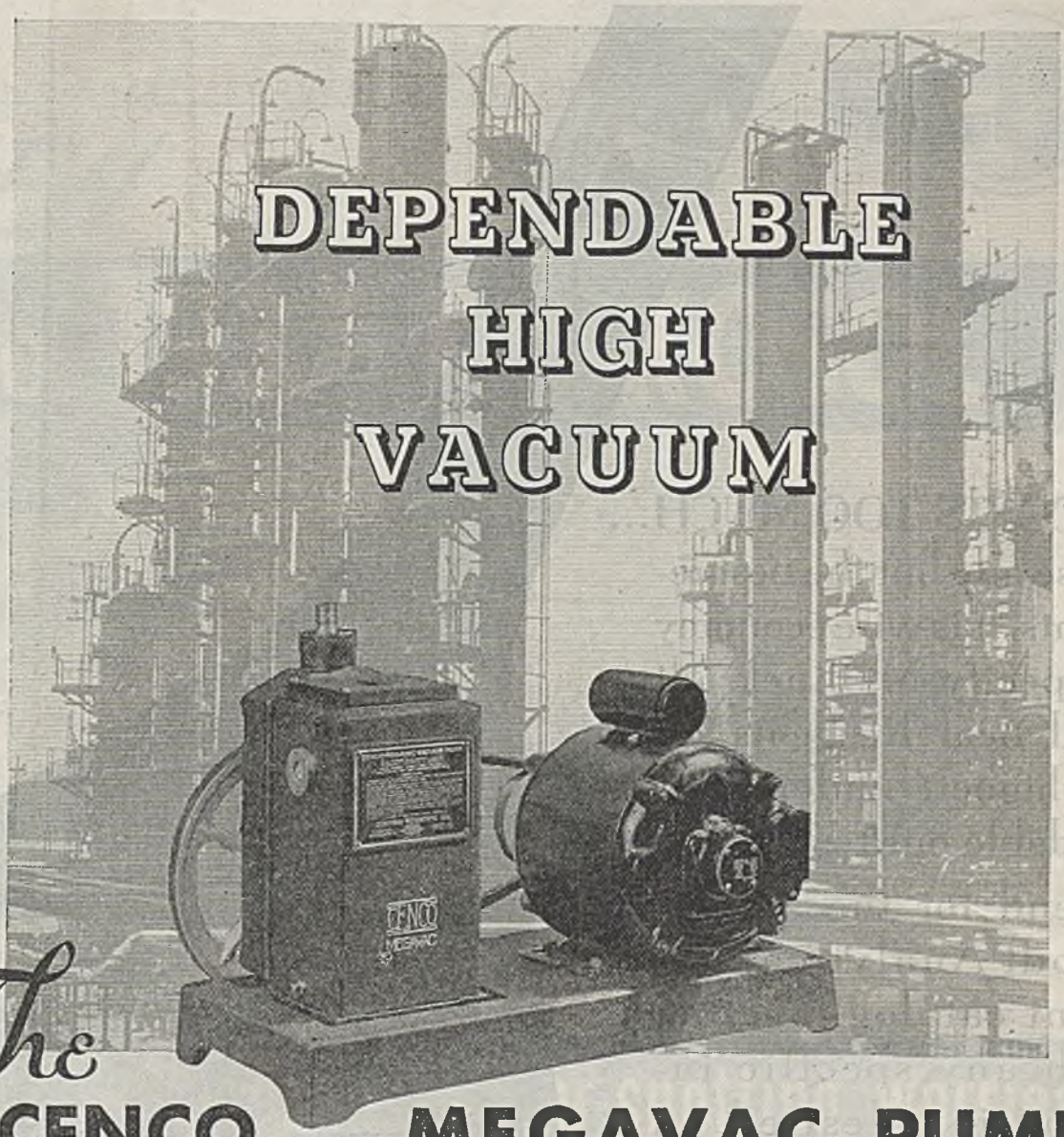

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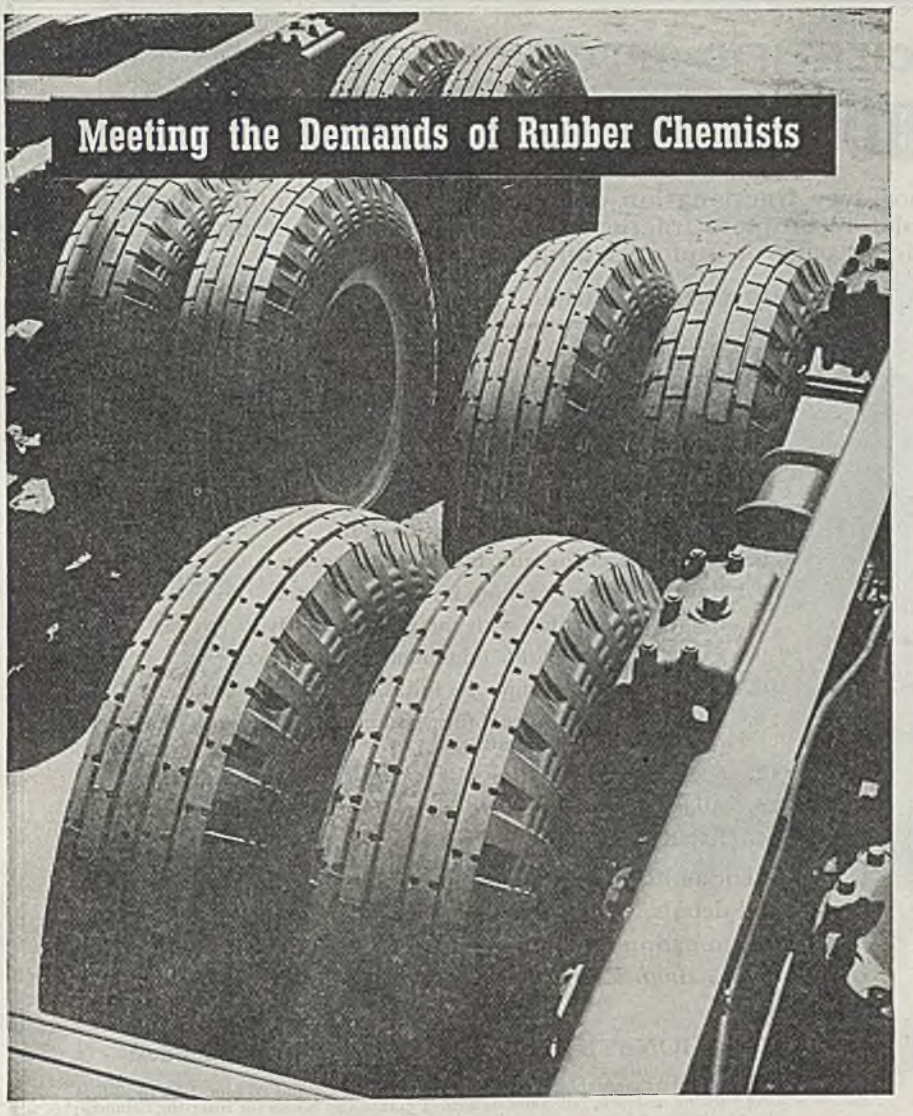

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Instrumentation in Analysis

In this issue we inaugurate a new monthly feature, Instrumentation in Analysis, prepared by Ralph H. Müller. Brief discussions of new instruments, methods, and apparatus of interest to analytical chemists, together with some discussion of their significance, field of application, and possible influence on the trend of future developments will appear over Dr. Müller's signature. It is recognized that many devices and methods, which are not primarily concerned with chemistry, will ultimately prove useful in analysis. This is particularly true in optical, electrical, electronic, and mechanical devices.

Dr. Müller is particularly well fitted by training and experience to cover the subject of Instrumentation in Analysis. He has been a member of the Radiation Laboratory of the Massachusetts Institute of Technology since 1942, and has done research in photochemistry, chemical physics, photoelectric photometry, electronics, instrumental methods of analysis and control, design of industrial and scientific instruments, and radar. He is well known to our readers as the author of comprehensive articles on photoelectric methods in analytical chemistry, American apparatus, instruments, and instrumentation, and instrumental methods of chemical analysis which appeared in 1939, 1940, and 1941. After receiving his Ph.D. from Columbia University and studying at Göttingen, he was on the staff of New York University from 1924 until he went to the MIT Radiation Laboratory to engage in highly secret research work for the war effort. In 1931 he received the silver medal of the American Medical Society for investigations on radium poisoning. Dr. Müller has been a member of the Advisory Board of the Analytical Edition for several years and extremely active in its deliberations.

It is felt by your editors that the introduction of Dr. Müller's column as a monthly feature is another step forward in a progressive and positive editorial program. The war stimulated greatly the development and use of instrumental methods of chemical analysis and unquestionably this trend will continue to grow in the future. There has been a long-felt need among analytical chemists for a timely, unbiased, and authoritative discussion and interpretation of new developments in the field of instrumentation.

Your editors and Dr. Müller will welcome suggestions and constructive criticisms from our readers. We also will welcome suggestions on other subjects of special interest to analytical chemists that might be developed into regular monthly features with treatment similar to Dr. Müller's presentation on instrumentation. We are here to serve the profession and the broad field of analytical chemistry.

Determination of Aromatics, Naphthenes, and Paraffins by Refractometric Methods

R. M. GOODING, N. G. ADAMS, AND H. T. RALL
Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.

Methods are described for determining aromatics, naphthenes, and paraffins in virgin naphthas and condensates boiling below 320° F. Most individual hydrocarbons can be estimated to 243° F. Efficient fractionation is used to produce narrow-boiling-range fractions containing relatively few individual hydrocarbons. Densities and refractive indices for the mercury g line and the sodium D line, determined for each fraction at 20° C., give specific dispersions and refractivity intercepts used for analysis of the samples. Aromatics are determined from specific dispersions and naphthenes, and paraffins are determined by use of modified Kurtz and Headington refractivity intercept–density charts. Aromatics can be determined from these charts with some loss in accuracy. Development of the charts from experimental and literature data is discussed and illustrated. Analyses of ten crude-oil naphthas are given.

THE Bureau of Mines, since early in 1942, has been analyzing various virgin naphthas and condensates to determine their possibilities as sources of aviation-gasoline base stocks, toluene, and other hydrocarbons. These analyses are based essentially upon fractional distillation of the naphthas or condensates, and refractometric examination of the distilled fractions. The final data obtained from such analyses indicate the quantities of aromatics, naphthenes, and paraffins boiling below 160° C. (320° F.) in the sample. The quantities of most individual hydrocarbons boiling below 117.22° C. (243° F.) can be determined. This report describes and illustrates the method of analysis adopted, shows the application of the method to the analyses of several crude oils, and indicates some uses of the results.

A study of the methods used and proposed for the determination of aromatics in saturated hydrocarbon mixtures indicated that aromatics in a crude oil could be conveniently and accurately determined from the specific dispersions of small narrow-boiling-range fractions obtained by distillation of the naphtha portion of the crude oil. Among others, Dixmier (*2*), Ward and Fulweiler (*9*), and Grosse and Wackher (*4*) have used specific dispersion in hydrocarbon analysis. The present method in which the specific dispersion is a measure of the quantity of aromatic material in a naphtha fraction, when that fraction contains only aromatics, naphthenes, and paraffins, is essentially a modification of that of Grosse and Wackher. Such a determination is possible because specific dispersions for naphthenes and paraffins are nearly equal and constant throughout the gasoline range, whereas the specific dispersions for aromatics, although not constant, are substantially higher than the values for naphthenes and paraffins.

The general equation for specific dispersion of a liquid is

$$S = \frac{n_a - n_b}{d} \times 10^4 \qquad (1)$$

where S is specific dispersion, n_a is the refractive index for light of wave length a, n_b is the refractive index for light of wave length b, d is the density, and 10^4 is a factor included for numerical convenience. All measurements of physical properties are made at one temperature, which for this work is 20° C. Although dispersion measurements of Grosse and Wackher were made for the F and C lines of hydrogen, the measurements used in this work are for the mercury g line and the sodium D line. The latter two lines are used because convenient and reliable mercury and sodium lamps are now commercially available and, since the value of the term $n_a - n_b$ is greater for these two lines than for the F and C lines of hydrogen, the accuracy of the method should be improved. A further modification of the method of Grosse and Wackher is in the use of very narrow-boiling-range fractions (usually less than 1° C.) rather than fractions having a boiling range of about 25° C. The determination of accurate values for the specific dispersions of pure aromatics, and of an average value for mixtures of naphthenes and paraffins, as well as the determination of aromatics in crude-oil naphthas, is discussed by Thorne, Murphy, and Ball (*8*).

The determination of the naphthene content of a sample is based on the use of the refractivity intercept, an empirical property originated by Kurtz and Ward (*6*). The present method is a modification of an analytical procedure proposed by Kurtz and Headington (*5*) using this property and applicable to mixtures containing both saturates and unsaturates.

The refractivity intercept is defined by the equation

$$R = n_D - 0.5d \qquad (2)$$

where R is the refractivity intercept, n_D is the refractive index for the sodium D line, and d is the density of the liquid, all measurements being made at 20° C. As described by Kurtz and Ward and as used by Kurtz and Headington, R is a constant for each hydrocarbon type or homologous series. If a sample contains only aromatics, naphthenes, and paraffins, the use of the refractivity intercept as an analytical tool depends upon the relationship, usually shown graphically, between the refractivity intercepts and densities of the sample and of the individual aromatics, naphthenes, and paraffins thought to be present. Four major modifications have been made in the method of Kurtz and Headington: (1) only aromatics and saturated hydrocarbons are considered in the scheme of analysis; (2) the graphical analysis charts cover an average boiling range of 10° C. instead of 30° C.; (3) very narrow-boiling-range fractions are analyzed; (4) individual values for refractivity intercepts are used for all compounds instead of a single value for each type.

After the aromatic and naphthene contents of a fraction containing only aromatics, naphthenes, and paraffins have been determined, the paraffin content of the fraction is obtained by difference. Aromatics can be determined by the use of refractivity intercept and density, but it is felt that the present determination of aromatics from specific dispersions is more accurate. A comparison of results by the two methods is given in Table I.

ANALYTICAL APPARATUS AND PROCEDURE

The accuracy of the analytical method described below depends in part on the apparatus, and its quality must be such that data of the requisite accuracy and precision are obtained. The equipment described in the following paragraphs has been found satisfactory for this work.

Two types of columns are used for the fractional distillation of samples. In one assembly the column proper is a glass tube 21 mm. in inside diameter packed with single-turn wire helices 2.4 mm. ($^3/_{32}$ inch) in diameter. The packed section is 244 cm. in length, and is insulated with asbestos listing and magnesia. A system of electrical heaters is incorporated in the insulation, so that the temperature of the insulation can be maintained at or slightly below the temperature of the vapor and liquid within the column. These temperatures are measured by 5 pairs of iron-constantan thermocouples spaced along the length of the column. The glass still pot is permanently sealed to the column proper and has a capacity of 4.5 liters. A total condenser at the top of the column provides reflux and liquid overhead product. The column was tested in the usual manner using methylcyclohexane and isooctane, and has an efficiency at total reflux equivalent to 88 theoretical plates.

The other distillation unit is a commercially available vacuum-jacketed glass column having 122 cm. of patented wire packing.

Table I. Comparison of Determination of Aromatics by Specific Dispersion and by Refractivity Intercept–Density Methods

	Volume Per Cent of Aromatics in Naphtha or Condensate														
	Carthage			Chapel Hill			Conroe			East Texas			Hull-Silk-Sikes (Strawn)		
Aromatic	Specific dispersion	Refractivity intercept	Difference	Specific dispersion	Refractivity intercept	Difference	Specific dispersion	Refractivity intercept	Difference	Specific dispersion	Refractivity intercept	Difference	Specific dispersion	Refractivity intercept	Difference
Benzene	2.05	1.78	0.27	0.54	0.40	0 14	1.94	1.90	0.04	0.24	0.16	0.08	0.16	0.15	0.01
Toluene	0.88	0.82	0.06	0.52	0.44	0.08	9.72	9.37	0.35	1.14	0.87	0.27	0.81	0.55	0.26
Ethylbenzene	0.16	0.12	0.04	0.32	0.23	0.09	0.37	0.34	0.03	0.38	0.25	0.13	0.31	0.20	0.11
m-Xylene + *p*-Xylene	0.54	0.50	0.04	0.43	0.33	0.10	3.52	3.42	0.10	1.33	1.15	0.18	0.81	0.55	0.26
o-Xylene	0.24	0.19	0.05	0.15	0.12	0.03	1.55	1.50	0.05	0.64	0.54	0.10	0.24	0.13	0.11
Isopropylbenzene	0.08	0.04	0.04	0.09	0.06	0.03	..	..	..	0.19	0.12	0.07	0.22	0.10	0.12
n-Propylbenzene	0.22	0.21	0.01	0.21	0.18	0.03	..	..	..	0.52	0.45	0.07	0.41	0.34	0.07
	Jennings			KMA (Strawn)			M nument			Old Ocean			Plymouth		
Benzene	1.03	0.94	0.09	0.24	0.24	0.00	0.13	0.08	0.05	1.02	0.92	0.10	0.16	0.11	0.05
Toluene	3.51	3.45	0.06	1.04	0.90	0.14	0.48	0.30	0.18	2.69	2.49	0.20	0.72	0.62	0.10
Ethylbenzene	0.48	0.41	0.07	0.34	0.30	0.04	0.44	0.33	0.11	0.51	0.43	0.07	0.35	0.32	0.03
m-Xylene + *p*-Xylene	3.48	3.38	0.10	1.19	1.05	0.14	0.50	0.31	0.19	2.79	2.46	0.33	0.75	0.58	0.17
o-Xylene	1.87	1.86	0.01	0.52	0.43	0.09	0.08	0.03	0.05	1.60	1.35	0.25	0.31	0.25	0.06
Isopropylbenzene	0.42	0.35	0.07	0.17	0.15	0.02	0.18	0.11	0.07	..	..	..	0.19	0.15	0.04
n-Propylbenzene	0.87	0.74	0.13	0.55	0.52	0.03	0.48	0.41	0.07	..	..	..	0.32	0.32	0.00
	Saxet			Segno			Slaughter			Wade City			Wasson		
Benzene	0.00	0.05	−0.05	0.59	0.54	0.05	4.60	4.12	0.48	0.10	0.08	0.02	2.29	1.98	0.31
Toluene	0.00	0.06	−0.06	3.22	3.07	0.15	4.80	4.50	0.30	0.79	0.66	0.13	4.44	4.16	0.28
Ethylbenzene	0.49	0.40	0.09	0.42	0.35	0.07	1.10	0.83	0.27	0.54	0.45	0.09	0.91	0.76	0.15
m-Xylene + *p*-Xylene	0.58	0.44	0.14	3.07	2.86	0.21	2.86	2.78	0.08	1.43	1.24	0.19	3.13	2.91	0.22
o-Xylene	0.07	0.06	0.01	1.67	1.54	0.13	0.78	0.72	0.06	0.91	0.75	0.16	1.19	1.05	0.14
Isopropylbenzene	0.16	0.00	0.16	0.48	0.41	0.07	0.34	0.27	0.07	0.29	0.21	0.08	0.47	0.39	0.08
n-Propylbenzene	0.27	0.26	0.01	0.88	0.72	0.16	0.81	0.74	0.07	0.74	0.71	0.03	0.85	0.79	0.06

The diameter of the wire packing is 22 mm. The still pot is a 5-liter flask with a spherical ground-glass joint. The vacuum jacket requires no auxiliary heating when the column is operating below 320° F. A total condenser fits into the top of the column and provides reflux and liquid overhead product. The fractionating efficiency of this column at total reflux is 50 theoretical plates at the vaporization rate used in these distillations. In all columns the temperature of the vapor at the top of the column is measured by means of iron-constantan thermocouples with a precision of 0.3° F. (0.17° C.). The peaks for particular compounds in the plot of volume per cent against temperature as measured by the thermocouples usually agree with the literature values for boiling points of the particular compounds to 1° F.

Refractive index measurements are made in a Bausch & Lomb precision oil refractometer using monochromatic light. Light is provided by commercially available lamps at the wave lengths of the mercury *g* line (4358 Å.) and the sodium D line (5893 Å.). The precision of these measurements is ±0.00010 unit of refractive index for routine determinations. Specific gravities are determined at 20° C./20° C. with a chainomatic Westphal balance using a 2-ml. glass plummet. The precision of these measurements is ±0.0002 unit of specific gravity. Specific gravities are converted to densities at 20° C.

A measured volume of the sample is introduced into the still pot. The volume of this charge may be from 2 to 4 liters, but usually is between 3 and 3.5 liters. The column is preflooded to increase separating efficiency, and then allowed to operate at the still-pot pressure maintained throughout the distillation for 1 hour or longer. Product withdrawal is begun after this stabilizing period, and is adjusted to give a take-off rate of 1 ml. per minute. A reflux ratio of 20 to 1 is maintained by an appropriate vaporization rate throughout the distillation. Fractions are collected every 8 or 9 minutes, and the temperature of the vapor at the top of the column is recorded at this time. This top temperature is considered as the uncorrected boiling point of the last portion of the material in one fraction, and of the first portion of the succeeding fraction. Distillation is continued until the corrected boiling point exceeds 320° F., or until the still pot is empty. After the distillation is stopped, the still pot is cooled, the column is allowed to drain, the residue is removed and its volume measured. Each distillation yields from 200 to 400 fractions, each representing approximately 0.25% by volume of the original charge.

The volume, the specific gravity, and the refractive index for the mercury *g* line and the sodium D line are determined for each fraction.

DETERMINATION OF AROMATICS AND NAPHTHENES

Refractive indices and densities of mixtures of aromatics with naphthenes, with paraffins, or with mixtures of naphthenes and paraffins are not additive either on a volume per cent basis or a weight per cent basis, but their additivity is more nearly linear using volume per cent as shown in Table II. For mixtures of aromatics, naphthenes, and paraffins the specific dispersions likewise are not additive, but are more nearly so using a weight per cent basis as shown by Figure 1. For this reason the determination of aromatics by the use of specific dispersions is made on a weight per cent basis and this weight per cent is then converted to volume per cent.

The equation for weight per cent aromatics in a fraction is

$$W = \frac{S_f - S_{np}}{S_a - S_{np}} 100 + C \qquad (3)$$

where W is weight per cent aromatics, S_f is the specific dispersion of the fraction, S_a is specific dispersion of the individual aromatic

Table II. Nonadditivity of Density and Refractive Index for Mixtures of Toluene with *n*-Heptane and with Methylcyclohexane

Composition of Blends in Terms of Nonaromatic Component		Deviations of Experimental Densities and Refractive Indices from Theoretical (Theoretical-Experimental × 10⁴)			
		Weight % Basis		Volume % Basis	
Weight % *n*-heptane	Volume %[a] *n*-heptane	d_4^{20}	n_D^{20}	d^{20}	n_D^{20}
100.00	100.00	0	0	0	0
98.98	99.19	5	3	2	1
96.98	97.60	13	8	2	1
94.97	95.98	20	13	2	2
89.97	91.89	38	25	3	5
79.98	83.50	69	45	5	7
70.17	74.85	92	61	7	10
50.30	56.15	113	76	7	13
29.98	35.13	100	69	6	13
19.99	24.02	77	54	4	10
10.02	12.35	43	32	1	7
5.02	6.27	23	17	1	4
3.03	3.80	13	11	−1	3
1.01	1.27	4	4	−1	1
0.00	0.00	0	0	0	0
Methylcyclohexane					
100.00	100.00	0	0	0	0
98.87	99.00	5	2	3	1
94.87	95.41	12	9	7	5
89.91	90.93	23	15	13	7
69.91	72.32	53	35	24	17
49.94	52.87	56	41	27	20
30.04	32.56	46	36	23	18
10.03	11.15	21	16	10	8
5.03	5.62	10	9	4	4
1.06	1.19	3	2	1	1
0.00	0.00	0	0	0	0

[a] Calculated from weight and density of components

Table III. Boiling Points, Specific Dispersions, and Densities of Aromatics

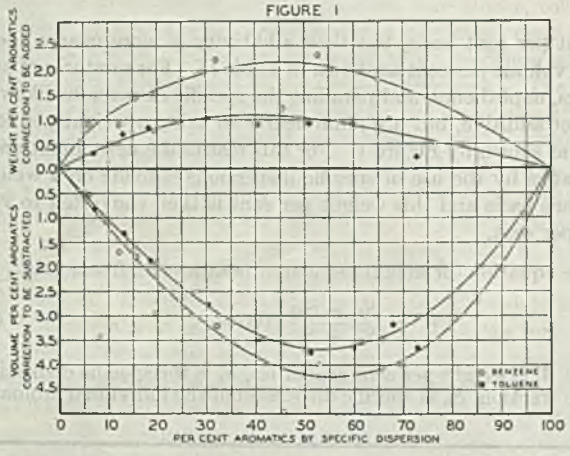
Aromatic	Boiling Point[a], 760 Mm. ° C.	° F.	Specific Dispersion[b], $(g - D)$	Density[b], 20° C.
Benzene	80.10	176.18	248.4	0.8790
Toluene	110.62	231.12	241.4	0.8669
Ethylbenzene	136.19	277.14	228.1	0.8671
p-Xylene	138.35	281.03	238.2	0.8610
m-Xylene	139.11	282.40	237.1	0.8641
o-Xylene	144.42	291.96	234.8	0.8800[a]
Isopropylbenzene	152.40	306.32	215.8	0.8619
n-Propylbenzene	159.22	318.60	216.0[c]	0.8619[a]

[a] From reliable but restricted data.
[b] See (*8*).
[c] Estimated value.

being determined, S_{np} is the average value of the specific dispersions of the naphthenes and paraffins, and C is an additive correction for the deviation from linearity of the property-composition relationship. The value of S_f is calculated from the refractive indices and density of the fraction by the equation

$$S_f = \frac{n_g - n_D}{d_f} \times 10^4 \qquad (4)$$

where n_g and n_D are the refractive indices of the fraction for the mercury g line and the sodium D line, and d_f is the density of the fraction.



The value of S_{np} is 122.4, the values of S_a are listed in Table III, and the value of C is taken from the curves in Figure 2. A discussion of these values is included in the paper by Thorne, Murphy, and Ball (*8*). The equation for converting weight per cent aromatics to volume per cent is

$$V = \frac{(W)(d_f)}{d_a} \qquad (5)$$

where V is volume per cent aromatics, d_f is the density of the fraction, and d_a is the density of the aromatic compound, given in Table III. The calculations for the per cent aromatics in each fraction are recorded to the nearest figure in the first decimal place.

For the naphthene determination, refractivity intercepts for each fraction are calculated by the use of Equation 2 and are then plotted with their corresponding densities on the proper member of a series of 14 graphical analysis charts extending over the temperature range from 97° to 320° F. The corrected boiling point determines which of the charts will be used in plotting the property values of the fraction, and the volume per cent of naphthenes in the fraction is read directly from the plot of these values on the chart. Percentages for the naphthenes are recorded only in whole numbers.

APPLICATION OF THE METHODS OF ANALYSIS

The distillation characteristics of mixtures of aromatics with naphthenes and paraffins are such that most of the individual

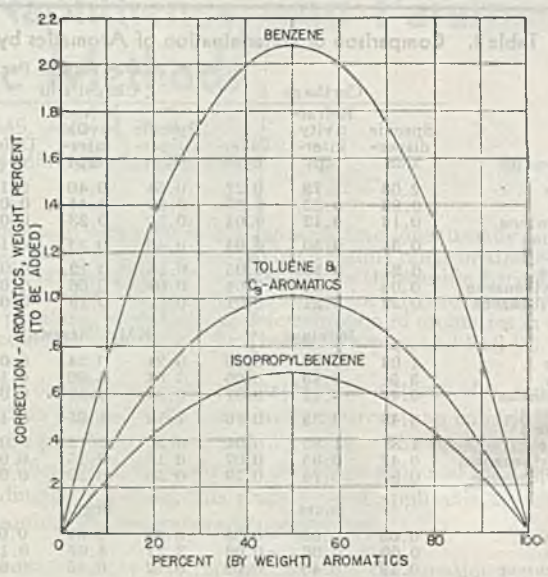


Figure 2. Curves for Correcting Aromatic Contents as Determined by Specific Dispersion Method

aromatic compound is distilled from a naphtha before the boiling point of the aromatic compound has been reached. Examination of the data from a large number of distillations has indicated the temperature limits within which the individual aromatic compounds are likely to be found. These limits for the individual compounds are: benzene, 146° to 185° F.; toluene, 203° to 251° F.; ethylbenzene, 251° to 273° F.; *p*-xylene and *m*-xylene, 273° to 283° F.; *o*-xylene, 283° to 295° F.; isopropylbenzene, 295° to 310° F.; and *n*-propylbenzene, 310° to 320° F. Equations 3, 4, and 5 are applied to all fractions within these ranges which have specific dispersions above 122.4 using the appropriate constants given in Table III for each aromatic compound. Because of the small difference in boiling point between *p*-xylene and *m*-xylene, making separation impossible under the distillation conditions employed, the constants for these two compounds are averaged, and the results of the determination for the range from 273° to 283° F. are expressed in terms of the mixture of the two. As indicated in Table III, the specific dispersion for *n*-propylbenzene was estimated, as none of the pure compound was available to make an experimental determination possible. However, since the densities and refractive indices (n_D) of isopropylbenzene and *n*-propylbenzene are practically the same, and since the specific dispersions for these two compounds calculated from the refractive indices for the hydrogen F and C lines are virtually identical (166.5 and 166.4), this estimated value of 216.0 should be within the experimental error of the true value, and the correction curve for isopropylbenzene in Figure 2 is used for *n*-propylbenzene. The summation of the percentages of aromatic in each fraction, based on the total amount of sample, yields the amounts of the individual aromatics in the sample.

To obtain greater precision in the determination of the naphthene content of each fraction, individual values for the refractivity intercepts of the pure compounds are used rather than the average values suggested by Kurtz and Headington.

Up to the present time the analysis of virgin naphthas has indicated that only those naphthenes that have 5- and 6-carbon-atom rings occur in these naphthas in detectable quantities. Such analyses have also indicated the absence of the *cis* form of the naphthene compounds, and the absence of the more highly branched paraffin hydrocarbons. This means that only about 34 individual aromatic and saturated hydrocarbons need be considered in the analysis of a naphtha in that portion of the material boiling between 97° and 243° F. From the above considerations and from information in the literature, about 70 compounds

should be considered in that portion of the naphtha distilling between 243° and 320° F.

A study of the boiling points of the compounds in the 97° to 320° F. range indicates certain fairly wide temperature intervals at which no material should distill, so that an efficient fractional distillation should show minima in the amount of distillate recovered at these temperature intervals. Examination of the data from more than 75 such distillations shows that such minima do occur, suggesting the use of these points as temperature divisions in the method of analysis.

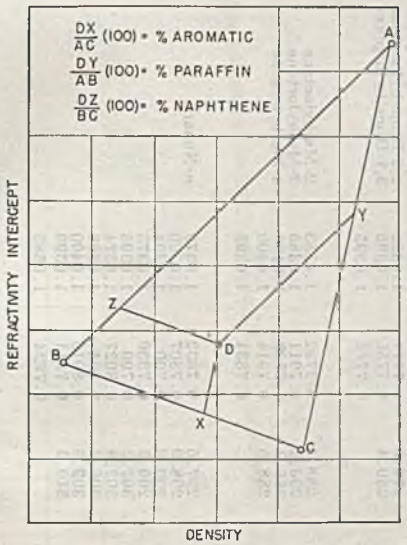


Figure 3. Graphical Analysis Diagram

On the basis of these points of minima and from a knowledge of the refractivity intercepts and densities of the individual hydrocarbons, together with a consideration of the boiling points and distillation characteristics of the aromatic compounds, the temperature range from 97° to 320° F. has been divided into 15 smaller ranges for analytical purposes. Graphical analysis charts, using refractivity intercepts and densities, have been constructed for 14 of these temperature ranges. No chart is necessary for naphthene analysis in the range from 135° to 146° F., since only paraffin hydrocarbons are present. Table IV indicates the temperature range of each division and the individual compounds, together with their physical properties, which have been used in defining the 14 charts.

If points *A*, *B*, and *C* in Figure 3 represent the refractivity intercept and density of a pure individual aromatic, paraffin, and naphthene hydrocarbon, respectively, then the composition of any fraction, *D*, containing only these 3 hydrocarbons can be determined from the geometrical position of point *D* within the triangle formed by points *A*, *B*, and *C*, provided that the properties which define each of the points are additive with relation to composition. As there are only 8 aromatic compounds in the boiling range considered, it was relatively easy to locate the aromatic points (*A* in Figure 3) on those of the 14 charts where aromatics must be considered.

For a number of boiling ranges the paraffins and naphthenes probably present are sufficiently well known and their constants sufficiently well established to make it possible to use their refractivity intercept and density values to establish points *B* and *C* in Figure 3, and therefore the slope and position of the paraffin-naphthene connecting line. Where there is insufficient information to permit this procedure, the slope and position of the line have been established by using data for distilled fractions free from aromatic material. The length of the line, and therefore the location of points *B* and *C*, are determined by a consideration of the paraffins and naphthenes which theoretically may be present and those which the data indicate most probably are present or absent. Figures 4, 5, 7, 8, 9, 10, 12, 13, 14, 16, 17, and 19 show some of the representative data used in defining the paraffin-naphthene base line of the graphical analysis triangles. These data are not continuous from one figure to the next, except as indicated, and were taken from a large number of distillations.

Figures 6, 11, 15, and 18 represent the finished form of 4 of the 14 graphical analysis charts used for the naphthene determinations except for the omission here of the smaller scale divisions ordinarily used, and show data for 4 different naphthas. These naphthas are from Saxet, Yates and Taylor-Link, and Conroe crude oils from Texas, and from Lance Creek crude oil from Wyoming. Each is distinctive in its composition characteristics. The Saxet naphtha, from the Corpus Christi area of Texas, contains an unusually high percentage of the naphthenic hydrocarbons. The Yates and Taylor-Link mixed sample from West Texas, containing about 75% of Yates material, has an abnormally low percentage of normal paraffins and a high percentage of isomeric paraffins. The Conroe, Texas, naphtha has an exceptionally high content of the aromatic hydrocarbons. The Lance Creek, Wyo., naphtha was completely dearomatized by filtration through silica gel before the distillation was made. The 14 graphical analysis charts are scaled in 1% divisions for aromatics and in 2% increments for naphthenes. Each of the 15 temperature ranges from 97° to 320° F. is discussed in detail below.

Figure 4. Temperature range, 97° to 135° F. Cyclopentane is the only naphthene found in this range; *n*-pentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are the paraffins present; and there is no aromatic. Cyclopentane, which occurs in most crude oils, usually is associated with a smaller quantity of 2,2-dimethylbutane. The total quantity of both compounds is always small. The temperature 135° F. seems to be the most suitable for the inclusion of all the cyclopentane in this range, and the exclusion of the major portion of the 2,3-dimethylbutane. In Figure 4 the paraffin and naphthene points, and therefore the connecting line, are defined by the appropriate constants for 2,2-dimethylbutane and cyclopentane. Two sets of data points for typical naphthas are also given by curves *A* and *B*, showing the change in composition of the successive fractions with increase in boiling point

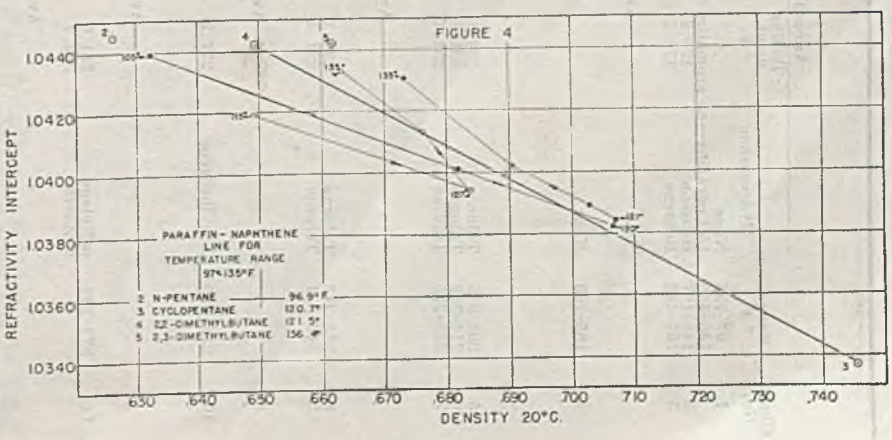
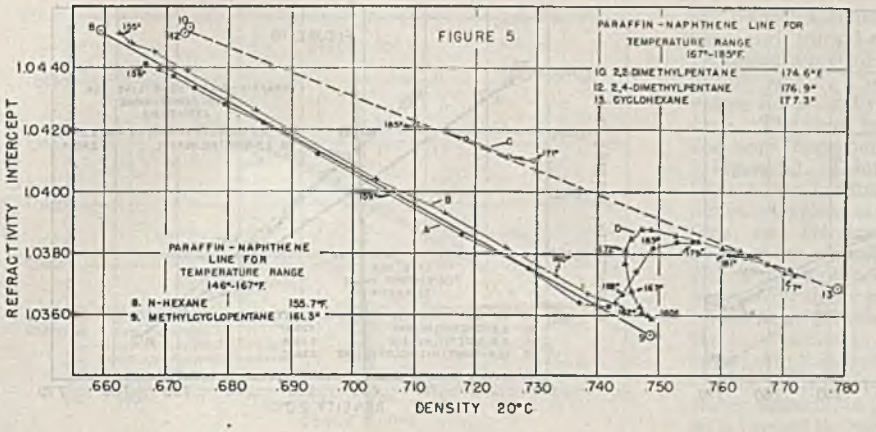
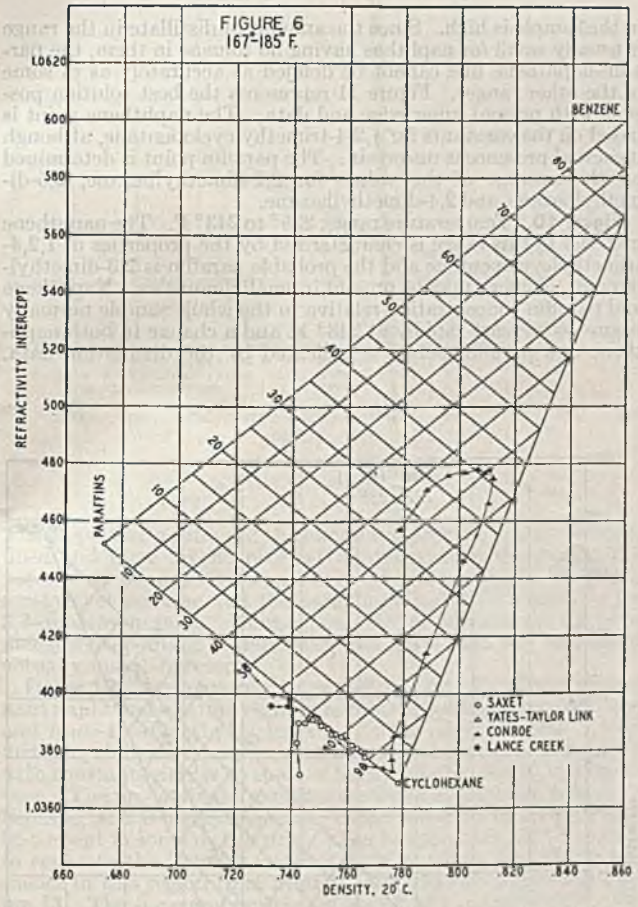


Table IV. Data Used in Constructing Refractivity Intercept–Density Charts

Chart No.	Range, ° F.	Aromatics: Hydrocarbon	Aromatics: Boiling point, ° F.	Aromatics: Density, 20° C.	Aromatics: Refractivity intercept	Naphthenes: Hydrocarbon	Naphthenes: Boiling point, ° F.	Naphthenes: Density, 20° C.	Naphthenes: Refractivity intercept	Paraffins: Hydrocarbon	Paraffins: Boiling point, ° F.	Paraffins: Density, 20° C.	Paraffins: Refractivity intercept
1	97–135	None	...	...	...	Cyclopentane	120.7	0.7454	1.0337	2,2-Dimethylbutane	121.5	0.6492	1.0442
	135–146	(All paraffins—no aromatics or naphthenes)											
2	146–167	Benzene	176.2	0.8790	1.0616	Methylcyclopentane	161.3	0.7486	1.0354	*n*-Hexane	155.7	0.6594	1.0452
3	167–185	Benzene	176.2	0.8790	1.0616	Cyclohexane	177.3	0.7786	1.0369	2,2-Dimethylpentane	174.6	0.6739	1.0453
										2,4-Dimethylpentane	176.9	0.6730	1.0451
			Av.	0.8790	1.0616			0.7786	1.0369			0.6735	1.0452
4	185–203	None	...	...	...	*trans*-1,3-Dimethylcyclopentane	195.4	0.745	1.0367	2,3-Dimethylpentane	193.6	0.6951	1.0445
						trans-1,2-Dimethylcyclopentane	197.4	0.752	1.0360	2-Methylhexane	194.1	0.6788	1.0455
										3-Methylhexane	197.5	0.6870	1.0452
							Av.	0.749	1.0364			0.6870	1.0451
5	203–215	Toluene	231.1	0.8668	1.0634	Methylcyclohexane	213.7	0.7694	1.0384	*n*-Heptane	209.2	0.6837	1.0459
6	215–222	Toluene	231.1	0.8668	1.0634	Ethylcyclopentane	218.2	0.7665	1.0366	2,2-Dimethylhexane	224.3	0.6953	1.0459
7	222–235	Toluene	231.1	0.8668	1.0634	1,2,4-Trimethylcyclopentane	235.0	0.7565	1.0373	2,2-Dimethylhexane	224.3	0.6953	1.0459
										2,4-Dimethylhexane	229.0	0.7003	1.0452
										2,5-Dimethylhexane	228.4	0.6935	1.0458
			Av.	0.8668	1.0634			0.7565	1.0373			0.6964	1.0456
8	235–243	Toluene	231.1	0.8668	1.0634	1,2,4-Trimethylcyclopentane	235.0	0.7565	1.0373	2,3-Dimethylhexane	240.1	0.7133	1.0449
9	243–251	Toluene	231.1	0.8668	1.0634	*trans*-1,3-Dimethylcyclohexane	248.2	0.7660	1.0399	2-Methylheptane	243.8	0.6979	1.0461
						trans-1,4-Dimethylcyclohexane	246.8	0.7625	1.0397	3-Methylheptane	246.1	0.7058	1.0456
						trans-1-Methyl-2-ethylcyclopentane	250.7	0.7696	1.0372	4-Methylheptane	243.9	0.7046	1.0456
			Av.	0.8668	1.0634			0.7660	1.0389			0.7028	1.0458
10	251–273	Ethylbenzene	277.2	0.8669	1.0624	*trans*-1,2-Dimethylcyclohexane	254.2	0.7760	1.0390	*n*-Octane	258.2	0.7026	1.0462
						Propylcyclopentane	267.4	0.7761	1.0385				
						Isopropylcyclopentane	259.5	0.7763	1.0378				
						Ethylcyclohexane	269.2	0.7879	1.0391				
			Av.	0.8669	1.0624			0.7791	1.0386			0.7026	1.0462
11	273–283	*p*-Xylene	281.0	0.8610	1.0653	1,1,3-Trimethylcyclohexane	277.4	0.7792	1.0398	2,5-Dimethylheptane	276.9	0.715	1.0462
		m-Xylene	282.4	0.8641	1.0652	1-Methyl-3-isopropylcyclopentane	279.9	0.7771	1.0392	2,6-Dimethylheptane	275.4	0.7089	1.0463
						1,3-Dimethyl-2-ethylcyclopentane	280.4	0.7756	1.0396	3,3-Dimethylheptane	279.2	0.725	1.0460
			Av.	0.8626	1.0653			0.7773	1.0395			0.7163	1.0462
12	283-295	*o*-Xylene	292.0	0.8800	1.0653	1-Methyl-2-isopropylcyclopentane	288.5	0.7792	1.0383	2-Methyloctane	289.9	0.7134	1.0464
						tert-Butylcyclopentane	293.4	0.7911	1.0385	3-Methyloctane	291.5	0.7207	1.0459
						1,2,4-Trimethylcyclohexane	286.2	0.7720	1.0406	4-Methyloctane	288.5	0.7199	1.0462
						trans-1,2,3-Trimethylcyclohexane	288.5	0.7914	1.0400				
			Av.	0.8800	1.0653			0.7834	1.0393			0.7180	1.0462
13	295–310	Isopropylbenzene	306.3	0.8617	1.0605	*trans*-1,2-Diethylcyclopentane	297.5	0.7832	1.0379	*n*-Nonane	303.4	0.7178	1.0465
						Isobutylcyclopentane	298.9	0.7807	1.0396				
						trans-1-Methyl-3-ethylcyclohexane	299.3	0.790	1.0394				
						1,3-Diethylcyclopentane	299.3	0.7850	1.0373				
						1-Methyl-4-ethylcyclohexane	302.2	0.790	1.0393				
						1,1-Diethylcyclopentane	302.9	0.8027	1.0374				
						1-Methyl-2-ethylcyclohexane	306.7	0.804	1.0368				
						Isopropylcyclohexane	309.9	0.8016	1.0400				
						sec-Butylcyclopentane	310.3	0.7941	1.0390				
			Av.	0.8617	1.0605			0.7924	1.0385			0.7178	1.0465
14	310-320	*n*-Propylbenzene	318.6	0.8619	1.0610	Propylcyclohexane	314.1	0.7933	1.0403	2,6-Dimethyloctane	317.5	0.7291	1.0461
						Butylcyclopentane	315.0	0.7847	1.0386	3,5-Dimethyloctane	317.9	0.7328	1.0467
										2,5-Dimethyloctane	318.2	0.7349	1.0453
										2,7-Dimethyloctane	320.0	0.7247	1.0468
			Av.	0.8619	1.0610			0.7890	1.0394			0.7304	1.0462





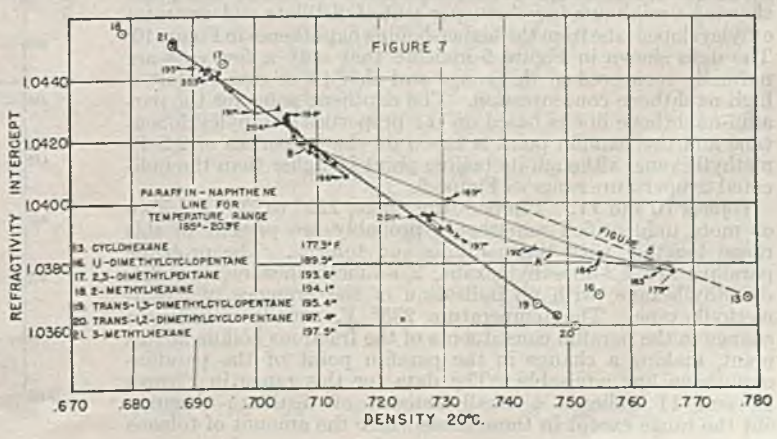
from *n*-pentane through mixtures containing cyclopentane to 2,3-dimethylbutane. Since no aromatic occurs in this range the paraffin-naphthene line suffices for the naphthene determination.

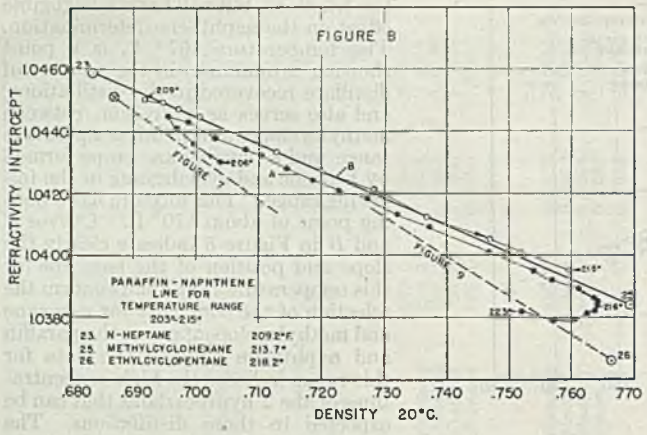
Temperature range, 135° to 146° F. Normally all material boiling in this range will be paraffinic, and no naphthene determination is required. The paraffins present are 2,3-dimethylbutane, 2-methylpentane, and 3-methylpentane and a procedure for estimating their relative quantities, based on refractive indices and densities, is outlined later. The temperature 146° F. was selected as the maximum that can be reached in all distillations without including some benzene.

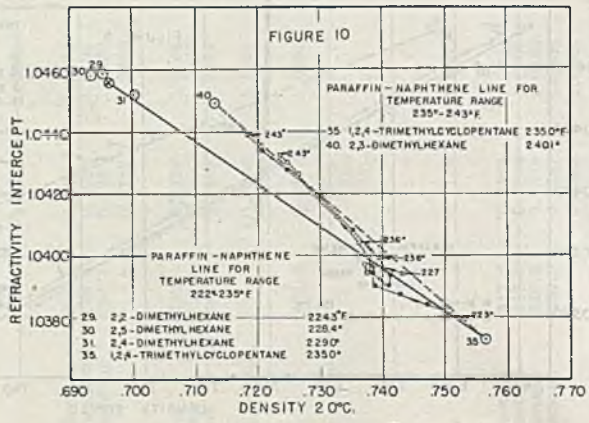
Figure 5. Temperature range, 146° to 167° F. Methylcyclopentane, *n*-hexane, and benzene are the compounds usually found in this range. Some 3-methylpentane may occur in the first few fractions, but will have a negligible effect on the naphthene determination. The temperature 167° F. is a point showing a minimum in the amount of distillate recovered in the distillations, and also serves as a division between methylcyclopentane in this temperature range and a possible azeotrope formed by benzene and cyclohexane in the following range. This mixture has a boiling point of about 170° F. Curves *A* and *B* in Figure 5 indicate clearly the slope and position of the base line for this temperature range and confirm the selection of the constants for *n*-hexane and methylcyclopentane as the paraffin and naphthene points. The data for this range indicate the high concentrations of the 2 hydrocarbons that can be expected in these distillations. The paraffin-naphthene base line shown in Figure 5 is combined with the aromatic point for benzene to obtain a triangle similar in form to the triangles shown in Figures 3 and 6.

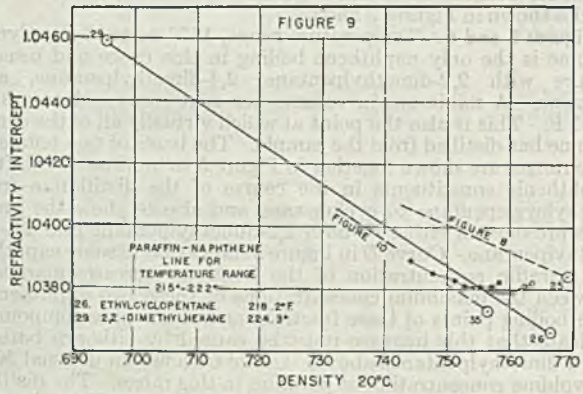
Figures 5 and 6. Temperature range, 167° to 185° F. Cyclohexane is the only naphthene boiling in this range and usually occurs with 2,2-dimethylpentane, 2,4-dimethylpentane, and benzene. A minimum in volume per cent recovered occurs at 185° F. This is also the point at which virtually all of the cyclohexane has distilled from the sample. The bases of two temperature ranges are shown together in Figure 5 to indicate the shift in naphthenic constituents in the course of the distillation from methylcyclopentane to cyclohexane and also to show the probable presence of either or both 2,2-dimethylpentane and 2,4-dimethylpentane. Curve *D* in Figure 5 shows that in some naphthas the paraffin concentration of the fractions increases markedly between the maximum concentrations of these two naphthenes. The boiling points of these fractions and of the pure compounds indicate that this increase must be caused by either or both of the 2 dimethylpentanes above. Curve *C* shows an unusual 50% by volume concentration of paraffins in this range. The distillation data in Figures 5 and 6 indicate that the paraffin and naphthene points were chosen properly.

Figure 7. Temperature range 185° to 203° F. Naphthenes boiling in this range are 1,1-dimethylcyclopentane, *trans*-1,3-dimethylcyclopentane, and *trans*-1,2-dimethylcyclopentane, and the paraffins are 2,3-dimethylpentane, 2-methylhexane, and 3-methylhexane. Present experience does not indicate the presence of either 3,3-dimethylpentane or 3-ethylpentane. The amounts of benzene or toluene found are negligible and their presence is unusual. The temperature 203° F. is another point in the distillations where a definite minimum in total volume per cent occurs, and is also a division between the isomeric heptanes and *n*-heptane. It is the lowest temperature at which toluene first appears in any of the distillations. Curves *A* and *B* in Figure 7 show the shift with increase in boiling point from cyclohexane in Figure 5 toward 2,3-dimethylpentane and 2-methylhexane in Figure 7, a reversal toward the 2 higher-boiling *trans*-dimethylcyclopentanes, and a final reversal in the paraffin direction toward 3-methylhexane. The required slope and position of the paraffin-naphthene line is defined by the data in Figure 7 and the paraffin and naphthene points selected fulfill these requirements. The paraffin point is an average of the values for 2,3-dimethylpentane, 2-









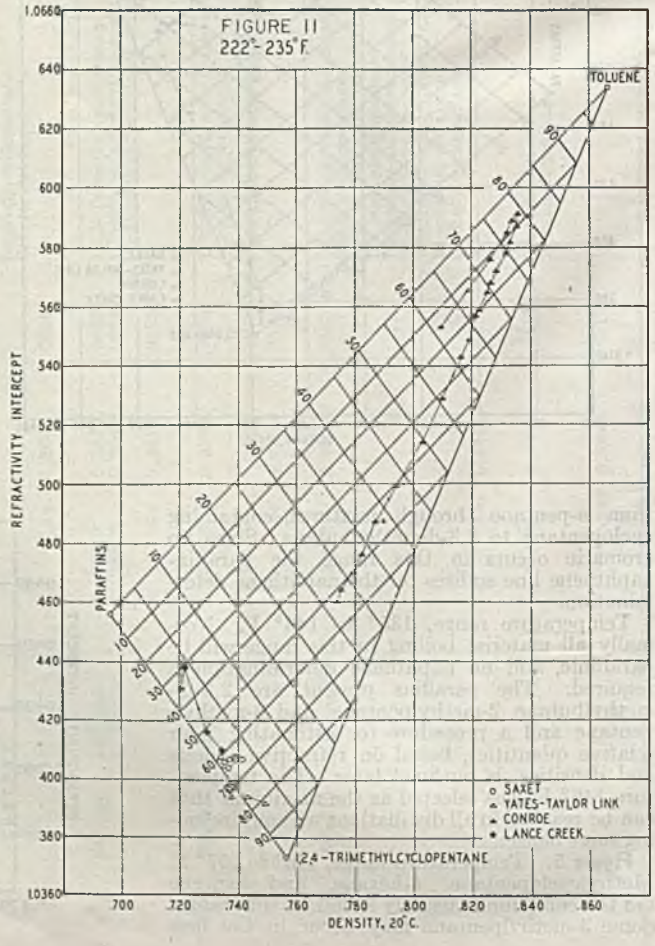
methylhexane, and 3-methylhexane and the naphthene point is an average of the values for *trans*-1,3-dimethylcyclopentane and *trans*-1,2-dimethylcyclopentane. The quantity of 1,1-dimethylcyclopentane in this range relative to the total amount of the other 2 naphthenes is usually small and consequently its constants were not used in the average for the naphthene point.

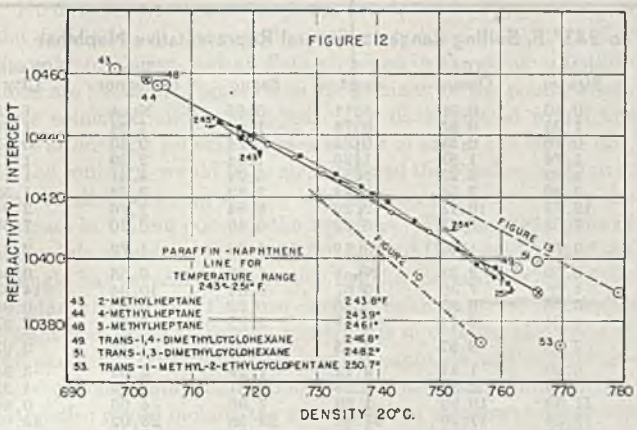
Figure 8. Temperature range, 203° to 215° F. Methylcyclohexane, *n*-heptane, and toluene are the only hydrocarbons usually present in this range. The temperature 215° F. separates methylcyclohexane from ethylcyclopentane in Figure 9, and *n*-heptane from the isomeric octanes. Curve *A* in Figure 8 shows the transition from Figure 7 to *n*-heptane in Figure 8. All data for this range show a change in concentration from *n*-heptane toward methylcyclohexane, both hydrocarbons usually occurring in high concentrations. Curve *A* in Figure 8 also shows a shift from methylcyclohexane in Figure 8 toward Figure 9. All the data indicate that the constants for methylcyclohexane and *n*-heptane define the paraffin-naphthene line for this range very accurately.

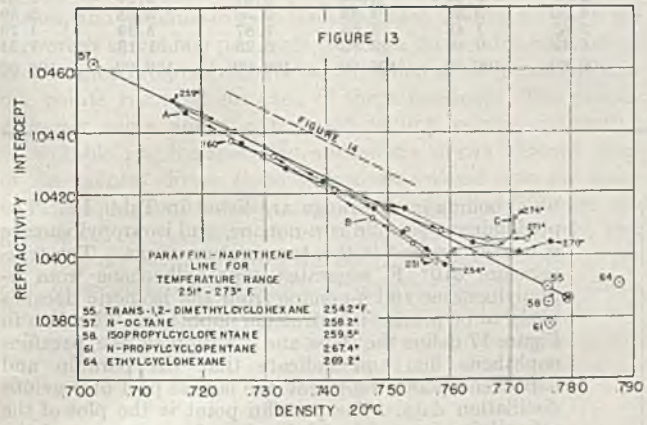
Figure 9. Temperature range, 215° to 222° F. Ethylcyclopentane, 2,2-dimethylhexane, and toluene are the hydrocarbons indicated in this range. The temperature 222° F. is at a point showing a minimum in volume per cent of distillate and separates ethylcyclopentane from the higher-boiling naphthenes in Figure 10. The data shown in Figure 9 indicate that only a few cuts are normally recovered in this range and that these cuts contain a high naphthene concentration. The napthene point for the paraffin-naphthene line is based on the properties of ethylcyclopentane and the paraffin point is based on the properties of 2,2-dimethylhexane, although its boiling point is higher than the indicated temperature range of Figure 9.

Figures 10 and 11. Temperature range, 222° to 235° F. Two or more unidentified naphthenes probably are present in this range together with the paraffins and toluene. The probable paraffins are 2,2-dimethylhexane, 2,5-dimethylhexane, and 2,4-dimethylhexane, with no indication of the presence of 3,3-dimethylhexane. The temperature 235° F. usually indicates a change in the paraffin constituents of the fractions boiling at this point, making a change in the paraffin point of the paraffin-naphthene line advisable. The data for this range in Figures 10 and 11 indicate a small amount of distillate throughout the range except in those cases where the amount of toluene in the sample is high. Since the amount of distillate in the range is usually small for naphthas having no toluene in them, the paraffin-naphthene line cannot be defined as accurately as in some of the other ranges. Figure 11 represents the best solution possible with present knowledge and data. The naphthene point is based on the constants for 1,2,4-trimethylcyclopentane, although its actual presence is uncertain. The paraffin point is determined by the average of the values for 2,2-dimethylhexane, 2,5-dimethylhexane, and 2,4-dimethylhexane.

Figure 10. Temperature range, 235° to 243° F. The naphthene material in this range is characterized by the properties of 1,2,4-trimethylcyclopentane and the probable paraffin is 2,3-dimethylhexane. Toluene may be present in small quantities. Naphthene and paraffin concentration relative to the whole sample normally begins to increase rapidly at 243° F. and a change in both naphthene and paraffin points is indicated by the distillation data.





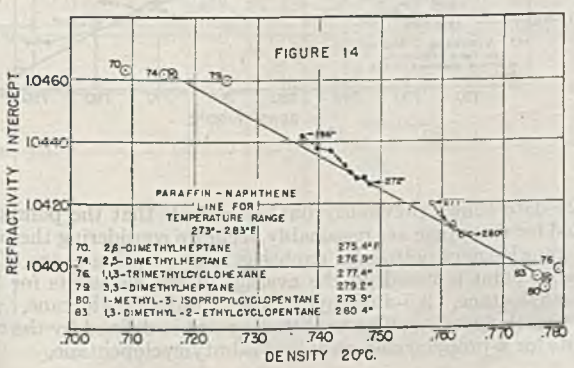


The slope and position of the paraffin-naphthene line are well defined and there are no reversals of direction in the data. The naphthene point is determined by the constants for 1,2,4-trimethylcyclopentane and the paraffin point by the constants for 2,3-dimethylhexane. Here again, the occurrence of 1,2,4-trimethylcyclopentane is uncertain, and more than one naphthene actually may be present.

Figure 12. Temperature range, 243° to 251° F. The predominant naphthenes in this region are *trans*-1,3-dimethylcyclohexane and *trans*-1,4-dimethylcyclohexane, with possibly some 1,1-dimethylcyclohexane, and one or more cyclopentane derivatives with constants similar to those of *trans*-1-methyl-2-ethylcyclopentane. The predominant paraffins are 2-methylheptane, 4-methylheptane, and 3-methylheptane. Small amounts of toluene may be present in some distillations. The temperature 251° F. serves to separate the isomeric octanes from *n*-octane, and the naphthenes in this region from *trans*-1,2-dimethylcyclohexane in Figure 13. The slope and position of the paraffin-naphthene line are well defined by the data in Figure 12. The naphthene point is based on the average of the refractivity intercepts and densities of *trans*-1,4-dimethylcyclohexane, *trans*-1,3-dimethylcyclohexane, and *trans*-1-methyl-2-ethylcyclopentane. Probably some 1,1-dimethylcyclohexane is present but the relative amount is usually small. The paraffin point is defined by the average of the values for 2-methylheptane, 4-methylheptane, and 3-methylheptane. The data for this range confirm this selection of paraffin and naphthene points.

Figure 13. Temperature range, 251° to 273° F. The principal naphthenic constituents in this range appear to be *trans*-1,2-dimethylcyclohexane, *n*-propylcyclopentane, isopropylcyclopentane, and ethylcyclohexane. The paraffin usually present in greatest concentration is *n*-octane, although small amounts of 2,-2-dimethylheptane and 2,4-dimethylheptane may occur. Ethylbenzene is usually present in this range. The temperature 273° F. serves as a division between ethylcyclohexane in this range and the naphthenes in Figure 14, and also as a relative division between ethylbenzene and the 2 aromatics in the next boiling range. Curves *A* and *B* in Figure 13 show a high concentration of naphthenic material in the first fractions of the range, the trend of the data toward the paraffin point because of the presence of *n*-octane, and the reversal near the boiling point of *n*-octane toward another region of high naphthenic concentration. Curves *A*, *B*, and *C* show the shift from Figure 13 toward Figure 14 in the higher-boiling fractions in this range. Curve *C* represents a naphtha almost devoid of the normal paraffins. The data define the paraffin-naphthene line rather well and indicate that the paraffin and naphthene points are properly located. The naphthene point is defined by an average of the constants for *trans*-1,2-dimethylcyclohexane, isopropylcyclopentane, *n*-propylcyclopentane, and ethylcyclohexane. The paraffin point is represented by the values for *n*-octane.

Figures 14 and 15. Temperature range, 273° to 283° F. There is no definite indication of the probable naphthenes in this range and the more probable paraffins are 2,6-dimethylheptane, 2,5-dimethylheptane, and 3,3-dimethylheptane. *p*-Xylene and *m*-xylene usually are present in the fractions distilling within the above temperatures. The temperature 283° F. is used to separate the dimethylheptanes from the methyloctanes, and *p*-xylene and *m*-xylene from *o*-xylene in the following temperature range. One set of data in Figure 14 shows an increase in paraffin concen-



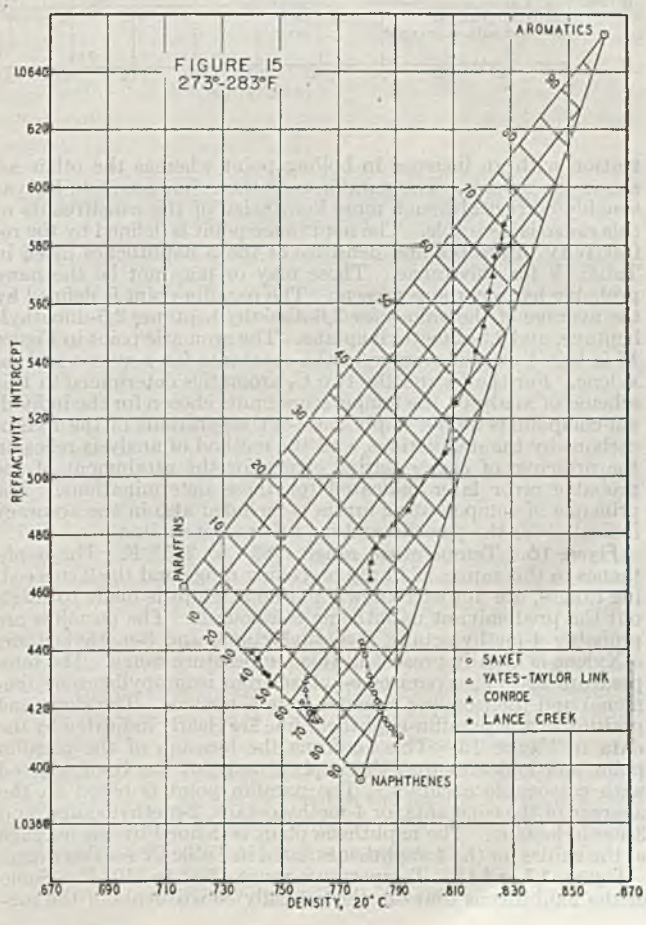
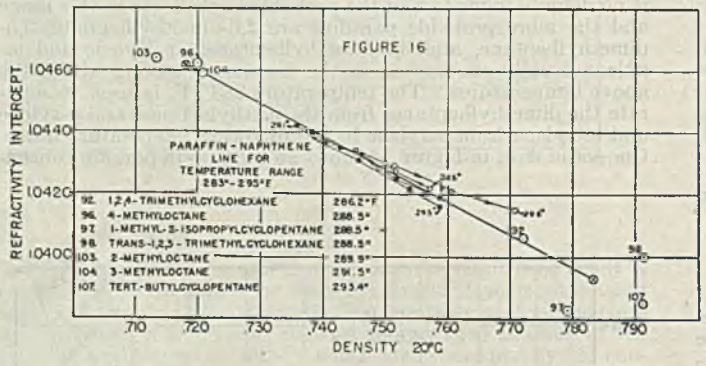


Table V. Volume Per Cent of Individual Hydrocarbons in the 97° to 243° F. Boiling Range for Several Representative Naphthas

Hydrocarbons	Coalinga	Conroe	Hastings	Jennings	KMA Strawn	Old Ocean	Saxet	Segno	Tom O'Connor	Wade City
n-Pentane[a]	0.44	0.33	0.89	1.12	0.40	0.36	1.11	0.55	None	1.28
Cyclopentane	1.76	0.96	1.23	0.67	1.25	0.85	0.73	1.08	1.04	1.36
2,2-Dimethylbutane	0.25	0.39	0.78	0.42	0.16	0.58	0.32	0.74	0.60	0.57
2,3-Dimethylbutane	2.21	1.46	1.97	2.05	1.74	1.88	1.25	1.94	2.09	1.27
2-Methylpentane	2.56	2.89	2.16	3.47	4.39	5.23	1.33	3.71	4.61	1.14
3-Methylpentane	1.89	2.09	1.81	1.03	3.80	3.36	0.88	2.22	2.62	1.52
n-Hexane	7.75	6.44	5.18	9.15	12.71	10.18	2.29	8.84	7.76	2.04
Methylcyclopentane	10.29	6.51	7.42	5.01	7.52	5.42	5.52	6.40	6.70	7.39
2,2-Dimethylpentane 2,4-Dimethylpentane	0.51	0.96	2.55	1.46	0.79	1.52	3.51	1.38	1.72	2.27
Benzene	2.22	3.27	0.16	3.61	0.59	2.28	None	1.82	0.58	0.38
Cyclohexane	7.63	10.40	13.66	7.13	4.68	7.30	15.07	9.64	10.94	14.93
1,1-Dimethylcyclopentane	1.17	0.35	0.70	1.00	0.45	0.83	1.30	0.59	0.68	0.96
2,3-Dimethylpentane 2-Methylhexane	2.69	3.45	4.53	6.14	5.81	6.71	2.39	5.32	5.79	2.27
trans-1,3-Dimethylcyclopentane	4.92	2.62	5.78	2.53	7.08	3.87	4.33	2.98	4.36	3.97
trans-1,2-Dimethylcyclopentane	7.05	1.59	2.35	1.02	5.29	1.41	3.12	1.29	2.64	3.94
3-Methylhexane	3.30	1.90	1.49	2.25	3.90	2.88	1.25	2.01	3.29	1.32
n-Heptane	5.94	6.90	2.43	8.42	11.32	10.92	1.69	7.96	4.96	0.86
Methylcyclohexane	14.55	22.00	32.39	18.07	12.29	17.20	37.48	21.58	23.02	35.62
Ethylcyclopentane	4.38	2.03	3.58	2.34	3.65	3.48	4.09	2.70	3.22	5.16
2,2-Dimethylhexane	0.57	0.71	0.77	2.39	0.93	1.51	1.35	1.27	1.51	1.39
2,5-Dimethylhexane 2,4-Dimethylhexane	0.56	2.70	2.02	2.13	0.51	1.04	2.11	1.69	0.33	1.19
Toluene	7.94	16.19	0.77	12.02	2.57	5.87	None	9.61	3.39	2.64
Trimethylcyclopentanes (?)	7.23	3.56	3.05	3.71	4.56	3.38	4.42	2.56	3.58	3.69
2,3-Dimethylhexane	1.30	0.22	1.33	2.39	2.49	1.45	1.66	1.87	3.39	1.23
A trimethylcyclopentane (?)	0.89	0.08	1.00	0.47	1.12	0.49	2.80	0.25	1.18	1.61
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[a] *n*-Pentane boiling below 97.0° F. not included in these figures.

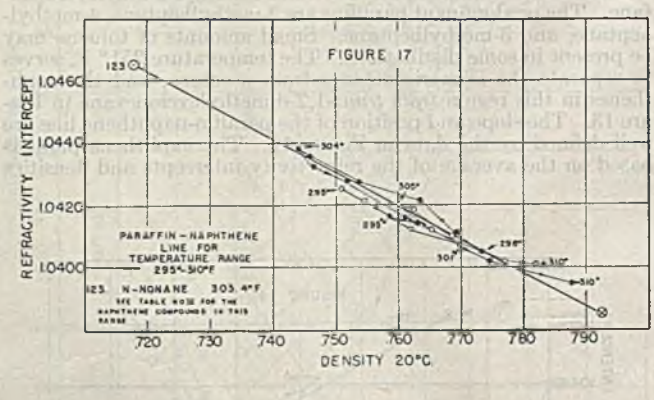


tration with an increase in boiling point whereas the other set shows the reverse. The paraffin-naphthene line seems to be reasonably correct although more knowledge of the constituents of this range is desirable. The naphthene point is defined by the refractivity intercepts and densities of the 3 naphthenes listed in Table IV for this range. These may or may not be the more probable hydrocarbons present. The paraffin point is defined by the average of the values for 2,6-dimethylheptane, 2,5-dimethylheptane, and 3,3-dimethylheptane. The aromatic point in Figure 15 is based on the average of the constants for *p*-xylene and *m*-xylene. For the C_8 and the two C_9 aromatics determined in this scheme of analysis, the temperature limits chosen for the individual compounds do not imply clear-cut separations of the hydrocarbons by the distillations, and the method of analysis relies on the principle of compensating errors for the attainment of the probable error later indicated for these determinations. The principle of compensating errors is included also in the accuracy indicated for the paraffin and naphthene determinations.

Figure 16. Temperature range, 283° to 295° F. The naphthenes in this range, as in the preceding range and the 2 succeeding ranges, are not well known and no attempt is made to single out the predominant naphthenic compounds. The paraffins are probably 4-methyloctane, 2-methyloctane, and 3-methyloctane. *o*-Xylene is usually present in this temperature range. The temperature 295° F. separates *o*-xylene from isopropylbenzene (cumene) and the isomeric nonanes from *n*-nonane. The slope and position of the paraffin-naphthene line are clearly indicated by the data in Figure 16. This confirms the location of the paraffin point and indicates that the naphthene point has been selected with reasonable accuracy. The paraffin point is based on the average of the constants for 4-methyloctane, 2-methyloctane, and 3-methyloctane. The naphthene point is defined by the average of the values for the 4 naphthenes listed in Table IV for this range.

Figures 17 and 18. Temperature range, 295° to 310° F. Some of the naphthenes that are theoretically constituents of the material boiling in this range are listed in Table IV. The predominant paraffin is *n*-nonane, and isopropylbenzene is usually present in this temperature range. The temperature 310° F. separates isopropylbenzene from *n*-propylbenzene and *n*-nonane from the isomeric decanes likely to be present in petroleum naphthas. The data in Figure 17 define the slope and position of the paraffin-naphthene line and indicate that the paraffin and naphthene points represent the largest part of previous distillation data. The paraffin point is the plot of the refractivity intercept and density of *n*-nonane, and the naphthene point is based on the average of the constants for the compounds listed in Table IV for this range.

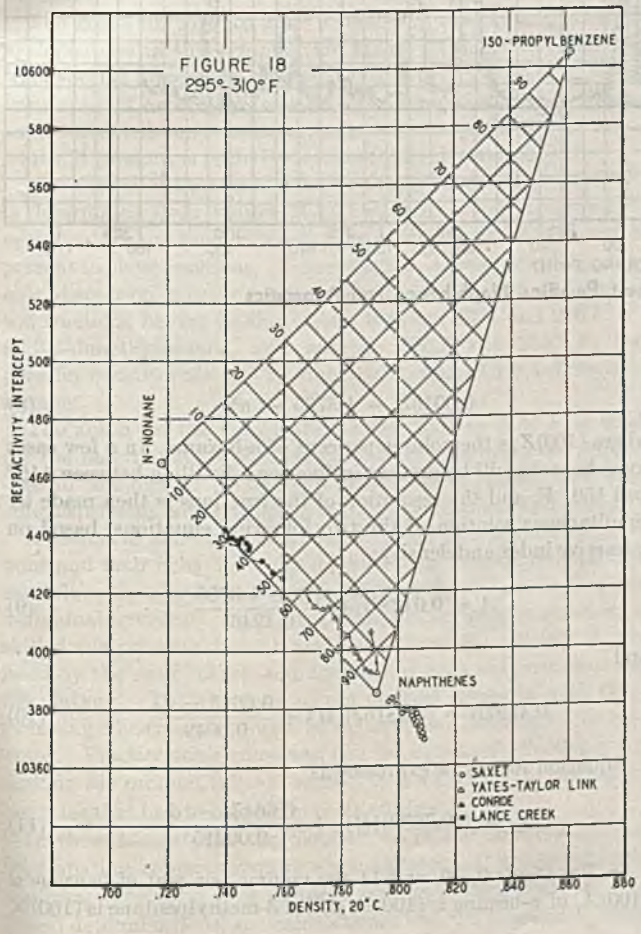
Figure 19. Temperature range, 310° to 320° F. The naphthenes in this range are represented by the values for *n*-propylcyclohexane and *n*-butylcyclopentane. The paraffins present are probably 2,6-dimethyloctane, 3,5-dimethyloctane, 2,5-dimethyloctane, and 2,7-dimethyloctane. *n*-Propylbenzene usually is present in the range. The temperature 320° F. was chosen to include all the *n*-propylbenzene in the naphthas. The data in Figure 19 do not define the paraffin-naphthene line as well as most of the

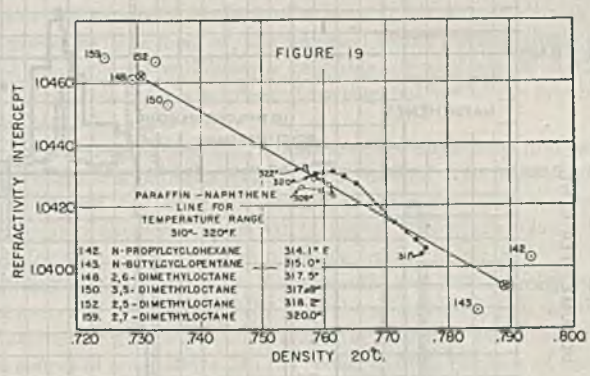


other data shown previously but do indicate that the points selected for this range are reasonably accurate considering the present knowledge of petroleum naphthas in this boiling range. The paraffin point is based on the average of the constants for 2,6-dimethyloctane, 3,5-dimethyloctane, 2,5-dimethyloctane, and 2,7-dimethyloctane. The naphthene point is defined by the constants for *n*-propylcyclohexane and *n*-butylcyclopentane.

No data for the Conroe naphtha are shown in Figure 18, since the distillation of this sample was discontinued at 295° F. For the sake of clarity, not all data obtained in the column distillations are shown in Figures 4 to 19, as many of the points would have coincided and overlapped. The data omitted would not have altered the general shape or extent of any of the curves but, on the contrary, would have strengthened the conclusions drawn. The small directional arrows indicated on the curves show the increase in boiling point of the fractions. The fact that some of the points shown on Figure 18 fall beyond the boundaries of the triangle has several implications: (1) the literature values of the constants for some of the pure compounds are in error; (2) undue weight was given to certain compounds in defining the shape of the particular triangle; or (3) certain naphthas will exhibit unusual characteristics not encountered in most cases. Unusual characteristics would include the appearance of significant quantities of bi- or dicyclic naphthenic compounds in the higher-boiling portion of the naphtha.

Having determined the volume per cent of aromatics, naphthenes, and paraffins in each fraction, these volume per cents are converted to volume per cents based on the total sample which are summed progressively for each fraction at the corrected boiling points recorded for each of these fractions. The volume sum per cents and the recorded boiling points are plotted on suitable graph paper and curves are drawn through each of the points. From these curves the volume sum per cents of aromatics, naphthenes, and paraffins are read at each degree from 97° to 320° F. The difference between the volume sum per cents for any 2 successive degrees is the volume per cent of aromatics, naphthenes, or paraffins distilled throughout that specific degree. From these data, curves indicating the volume per cent per Fahrenheit degree of each of the hydrocarbon types are plotted as shown on Figure 20. These charts show the results of the analysis in graphical form. The amounts of the individual aromatics, and the total amounts of naphthenes and paraffins have been determined from the data obtained, and the amounts of individual naphthenes and paraffins, or any desired group of compounds, may be estimated from the curves shown on Figure 20. Further examination of the data obtained by these analyses will give the amounts of most of the individual hydrocarbons having boiling points below 243° F. Table V gives the amounts of the individual hydrocarbons boiling below 243° F. in





10 representative naphthas as determined by the procedure outlined in the following paragraphs. A paper in preparation will give additional analyses together with some correlations that have been obtained from a study of the data. In general, the data will substantiate most of the conclusions drawn by Forziati, Willingham, Mair, and Rossini (*3*). Unfortunately, two of the samples indicated in Table V, Saxet and Wade City, were prepared by the refineries in such a manner that the total quantity of hexanes naturally occurring in the crude oils was not retained in the naphthas. This was indicated by the Engler distillation initial boiling points of the samples which were 170° and 162° F., respectively. A study of similar analyses reported by other laboratories indicates that in some cases a similar deficiency must have existed in the samples analyzed.

PROCEDURE FOR ESTIMATING INDIVIDUAL HYDROCARBONS IN TEMPERATURE RANGE 97° TO 243° F.

The estimations will not include any material having boiling points below *n*-pentane, and *n*-pentane will be indicated only in such amount as occurs in a mixture with higher-boiling material. Therefore the first fraction considered in this procedure is that fraction whose boiling point shows a decided rise, 5° or more, above the boiling point of *n*-pentane at about 97° F. An increase in the refractive index for the sodium D line (n_D^{20}) will accompany this temperature rise. This increase will reach a peak at about 121° F. and then decrease until the reading is 1.3750 or lower, at approximately 136° F. From 97° to 136° F. the material present in the fractions will consist of cyclopentane and *n*-pentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. The total quantity of cyclopentane and 2,2-dimethylbutane is determined by the equal-area method of division from a plot of temperature against volume per cent distilled from 97° to 136° F. The difference between this quantity and the amount of cyclopentane determined from Figure 4 is the amount of 2,2-dimethylbutane in the sample.

From the point where the refractive index recedes to 1.3750 at about 136° F. to the point where the index and the density reach a minimum due to a maximum concentration of 2-methylpentane at about 141° F., all the material in the fractions will be 2,3-dimethylbutane and 2-methylpentane. The percentage of 2,3-dimethylbutane is calculated from the equation

$$0.0036Y = n_D^{20} - 1.3714 \qquad (6)$$

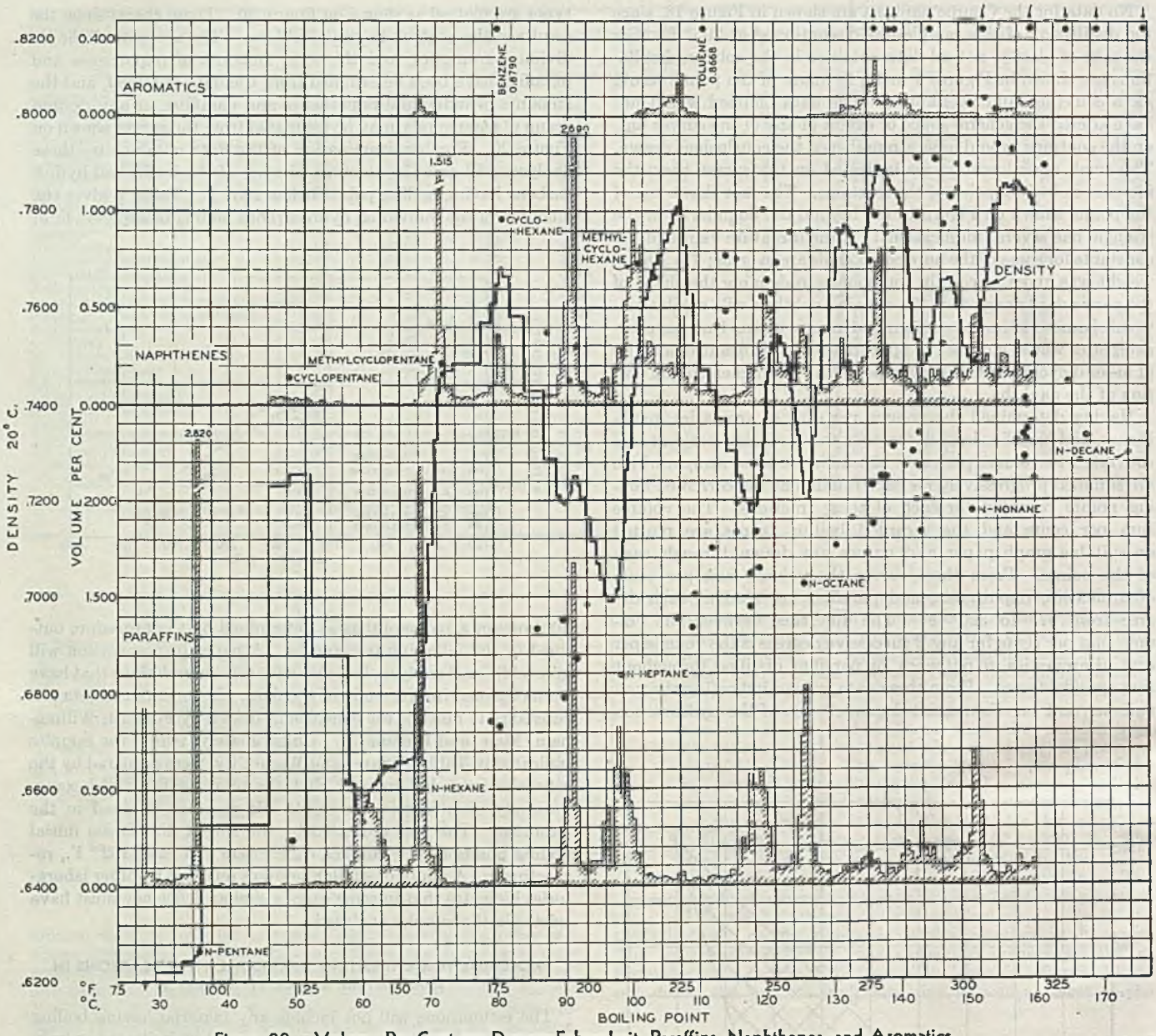


Figure 20. Volume Per Cent per Degree Fahrenheit, Paraffins, Naphthenes, and Aromatics

where (100)Y = volume per cent of 2,3-dimethylbutane and n_D^{20} is the refractive index of the fraction. If there are several fractions in this minimum region, Equation 6 is used to the middle of the region.

From this minimum to about 145° F. the material is 2-methylpentane and 3-methylpentane, and the amount of 2-methylpentane is determined by use of the equation

$$0.0051W = 1.3765 - n_D^{20} \quad (7)$$

where (100)W is the volume per cent of 2-methylpentane. Equation 7 is used up to and including that fraction showing a "low" in the volume per cent of 2-methylpentane indicated by the equation, which occurs at about 145° F. An increase in the amount of 2-methylpentane shown by the use of the equation indicates that n-hexane is responsible for this increase.

From the above "low" in the amount of 2-methylpentane calculated to a temperature of 150° F., the fractions usually contain only 3-methylpentane and n-hexane, the amount of n-hexane being calculated by use of the equation

$$0.0016Z = 1.3765 - n_D^{20} \quad (8)$$

where (100)Z is the volume per cent of n-hexane. In a few cases some benzene will be present in fractions distilling between 146° and 150° F. and the resolution of the fractions is then made by simultaneous solution of the two following equations, based on refractive index and density:

$$A = 0.0128B + \frac{n_D^{20} - 1.3765}{0.1246} \quad (9)$$

and

$$0.4392B = (43.8163)(H) + \frac{0.6643 - d_f}{0.0049} \quad (10)$$

Equation 10 may be expressed as

$$B = (99.7639)(H) + \frac{0.6643 - d_f}{0.00215} \quad (11)$$

In Equations 9, 10, and 11 the volume per cent of benzene is (100)A, of n-hexane is (100)B, and of 3-methylpentane is (100) ×

$(1 - A - B)$. H is from Equation 9 and is $\left(\frac{n_D^{20} - 1.3765}{0.1246}\right)$. All material in the temperature range from 150° to 167° F. will be *n*-hexane, methylcyclopentane, and benzene, if benzene is present in the sample. Methylcyclopentane is determined in the usual manner by use of the triangular graph for this temperature range. The base of this triangle is shown in Figure 5. Benzene is determined by the use of the specific dispersion equations, and by difference the remainder of the material in the fraction is *n*-hexane.

All material in the range 167° to 185° F. is cyclohexane, 2,2-dimethylpentane, 2,4-dimethylpentane, and benzene, if present. No differentiation is made between the 2 dimethylpentanes, cyclohexane is determined by the use of Figure 6, and benzene by the specific dispersion equations.

No aromatics occur in the fractions having boiling points between 185° and 203° F. The total amounts of naphthenes and paraffins in the range are determined from the use of Figure 7. All the naphthenic material in the fractions boiling between 185° and 191.5° F. is 1,1-dimethylcyclopentane. All paraffinic material within the range 185° to 196.5° F. is a mixture of 2,3-dimethylpentane and 2-methylhexane and is reported as such. From 191.5° to 196.5° F. the naphthenic component is *trans*-1,3-dimethylcyclopentane. The paraffinic material distilling between 196.5° and 203° F. is 3-methylhexane and the naphthenic material in this range is *trans*-1,2-dimethylcyclopentane. If Figure 7 indicates that the first fraction in this range from 185° to 203° F. still contains cyclohexane as the predominant naphthene, the naphthene material should be recorded as cyclohexane instead of 1,1-dimethylcyclopentane.

The triangular graph constructed on the base shown in Figure 8 is used for the determination of the amount of methylcyclohexane in the sample and is used from 203° to 215° F. Toluene is calculated from specific dispersions, and *n*-heptane is obtained by difference.

The graph for 215° to 222° F. indicates the amount of ethylcyclopentane in this temperature range. Toluene is calculated from specific dispersions, and the remainder of the material in the fractions is 2,2-dimethylhexane. (The amount of ethylcyclopentane indicated may include some other naphthenic material, which, if present, is probably a trimethylcyclopentane.)

The naphthenic material in boiling range from 222° to 235° F. is determined from Figure 11 and is recorded as a trimethylcyclopentane mixture. Two or more of these compounds may be present in these fractions. Toluene again is determined by specific dispersion measurements. The balance of the material in the fractions having boiling points between 222° and 226.3° F. is 2,2-dimethylhexane, and between 226.3 and 235° F. the paraffin constituents are 2,5-dimethylhexane and 2,4-dimethylhexane.

The graph for the temperature range 235° to 243° F. is used for the determination of what probably is a trimethylcyclopentane in this region. Toluene, if present, is calculated from specific dispersions, and remaining material is 2,3-dimethylhexane.

A technical aide without a knowledge of petroleum hydrocarbons and their behavior when distilled from petroleum naphthas can follow the above procedure for estimating the amounts of the individual hydrocarbons in a naphtha, but for greater accuracy a skilled analyst should check and complement the procedure outlined by the use of other combinations of data obtained in these distillations. The accuracy of the method increases with fractionating efficiencies and with larger charges of sample to the columns. Fractionating efficiency can be increased effectively by making the product take-off rates 2 to 5 ml. per hour instead of the rates that had to be used in these studies.

In these laboratories the distillations of the naphthas in the fractionating columns require approximately 50 hours for each naphtha. The total time required for the distillation, the analytical determinations, the calculations, and the plotting is from 80 to 100 hours. The distillations and analytical determinations require the services of technical personnel, whereas the calculations and plotting can be done by high-school students with a minimum of supervision.

ACCURACY OF THE METHOD

The accuracy of the determination of the aromatics by the use of specific dispersions is discussed by Thorne, Murphy, and Ball (*8*), and has been checked by analysis of synthetic mixtures containing known amounts of the individual aromatic compounds. When the aromatic content of a normal virgin naphtha is determined by this method, the reported result for any single aromatic compound will have a probable error of about ±0.2%. This probable error was checked by the analyses of the synthetic mixtures.

The accuracy of the determination of the naphthene and paraffin content of a naphtha has not been checked experimentally but from factors that can be estimated, it is believed that the determination of these two types will be within 10% of the reported result for that portion of the naphtha boiling below 243° F., and within 25% for that portion between 243° and 320° F. The greatest source of error below 243° F. is the nonadditivity of mixtures of aromatics with naphthenes and with paraffins, while the greatest source of error above 243° F. seems to be in the lack of knowledge as to the constitution of this portion of the naphtha.

For the estimations of individual naphthene and paraffin hydrocarbons it is felt that the estimations are correct to ±0.3% by volume of the total amount of sample charged to the columns when the volume per cent of the individual hydrocarbon is below 3% of the charge. When the amount is more than 3%, the accuracy of the estimate should be within ±10% of the amount reported. While overlapping of compounds into adjacent fractions occurs at the temperature divisions used in the scheme of analysis due to the holdup of the columns and a lack of sufficient fractionating efficiency, such overlapping is compensatory and should not be enough to cause errors exceeding the above limits.

The possible effects of the presence of sulfur compounds on the determinations are discussed in a Bureau of Mines report by Ball and Thorne (*1*). The conclusion reached is that 0.2% by weight of sulfur in a naphtha will not affect the final results of analyses for the three hydrocarbon types. Another of this series of papers by the Bureau of Mines (7) discusses a rapid method of analyzing naphthas for benzene, toluene, and seven-carbon-atom naphthenes by the use of specific dispersions and refractivity intercept–density diagrams.

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Determination of Total Solids in Resin Solutions

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Total solids in solutions of heat-stable resins in volatile solvents can be determined rapidly and with an average accuracy of 0.3% by first dissolving samples in a suitable nonvolatile, high-boiling solvent and then heating them in vacuo at 100° C. for 20 to 30 minutes while they are being agitated. If the proper high-boiling solvent were selected, this general method could be extended to the determination of any nonvolatile stable material in admixture with any volatile substance.

A NEW method for the routine determination of total solids in resin solutions has been developed, which is applicable to solutions of all resins, provided the resins do not change in molecular weight through the evolution of gases or moisture on heating. This "solution-evacuation" method consists essentially of dissolving a sample of resin solution in a high-boiling solvent, heating the resulting solution under vacuum to remove only the solvent in which the resin was dissolved originally, but not the high-boiling solvent, and observing the loss in weight of the system. The solution-evacuation method is much more rapid and accurate than any of the usual methods which depend upon heating at atmospheric pressure, either alone (*1*, *2*) or after the addition of a suitable high-boiling liquid (*4*, *5*, *6*), or upon heating in vacuo (*3*).

As a possible means of determining total solids, the measurement of several physical constants of resin solutions was considered. Among these, specific gravity and refractive index seemed most likely to give a useful method, but proved to be impractical. The high viscosity of the solutions made the determination of specific gravity with a Westphal balance practically impossible and the filling of a pycnometer a long and difficult task. The correlation between refractive index and total solids was only approximate and offered no promise of giving the necessary accuracy.

The resins from which solutions were prepared were definitely acidic; consequently, the acid numbers of their solutions possibly could give a measure of the total solids. However, the acid number could not be measured with the desired accuracy without very careful work. The acid number of the resins was about 60, that of the solutions was about 45. Thus, an error of one unit in the measurement of the acid number corresponds to a variation in the total solids of nearly 2%. Furthermore, usual small variations in the acid number of the solid resin also would cause an error in this method.

Direct methods also were considered. Evaporation of the solvent in a vacuum oven offered only a slight advantage over an air oven, because of poor conduction of heat to the sample.

The solution-evacuation method, like the direct methods, involves separating the solvent from the solid resin. However, in order to accomplish this rapidly and completely, without entrainment as occurs in the oven method, the sample of resin solution must be dissolved in dibutyl phthalate. This technique keeps the system, from which the solvent is being removed, liquid throughout the determination. The solution in dibutyl phthalate, contained in a small Erlenmeyer flask, is heated and evacuated, and its loss in weight determined. This loss in weight is the weight of the volatile solvent. Thus, the per cent total solids of the sample is calculated readily. Such determinations require 35 minutes to 1 hour. The average accuracy and precision of the results, expressed as per cent total solids, are 0.2%.

In order to remove the volatile solvent completely from the solution and at the same time avoid mechanical loss of any part of the sample, it was found necessary to provide some surface at which the bubbles of solvent vapor could readily form. This was accomplished by placing about 6 polished steel balls in the flask and slowly rocking it.

Although the solution-evacuation method has been applied only to solutions of resins in nonaqueous solvents, it is probable that its use could be extended to water solutions if one of the commercially available polyethylene glycols were used to replace the dibutyl phthalate. In fact, by adding a suitable high-boiling solvent to the sample, this method could be applied in the determination of nonvolatile stable material in admixture with any volatile substance.

APPARATUS

An apparatus was designed to rock two flasks in an oil bath in such a manner that the axis of rotation passes through the base of the flasks. This arrangement prevents any unnecessary motion of the flasks and attendant splashing of the hot oil. The power for this rocking is supplied by a small electric motor with a reduction gear assembly. (The motor used in this investigation was a Ratiomotor, Type MB58328, manufactured by the Boston Gear Works, Philadelphia, Pa.) The rocking arm is attached to an eccentric on the motor by means of a connecting rod. The built-in reduction gear on this motor gives the driving shaft a speed of 50 r.p.m. The frame for holding the flasks was designed to allow the flasks to be raised from and lowered into the oil bath. Figure 1 shows the construction of the rocking device.

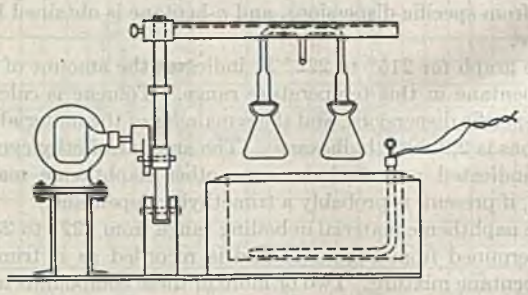

Figure 1. Construction Details of Rocking Device

The oil bath is constructed of sheet steel and is lagged with a 1.25-cm. (0.5-inch) layer of 85% magnesia. The bath liquid is heated with a 200-watt tubular immersion heater bent and placed to deliver the heat near the bottom of the bath. The heat input is controlled by a small (5-ampere) Variac.

Fifty-milliliter Erlenmeyer flasks fitted with 25/15 spherical joints are attached by means of clamps to a two-outlet manifold also fitted with spherical joints each of the same size. This manifold is attached to the rocking device and is connected by means of heavy-walled rubber tubing to a manometer and two solvent traps of conventional design. The two solvent traps are connected in series and are cooled in a mixture of dry ice and Cellosolve. The system is evacuated by means of a Hy-vac oil pump. The vacuum system also contains a needle valve which opens to the atmosphere and is connected to the system between the manometer and flasks. This valve permits the control of the pressure in the flasks by bleeding air into the system. Figure 2 shows the relationships of the various parts of the apparatus.

REAGENT

Any good grade of dibutyl phthalate may be used in this determination. All the grades tested contained small amounts of volatile matter. It is highly advantageous to reduce the amount of volatile matter from its normal value of 23 to 25 mg. per 10 ml. to about 5 mg. per 10 ml. by sparging it with dry air for 48 hours.

PROCEDURE

Place about 6 steel balls, 0.77 cm. ($^5/_{16}$ inch) in diameter, in a 50-ml. Erlenmeyer flask, add 10 ml. of dibutyl phthalate, and weigh (W_1). Add 2 to 3 ml. of the resin solution, using a 5-ml. pipet with the tip cut off, and taking care to get all the resin solution into the dibutyl phthalate with none of the resin on the side of the flask or the joint. This operation is made easier if the solution adhering to the outside of the pipet is removed with a paper towel or other suitable material before the sample is delivered to the flask. Weigh the flask after adding the resin solution (W_2). Then, $W_2 - W_1$ represents the weight of the sample. All weighings are made to the nearest milligram. A second flask is charged in the same way.

Set the flasks firmly in place on the apparatus and clamp them in position. Lower them into the bath, which is maintained at 100° ± 2° C. by means of the Variac. With the needle valve open, start the vacuum pump and set the rocking device in motion. By closing the needle valve, slowly reduce the pressure in the flasks at such a rate that moderate boiling of the solution is maintained. The full vacuum of the pump should be attained in 5 minutes. Continue the determination for the time required by the sample being examined.

Admit air to the apparatus by opening the needle valve; then stop the pump and rocking device. Remove the flasks and allow them to cool. Remove the adhering oil by rinsing the flasks with methyl acetate or other suitable solvent and wiping them carefully with tissue paper. Weigh the cooled flasks (W_3). Then, $W_3 - W_1$ is the weight of the solids. Run a blank to determine the loss in weight of the dibutyl phthalate.

$$\frac{(W_3 - W_1 + B) \times 100}{W_2 - W_1} = \% \text{ total solids}$$

where B represents the blank value for a particular lot of dibutyl phthalate.

APPLICATION OF THE METHOD

In order to establish the proper conditions for the determination of total solids of a variety of resin solutions, as well as to ascertain the practical accuracy of the method, a series of solutions of known total solids content was prepared and analyzed.

A weighed amount of Flexalyn (diethylene glycol ester of rosin, registered in U. S. Patent Office by Hercules Powder Company) was dissolved in sufficient 50 D solvent (principally xylenes) to give approximately an 80% solution. The resin was dissolved by heating under a reflux condenser. After being cooled, the solution was weighed and its actual solids content was calculated. The total solids in this solution was determined experimentally by the foregoing procedure. The sample sizes usually were between 1.5 and 2.0 grams and the final pressure was 5 mm. or less. The effects of time of heating, temperature of the oil bath, and variations in sample size were studied.

The results of these experiments (Table I) indicate that correct results are obtained when the solutions are heated for 45 minutes at 100° C. or for 30 minutes at 110° C.

Solutions of Petrex 5 (a glycol ester of a terpene–maleic anhydride adduct, registered in U. S. Patent Office by Hercules Powder Company), a hard resin, in ethyl acetate, ethyl alcohol, methyl ethyl ketone, and toluene were prepared in the manner described for Flexalyn solutions. Since the Petrex 5 itself contained volatile substances, the solid resin was first analyzed by the solution-evacuation procedure and found to lose 0.8% of its weight. This value was used as a correction factor in calculating compositions of solutions of Petrex 5 in the various solvents.

Table I. Total Solids of Flexalyn Solutions in 50 D Solvent (Chiefly Xylenes)

Time of Heating under Vacuum	Temperature of Bath	Total Solids in Flexalyn Solution		
		Calcd	Found	Average found
Min.	° *C.*	%	%	%
20	100 ± 1	79.9	80.8, 81.1	81.0
30	100 ± 1	79.9	80.9, 80.7 86.8[a], 80.7	80.8
45[b]	100 ± 1	79.9	80.1, 79.6 79.7, 79.7 80.1, 80.2	79.9
20	110 ± 2	79.9	80.9, 81.0 80.3, 80.3	80.6
30[c]	110 ± 2	79.9	79.8, 79.7 79.7, 80.0 80.3, 80.3	80.0

[a] Arbitrarily rejected in computing average.
[b] Sample sizes ranged from 1.3 to 2.9 grams.
[c] Sample sizes ranged from 1.3 to 3.7 grams. High values, 80.3 and 80.3, were obtained on samples of 3.65 and 3.67 grams.

Table II. Total Solids of Petrex 5 in Various Solvents

Sample Weight	Time of Heating under Vacuum	Temperature of Bath	Total Solids in Solution	
			Calcd.	Found
Grams	*Min.*	° *C.*	%	%
		In Ethyl Acetate		
2.195	30	100	73.6	73.8
2.160	30	100	73.6	73.8
2.236	20	100	73.6	73.7
2.309	20	100	73.6	73.5
2.312	20	110	73.6	73.7
2.194	20	110	73.6	73.6
		In Ethyl Alcohol		
1.770	30	100	74.4	74.9
2.008	30	100	74.4	74.8
1.867	30	100	74.4	75.0
2.480	30	100	74.4	74.9
2.112	20	100	74.4	74.9
2.183	20	100	74.4	74.9
2.278	15	110	74.4	74.5
2.485	15	110	74.4	74.8
		In Methyl Ethyl Ketone		
1.993	30	100	74.6	74.5
2.059	30	100	74.6	74.6
2.030	20	100	74.6	74.8
2.359	20	100	74.6	74.7
2.156	20	110	74.6	74.5
2.323	20	110	74.6	74.6
		In Toluene		
2.108	30	100	74.1	74.0
2.500	30	100	74.1	73.6
1.894	30	100	74.1	73.7
2.746	30	100	74.1	73.4
2.042	20	100	74.1	73.7
2.841	20	100	74.1	73.8
3.181	15	110	74.1	73.7
3.116	15	110	74.1	73.8

The results presented in Table II show that the solvent can be completely removed from these solutions at either 100° or 110° C. by heating for 20 minutes or longer. The values for Petrex 5 in ethyl alcohol are slightly high. It may be that in preparing the solution by heating the resin, which is appreciably acidic, a small amount of the alcohol may have been esterified.

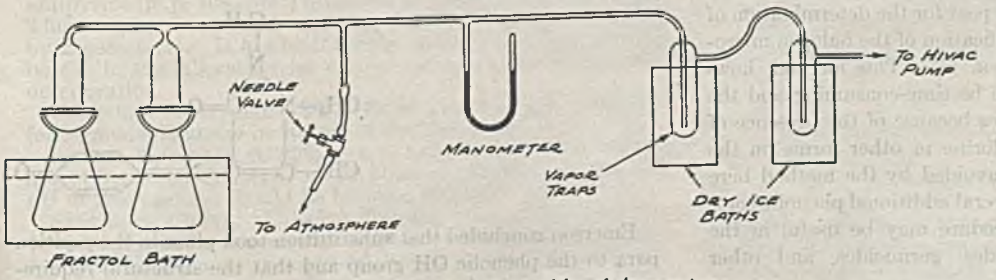

Figure 2. Complete Assembly of Apparatus

Solutions of Petrex 7HT (a glycol ester of a terpene–maleic anhydride adduct, registered in U. S. Patent Office by Hercules Powder Company), a soft resin, in ethyl acetate, ethyl alcohol, methyl ethyl ketone, and "mixed solvent" (chiefly toluene) were prepared as described for Flexalyn. The solid resin, when analyzed by the solution-evacuation procedure, lost 1.60% of its weight. This value was used as a correction factor in calculating the compositions of the

Table III. Total Solids of Petrex 7HT in Various Solvents

Sample Weight	Time of Heating under Vacuum	Temperature of Bath	Total Solids in Solutions	
			Calcd.	Found
Grams	*Min.*	*° C.*	*%*	*%*
		In Ethyl Acetate		
2.226	30	100	73.3	73.5
2.134	30	100	73.3	73.5
2.233	20	100	73.3	73.8
2.328	20	100	73.3	73.8
2.245	15	110	73.3	73.4
2.272	15	110	73.3	73.3
		In Ethyl Alcohol		
2.023	45	100	74.3	74.8
2.263	45	100	74.3	74.7
2.074	30	100	74.3	74.9
1.980	30	100	74.3	75.0
2.221	30	110	74.3	75.0
2.252	30	110	74.3	74.8
2.229	15	110	74.3	75.3
2.026	15	110	74.3	75.3
		In Methyl Ethyl Ketone		
2.350	30	100	74.4	74.5
2.159	30	100	74.4	74.5
2.532	20	100	74.4	74.6
2.162	20	100	74.4	74.7
1.998	15	110	74.4	74.3
2.459	15	110	74.4	74.3
		In Mixed Solvent (Chiefly Toluene)		
1.756	30	100	73.5	73.3
1.932	30	100	73.5	73.3
2.963	30	100	73.5	73.4
2.540	30	100	73.5	73.3
2.320	20	100	73.5	73.3
2.396	20	100	73.5	72.9
2.651	20	100	73.5	73.4
2.711	20	100	73.5	73.4
2.399	15	100	73.5	73.7
2.601	15	100	73.5	73.3

solutions of Petrex 7HT in the various solvents. These solutions were analyzed by the solution-evacuation method.

The data obtained on these solutions (Table III) are similar to those obtained with the other solutions. Again the slightly high values obtained when using alcohol as solvent may be explained on the basis of esterification.

The data recorded in Tables II and III are all consecutive results; none has been discarded. They indicate that analyses by this procedure, expressed as per cent total solids, have an average accuracy and precision of 0.2%.

SUMMARY

This paper describes a new technique for the determination of the total solids in solutions of synthetic resins in nonaqueous solvents, which has been used as a routine control method for nearly two years. Results of higher accuracy are obtained more rapidly than by any method previously used. It is possible that this method can be extended to aqueous solutions by using one of the polyethylene glycols in place of dibutyl phthalate.

ACKNOWLEDGMENT

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Quantitative Determination of Phenolic Fungicides

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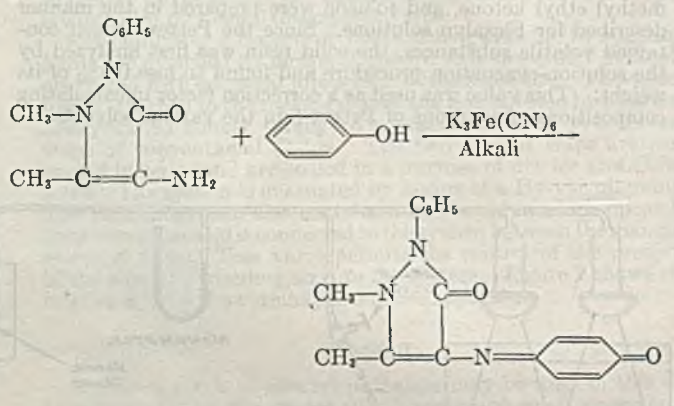
The color reaction of 4-aminoantipyrine with the textile mildew preventive 2,2′-methylenebis[4-chlorophenol] in the presence of potassium ferricyanide and dilute sodium carbonate has been found adaptable to quantitative analysis for this phenolic material and has been used for its determination in fabric. Absorption curves and standard calibration curves are given for several other commercially important phenols, with the suggestion that this color reaction may find application in the quantitative determination of many phenolic fungicides, germicides, and other materials.

RECENTLY certain fungicidal materials have come into extensive use as mildew preventives for fabrics destined to be used in tropical areas (*4*). One of the compounds which has been most widely used for this purpose is 2,2′-methylenebis[4-chlorophenol], known to the textile trade as Compound G-4. The method most commonly used in the past for the determination of this compound on fabric is a modification of the halogen microprocedure of Willard and Thompson (*5*). This method, however, has been found in practice to be time-consuming and the results to be uncertain in some cases because of the presence of inorganic or organically bound chlorine in other forms on the fabric. Both these difficulties are avoided by the method here described. Preliminary data on several additional phenolic compounds suggest that the new procedure may be useful in the determination of phenolic fungicides, germicides, and other materials.

The reaction used is based on the observation made by Emerson that 4-aminoantipyrine condenses with aromatic amines (*1*) in the presence of acid oxidizing agents and with phenols (*2*, *3*) in the presence of alkaline oxidizing agents to yield a series of antipyrine dyes. On the basis of this reaction Emerson proposed a color test for phenols (*2*). The structure suggested for the dyes produced in the reaction is shown in the following example for phenol:



Emerson concluded that substitution took place in the position para to the phenolic OH group and that the structural requirements for the reaction were as follows:

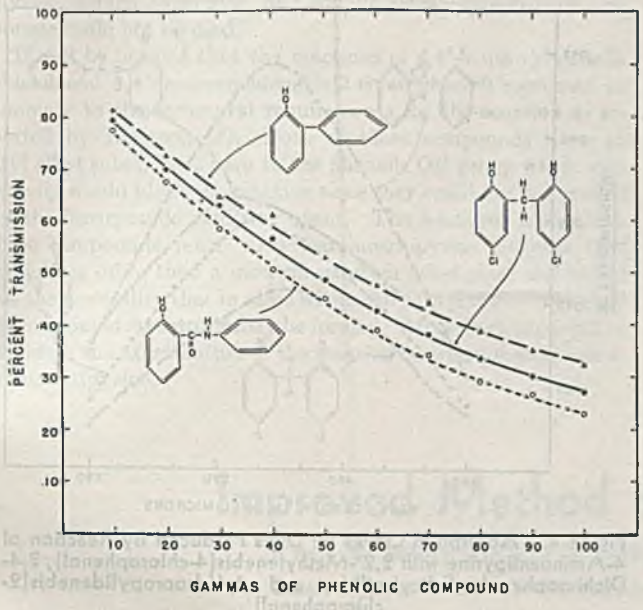


Figure 1. Standard Calibration Curves for Dyes Produced by Reaction of 4-Aminoantipyrine with o-Phenylphenol, 2,2′-Methylenebis[4-chlorophenol], and Salicylanilide

Filters used for data in Figures 1, 2, and 3 are those suggested in text where reactions of various compounds with 4-aminoantipyrine are described

1. At least one free phenolic group must be present.
2. The position para to the phenolic OH must either be unsubstituted, or substituted by halogen, carboxyl, sulfonic acid, hydroxyl, or methoxyl, which groups are expelled in the reaction. Substitution in the para position by alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde groups blocks the reaction.

Under certain conditions the reaction of 4-aminoantipyrine with phenols is readily amenable to quantitative treatment in the determination of phenolic fungicides. A method for the determination of 2,2′-methylenebis[4-chlorophenol] on fabric is presented below and absorption and standard calibration curves are given for *o*-phenylphenol, salicylanilide, 2,2′-methylenebis-[3,4,6-trichlorophenol], 4,4′-isopropylidenediphenol, 4,4′-isopropylidenebis[2-chlorophenol], 2,4-dichlorophenol, pentachlorophenol, and tetrabromo-*o*-cresol.

DETERMINATION OF 2,2′-METHYLENEBIS[4-CHLOROPHENOL]

This compound reacts with 4-aminoantipyrine in an alkaline oxidizing medium to form a red dye. Under the conditions described below the dye develops almost immediately and is relatively stable for several hours. The standard calibration curve, made with an Aminco Type F photometer, balanced against distilled water, and the absorption curve, taken with a Coleman Model 10S spectrophotometer, are shown in Figures 1 and 4, respectively. The procedure for determination of this compound in fabric is presented below.

Solutions. 4-Aminoantipyrine, 2%. Two grams of 4-aminoantipyrine (m.p. 108–109°) dissolved in 100 cc. of distilled water. This compound is made from antipyrine by the method described by Emerson (*1*). It has been kept in solution in stoppered dark bottles in the laboratory for several months without noticeable deterioration.

Potassium ferricyanide, 8%. Eight grams of C.P. potassium ferricyanide dissolved in 100 cc. of distilled water.

Sodium carbonate, 0.025%. C.P. anhydrous sodium carbonate (4.5 grams) dissolved in 18 liters of distilled water. The pH of this solution should be between 10.4 and 10.6.

Standard Curve. Dissolve 200 mg. of 2,2′-methylenebis-[4-chlorophenol] in 100 cc. of acetone in a volumetric flask, place 1 cc. of this solution in a second 100-cc. volumetric flask, and dilute to the mark with sodium carbonate solution. This solution, containing 20 micrograms of G-4 per cc. is used to obtain suitable aliquots covering the range of 20 to 100 micrograms. Place each aliquot in a 25-cc. volumetric flask and add 0.5 cc. of aminoantipyrine reagent. Dilute to the mark with the sodium carbonate solution, add 0.25 cc. of 8% potassium ferricyanide, and shake vigorously. After 5 minutes, pour the solution into a colorimeter tube and measure the color, using a suitable filter (green, about 500 millimicrons). The same grade of product should be used in making up the standard curve as was applied to the cloth sample in question.

Fabric Analysis. For samples of cloth containing up to 2% of compound G-4, weigh a 1-gram sample of the very finely cut material to the nearest milligram, and place the sample in a 200-cc. beaker. Add 50 cc. of 0.25% sodium carbonate solution and heat to gentle boiling. Boil gently for 5 minutes. Pour the hot solution off the fabric into a 200-cc. volumetric flask (Pyrex). Repeat the extraction twice with 50 cc. of the sodium carbonate solution, each time boiling for 5 minutes and combining the extracts with the first one in the volumetric flask. Dilute the solution to near the mark with the sodium carbonate solution, using the diluent to wash the textile material twice. Cool the flask to room temperature and dilute exactly to the mark. Filter about 20 cc. through a dry filter and use the proper aliquot of this solution (usually 1 to 2 cc.) to get a reading on the standard curve. Place the aliquot in a 25-cc. volumetric flask and add 0.5 cc. of 2% 4-aminoantipyrine solution. Dilute to the mark with 0.025% sodium carbonate solution, add 0.25 cc. of 8% potassium ferricyanide solution, shake vigorously, and after 5 minutes pour into a colorimeter tube and measure the color. After mixing the re-

Table I. Comparative Determination of 2,2′-Methylenebis[4-chlorophenol] (Compound G-4) on Fabric

(By the Willard and Thompson halogen microprocedure and the 4-aminoantipyrine method. The replicates in the aminoantipyrine method are different individual samples cut from a single piece of cloth.)

Sample No.	Per Cent on Fabric: Aminoantipyrine method	Per Cent on Fabric: Willard-Thompson method
1	0.89	0.99
	0.91	
	0.88	
	0.87	
2	1.76	1.75
	1.73	
	1.76	
	1.74	
3	1.10	1.07
	1.05	
	1.07	
	1.06	
4	1.68	1.69
	1.67	
	1.64	
	1.68	

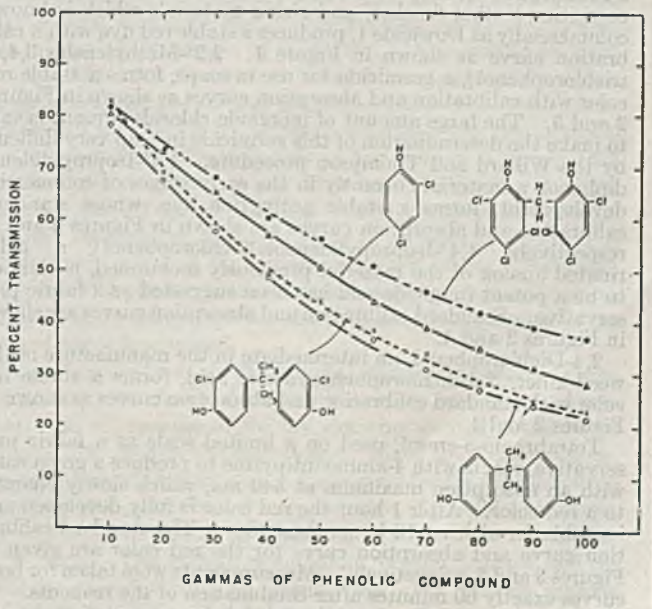


Figure 2. Standard Calibration Curves for Dyes Produced by Reaction of 4-Aminoantipyrine with 2,2′-Methylenebis[3,4,6-trichlorophenol], 4,4′-Isopropylidenediphenol, 4,4′-Isopropylidenebis[2-chlorophenol], and 2,4-dichlorophenol

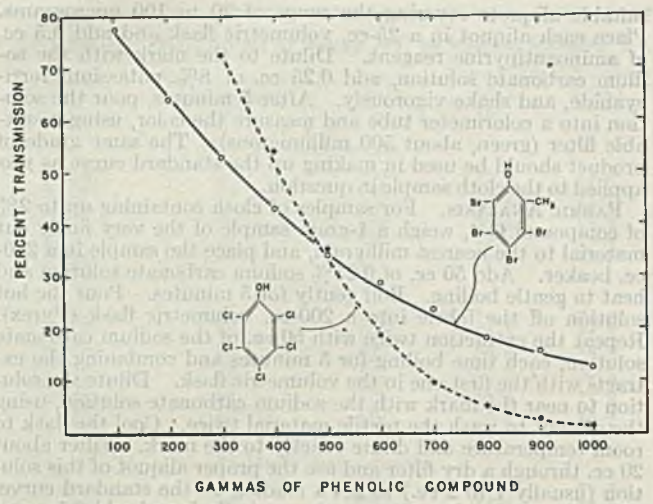


Figure 3. Standard Calibration Curves for Dyes Produced by Reaction of 4-Aminoantipyrine with Pentachlorophenol and Tetrabromo-o-cresol

agents, the tubes should not be exposed to direct sunlight or strong artificial light, as this sometimes causes fading of the colors.

A comparison of results obtained on analyzing four samples of fabric by the Willard and Thompson method (chlorine determination) and the 4-aminoantipyrine method is given in Table I. It was found that the colorimetric determinations could be made on 16 samples of fabric in less than 2 hours, including weighing of samples, extraction, development, and measurement of color.

DATA ON OTHER PHENOLS

Absorption curves and standard calibration curves were made for a group of other phenols according to the methods described above for Compound G-4. The several standard calibration curves are shown in Figures 1, 2, and 3, and the absorption curves in Figures 4 and 5.

Salicylanilide, a fabric preservative known commercially as Shirlan, produces a red dye which fades very gradually; calibration and absorption curves are shown in Figures 1 and 4. *o*-Phenylphenol, an industrial preservative for casein paints, cosmetics, leather finishes, and sizing materials which is known commercially as Dowicide 1, produces a stable red dye with a calibration curve as shown in Figure 1. 2,2′-Methylenebis[3,4,6-trichlorophenol], a germicide for use in soaps, forms a stable red color with calibration and absorption curves as shown in Figures 2 and 5. The large amount of inorganic chloride present is said to make the determination of this germicide in soap very difficult by the Willard and Thompson procedure. 4,4′-Isopropylidenediphenol, a material currently in the early stages of commercial development, forms a stable antipyrine dye, whose standard calibration and absorption curves are shown in Figures 2 and 5, respectively. 4,4′-Isopropylidenebis[2-chlorophenol], a chlorinated analog of the material previously mentioned, is claimed to be a potent fungicide and has been suggested as a fabric preservative. Standard calibration and absorption curves are shown in Figures 2 and 4.

2,4-Dichlorophenol, an intermediate in the manufacture of the weed-killer, 2,4-dichlorophenoxyacetic acid, forms a stable red color with standard calibration and absorption curves as shown in Figures 2 and 4.

Tetrabromo-*o*-cresol, used on a limited scale as a fabric preservative, reacts with 4-aminoantipyrine to produce a green color with an absorption maximum at 540 mμ, which slowly changes to a red color. After 1 hour the red color is fully developed and is stable for at least 12 hours thereafter. The standard calibration curve and absorption curve for the red color are given in Figures 3 and 5, respectively. Measurements were taken for both curves exactly 60 minutes after combination of the reagents.

Pentachlorophenol, a wood and fabric preservative known under the trade name of Dowicide 7, reacts with 4-aminoantipyrine to give a green color which gradually fades to colorless over a period of 2 hours. A satisfactory calibration curve could be obtained by measuring the color at 30 minutes after development of color, using a 640 filter (Figure 3). In this reaction it was found that 0.5 cc. of the potassium ferricyanide solution and 0.75 cc. of the aminoantipyrine solution gave the best development of color.

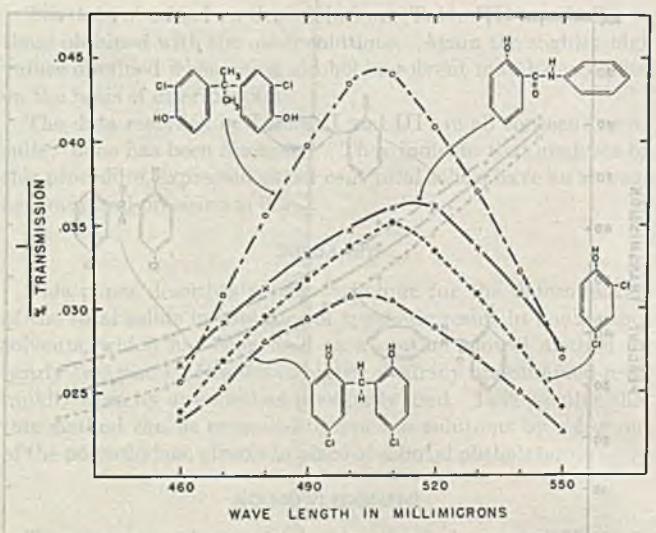


Figure 4. Absorption Curves for Dyes Produced by Reaction of 4-Aminoantipyrine with 2,2′-Methylenebis[4-chlorophenol], 2,4-Dichlorophenol, Salicylanilide, and 4,4′-Isopropylidenebis[2-chlorophenol]

100 micrograms of phenolic compound used to develop color

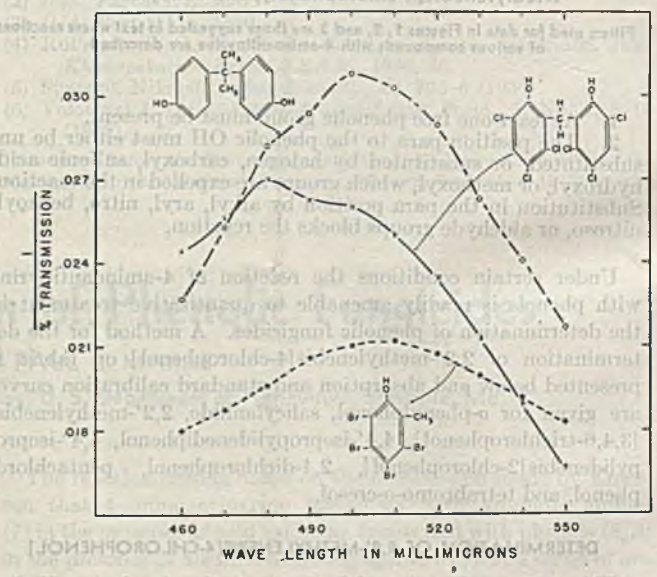


Figure 5. Absorption Curves for Dyes Produced by Reaction of 4-Aminoantipyrine with 4,4′-Isopropylidenediphenol, 2,2′-Methylenebis[3,4,6-trichlorophenol], and Tetrabromo-o-cresol

For first two compounds 100 micrograms of each compound were used to develop color, as described in section on standard curves. For tetrabromo-o-cresol 400 micrograms of phenolic compound were used.

DISCUSSION

It can be seen from the data presented that 4-aminoantipyrine promises to be a very useful reagent for the quantitative estimation of phenols. The only element appearing to require special care in the analysis is the pH of the reaction medium. Deviations of 0.5 of a pH unit in either direction from the limits given caused changes in both the intensity and stability of the color produced. Attempts to utilize buffer mixtures were not successful, since the ions used in the buffer mixtures interfered with the development of the color. Thus boric acid–sodium hydroxide,

glycine–sodium hydroxide, and sodium tetraborate–sodium carbonate could not be used.

It will be noticed that the reactions of 4,4′-isopropylidenediphenol and 4,4′-isopropylidenebis[2-chlorophenol] represent an anomaly to the structural requirements for the reaction as reported by Emerson (*2*). Both of these compounds have an aryl alkyl substituent para to the phenolic OH group which supposedly would block the reaction since they could not be expelled by the ferricyanide oxidizing agent. The readiness with which these compounds react with 4-aminoantipyrine suggests that something other than a para substitution takes place and brings out the possibility that in cases where the para position is blocked ortho-quinoid structures may be formed. More work is needed to elucidate the exact nature of the reaction between phenols and 4-aminoantipyrine.

ACKNOWLEDGMENT

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Improved Method of Flame Photometry

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An improved flame photometer, employing a dual optical system, has been devised. With this instrument the internal standard principle often employed in spectral analysis may be used. Since by this method light intensity ratios are measured rather than absolute light intensities, the disturbing effects caused by gas and air pressure fluctuations, by the presence of foreign ions and molecules, and by viscosity differences are considerably reduced. The construction and performance of this photometer are discussed in detail.

IN A recent paper (*1*) a rapid analytical technique for the determination of sodium and potassium in aqueous solution was presented. An instrument known as the flame photometer was described, and the analytical procedure explained. Briefly, the method consists of atomizing an aqueous solution of the metal into the base of a gas burner, whereupon the vapor is carried into the flame and ignited. The light arising from the flame characteristic of the element being determined is filtered free of other radiation and is brought to fall upon a photocell. By measuring the intensity of the light produced with solutions of known concentration and preparing a calibration curve of intensity versus concentration, the metal content of other solutions may subsequently be determined by making use of the curve.

The prime requisite of successful flame photometry by this method is the establishment of constant atomization and burning conditions in the instrument. Considerable investigative work led to a design of instrument which would fulfill this condition with reasonable satisfaction. In the flame photometer previously described, these problems had been solved to obtain an average accuracy of ±3% of the total element present in the sample in a single determination. The errors made were found to be almost entirely random—i.e., equal number positive and negative—and it could be assumed that they came entirely from momentary variations of light intensity in the flame.

In the early course of this work, however, it was noted that an error far more serious in nature than this instrumental error could arise when excessive amounts of certain ions were introduced into solutions containing sodium or potassium—for example, the presence of 1% sulfuric acid in a solution containing 100 p.p.m. of sodium reduced the light emitted by the flame by some 15%. It was further noted that acids, salts, or indeed almost any foreign molecule, similarly reduce the apparent sodium content of solutions as analyzed by the flame photometer.

The most obvious manner in which to correct this type of error is to compound the standard solutions used in calibrating the instrument in such a manner that these standards contain quantities of the interfering molecules in proportions similar to those quantities contained in the solutions to be analyzed. This procedure has been adopted, and in applications where one can accurately predict the composition of the solutions submitted for analysis, it has been satisfactory.

It is apparent, however, that such a procedure is not altogether convenient, since it requires the compounding of a series of standard solutions for each type of unknown which the laboratory must analyze. In other cases, where the chemical composition of unknowns may vary considerably from one sample to the next, the procedure is not feasible. For these reasons, a method was sought which would eliminate as nearly as possible the effect of foreign molecules upon the quantitative determination of the alkali metals.

In the usual spectrographic method of analysis it has been common practice to employ what is termed an "internal standard" (*3*) element to reduce the effect of variation of the light source, and other disturbing influences, upon the accuracy of the results obtained. The method consists of purposely adding to each sample to be analyzed a fixed quantity of some element (the internal standard) not normally occurring in the sample, before bringing the sample to excitation. Upon excitation, light is emitted by both the element being determined and the internal standard, and the ratio of the intensities of these two characteristic lights emitted is subsequently determined by photography and densitometry. The principle of the method is simply that any change in the source or any other factor influencing the light intensity emitted by one element similarly affects the internal standard element, so that the ratio of intensities obtained is constant regardless of the experimental conditions. Naturally it is advantageous to choose as an internal standard an element which bears excitation characteristics as similar as possible to the element being determined.

In attempting to apply the internal standard method to flame photometry, the choice of a suitable element as a standard was rather limited, because of the few elements excited at the flame temperatures used in the instrument. Since the flame photometer was primarily designed as an instrument for the determination of sodium and potassium, it was desirable, if possible, to choose one of the alkali metals as a standard rather than an alkaline earth metal. The spectra of rubidium, cesium, lithium, and indium were investigated as possibilities. For various reasons such as the intensity of light emitted by the element, the problem of filtering the characteristic radiation emitted, and the wavelength sensitivity of the photodetecting device to be employed,

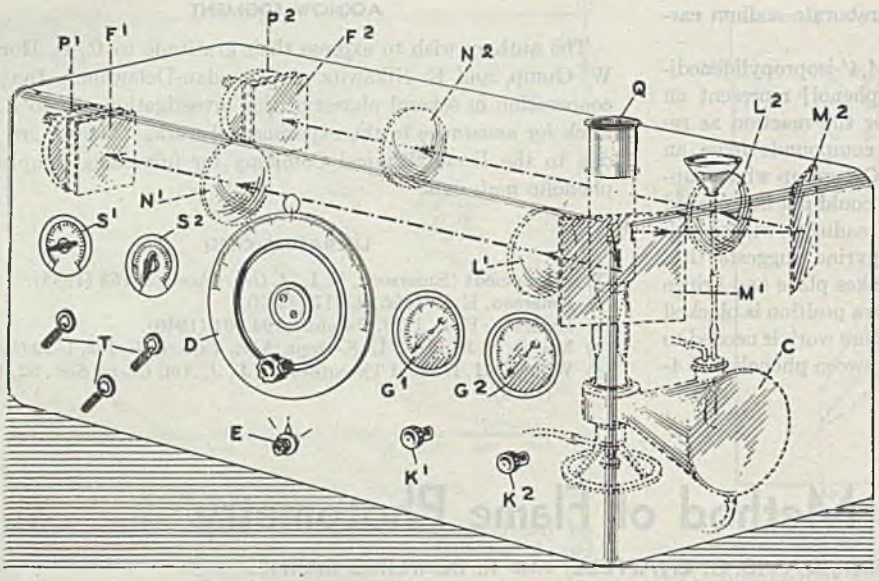

Figure 1. Internal Standard Flame Photometer

Q, chimney. M^1, M^2, mirrors. L^1, L^2, N^1, N^2, Fresnel lenses. F^1, sodium or potassium filters. F^2, lithium filters. P^1, P^2, barrier layer photocells. *C*, atomizing chamber. G^1, G^2, gas and air pressure gages. K^1, K^2, gas and air regulator knobs. *D*, main potentiometer dial. *E*, compensating rheostat. *T*, toggle switches. S^1, S^2, sensitivity adjustment, coarse and fine

all except lithium were rejected. The only serious objection to the use of lithium is the fact that the element is relatively abundant and may therefore occur as an impurity in certain types of samples, especially those of mineral origin. The light emitted by lithium is sufficiently intense, and the only line emitted (6708 Å.) is favorably placed about equidistant in the spectrum between the lines of sodium and of potassium. The problem of filtering the three radiations sufficiently free from one another was accomplished with Corning glass filters and a special liquid filter developed in these laboratories (*4*) which consists of cupric chloride dissolved in concentrated hydrochloric acid.

INTERNAL STANDARD FLAME PHOTOMETER

To test the internal standard method as applied to flame photometry, it was necessary to construct a special instrument housing two light paths and two photocells. The instrument built (Figure 1) was similar in general design to the flame photometer previously described (*1*).

Light leaves the flame through two rectangular apertures on opposite sides of the chimney, *Q*, each beam being reflected into an optical system similar to that previously used. The lens, L^1 or L^2, nearest the chimney casts an enlarged image of the aperture on the second lens, N^1 or N^2, filling this lens as nearly as possible with the rectangular image produced. The second lens casts a slightly reduced image of the first lens upon a round photocell, P^1 or P^2, just filling the active area. This system provides high light-gathering power yet allows the photocells to be well removed from the heat of the source. The barrier layer photocell has been retained as the light-detecting device. Before one photocell is placed the set of lithium filters, while sodium or potassium filters may be interchanged before the other photocell. [If desired, separate light paths and photocells may be provided for the sodium and potassium (making a total of three optical systems) and the desired sodium or potassium cell switched into the circuit electrically.]

Gas and air supplied to the burner and atomizer, respectively, are regulated and measured by appropriate regulators and gages, G^1 and G^2. The stainless steel hypodermic needle atomizing unit, and the conical-shaped atomizing chamber, *C*, used in the previous instrument were left unchanged.

The circuit used for measuring the ratio of the light intensities between the internal standard and the element being determined is shown in Figure 2. (Actually the circuit employed is not a true ratio-measuring device but rather a compensated circuit. At balance, however, the potentiometer reading obtained is very nearly proportional to the ratio of the light intensities on the two photocells.) Several of the "bucking circuit" arrangements suggested in the literature (*2*) were tried but none proved satisfactory at the low light levels encountered in the photometer. The circuit used maintains a resistance of some 10,000 ohms across each photocell, which seems about proper for the damping characteristics of the galvanometer. The 10,000-ohm potentiometer, *D*, was coupled to a 20-cm. (8-inch) circular dial on the front panel, making possible the reading of the potentiometer to within $\pm 0.2\%$ of full scale. A small 500-ohm rheostat, *E*, was added to one end of the slide wire for slight compensating adjustments found necessary from time to time during operation. The box-type galvanometer used in the previous instrument (G.E. 32C-245-G9) made a satisfactory null indicator for the instrument. As formerly, the galvanometer was connected to the photometer by jacks.

Also shown in Figure 2 is the circuit used in the previous method of flame photometry. Although not shown, the instrument was so arranged that either circuit shown in Figure 2 could be utilized by merely throwing toggle switches, *T*. The instrument could thus be used as previously described—to measure the direct or absolute intensity of the sodium or potassium wave lengths, now termed the "absolute method" of flame photometry, or the ratio of light intensities of sodium versus lithium or potassium versus lithium, termed the "internal standard method" of flame photometry. This arrangement was very convenient in making comparisons of the two methods.

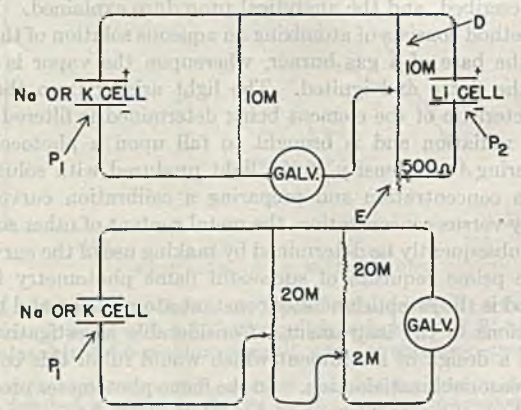

Figure 2. Circuits of Internal Standard Flame Photometer

Ratio circuit above, absolute circuit below

ANALYTICAL PROCEDURE

The procedure employed in making use of the internal standard method is similar in principle to that employed in the absolute method, in that the instrument is first calibrated with solutions of known concentration. All the standards, however, are prepared to contain a fixed amount of a soluble lithium salt. Lithium sulfate has generally been employed for this purpose, as the salt is rather easily prepared in a form relatively free of sodium and potassium.

Reagent quality lithium sulfate is precipitated as the fluoride by adding ammonium fluoride in slight excess. The lithium fluoride is then washed with cold distilled water, dried, and con-

verted back to the sulfate in platinum ware by the addition of concentrated sulfuric acid and heating. Since the sodium and potassium fluorides are several times more soluble than the lithium salt, the procedure appears satisfactory.

In practice, all sodium standards were made to contain 1000 p.p.m. of lithium, and amounts of sodium ranging from 0 to 90 p.p.m. (It was found by experiment that this quantity of lithium gives an electrical response equal to the response of 95 p.p.m. of sodium with the particular filters and photocells employed in the instrument.) The standards thus prepared are successively introduced into the instrument and in each case the potentiometer is so adjusted as to cause no current to flow through the galvanometer. A potentiometer dial reading is taken for each standard and a calibration curve is prepared. The curve obtained is smooth, and fairly linear (Figure 3).

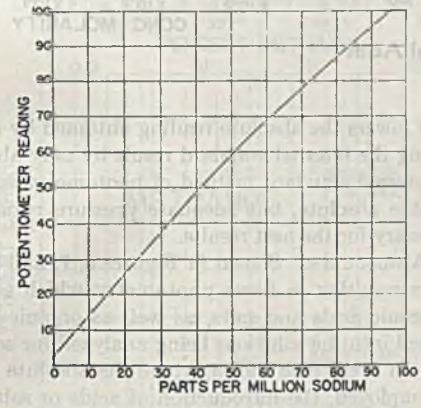

Figure 3. Typical Calibration Curve for Sodium as Obtained by the Internal Standard Flame Photometer

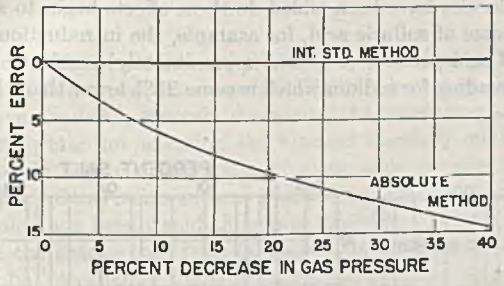

Figure 4. Effect of Variation of Gas Pressure

To determine the sodium content of a sample, an aqueous solution is appropriately pipetted into a volumetric flask, so that upon dilution the sodium content will fall below 90 p.p.m. A sufficient quantity of a stock lithium sulfate solution is then added to bring the lithium concentration to 1000 p.p.m. upon dilution. The sample thus prepared when introduced into the instrument yields a potentiometer reading which is readily converted into parts per million of sodium by use of the calibration curve.

In actual operation the calibration curve remains well fixed after establishment. The standard solution containing 0 p.p.m. of sodium and 1000 p.p.m. of lithium will read near the lower end of the main potentiometer scale and the 90 p.p.m. of sodium standard will read near the upper end of the scale. When employing the flame photometer for analysis it will be found wise to check the upper and lower ends of the scale occasionally with the standard solutions. Unless the flame in some manner becomes contaminated with sodium (dust in the atmosphere, etc.), the lower end of the calibration curve will remain well anchored. If drift occurs at the upper end of the scale, compensation may be made by adjustment of the secondary slide wire, E, to restore the original reading of the standard.

A similar procedure is used in the determination of potassium, with the exception that the solutions are prepared to contain 200 p.p.m. of lithium. This amount of lithium balances about 95 p.p.m. of potassium. The lithium concentrations chosen were such as to balance convenient working concentrations of sodium and potassium, but more or less lithium may be added to prepare a series of standards covering greater or lesser ranges of concentration of sodium and of potassium.

The amount of sample required for a single sodium or potassium determination is about the same as that required by the previous instrument (*1*). Samples of as little as 3 ml. of solution have been analyzed, but a larger quantity of sample (say 10 ml.) is preferred. Although the authors prefer working in a concentration range of 1 to 100 p.p.m. of sodium or potassium, concentrations as low as 0.1 p.p.m. of sodium or 0.5 p.p.m. of potassium have been determined. In working at concentrations below 5 p.p.m. of sodium or potassium a special set of standard solutions containing less lithium should be used for calibration of the instrument.

ACCURACY

In order to determine the accuracy of the internal standard method of flame photometry, a series of 100 solutions containing known concentrations of sodium was prepared and analyzed by the method. A similar series was studied in the case of potassium. These solutions were prepared from C.P. sodium and potassium chlorides and lithium sulfate prepared as previously described. The average error of a single determination of sodium was $\pm 1.24\%$, while for potassium a figure of $\pm 1.01\%$ was obtained. The sign of the error was found to be random. These figures show conclusively the superiority of the internal standard method over the absolute, for in a similar experiment using the absolute method, the average error of a single determination was shown to be $\pm 3\%$ of the amount of element present.

Further experiments have been conducted which show the superiority of the internal standard method with respect to common interferences which may beset the absolute method. These detrimental effects may be divided into at least four classes: effect of variation of gas pressure, effect of variation of air pressure, effect of foreign molecules and ions, and effect of viscosity of the sample.

In order to determine the magnitude of these various effects, standard solutions were prepared and analyzed by both the internal standard and the absolute method. These solutions all contained 50 p.p.m. of sodium (as the chloride) plus varying amounts of the interfering substances (except in the case of the effect of sodium chloride, in which case 50 p.p.m. of potassium was the concentration chosen). The standards used in the evaluation of the internal standard method contained, in addition, 1000 p.p.m. of lithium.

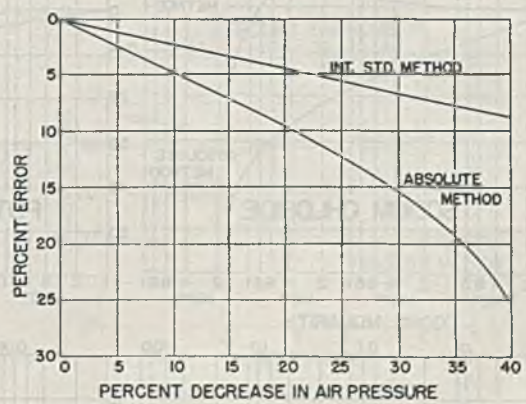

Figure 5. Effect of Variation of Air Pressure

In a separate series of experiments, it was subsequently shown that the percentage error produced by a given quantity of interfering ion or molecule is independent of the amount of sodium or potassium present in the sample over a concentration range of 10 to 100 p.p.m.

INTERFERENCES

GAS PRESSURE. The effect of lowering the gas pressure from that normally used in the operation of the flame photometer [0.21

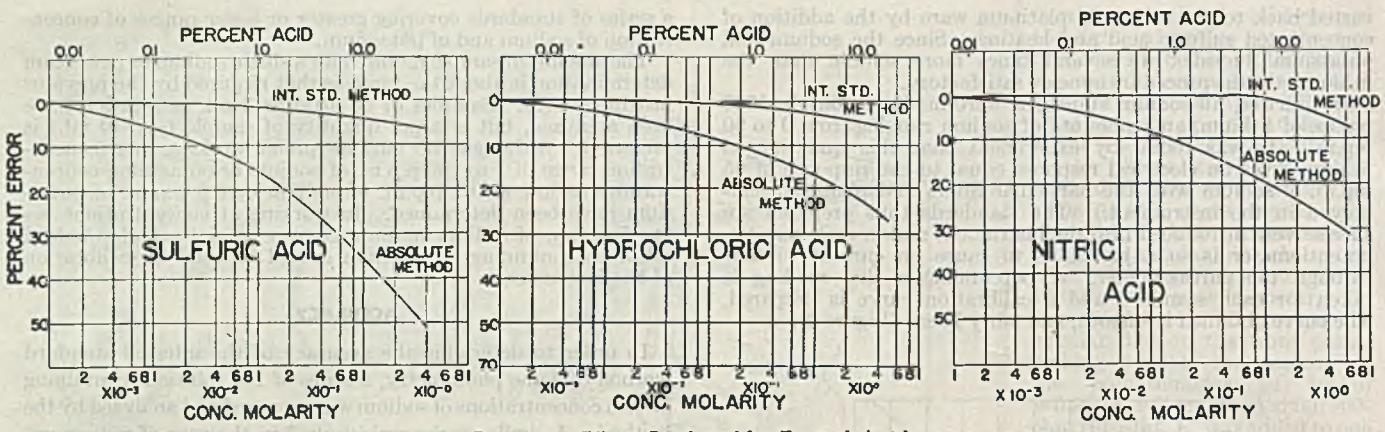

Figure 6. Effects Produced by Typical Acids

kg. per sq. cm. (3 pounds per sq. inch) of propane] is shown graphically in Figure 4. It is immediately noted that the gas pressure may be lowered by 33% [from 0.21 kg. per sq. cm. (3 pounds) down to 0.14 kg. per sq. cm. (2 pounds)] using the internal standard method with no appreciable change in the quantity of metal determined in a sample, while a similar change of gas pressure lowers the result obtained in using the absolute method by some 12.5%. The obvious superiority of the internal standard method should now make feasible the operation of flame photometers directly from city gas mains where variations in gas pressure previously made such operation very questionable.

Air Pressure. That variations of flame photometer readings are much more dependent upon air pressure fluctuations than upon gas pressure changes is immediately apparent from a study of Figure 5. The internal standard method does not completely eliminate the effect of variations in air pressure at any range. The magnitude of the effect, however, is reduced by a factor of about 2.5. Thus, a reduction of air pressure from the standard operating pressure of 1.05 to 0.84 kg. per sq. cm. (15 to 12 pounds per sq. inch) lowers the absolute reading obtained by some 10% while reducing the internal standard result by only about 3.5%. Again the internal standard method of photometry is distinctly superior to the absolute, but adequate pressure regulation will remain necessary for the best results.

Foreign Molecules. Shown in Figures 6, 7, and 8 are plots of the errors resulting in flame photometry which occur when certain inorganic acids and salts, as well as organic molecules, are introduced into the solutions being analyzed for sodium and potassium. In every case shown, where the absolute method of analysis is employed, the introduction of acids or salts into the solution reduces the light emitted by the sodium or potassium. If a sufficient quantity of the interfering substance is added, the internal standard method also will usually produce a low result, but not until considerably higher concentrations of the interfering molecules have been added do these effects begin to appear. In the case of sulfuric acid, for example, the introduction of 0.2 mole of acid per liter (2% acid approximately) results in an absolute reading for sodium which is some 21% lower than the true

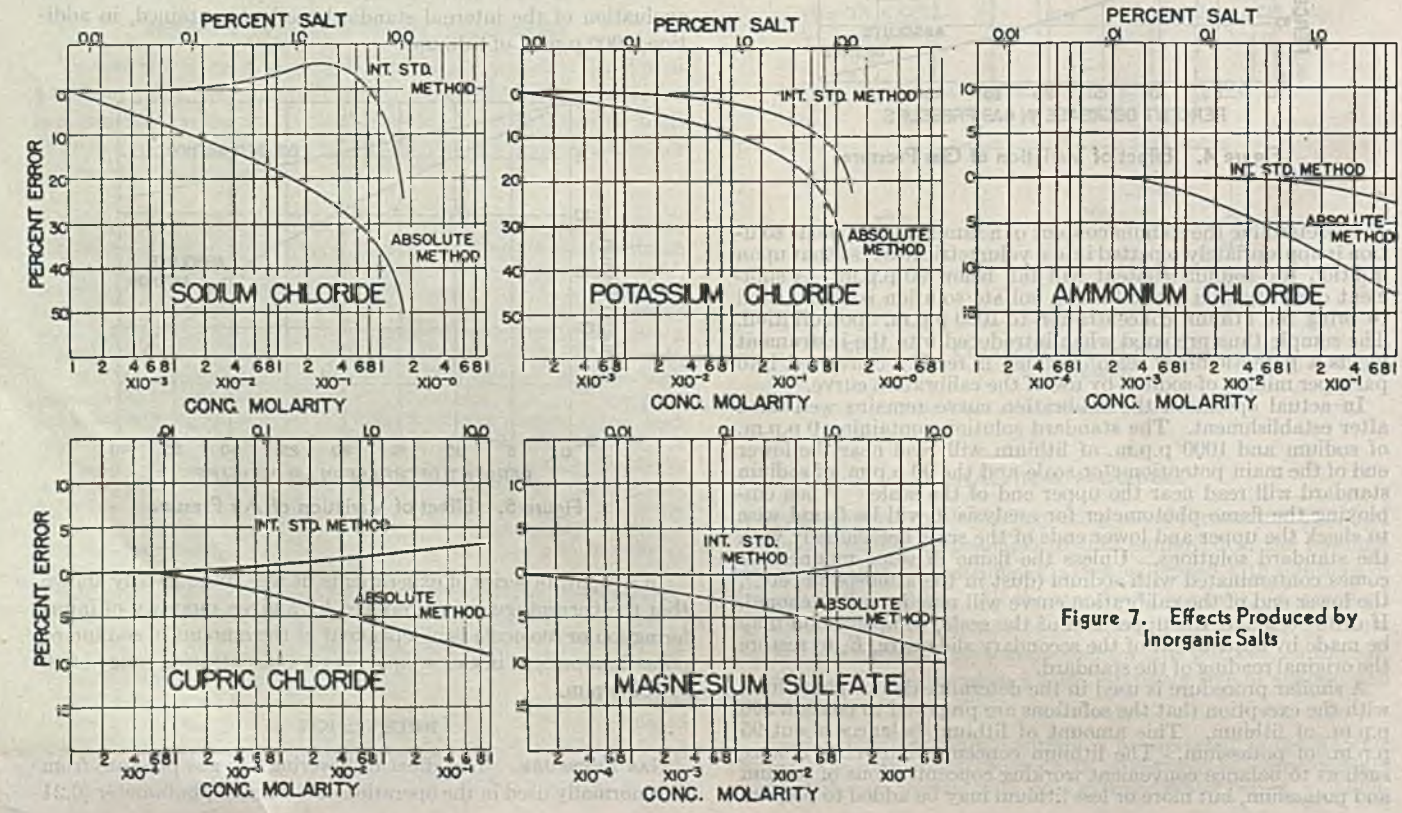

Figure 7. Effects Produced by Inorganic Salts

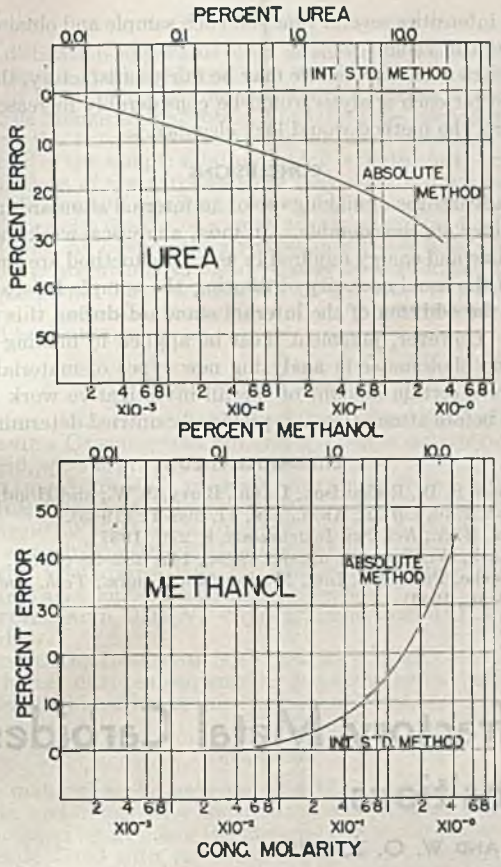

Figure 8. Effect Produced by Organic Molecules

value, while by the internal standard method the result obtained is but 1.5% lower than normal. Hydrochloric and nitric acids behave similarly, severely depressing the absolute readings obtained while not affecting the internal standard method until relatively high concentrations of these acids are present in the sample. Other acids such as phosphoric, hydriodic, and hydrobromic have been found to behave similarly. It may be noted from the graphs that from 50 to 200 times the amount of acid may be tolerated by the internal standard method as by the absolute—i.e., before an equal suppression of the result is noted.

Salts of most types depress the readings obtained by the absolute method of flame photometry much as do the acids. The effects of five different salts are shown in the graphs—namely, ammonium chloride, sodium chloride, potassium chloride, magnesium sulfate, and cupric chloride. These salts begin to depress the absolute readings when present at approximately the same range of concentration as do the acids. It is obvious, therefore, that the neutralization of an acid in a sample with, for example, ammonium hydroxide, will not lessen the ill effect of the acid.

Potassium chloride affects the determination of sodium much as does ammonium chloride. Similarly, sodium chloride will depress the readings obtained in a potassium determination if present in sufficient quantity. This effect should especially be remembered if any attempt is made to determine a trace of one of these elements when combined with large quantities of the other.

Of interest also are the effects produced by two of the salts, the magnesium sulfate and the copper chloride, which tend to raise the result obtained by the internal standard method rather than to produce a low answer as they do by the absolute method. Two explanations for this behavior are possible: either that the salts depress the light emitted by lithium to a greater extent than that by sodium, or that a certain small amount of light is emitted by copper and magnesium which will pass the sodium filter. The former reason may apply to the magnesium in the case of sodium determinations, but the latter reason may apply to the copper salt, as it is known that copper salts do emit a green band, some of which may pass through the sodium filters.

Figure 8 shows the effects produced by two common organic molecules. Urea behaves very similarly to the acids and salts—the effect quantitatively being of the same order of magnitude. Methanol, however, behaves in a manner entirely different from any substance previously mentioned in that it increases the light emitted by the flame. Ethanol has been observed to exhibit a similar behavior.

Viscosity. As might be expected, samples which contain sodium or potassium and some additional agent which considerably increases the viscosity of the sample tend to read lower than solutions of sodium or potassium of normal viscosity—when the determination is made by the absolute method. The explanation is obvious in that the absolute method depends upon a constant rate of atomization in the standards and in the unknowns. Higher viscosities decrease the rate of atomization of the sample, so that fewer atoms are introduced into the flame in a given time, and consequently less light is emitted by the flame.

Figure 9 shows the comparative effects of viscosity upon the internal standard and absolute methods. Sucrose was added to the samples to increase the viscosity. In an extreme case where 40% sucrose was added to the sample (viscosity 5.1 centipoises) the absolute method produced a result 42% below the true value, while the result obtained by the internal standard method was but 11% low.

A study of the flow rates of the solutions through the atomizer shows that the light emitted is decreased by a lesser amount than would be expected from the decrease in the rate of atomization. Undoubtedly the presence of the sucrose gives rise to some type of interference, apparently behaving as does methanol—that is, to produce more light.

Surface Tension. It was thought probable that variations in the surface tension of solutions might give rise to some change of the atomization characteristics of solutions being atomized into the flame photometer and hence lead to an increase or decrease in the light emitted by the flame. The effect of surface tension was studied by adding the ammonium salt of Aerosol OT (a product of the American Cyanamid Company; the ammonium salt was specially prepared in these laboratories) to solutions of sodium and potassium chlorides. Using the absolute method, no effect was observed upon the light emitted by the flame although the surface tension varied from that of water (ca. 72 dynes per centimeter) down to 28 dynes per centimeter. An explanation might lie in the known fact that a time factor is involved in lowering of the surface tension of freshly formed surfaces when surface-active agents are used to lower the tension. If this factor does explain the failure of surface-active agents to alter the atomization characteristics of a solution, there then remains a

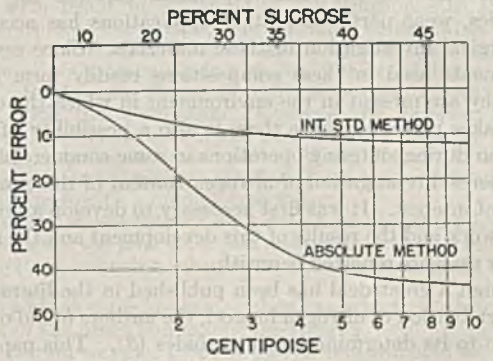

Figure 9. Effect of Viscosity

question as to whether the surface tension of a solution introduces an effect upon the light emitted by a flame. For example, the increased amount of light emitted by a solution containing alcohol may be partly due to the altered surface tension of the solution. At the present time, no attempt has been made to study this effect further.

PROPOSED ALTERNATIVE PROCEDURE

Certain analysts in considering the internal standard type of flame photometer may propose that the previously described type of flame photometer, employing a single photocell, be used in a quasi-internal standard method by adding lithium to each sample and measuring individually the intensity of the lithium and sodium lines. This, of course, could be readily accomplished if a suitable method of mechanically interchanging the filters before the photocell were devised.

Such a procedure might serve well in eliminating the effects of foreign ions and molecules upon the flame, but would not eliminate the effects of variations in gas, air pressure, or other momentary changes which constantly alter the intensity of the flame. The error introduced by variation of the flame could, of course, be substantially reduced by alternately measuring the sodium and lithium intensities several times on each sample and obtaining an average ratio value.

Although such a procedure may be fairly satisfactory, the time involved for each analysis would be considerably increased, and in general the method would lack elegance.

CONCLUSIONS

The advantages of making use of an internal standard in flame photometry are considerable. In most analytical work the additional time and energy required in using the method are small because of the usual necessity of diluting the sample before analysis and the addition of the internal standard during this step is simple. However, judgment must be applied in making use of the flame photometer in analyzing new types of materials, and therefore a certain amount of careful investigative work should be done before attempting any previously untried determination.

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Determination of Nitrogen in Refractory Metal Carbides and Their Compositions

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A procedure is described for determining nitrogen in refractory metal carbides by the solution and distillation method. No special apparatus is required and very precise results are obtained. The nitrogen contents of several representative carbides and compositions are given.

THE great increase in the past few years in the use of cemented compositions of the refractory metal carbides for cutting tools, dies, wear parts, and other applications has accelerated metallurgical investigation of these materials. Since several of the elements used in these compositions readily form nitrides when they are present in the environment in which the carburization takes place and since there is also a possibility of nitride formation during sintering operations in some commercially used atmospheres, investigation of nitrogen content of these materials seemed of interest. It was first necessary to develop a procedure for this work and the results of this development and the method as finally used are reported herewith.

Although a great deal has been published in the literature on the determination of nitrogen in steel, the authors found only one reference to its determination in carbides (*3*). This paper incidentally contains a very complete and worth-while bibliography on the determination of nitrogen in iron and steel. Phragmen and Treje (*3*) investigated both the vacuum fusion and solution and distillation methods. In the case of the solution and distillation method they used a refluxing technique for solution with special apparatus and sulfuric acid plus potassium bisulfate as the solution agents. For titanium carbide their results show a much lower recovery with the solution and distillation method than for the vacuum fusion procedure using sodium peroxide. Hence, when applied to titanium carbide, which is a constituent of many commercial carbide compositions and is a very likely source of nitrogen, the solution and distillation procedure of Phragmen and Treje appears unsatisfactory.

It was the authors' desire to develop a solution and distillation method without the use of special apparatus, but it is obvious that the problem would be one of developing a method of obtaining complete solution. These carbides and their compositions are very refractory and are ordinarily insoluble without resort to oxidizing reagents or fusion. As shown in Table I, several unsatisfactory procedures and modifications were investigated.

Table I. Procedures Investigated

	Solution Method	Results
1.	Fuming sulfuric acid plus sodium sulfate (*2*)	Partial solution and low results
2.	Fuming sulfuric acid plus sodium thiosulfate	Usually incomplete solution. Erratic results
3.	Fusion with potassium bisulfate and solution of melt in hydrochloric acid	Results low when fusion was complete
4.	Fuming with sulfuric acid plus potassium bisulfate plus hydrofluoric acid	Very destructive to glassware
5.	Heating in a stream of hydrogen with copper oxide and lead oxide catalysts and absorption of ammonia in sulfuric acid	Results very low

The use of perchloric acid as recommended in some procedures for determining nitrogen in alloy steels was not tried, inasmuch as there has always been a question of the loss of nitrogen by oxidation in even short periods of fuming. Since extended periods were necessary for these materials, the loss of nitrogen seemed certain.

It was then found that by a careful technique, extended fuming with a mixture of sulfuric acid, potassium bisulfate, and either cuprous oxide or selenium oxychloride could be carried out and complete solution could be obtained. In some instances this required as much as 184 hours for the solution of a 1-gram sample but there was no evidence of loss of ammonia. This procedure was adopted as described in detail in this paper.

APPARATUS

The distillation apparatus used is shown in Figure 1. This apparatus is a combination of that described by Lundell, Hoffman, and Bright (*2*), and one developed a number of years ago at Battelle Memorial Institute. The large tube leading from the funnel to the bottom of the distillation flask facilitates the introduction of the sample solution, which is particularly necessary with solutions of the carbides since they often contain insoluble matter. The small capillary tube extending near the bottom of the flask permits the use of a small stream of carbon dioxide–free air (obtained by passing the air through a tower filled with carbon dioxide absorbent) to ensure steady distillation and freedom from bumping. The construction of the trap is particularly effective in preventing carry-over of any of the strong sodium hydroxide solution.

SOLUTIONS REQUIRED

Ammonia-Free Water prepared over Devarda's alloy (*4*).

Selenium Oxychloride Solution, 1.2% in concentrated sulfuric acid, specific gravity 1.84.

Tartaric Acid, 50%, prepared with ammonia-free water.

Sodium Hydroxide Solution, 60%. Dissolve 600 grams of the reagent in 1000 ml. of distilled water and digest overnight on the water bath with a zinc-copper couple.

Sodium Hydroxide, 0.01 *N*. Standardize against Bureau of Standards acid potassium phthalate, No. 84.

Sulfuric Acid, 0.01 *N*. Standardize against 0.01 *N* sodium hydroxide.

Methyl Red Indicator Solution, 0.1% in 95% ethyl alcohol.

For higher nitrogen contents 0.1 *N* sodium hydroxide and sulfuric acid prepared in the same manner are used.

PROCEDURE

The material to be analyzed should be as finely divided as possible, and in any case under 200 mesh. This may be readily accomplished by grinding the material in a motor-driven mortar and pestle fitted with cemented carbide insert and tip, respectively. The composition used should be of the straight tungsten carbide type to minimize contamination.

Transfer a carefully weighed 1.0-gram sample to a dry 250 ml. Erlenmeyer flask and add 15 grams of potassium bisulfate, reagent grade, 30 ml. of sulfuric acid, and 1 ml. of selenium oxychloride solution. Place the flask on a hot plate regulated at a temperature to keep the solution just fuming, and invert a small beaker over the neck of the flask. In this way fuming can be continued for many hours without replenishing the acid. Continue the heating until solution is complete and cool to room temperature. Any undissolved residue may be readily detected by observing whether black residue remains when the flask is swirled. Carefully add 50 ml. of 50% tartaric acid solution and then 75 ml. of ammonia-free water. Boil gently for 5 minutes or until all soluble salts are dissolved.

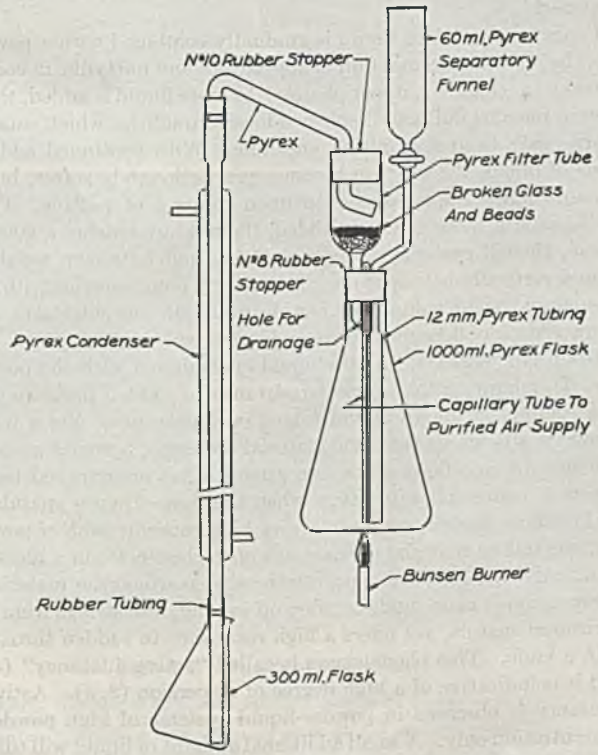

Figure 1. Nitrogen Distillation Apparatus

Table II. Typical Results

Material	General Composition	N_2 Found, %
Tungsten carbide + ammonium sulfate solution[a]		2.056
Titanium carbide		0.982
		0.978
Tungsten carbide 1		0.127
		0.113
		0.119
Tungsten carbide 2		0.122
		0.119
		0.122
		0.121
		0.121
Titanium nitride		16.24
		16.19
Cemented carbide composition	W + Ti + Cb + Ta	0.0252
		0.0252
	W + Ti + Cb + Ta	0.0258
		0.0258
	W + high Ti	0.35
	W + low Ti	0.11
		0.11

[a] Equivalent to 2.067% nitrogen.

When solution is nearly complete, prepare the distillation apparatus. Rinse out the entire distillation flask assembly with ordinary distilled water and measure 150 ml. of 60% sodium hydroxide solution into the flask. Add 400 ml. of distilled water and assemble the apparatus. Place a 300-ml. Erlenmeyer flask under the condenser outlet tube and start a gentle stream of air through the apparatus. Then apply the heat and continue to heat at as rapid a rate as is consistent with the operation of the trap until 150 to 200 ml. of distillate have been collected. Remove the flask and discard. Rinse the outlet tube down with ammonia-free water, place under the outlet tube a flask, rinsed with ammonia-free water, to which a few drops of methyl red indicator solution have been added, and distill over 50 ml. If the indicator remains pink the system is free of ammonia and distillation of the sample may proceed.

Remove the heat from the distillation flask, remove the collecting flask, and substitute another rinsed flask into which 5 ml. of 0.01 *N* sulfuric acid (or 0.1 *N*) have been pipetted. Also add 4 drops of methyl red indicator solution to the flask. Increase the air flow slightly and transfer the solution of the sample to the funnel. Slowly open the funnel stopcock and allow the solution to flow into the flask at such a rate that the reaction is not too violent with resultant splashing of the solution into the trap. Some dilution of the sample solution may be desirable. When the solution is all transferred, rinse the sample flask and funnel three times with ammonia-free water, finally adding a total of 500 ml. Replace the flame, slow the air stream somewhat, and proceed with the distillation. Observe the receiver for any evidence of neutralization of the acid and add more by pipet as needed to keep the indicator pink. When 200 ml. of distillate have been collected, remove the flask from the outlet tube while rinsing it down with ammonia-free water.

Titrate the excess sulfuric acid with 0.01 *N* sodium hydroxide (or 0.1 *N*) until the pink color just disappears. Add 2 more drops of methyl red indicator solution and continue titrating to a full yellow color.

Carry a blank using the same volume as in a sample run through all steps of the operation except the fuming.

On a 1-gram sample, 1 ml. of 0.01 *N* sulfuric acid used to absorb ammonia is equivalent to 0.0140% nitrogen in the sample.

RESULTS

Typical results obtained (Table II) show clearly that the reproducibility is excellent and that added known amounts of ammonia are recovered. Unfortunately, there are as yet no standards available for this class of materials, so that the procedure could not be tested in this manner.

In lieu of the use of standards, some confirmatory results are included. Tungsten carbide is shown not to contain much nitride and this confirms the statement made by Kieffer and Hotop (*7*) that tungsten does not form nitrides below 2300° C. Tantalum and columbium might be expected to behave similarly.

Hence, titanium is the greatest source of nitrogen in these compositions and the results show that titanium nitride is decomposed, so that even were the sample not completely decomposed, the nitride would be recovered.

ACKNOWLEDGMENT

The authors wish to thank Chester M. Alter of the Boston University Graduate School, Boston, Mass., and Metal Hydrides, Inc., of America, for supplying the sample of titanium nitride.

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Evaluation of Dispersions by a Novel Rheological Method

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A technique for the rapid evaluation of dispersions and dispersing agents is presented. The test comprises mixing the dry powder with the dispersing solution, measuring the amount of liquid required to produce two characteristic and reproducible consistencies, and observing the rheological phenomena of the mixture. A good dispersion displays active dilatancy at high powder concentrations. A poor dispersion or flocculate is plastic over a wide range of concentrations and never displays any flow tendencies. A fair dispersion displays passive dilatancy at high concentrations and visible thixotropy at lower powder concentrations.

FINELY subdivided insoluble solids such as pigments display widely different characteristics when mixed with relatively small amounts of liquid. The fact that it requires more liquid to moisten some pigments than to moisten others is the basis of the oil absorption test (*6*) commonly used in the paint and allied industries. It is likewise known that the consistency of a given powder-liquid system can be changed by dispersing (deflocculating) the clusters of powder particles present in the mixture. Deflocculation is accompanied by such a sharp reduction in yield value that a stiff paste becomes fluid (*7*). Consequently a paste of higher powder concentration can be produced in a dispersed than in a flocculated system.

As used in this paper the term "dispersion" denotes a powder-liquid system in which the primary particles are largely independent of each other. Used in this manner its meaning is not identical with the generic term, "dispersion", often applied to any two-phase system, flocculated or otherwise. A "flocculate" denotes a powder-liquid system in which the primary powder particles are held together in clusters by adhesion tension (*1*, *8*). Clear distinction is made in this paper between "dispersing agents" which serve the function of deflocculating or dispersing flocculated systems, and "wetting agents" whose function it is to aid in wetting water-repellent particles by a mechanism of lowering surface and interfacial tension.

The authors have studied more closely the changes in consistency brought about by variations in the state of flocculation or deflocculation (dispersion) of a concentrated powder-liquid system. Like Fischer and Jerome (*3*), they find that qualitative and quantitative differences in the rheological behavior (consistency) of the mixture are so pronounced and typical that these characteristics, in turn, can be used as a measure of dispersion.

Based on this observation, a simple and comprehensive technique for evaluating dispersions and dispersing agents has been developed. Such a method should be welcome to those active in the field of dispersion where, at present, guesswork in evaluating dispersions is often used for want of a simple and quick testing method.

SCOPE

The method of testing for dispersion here presented applies to dry, insoluble powders incorporated into a continuous liquid phase. (Powders which swell in the liquid medium, such as clays in water, can be tested only after they reach their swelling equilibrium. The results must be interpreted with caution.) The test comprises mixing the powder with the dispersing solution, measuring the amount of liquid required to produce two characteristic and reproducible consistencies, the "wet point" and the "flow point", and observing the attendant rheological properties of the mixture. Thus far, the test has been used chiefly for aqueous systems, and the present paper deals with this method of testing for dispersion only as it applies to aqueous systems. However, with but minor modifications, the test can be used for nonaqueous systems as well. In some of its aspects it is an art more than a scientific method. Its chief limitation is that it tests dispersions at high concentration, and the results cannot always be applied to more dilute dispersions. However, discrepancies between the degree of deflocculation of such mixtures at high and at low concentration seem to be the exception rather than the rule.

RHEOLOGICAL DESCRIPTION

The rheological behavior of concentrated powder-liquid systems falls into three distinct, recognizable groups, depending on whether the powder is flocculated, well dispersed, or only partly dispersed.

FLOCCULATES. As a liquid is gradually combined with a powder, the mixture becomes dull in appearance and puttylike in consistency (see Figure 1, upper photo). As more liquid is added, the system remains dull and displays adhesive qualities which cause sharp peaks to appear during kneading. With continued additions of liquid, the mixture becomes proportionately softer, but remains dull in appearance even upon tapping or patting. Finally, as still more liquid is added, the mixture reaches a stage where, though pastelike, it falls or drops under its own weight from a vertically held spatula. This plastic flow behavior with a pronounced yield value over a wide range of concentrations is characteristic of flocculates or poor dispersions.

GOOD DISPERSIONS. As the liquid is combined with the powder, the mixture displays great resistance to sudden pressure or to kneading, turning dull and ridged in appearance. Yet a few moments afterwards the same material coalesces, becomes glossy and smooth, and flows of its own accord if left undisturbed (see Figure 1, center photo). Even when the flow—from a spatula, for instance—is slow, owing to a very high concentration of powder, the falling material spreads out on a glass plate in a glossy pool. At slightly lower concentrations of powder, the material becomes much more fluid, running off in long, fine strings from a horizontal spatula, yet offers a high resistance to sudden thrusts with a knife. This phenomenon is called "active dilatancy" (*4*) and it is indicative of a high degree of dispersion (*2*, *5*). Active dilatancy is observed in powder-liquid systems of high powder concentration only. A small additional amount of liquid will turn such a mixture into a mobile fluid. In the dilatancy range, the

quality of the dispersion can be judged by the degree of spontaneous flow. The longer and finer the honeylike strings of the mixture, with a given powder at a given concentration, the better the dispersion.

Fair Dispersions. As the liquid is gradually combined with the powder, the resultant mixture appears dull, as is likewise true in a flocculate. Yet when gently tapped, the material turns glossy and begins to flow, but ceases its flow as soon as the disturbance is discontinued (see Figure 1, lower photo). This phenomenon is called "passive dilatancy" (*4*). When more liquid is added, the material loses its resistance, and when agitated, seems mobile. Yet when left undisturbed, it sets—i.e., it is visibly thixotropic (*9*) and displays the reversible isothermal sol-gel transformation which characterizes all thixotropic systems. When dropped, it shows the rounded peaks and craters typical of such systems. Even when rather dilute, it will neither flow in strings nor spread out in a thin layer when poured onto a glass plate.

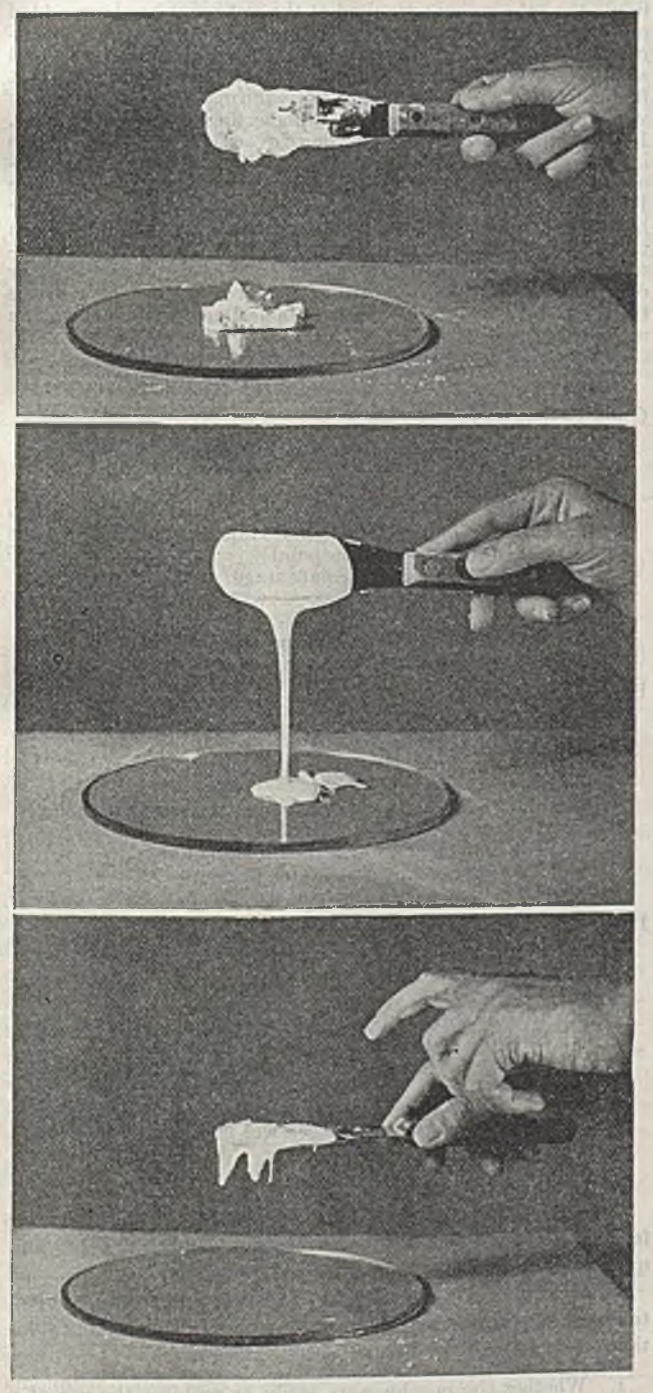

Figure 1. Powder-Liquid Dispersions

Upper. Mixture of 85% water and 15% powder by volume. Plastic, poor dispersion
Center. Mixture of 60% dispersing agent solution and 40% powder by volume. Actively dilatant, good dispersion
Lower. Mixture of 65% dispersing agent solution and 35% powder by volume. Passively dilatant, fair dispersion

RELATIONSHIP OF GOOD, FAIR, AND POOR DISPERSIONS

While concentrated powder-liquid systems show the three general types of rheological behavior outlined above, no sharp line of demarkation between these groups exists. In fact, even within the same powder-liquid system, there may be produced—with an electrolyte, for instance—a continuous change from good dispersion (complete deflocculation) on one end of the scale, to complete flocculation or poor dispersion on the other end of the scale. This transition is accompanied by a corresponding change in rheological properties, both dilatancy and thixotropy.

If thixotropy be defined in terms of time of solidification (*4*), a poorly dispersed, plastic suspension may be regarded as an extreme case of thixotropy—viz., one in which the time of solidification is infinitely short and therefore thixotropy cannot be measured directly. At the other end of the scale, a good dispersion may be regarded as a thixotropic system in which the time of solidification is too long to be measured. In intermediate states, however, the association of particles takes place in measurable time intervals—e.g., in minutes. In these cases the time of solidification becomes tangible and thixotropy clearly noticeable.

The time of solidification of a suspension depends not on the degree of deflocculation alone, but also on concentration. In a given system, the time of solidification at high powder concentration is always shorter than at lower concentrations. Hence the concentrated powder-liquid systems described above, which stop flowing when vibration ceases, at lower concentrations turn visibly thixotropic—i.e., they will require many seconds or some minutes to set up. Passive dilatancy is merely a case of a rapid sol-gel transformation superimposed on dilatant flow.

Passive dilatancy at high powder concentration and visible thixotropy at lower powder concentration are indicative of a state intermediate between flocculation and dispersion. The residual forces between particles are strong enough to set up a loose network of particles, yet minor external forces are sufficient to break down the structure and to permit the particles or small clusters of particles, at least temporarily, to be independent of each other. This state of conditional dispersion is designated here as "fair dispersion".

For practical purposes—for maintaining a stable suspension, for instance—a system displaying some thixotropy is often preferable to a good dispersion displaying no thixotropy because a slight gelling of the system prevents the settling and hard caking of the powder.

EXPERIMENTAL PROCEDURE

Different though their rheological properties be, two characteristic consistencies can be produced in any concentrated powder-liquid system. These consistencies, "wet point" and "flow point" are wholly arbitrary but are easily reproducible and can, therefore, be used conveniently as markers. The wet point is defined as that stage in the moistening of a powder where the minimum amount of liquid is used to form a coherent mass. [The wet point corresponds roughly to the end point of the oil absorption test which measures the amount of oil required by a specified amount of pigment to form a paste (*6*).] The flow point is defined as that stage in the moistening of a powder where the minimum amount of liquid is used which will cause all or a substantial part of the powder-liquid mixture to flow or fall repeatedly from the vertical blade of a horizontally held spatula. The test is based on determining the amount of liquid required at the wet point and at the

flow point and observing the rheological characteristics at and between the two points.

EQUIPMENT. A glass plate, preferably a thick, round plate about 20 cm. (8 inches) or more in diameter.

A stainless steel spatula, preferably one with a broad, short, not too flexible blade—e.g., 10 cm. (4 inches long) and 3.1 cm. (1.25 inches) wide.

A buret with subdivisions of 0.1 cc.

A balance with accuracy of 0.1 gram.

WET POINT DETERMINATION. Weigh out the powder to be dispersed. If it is bulky and light, use 10 grams; if it is dense and heavy, use 20 grams. Place the powder on a glass plate and make a crater in the center of the powder. From a buret add some dispersing solution to the powder, running it into the crater until a little pool forms. Cover the pool with dry powder from the periphery and wait a few seconds until the liquid has soaked in. Then start kneading vigorously with the spatula until as much powder as possible has been wet. Where a water-repellent powder—e.g., sulfur—is to be dispersed it may be advisable to use a wetting agent in conjunction with the dispersing agent, as would be necessary in actual production. If a large proportion of the powder still remains dry, add more solution from the buret in an amount estimated to wet nearly all the remaining dry powder.

When the point is reached where nearly all the powder is moistened, interrupt the kneading action and scrape the material together into one heap and try by patting, pressing, and troweling with the spatula to form a moist, coherent mass. As that point is approached, add the solution dropwise with intermittent kneading and patting, so as not to overshoot the point where just enough and no more liquid is present to form all the powder into a coherent mass. Since the amount of liquid required at this point, the wet point, varies widely with different powders, an inexperienced operator may, at first, overshoot it and have to repeat the test, but with a little experience he will learn to approach the wet point rapidly and then reach it with a few more drops.

FLOW POINT DETERMINATION. After recording the volume of liquid needed to produce the wet point, add more dispersing solution dropwise and continue the kneading throughout until the flow point is reached and the requisite amount of liquid likewise recorded.

For well-dispersed systems the flow point is defined as the stage where a substantial portion of the material first flows off a vertically held spatula blade without producing jagged flow edges. Zinc oxide or barium sulfate dispersed with dialyzed waste sulfite liquor, in aqueous systems, and titanium dioxide dispersed with a 5% solution of a short oil oxidizing type alkyd in xylene, in nonaqueous systems, are good examples of this type of system.

The most characteristic feature of good dispersions is that here the flow point lies very close to the wet point. The better the dispersion, the narrower the gap between the two points until in some cases the wet point and flow point become practically indistinguishable.

For poor dispersions or for out-and-out flocculated systems, the flow point is reached when the paste drops off the vertically held spatula blade. This falling or dropping off is clearly different from the flow of good dispersions. Sometimes the whole mass comes off at once, leaving the spatula bare. More often, an appreciable amount of the mixture remains on the spatula. An example of a flocculated system is a mixture of zinc oxide and water, or, in nonaqueous systems, titanium dioxide in xylene.

In poorly dispersed or flocculated systems, the gap between wet point and flow point is very wide—in fact, so wide that sometimes the test is discontinued before the flow point is reached.

For fair dispersions, the flow point is harder to define and less reproducible than for either well or poorly dispersed systems. The material never really flows spontaneously but drops. Yet just as it breaks away from the spatula, it shows an elongation along the edge as though it were going to flow. The phenomenon is hard to describe but is easily recognized after a little experience. Usually, only part of the dispersion on the spatula comes off, especially if not all the material has been scraped up at the same time. This is due to the thixotropic character mentioned above, which introduces a time factor and also makes the flow point vary somewhat with the kind of kneading and mixing action given to the material. Often, by the time the first part of the material has left the spatula, the rest has set up. An example of a fair dispersion is a mixture of a rutile type titanium dioxide in a solution of dialyzed waste sulfite liquor.

The gap between wet point and flow point in fair dispersions is wide enough to be measured easily—in fact, sometimes it is so wide that one may think the system is flocculated. To decide definitely whether it is dispersed or not, the tapping test mentioned below should be made in all cases where the addition of a small amount of liquid to the wet paste does not produce flow point consistency—i.e., in all except actively dilatant systems.

Tapping at Intermediate Stage. When about 10 to 20% more liquid than the amount required at the wet point has been added and the material does not flow but remains dull and merely becomes softer, some of it is placed at the tip of a horizontally held spatula. The horizontal blade is tapped repeatedly, gently at first and if this is not sufficient to cause the material to move, more vigorously, near the handle with the index finger of the other hand. If the mixture turns glossy and flows over the edges of the blade in bands or strings when so tapped and flow is arrested in midair when tapping ceases, the material is passively dilatant (see Figure 1, lower). It is partly dispersed, or at least it can easily be made to disperse by such means as dilution and agitation, even though for a limited period of time only. However, if the material stays on the spatula and rises on it in scroll-like form or otherwise tends to decrease its surface area in contact with the blade, it is flocculated or contains some flocculated material in appreciable amount.

CHARACTERISTICS OF POWDER-DISPERSING SOLUTION MIXTURES

GOOD DISPERSIONS

1. *At the Wet Point*
   - *a.* Shine without tapping or upon light tapping
   - *b.* Are dry and hard to knead
2. *At the Intermediate Stage* (defined as that mixture which contains about 10 to 20% more liquid than the wet point and has not reached flow point)
   - *a.* Lack distinct intermediate stage
3. *At the Flow Point*
   - *a.* Flow without tapping
   - *b.* Offer resistance to sudden pressure
4. Have a very small gap between wet point and flow point

FAIR DISPERSIONS

1. *At the Wet Point*
   - *a.* Shine on sharp tapping
2. *At the Intermediate Stage*
   - *a.* Flow on tapping only
   - *b.* Show some resistance to sudden pressure occasionally
3. *At the Flow Point*
   - *a.* Fall with elongation at the breaking line
   - *b.* Show no resistance to sudden pressure
   - *c.* Show visible thixotropy

POOR DISPERSIONS AND FLOCCULATES

1. *At the Wet Point*
   - *a.* Remain dull even on tapping
2. *At the Intermediate Stage*
   - *a.* Rise on tapping
   - *b.* Show no resistance to sudden pressure
   - *c.* Possess marked plasticity (high yield value)
3. *At the Flow Point*
   - *a.* Fall without elongation at breaking point
4. Have a very large gap between wet point and flow point

EVALUATION

With the above-described testing procedure all pertinent information as to the quality of the dispersion and the quality and quantity of the dispersing agent needed can be obtained.

As a first step, every new powder to be tested becomes subject to a preliminary test with pure water instead of dispersing solution. This blank test will establish:

1. Whether the powder wets easily or requires the use of a combination dispersing-wetting agent
2. Whether the powder is flocculated or, like starch, for instance, has self-dispersing qualities. In the latter case, dispersing agents can be expected to have a limited effect, if any, while in flocculated systems pronounced changes can be brought about by the use of suitable dispersing agents.

Table I. Effect of Several Dispersing Agents on Some Representative Pigments

Pigment (20 Grams)	Dispersing Agent: Description	Concentration	Wet Point	Flow Point	Difference	Rheological Behavior	Dispersion Quality	Pigment Concentration at Flow Point
		%	Cc.	Cc.	Cc.			% by volume
ZnO[a]	Water	..	6.3	20.9	14.6	Rises on tapping	Poor	14.9
	Dialyzed waste sulfite liquor	2	5.3	6.1	0.8	Flows on tapping	Fair	37.5
		3	4.8	5.4	0.6	Flows	Good	40.3
		5	5.2	5.4	0.2	Flows	Good	40.3
		7	5.1	5.4	0.3	Flows	Good	40.3
TiO_2[b]	Water	..	9.0	16.9	7.9	Rises on tapping	Poor	21.8
	Dialyzed waste sulfite liquor	2	8.6	10.6	2.0	Flows on tapping	Fair	30.7
		3	8.5	9.8	1.3	Flows on tapping	Fair	32.4
		5	8.0	9.3	1.3	Flows on tapping	Fair	33.5
		7	8.3	9.7	1.4	Flows on tapping	Fair	32.6
	Sodium salt of polymerized polyaryl sulfonic acids	3	8.9	12.2	3.3	Rises on tapping	Poor	27.8
		5	8.4	11.8	3.4	Rises on tapping	Poor	28.4
Fe_2O_3[c]	Water	..	6.2	19.4	13.2	Rises on tapping	Poor	16.7
	Dialyzed waste sulfite liquor	5	6.1	7.1	1.0	Flows	Good	35.4
	Modified glucoside extract	5	6.1	9.3	3.2	Rises on tapping	Poor	29.5
$PbCrO_4$[d]	Water	..	6.4	13.7	7.3	Rises on tapping	Poor	19.5
	Modified glucoside extract	5	6.2	8.3	2.1	Flows	Good	28.5
	Sodium salt of sulfonated condensed naphthalene	5	6.2	10.0	3.8	Rises on tapping	Poor	24.9
Furnace black[e]	Water	..	24.7	35.7	11.0	Rises on tapping	Poor	23.7
	Modified glucoside extract	3	20.2	21.5	1.3	Flows	Good	34.1
		5	19.4	24.7	5.3	Flows on tapping	Fair	31.0
		7	19.2	29.9	10.7	Flows on tapping	Fair	27.1
Carbon black[f]	Water	..	34.6	67.4	32.8	Rises on tapping	Poor	14.1
	Modified glucoside extract	5	28.0	29.0	1.0	Flows on tapping	Fair	27.7
		10	28.8	30.8	2.0	Flows on tapping	Fair	26.5
$BaSO_4$[g]	Water	..	6.5	12.2	5.7	Rises on tapping	Poor	27.6
	Sodium salt of sulfonated condensed naphthalene	5	5.7	6.7	1.0	Flows	Good	41.0
Hansa yellow[h]	Water	..	19.2	45.8	26.6	Rises on tapping	Poor	23.9
	Dialyzed waste sulfite liquor + wetting agents	5	17.0	19.8	2.8	Flows	Good	42.1

[a] Zinc oxide, lead-free, 592 American Process, New Jersey Zinc Co.
[b] Titanium dioxide, pure, rutile, 350-OR, United Color & Pigment Corp.
[c] Iron oxide, precipitated, C. K. Williams & Co.
[d] Lead chromate, medium, C.P., United Color & Pigment Corp.
[e] Furnace black, Furnex, Binney & Smith Co.
[f] Carbon black, Raven 15 Black, Binney & Smith Co.
[g] Barium sulfate, precipitated, C. J. Osborn Co.
[h] Hansa Yellow, Horicon X-1351, Imperial Paper & Color Corp.

Steps in Evaluation. *A. Which of a number of dispersing agents produces the best dispersion with a given powder?*

A single test with a solution of 5% concentration is generally sufficient to answer this question. The agent which requires the smallest amount of liquid to go from wet point to flow point and displays the highest degree of dilatancy for a given powder is, as a rule, the most powerful dispersing agent. Final judgment, however, should be reserved until at least three determinations at different concentrations of dispersing agent have been made.

In many cases, too, the total amount of liquid used at the wet point and flow point is a good measure of dispersion. The less liquid required for a given powder, the better the dispersion. When it comes to a close comparison of several good dispersions, not infrequently an agent requiring slightly less liquid to reach the flow point shows the wider gap between wet point and flow point and less dilatancy. Careful checks against other dispersion tests indicate that the size of the gap and the rheological behavior are more significant as to degree of dispersion at high powder concentration than the absolute amount of liquid required. On the whole, however, the rheological characteristics of a mixture conform to the concentration rule, according to which the better dispersion requires less liquid at the flow point than the poorer dispersion.

B. What is the minimum amount of dispersing agent needed for optimum dispersion of a given powder?

This is determined by making successive tests, each test with the dispersing solution at a different concentration. By going stepwise from excess strength to insufficient strength of solution and measuring in each case the amount of liquid used at the flow point, data are provided (Table I) for a curve in which the amount of liquid used is plotted as ordinate and the concentration of the dispersing agent as abscissa (see Figure 2).

The flow point curves show an inflection where the strength of the solution becomes insufficient to disperse all the particles, and sometimes they also bend upward away from the abscissa in the region of higher concentration of the dispersing agent. This means that in some cases an excess as well as a deficiency of dispersing agent can be detrimental to the quality of the dispersion, a fact which underlines the necessity of making a quantitative test in every instance and not drawing conclusions prematurely from a single test. This is clearly shown in Table I, which demonstrates the effect of several dispersing agents in varying concentration on some representative pigments.

Carbon black (Furnex from Binney & Smith) dispersed with a 7% solution of a modified glucoside extract shows passive dilatancy and fair dispersion and with a 3% solution, strong active dilatancy and good dispersion.

Where the curve runs through the minimum, or where it shows its point of inflection, there lies the "optimum"—i.e., at that concentration the best possible dispersion can be produced with the least amount of dispersing agent. (The corresponding wet point curve runs more nearly as a straight line, indicating that the wet point is almost the same for dispersed as for undispersed systems and therefore cannot be used to determine the optimum point. However, the wet point curve is significant as a point of reference. By plotting it along with the flow point curve, the quality of the dispersion can be seen at a glance. The better the dispersion, the closer the two curves approach each other, especially at the point of inflection. The absolute amount of liquid required at wet point or flow point is not characteristic and varies greatly from one powder to the next.) Sometimes there is no sharp point of inflection; instead, the curve turns upward gradually. In that case a decision must be made as to how much of the quality of the dispersion is to be sacrificed for economy's sake.

Calculations. With the data obtained from the curve one can easily calculate the percentage of dispersing agent required for best dispersion—for example, where 20 grams of powder are used in the test and the point of inflection lies at 5.4 cc. for a 3% solution, $\frac{5.4 \times 3.0}{100}$ or 0.162 gram of dispersing agent is required for 20 grams and 5×0.162 gram or 0.810 gram of dispers-

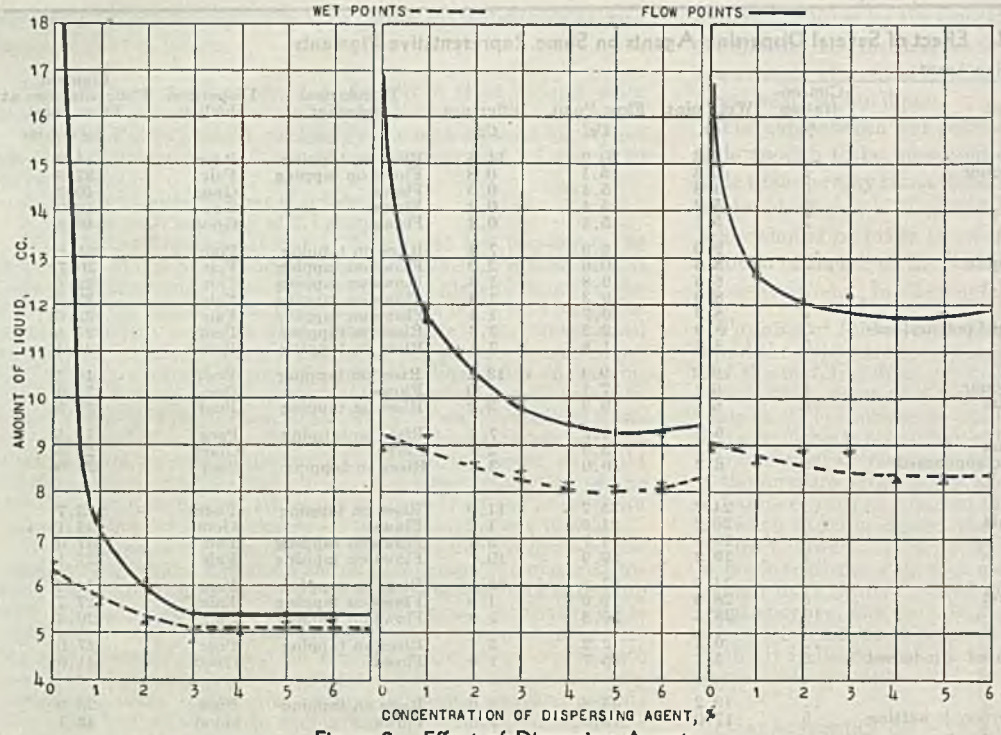

Figure 2. Effect of Dispersing Agents

Left. Good dispersion. 20 grams of ZnO dispersed with dialyzed waste sulfite liquor
Center. Fair dispersion. 20 grams of rutile TiO_2 dispersed with dialyzed waste sulfite liquor
Right. Poor dispersion. 20 grams of rutile TiO_2 dispersed with a sodium salt of polymerized polyaryl sulfonic acid

ing agent for 100 grams of the powder. For accurate calculations this last figure should be multiplied by the specific gravity of the solution, but for practical purposes, at the low concentrations used, the difference between milliliters and grams can be neglected.

C. What is the highest concentration of powder that can be obtained in a dispersion with a given dispersing agent?

This can likewise be calculated from the flow point curve.

Taking the amount of liquid, X, required at the optimum point for an amount of powder, Y, the concentration of powder in the dispersion is $\frac{100\ Y\ \%}{X+Y}$. In the example given above, the concentration would be $\frac{20 \times 100\%}{20+5.4} = 78.7\%$ by weight (40.3% by volume). In other words, 100 grams of dispersion of flow point consistency can be produced with 78.7 grams of powder, 0.637 gram of active dispersing agent, and 20.7 grams of water.

D. What is the effect of extraneous substances on a dispersion?

Dispersions are very sensitive towards extraneous substances. The adverse effect of electrolytes is well known (*2*). Polyvalent cations and acids especially will flocculate dispersions of the common type (negative charge). Not so well known, however, is the fact that many wetting agents also affect the dispersion detrimentally, while other combinations of surface-active compounds produce a greater dispersing effect than either one of the components. To make things still more complicated, such a beneficial combination may disperse nine powders very well and flocculate the tenth, although this one powder is chemically closely related to the others. In view of this unpredictable behavior of dispersions, it is essential to be able to determine the influence of each component separately.

The testing procedure is as follows:

Prepare about 50 grams of the dispersion at flow point consistency, using the dispersing agent which has been found most effective. Take a small part of that dispersion, add a few drops of one of the other liquid components in question, and mix with the spatula. If the rheological characteristics remain unchanged or the mixture becomes slightly more fluid because of the extra amount of liquid added, the compound has not affected the state of dispersion.

If the liquid added, preferably in concentrated solution, strongly liquefies the mixture, it has a dispersing effect. If, on the other hand, the dispersion becomes stiffer, dry, and loses its flow, the added substance detrimentally affects the dispersion.

In this way, the influence of each of the liquid components is quickly determined with a small portion of the original mixture and the formulation can be adjusted accordingly. This procedure has to be followed in all cases where the water-repellent nature of the powder calls for the use of wetting agents and where a good dispersion cannot be achieved with combination wetting-dispersing agents of known general compatibility. Under these conditions it will be necessary to prepare at least one dispersion of flow point consistency without a wetting agent and to try the effect of a number of wetting agents on it, as set forth above. To reach the wet point by the use of a dispersing agent alone takes considerably more time and effort than it does with pigments which are not water-repellent, but once reached, the wet point value is the same as that found so much more easily by the addition of wetting agents.

E. How shall dispersions consisting of more than one powder be tested?

A testing procedure similar to that used above may be followed. Dispersions of each of the component powders are made up singly at flow point consistency and then are combined one by one. If the combination results in loss of flow and causes the system to turn dull and stiff, the dispersion has been affected adversely. But again, the flocculated or flocculating component is clearly recognized and can be eliminated altogether, or, if that is not possible, a dispersing agent can usually be found which, though it may not be the most powerful dispersing agent for each component, avoids trouble in the complete formula.

Such testing procedure is unnecessary if sufficient dispersion data on the individual powders are available. The most suitable dispersing agent can be found by comparing the effect of each dispersing agent on each of the powders and selecting the one with the best over-all performance. This is demonstrated in Table II, in which the pertinent test data of four typical dispersing agents for zinc oxide and titanium dioxide are given.

While all four agents produce good dispersions of zinc oxide, D is more effective than A, B, or C as judged from the small gap between wet point and flow point. However, D produces a poor dispersion of titanium dioxide. Hence, where a dispersion of titanium and zinc oxide is called for, D is unsuitable in spite of its excellence as a zinc oxide dispersant. Agent B is obviously the one to be chosen for the best over-all result.

Time Required. After standard solutions of the dispersing agents are prepared, each test should take no more than 7 to 10 minutes. Hence, the quantitative evaluation of a dispersing agent with respect to one powder can be carried out in about an

Table II. Variation in Dispersing Efficiency of Various Dispersing Agents Acting on Different Powders

Dispersing Agent, 5% Solution	20 Grams of ZnO				20 Grams of TiO_2			
	Wet point	Flow point	Δ[a]	Dispersion	Wet point	Flow point	Δ[a]	Dispersion
	Cc.	Cc.			Cc.	Cc.		
Agent A	4.7	5.2	0.5	Good	7.1	8.2	1.1	Fair
Agent B	4.7	4.9	0.2	Good	7.6	8.0	0.4	Good
Agent C	4.5	4.7	0.2	Good	8.4	11.8	3.4	Poor
Agent D	4.3	4.4	0.1	Good	8.2	12.2	4.0	Poor

[a] Δ = flow point minus wet point, cc.

hour's time, while a qualitative, or partial test as in A above can be made in just a few minutes.

PRECISION

Once the necessary technical skill has been acquired by an operator, which takes no more than a day or two, the quantitative experimental error becomes surprisingly small. For good dispersions, he can usually reproduce his results within a margin of 2%. For poor dispersions it may be as much as 5% and in some cases even slightly more.

The variation in results between two operators is also small. It depends primarily on how quickly, thoroughly, and energetically the mixing is performed, but different operators will never disagree as to the general character of the dispersion—that is, whether the dispersion is good, fair, or poor.

Tests were made with powders of widely different particle size, some with fine powders of an average particle size of 0.1μ and other tests with powders of an average particle size of 50μ. Within this particle-size range, the test proved to be fully applicable.

In view of the high reproducibility of the results, and considering the differences in the surface characteristics of different powders, it becomes understandable that the test can be used successfully for the rapid identification of pigments, and even for the identification of different modifications of the same pigment.

The test reveals the dispersing agent, among a number tested, which produces the best dispersion with a given powder or mixture of powders; the minimum amount of dispersing agent required to achieve optimum dispersion; the highest concentration of powder that can be obtained in a dispersion with a given dispersing agent; the effect of extraneous substances on a dispersion; and the effect of a mixture of powders on a dispersion.

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Separation of Acids by Chromatographic Adsorption of Their *p*-Phenylphenacyl Esters

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IN STUDYING the volatile flavor and odor constituents of pineapple (*5*), small amounts of ester mixtures were obtained which were difficult to separate sharply. Subsequently, the hydrolysis of these esters yielded mixtures of acids whose derivatives were in turn difficult to purify, especially when the quantity of available material was small. This necessitated the development of a method for separating small amounts of acids or their derivatives.

Various attempts have been made to separate the fatty acids directly by chromatography.

Cassidy (*1*) separated lauric, myristic, palmitic, and stearic acids on a carbon column from petroleum ether solution, and Swift *et al.* (*14*) purified methyl linoleate by passing cottonseed oil through alumina. All these separations involve colorless compounds, thus resulting in the consequent difficulties of separating the colorless bands. Cassidy (*1*) tried unsuccessfully to separate the *p*-aminoazobenzene derivatives of the higher fatty acids. Smith (*13*) separated formic, acetic, propionic, butyric, and valeric acids using an indicator to locate the bands on the column. In addition, Manunta (*10*), Kaufmann (*7*), Kaufmann and Wolf (*8*), Kondo (*9*), Papps and Othmer (*11*), Holmes and McKelvey (*6*), Rykhlikov (*12*), Elder and Springer (*3*), and Gyani and Ganguly (*4*) have made contributions in this field.

In searching for a method of purifying small amounts of acids or their derivatives, it was found that the highly purified *p*-phenylphenacyl derivatives (*2*) of the acids have a blue fluorescence in ultraviolet light. These derivatives can be adsorbed on silicic acid, resulting in the separation of acids differing by one CH_2 group, at least in the lower members.

Adsorption was made from a 1 to 1 benzene–petroleum ether (80° to 90° C.) mixture and development made with the same solvent. The refractive index of this mixture is such that it makes the adsorbent translucent (*15*).

The adsorbent used in this case was Merck's silicic acid (reagent grade). Different batches were found to vary in adsorption power. However, by evacuating a 10-cm. layer in a desiccator over phosphorus pentoxide for 4 minutes with a Hyvac pump, a fairly uniform product was obtained. Reactivation of the adsorbent was accomplished in the same manner after air-drying the acetone-eluted material.

The separations reported here were made with mixtures of derivatives, each of which had been previously chromatographed by itself to obtain a pure product. Derivatives which had been recrystallized only to a constant melting point still contained sufficient impurities to produce a yellow to white fluorescence.

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It was found advantageous to treat an alcohol solution of the derivatives with a decolorizing charcoal which adsorbed some highly fluorescent impurities that were removed with difficulty by adsorption on silicic acid. On chromatographing a charcoal-treated derivative under ultraviolet light, the white to yellow band which first appeared gradually developed, so that a blue band appeared beneath the more highly colored zone. This blue band was cut into sections and eluted with purified acetone. A bright fluorescent zone at the top of the column was due to traces of impurities which were strongly adsorbed. Any excess *p*-phenylphenacyl bromide was washed out ahead of the acid derivative.

For the separations 1.2 × 25 cm. columns were employed, using pressure to develop the chromatograms. The columns were wet with benzene–petroleum ether (80° to 90° C.) mixture and the derivatives added in a small quantity of the same solvent. This preliminary adsorption was accomplished with a pressure of 0.35 kg. per sq. cm. (5 pounds per square inch). The solvent mixture was then added and the pressure increased to 1 kg. per sq. cm. (15 to 20 pounds per square inch). The columns were equipped with a reservoir of solvent, so that there was no interruption during development.

The higher molecular weight derivatives were less strongly adsorbed than the lower members, so that a uniform series of separations was obtained from acetic to capric acids, inclusive. Each member could be separated from the one preceding or following it, the higher carbon member always being lower on the column. Similarly isobutyric, isovaleric, and isocaproic *p*-phenylphenacyl esters could be separated from one another and gave the same sequence. The capric and undecylic derivatives could not be separated, nor could the lauric and myristic derivatives.

Table I. Acid Mixtures Whose *p*-Phenylphenacyl Esters Have Been Separated by Chromatographic Adsorption

Acetic-propionic	*n*-Valeric–ethyl methyl acetic
Acetic-butyric	*n*-Valeric–trimethyl acetic
Acetic-valeric	Isovaleric–ethyl methyl acetic
Propionic-butyric	Isovaleric–trimethyl acetic
Propionic-caproic	Isovaleric-isocaproic
Propionic-heptylic	Caproic-isovaleric
Butyric-isobutyric	Caproic-heptylic
Butyric-valeric	Caproic–trimethyl acetic
Butyric-caproic	Caproic-caprylic
Butyric-isovaleric	Heptyllic-caprylic
Isobutyric-isovaleric	Heptyllic-capric
Isobutyric-*n*-valeric	Caprylic-pelargonic
n-Valeric–isocaproic	Caprylic-capric
n-Valeric–*n*-caproic	Pelargonic-capric

The separation of the lower members was characteristic. If a mixture of two of these chromatographically pure derivatives was placed on the column, there first appeared a whitish band which gradually narrowed as development continued with the appearance of blue bands above and below the white band. As the white band disappeared, separation was completed. In going further up the series this characteristic white band is not seen and the separations become less sharp. With the lower members the separation is quantitative.

To illustrate this, 16.9 mg. of butyric derivative and 17.1 mg. of acetic derivative were chromatographed on a column measuring 1 × 18 cm. After development the column under ultraviolet light consisted of the following bands: 2.5 cm. colorless, 2.5 cm. blue, 0.6 cm. colorless, and 2.5 cm. blue (listed from the top downward). From the upper blue band 16.3 mg. of acetic derivative melting at 110.5–111° C. were obtained. The lower blue band yielded 16.8 mg. of butyric derivative melting at 81.5–82° C.

In a similar manner, 27.2 mg. of acetic derivative and 21 mg. of *n*-propionic derivative were separated on a column measuring 1.2 × 25 cm. After development the upper 5-cm. blue band was separated from the 4.5-cm. lower blue band by a 1.9-cm. colorless zone. The upper blue band yielded 26.8 mg. of derivative melting at 110–111° and the lower band yielded 20.7 mg. of derivative melting at 102–103° C.

With the higher members, the adsorbed derivatives formed a continuous band. Sectioning of this with subsequent elution yielded a pure top and bottom section with the intervening sections showing various stages of mixtures.

The *n*-butyric derivative (m.p. 82° C.) can be separated from the isobutyric derivative (m.p. 89°). Ten milligrams of each of these were placed on a 1.2 × 25 cm. column, and after development the blue zone was cut into 7 equal sections. The eluted material from the two top sections melted at 78.6–80° and 78–78.9° C., respectively. On rechromatographing these the melting point was raised to 81–82°. The material from the lowest section of the first column melted at 85–87°, thus placing the iso derivative beneath the normal derivative. Isobutyric *p*-phenylphenacyl ester showed only a partial separation from the *n*-valeric derivative; the material from the upper part of the band melting at 82–84° compared to an expected value of 88–89.5° and that from the bottom part melting at 64–66° instead of 69° C. Although the *n*-valeric ester could not be separated from isovaleric ester, isovaleric ester was separated from the methyl ethyl acetic ester. In this case the latter appeared beneath the isovaleric. In turn methyl ethyl acetic ester gave a partial separation from that of *n*-valeric. Trimethyl acetic was separated from valeric, isovaleric, and *n*-caproic derivatives, and in each case appeared at the bottom of the blue zone.

Table I lists the separations which have been accomplished with this method. By using the method, it was possible to raise the melting point of the *n*-valeric derivative from 63.5° to 69° C. In addition, the *p*-phenylphenacyl ester of trimethyl acetic acid has been prepared for the first time. It melts at 113.1–114° C.

SUMMARY

The *p*-phenylphenacyl esters when highly purified have a blue fluorescence in ultraviolet light. These derivatives can be separated from one another on silicic acid. Each member from acetic to capric, inclusive, could be separated from the one preceding or following it, the higher carbon member always appearing at the bottom of the column. The iso acids with four, five, and six carbon atoms formed a similar series. The isobutyrate derivative could be separated from the *n*-butyrate, but the isovalerate could not be separated from the valerate ester. In contrast with this, methyl ethyl *p*-phenylphenacyl acetate was separated from the isovalerate. The trimethyl acetate was separated from the valerate, the isovalerate, and the *n*-caproate. Neither the capric and undecylic, nor the lauric and myristic derivatives could be separated.

By this method the melting point of the *p*-phenylphenacyl derivative of *n*-valeric acid has been raised from 63.5 to 69° C. The *p*-phenylphenacyl ester of trimethyl acetic acid melts at 113.1–114° C.

ACKNOWLEDGMENT

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Determination of Specific Surface by Permeability Measurements

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The effect of varying porosity on air permeability of powders has been investigated. The present experimental data indicate that the relation between permeability, specific surface, and porosity may be represented by the following modification of Kozeny's equation:

$$K = \frac{g(1+a)}{5\eta S_0^2} \times \frac{\left(\epsilon - \frac{a}{1+a}\right)^3}{(1-\epsilon)^2}$$

For certain pulverized materials, such as ground limestone, quartz, and portland cement, $\frac{a}{1+a}$ was found to be approximately 0.11.

THE industrial importance of the state of subdivision of many substances has led to the development of various methods of determining particle size. The permeability of beds of powdered materials has recently been investigated as a property by which the particle size or specific surface of such materials may conveniently be measured.

Carman (*5*) utilized the permeability to liquids, while Gooden and Smith (*6*), Lea and Nurse (*9*), and Blaine (*3*) used air as the permeating fluid.

The relationship, developed by Kozeny (*7*) and Carman, upon which this work is based is

$$K = \frac{g\,\epsilon^3}{5\eta S_0^2(1-\epsilon)^2} \qquad (1)$$

where K = permeability of the porous medium or apparent linear rate of flow (volume rate divided by bed area) per unit pressure drop (expressed as grams per sq. cm. per cm.) across the bed (cm.^{4} per gram sec.)
g = acceleration due to gravity, cm. per sec.^{2}
ϵ = porosity or fractional void of bed (dimensionless)
η = absolute viscosity of fluid, grams per cm. sec.
S_0 = specific surface of powder, cm.^{2} per cm.^{3}

Lea and Nurse (*9*) developed an apparatus for measuring the air permeability of powdered materials and modified Equation 1 to express specific surface directly in terms of the apparatus constants and the manometer readings:

$$S_w = \frac{14}{\rho_1}\left[\frac{\epsilon^3 A h_1}{(1-\epsilon)^2 LCh_2}\right]^{1/2} \qquad (2)$$

where S_w = specific surface, sq. cm. per gram
ρ_1 = density of material tested
A = cross-sectional area of bed of material
L = depth of bed
C = constant for flowmeter capillary
h_1 = manometer reading across bed
h_2 = manometer reading across capillary

Although Carman has presented evidence tending to show that these equations are valid, and that variations of permeability with porosity are represented by the porosity function, $\frac{\epsilon^3}{(1-\epsilon)^2}$, over a wide range, the work of Blaine (*3*) and that of the Working Committee on Fineness of A.S.T.M. Committee C-1 on Cement (*2*) as well as preliminary tests made in this laboratory have indicated that for fine powders the permeability changes disproportionately with the porosity function.

Experiments were made to determine the effect of varying porosity on the air permeability. The apparatus used was essentially similar to that described by Lea and Nurse (*9*). The permeability cell had an inside diameter of 1.69 cm., and was filled to a depth of 3.00 cm. The capillary tube had a constant $C = 2.64 \times 10^{-6}$. Correction was made for the resistance of the cell membrane, which was of the order of 1% of the resistance of the bed of powder, in the calculation of the ratio of h_1/h_2.

For any given powder and cell S_w, ρ_1, A, L, and C in Equation 2 may all be considered constant. Then Equation 2 may be written

$$\left(\frac{h_2}{h_1}\right)^{1/3}(1-\epsilon)^{2/3} = k\epsilon \qquad (3)$$

where $k = \left(\frac{14}{\rho_1 S_w}\right)^{2/3}\left(\frac{A}{LC}\right)^{1/3}$

If the porosity function holds and Equations 2 and 3 are valid, a plot of $(h_2/h_1)^{1/3}(1-\epsilon)^{2/3}$ versus ϵ should yield a straight line intersecting both axes at the origin. The data obtained on pulverized quartz powder of varying fineness are plotted in Figure 1, and the data obtained on several other materials are plotted in Figure 2. In general the points fall in straight lines intersecting the x-axis to the right of the origin. In the case of the pulverized quartz the intercept is independent of the fineness. These plots are entirely equivalent to those of Powers (*10*), who plotted $Q^{1/3} \times$

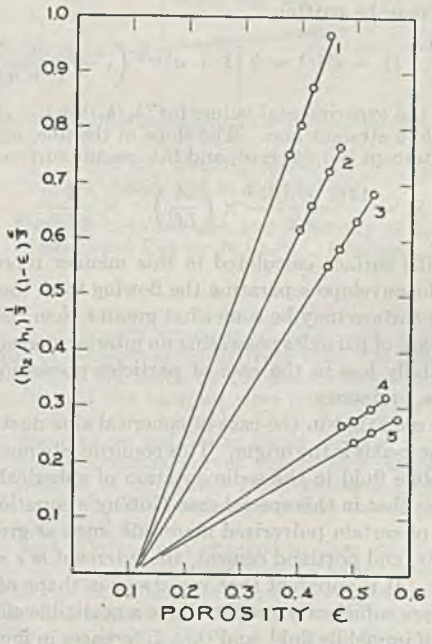

Figure 1. Permeability of Pulverized Quartz

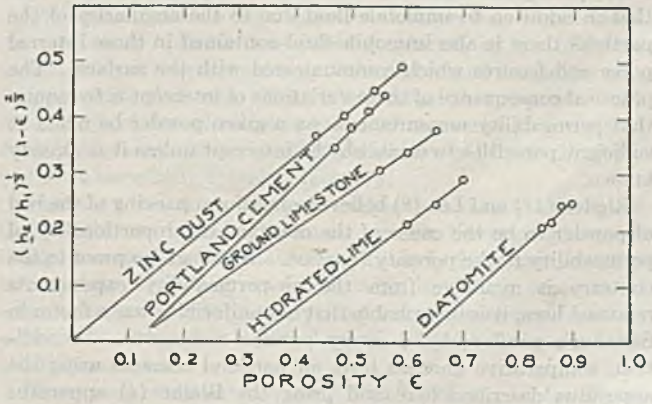

Figure 2. Permeability of Various Materials

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$(1 - \epsilon)^{1/3}$ versus ϵ, as Q, the volume rate, is proportional to the linear rate, and in the case of sedimentation the hydraulic gradient is proportional to the solids content $(1 - \epsilon)$. Powers found that the bleeding of portland cement pastes may be represented by a relationship based on Kozeny's equation if it is assumed that part of the fluid is immobile and does not flow. Steinour (*13*) has also demonstrated that the same relationship holds in the case of nonflocculated suspensions of emery powders and has shown the probable explanation of this phenomenon to be simple stagnation of fluid behind angular particles—that is, failure of fluid stream to trace out angularities of particles.

In view of the similarity of these plots with those of Powers it would appear reasonable to assume that the same inferences apply to the flow of a fluid through a bed of powder as apply to the sedimentation of powdered materials suspended in a fluid. Then, following the work of Steinour, if it is considered that the immobile fluid ϵ_i is proportional to the volume of solids—that is, $\epsilon_i = a(1 - \epsilon)$—then $\epsilon - a(1 - \epsilon)$ may be substituted for ϵ in Equation 1 to yield

$$K = \frac{g(1 + a)}{5\eta S_0^2} \times \frac{\left(\epsilon - \frac{a}{1 + a}\right)^3}{(1 - \epsilon)^2} \qquad (4)$$

Similar substitution in Equation 2 yields

$$S_w = \frac{14}{\rho_1}\left[\frac{(1 + a)\left(\epsilon - \frac{a}{1 + a}\right)^3}{(1 - \epsilon)^2} \times \frac{Ah_1}{LCh_2}\right]^{1/2} \qquad (5)$$

If, as before, it is considered that $\left(\frac{14}{\rho_1 S_w}\right)^{2/3}\left(\frac{A}{LC}\right)^{1/3} = k$,

Equation 5 may be written

$$\left(\frac{h_2}{h_1}\right)^{1/3}(1 - \epsilon)^{2/3} = k\,(1 + a)^{1/3}\left(\epsilon - \frac{a}{1 + a}\right) \qquad (6)$$

A plot of the experimental values for $(h_2/h_1)^{1/3}(1 - \epsilon)^{2/3}$ versus ϵ should yield a straight line. The slope of the line, $m = k\,(1 + a)^{1/3}$, the intercept is $a/(1 + a)$, and the specific surface,

$$S_w = \frac{14(1 + a)^{1/2}}{\rho_1} \times \left(\frac{A}{LC}\right)^{1/2} \times \frac{1}{m^{3/2}} \qquad (7)$$

The specific surface calculated in this manner represents the surface of the envelope separating the flowing from the immobile fluid. This surface may be somewhat greater than the true surface in the case of particles possessing no interior angles, or it may be substantially less in the case of particles possessing internal angles, pores, or fissures.

It will be seen that in the case of spherical zinc dust the intercept with the x-axis is the origin. This confirms Steinour's finding of no immobile fluid in the sedimentation of spherical particles, and indicates that in this special case Kozeny's equation is valid. In the case of certain pulverized materials, such as ground limestone, quartz, and portland cement, the intercept is $\epsilon = 0.11$ approximately. It is apparent that variations in shape of this class of particles are sufficiently small to have a negligible effect on the proportion of immobile fluid, and that differences in fineness have no effect. However, in the case of materials of high porosity, the intercept is greater than $\epsilon = 0.11$ and is varying. It is probable that in addition to immobile fluid due to the angularity of the particles there is also immobile fluid contained in those internal pores and fissures which communicated with the surface. The practical consequence of these variations of intercept is to require that permeability measurements on a given powder be made at sufficient porosities to establish the intercept unless it is already known.

Rigden (*11*) and Lea (*8*) believe nonuniform packing of the bed of powder to be the cause of the observed disproportionality of permeability to the porosity function. Although no proof to the contrary is available from the air-permeability experiments reported here, it is improbable that nonuniformity was a factor in Steinour's nonflocculated emery powder suspension. In addition, comparative fineness tests on portland cements using the apparatus described here and using the Blaine (*4*) apparatus gave excellent agreement when calculated by Equation 5 and the equivalent equation for the Blaine apparatus, regardless of the porosity of test. It is thought improbable that if nonuniform packing were present to any effective degree its magnitude should be dependent only on the porosity and not on the dimensions of the cell.

The possibility that the observed phenomena might result from simple adsorption of fluid on the surface of the particles is thought to be eliminated by the fact that the ratio of immobile fluid to solid volume was observed not to increase with increasing surface area and by the fact that the fluid layer of any reasonable thickness can be calculated to possess a volume too small to be detected by the methods used. Capillary attraction in the interstices may likewise be eliminated by the fact that no increase is observed with increasing surface area and by the absence of the effect in the case of spherical particles.

Table I. Specific Surface of Various Materials

Material	Surface *Sq. cm./g.*
Pulverized quartz 1	626
Pulverized quartz 2	958
Pulverized quartz 3	1430
Pulverized quartz 4	5000
Pulverized quartz 5	6330
Zinc dust	1400
Portland cement	2570
Ground limestone	5800
Hydrated lime	5800
Diatomite	6340

Table II. Comparison of Methods of Calculating Surface of Portland Cement

Method	Surface *Sq. cm./g.*	Ratio to Wagner Surface
Wagner turbidimeter	1870	...
Equation 2, $\epsilon = 0.47$	3670	1.96
Equation 2, $\epsilon = 0.50$	3510	1.88
Equation 2, $\epsilon = 0.53$	3410	1.82
Equation 2, $\epsilon = 0.56$	3350	1.79
Equation 7	2570	1.33

The specific surfaces of the materials shown in Figures 1 and 2 were calculated by Equation 7 and are given in Table I. The surface of the portland cement calculated from the data at each porosity by Equation 2 and that determined by the Wagner turbidimeter (*1*) is compared with that calculated by Equation 7 in Table II. Surfaces obtained by other sedimentation and elutriation methods by Roller and Roundy (*12*) and others are usually higher than those given by the Wagner turbidimeter by factors of from 1.2 to 1.5, and application of Equation 5 or 7 yields similar values.

ACKNOWLEDGMENT

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Factors Influencing Estimation of Free Fatty Acids in Dried Egg Powders

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At the normal pH of dried whole egg, fatty acids liberated during storage are incompletely estimated by the A.O.A.C. procedure for determination of acidity of the ether extract. In addition, the contribution of the extracted cephalin to the acidity of the ether extract may obscure significant percentage increases in the free fatty acidity of the egg powder. The necessity for drying the egg powder as required in the A.O.A.C. procedure is re-emphasized.

A CURRENT study in this laboratory of lipolytic activity in stored dried egg powders necessitated the use of a specific method for measuring glyceride hydrolysis. The method of the Association of Official Agricultural Chemists for the acidity of the ether extract of dried egg powder (*2*, page 314) has been generally used for this purpose and the results obtained have been reported variously as free fatty acids or as increases in the acidity of the ether extract (*3*, *4*, *5*, *11*, *19*). Briefly, this method consists of drying the egg powder to constant weight at 55° C. and under a pressure not exceeding 125 mm. of mercury. Samples of about 2 grams each are extracted with anhydrous ether, the ether is evaporated, and the residual oils are weighed and dissolved in neutral benzene and titrated to the phenolphthalein end point with 0.05 *N* sodium ethylate. The preliminary drying of the powder has been deemed unnecessary and omitted by several investigators (*3*, *5*, *11*).

The data presented here show that the indiscriminate use of results thus obtained, as a measure of either lipolysis or free fatty acid content, may be misleading.

METHODS

Phosphorus was determined according to the method of Allen (*1*). The micro-Kjeldahl procedure was used for total-nitrogen determinations. Amino nitrogen was determined by the Van Slyke manometric method, with 3-minute reaction times; *d,l*-alanine (Merck's) standards were assayed with each run. The formol titration, carried out electrometrically with the Beckman Laboratory Model pH meter, was also used to evaluate amino nitrogen; ethanolamine (redistilled) standards assayed by this procedure were titrated to the extent of 82% and this correction factor was therefore applied. Choline was determined by the reineckate method as modified by Glick (*12*). The pH of dried egg powder was evaluated with the Beckman meter on an emulsion of 1 gram with 3 grams of boiled distilled water. Apparent moisture content of the egg powder was determined by the A.O.A.C. method (*2*, page 308).

RESULTS

INCOMPLETE RECOVERY OF FATTY ACIDS. To estimate the total splitting of glyceride linkages it is essential to determine the liberated fatty acid, whether present as the free acid or the salt. At the pH of freshly dried whole egg (8.5 to 9) it is conceivable that the fatty acids liberated during storage, being weak acids, would react with the egg buffers to form salts. These salts—e.g., sodium oleate—would not, of course, contribute to the acidity of the ether extract, and the result would be incomplete measure of lipolysis.

Table I. Recovery of Added Oleic Acid

Added Oleic Acid *Mg./2 g. egg*	Resultant pH (Liquid)	pH Dried Egg, 1 G. Egg + 3 G. H_2O	Acidity of Ether Extract *Mg. oleic acid/2 g. egg*	Recovered Oleic Acid *Mg./2 g. egg*	Recovered Oleic Acid %
0	7.7	8.9	15.10	...	...
9.7	7.4	8.7	20.65	5.55	57
23.8	7.2	8.4	29.95	14.85	62
37.7	7.0	8.0	39.00	23.90	63
	Adjusted pH (Liquid)				
0	4.5	4.5	22.7	...	...
9.5	4.5	4.5	32.1	9.4	99
23.4	4.5	4.5	45.3	22.6	97
37.7	4.5	4.5	58.5	35.8	95

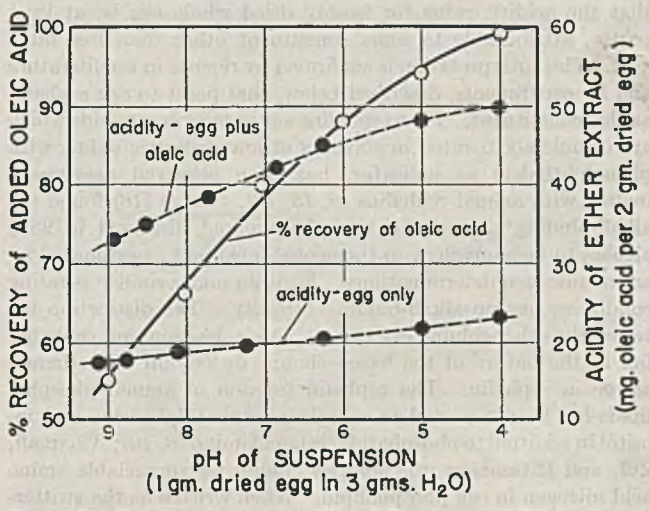


Figure 1. Relation between pH and Recovery of Oleic Acid from Dried Egg by A.O.A.C. Method

To determine the recovery of fatty acids as a function of the pH of dried egg, known amounts of oleic acid were added in ether solution to aliquots of whole fresh eggs, the mixtures were adjusted to various pH levels by the careful addition of 3 *N* hydrochloric acid, and the samples were lyophilized (dried in the frozen state under high vacuum). Oleic acid was used, since it has been reported to constitute about 50% of the egg fatty acids (*7*, *17*), and titration curves run in this laboratory have shown the mixture of egg fatty acids to have approximately the same pK as oleic. The dried egg powders contained 27 mg. of added oleic acid per 2 grams.

The oleic acid solution was checked against standard sodium ethylate. A set of controls, containing no added oleic acid, was prepared from the same batch of egg to cover the same range of pH. At least three 2.0-gram samples of each preparation were extracted with anhydrous ether for 4 hours in Soxhlet extractors and the acidity of the ether extracts was measured by the A.O.A.C. method.

The results are shown in Figure 1. The recovery of the added oleic acid at any pH was determined graphically by the difference in the acidity of the ether extracts of the control and the sample containing added oleic acid. Thus it was found that approximately 55 to 60% of the added oleic acid was recovered at the pH of freshly dried egg and that acidification below pH 5 was necessary to obtain essentially complete recovery.

That the pH change, which would be effected by the liberation of free fatty acid, is insufficient to increase the recovery appreciably is exemplified by the data in Table I, showing incomplete but slightly increasing recoveries with increasing amounts of added oleic acid. The recovery from samples prepared from the same batch of egg, but acidified to pH 4.5 prior to drying, is essentially complete.

DISTRIBUTION OF ACIDITY OF ETHER EXTRACT. From Figure 1 it is evident that the rate of increase of oleic acid recovery with

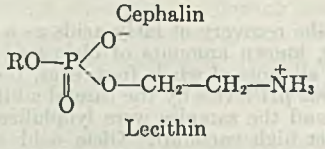
Table II. Analyses of Ether-Extracted Oils

Egg	H_2O	0.05 *N* Sodium Ethylate			Nitrogen			Phosphorus			Molecular Ratio, N/P			Oil Yield
		Whole oil	Acetone-soluble	Acetone-insoluble	Whole oil	Acetone-soluble	Acetone-insoluble	Whole oil	Acetone-soluble	Acetone-insoluble	Whole oil	Acetone-soluble	Acetone-insoluble	
	%	*Mg./g.*			*Mg./g.*			*Mg./g.*						%
Spray-dried A[a]	4.6	1.24	0.44	7.04	2.34	0.32	17.2	4.48	0.52	33.5	1.15	1.36	1.13	..
Spray-dried B[a]	3.7	1.41	0.48	7.16	2.92	0.39	18.6	5.12	0.56	33.4	1.25	1.55	1.23	..
Lyophilized[a]	1.7	1.45	0.43	8.44	2.26	0.24	16.0	4.62	0.42	33.3	1.09	1.27	1.06	..
A, stored[a]	5.6	4.00	3.72	6.32	2.22	0.59	15.9	4.58	1.14	33.6	1.07	1.14	1.06	..
Spray-dried A[b]	...	1.08	0.41	7.82	1.89	0.33	17.7	3.70	0.60	35.0	1.13	1.22	1.12	37.0
Spray-dried B[b]	...	1.22	0.46	7.06	2.52	0.38	18.8	4.48	0.62	33.9	1.24	1.35	1.23	37.1
Lyophilized[b]	...	1.22	0.41	8.01	2.01	0.33	16.0	4.05	0.55	33.3	1.10	1.33	1.05	37.7
A, stored[b]	...	3.60	3.33	5.95	1.93	0.56	15.6	3.93	0.96	33.6	1.09	1.29	1.03	36.8

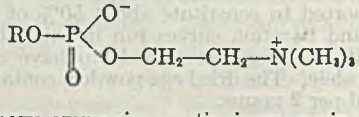
[a] Extracted without preliminary drying.
[b] Extracted after drying 24 hours at 55° C. and less than 3 mm. of Hg; residual moisture content, approximately 0.8%.

decreasing pH is considerably greater than the rate of increase in the acidity of the ether extract of the controls, thus indicating that the acidity value for freshly dried whole egg is, at least partly, attributable to some constituent other than free fatty acid. This interpretation is confirmed by reports in the literature and by experiments, described below, that point to egg cephalin as this constituent. That cephalins act as monobasic acids which are completely titrated in solvents of low dielectric value, with phenolphthalein as indicator, has been observed previously, mainly with animal cephalins (*9*, *13*, *18*). Jukes (*16*) found the alkali-binding capacity of egg phospholipid dissolved in 98% alcohol to be equivalent to the cephalin content as estimated by amino nitrogen determinations. Lecithin under similar titrating conditions has no alkali-binding capacity. The distinction between the ether-soluble egg phospholipids, lecithin and cephalin, lies in the nature of the base—choline in lecithin and ethanolamine in cephalin. The cephalin fraction of animal phospholipids has been reported to contain phosphatidyl serine and inositol in addition to phosphatidyl ethanolamine (*6*, *10*); Chargaff, Ziff, and Rittenberg (*6*), however, found no appreciable amino acid nitrogen in egg phospholipid. When written as the zwitterion structure, they may be represented, according to Fischgold and Chain (*9*), as follows:

Cephalin



Lecithin



The quaternary ammonium cationic group in lecithin is the ion of a very strong base and is not titrated in the A.O.A.C. method, whereas the primary amino group of cephalin is the cation of a weak base and is completely titrated to the $—NH_2$ form by sodium ethylate.

To determine the extent to which egg cephalin contributes to the acidity of the ether extracts, extracts prepared from four egg powders were analyzed. Two of these were commercially spray-dried products; one was prepared in this laboratory by lyophilizing whole-egg mix from several dozen Grade A fresh eggs; the fourth was a commercial spray-dried powder containing 5% moisture which had been stored at 98° F. for 9 months. Extractions were made at the moisture level of the samples as received, and also after a preliminary drying (Table II). Approximately 80 grams of each preparation were extracted with anhydrous ether in a Soxhlet extractor for a period extending 2 to 3 hours after the extracts appeared colorless. The extracts were centrifuged to remove any ether-insoluble material passing through the paper extraction thimbles. The ether was evaporated on the steam bath and traces of solvent were removed by drying in a vacuum oven at 70° C. and 3 mm. of mercury for 1 hour. To a 20-gram portion of each oil were added 180 ml. of ice-cold acetone and the turbid mixture was allowed to stand 2 hours in an ice-water bath. It was then centrifuged and the acetone-insoluble portion twice kneaded in 10-ml. portions of ice-cold acetone and centrifuged. The supernatant acetone solutions were combined and the solvent was removed from both fractions by evaporation on the steam bath, followed by vacuum-oven drying.

Yields, acidity, nitrogen, and phosphorus values for the whole oils and the fractions prepared therefrom are given in Tables II and III. The upper half of each table contains data for the eggs extracted without the preliminary drying. The acidities were determined by titration of benzene solutions to the phenolphthalein end point.

For the oils obtained from the three unstored egg powders, the acetone-insoluble fraction represents about 13% by weight of the original oil but contains about 70% of the acidity. This material is essentially phospholipid, as evidenced by the nitrogen and phosphorus contents and ratios. The slightly low nitrogen and phosphorus values are not unexpected, since impurities such as saturated triglycerides are removed with difficulty from the phospholipid by acetone trituration (*14*, *20*). The acetone-insoluble fraction from the stored egg powder represents 11% of the oil but contains only 17% of the acidity.

The acetone-soluble fractions, containing the free fatty acids, represent 26 to 32% of the original acidity for the unstored eggs, and 83% for the stored eggs, indicating large amounts of free fatty acid in the latter sample. Part of the acetone-soluble acidity may still be due to phospholipid, since about 10% of the nitrogen and phosphorus of the oils from the unstored egg powders and 23% for the oil from the stored sample remain in this fraction. The higher nitrogen and phosphorus content of this latter sample may be attributed to the increased solubility of the phospholipid in acetone imparted by the presence of large amounts of free fatty acid (*15*). It is difficult to account for the very considerable deviation of some of the nitrogen-phosphorus ratios from 1.0; however, as is shown later, these high ratios do

Table III. Distribution of Acidity, Nitrogen, and Phosphorus in Ether-Extracted Oils

Egg	H_2O	Yield of Whole Oil, %		Acidity, % of Total		Nitrogen, % of Total		Phosphorus, % of Total	
		Acetone-soluble	Acetone-insoluble	Acetone-soluble	Acetone-insoluble	Acetone-soluble	Acetone-insoluble	Acetone-soluble	Acetone-insoluble
	%								
Spray-dried A[a]	4.6	88.5	12.0	31	68	12	88	10	90
Spray-dried B[a]	3.7	85.9	13.9	29	71	12	88	9	91
Lyophilized[a]	1.7	87.2	12.8	26	74	9	91	8	92
A, stored[a]	5.6	89.3	10.7	83	17	23	77	22	78
Spray-dried A[b]	...	91.0	9.0	35	65	16	84	15	85
Spray-dried B[b]	...	88.7	11.6	33	67	13	87	12	88
Lyophilized[b]	...	89.4	10.7	30	70	15	85	12	88
A, stored[b]	...	90.8	9.1	85	15	26	74	22	78

[a] Extracted without preliminary drying.
[b] Extracted after drying 24 hours at 55° C. and less than 3 mm. of Hg; residual moisture content, approximately 0.8%.

Table IV. Alkali-Binding Capacity and Amino Nitrogen of Acetone-Insoluble Fractions

	Milliequivalents per Gram				% of Total N as NH_2N		
Egg	Sodium ethylate	Van Slyke NH_2N (hydrolyzed)	Formol NH_2N (hydrolyzed)	Van Slyke NH_2N (unhydrolyzed)	Sodium ethylate	Van Slyke (hydrolyzed)	Formol (hydrolyzed)
Spray-dried A	0.35	0.39	0.41	0.27	30	32	33
Spray-dried B	0.36	0.39	0.37	0.31	27	29	28
Lyophilized	0.42	0.44	0.44	0.40	37	38	38
A, stored	0.31	0.28	0.30	0.10	27	25	28

not invalidate the conclusions to be drawn as regards the contribution made by cephalin to the apparent acidity of the acetone-soluble oil.

The lower halves of Tables II and III show that drying prior to ether extraction results in appreciably lower acidities of the ether extracts. This result is correlated with the lower percentage of phospholipid in these oils. The effect of the moisture content of the egg at the time of extraction on the resulting acidity of the ether extract will be discussed in more detail later.

Alkali-Binding Capacity and Amino Nitrogen of Acetone-Insoluble Fraction. It has been determined that approximately 70% of the acidity of the ether extract from fresh egg powders resides in the acetone-insoluble (phospholipid) fraction of the extracted oil. Presumably, under the conditions of extraction and subsequent titration, the primary amino group of the cephalin constituent is responsible for the alkali-binding capacity, since no other reactive compounds have been reported in egg which would appear in this fraction. The amino nitrogen content was determined according to the method of Van Slyke, on weighed portions dissolved in glacial acetic acid and on aliquots of hydrolyzed material, and also by the formol titration method on the hydrolyzate.

For the hydrolysis, weighed portions of the phospholipid were refluxed with 2 *N* sulfuric acid for 48 hours; the fatty acids were removed by filtration and washed with hot 2 *N* sulfuric acid and the filtrate was made up to volume. The data given in Table IV show satisfactory agreement between the equivalents of alkali-binding capacity and amino nitrogen content as determined on the hydrolyzed phospholipid. Thus, for the acetone-insoluble fractions obtained from the unstored spray-dried powders, both the alkali-binding and amino nitrogen equivalents indicate that about 30% of the total nitrogen exists as cephalin. For the lyophilized egg sample, the value is higher, both measurements indicating a cephalin content of about 38%. The Van Slyke values on the unhydrolyzed phospholipids are lower, notably so for the stored egg powder. This finding is in agreement with the report of Chargaff *et al.* (*6*) that the amino nitrogen of various phospholipid preparations, including egg, decreased on storage, but that hydrolysis of the stored preparations gave considerably higher values. The agreement between the sodium ethylate equivalence values for the unhydrolyzed phospholipid and the amino nitrogen values for the hydrolyzed phospholipid suggests that the disappearance of the amino group may have been due to the formation of an amide that is easily hydrolyzed by alkali. Chargaff *et al.* (*6*) postulated amide formation in their study but did not test its lability to alkali.

Acidity of Acetone-Soluble Fractions. It has been noted (Table III) that about 10% of the nitrogen and phosphorus in the ether-extracted oils from the unstored egg powders remained in the acetone-soluble fractions. In order to correct the acidity of this fraction for nonfree-fatty-acid acidity, the cephalin content was estimated by amino nitrogen determinations and also by determining the difference between equivalents of total phosphorus and choline. The analyses were carried out on hydrolyzates prepared by autoclaving weighed portions of the acetone-soluble oils in 3 *N* hydrochloric acid for 4 hours at 250° F.; the fatty acids were removed with ether. From the average value of the two independent determinations (Table V) cephalin was found to represent about 23% of the acidity of the acetone-soluble fractions of the fresh egg oils, leaving the bulk of the acidity to be accounted for by free fatty acids. The acetone-soluble fraction from the stored egg powder contained less than 3% of its acidity as cephalin; the free fatty acid content was approximately 10 times that for the corresponding fractions for the unstored egg powders.

Converted back to the whole oil basis, the data of Table VI show that not more than about 22 to 26% of the acidity of the ether extract from fresh egg powder is due to free fatty acids.

Table V. Alkali-Binding Capacity of Acetone-Soluble Fractions

(Milliequivalents per Gram of Acetone-Soluble Oil) × 20

Egg	Choline	Total P − choline[a]	Formol NH_2N	Na ethylate	Approximate cephalin[b]	Net free fatty acids
Spray-dried A	0.27	0.12	0.085	0.41	0.10	0.31
Spray-dried B	0.29	0.11	0.080	0.46	0.10	0.36
Lyophilized	0.24	0.11	0.092	0.41	0.10	0.31
A, stored	0.55	0.07	0.081	3.33	0.08	3.25

[a] Total milliequivalents of phosphorus per gram of acetone-soluble oil minus milliequivalents of choline per gram of acetone-soluble oil taken to equal milliequivalents of cephalin; assumed that only negligible amounts of phospholipid other than lecithin and cephalin are present.
[b] Mean of values in columns 2 and 3.

Table VI. Summary of Acidity Fractionation

	Ml. of Sodium Ethylate (0.05 *N*) per Gram of Ether Extract	Acidity Due to			% of Acidity Due to		
Egg		Acetone-insoluble cephalin	Acetone-soluble cephalin	Free fatty acids	Acetone-insoluble cephalin	Acetone-soluble cephalin	Free fatty acids
Spray-dried A	1.08	0.70	0.09	0.28	65	8	26
Spray-dried B	1.22	0.82	0.09	0.32	67	7	26
Lyophilized	1.22	0.86	0.09	0.27	71	7	22
A, stored	3.60	0.54	0.08	2.97	15	2	83

Moisture Content and Acidity of the Ether Extract. Vacuum-oven drying of the four egg powders before extraction with ether resulted in appreciably lower acidities of the ether extracts and the data showed that this lower acidity was correlated with reduced phospholipid content of the oil. Additional data were obtained on one batch of egg powder adjusted to four moisture levels. A commercial spray-dried powder was dried in a vacuum oven at 55° C. with a pressure of about 3 mm. of mercury for 24 hours, resulting in a powder containing 0.86% moisture. Portions of this powder were adjusted to 0.31, 1.75, and 4.99% moisture by being held over Anhydrone, 71% sulfuric acid, and 51% sulfuric acid, respectively, in evacuated desiccators. Ether extracts were obtained as before. With increasing moisture content the acidity of the ether extract increases. This can be correlated with increased phospholipid extraction, as evidenced by greater acetone-insoluble nitrogen and phosphorus contents of the oils (Table VII). The acetone-soluble oil yield is not appreciably affected. Thus, if we assume that the increased phospholipid extracted contains cephalin, it is apparent that the increased acidities are attributed to increased extraction of phospholipid.

DISCUSSION

The incomplete extraction of liberated fatty acids results in low absolute values for increases in fatty acidity of the egg powder during storage or lipolysis studies. This source of error can be eliminated by reconstituting, acidifying to pH 4.5, and drying the egg in the frozen state under vacuum, prior to extracting the oil.

Table VII. Acidity and Composition of Ether Extract as Related to Moisture Content

	0.05 *N* Sodium Ethylate per Gram of Ether Extract	Dry Egg Basis		Whole Oil Basis			
		Acetone-insoluble	Acetone-soluble	Acetone-insoluble	Acetone-soluble		
H_2O						N	P
%	*Ml.*	%	%	%	%	%	%
0.31	0.93	3.5	33.2	9.5	90.5	0.178	0.352
0.86	1.08	3.5	32.7	9.8	90.2	0.195	0.362
1.75	1.17	4.0	32.7	10.8	89.2	0.204	0.382
4.99	1.28	4.7	33.1	12.4	87.6	0.240	0.458

In the measurement of the free fatty acid content of egg oil, and of animal lipoids and certain vegetable oils, the alkali-binding capacity of cephalin must be taken into account, since in many cases it constitutes the major portion of the acidity of the whole ether extract. This fact was recognized recently by Hutt and Weatherall (*15*) in estimating the free fatty acid content of commercial lecithins and by Fairbairn (*8*) in lipolytic enzyme studies on phospholipids. Acetone precipitation suffices to remove the greater portion of the cephalin and, if complete elimination of cephalin is deemed necessary, alcoholic magnesium chloride in conjunction with acetone can be used (*8, 14*).

In egg oil, the cephalin contributes a large portion (60 to 70%) of the acidity of the whole ether extract, thus obscuring significant percentage increases in the free fatty acidity of the egg—i.e., the percentage increase in the acidity of the whole ether extract may be relatively small while there may be a significantly large increase in the free fatty acidity. For example, as shown in Table IV, the difference between the acidities of ether extracts of lyophilized (unstored) and stored egg was about 3-fold; correction for the cephalin titer increased this to greater than 10-fold.

Interpretation of the acidity of the ether extract is further complicated by the variable ether extraction of cephalin at different moisture levels (Tables II and VII). Difficulty in obtaining reproducible results on the same lot of egg powder at the same moisture level, due to inconsistent extraction of phospholipid, has been observed.

ACKNOWLEDGMENT

The authors are indebted to Julia S. Furlow for carrying out the Van Slyke amino nitrogen determinations.

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Determination of Carotenoids and Lipid Amine-Aldehyde Products in Dehydrated Egg

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A spectrophotometric method for the determination of carotenoid content and a fluorometric method for the determination of ether-soluble brown products in powdered eggs are described. The development of brown lipid substances in stored egg powders introduces errors into the direct photometric measurement of carotenoids; however, these errors are minimized by the spectrophotometric procedure described. Both determinations can be performed upon a single ether extract of egg powder.

LOSS of carotenoid indicates oxidative degradation in stored egg powder (*1*). The concentration of fluorescent lipid amine-aldehyde products in egg powders is also of interest, since recent studies have found correlation coefficients between lipid fluorescence values and palatability of −0.79 to −0.98 (*9*).

In connection with the research program on the evaluation of miscellaneous egg powders in this laboratory, the quantitative methods described below were devised for determination of carotenoids and brown products. Previously published methods for spectrophotometric determination of carotenoids in dehydrated egg (*5, 8*) have involved saponification and isolation of the carotenoids in the unsaponifiable fraction. This step has been desirable, since brown substances in lipid extracts of stored powders interfere with spectrophotometric determination of carotenoid. Brown substances, including the lipid amine-aldehyde products, can be separated from the carotenoids by saponification and solvents partition; the lipid amine-aldehyde products have been measured spectrophotometrically and fluorometrically in the acid aqueous portion of the saponifiable fraction (*1, 3*).

In the present paper a combined spectrophotometric and fluorometric method is presented by which carotenoids and lipid amine-aldehyde products can be determined directly upon the ether extract of egg powder without recourse to saponification and solvents partition.

SPECTROPHOTOMETRIC METHOD FOR CAROTENOID CONTENT

The problems of spectrophotometric determination of carotenoids in ether extracts of stored egg powders can be illustrated by the absorption curves of Figure 1. The absorption curve of the sample stored for 9 months at 15° F. is hardly distinguishable from that of a freshly dehydrated egg. In the sample stored for 9 months at 98° F. the carotenoid maxima are barely visible when superimposed upon the broad general absorption band of brown substances. It is obvious that calculation of carotenoid content from the observed density at a single wave length, while justifiable in the case of the sample stored at 15° F., would intro-

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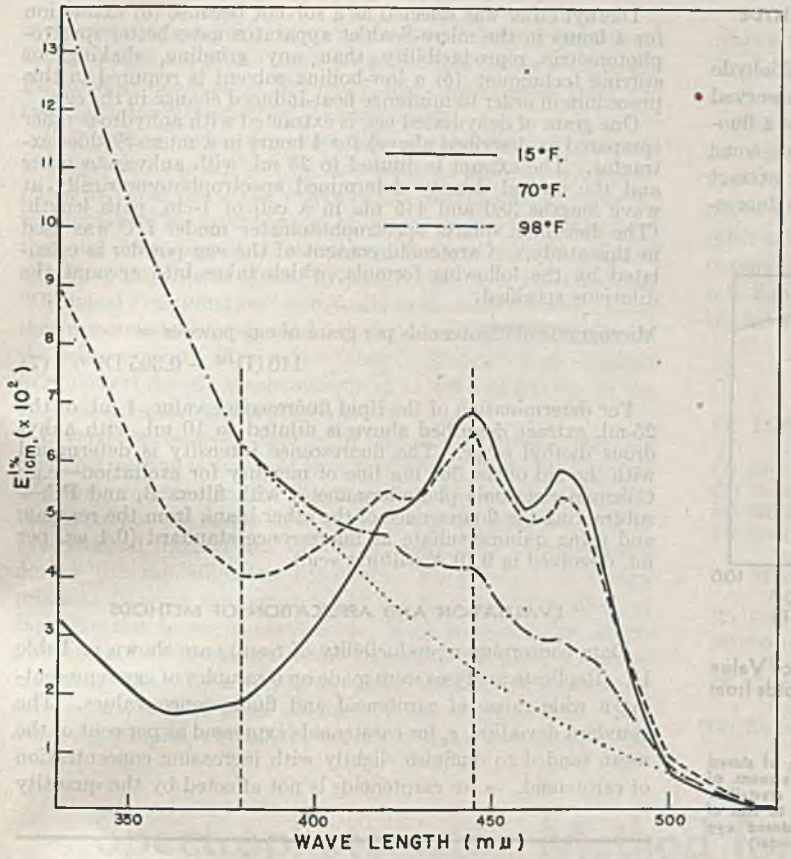

Figure 1. Absorption Spectra of Ether Extracts of Egg Powders Stored 9 Months

λ380 mμ and λ445 mμ are indicated by vertical lines. Dotted line is a hypothetical curve representing absorption due to brown products alone

duce large errors in the case of the sample stored at the higher temperatures.

The spectrophotometric method described here is based on the assumption that absorption by ether extracts of egg powders is due to two components, the carotenoid pigment and the brown substances which develop during storage. Each of these components is actually a complex mixture of substances of similar absorption properties. The simplification of considering the absorbing system as a binary mixture permits a rapid, reliable spectrophotometric determination of carotenoid content.

Density measurements are made at λλ 380 and 445 mμ, corresponding to a minimum and a maximum, respectively, in the carotenoid absorption curve. These densities can be expressed by the usual simultaneous equations for a binary mixture to which the Beer-Lambert law is applicable (*6*):

$$D^{445} = \alpha_x^{445} C_x l + \alpha_B^{445} C_B l \quad (1)$$

$$D^{380} = \alpha_x^{380} C_x l + \alpha_B^{380} C_B l \quad (2)$$

x and B refer to carotenoid and brown pigment, respectively; the numbers refer to the wave lengths; D, α, C, and l have their usual meanings of density, absorption coefficient, concentration, and path length. α as used here is defined by the equation

$$\alpha^\lambda = \frac{\log \left(\frac{I_0}{I}\right)_\lambda}{Cl} = \frac{D^\lambda}{Cl} \quad (3)$$

Since a path length of 1 cm. was used in these experiments, the solutions of Equations 1 and 2 for carotenoid content can be written

$$C_x = \frac{D^{445} - \left(\frac{\alpha_B^{445}}{\alpha_B^{380}}\right) D^{380}}{\alpha_x^{445} - \left(\frac{\alpha_B^{445}}{\alpha_B^{380}}\right) \alpha_x^{380}} \quad (4)$$

Since the absorption coefficients of the brown material appear in Equation 4 only as the ratio $\frac{\alpha_B^{445}}{\alpha_B^{380}}$, values for the individual coefficients are unnecessary. The ratio used is $\frac{D^{445}}{D^{380}}$ obtained on extracts of egg powders in which brown substances had developed and carotenoids had been largely destroyed. Correction is made for absorption due to the small amounts of remaining carotenoids by drawing through the region of carotenoid absorption a hypothetical curve (the dotted line of Figure 1) representative of absorption due to brown products only. The position of this curve on either side of the range of carotenoid absorption is given by the height of the total lipid extract curve; its shape conforms to what is known of the absorption curve of brown lipid materials in egg (*1*). The average value thus found for the ratio $\frac{\alpha_B^{445}}{\alpha_B^{380}}$ was 0.395 in six determinations which ranged from 0.37 to 0.45.

A slightly lower value for this ratio was obtained by the following method. The carotenoid contribution to total density at λλ 445 and 380 mμ was estimated as the total densities of the unsaponifiable fraction at these wave lengths (*1*). These densities were subtracted from the corresponding densities of the total extract to give densities due to brown substances alone, from which the ratio $\frac{\alpha_B^{445}}{\alpha_B^{380}}$ was calculated. However, the graphic method of correcting for residual carotenoid content is preferred because it is not influenced by any loss of carotenoid by isomerization or destruction during saponification.

The value used for the absorption coefficient, $\alpha_x^{445} = 255.5$, is Zscheile's for lutein in ethanol (*10*). Since the absorption of egg carotenoids in ether was found not to differ significantly from that in ethanol, the use of Zscheile's value would introduce little error. However, calculation of a coefficient for a 3 to 1 mixture of lutein and zeaxanthin as performed by Schrenk (*8*) would give a slightly lower result.

The coefficient α^{380} was estimated by measuring the ratio of densities $\frac{D^{445}}{D^{380}}$ on various freshly dehydrated egg samples containing no brown substance. The average of 25 determinations was 3.65. By combination of this average with the figure above for α_x^{445} the value $\alpha_x^{380} = 70$ is obtained. Substitution of these numerical values into Equation 4 gives finally the carotenoid content in grams per liter.

$$C_x = \frac{D^{445} - 0.395\, D^{380}}{227.8} \quad (5)$$

Solution of Equations 1 and 2 for C_B is not useful at present, since there is no satisfactory method of finding absolute values of the absorption coefficients α_B^{445} and α_B^{380}. However, relative values of the concentration of brown substances can be found by using Equation 2 (with $l = 1$ cm.) in the form

$$D_B^{380} = \alpha_B^{380} C_B = D^{380} - 70\, C_x \quad (6)$$

Investigations made for the purpose of evaluating this method have shown that the quantity D_B^{380} increases during storage at low temperatures while the fluorescence value described below remains constant. Thus the value D_B^{380} probably does not measure the same material that is determined by the fluorescence value. The spectrophotometric procedure for determination of lipid amine-aldehyde products cannot be recommended therefore before the completion of further studies designed to improve its specificity.

FLUOROMETRIC METHOD FOR BROWN LIPID AMINE-ALDEHYDE PRODUCTS

Previous work has demonstrated that the lipid amine-aldehyde products are primarily responsible for the fluorescence observed in ether extracts of dehydrated egg (*1*). Development of a fluorometric method for estimating these products requires some general information about fluorometric behavior of egg extract as well as a practical technique for controlling extraneous fluorescence.

In the development of the procedure, the influence of two factors upon the fluorescence value of extracts of egg lipids has been studied: the effect of variable carotenoid content in lipid extracts and the effect of dilution upon the measured fluorescence value. In the procedure herein described the fluorescence value is defined as fluorescence of solution minus fluorescence of solvent on a scale such that fluorescence of the standard (0.4 microgram of quinine sulfate per ml.) equals 100.

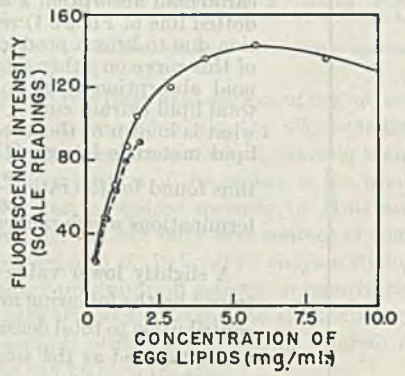

Figure 2. Change in Fluorescence Value with Concentration of Brown Lipids from Stored Egg

Open circles represent ether solutions of stored egg lipids. Half-filled circles show amount of deviation caused by introduction of crystalline α-carotene in concentration equivalent to that of carotenoid in extracts of average unstored egg (approximately 50 μg./gram of powder)

Table I gives fluorescence values of a standard egg oil solution to which increasing amounts of α-carotene have been added. (The oil, obtained by ether extraction of freshly lyophilized egg, had become highly discolored and had lost all its carotenoid after being stored for 11 days at 145° F.) Since carotene has approximately the same molecular weight and the same absorption properties as lutein, the chief carotenoid of egg, the data in Table I provide a basis for estimating the validity of fluorescence values obtained in the presence of variable amounts of carotenoid pigment. The solution of 0.4 microgram per ml. of carotene corresponds to the extract of an egg with extremely high pigmentation. It is apparent from the table that the presence of egg carotenoid does not invalidate fluorescence measurement.

In Figure 2 the open circles show the change in fluorescence with concentration of the egg oil, which represents the concentration of brown lipid amine-aldehyde material. Fluorescence intensities below 50 are in approximately linear relation with concentration of fluorescent material. Above this value deviations from linearity increase and the curve goes through a maximum. The curve, carried only to 10 mg. per liter in Figure 2, continues to fall; for a concentration of 145 mg. per liter the fluorescence is only 20. Similar curves for other fluorescent materials have been published (*4*). It is therefore evident that this fluorescence method must be considered strictly empirical; the ratio of grams of egg extracted to volume of fluorescent solution must be held constant.

COMBINED SPECTROPHOTOMETRIC AND FLUOROMETRIC PROCEDURE

All the glassware used, including the Soxhlet condensers, must be frequently and thoroughly cleaned with dichromate-sulfuric acid. The thimbles and cotton are ether-extracted for 2 hours before use, dried, and kept free from dust. Fluorescence of ether is reduced to a minimum by redistillation after refluxing over a lead-sodium alloy. (Because of its high fluorescence, commercial anhydrous ether is not a suitable solvent.) In this way extraneous fluorescence is reduced to a low, constant value.

Diethyl ether was selected as a solvent because (*a*) extraction for 4 hours in the micro-Soxhlet apparatus gave better spectrophotometric reproducibility than any grinding, shaking, or stirring technique; (*b*) a low-boiling solvent is required in this procedure in order to minimize heat-induced change in the egg.

One gram of dehydrated egg is extracted with anhydrous ether (prepared as described above) for 4 hours in a micro-Soxhlet extractor. The extract is diluted to 25 ml. with anhydrous ether and the optical density determined spectrophotometrically at wave lengths 380 and 445 mμ in a cell of 1-cm. path length. (The Beckman quartz spectrophotometer model DU was used in this study.) Carotenoid content of the egg powder is calculated by the following formula, which takes into account the dilutions specified:

$$\text{Micrograms of carotenoids per gram of egg powder} = 110\,(D^{445} - 0.395\,D^{380}) \quad (7)$$

For determination of the lipid fluorescence value, 1 ml. of the 25-ml. extract described above is diluted to 10 ml. with anhydrous diethyl ether. The fluorescence intensity is determined with the aid of the 365 mμ line of mercury for excitation—e.g., Coleman electronic photofluorometer with filters B_1 and PC_1—subtracting the fluorescence of the ether blank from the reading, and using quinine sulfate as fluorescence standard (0.4 μg. per ml. dissolved in 0.10 *N* sulfuric acid).

EVALUATION AND APPLICATION OF METHODS

Data concerning reproducibility of results are shown in Table II. Replicate analyses were made on 6 samples of egg representing a wide range of carotenoid and fluorescence values. The standard deviation, σ, for carotenoids expressed as per cent of the mean tended to diminish slightly with increasing concentration of carotenoid. σ for carotenoids is not affected by the quantity

Table I. Effect of Added Carotene on Fluorescence of a Discolored Egg Oil in Ether Solution

Concentration of Carotene μg./ml.	Fluorescence	Concentration of Carotene μg./ml.	Fluorescence
0	96	0.4	86
0.1	93	0.5	85
0.2	89	1.6	65
0.3	87	2.7	54

Each liter of solution contained 1.74 mg. of an oil obtained by ether-extraction of freshly lyophilized egg and stored 11 days at 145° F.

Table II. Reproducibility of Spectrophotometric and Fluorometric Methods

Sample No.	H_2O, %	No. of Replicates	Spectrophotometric Carotenoid content, mean μg./gram dried egg	σ as % of mean	Fluorometric Lipid fluorescence value	σ as % of mean
1	5	6	9.48	4.08	75.4	9.75
2	2.5	8	11.1	2.85	40.2	5.48
3	0.7	7	28.3	3.78	22.0	8.54
4	2.6	8	53.3	4.20	40.6	7.11
5	2.5	6	60.0	4.82	3.10	13.98
6	5	6	108	5.04	7.08	2.53
			Av. % of mean	4.13		7.90

Table III. Application of Spectrophotometric Method to a Storage Experiment

Storage Conditions Temp.	Duration	Spectrophotometric Method—Carotenoids Direct (λ 445)	Chemical fractionation (λ 445)	Binary (λ 445, 380)	Difference from Chemical Direct method	Binary
° F.	Months	μg./gram dried egg	μg./gram dried egg	μg./gram dried egg	%	%
15	1	29.3	25.3	28.9	13.4	12.4
15	6	27.4	24.7	27.2	9.8	9.2
15	9	28.7	25.7	28.6	10.5	10.1
70	1	26.35	23.4	26.8	11.4	12.7
70	3	27.3	23.3	25.7	14.6	9.3
70	6	25.2	21.2	22.3	16.0	5.0
70	9	25.3	18.2	21.2	28.1	14.2
98	1	27.5	20.95	21.7	23.8	3.4
98	3	30.3	19.8	21.15	34.6	6.3
98	6	29.2	18.0	19.2	38.2	6.3
98	9	18.0	9.2	9.5	48.8	3.1

of fluorescent material or by moisture level. Since σ for fluorescence intensity is higher than for carotenoid concentration, the fluorometric method is obviously less reproducible than the spectrophotometric method for carotenoids.

Spectrophotometric determinations of the carotenoid contents of dehydrated egg samples by three different procedures are compared in Table III. The values in the column labeled "Direct" were obtained by measurement of optical density at λ 445 mμ of the total ether extract on the assumption that all absorption at this wave length was caused by carotenoid. The values labeled "Chemical Fractionation" were found in the same manner, except that measurements were made on the unsaponifiable fraction of the ether extract. The values labeled "Binary" were obtained from optical density measurements at $\lambda\lambda$ 445 and 380 mμ on the total ether extract and use of Equation 5.

Divergence between results by the direct method and the chemical method is due to at least two errors. These are the positive error inherent in the direct method due to absorption by brown substances in the lipid extracts and the negative error in the chemical method due to loss or destruction of carotenoids during the saponification procedure. Samples low in brown products (storage temperature 15° F.) show only the effect of saponification losses in carotenoid. With these samples, therefore, the binary procedure herein described will prevent carotenoid destruction by avoiding saponification and will produce results comparable to those obtained by the direct method. The other egg samples, which have developed brown discoloration, are subject to both the absorption error and the saponification error. Since these two types of error are eliminated by the binary method, it thus has the advantages of both accuracy and rapidity.

Although the spectrophotometric and fluorometric procedures have been described as a combined method to be used on the same extract, either determination can be made separately or in connection with any other procedure that may be of interest. The ether-extracted egg powder residue, for instance, is suitable for obtaining additional information by means of reflectance and salt fluorescence procedures (*7*, *9*). Some results obtained by the use of the latter techniques will be published separately (*2*).

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Spectrophotometric Method for Estimating Gossypol in Crude Cottonseed Oil

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Spectral absorption curves of the dianilino derivative of pure gossypol and that of the gossypol in an expeller and hydraulic crude cottonseed oil are given. A rapid spectrophotometric method having the accuracy and precision of the gravimetric method for estimating the gossypol content of crude cottonseed oil is presented. The time required for the analysis is less than 2 hours.

THE gravimetric method for the determination of gossypol is based upon the reaction of gossypol with aniline to form a relatively insoluble dianilino derivative. The reaction, however, proceeds rather slowly; and, in the presence of cottonseed oil, the recovery of gossypol is not completely quantitative. Royce (*2*) has proposed a method in which the dianilino-gossypol is precipitated in the presence of pyridine. The precipitate contains two molecules of pyridine of crystallization, which is less soluble; consequently, the recovery of gossypol is improved, but 7 to 20 days are required for complete precipitation. The method has been modified by Royce and Kibler (*4*), and further modified by Royce, Harrison, and Deans (*3*) and by Halverson and Smith (*1*). The latter, with the use of heat and constant agitation of the mixture, were able to shorten the time required for precipitation to 72 hours, with an over-all time of 5 days required for the determination.

This paper presents a colorimetric method that requires about 1.5 hours for the determination of gossypol which has a precision approaching that of the gravimetric method. This method is based on the reaction of gossypol with aniline; but, in contrast with the gravimetric method, the dianilino-gossypol is soluble in the reagents used at the concentration required by the spectrophotometric method.

EXPERIMENTAL

A standard solution of pure gossypol was prepared by dissolving 50 mg. of pure gossypol in about 10 to 15 ml. of peroxide-free ethyl ether, adding 5 grams of Wesson oil, and removing the ether under reduced pressure while warming the flask in warm water not above 60° C. The Wesson oil solution was made to 500 ml. with Skellysolve B.

Aliquots of this solution were used for preparation of a standard transmittance-concentration curve and a spectral absorption curve. The spectral absorption curve was obtained by pipetting 2-ml. aliquots of this solution into each of two 25-ml. volumetric flasks. One of these aliquots was made to volume with Skellysolve B to be used as a blank for preparing the absorption curve. The color was developed in the other aliquot after diluting to 5 ml. and heating with 0.5 ml. of aniline for 40 minutes as described under Procedure. After diluting to volume, the spectral absorption curve 1, Figure 1, was determined with the Beckman spectrophotometer, using the hydrogen discharge tube.

An average value, for 13 determinations, of 0.621 for $\log \frac{I_0}{I}$ at 440 mμ was obtained for 0.2 mg. of pure gossypol in 25 ml. when the color was developed with aniline as described under Procedure and when square cuvettes with a depth of 0.999 cm. were used on the Beckman spectrophotometer. The $E_{1\ cm.}^{1\%}$ value at 440 mμ is 776. The concentration of gossypol in grams per 100 ml. may be obtained from $\frac{\log \frac{I_0}{I} \text{ at } 440\ m\mu}{776 \times \text{cm. depth}}$. From this equation, the amount of gossypol in the aliquot of cottonseed oil taken for analysis may be obtained and the gossypol content calculated.

A spectral absorption curve was determined with the Beckman spectrophotometer for the gossypol contained in a crude cottonseed oil produced by the expeller process and in one obtained by the hydraulic process. These oils are designated as expeller and hydraulic oils throughout this paper. In order to compare the absorption curves of the gossypol obtained from these oils with pure gossypol, the observed $\log \frac{I_0}{I}$ values for the gossypol in these oils at the various wave lengths were multiplied by the ratio ob-

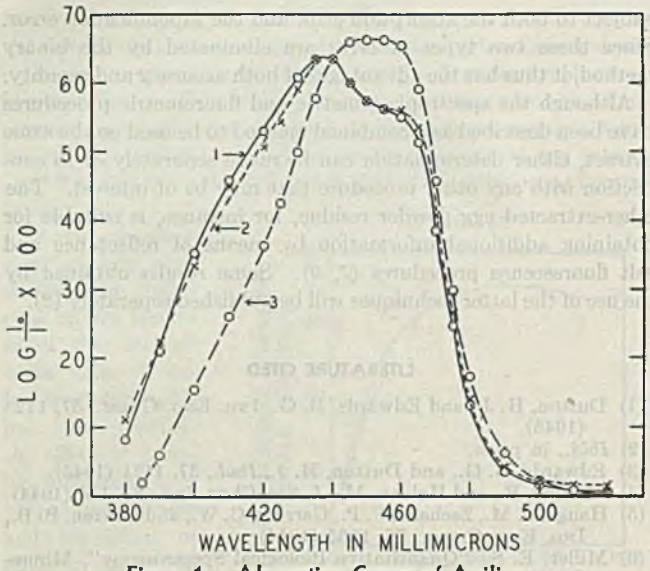

Figure 1. Absorption Curves of Aniline

1. Pure gossypol in Skellysolve B. 2. Expeller cottonseed oil in Skellysolve B. 3. Hydraulic cottonseed oil in Skellysolve B. In each case absorption read against respective untreated solution

tained by dividing the log $\frac{I_0}{I}$ value for pure gossypol at 440 mμ by the corresponding value obtained from the respective crude oil at this wave length. Curve 2, Figure 1, for the expeller oil follows that of pure gossypol, indicating that the material represented by curve 2 is gossypol. In the case of the hydraulic oil represented by curve 3, the maximum occurs between 445 and 455 mμ with a broad, rounded peak compared to the maximum between 435 and 440 mμ for the pure gossypol and the expeller oil. The absorption for the hydraulic oil is less than for the pure gossypol and the expeller oil in the region between 385 and 440 mμ and is about the same in the region from 470 to 520 mμ. The difference between the maximum of pure gossypol and the hydraulic oil is not sufficient to affect the analysis of gossypol by the spectrophotometric method. This shift of the curve to the right is similar to that occurring with extracts of cottonseed meal (*5*) and is probably due to a slight change in the molecule.

The standard transmittance-concentration curve was prepared by transferring three aliquots each of 0.2, 0.3, 0.5, 0.75, 1.0, 1.5, and 2.0 ml. of the standard gossypol solution to 25-ml. volumetric flasks. One flask containing each level of the standard gossypol solution was diluted to volume with Skellysolve B and used as a blank in the Coleman double monochrometer spectrophotometer. The aliquots in the other volumetric flasks were diluted to 5 to 6 ml. with Skellysolve B, and 0.5 ml. of freshly distilled aniline (water-white) was added; then the color was developed with aniline as described under Procedure. The per cent transmittance was read on the Coleman spectrophotometer at 440 mμ. The per cent transmittance plotted against concentration (0.02 to 0.20 mg. of gossypol in 25 ml.) on semilog paper gives a straight line and, therefore, obeys Beer's law. This line is represented by the following equation: concentration of gossypol in mg./25 ml. $= \frac{2.00000 - \log T}{5.171}$. A table may be prepared from this equation for converting transmittance readings to the corresponding weight of gossypol.

PROCEDURE

Filter the crude cottonseed oil under reduced pressure through a layer of washed Hyflo Super-Cel about 2 mm. thick placed over a disk of filter paper in a Hirsch funnel. (It is necessary to wash the Hyflo Super-Cel with hydrochloric acid to remove the traces of iron present, as iron destroys the gossypol. Boil 100 grams of Hyflo Super-Cel with 600 ml. of distilled water and 50 ml. of concentrated hydrochloric acid for 10 to 15 minutes, filter through a large Büchner funnel, and wash well with distilled water. Repeat the process and dry.) Prepare the layer of Hyflo Super-Cel by pouring a suspension of the Super-Cel in Skellysolve F or B over the paper disk while suction is applied. Discard the first few milliliters of oil filtered. The oil may be collected in a test tube placed in the suction flask. Pipet 5 ml. of the filtered crude oil into a 100-ml. volumetric flask, wiping the outside of the pipet with a clean cloth before adjusting to the mark. After draining, rinse the pipet into the volumetric flask with a stream of Skellysolve B from a wash bottle. Make to volume with Skellysolve B. Transfer two 3-ml. aliquots to 25-ml. volumetric flasks. Dilute one of the aliquots to volume with Skellysolve B to be used as the blank in the spectrophotometric determination of gossypol. Dilute the other aliquot to 6 ml. with Skellysolve B and add 0.5 ml. of freshly distilled aniline (water-white); then heat for 40 minutes on the metal top of the steam bath. Adjust the heating so only a small amount of steam is escaping from the bath. This causes only slight loss of Skellysolve B during the heating. This heating may also be done in a water bath at 60° to 65° C.

As the flasks are removed from the steam bath, add about 10 ml. of Skellysolve B to prevent the aniline from separating. Allow to cool, then make to volume with Skellysolve B and mix. Read the per cent transmittance on the Coleman double monochrometer spectrophotometer at 440 mμ, using the aliquot diluted with Skellysolve B as a blank. Scale the weight of gossypol in the 25 ml. from the standard curve or read it from the prepared conversion table. This value represents the weight of gossypol in the aliquot taken. The 3-ml. aliquot is equivalent to 0.15 ml. of oil. The specific gravity, 0.925, of cottonseed oil times the volume gives the weight of oil used in the determination ($0.925 \times 0.15 = 0.1388$ gram). The per cent gossypol is found by multiplying the weight of gossypol found in the aliquot by 100 and dividing by the weight of oil used.

The dianilino-gossypol color has remained stable for as long as 40 hours. Care must be exercised to prevent the blanks from becoming contaminated with aniline.

Three hydraulic oils were analyzed for the gossypol content by the gravimetric method of Halverson and Smith (*1*) and by the spectrophotometric method described above. Some of the determinations were made on the Beckman spectrophotometer, calculating the weight of gossypol from the extinction coefficient. The results are presented in Table I. There were no significant differences in the per cent gossypol found by the two methods. The variation in the gravimetric method is greater than that for the spectrophotometric method. The gravimetric method required 120 hours for completing the analysis, while the spectrophotometric method required less than 2 hours. This simple, quick method using common and inexpensive reagents is suitable for routine analyses as well as for more exacting work. When the concentration is too great to read on the spectrophotometer, aliquots from the blank and determination may be diluted with Skellysolve B to bring them within the reading range of the instrument.

The author is indebted to the Buckeye Cotton Oil Company, subsidiary of the Procter & Gamble Company, for the oil used in this investigation and to J. O. Halverson for suggestions.

Table I. Per Cent Gossypol in Crude Cottonseed Oil

Sample No.		Gravimetric	Spectrophotometric
		%	%
1		0.0168	0.016
		0.0177	0.016
		0.0168	0.017
			0.017
			0.017[a]
			0.016[a]
			0.017[a]
			0.017[a]
	Av.	0.0171	0.0166
2		0.0455	0.050
		0.0542	0.050
		0.0549	0.053[a]
		0.0518	0.053[a]
		0.0530	0.054[a]
		0.0524	0.053[a]
	Av.	0.0520	0.0522
3		0.0555	0.050
		0.0561	0.050
		0.0542	0.049
		0.0505	0.051
		0.0508	0.051[a]
		0.0528	0.051[a]
			0.052[a]
			0.052[a]
	Av.	0.0533	0.0508

[a] Determined by Beckman spectrophotometer.

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Estimation of Gossypol in Cottonseed Meal and Cottonseed Meats

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Spectral absorption curves are presented for the aniline derivative of pure gossypol and gossypol extracted from cottonseed meal and cottonseed meats with 60% alcohol containing ether in the Waring Blendor. These curves represent the difference between the absorption spectra of the aniline derivative of gossypol and of gossypol or gossypol extracts at the same concentration. The absorption curve for the cottonseed meats extract is practically identical with that of pure gossypol except in the region of 380 to 410 mμ. The curve for the cottonseed meal extract is shifted slightly to the right but is very similar to that of pure gossypol.

Cottonseed meal samples were extracted by allowing them to stand 10 minutes in 30% alcohol, then adding sufficient 72% alcohol to give a 60% alcohol to which ether was added. After blending for 5 minutes in the Waring Blendor, the extracts were filtered and made to 100 ml. Aliquots were taken for the blanks and determinations. The dianilino-gossypol color was developed in the latter by heating after adding aniline, then the per cent transmittance was read on the Coleman spectrophotometer, from which the gossypol content was determined. Duplicate determinations of gossypol in cottonseed meal or cottonseed meats may be completed in 2 hours with readily reproducible results.

A NUMBER of methods, both gravimetric (*2*, *6*, *7*) and spectrophotometric (*1*, *5*), for the estimation of gossypol in cottonseed meal and cottonseed meats have been published. The gravimetric methods depend on the reaction of gossypol with aniline to form a relatively insoluble dianilino derivative. Lyman, Holland, and Hale (*5*) reported a colorimetric method based on this reaction. Boatner, Caravella, and Kyame (*1*) proposed a spectrophotometric method for estimating the gossypol content of cottonseed meal and cottonseed meats based on the reaction of gossypol with antimony trichloride. All these methods require a considerable period of time varying from 48 to 120 hours for completing the analysis. The amount of gossypol found depends upon both the extractant and the length of time the extraction is continued.

Three processes of extraction have been used: simple equilibration, intermittent flushing in the Soxhlet-type extractor, and continual washing in the Butt extractor. The gossypol content of cottonseed meal determined by the latter two methods depends somewhat on the moisture content of the meal and the amount of alcohol and water in the ether used for the extraction. In order to obtain satisfactory reproducible results, the methods cited must be followed with care. Moreover, the gossypol found in a given sample of cottonseed meal varies considerably when determined by the different methods.

A rapid method is proposed for determining the gossypol content of cottonseed meal or cottonseed meats in which the extraction is carried out in a Waring Blendor with 75 ml. of 60% ethyl alcohol containing 15 ml. of ethyl ether. The filtrate is made to volume and aliquots are taken for the spectrophotometric determination by a modification of the dianilino-gossypol method of Lyman, Holland, and Hale (*5*). This modification gives a more complete development of the dianilino-gossypol color which is stable for 24 hours or longer. Duplicate or triplicate determinations of gossypol in a sample of cottonseed meal may be completed in 2 hours; cottonseed meats require slightly less time. The results are readily reproducible. The composition of the extractant need not be held to extremely narrow limits. Values almost as high as those given in Table I were obtained with an 85% alcohol mixture. The 60% alcohol mixture has much better foaming characteristics, which gives a good suspension of the sample in the solvent and results in less splashing.

EXPERIMENTAL

In the work reported here, 25 mg. of pure gossypol were dissolved in 5 to 10 ml. of peroxide-free ether; most of the ether was removed under reduced pressure, and the solution diluted to 250 ml. with 95% alcohol. This, or a similar solution, was used for the standard transmittance-concentration and spectral absorption curves. Aliquots of 2 ml. of this solution were pipetted to two 25-ml. volumetric flasks. The color was developed in one of the flasks by heating the aliquot with 0.5 ml. of aniline for 40 minutes at 60° to 65° C., as outlined under Procedure, and the other was used as a blank for running a spectral absorption curve on a Beckman spectrophotometer, using the hydrogen discharge tube. This is represented by curve 1, Figure 1.

Three preparations of pure gossypol containing 0.2 mg. in 25 ml. gave an average value of 0.569 for $\log \frac{I_0}{I}$ at 445 mμ when the color was developed with aniline and read on the Beckman spectrophotometer using square cuvettes having a depth of 0.999 cm. The $E^{1\%}_{1\text{ cm.}}$ value at 445 mμ is 712. The concentration of gossypol

$$\text{in grams per 100 ml.} = \frac{\log \frac{I_0}{I} \text{ at 445 m}\mu}{712 \times \text{depth in cm.}}.$$

The amount of gossy-

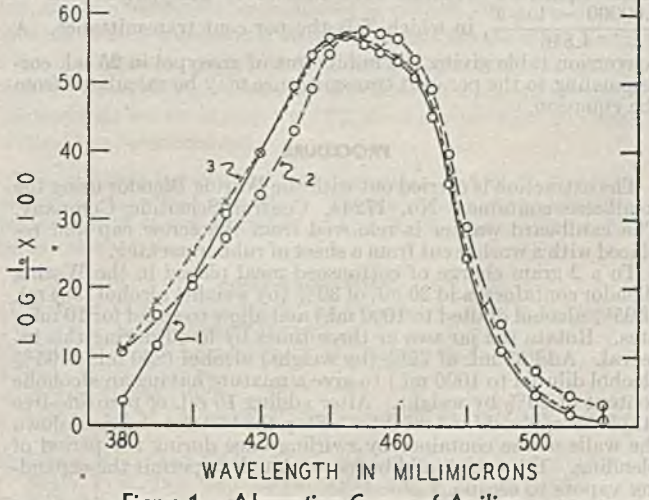

Figure 1. Absorption Curves of Aniline

1. Pure gossypol in alcohol-ether mixture. 2. Gossypol extracted from cottonseed meal with an alcohol-ether mixture. 3. Gossypol extracted from cottonseed meats with an alcohol-ether mixture. In each case absorption read against respective untreated solution

pol in the aliquot taken from the cottonseed meal or meats extract may be obtained from the above equation and the per cent gossypol content calculated.

Following the same procedure, a spectral absorption curve was obtained for the gossypol extracted from cottonseed meal by the proposed method. An absorption curve was likewise obtained for cottonseed meats. In order to compare these absorption curves with that of pure gossypol, the $\log \frac{I_0}{I}$ values observed at the various wave lengths of each extract were multiplied by the ratio obtained when the $\log \frac{I_0}{I}$ value of pure gossypol at 445 mμ was divided by the corresponding value of the respective extracts at this wave length. In this manner, curves 2 and 3, Figure 1, were obtained for the gossypol extracted from cottonseed meal and cottonseed meats, respectively. Curve 2 for the cottonseed meal is shifted slightly to the right with the maximum absorption at 450 mμ compared to 445 mμ for pure gossypol. A similar shift to the right occurs when hydraulic-expressed crude cottonseed oil is the source of the gossypol (*8*). This shift is so slight and the general character of the curve is so similar to that of pure gossypol in the region of 445 to 510 mμ that the absorption of the cottonseed meal extract in this region must be attributed to the gossypol present. This shift, however, may be due to a slight modification of the gossypol molecule. This divergence has no effect on the spectrophotometric estimation of gossypol in cottonseed meal. Curve 3, Figure 1, for cottonseed meats follows that for pure gossypol almost exactly in the region of 420 to 510 mμ. There appears to be slightly greater absorption in the region between 370 and 440 mμ for the aniline derivative of cottonseed meal extracts than for pure gossypol.

A standard transmittance-concentration curve was prepared by transferring three aliquots each of 0.2, 0.3, 0.5, 0.75, 1.00, 1.5, and 2 ml. from a standard gossypol solution containing 25 mg. of pure gossypol in 250 ml. of 95% alcohol, prepared as previously described, to 25-ml. volumetric flasks. Three preparations of pure gossypol were used for this curve. One of the flasks containing each aliquot was made to volume with 72% alcohol, by weight in water, to which 70 ml. of ether per 1000 ml. were added and used as a blank for the spectrophotometric determination. Five milliliters of the above alcohol-ether mixture and 0.5 ml. of freshly distilled aniline were added to each of the other flasks and the color developed as described under Procedure. The transmittance was read in the Coleman double monochrometer spectrophotometer at 445 mμ, using the blanks containing the corresponding amount of gossypol. The values were expressed as milligrams of gossypol per 25 ml. The standards follow Beer's law, giving a straight line when per cent transmittance *vs.* concentration is plotted on semilog paper. This line is represented by the linear equation: concentration in mg. of gossypol/25 ml. $= \frac{2.00000 - \log T}{4.846}$, in which T is the per cent transmittance. A conversion table giving the milligrams of gossypol in 25 ml. corresponding to the per cent transmittance may be calculated from the equation.

PROCEDURE

The extraction is carried out with the Waring Blendor using the small-size container, No. 17244, Central Scientific Company. The cardboard washer is removed from the screw cap and replaced with a washer cut from a sheet of rubber packing.

To a 2-gram charge of cottonseed meal placed in the Waring Blendor container, add 20 ml. of 30% (by weight) alcohol (384 ml. of 95% alcohol diluted to 1000 ml.) and allow to stand for 10 minutes. Rotate the jar two or three times by hand during this interval. Add 55 ml. of 72% (by weight) alcohol (830 ml. of 95% alcohol diluted to 1000 ml.) to give a mixture having an alcoholic content of 60% by weight. After adding 15 ml. of peroxide-free ethyl ether, blend for 5 minutes. Stop the blender and rinse down the walls of the container by swirling once during the period of blending. The cap should be loose enough to permit the expanding vapors to escape.

After blending, remove the cap, swirl the jar to suspend the residue, and pour into a 250-ml. beaker. Rinse the cap and jar with a stream of the alcohol-ether mixture (1000 ml. of 72% alcohol by weight to 70 ml. of ether), used for washing and making dilutions, from a wash bottle and transfer the washing to a second beaker to be used to wash the first beaker and residue after filtering through a filter tube (Corning 9480). Insert the filter tube and a bent glass tube for the application of suction in a two-holed rubber stopper placed in the top of a bell jar.

Prepare the filter by inserting a porcelain disk in the filter tube and, with vacuum applied, pour a layer of asbestos over it, followed by a layer of washed Hyflo Super-Cel about 2 mm. thick. (It is necessary to wash the Hyflo Super-Cel with hydrochloric acid to remove the traces of iron present, as iron destroys gossypol. Boil 100 grams of Hyflo Super-Cel with 600 ml. of distilled water and 50 ml. of concentrated hydrochloric acid for 10 to 15 minutes and filter, using a large Büchner funnel. Wash well with distilled water. Repeat the process and dry.) Suspend the washed Hyflo Super-Cel in 72% alcohol for preparing the filter. Receive the filtrate in a 100-ml. volumetric flask, containing 5 ml. of ether, placed under the bell jar. This ether replaces that lost during the filtration and prevents a slight turbidity due to the separation of oil from the mixture. Wash the first beaker and residue with the washings from the blender jar and then wash a second time with the alcohol-ether mixture from the wash bottle. Allow to cool and make to volume with the alcohol-ether mixture.

Table I. Gossypol Content of Cottonseed Meal and Cottonseed Meats

Sample No.		Gravimetric %	Blendor %	Lyman *et al.* %
2933		0.110	0.082	0.038
		0.118	0.083	0.038
		0.088	0.080	0.043
		0.109	0.088	0.037
		0.099	0.085	
		0.096	0.086	
	Av.	0.103	0.084	0.039
3039		0.117	0.077	
		0.103	0.081	...
			0.084	
	Av.	0.110	0.081	
3040		0.157	0.109	
		0.152	0.115	...
			0.118	
	Av.	0.155	0.114	
3041		0.100	0.072	
		0.096	0.074	...
			0.071	
	Av.	0.098	0.072	
3042		0.098	0.074	
		0.105	0.077	...
			0.071	
	Av.	0.102	0.074	
3043		0.099, 0.101	0.103	0.064
		0.092, 0.105	0.101	0.044
		0.107, 0.088	0.099	0.052
		0.106, 0.107	0.100	0.056
		0.111, 0.117	0.102	
		0.113, 0.116	0.100	
	Av.	0.105	0.101	0.052
3044		0.065, 0.059	0.053	0.025
		0.054, 0.053	0.052	0.026
		0.063, 0.051		
		0.067, 0.064		
		0.067, 0.070		
		0.061, 0.066		
	Av.	0.061	0.053	0.026
3073		0.095	0.098	0.040
		0.099	0.096	0.050
			0.102	0.055
				0.059
	Av.	0.097	0.099	0.051
3074		0.131	0.135	0.080
		0.123	0.128	0.080
		0.108	0.130	0.071
		0.103		0.083
		0.098		
	Av.	0.113	0.131	0.076
3096		0.087	0.058	0.051
		0.087	0.059	0.045
			0.061	
	Av.	0.087	0.059	0.048
3095		0.813	1.04	
		0.818	1.00	
		0.824	1.04	...
		0.818	1.04	
		0.827	1.03	
	Av.	0.820	1.03	

Two blender jars are advantageous, since one charge may be allowed to stand in the 30% alcohol while another one is being blended and filtered.

Use a charge of 0.2500 gram of cottonseed meats for the determination and mix the 20 ml. of 30% and the 55 ml. of the 72% alcohol before adding; otherwise a sticky paste is obtained which is not readily extracted. The 15 ml. of ether may be added directly to the jar. Blend the meats immediately, after which proceed as with cottonseed meal.

Transfer two 5-ml. aliquots to 25-ml. volumetric flasks. Dilute one of the aliquots to volume with 72% alcohol containing ether (1000 to 70 ml.) to be used as the blank in reading the transmittance of the gossypol with the spectrophotometer. Add to the other aliquot 0.5 ml. of freshly distilled aniline and heat on the metal top of the steam bath for 40 minutes. Adjust the steam so that only a small amount of steam is escaping. (This heating may be done in a water bath at about 65° C.) Remove from the steam bath, add 5 to 10 ml. of the 72% alcohol-ether mixture, and allow to cool. Then make to volume with the alcohol-ether mixture. Mix and read the intensity of color as per cent transmittance on the spectrophotometer at 445 mμ using the blank prepared from the extract. Take care to avoid contaminating the blanks with aniline.

The weight of gossypol in milligrams in 25 ml. may be scaled from the standard transmittance-concentration curve or read from the prepared conversion table. The value obtained is the per cent of gossypol in cottonseed meal. In the case of cottonseed meats, the milligrams of gossypol found per 25 ml. times 8 gives the per cent of gossypol.

The gossypol content of 10 samples of cottonseed meal was determined by the proposed method and compared with values obtained by the gravimetric method of Halverson and Smith as revised by Smith (*7*). Some of these meals were also run by the Lyman, Holland, and Hale colorimetric method. The results are shown in Table I. On the whole, the gravimetric values are slightly higher than those by the proposed method; however, the values for samples 3043, 3044, 3073, and 3074 are as high as those by the gravimetric method.

DISCUSSION

The mean difference in gossypol content as determined by the two methods was 0.0122 ± 0.0054% for all the samples of meals. The difference for individual samples of cottonseed meal, however, varied from 0.0408 to −0.0177%. This variation indicates that the ratios between the values of the two methods are not precisely the same for the different samples of meal. The variation for the gravimetric method for cottonseed meals 3043 and 3044 may be partially due to the use of different lots of ether for the extraction of the meal without modifying it to the optimum composition of 96.5% ether, 2.3% alcohol, and 1.1% water (*4*). All the meals used for the gravimetric method had a moisture content of 20 to 22%, which is the optimum for extracting gossypol from cottonseed meal by the method used (*3, 4, 5*).

The standard deviation for the proposed method was 0.0025% when the intensity of color was determined on two aliquots from the same extract. With one aliquot, the value would have been about 0.0027%, while one aliquot from each of two separate extracts would have had a standard deviation of about 0.0019%; therefore, it is recommended that two separate charges of cottonseed meal be carried through the entire process with the color being developed in only one aliquot from each extract. For control work involving large numbers of samples, however, single determinations should be satisfactory.

Gossypol contents of six of these cottonseed meals were determined by the method of Lyman, Holland, and Hale (*5*). The meals were extracted for 72 hours with peroxide-free ether containing 2.3% alcohol and 1.1% water (Table I). In all cases, the Lyman, Holland, and Hale method gave lower values than the proposed or the gravimetric methods; however, these authors have stated that higher values may be obtained if 20% moisture is added to the meal.

The value for cottonseed meats, No. 3095, by the proposed method was higher than by the gravimetric method, being 1.03 and 0.822%, respectively (Table I). However, 1.04 and 1.06% gossypol was found in these meats when they were extracted with ethyl ether as in the gravimetric method and the extracts subjected to the colorimetric procedure for oils (*8*) after removal of the ether and taking up in Skellysolve F. These values obtained for the ether extracts are practically identical with those obtained when the extraction was done in the blender, and are appreciably higher than those yielded by the gravimetric method. Boatner, Caravella, and Kyame (*1*) have reported that the antimony trichloride spectrophotometric method gives a higher value for some cottonseed meats than the gravimetric method. This indicates that some of the gossypol is not precipitated although it gives the color reaction with aniline. The spectral curve for this aniline derivative follows that of pure gossypol in the region of 420 to 520 mμ.

In the proposed method, the extraction is completed in 15 minutes with a mixture of alcohol, water, and ether (respectively, 51.6, 34.4, and 14.0%) in the Waring Blendor while 72 hours are required by the method of Lyman, Holland, and Hale using the Butt extractor with ether containing 2.3% alcohol and 1.1% water. The extract obtained by the proposed method is filtered and made to volume with the alcohol-ether mixture, as compared to the Lyman, Holland, and Hale method in which the ether is removed and the gossypol taken up in *N* butyl alcohol. These methods also differ in that the proposed method requires only one fourth as much aniline and that heat is used to promote the complete color development which is stable for a considerable time. In the Lyman, Holland, and Hale method, the color appears to develop more readily for pure gossypol than for that extracted from cottonseed meal. About 20 to 24 hours are required to reach the maximum color intensity by the latter. Ethyl alcohol solutions have advantages over *N* butyl alcohol from a manipulation standpoint.

The extraction was carried out on cottonseed meal No. 2933 with 75 ml. of alcohol adjusted to 56.5, 60, 70, 75, and 85%, and 15 ml. of ether after soaking in 24 or 30% alcohol for 10 minutes. The differences in the amount of gossypol found were very slight for the 56.5 to 75% alcohol, while that for the 85% was 0.014% lower than for the 60. This indicates that during the blending operation the concentration of the alcohol mixture may be permitted to vary a few per cent without affecting the results. Allowing the charge of cottonseed meal, but not cottonseed meats, to stand for 10 minutes before blending softens the meal, which facilitates the extraction of gossypol. Thirty per cent alcohol is more effective than 50 for this purpose.

The filtered extracts will become slightly turbid if too much ether is lost during the filtration. Aliquots used for the blanks will also become turbid when diluted to volume with a mixture of 1000 ml. of 60% alcohol and 70 ml. of ether. On the other hand, if the dilutions are made with 95% alcohol, turbidity frequently occurs. These difficulties are not encountered when all dilutions and washings are made with the 72% alcohol-ether mixture (1000 to 70 ml.) as recommended.

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Chemical Determination of Vitamin A in Mixed Feeds and Feedstuffs

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The antimony trichloride colorimetric reaction for determining vitamin A has been modified in order to correct for the color produced by nonvitamin A materials. The system of correction depends upon the action of light on the kinetics of the antimony trichloride reaction and the use of a preliminary chromatographic purification.

THE analysis of mixed feeds for their vitamin A content is complicated by the relatively low vitamin A level often present, the large number of different ingredients present in the mixture, and the wide variation in the physical and chemical characteristics of these ingredients. These complications have prevented the use of spectrophotometric methods for vitamin A measurement. The blue color reaction produced by vitamin A with antimony trichloride offers the best approach to the problem at the present time.

The antimony trichloride blue color reaction of Carr and Price (*3*) has high sensitivity to small amounts of vitamin A. This method as modified by Dann and Evelyn (*5*) has been widely used as the basis for a number of analytical methods adapted to a variety of materials. Oser, Melnick, and Pader (*7*) have used the blue color test in vitamin A measurements on food products in a procedure involving the use of an internal standard designed to correct for the presence of reaction inhibitors, temperature effects, reagent variations, turbidity, and extraneous color. Corbet, Geisinger, and Holmes (*4*) very early listed a large group of materials known to give a color reaction with antimony trichloride under conditions of the usual vitamin A test.

The reaction has been utilized for the quantitative measurement of vitamin D and some of the related sterols and the blue color produced by carotene and the xanthophyll pigments is common knowledge. Dann and Evelyn (*5*) attempted to correct for the reaction of carotene with antimony trichloride and the resultant interference with the vitamin A test. Oser, Melnick, and Pader (*7*) attempted to distinguish quantitatively between the blue color produced by the reaction of carotene and that produced by the reaction of preformed vitamin A by the difference in the intensity of the two color reactions with time. These authors found that the blue color of the reacted vitamin A faded almost completely in 2 hours, whereas the blue color of carotene increased in intensity over this period of time.

The present authors in an attempt to duplicate this work found that the period required for vitamin A blue color destruction was greatly influenced by both light and temperature conditions. The effect of temperature was noted by Norris and Church (*6*) and is a normal behavior, but the action of light has only recently been reported by Caldwell and Parrish (*2*) and appears to offer an explanation for some of the discrepancies in the vitamin A literature in regard to the rate of fading of the blue color.

Some types of mixed feeds and certain feed ingredients when reacted with antimony trichloride give strong color reactions of nonvitamin A origin that interfere greatly with the vitamin A tests. The action of light on the course of these nonvitamin A color reactions has been found to differ so greatly from the action on the true vitamin A blue color as to provide a means of differentiating between the color reaction of vitamin A and any interfering color reactions simultaneously produced.

ANALYTICAL PROCEDURE

REAGENTS. Antimony trichloride reagent, 90 grams of reagent grade antimony trichloride in 240 ml. of reagent grade chloroform.

Aqueous potassium hydroxide, 50 grams of reagent grade pellets in 50 ml. of distilled water.

Calcium phosphate, dibasic, should be tested to retain vitamin A and pass β-carotene (Mallinckrodt A. R. grade).

Skellysolve F, petroleum ether, boiling range 30° to 60° C.

EXTRACTION. Place a weighed 10-gram sample of feed in a 20 × 80 mm. paper extraction thimble and extract (all operations on vitamin A solutions should be carried out in subdued artificial light, preferably in amber glassware) for 4 hours in a Butt-type extraction tube with 35 ml. of Skellysolve F placed in a 100-ml. extraction flask. Other types of extraction equipment may require different volumes and extraction times.

Evaporate off the solvent from the extract under a vacuum, add 30 ml. of 95% ethyl alcohol and 3 ml. of aqueous potassium hydroxide solution, and bring to a boil in a water bath. Cool and wash contents of flask into a 250-ml. separatory funnel with a minimum amount of Skellysolve F. Add 30 ml. of distilled water and sufficient Skellysolve F to make 25-ml. total volume of the latter. Shake and draw off the lower phase after settling, and transfer the Skellysolve phase to a clean 125-ml. flask. Repeat the extraction of the aqueous phase with 3 more 25-ml. portions of Skellysolve and combine the extracts in a clean 250-ml. separatory funnel. Wash free from alkali by repeated washings or with a continuous spray washing device. Filter alkali-free extract into a 300-ml. long-necked round-bottomed flask through about 15 grams of anhydrous sodium sulfate on a filter paper, and wash the filter paper with additional solvent.

PURIFICATION. If little or no color is present in the final extract, this step may be omitted. If an appreciable amount of colored pigments is present, evaporate the extract down to a 5-ml. volume under a vacuum and wash into a chromatographic column with a minimum volume of Skellysolve.

Prepare a 16 × 150 mm. chromatographic column with a 7.5-cm. (3-inch) layer of dibasic calcium phosphate, topped by a 2.5-cm. (1-inch) layer of calcium carbonate. The dibasic calcium phosphate should be tested prior to use and shown to retain vitamin A without destruction and to pass β-carotene using Skellysolve F as a solvent. The Skellysolve should be free from ether, alcohol, or other solvents and should be as dry as possible.

After the extract passes into the column, wash at once with Skellysolve F and continue washing until all carotene passes through the column. This is indicated by a colorless filtrate. This solution may be retained and the carotene measured.

The appearance of the column at this point shows a sharp colored layer at the extreme top, usually followed by a series of lines and a broad colored band, all in the carbonate layer. Remove all these with care, except for the lowest portion of the broad colored band, by digging out the adsorbent with a suitable instrument.

Change the receiving flask on the column and elute the vitamin A by passing 25 ml. of ether slowly through the column or until all the remaining yellow lines pass through the column. This eluate is to be used for the vitamin A reading.

COLOR REACTION. Divide the eluate from the column, or the original extract if the column purification was not required, into two equal portions of any convenient volume. At this point it is desirable to estimate the approximate vitamin A content of the material being tested, in order that the final solution concentration of vitamin A will be approximately 15 units per ml., a concentration most suitable for measurement. A volume factor, x, is approximated from the formula:

$$x = \frac{\text{(approximate units of vitamin A per gram in feed)} \times \text{(weight of sample)}}{30}$$

by which x is found to the nearest whole number (but not less than 2). To one portion of the solution add $10x$ units of a vitamin A solution (obtained from a dilution of Distillation Products vitamin A concentrate capsules, Control No. PC-3, checked spectrophotometrically). Evaporate both fractions to dryness under a vacuum and dissolve each fraction in exactly x ml. of dry chloroform. By this system one portion of the sample has been fortified with an internal standard equipment to 10 units per ml.

Reaction readings are made on the Evelyn photoelectric colorimeter, using a 620 mμ filter. Set a reagent blank containing 1 ml. of chloroform plus 10 ml. of antimony trichloride reagent to a reading of 100% transmission and find the corresponding reference no cell reading with blank solution tube removed. This

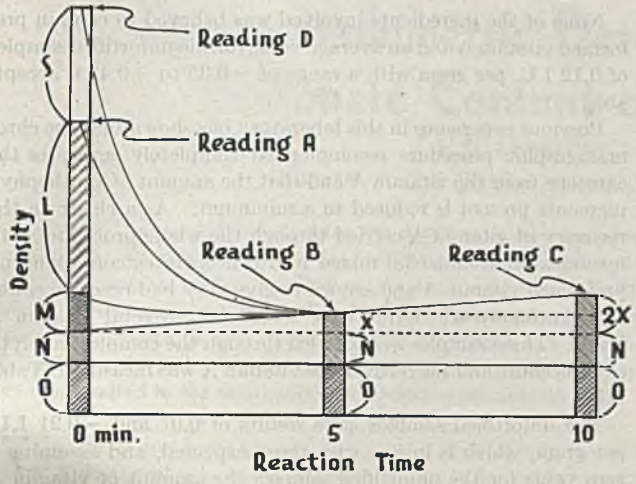

Figure 1. Derivation of Vitamin A Calculation Formula

reading is used for subsequent settings for a series of readings on any one day with the same reagent.

Place a 1-ml. sample of the unfortified unknown in a reaction tube in the instrument, add 10 ml. of antimony trichloride reagent, and take a reading as soon as the galvanometer can be read (reading A). Place the reacted solution immediately in a glass-walled water bath (a rectangular battery jar is suitable) kept at 30° C. midway between two 150-watt reflector flood lamps placed at a distance of 30 cm. (12 inches) between the two bulb faces.

After exactly 5 minutes read the reaction tube again (reading B) and immediately return it to the water bath. At the end of exactly 10 minutes obtain a third reading (reading C).

React a 1-ml. sample of the vitamin A–fortified sample as above with 10 ml. of antimony trichloride and take only the initial reading (reading D). According to the data of Baxter and Robeson (*1*), confirmed by the authors, this reading should not exceed a photometric density of 0.523, corresponding to a transmission of 30% in order to stay within the linear range for a vitamin A standard curve.

Dilute a second 1-ml. aliquot of the unknown (if necessary a part of the fortified sample can be mixed with the unfortified for this reading) with 10 ml. of chloroform and read at 440 mμ (reading E) against a blank of pure chloroform set to 100% transmission. Reading E is made to correct for the interference of certain carotenoid pigments which give color reactions with antimony trichloride. Calculate vitamin A concentration from the following formula in which all readings have been converted to photometric densities:

$$\text{Units of vitamin A per gram} = \frac{10(A - 2B + C - 0.067\,E)(2x)}{(D - A)\ (\text{wt. of sample})}$$

The factor 0.067 in this formula is explained below and should be determined by the user for the particular type of carotenoid pigments most commonly encountered (from alfalfa, corn gluten, etc.) and with the particular filters used in making the readings.

BASIS OF COLOR-READING PROCEDURE

The vitamin A blue color reaction with antimony trichloride is usually read at about 620 mμ within 10 seconds after addition of the reagent to the A source. Unfortunately, if the vitamin A solution contains any considerable amounts of impurities of a variety of types, these impurities will produce colored reactions simultaneously with the formation of the vitamin A blue color. The best available means of purification do not completely remove these interfering materials from feed extracts.

These interfering materials can be grouped into three broad reaction types:

1. Materials which produce a high initial color intensity which fades with time, similar to vitamin A itself. This is indicated by decreasing light absorption with time.
2. Materials which produce a low initial color intensity which increases with time. This is indicated by increasing light-absorption values.
3. Materials which produce a color reaction of an intensity relatively constant with respect to time. This is indicated by constant light-absorption values.

All classes of interference would be made up of one of these types or some combination of several types.

If vitamin A–antimony trichloride reaction solutions are subjected to controlled light of high intensity at constant temperature, as outlined in the quantitative procedure, the blue color fades very rapidly, and at the end of 5 minutes has completely disappeared. If reacted solutions of pure vitamin A are read at 620 mμ, the difference between the initial photometric density and that after 5 minutes is directly proportional to the A concentration over a wide range of concentration values.

Extracts of feedstuffs known not to be sources of vitamin A have been tested under similar conditions with the following observed groupings:

1. Reacting materials which showed decreasing color intensities with time were mostly carotenoid in nature and had attained minimum values of photometric density at 620 mμ within 5 minutes. Moreover, the difference between the initial absorption at 620 mμ and the absorption after 5 minutes in each case was quantitatively related to the yellow color present in the unreacted solution. The latter could be measured by reading at 440 mμ.
2. Materials which showed increasing color intensities with time increased in photometric density at approximately a uniform rate for short periods of time. The increase during the period 0 to 5 minutes was approximately the same as that for 5 to 10 minutes. In all cases this increase in photometric density at 620 mμ was relatively slow as compared with the rapid decreases observed for vitamin A and carotenoids and the difference between the changes in the two time intervals was negligible.
3. Materials which possessed a color of their own unrelated to the antimony trichloride reaction or which reacted to produce a color that did not change with short intervals of time.

Utilizing the facts ascertained in these observations, it was decided that a procedure could be developed for reading vitamin A in the presence of all three types of interfering materials. This is best explained by means of Figure 1.

Readings are made under controlled conditions of light exposure and temperature immediately after reaction (reading A), after 5 minutes' exposure (reading B), and after 10 minutes' exposure (reading C). In addition, a second portion of the extract being tested is reacted in the presence of a known addition of pure vitamin A (reading D) and an independent reading is made at 440 mμ (reading E) of the diluted, but unreacted, sample to be used as a correction for carotenoids present.

Reading A is composed of the sum of the absorptions produced by an unknown amount of vitamin A, represented by amount L, and the three types of interfering colored reactions previously mentioned, and represented by quantities M, N, and O, indicating decreasing color, increasing color, and stable color, respectively. Reading B, at the end of 5 minutes, shows that L and M have faded out completely, O has remained constant, and N has increased by increment X. At the end of 10 minutes, represented by reading C, an additional increment, X, has been added to the value of original quantity N, making its value $N + 2X$.

$$\text{Reading } A = L + M + N + O \quad (1)$$
$$\text{Reading } B = X + N + O \quad (2)$$
$$\text{Reading } C = 2X + N + O \quad (3)$$

from which the formula $L = A - 2B + C - M$ may be derived. M may be derived by a separate reading (reading E) of the carotenoid color at 440 mμ which will bear a relationship, K, to the blue color produced at 620 mμ for any particular group of pigments and pair of filters.

Hence, $$M = KE$$

or $$L = A - 2B + C - KE$$

To compensate for the fact that certain materials may inhibit the amount of absorption L produced by the antimony trichloride reaction with vitamin A, a known increment (10 units = S) of A is added to a second fraction of the original solution and after adjusting to the same volume for reaction, reading D is obtained.

All color produced by preformed vitamin A has completely faded at the end of 5 minutes. Thus, after this period of time the sample with the added increment of vitamin A will read the same as the sample without the vitamin A increment (Figure 1). This fact makes it possible to use the principle of the internal standard with its attendant advantages as stated by Oser, Melnick, and Pader (*7*).

$D - A$ equals the amount of absorption produced by 10 units of vitamin A under the same reaction conditions as in the case of L absorption, produced by the unknown amount of vitamin A.

For low concentrations of vitamin A the readings given in terms of photometric density are directly proportional to the amount of vitamin A present.

$$\text{Therefore} \qquad \frac{\text{Units of vitamin A}}{10} = \frac{L}{D - A}$$

$$\text{or} \qquad \text{Units of vitamin A} = \frac{10(A - 2B + C - KE)}{D - A}$$

The value of K is derived by reacting with antimony trichloride and reading at 620 mμ portions of a series of solutions of varied carotenoid concentration and reading dilutions of the same solutions at 440 mμ. The reacted absorption values are plotted against the dilution absorption values and a straight-line relationship is found. The ratio of the photometric density at 620 mμ to that at 440 mμ is the value of K desired. This was found to be 0.067 for the authors' instrument for the carotenoids of alfalfa, the major carotenoid source in feeds. This value was obtained after a chromatographic column treatment and readings obtained according to the procedure given. The chromatographic treatment removes pure carotene and only the related pigments are present.

Table I. Composition of Feed Mixtures

Ingredient	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
	%	%	%	%	%	%
Soybean oil meal	30	30	30	30	30	...
Corn meal	50	50	50	...	...	...
Tankage	20	...	...	...	10	20
Fish meal	...	20	...	20	20	30
Ground oats	...	...	...	30	...	...
Alfalfa	...	...	20	20	20	30
Wheat germ	...	...	...	...	20	20
Total	100	100	100	100	100	100

RECOVERY OF ADDED VITAMIN A

In order to check on the accuracy of the reading procedure, samples of feedstuff mixtures (Table I) were prepared containing varying proportions of typical feed materials. Some of the mixtures were prepared with abnormally large amounts of certain types of ingredients known to interfere with vitamin A measurement.

Portions of these mixtures were extracted and purified on chromatographic columns. Each extract was divided into two equal portions, each equivalent to 8 grams of original sample and one portion was fortified with 100 I.U. of vitamin A or 12.5 I.U. per gram of sample. The two portions of each sample were then treated as separate samples and their vitamin A content was read and calculated by the procedure given. The value of X for calculation is 2.5. According to the procedure later adopted a whole number, in this case 3, is recommended.

Table II shows the results obtained on this experiment. The average recovery obtained, 12.61 I.U. per gram, checks well with a theoretical recovery of 12.5. The range 11.62 to 13.60 is within the range to be expected from a reading procedure depending upon five independent readings.

Table II. Recovery of Added Vitamin A

Sample No.	Reading A	Reading B	Reading C	Reading D	Reading E	Vitamin A Found	Recovery	Error
						I.U./g.	*I.U./g.*	*I.U./g.*
1	0.027	0.022	0.032	0.214	0.034	0.43	...	...
1F[a]	0.382	0.034	0.043	0.540	0.034	14.03	13.60	+1.10
2	0.032	0.041	0.056	0.214	0.045	0.10	...	...
2F[a]	0.387	0.051	0.062	0.551	0.045	13.10	13.00	+0.50
3	0.149	0.122	0.122	0.328	0.403	0.00	...	...
3F[a]	0.485	0.131	0.131	0.661	0.403	11.62	11.62	−0.88
4	0.161	0.144	0.149	0.340	0.475	−0.35	...	...
4F[a]	0.512	0.158	0.161	0.671	0.475	12.77	13.12	+0.62
5	0.174	0.155	0.172	0.358	0.462	0.17	...	...
5F[a]	0.509	0.164	0.181	0.677	0.462	12.32	12.15	−0.35
6	0.201	0.177	0.197	0.381	0.495	0.38	...	...
6F[a]	0.530	0.184	0.204	0.696	0.495	12.54	12.16	−0.34
					Av.	0.12	...	
						12.73	12.61	

[a] Same as samples 1, 2, etc., except 12.5 I.U. per gram added vitamin A.

None of the ingredients involved was believed to contain preformed vitamin A and an average value for the unfortified samples of 0.12 I.U. per gram with a range of −0.35 to +0.43 is acceptable.

Previous experience in this laboratory has shown that the chromatographic procedure recommended completely separates the carotene from the vitamin A and that the amount of xanthophyll pigments present is reduced to a minimum. As a check on the recovery of vitamin A carried through the whole procedure, two formulas for commercial mixed feed concentrates containing no preformed vitamin A and known to give very bad reaction colors with antimony trichloride were fortified at several vitamin A levels. These samples were carried through the complete analytical procedure and the recovery of vitamin A was measured (Table III).

The unfortified samples gave results of 0.07 and −0.21 I.U. per gram, which is in line with those expected, and assuming a zero value for the unfortified samples the amount of vitamin A lost in the complete procedure varied from 0.74 to 0.88 I.U. of vitamin A per gram of sample. Since this is the combined loss of the extraction, saponification, and column procedure, plus losses in transferring and evaporation, it appears to be satisfactory for this type of procedure. However, this loss is apparently an absolute one and for very low potency feeds it may result in a high percentage error.

No attempt is made in this paper to measure vitamin A activity other than that produced by preformed vitamin A. Carotene can be measured on the first eluate from the chromatographic column but the problems involved in the separation and measurement of different carotenoids having vitamin A activity and the subsequent conversion into units of preformed vitamin A are at present only partially solved.

Table III. Recovery of Added Vitamin A from Mixed Feeds

Sample	Added Vitamin A	Total Vitamin A	Loss of Vitamin A
	I.U./g.	*I.U./g.*	*I.U./g.*
Feed A	...	0.07	...
Feed A	8.20	7.32	0.88
Feed A	10.24	9.48	0.76
Feed A	16.40	15.52	0.88
Feed B	...	−0.21	...
Feed B	10.24	9.50	0.74

SUMMARY

A modification of the antimony trichloride method for the determination of vitamin A in feeds and feedstuffs compensates for the presence of interfering reacting materials by means of the differential effect of light on the kinetics of the antimony trichloride reaction of vitamin A and the interfering materials, respectively. A chromatographic procedure suitable for the preparation of feed extracts intended for color reaction is given. The principles of the procedure appear favorable for use in a variety of applications in the determination of vitamin A in human foods.

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Direct Volumetric Determination of the Organic Sulfonate Content of Synthetic Detergents

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A method has been developed for the quantitative determination of sodium alkylbenzene sulfonates, which is applicable to commercial detergents containing alkyl or alkylaryl sulfonates. Under standardized conditions *p*-toluidine hydrochloride reacts with these organic sulfonates to give amine-sulfonate salts which can be subjected to rapid and relatively precise quantitative analytical determination suited to the requirements of industrial laboratories.

THE usual methods for obtaining the active organic content of a detergent mixture are relatively long and produce results calculated by "difference" methods (*2*, *4*). In a search for a rapid and direct mode of analysis for production control to overcome the time disadvantages of these methods a procedure has been developed which has considerable merit for the analysis of certain detergents of either the alkyl sulfonate or alkylaryl sulfonate type. ("Alkyl" is used throughout to indicate hydrocarbon species obtained by fractional distillation of petroleum.) The new method employs the familiar qualitative reaction of amines and aryl sulfonic acids (*5*, *7*) with modifications to obtain quantitative results of relatively high precision and accuracy under standardized conditions.

METHOD FOR ALKYLBENZENE SULFONATES

A neutral detergent mixture containing the sodium salts of alkylbenzene sulfonic acids as the active organic ingredient may be reacted in aqueous medium with an amine salt of a strong inorganic acid to produce the sulfonic acid salt of the amine and the sodium salt of the inorganic acid. Removal of the sulfonate-amine complex into a water-immiscible phase will displace the equilibrium to favor completion of the reaction. The homologous nature of the organic species in most commercial detergents facilitates this removal by prevention of crystallization. The organic sulfonate can then be determined by suitable treatment of the solvent extract of the reaction mixture. Direct titration with standard alkali in the presence of a suitable indicator has been found rapid and convenient. The weakly basic amine does not interfere. The main reactions may be presented as follows:

$$RC_6H_4SO_3NA + CH_3C_6H_4NH_2.HCl \longrightarrow CH_3C_6H_4NH_2.RC_6H_4SO_3H + NaCl$$

$$CH_3C_6H_4NH_2.RC_6H_4SO_3H + NaOH \longrightarrow RC_6H_4SO_3Na + CH_3C_6H_4NH_2 + H_2O$$

After numerous trials with various amine salts and solvents, *p*-toluidine hydrochloride and carbon tetrachloride were selected for greatest ease of manipulation. The following specific procedure was devised for application to solid detergents containing 30 to 60% sodium alkylbenzene sulfonate and remainder of neutral inorganic salts.

A weighed sample containing 3 to 4 grams of the organic material is transferred to a 250-ml. (Corning No. 6340) separatory funnel (stem cut to 1.25 cm., 0.5 inch). Fifty milliliters of C.P. carbon tetrachloride and 100.0 ml. of an aqueous solution containing 3.40 grams of *p*-toluidine hydrochloride (*1*) are added; the funnel is then stoppered and shaken mechanically at room temperature for about 5 to 10 minutes or until all the solid phase has disappeared. Complete layer separation is effected by a few minutes of settling. The carbon tetrachloride layer is carefully drawn off, and the aqueous phase is extracted a second time using a brief shaking with an additional 25 ml. of carbon tetrachloride. The carbon tetrachloride extracts are combined in 100 ml. of 95% ethanol previously just neutralized with 0.1 *N* sodium hydroxide to a faint purple end point using *m*-cresol purple as the internal indicator. The resulting solution is titrated in a glass-stoppered, 500-ml. Erlenmeyer flask with 0.1 *N* sodium hydroxide until the emulsion obtained by vigorous intermittent shaking during titration tends to remain a lavender color. (Alcohol is used for facilitating the titration reaction and discerning the end point; formulas 2B and 3A are satisfactory.)

The organic content of the sample is calculated from the "% organic" equivalent of the standard sodium hydroxide solution found by carrying out the above determination on a suitable reference sample of known organic content.

SAMPLE CALCULATION. A reference sample was found to have an organic content of 40.0% when analyzed by "difference" [100% − (% sodium sulfate + % moisture + % sodium chloride + % ether-soluble)]; it required 67.32 ml. of 0.10 *N* sodium hydroxide per 6.000-gram sample by the procedure described; therefore, the factor for converting ml. of 0.10 *N* sodium hydroxide to per cent of organic material in unknown samples of the same organic constitution $= \frac{40.0}{67.32} = 0.594$ per 6 grams of sample.

A 6.000-gram sample of an unknown required 92.00 ml. of 0.10 *N* sodium hydroxide; hence its organic content = ml. of NaOH × 0.594 = 54.6%.

In order not to confine narrowly the apparent applicability of the method, calculations on a stoichiometric basis are avoided in the general procedure. Because the weight of the average of the alkyl groups is not always definitely known or is subject to variation with modifications of manufacturing processes and because of the empirics of reagent volumes in this method, some products may not be accurately analyzed when calculated factors are employed.

DISCUSSION OF VARIABLES

When the initial concentration of *p*-toluidine hydrochloride is fixed for a series of determinations in which only the weight of sample is varied, the alkali equivalent per gram of sample remains constant when the molecular ratio of amine to sulfonate exceeds about 2.5.

When the outlined analytical procedure is applied to a series of duplicate samples, except that the *p*-toluidine hydrochloride concentration in the amine reagent is varied, it appears that the alkali equivalent per gram of sample is regularly affected by the initial concentration of the amine hydrochloride. Data from such a series are plotted in Figure 1. Physical limitations fix the range of reagent concentration. The amine salt in concentrations above about 8% on a weight-volume basis causes phase separation difficulties; when its initial concentration is much below 2.5 times the molar concentration of the sulfonate and below about 3.4 grams per 100 ml. of reagent, sufficient detergent remains unreacted to cause emulsification. It is not known why the curve of Figure 1 does not become parallel with the abscissa at the point demanded by theory, but since a continuous line function is exhibited over a wide range of amine concentrations and since chlorides can be qualitatively detected in the carbon tetrachloride extract, it is likely that, although *p*-toluidine hydrochloride is in-

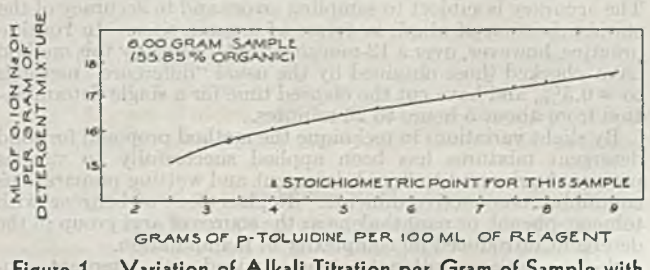

Figure 1. Variation of Alkali Titration per Gram of Sample with Initial Concentration of *p*-Toluidine Hydrochloride

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Table I. Analysis of Commercial Products by *p*-Toluidine Hydrochloride Method

Product	Type of Molecule (*5*, *6*, *8*)	Ml. of 0.10 *N* NaOH per Gram
Santomerse 1	Alkylaryl sulfonate	10.3
Santomerse 3	Alkylbenzene sulfonate	26.2
Santomerse D	Alkylbenzene sulfonate	26.8
MP 189	Alkyl sulfonate	9.7
SV 1959	Alkyl sulfonate	23.8
Ultrawet A	Alkyl sulfonate	28.7
Nacconol NR	Alkylbenzene sulfonate	11.1
Nacconol HG	Alkylbenzene sulfonate	15.2
Nacconol F	Alkylbenzene sulfonate	12.8
Naccolene F	Alkylbenzene sulfonate in solvent	2.7
Naccosol A	Alkylnaphthalene sulfonate	26.7

soluble in carbon tetrachloride, it is taken into the solvent layer in slight amounts by small changes in miscibility related to an effect of *p*-toluidine hydrochloride concentration.

However, by strict adherence to volume and reagent concentration in a procedure with any specified concentration of amine hydrochloride in the graphed range, one may obtain reproducible results for alkali equivalent per gram of sample when the weight of sample is varied within its practical limits. Notwithstanding, the reagent concentrations at which there apparently is stoichiometric relationship have been selected for the authors' use to avoid occult errors. These concentrations were determined from application of the method to mixtures of commercial detergent with pure sodium dodecylbenzene sulfonate, the former being employed in admixture to prevent formation of a crystalline product by the latter.

When the stoichiometric point is found by use of a suitable pure compound of known molecular weight, the average molecular weight of the mixture of homologs in a commercial detergent can be found; hence, conditions at which the metathetical amount of alkali is used at the titration end point can then be determined for other detergent mixtures for which a standard factor may be desired to convert titrations to per cent organic content.

The data in Figure 1 illustrate those obtained on portions of a detergent sample for which the average molecular weight had been calculated. The point of apparent stoichiometric relationship chosen for fixing reagent quantities and volume was selected by use of this calculation.

For only routine or occasional analytical purposes it is not necessary to determine the optimum amine salt concentration; if a desired reference sample is run with the unknown under identical conditions of volume and amount of reagents, the concentration may be between 3 and 8%.

Perchlorocthyle ne may readily be used to replace the carbon tetrachloride, but other solvent substitutions should be made only after an adequate study of the effects involved.

In the presence of colored materials which are otherwise negligible in effect, a pH meter and glass electrode may be used to determine the titration end point in an open vessel if vigorous stirring is provided.

RESULTS

Determinations by five analysts using fifty-seven samples of detergent of known organic content (35 to 55%) established that the *p*-toluidine method as outlined above is precise to ±0.23%. The accuracy is subject to sampling errors and to accuracy of the standardization of alkali in terms of organic titer. In routine practice, however, over a 12-month period, results by this method have checked those obtained by the usual "difference" methods to ±0.5%, and have cut the elapsed time for a single determination from about 5 hours to 20 minutes.

By slight variations in technique the method proposed for solid detergent mixtures has been applied successfully to various process slurries and to liquid detergent and wetting preparations containing nonreactive diluents. Replacement of benzene with toluene, phenol, or naphthalene as the source of aryl group in the detergent introduced no complexity of manipulation.

Sodium benzene sulfonate alone or mixed with detergent samples remained undetected under the conditions of the method.

A few of the commercial detergents tested for adaptability to the outlined procedure are listed in Table I. Data were not available on all the samples for drawing inferences about accuracy from the titration values, so such calculations were omitted entirely. Each sample seemed to have sufficient homologous nature to make it amenable to this procedure without the undesirable crystallizing effects exhibited by such compounds as pure dodecylbenzene sodium sulfonate.

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New Standard Samples

The National Bureau of Standards, Washington 25, D. C., has inaugurated a series of standard samples for use in the preparation of buffer solutions of known pH values from 0° to 60° C., and in the calibration of instruments for the measurement and control of pH. Three standards of this series are now available, acid potassium phthalate, potassium dihydrogen phosphate–disodium hydrogen phosphate, and borax (sodium tetraborate decahydrate). The two phosphates are intended to be used together. Four new standard steels have also been added to the list. Table I shows sample numbers and fees of the new standards.

Orders should give both the number and the name of the sample wanted. No samples of smaller size than those listed are distributed, and remittance should accompany order.

The bureau now issues more than 300 different kinds of standard samples, comprising steels, irons, ferroalloys, nonferrous alloys, ores, ceramic materials, certain high-purity chemicals, hydrocarbons, paint pigments for color, oils for viscometer calibrations, certain reference standards, and melting-point standards. Complete information is given in the Supplement to Circular C398, which can be obtained free of charge upon application to the bureau.

Table I

Sample No.	Material	Recommended Concentration *Mole/liter of solution*	pH Value at 25° C.	Approximate Weight of Sample *Grams*	Price per Sample
185	Acid potassium phthalate	0.05	4.005	60	$3.00
186	Potassium dihydrogen phosphate (186-I)	0.02	6.866	60	6.00
	Disodium hydrogen phosphate (186-II)	0.02			
187	Borax	0.01	9.177	30	3.00
139	Steel (N.E. 8637) (approximately 0.5 Ni, 0.5 Cr, 0.17 Mo)			150	3.00
152	Steel (B.O.H.) (tin-bearing approximately 0.04 Sn)			150	2.00
155	Steel (approximately 0.5 Cr, 0.5 W)			150	3.00
156	Steel (N.E. 9450) (approximately 1.4 Mn, 0.5 Ni, 0.4 Cr, 0.13 Mo)			150	3.00

Colorimetric Determination of Nickel in Bronzes

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A method is described for the colorimetric determination of nickel in bronzes. Copper is separated by precipitation with ammonium hypophosphite and subsequent filtration. The nickel is then determined by measurement of the color produced by dimethylglyoxime in the presence of citric acid, iodine, and ammonia. The method is rapid (one determination can be completed in less than 30 minutes) and of sufficient accuracy for routine purposes.

VARIOUS color reactions have been suggested for the colorimetric determination of nickel but dimethylglyoxime is so far still the best reagent for this particular purpose. This reaction is based on the fact that a red or reddish-brown solution is produced when dimethylglyoxime is added to an alkaline solution containing nickel, provided that it has previously been treated with an oxidizing agent such as bromine water or iodine solution. The colored compound is nickelic (IV) dimethylglyoxime. Its color depends on the method of preparation—i.e., whether the oxidant was added to the solution when it was still acid or after it had been made alkaline.

Feigl (*3*) first described this reaction and Rollet (*14*) suggested a few modifications in order to make it suitable for colorimetric purposes. Subsequent investigators have used it for the determination of nickel in steel (*2, 5–12, 14, 16*), where its use has become extensive. The interference of iron can easily be eliminated by adding citric or tartaric acid. However, the method is not directly applicable in the presence of considerable amounts of copper, and as far as the present authors can ascertain, there have been only three methods described in the literature for its application to the determination of nickel in bronzes (*1, 4, 13*).

Haywood and Wood (*4*) recommend the direct colorimetric determination of nickel in the presence of copper. By the use of special filters and a suitable blank the difficulties arising from the presence of copper are overcome, but this method can be used only for nickel contents up to 5%.

There is an earlier reference by Dietrich (*1*) to a similar method, but apart from stating that nickel is determined in an aliquot portion of the solution used for copper, the only information given is that bromine water, ammonia, and dimethylglyoxime are required. Results could be obtained within 10 to 15 minutes for nickel contents up to 15%.

Ochotin and Sytschoff (*13*) developed a method for the colorimetric determination of nickel in alloys, which they claim to be rapid and accurate enough for routine analysis. But they state that if copper is the major constituent of such an alloy a separation—e.g., by electrolysis—has to be carried out although this separation need not be quantitative. After removal of the copper the nickel is precipitated by dimethylglyoxime. The solution containing the precipitate is then transferred to a separating funnel and treated with ether, with the effect that the entire precipitate becomes dispersed in the ether. The aqueous solution is then drained off and alcohol and collodion are added to the ether suspension. The resulting colored solution is compared with standard solutions of known nickel content prepared under similar conditions. This method was tried out but the separation with ether was tedious and investigations to find a more practical method were continued.

Since the method for steel was not directly applicable to bronzes on account of the interference of the copper, the problem was to find a quick method of separating this element. As small quantities of copper are not detrimental, such a separation need not necessarily be quantitative. The usual methods of separating copper—i.e., by electrolysis or by gassing with hydrogen sulfide—were not adopted, as the former requires the use of additional apparatus and the latter is objectionable on account of the obnoxious fumes of the hydrogen sulfide, and the tendency of copper sulfide to become colloidal makes it difficult to filter. A search through the literature was, therefore, carried out to find other suitable methods of separation. It was found that Turbin (*15*) had attempted to separate copper and nickel by means of iron powder. This was tried out but results were not very promising. Next, an attempt was made to reduce the copper by means of a sugar solution in the presence of alkaline sodium potassium tartrate. This reaction is commonly used for the determination of sugar in urine and it was considered that it might well be applied in the reverse direction. The tests were fairly successful and the only disadvantage appeared to be caramelization of the sugar which made it necessary to boil the solution afterwards with nitric acid in order to destroy the color.

Finally, another method was investigated using a solution of ammonium hypophosphite as reducing agent. This effectively precipitates the copper at low acid concentrations, yielding a precipitate which is easy to filter. Although the copper is not quantitatively removed in this way, the small amount which remains does not seriously affect the subsequent colorimetric determination of nickel. An excess of hypophosphite has no influence on the reaction, as sufficient iodine is added for its complete oxidation.

REAGENTS USED

Ammonium hydroxide, specific gravity 0.88.
Ammonium hypophosphite solution, 5%.
Citric acid solution, 10%.
Dimethylglyoxime solution, 1% in alcohol.
Iodine solution, 0.1 *N*: 12.69 grams in 50 ml. of water containing 25 grams of potassium iodide. Solution made up to 1000 ml.
Nitric acid, 1 to 1.

PROCEDURE

Transfer 0.1 gram of fine drillings of the alloy to a 100-ml. beaker and add 2 ml. of nitric acid. Heat until solution is complete and then evaporate gently until a greenish color is obtained. Dilute to 20 ml. with distilled water and add 5 ml. of ammonium hypophosphite solution. Heat to boiling and boil for 3 minutes, then remove from hot plate and allow to cool. Filter through a Whatman No. 541 filter paper (11-cm.) and wash with tepid water until bulk is approximately 150 ml. Cool the filtrate, transfer to a 250-ml. volumetric flask, and make up to the mark. Transfer 25 ml. of this solution to a 100-ml. volumetric flask and add in the following order, shaking well after each addition:

10 ml. of citric acid
2 ml. of iodine solution
10 ml. of ammonium hydroxide solution
4 ml. of dimethylglyoxime solution

Finally make up to 100 ml. with distilled water.

Shake the flask well and allow to stand for at least 10 but not more than 30 minutes, and measure the color produced by means of a Zeiss Pulfrich photometer, using the photometer filament lamp with filter S53 (having a mean transmission of 5300 Å.), and distilled water as comparison. (Any other type of colorimeter may be used with suitable filters.)

The method as described above was found to be applicable for nickel contents up to 5%. For nickel contents between 5 and 10% a 10-ml. aliquot should be taken and the result multiplied by 2.5. For nickel contents above 10%, proportionately smaller aliquots should be taken.

This method was first investigated on standard solutions containing a known amount of nickel and copper (Table I). Solution A contained 10 grams of copper per liter and solution B contained 0.2 gram of nickel per liter. These solutions were mixed in the proportions indicated and treated in the way described above.

The graph based on these figures was found to be a straight line passing through the origin, proving that the color is strictly proportional to the concentration of nickel, and thus truly follows Beer's law.

Table I. Determination of Nickel in Standard Solutions

Solution	Ni, Mg.	Cell, Mm.	Reading	K
1. 10 ml. A + 5 ml. B	1.0	30	0.36	0.12
2. 10 ml. A + 10 ml. B	2.0	30	0.76	0.253
3. 10 ml. A + 15 ml. B	3.0	10	0.36	0.36
4. 10 ml. A + 20 ml. B	4.0	10	0.49	0.49
5. 10 ml. A + 25 ml. B	5.0	10	0.63	0.63
6. 10 ml. A + 30 ml. B[a]	6.0	20	0.58	0.725

[a] 10-ml. aliquot taken and reading multiplied by 2.5; hence: Adjusted coefficient = 0.725

Table II. Determination of Nickel in Standard Bronze

Standard	Cell	Reading		Ni (from Standard Graph)	Ni (Gravimetric)	Deviation
	Mm.		K	%	%	%
HAR	30	0.21	0.07	0.55	0.50	+0.05
HAS	30	0.99	0.33	2.67	2.66	+0.01
HAT	30	1.00	0.33	6.75	6.72	+0.03
HAU	10	0.40	0.40	7.98	7.92	+0.06
DTD 174	30	0.50	0.167	1.37	1.35	+0.02
DTD 164	30	0.02	0.34	2.76	2.75	+0.01
DTD 197	10	0.63	0.63	5.13	5.10	+0.03
DTD 412	10	0.60	0.60	4.90	4.88	+0.02
DTD 498	30	0.84	0.28	2.27	2.22	+0.05
DTD 504	30	0.78	0.26	2.10	2.05	+0.05
P-bronze	30	1.22	0.407	3.30	3.28	+0.02
Mn-bronze	30	0.50	0.167	1.34	1.14	+0.20
Ni-bronze	30	1.30	0.433	17.6	17.5	+0.10

The method was then tried out for a number of standard bronzes, the nickel content of which had previously been obtained gravimetrically (Table II).

In the case of the high-nickel bronze, the solution was made up to 500 ml. and a 10-ml. aliquot taken. The reading was then multiplied by 5. The results corresponded well with the gravimetric values, the greatest accuracy being found for nickel contents above 3%.

The time required for a single determination is approximately 30 minutes, and very much less if a batch of samples is investigated at the same time.

ACKNOWLEDGMENT

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Removal of Peroxides from Organic Solvents

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A rapid and efficient method for removal of peroxides from organic solvents by means of activated alumina is presented. Since no moisture is added, the method is directly applicable to dioxane and anhydrous solvents.

THE autoxidation of ethers and certain other organic solvents during storage gives rise to the formation of peroxides. The distillation of any of a wide variety of ethers containing appreciable quantities of peroxide may result in dangerous explosions (*14*). Peroxide-containing isopropyl ether appears to be particularly hazardous in this respect, violent explosions of its distillation residues having occurred as a result of heating at temperatures well below 100° C. or even from mechanical shock alone (*3*, *7*).

The octane numbers of synthetic gasolines are appreciably lowered by the formation of peroxides during storage, but can be largely restored by removal of the peroxides (*1*, *11*).

The use of peroxide-containing liquids as solvents for substances which are easily oxidized necessitates the prior removal of the accumulated peroxides. A large number of methods for accomplishing such purifications have been proposed from time to time.

Peroxides, aldehydes, unsaturated compounds, and acids can be effectively removed from impure ether by shaking with aqueous silver hydroxide precipitated *in situ* with an excess of alkali (*12*). A commonly used laboratory method of freeing ethyl ether of peroxides consists in treating the ether with an aqueous solution of ferrous sulfate (*14*). Aqueous solutions of sodium bisulfite, acidified potassium iodide, sodium sulfite (*14*), and potassium permanganate (*7*) have also been recommended. Peroxides may also be eliminated from ether by distilling over either alkaline pyrogallol or alkaline permanganate and then passing a fine spray of the condensed ether through a strongly alkaline solution of either reagent (*8*). All these methods have the disadvantage of necessitating the addition of water which, if an anhydrous solvent is desired, must subsequently be removed. Furthermore, they are not suitable for the treatment of many water-miscible liquids such as dioxane or some of the monoalkyl ethylene glycol ethers (Cellosolves).

The purification of ether with alkali metals (*10*) or hydroxides (*6*, *10*) eliminates both peroxides and aldehydes but, in common with the above methods, also requires a distillation procedure. Two recently developed methods for destroying peroxides are applicable to dioxane as well as to some of the acyclic ethers (*8*). These consist in shaking the dioxane with stannous chloride and distilling off the dioxane and refluxing with lead dioxide and filtering through a tight filter paper.

The only previous report on the use of an adsorbent for the elimination of peroxides in ether appears to be that of Rae (*9*) who found that when peroxide-containing ether was shaken with 1.1% of animal charcoal and allowed to stand, the peroxides gradually decreased and in 54 days finally disappeared. Harris and Welch (*4*) found that certain carbons removed the compounds which were responsible for a positive Kreis test in a cottonseed oil.

Activated alumina has previously been recommended for the continuous commercial drying of organic liquids (*2*). In connection with the chemical study of certain oxygen-labile steroids in these laboratories, it was found that peroxides could be completely and quickly removed from many organic solvents by merely passing them through a vertical column of activated

alumina. The peroxides were not decomposed or converted into other products by the alumina, but were removed from solution by adsorption. The aldehyde contents were also reduced by this treatment, as was evidenced by testing with 2,4-dinitrophenylhydrazine. The purified solvents did, however, give positive reactions with the Schiff fuchsin-aldehyde reagent. Because the urgency of other problems prevents undertaking a more comprehensive study of the removal of peroxides and aldehydes by adsorbents and because of the potential usefulness of this technique to others, the results are being published at this time.

PROCEDURE

Grade F-20 chromatographic Alorco activated alumina (−80-mesh) was supported in an upright chromatographic adsorption tube by a clean cotton plug. The dry alumina was poured into the tube while the tube was being jarred to obtain good settling of the adsorbent. A wisp of cotton placed on top of the adsorbent protected the surface of the adsorbent from agitation.

A generous layer of the solvent to be purified was placed on top of the adsorbent, the remainder of the solvent then being added by means of a dropping funnel fitted into the top of the tube with a rubber stopper. The flow of the liquid through the column was greatly accelerated by means of air pressure applied to the liquid in the dropping funnel. The compressed air which furnished the air pressure was passed through a safety bottle of the type commonly used in reduced pressure distillations. The valve of the safety bottle was left open. This prevented the building up of objectionable pressures. The pressure was regulated satisfactorily by adjustment of the valve in the compressed air line.

Determination of Peroxides. Peroxide values of the original solvents as well as of successive portions of solvents which had passed through the alumina columns were determined by an iodometric method based on Wheeler's method of determining peroxides in fats and oils (*13*). Five to 50 ml. of solvent, depending upon its peroxide content, were mixed with 30 ml. of a 40 to 60 chloroform–glacial acetic acid mixture. One milliliter of saturated aqueous potassium iodide solution was added and the flask was rotated for 1 minute. At the end of the 1-minute interval, 50 ml. of water were added and the mixture was immediately titrated with 0.01 *N* sodium thiosulfate, using starch as an indicator.

Table I. Comparison of Iodometric and Permanganate Methods for Determination of Peroxides in Solvents

Solvent	Peroxide Content I Iodometric method	Peroxide Content II Permanganate method	II/I
	Micromoles of O_2 per liter		
Aqueous H_2O_2 1	10,000	10,600	1.06
Aqueous H_2O_2 2	333,000	349,100	1.05
Aqueous H_2O_2 2 + formaldehyde[a]	304,400	294,600	0.97
Aqueous H_2O_2 2 + acetaldehyde[a]	155,700	338,200	2.2
Ethyl ether 1	0.0	0.0	...
Ethyl ether 1 + formaldehyde[a]	0.0	0.0	...
Ethyl ether 1 + acetaldehyde[a]	0.0	0.0	...
Ethyl ether 1 + H_2O_2	6,200	9,200	1.5
Ethyl ether 9[b]	4,600	7,850	1.7
Ethyl ether 9 + formaldehyde[a]	4,020	8,510	2.1
Ethyl ether 9 + acetaldehyde[a]	3,840	9,160	2.4
Ethyl ether 2	6,700	9,200	1.4
Ethyl ether 2 + cinnamaldehyde[a]	6,800	138,600	20.4
Ethyl ether 3	127	130	1.02
Ethyl ether 3 through Al_2O_3	0.0	0.0	...
Ethyl ether 4	56,100	63,800	1.1
Ethyl ether 5	46,800	88,100	1.9
Ethyl ether 5 through Al_2O_3	0.0	0.0	...
Skellysolve F	0.0	0.0	...
Dioxane	95,600	36,600	0.4
n-Butyl ether	56,200	12,400	0.2

[a] Solvent allowed to stand 30 minutes after addition of aldehyde before being titrated.
[b] Ether prepared by adding some ether having a very high peroxide content to peroxide-free ether.

Omitting the chloroform–acetic acid mixture and supplying the necessary acid by the addition of 1 ml. of glacial acetic acid did not yield good results—i.e., in some cases (*n*-butyl ether) no satisfactory end point could be obtained and in some cases where a very sharp end point was obtainable (dioxane) the values were low.

The determination of adsorbed peroxide was made on the alumina after its removal from the tube. The peroxides were eluted by shaking the alumina briefly with sufficient chloroform–acetic acid mixture (30 ml. for 18.5 grams of alumina). One milliliter of saturated potassium iodide solution was added and the determination was carried out by the procedure used in determining the peroxides in solvents.

Table II. Removal of Peroxides from Ethers

[1.9 × 33 cm. Al_2O_3 columns (82 grams of Al_2O_3)]

Solvent	Peroxide Content	Volume Completely Freed from Peroxide	Peroxide Removed Per column	Peroxide Removed Per 100 gm. Al_2O_3
	Micromoles O_2/l.	*Ml.*	*Micromoles O_2*	*Micromoles O_2*
Ethyl ether 3 (absolute)[a]	127	700[a]	88.9[a]	...[a]
Ethyl ether 6[b]	1,870	200	374	460
Ethyl ether 7[c]	3,670	250	918	1,120
Ethyl ether 8[d]	31,490	100	3,150	3,840
n-Butyl ether[e]	61,930	350	21,680	26,400
Dioxane 1[f]	37,500	200	7,500	9,150
Dioxane 2[g]	299,600	100	29,960	36,500

[a] Total supply 700 ml. Al_2O_3 column was still able to remove peroxide completely when all available solvent had been treated.
[b] U.S.P. ether in clear glass bottle several months.
[c] U.S.P. ether in clear glass bottle, then dried with $CaCl_2$.
[d] J. T. Baker ethyl ether, "for fat extraction, purified, dried", in a partly filled amber glass bottle in dark for over 3.5 years.
[e] In amber glass bottle over 3.5 years.
[f] Contained no peroxides when received. Opened to admit air, closed, shaken, and allowed to stand in original amber glass bottle for one month.
[g] In screw-top metal container for over 2.5 years.

The iodometric method of determining peroxides in solvents was compared with the permanganate titration method of King (*5*). Table I shows that the permanganate method gave consistently higher results with ethyl ether but that the ratio of these results to those obtained by the iodometric method varied widely for different samples of ether. These differences in results are thought to be due partly to the titration of substances other than peroxide by the potassium permanganate and partly to a possible incomplete recovery of peroxide by the iodometric method. The potassium permanganate titrations for peroxide in dioxane and *n*-butyl ether unexpectedly gave much lower results than the iodometric method, possibly because of a greater stability of these peroxides toward potassium permanganate. All solvents which were shown to be free of peroxides by one method were negative by both methods.

The authors have made no attempt to determine the reasons for the discordant results obtained by the two methods. Because the iodometric method was more convenient and was satisfactory for their purposes, the results reported below were all obtained by this method.

RESULTS

A number of ethers were passed through 1.9 × 33 cm. columns of activated alumina containing about 82 grams of the adsorbent. Peroxide determinations were made on successive 50-ml. portions of each solvent after it had passed through the alumina. Table II shows the volumes of these solvents which were completely freed from peroxides by passage through such a column.

On continuing to pass the solvents indicated in Table II other than ether 3 through the columns, succeeding portions of each solvent contained increasing amounts of peroxide—i.e., the volumes indicated in the table exhausted the ability of the alumina to remove peroxides completely from the respective solvents. Larger columns can, of course, be used to free proportionately larger volumes of solvent from peroxides.

The 700 ml. given in the table for ethyl ether 3 also represent the total supply of this ether which was at hand. It is likely that a very much larger volume of this solvent could have been purified had it been available.

A comparison of ethers 6 and 7 indicates that the moisture content of the ether affects the efficiency of the peroxide removal.

A larger volume of the dried ether was purified even though its peroxide content was double that of the other.

Activated alumina appears to vary in its efficiency for removing peroxides with the nature of the solvent being purified. Thus, its capacity for removing peroxides was much greater for *n*-butyl ether than for ethyl ether.

Activated alumina seemed to work more efficiently with the solvents having the higher peroxide contents. Other factors such as aldehyde or acid content may, however, have been partly responsible for this. The effect of the rate of flow of the solvent was not investigated.

Three Skellysolve petroleum fractions, which contained peroxides, were freed from peroxides by passing each through 18.5 grams of activated alumina in separate columns 1.5 × 10 cm. in size. The peroxides had developed in the petroleum fractions by autoxidation after being redistilled and stored in partly filled clear glass containers exposed to daylight for several months. The volumes which were treated are indicated in Table III. Because these volumes exhausted the available supply of peroxide-containing Skellysolves, the total capacity of the columns for completely removing peroxides from these solvents could not be determined; in no case was the peroxide-removing capacity of the column exhausted.

Table III. Removal of Peroxides from Petroleum Fractions

[1.5 × 10 cm. Al_2O_3 columns (18.5 grams of Al_2O_3)]

Petroleum Fraction	Peroxide Content	Volume Treated and Completely Freed of Peroxide	Peroxide Removed
	Micromoles O_2/l.	*Ml.*	*Micromoles O_2*
Skellysolve B	154.0	648[a]	99.8
Skellysolve C	33.6	600[a]	20.2
Skellysolve F	48.0	650[a]	31.2

[a] These volumes exhausted supply of solvents. Much larger volumes probably could have been purified had they been available.

That activated alumina removes peroxides from solvents by adsorption rather than by decomposition is clearly indicated in Table IV. The "peroxide removed from solvent" was calculated from the difference in the peroxide content of the solvent before and after passing through the alumina column. The "adsorbed peroxide" was determined by titrating the alumina itself after passage of the organic liquid.

The removal of peroxides from organic solvents by means of activated alumina appears to have certain advantages over most of the methods which have been reported. The fact that the elimination of peroxides by alumina takes place by adsorption is of decided advantage in purifying solvents in those instances where the presence of peroxide decomposition products might be objectionable. The method is simple and rapid and requires no equipment not readily available. Since no moisture is added to the solvent to be purified, the method is directly applicable to dioxane and to anhydrous solvents.

Table IV. Adsorption of Peroxides

(18.5 grams of Al_2O_3)

Solvent	Peroxide Removed from Solvent	Adsorbed Peroxide Found in Alumina by Titration
	Micromoles O_2	*Micromoles O_2*
Ethyl ether	87.4	86.4
Methyl Cellosolve	34.6	35.4
Skellysolve B	99.8	96.0
Dioxane	2,990.0	3,040.0

ACKNOWLEDGMENT

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A Constant Reflux Ratio Distilling Head

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ONE of the most troublesome problems in carrying out a distillation of laboratory or pilot-plant scale is the maintenance of a constant reflux ratio. In any distillation upon which calculations are to be made and on many precise analytical distillations as well, it is essential that the reflux ratio be constant and known.

The simplest and most common way of obtaining reflux ratio is use of a stopcock to remove a fraction of the liquid from the total condensate. Partial constriction of a capillary with mercury (*6*) or a nonlubricated glass value (*8*, *10*) has been used to eliminate the stopcock (*6*). Some shortcomings and operating difficulties associated with still heads which depend upon throttling of product for reflux control are (*4*):

1. The reflux must be laboriously and painstakingly controlled by manual adjustment of the stopcock.
2. The reflux ratio must be determined by drop-counting—a time-consuming and often inaccurate process.
3. Accumulation of dirt particles, grease, or drops of insoluble, high surface tension liquid such as water in the regulating stopcock greatly affects the reflux ratio, usually requiring interruption of the distillation.
4. The reflux ratio varies with the rate of distillation, since the rate of product take-off remains fixed.
5. A heterogeneous (two-phase) system cannot be distilled because more of one layer, usually the lower, is removed and equilibrium is thus destroyed.

The accumulative effects of these difficulties result in frequent, sometimes almost constant, attention to each still in order to get satisfactory distillation; uncertainty and variability of the conventional still head, making it difficult to do a reproducible and good analytical distillation; near impossibility of carrying out a

distillation suitable for precise calculation; and inability to handle a distillation yielding a heterogeneous overhead product.

Throttling the vapor instead of the condensed product eliminates the difficulty encountered with heterogeneous distillates.

A constant reflux ratio has been obtained by the use of intermittent take-off, by dividing the condensate into two streams, or by dividing the condensing surface into proportional parts. The intermittent take-off type usually employs a solenoid operated by a timing device. The removal of a portion of the condensate is effected by a swinging funnel (*2*), a swinging wire, a ball and seat, or a plunger and seat (*7*). One of the latest intermittent arrangements utilizes pressure change to withdraw the product (*9*). Most of these devices are not easily built and in addition have the difficulties associated with a complex system and many moving parts.

Dividing the condensed phase into two streams has been accomplished by capillaries (*1*) or by a glass arc (*5*).

Heads separating reflux by means of proportional condensing surfaces are of two general types. One type consists of a number of vertical tubes in parallel arranged similar to a tube bundle heat exchanger. The vapor is condensed on the inner surface of the tubes. Funnels are placed under a few of the tubes to catch the distillate, the condensate from the remaining tubes being returned as reflux. The Corad type head (*3*) condenses the vapor on the inside of one tube which is divided by means of vertical strips into several parallel surfaces. The condensate from one surface is taken off as product while the remainder is returned as reflux to the column. These heads operate very satisfactorily, but they are not easily fabricated from glass.

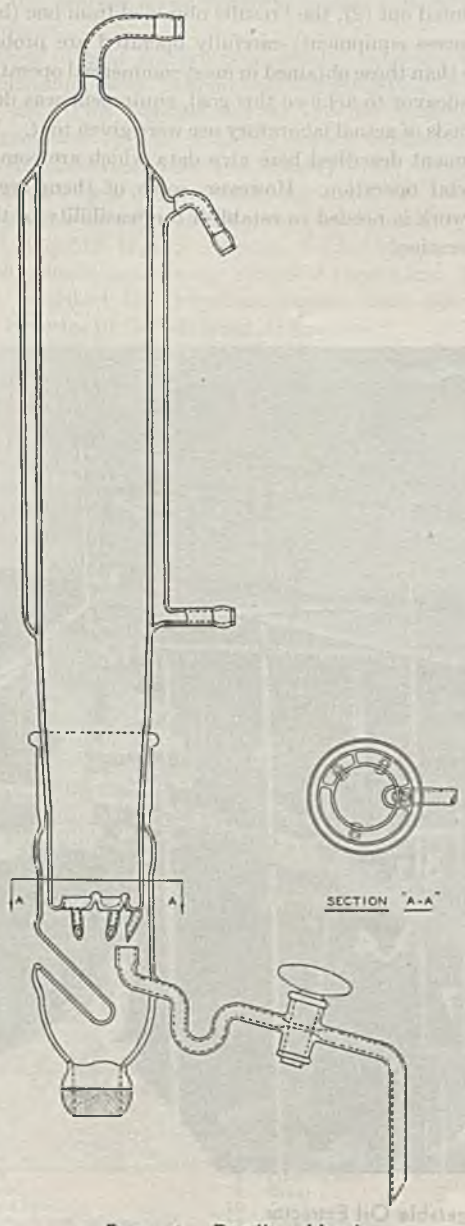

Figure 1. Distilling Head

A distilling head of the nonintermittent type has been designed (Figure 1) which gives a constant reflux ratio regardless of distillation rate, has no moving parts, and can be readily built by a skilled glass blower. The vapor is condensed on the concave (inside) surface of a vertical tube which has a gutter or trough around its lower inside perimeter. The trough is divided into sections and each section has a hole and its own downspout or drip. The downspouts are arranged to lie in a circle and either they or the receiving cup may be rotated to take product from any (or none) of the downspouts. The length of the section of trough compared with the total trough length determines the reflux ratio obtained from each section.

Figure 1 shows the arrangement when the receiving cup is fixed and the downspouts are rotatable by means of a standard-taper ground-glass joint. The head shown had the condensing section made from 48-mm. tubing, the lower chamber from 56-mm. tubing; the downspouts, 5-mm. tubing; a 55/50 standard-taper joint to rotate the downspouts, and a 35/25 ground-glass ball joint to attach it to the distilling column. The trough was divided into four sections, approximately 180, 90, 60, and 30 degrees. This would give reflux ratios (amount returned: amount removed) of 1 to 1, 3 to 1, 5 to 1, and 11 to 1. Calibration of the head gave actual reflux ratios of 0.9 to 1, 3.8 to 1, 5.2 to 1, and 8.5 to 1. The only critical dimension seems to be the diameter of the downspout giving the lowest reflux ratio. It must be sufficient to prevent trough overflow up to column capacity. The condensing tube must be clean and smooth and be kept vertical, so that channeling will not occur. The head operates satisfactorily under vacuum, provided the receiver is connected by an additional line to the vent at the top of the condenser. Heterogeneous distillates are handled without difficulty.

This type of distilling head has the following advantages:

It gives a constant reflux ratio regardless of distillation rate Almost any reflux ratio can be obtained by proper design.
It requires no attention while in operation.
It has no moving parts or auxiliary equipment. It does not have excessive holdup and its cost of construction is low.
It can be operated under vacuum or pressure, and can handle heterogeneous as well as homogeneous condensates.
It can be readily built by a skilled glass blower without recourse to special tools or parts.

The number of reflux ratios obtainable with a single head is limited by the number of downspouts that can be built into the head.

ACKNOWLEDGMENT

The advice and cooperation of W. E. Barr, glassblower, are gratefully acknowledged.

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Laboratory Study of Continuous Vegetable Oil Extraction

Countercurrent Extractor, Rising-Film Evaporator, and Oil Stripper

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Apparatus useful for studies of continuous vegetable oil extraction in the laboratory are described in a continuous countercurrent extractor capable of supplying essential data, such as completeness of oil extraction, contact time, solvent-to-solid ratio, miscella composition, and solvent carry-over; a rising-film evaporator of the natural circulation type provided with a separator for continuous oil removal; and a new and efficient oil stripper providing turbulence and thin films by operating against gravity and against surface tension.

THE development of apparatus for the laboratory study of continuous countercurrent extraction of vegetable oils with ethanol stems from difficulties encountered in obtaining pertinent information by the usual batch-extraction methods both in the laboratory and in the pilot plant. These difficulties include the lack of information regarding the requisite ratio of solvent to solid, proper contact time between them in the extraction step, the deleterious effect on the oil and by-products caused by prolonged heating encountered in batch concentration, and the difficulties due to overheating and foaming encountered in stripping the last portions of solvent from the oil.

These difficulties are discouraging to anyone attempting to evaluate in the laboratory any solvent for use in oil extraction. However, the value of results from laboratory-size equipment capable of continuous operation is of course enhanced when essential details of plant operation are duplicated, since, as has been pointed out (*2*), the "results obtained from one (laboratory-scale process equipment) carefully operated are probably more accurate than those obtained in most commercial operating tests". In an endeavor to achieve this goal, equipment was devised and trial periods of actual laboratory use were given to it. The pieces of equipment described here give data which are comparable to commercial operation. However, some of them are new and further work is needed to establish the feasibility of their large-scale operation.

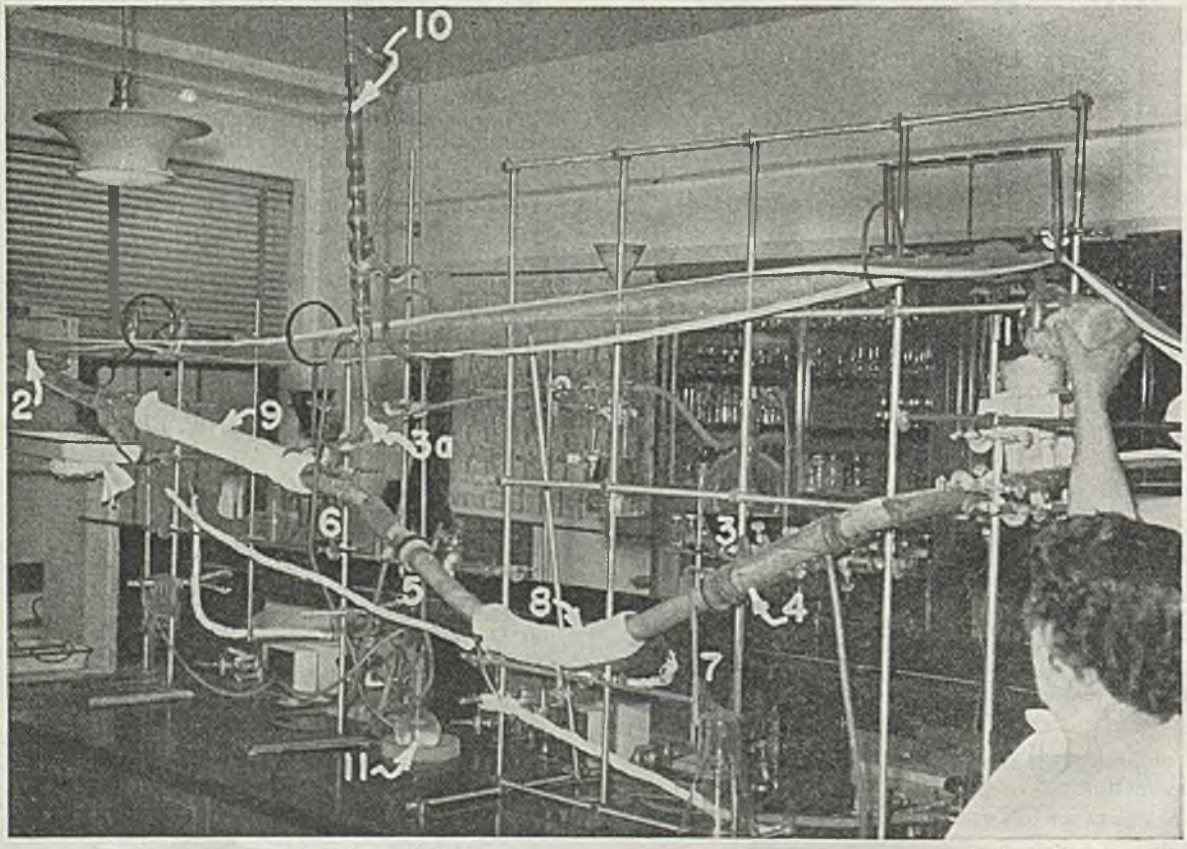

Figure 1. Continuous Countercurrent Vegetable Oil Extractor

The essential details of the equipment may be considered as a group of three divisions which may be designated as the extraction unit (including the dryer), the solvent- and by-product-recovery unit, and the oil-stripping unit.

In order to accumulate information for a materials balance, the extraction unit must contain means for uniform input of solvent and oil-bearing solid and control over products to permit analytical determination of the effect of the extraction. Furthermore, the solvent and solid feed must be variable over such ranges as to permit the extraction study to include significant solvent-to-solid ratios. Variability of the speed of the solids conveyor is also essential for determination of the proper time of contact between solvent and oil-bearing solid.

Important to the separation and recovery of the major fraction of the solvent is the effect of heat on the dissolved substances. This effect varies with the variety of oil extracted, since some oils undergo changes, such as permanent darkening, more readily than others. The heat effect varies also with the solvent used, since that determines the quantity and character of material other than oil which is dissolved. In any case, heating of prolonged duration, such as occurs in the pot-still type of batch concentration, is avoided in commercial practice by using the falling film, packed column, or rising-film type of evaporator where the liquid in the process of evaporation passes rapidly over the heated surfaces.

The effects of heat receive even greater emphasis when the solvent remaining after evaporative concentration is stripped from the oil. This residual solvent can be removed under ordinary pressures only at relatively higher temperatures than prevail in the first stage of concentration (*3*). By sweeping with steam or an inert gas under reduced pressures, the temperature can be greatly reduced, and this procedure is usually followed with the falling-film type of stripper, the bubble-cap tower, or the packed column used as the stripping apparatus. The new apparatus described for stripping solvents from oils may be evaluated in terms of the following discussion.

The process of stripping proceeds with greatest rapidity when thin films are presented to the heating surfaces and to the stripping atmosphere. Under such condition, heat transfer and diffusion of solvent-to-free liquid surfaces take place most rapidly. The production of thin films in any equipment in which the liquid flows freely over a surface is complicated by the surface tension forces which cause the liquid to attempt to occupy the volume having the smallest surface area, with the result that frequently the falling film becomes a meandering trickle of appreciable thickness. Similarly, capillarity, because of the proximity of surfaces in packed columns, partially circumvents the production of thin films. This latter effect leads also to channeling of the descending liquid and of the rising atmosphere.

EXTRACTION UNIT

A photograph of the continuous countercurrent extraction unit including the meal dryer is shown in Figure 1. Figure 2 is described as to construction and operation by considering the conveyor system, solvent system, and drying system, in that order.

The conveyor is made from ordinary 16-mesh galvanized iron window screen of the Pearle type by cutting a strip 12.1 cm. (4.75 inches) wide by 8.53 meters (28 feet) long and binding the edges with cloth to prevent raveling. It is made continuous by lapping the ends on a bias cut and stapling them with a paper stapler. In operation, it has been far more satisfactory and durable than originally anticipated, since the present conveyor has had an almost daily use of 6 or 7 hours for about 10 months and will evidently survive many months more.

In conveying the oil-containing solid through the body of the extractor, which consists of 45-mm. tubing bent in the shape shown, the screen closes around the solid completely, and it is essential that the quantity of material be sufficient to fill the tube, or the solvent will channel past too freely. The charging operation is shown at 1, where a weighed quantity of material is fed into a hopper which is maintained at a constant height above the moving screen, thus supplying a uniform feed to the extractor. A tabulation of the quantity of solid required to maintain a given level of material in the hopper supplies information as to the grams fed per hour. The rate of solid feed is regulated by the speed of the conveyor, and that, in turn, is regulated by the time of contact desired between the solid and solvent. The screen belt conveyor is pulled through the system by passing the belt between rubber rolls 2, which are driven by a variable-speed motor (not shown) through speed-reducing gears, so that any contact time from 0.5 hour up to more than 1.5 hours may be obtained.

Table I. Performance of Oil Extractor

Solvent	Temperature	Solvent-to-Solid Ratio[a] (Weight)	Contact Time, Min.	Oil Left in Residue, %
Hexane (Skelly B)	Room	1.2/1	55	0.39
Ethyl alcohol (absolute)	Boiling	2.12/1	65	0.62
Isopropyl alcohol (absolute)	Boiling	1.27/1	65	0.54

[a] Feed rate of flakes 267 grams per hour.

The solvent is metered to the extractor by a small gear pump driven by a variable-speed motor through speed-reducing gears. Since the gear pump would not meter nonlubricating liquids, it was used to meter lubricating oil into a closed container, and the displaced air was used to meter solvent to the extractor. This displacement system is shown at 3 with the point of entrance of the solvent into the extractor at 3*a*. The solvent maintains a liquid level in the extractor from 4 to 5. From 5 to 6, miscella (solution) drain back and fresh solvent wash takes place, while the miscella outlet is located at 7. The outlet take-off tube is joined to the top side of the extractor tube to permit settling of fines. Hot extractions may be carried out by passing steam through a neoprene coil, 8, surrounding the center section of the extractor.

The major portion of solvent remaining on the extracted solid is removed in dryer 9, which is constructed of 65-mm. glass tubing in order to accommodate copper heating coils in addition to the conveyor belt and its charge. At the end of the dryer nearest the extractor, the size of the tubing is reduced to 45 mm. in order to make a smooth and tight connection to the extractor. At a point just before the reduction in size of the tubing, a short piece of 20-mm. tubing ending in a male 24–40 ground-glass joint is

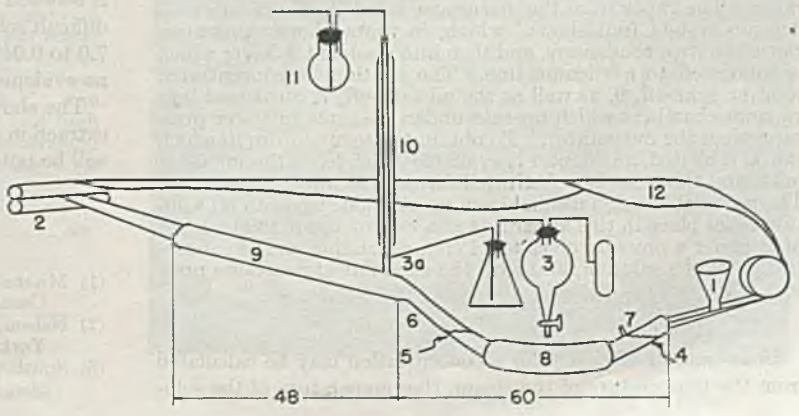

Figure 2. Continuous Countercurrent Vegetable Oil Extractor

1. Solid feed
2. Drive rolls
3. Solvent feed
4 to 5. Liquid level
5 to 6. Drainback and solvent wash
7. Miscella outlet
8. Heating coil
9. Dryer
10. Condenser
11. Trap to aspirator

joined to the dryer. This line is continued to a junction with the solvent inlet, 3*a*, and on to condenser 10, which in turn is connected through wash bottle 11 to a water aspirator. This aspirator is adjusted to cause a very gentle movement of air over the heated solvent-wet solid in the dryer and up through the condenser, where the entrained solvent vapors are condensed and flow down with the solvent feed into the fresh solvent wash portion of the extractor. The conveyor turns over during passage through the dryer and, on emerging, opens up to discharge the dried solid into a tray.

The efficiency of the extractor for extracting soybean oil is clearly indicated in Table I. Commercial-scale operation is predicated on leaving a residual oil content of 1% or less. Vapors of solvent in use are not detectable around extractor.

Information required for a materials balance can be obtained with this apparatus, as well as the solvent-to-solid ratios and contact times involved in reducing the oil content any desired amount.

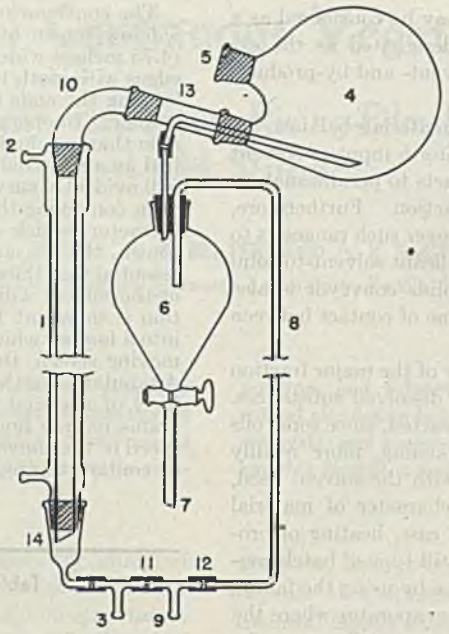

Figure 3. Continuous Natural Circulation Concentrator

1. Heating surface
2. Steam inlet
3. Solution inlet
4. Disengager
5. Disengager vapor outlet
6. Separator
7. Oil take-off
8. Return line
9. Solution take-off
10. 75° angle adapter
11, 12. Rubber connections
13. Disengager outlet
14. Reducing adapter

CONTINUOUS NATURAL CIRCULATION CONCENTRATOR

The rising-film evaporator, capable of continuous operation with natural circulation, is illustrated in Figure 3 and was assembled from standard glass equipment listed in glass-equipment catalogs. This availability, the versatility offered by a separator in the system, and the ease of conversion to an oil stripper are advantages over a setup (*1*) requiring construction of special units.

In the evaporating unit, steam is introduced at 2 into the outer jacket of a West-type condenser, 1, so that when the solution, which is fed into the bottom of the condenser through reducing adapter 14, reaches the heated surface, the sudden formation of solvent vapors causes it to be thrown violently up the condenser and through the 75° angle adapter, 10, and the gas-inlet adapter, 13, into the two-necked, 2-liter, round-bottomed flask serving adequately as a centrifugal disengager. This oil and unevaporated solvent are led into the 1-liter separatory funnel, 6, which is of importance in the concentration of partially miscible liquids such as alcohol and soybean oil. In this instance, at the temperature of the concentration, the oil separates in large drops which settle into a clear oily layer at the bottom of the separator, while the supernatant solution is led by line 8 back to the evaporator. The vapor from the disengager is led through 5 to a condensing system (not shown) which, in the authors' apparatus, consists of two condensers, and then into a solvent receiver which is connected to a vacuum line. The continuous concentrated solution take-off, 9, as well as the oil take-off, 7, must lead into vacuum chambers which operate under the same or lower pressures than the evaporator. To obtain the temperature to which the oil is heated, an adapter is available which has a thermometer inlet, and this may be substituted for the 75° angle adapter, 10. The removal of ethyl alcohol from an alcoholic soybean oil solution takes place in this apparatus at a rate of about 1800 ml. per hour under a pressure of 12 to 24 cm., depending on the concentration of the solution, and with the steam at atmospheric pressure.

Heat-transfer efficiency for a concentration may be calculated from the temperature of the steam, the temperature of the solution, the latent heat of vaporization of liquids, the area of the heating surface, and the rate of distillation of the solvent. Foaming is not a problem with this evaporator.

CONTINUOUS OIL STRIPPER

In order to avoid the previously described difficulty of obtaining films with the usual oil strippers, a stripper was devised which can be assembled from standard glass equipment or utilize the apparatus described in Figure 3.

In utilizing the latter apparatus, it is necessary only to put regulatory clamps over the rubber connections, 11 and 12. The clamp at 12 is entirely closed, and that at 11 is used to regulate the incoming flow of inert stripping atmosphere introduced at 9. The oil solution to be stripped is introduced at 3.

Stripping atmosphere and oil solution are introduced at the bottom of a tube which offers the only means of escape for the atmosphere, and, therefore, the gas rises through the tube as a series of bubbles, carrying with them a quantity of liquid. The stripping atmosphere is introduced too rapidly for the operation to be similar to the usual air lift, and, therefore, the quantity of liquid separating the bubbles is small, and their rise is very rapid, causing the liquid to spread on the surface of the heated tube until, finally, the thin bubbles break. This effect may be controlled, so that bubbles with film surfaces are continuously forming and breaking against the sides of the tube, in such a fashion that the liquid appears to be pushed against the sides in thin layers and, finally, is thrown over the top of the tube. As observed through the glass tubes, the operation takes place in a complex manner which bears no resemblance to the normal action of an air lift nor of a rising-film evaporator. The action supplies a force in active operation against the surface forces which come into control when a liquid flows freely over a surface, and thereby this stripper acts to overcome the contractile effect produced by those forces.

Since relatively large surfaces of solution are exposed, the stripping action has been found very successful. For example, the authors have been able to reduce the solvent content of an alcoholic soybean oil solution from 5 to 0.04% by operating the system under a pressure of 60 cm. with the heating tube and stripping atmosphere heated with steam at atmospheric pressure. A solution containing trichloroethylene, which is one of the most difficult solvents to remove from vegetable oils, was reduced from 7.0 to 0.04% in one passage. In this latter case, the oil showed no evidence of having been overheated.

The above-described equipment is now in use on a study of oil extraction of soybeans with ethanol and the results of this study will be published soon.

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Tropical Testing Chamber

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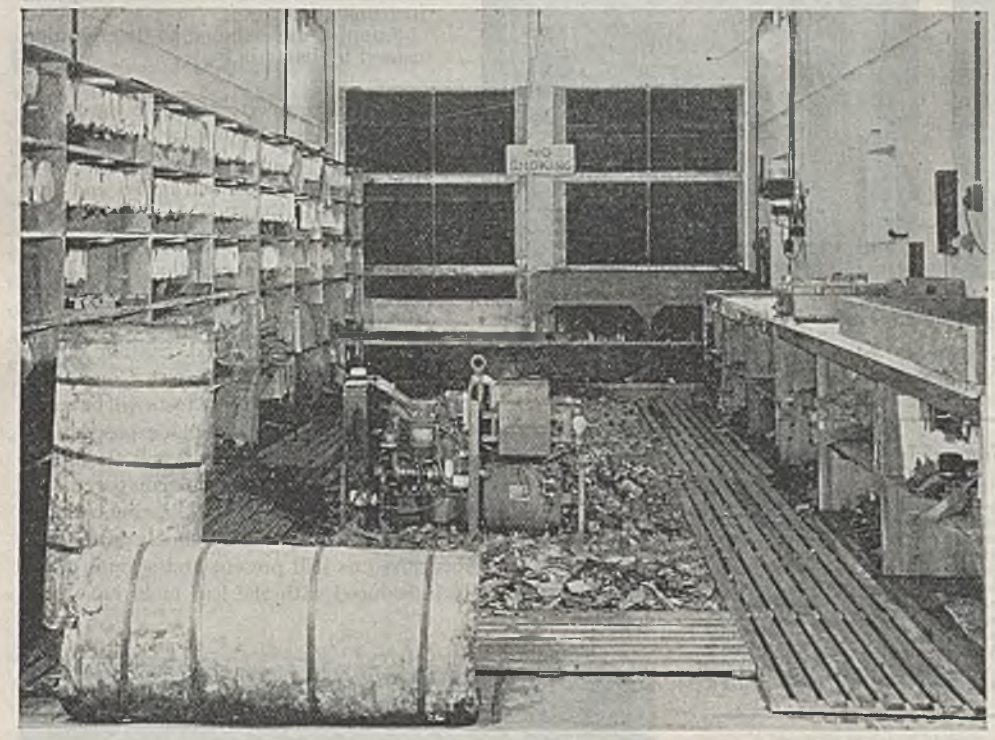

Figure 1. Interior View of Tropical Testing Chamber

THE tropical testing chamber of the Engineer Board was established at Fort Belvoir in the latter part of 1944 because the Corps of Engineers needed to test the resistance to tropical deterioration of a large number of items of equipment, as cork, fabrics, optical glass, leather, protective coatings, plastics, rubber (both natural and synthetic), wood and wood products (such as paper), and materials used in electrical and electronic equipment and in mapping equipment.

The tropical testing chamber may be considered analogous to a pilot plant in industry. In such an analogy, a pure culture test would be comparable to a laboratory batch in industry, and a tropical field test comparable to a plant batch. In the large tropical chamber end items of equipment can be tested, which is particularly important in the case of such matériel as optical instruments and electrical and electronic equipment.

The tropical testing chamber is 14 feet in width, 32 feet in length, and 12 feet in height. The wall construction consists of three layers, an outer layer of brick 9 inches thick, a middle layer of asphalt-impregnated mineral wool 4.5 inches thick, and an inner layer of Transite 0.375 inch thick. The outer layer of the ceiling is an asphalt slag roof; next is a layer of Celotex, 1.5 inches thick; next, a metal deck; under the metal deck is a layer of asphalt-impregnated mineral wool 6 inches thick; under the mineral wool is a 2-foot air space for circulation of air; and finally, a Transite ceiling 0.375 inch thick. The chamber has double doors which are 9 feet wide and 11 feet high and a single pedestrian door. The humidity and temperature within the room are controlled by heating and cooling coils through which the air is blown. A fan produces an air movement with a velocity of 4 to 5 miles an hour. Water vapor sprays are provided at the back of the coils.

Figure 1 is a photograph of the interior of the chamber taken through the double doors, showing the heating and cooling coils at the rear. On one side are wooden shelves and on the other is a bench with two additional shelves below it. At the end of the chamber opposite the large double doors are three soil burial beds 4 feet wide by 7 feet long by 10 inches deep. One of the beds is mounted on rollers over the other two beds. On the floor is abundant leaf mold, providing a source of food for the fungi. Wooden walkways make all parts readily accessible. Figure 1 shows an electrical generator set and two rolls of asphalt-coated burlap being exposed on the floor.

A definite temperature and humidity cycle is maintained in the tropical testing chamber. For 18 hours, the relative humidity is maintained at 90 ± 2% and the temperature is held at 85° ± 1° F. For 6 hours, the relative humidity is maintained at 95 ± 2% and the temperature is held at 75° ± 1° F. This cycle is shown graphically in Figure 2.

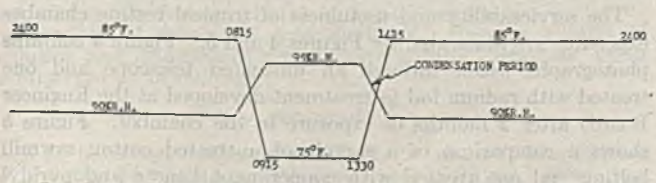

Figure 2. Temperature-Humidity Cycle of Testing Chamber

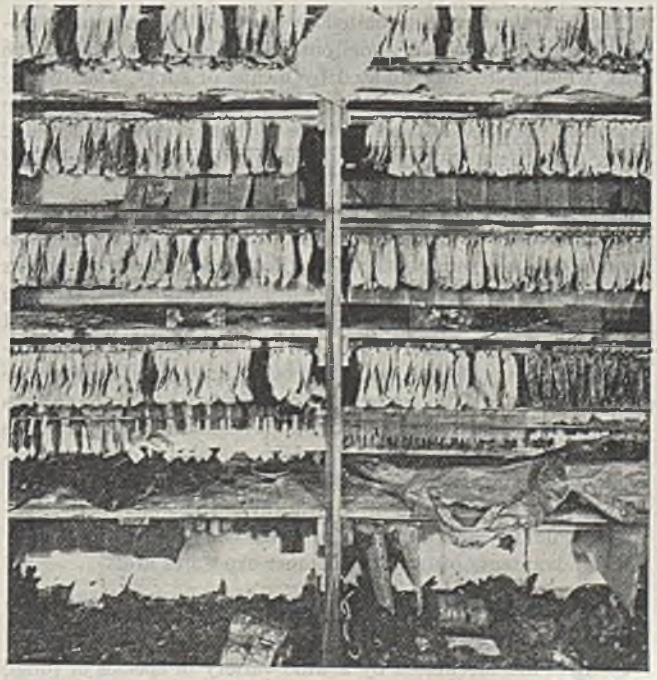

Figure 3. Samples Being Exposed in Testing Chamber

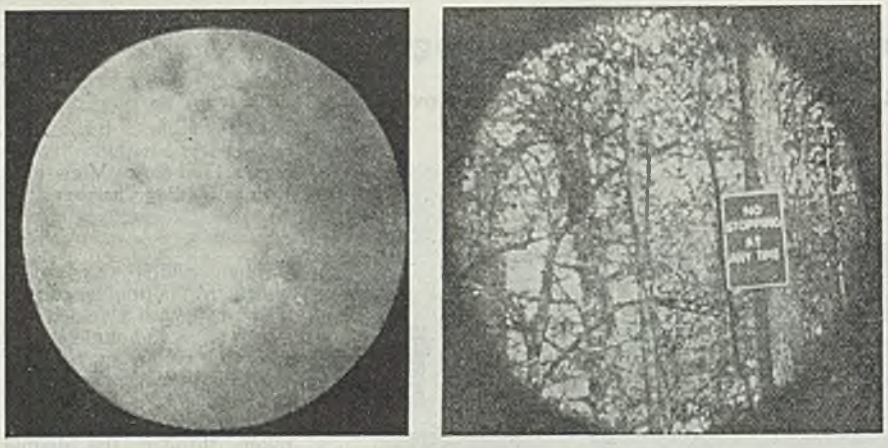

Figure 4. Photographs Taken through Telescopes after 2 Months' Exposure in Chamber

Left. Untreated telescope. *Right.* Telescope treated with radium foil

Table I. Fungi Introduced into Tropical Testing Chamber

Species	Source	Species	Source
Chaetomium globosum	Local	*Penicillium sp.*	India
Aspergillus niger	Hollandia	*Penicillium expansum*	Local
Trichoderma lignorum	South Pacific	*Penicillium sp.*	New Guinea
Aspergillus oryzae	South Pacific	*Aspergillus oryzae*	China
Mucor sp.	South Pacific	*Penicillium sp.*	South Pacific
Penicillium sp.	South Pacific	*Chaetomium sp.*	New Guinea
Aspergillus 19B	South Pacific	*Aspergillus niger*	South Pacific
Memnoniella echinata	New Guinea	*Aspergillus niger*	Local
Penicillium luteum	India	*Spicarios sp.*	South Pacific
Stemphylium sp.	New Orleans	*Chaetomium sp.*	South Pacific
Memnoniella sp.	South Pacific	*Mucor sp.*	South Pacific
Metarrhizium glutinosum	New Orleans	*Aspergillus versicolor*	South Pacific

A relative humidity of 90% at 85° F. is ideal for the growth of most fungi and is typical of tropical conditions.

A relative humidity of 95% at a temperature of 75° F. was chosen because it provides a temperature drop and a relative humidity rise comparable to conditions which occur in the tropics.

Cycling provides breathing for partially closed systems such as optical instruments.

Cycling causes condensation which provides a film of water ideal for fungus growth and excellent conditions for the corrosion of metals.

The chamber was inoculated by the addition of spore suspensions of 24 species of fungi obtained chiefly from the Pacific area, which were disseminated by means of spray, and by the native fungi occurring on the leaf mold placed on the floor of the chamber. The list of the 24 species of fungi is given in Table I. Other fungi were undoubtedly brought into the chamber by the air and by test specimens.

Wooden shelves are employed for the shelf exposure of materials because wood provides a source of nutrient for fungi, and also because exposure on wooden shelves duplicates storage conditions in the field. Such items as fabrics, small pieces of cork, etc., are hung from glass rods with glass hooks. Packaged materials and large objects are placed directly on the shelves. Figure 3 provides a close-up of test specimens being exposed in and on the wooden shelves. The center of the chamber is used for the exposure of large pieces of equipment. The soil burial beds in the room provide soil exposure tests which are likely to be more reproducible than usual because of the close control of the water content and temperature of the soil made possible by the controlled humidity and temperature in the chamber.

The advantages of tropical chamber exposures are:

Samples are exposed under conditions approximating those in nature.

Samples are constantly reinoculated with fungus spores.

Samples are inoculated by a wide variety of species of fungi, so that after one grows, others may follow, if a breakdown of the fungicide is caused by the first fungi.

The end item is exposed in its entirety.

Samples are exposed to deterioration caused by moisture from condensation.

Samples are exposed to deterioration aided by mites and other insects which are present in the chamber (mites are desirable in testing such items as optical instruments).

Samples are exposed to deterioration caused by bacteria.

It is desirable to correlate the results of tropical chamber tests with other types of testing. Comparisons with tropical field tests and with soil burial and pure culture tests are being made. As part of a study of commercially available fungicides applied to fabrics that is now being carried out at the Engineer Board, ten thousand fabric samples are being sent to the Panama Field Station of the National Defense Research Committee, and the results of these tests will be correlated with the results obtained from similar samples exposed in the chamber. Cork, leather, and optical instruments will also be exposed in the chamber at Panama and the results compared.

The fungi that are now present in the tropical testing chamber are being identified. Eight of the species originally introduced have already been recognized as still present and several others which were probably introduced with the leaf mold have been identified.

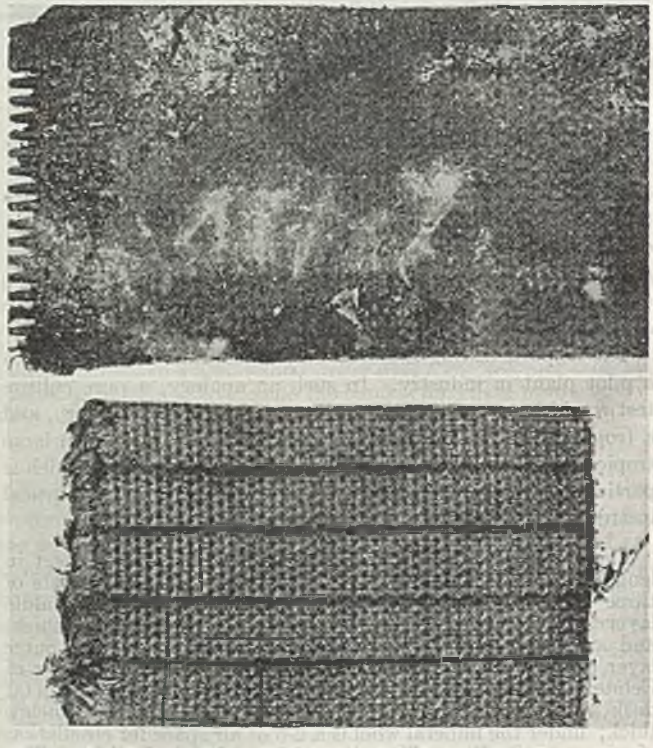

Figure 5. Cotton Sawmill Belting after 2 Months' Exposure in Chamber

Upper. Untreated belting
Lower. Belting treated with copper naphthenate and pyridyl mercuric stearate

The serviceability and usefulness of tropical testing chamber exposures are illustrated by Figures 4 and 5. Figure 4 contains photographs taken through an untreated telescope and one treated with radium foil (a treatment developed at the Engineer Board) after 2 months of exposure in the chamber. Figure 5 shows a comparison of a sample of untreated cotton sawmill belting and one treated with copper naphthenate and pyridyl mercuric stearate after two months of exposure in the chamber.

Semimicro-Kjeldahl Procedure for Control Laboratories

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NITROGEN analyses must often be run either on a very limited amount of sample or in the shortest possible time. While the usual macroprocedure is not satisfactory under these conditions, micromethods often cannot be employed because of limitations on equipment and personnel. In recent years sufficient improvement and simplification have been made in the semimicromethod to permit its use in almost any laboratory. Among the modifications which have been made are the distillation unit of Redemann (*4*), the adaption of the Winkler boric acid method to the semimicro scale by Wagner (*6*), the introduction of an improved indicator for use in presence of boric acid by Ma and Zuazaga (*1*), and the discovery of highly efficient digestion catalysts of the mercury-selenium type by Osborn and Krasnitz (*3*).

Table I. Determination of Nitrogen in Simple Compounds

Compound	% Nitrogen Found	Theory
Acetanilide	10.44 10.34	10.36
p-Bromoacetanilide	6.47 6.43	6.54
Benzanilide	7.14 7.07	7.10

This paper describes a procedure which incorporates these recent modifications and may be used with equipment available in almost any laboratory. The procedure has been checked by two different laboratories and has given excellent results for more than 3 years.

APPARATUS

The balance employed should be adjusted to give a precision of 0.1 mg. or better when weighings are conducted by the method of swings. All weights used should be checked to assure accuracy within the precision of the balance.

Samples are introduced into the digestion flask by means of a long-stemmed weighing tube (*2*) to prevent errors resulting from particles of sample adhering to the neck of the flask and escaping decomposition.

A digestion rack can be made by attaching six buret clamps to an iron bar which is clamped to a ring stand. The 100-ml. Kjeldahl flasks are heated with a Bunsen or Fisher burner.

The Redemann distillation unit can be made by a glassblower of ordinary skill or may be purchased from Scientific Glass Apparatus Co., Bloomfield, N. J., catalog No. M-1285.

REAGENTS

Catalyst Mixture. Grind together 150 grams of anhydrous potassium sulfate, 5 grams of metallic selenium, and 10 grams of mercuric oxide.

Mixed Indicator. Prepare 0.1% bromocresol green and 0.1% methyl red solutions in 95% alcohol separately. Mix 10 ml. of bromocresol green solution with 2 ml. of methyl red solution.

Boric Acid, 4%. Dissolve 20 grams of boric acid in 500 ml. of boiling distilled water.

Sodium Hydroxide, 48%. Dissolve 480 grams of sodium hydroxide in 520 ml. of distilled water and allow to stand until carbonate-free.

Sodium Thiosulfate, 44%. Dissolve 88 grams of sodium thiosulfate pentahydrate in 112 ml. of distilled water.

Standard Hydrochloric Acid, 0.015 *N*. Prepare a 0.015 *N* solution and standardize against pure sodium carbonate, using methyl red as an indicator.

PROCEDURE

A 15- to 50-mg. sample (30 to 50 mg. for balance with precision of 0.1 mg., 15 to 25 mg. with precision of 0.03 mg.) is weighed into a 100-ml. Kjeldahl flask, and 4 ml. of concentrated sulfuric acid and about 1.5 grams of catalyst mixture are added. Digestion is started with a low flame, gradually increasing the heat until the mixture boils briskly. For most samples the solution becomes clear after about 10 minutes heating. Digestion is continued for 25 minutes after clearing; for difficult compounds such as pyridine derivatives the afterboil should be extended to 1 hour. The flask and contents are cooled to room temperature, 20 ml. of water are added, and the solution is well mixed.

A blank flask is fitted into place in the distillation unit and the apparatus is well steamed. The blank flask is replaced by the flask containing the sample and a moderate current of steam is passed over until the apparatus is completely filled with steam. A 125-ml. Erlenmeyer flask containing 10 ml. of 4% boric acid solution and 3 drops of mixed indicator is placed under the delivery tube, with the tip of the delivery tube below the surface of the acid. During the course of several minutes 12 ml. of 48% sodium hydroxide solution are slowly added. Dropwise addition of base is necessary until most of the acid is neutralized to prevent too violent a reaction. About 4 ml. of sodium thiosulfate solution are added immediately after the base and the solution is steam-distilled as rapidly as possible. After 25 to 30 ml. of distillate have been collected, the receiver is lowered and about 5 ml. of additional distillate are collected.

Table II. Determination of Nitrogen in Ring Compounds

Compound	% Nitrogen Found	Theory
Pyridine hydrochloride	11.99 11.93	12.12
2-Aminopyridine	29.54 29.55	29.76
2-(Pyridyl-2) ethyl phenyl amine	14.06 13.90	14.13
2-Chloroquinoline	8.54 8.53	8.57
Triphenyltriazine	13.46 13.52	13.51
2-Benzoyl-5-phenyl-glyoxaline	11.27 11.23	11.29
2,5-Diphenyl-3-keto-3,4-dihydropyrazine	11.33 11.24	11.29
2-Methyl-4-phenyl-5-keto-dihydroglyoxaline	15.93 16.10	16.09

The boric acid solution changes from pink to a bluish green as soon as it comes in contact with ammonia. The solution is titrated with 0.015 *N* acid. Since the true end point is difficult to detect, the titration is continued until a faint pink color appears. The volume of acid required to produce a pink color of this same intensity is determined by adding standard acid to a solution of the same volume, containing the same quantity of boric acid and indicator. The blank (usually about 0.20 ml. of 0.015 *N* acid) is subtracted from the volume of acid required to titrate the sample.

Table III. Determination of Nitrogen in High Polymeric Materials

Polymer	% Nitrogen Found	Calculated[a]
Butadiene-acrylonitrile 70/30 copolymer	7.69 7.64	7.65
Butadiene-acrylonitrile 60/40 copolymer	9.15 9.06	9.14
Butadiene-2-vinylpyridine 75/25 copolymer	3.26 3.25	3.27
Butadiene-2-vinylpyridine 60/40 copolymer	5.16 5.19	5.00
Butadiene-2-vinylpyridine 50/50 copolymer	6.19 6.32	6.27
Chloroprene-2-vinylpyridine copolymer	1.34 1.32	1.30
Polymeric salt of sebacic acid and *p*-xylylenediamine	8.02 8.13	8.28
Polyhexamethylene adipamide (nylon)	12.03 11.99	12.11

[a] Calculated values were obtained from analysis of polymer by an independent method such as Dumas nitrogen or determination of carbon-hydrogen ratio.

RESULTS

Table I indicates that the procedure gives excellent results.

With the exception of compounds which contain a nitrogen to nitrogen or a nitrogen to oxygen linkage, practically all organic nitrogen compounds can be analyzed by the Kjeldahl method. So far the authors have encountered no exceptions to this rule. In Table II analytical results are listed for a number of nitrogen ring compounds including several pyridine derivatives. For pyridine compounds the digestion time had to be extended to about one hour. Shirley and Becker (*5*) observed that the use of a copper sulfate catalyst gave low results with pyridine-type compounds while correct results were obtained with a mercury or mercury–selenium oxychloride catalyst. This observation has been confirmed by the authors.

The literature contains little information as to the reliability of the Kjeldahl method for high polymeric materials. All high polymeric materials investigated by the authors to date have given the correct results by this method. However, the same limitations as to structure should apply for high polymers as for the usual compounds. Table III gives analytical results for a number of high polymeric substances.

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Sensitive and Selective Test for Gallotannin (Tannic Acid) and Other Tannins[1]

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A VIOLET flocculent precipitate is slowly produced when an ammoniacal solution of tannic acid is warmed with a solution of ferrous α,α'-dipyridyl sulfate, $Fe(\alpha,\alpha'\text{-dip})_3SO_4$. The precipitate, which filters well, forms quickly if the ammoniacal solution or suspension is treated with acetic acid and warmed. Precipitation is complete, as shown by the negative response of the filtrate to the most common tannic reagent—i.e., ferric chloride plus sodium acetate (*2*). A solution of ferrous α,α'-phenanthroline sulfate, $Fe(\alpha,\alpha'\text{-phen})_3SO_4$, shows a similar reaction toward tannic acid.

Attempts to isolate precipitates of constant composition have not been successful. Nonetheless, the chemical basis of this new reaction of tannin deserves consideration. Some of the factors involved are: the phenolic nature of the tannin, the colloidal character of aqueous tannin solutions, the autoxidation of these solutions at pH greater than 7, and the ability of $Fe(\alpha,\alpha'\text{-dip})_3^{++}$ ions to combine with voluminous and complex anions to form red, slightly soluble salts (*1*).

Of the possible types of reaction, the writers believe the most probable to be the formation of an adsorption complex by combination of the oxidation products of the tannin with Fe $(\alpha,\alpha'\text{-dip})_3(OH)_2$, or $Fe(\alpha,\alpha'\text{-phen})_3(OH)_2$. Adsorption compounds of tannin with hydrous metal oxides have been reported and used for analytical purposes (*3*, *4*). The assumption that it is not tannin itself, but rather an oxidation product (of unknown composition) which takes part in this reaction, is supported by the observation that no precipitate is formed if air is excluded, or if much alkali sulfite is present. This is also in agreement with the fact that the deposition of the violet precipitate occurs gradually, and the precipitate always forms first at the upper surface of the liquid. This effect is seen distinctly if the solution of tannic acid is not extremely dilute.

The probability that autoxidation of tannic acid is responsible for the reaction with $Fe(\alpha,\alpha'\text{-dip})_3^{++}$ ions made it likely that other autoxidizable phenolic compounds would exhibit an analogous behavior. Trials showed that ammoniacal solutions of pyrogallol give a very strong reaction. Gallic acid, in cold saturated (1%) solution, gives a visible response, though much less decided than tannic acid and pyrogallol at this dilution. Hydroquinone reacts weakly. Phloroglucinol, resorcinol, and pyrocatechol give no response. These findings led to the expectation that vegetable tannins would behave toward $Fe(\alpha,\alpha'\text{-dip})_3SO_4$ as tannic acid does, since they are all phenolic in nature, and their alkaline solutions are said (*2*) to absorb oxygen. This prediction has been realized with all the natural tanning agents that have been tested thus far, though the number of varieties available has not been large. Consequently, this reaction applies to gallotannin and to other tannins. As will be seen, the nature of the response to the tannin reaction with $Fe(\alpha,\alpha'\text{-dip})_3SO_4$ is not determined by whether the test material is a pyrogallol- or catechutannin. Synthetic tans, which mostly are condensation products of formaldehyde and sulfonated phenols, give no response.

[1] Translated from the German manuscript by Ralph E. Oesper, University of Cincinnati, Cincinnati, Ohio.

DETECTION OF TANNIC ACID (GALLOTANNIN)

REAGENT. Dissolve 0.25 gram of α,α'-dipyridyl and 0.146 gram of ferrous sulfate heptahydrate in 50 ml. of water. The solution keeps well in closed containers. Before the test, it is well to render a portion of the reagent ammoniacal and boil. Remove the resulting slight precipitate of hydrous ferric oxide by filtering or centrifuging. This purification is essential when testing for small quantities of gallotannin or other tannins.

PROCEDURE. *Test Tube Reaction.* Treat 1 ml. of the test solution with an equal volume of ammoniacal reagent solution and bring the mixture to boiling. Add acetic acid until the odor of ammonia vanishes and again heat the solution to boiling. A flocculent violet precipitate forms. If only minute quantities of the tannin are present, the precipitate has a brownish tinge. Turbidities produced by minute amounts of precipitate can be easily discerned in the red solution, if the test tube is held toward an intense source of light and a sheet of frosted glass interposed. Identification limit, 8 micrograms of tannic acid; limiting concentration, 1 to 125,000.

Drop Reaction. Place one drop of the test solution in a small (0.05-ml.) centrifuge tube, add 2 drops of reagent solution and suspend the tube in boiling water for several minutes. After acidifying with acetic acid, again warm the solution and then centrifuge. Any precipitate collects in the constricted end of the tube. Very tiny precipitates are readily seen if, after centrifuging, the tube is held against white paper. A blank test is recommended when small amounts of tannic acid are suspected. Identification limit: 1 microgram of tannic acid; limiting concentration: 1 to 50,000.

The test for tannic acid can alternatively be carried out as follows:

Make the test solution ammoniacal, warm, acidify with acetic acid, and then add the reagent solution. This procedure is not so sensitive as those already outlined.

The nonspecific phenol reaction of tannic acid with dilute sodium acetate–ferric chloride solution is not so sensitive as the test described here. As a test-tube reaction the identification limit is 25 micrograms; the limiting concentration is 1 to 40,000. The corresponding figures for the drop reaction on a spot plate are 1 microgram and 1 to 50,000. Hence the new test is three times as sensitive as the ferric-phenol reaction when carried out in a test tube, and just as sensitive as the latter when spot test techniques are used.

DETECTION OF NATURAL TANNINS AND DIFFERENTIATION FROM SYNTHETIC TANS

The test solution (0.5%) is prepared from the solid specimen. One milliliter of the filtered liquid is carried through one of the procedures as outlined. When testing extracts of tanning agents, test portions are prepared by diluting the specimen 1 to 10 and 1 to 100, and 1-ml. portions are used. The behavior of all solutions toward ammonia and acetic acid should be determined before adding the reagent. If a precipitate appears on adding acetic acid to the warm ammoniacal solution, it should be removed, and the test tube procedure carried out on the filtrate after again making the solution ammoniacal. The test with $Fe(\alpha,\alpha'\text{-dip})_3\text{-}SO_4$ was tried on a variety of tanning materials. The following natural tannins gave a positive reaction: gallotannin; tara powder; gambier; myrobalan; quebracho; and extracts of wattle, mangle, sumac, and fustic. In marked contrast the following synthetic tanning agents gave a negative reaction: orotan N, syntan A, syntan S, mertanol 7 L, maxyntan, and tanasol. These findings indicate that this test is suitable for distinguishing commercial natural from synthetic tanning agents.

Similar differentiating tests were also made on finished, mostly colored, leathers. About 0.5 gram of the leather was cut into tiny bits and boiled in 2 ml. of ammonia water for 2 minutes. The clear filtrate was carried through the test procedure. Preliminary tests with ammonia and acetic acid were made in all cases. This step is indispensable when testing leathers colored with coal-tar dyes, because the addition of the reagent to the ammoniacal solutions of many acid dyes results in a precipitate that does not dissolve in acetic acid. If the preliminary test produces a precipitate, it is filtered off, and the tannin test is made on the clear filtrate after it is again made ammoniacal.

In 19 out of 20 cases, the test revealed the nature (vegetable or synthetic) of the tanning agent. The single exception was a leather that had been tanned with a sulfited quebracho extract; it gave a negative response. Further studies will be necessary to determine whether the test fails with leathers tanned with strongly sulfited tannin extracts. A trial with a technical sulfited quebracho extract showed that it still gives a distinct tannin reaction at a dilution of 1 to 1000.

DETECTION OF TANNINS IN BEVERAGES

Three milliliters of the samples were taken for the tests. Positive reactions were given by 4 varieties of red wine (tart, sweet); 3 varieties of white wine (tart, sweet); and water extracts of tea, maté, and guarana. Negative responses were obtained with Cinzano (Italian origin); beer (light, dark); and water extracts of coffee (raw, roasted).

ACKNOWLEDGMENT

The samples of leather, and of the natural and synthetic tanning agents, were donated by Cortume Carioca, Rio de Janeiro. The authors express their gratitude to this firm for its cooperation.

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Gas Bubble Releaser for Use in Dumas Nitrogen Determination Azotometers

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A RATHER common and annoying occurrence in running a Dumas nitrogen determination is the sticking of gas bubbles to the surface of the mercury in the azotometer. This has been attributed to too narrow an opening of the gas inlet of the nitrometer, too short a distance between the gas inlet and the level of the mercury, excessive greasing of the gas inlet stopcock (*3*), and the use of perfectly pure clean mercury when the azotometer is first filled (*4*).

Flaschenträger (*1*) and Weygand (*5*) say that this difficulty can be overcome by the addition of powdered copper oxide to the surface of the mercury. Nichols (*2*) suggests the use of mercurous oxide for the same purpose. None of these measures, which are preventive in character, has been found completely reliable.

A simple direct method for releasing gas bubbles already sticking to the mercury has been used effectively in this laboratory for over a year.

A piece of steel or iron wire about 1 cm. long, slightly curved, is placed in the azotometer so that it rests on the surface of the mercury. Whenever gas bubbles are to be released, the piece of wire is swept over the mercury by means of a small permanent-type magnet held outside the azotometer near the level of the mercury and opposite the wire. The wire is attracted to the magnet and, in passing over the surface of the mercury, releases the bubbles. The wire can thus be moved back and forth simply by placing the magnet in the proper position opposite it. To facilitate this operation two magnets can be used. These are held on opposite sides of the azotometer and brought near the azotometer alternately.

In addition, this device can be used to break up small bubbles at the potassium hydroxide solution-gas interface. This is done by attracting the wire to the magnet and moving it up slowly to the interface. By moving the wire up and down through the interface, the gas bubbles are broken. Large gas bubbles stuck or moving up very slowly in the graduated portion of the azotometer can be released also by this means.

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NOTES ON ANALYTICAL PROCEDURES

Determination of Reducing Sugars

Mathematical Expression of Reducing Action in the Lane and Eynon and Volumetric Ferricyanide Methods

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IN THE determination of reducing sugars by direct titration against Fehling solution according to Soxhlet, Violette, or Pavy, it has been generally assumed that the concentration, x, of sugar solution, multiplied by the volume, y, required for complete reduction of a fixed quantity of copper solution, is constant ($xy = C$). But Soxhlet (*6*) showed as early as 1878 that this simple relationship holds only if the concentration of the unknown sugar solution is approximately the same as that used for standardization of the Fehling solution. Later, Lane and Eynon (*4*) found that the "factor" (C/100) may vary as much as 5% for a range of 15 to 50 ml. of sugar solution used.

When it became apparent about two years ago that copper salts might be difficult to obtain, it was decided to devise a substitute for the Lane and Eynon method, and alkaline ferricyanide solution was tried, as first proposed by Ionescu and Vargolici (*1*), with methylene blue as indicator of complete reduction. When the results were plotted by Louis Sattler, of this laboratory, it was discovered that there is a straight-line relationship not between x and y, but between their logarithms, and that the results can be expressed by the equation

$$\log y = \log b - m \log x \qquad (1)$$

or

$$y = bx^{-m} \qquad (2)$$

where b and m are constants. The original equation, $xy = C$, or $y = C/x$, is a special case of the general equation $y = C/x^m$, with $m = 1$.

EQUATIONS FOR LANE AND EYNON METHOD

To test the validity of this law of reducing action for the Lane and Eynon method, the values of m and log b were calculated by the method of averages from 18 pairs of values for milligrams of sugar in 100 ml. of solution and the corresponding titers given in the Lane and Eynon tables (*3*). A detailed comparison between the figures in the table for invert sugar alone, with 10 ml. of Fehling solution, and those calculated from the equation is shown in Table I. In this particular case m was found to be 1.0341, and log b = 3.7886.

Table I. Comparison between Lane and Eynon Titers and Those Calculated from Equation 1 for Invert Sugar Alone

(10 ml. of Fehling solution)

Sugar in 100 Ml.	Sugar Solution, L. & E.	Sugar Solution, Equation 1	Difference
Mg.	*Ml.*	*Ml.*	*Ml.*
336	15	15.00	0.00
298	17	16.98	−0.02
267	19	19.03	+0.03
242.9	21	20.98	−0.02
222.2	23	23.00	0.00
204.8	25	25.02	+0.02
190.4	27	26.98	−0.02
177.6	29	29.00	0.00
166.3	31	31.04	+0.04
156.6	33	33.03	+0.03
147.9	35	35.04	+0.04
140.2	37	37.03	+0.03
133.3	39	39.01	+0.01
127.1	41	40.98	−0.02
121.4	43	42.98	−0.02
116.1	45	45.01	+0.01
111.4	47	46.97	−0.03
107.1	49	48.92	−0.08
Average difference			±0.023
Maximum difference			−0.08

Table II. Constants in Equation 1 for Reducing Effect of Various Sugars, as Determined by Lane and Eynon

	m	log b	$\frac{m}{\log b}$	Deviation Average	Deviation Maximum
				Ml.	*Ml.*
	10 ml. of Fehling solution				
Invert sugar	1.0341	3.7886	0.2730	0.023	0.08
Plus 1 gram of sucrose	1.0166	3.7405	0.2718	0.013	0.04
Plus 5 grams of sucrose	1.0030	3.6848	0.2722	0.012	0.04
Plus 10 grams of sucrose	0.9830	3.6240	0.2713	0.067	0.21
Plus 25 grams of sucrose	0.9552	3.5308	0.2698	0.109	0.28
Dextrose	1.0354	3.7789	0.2740	0.017	0.04
Levulose	1.0315	3.7966	0.2717	0.023	0.06
Maltose hydrate	0.9759	3.8444	0.2512	0.008	0.03
Lactose hydrate	1.0010	3.8348	0.2610	0.057	0.14
	25 ml. of Fehling solution				
Invert sugar	1.0124	4.1270	0.2453	0.018	0.05
Plus 1 gram of sucrose	1.0086	4.1130	0.2452	0.009	0.04
Dextrose	1.0121	4.1138	0.2458	0.022	0.05
Levulose	1.0108	4.1362	0.2444	0.016	0.04
Maltose hydrate	0.9597	4.1932	0.2289	0.024	0.05
Lactose hydrate	0.9750	4.1593	0.2344	0.016	0.04

In Table II the values of m and log b, calculated as explained, are shown for all the sugars and sugar mixtures studied by Lane and Eynon, together with the maximum and average deviations of the calculated titer from that given in their tables.

In two of the equations the value of m is so close to unity that the formula $y = C/x$ could be used without serious error. The ratio of m to log b for invert sugar is about midway between the ratios for dextrose and levulose. With increasing quantities of sucrose added to invert sugar both m and log b decrease, m more rapidly than log b, as shown by the ratio between the two.

The agreement between the titers given in the Lane and Eynon tables and those calculated is remarkably close, the average deviations being in most instances around 0.02 ml. or less and the maximum deviations well within 0.1 ml. Larger discrepancies are found in the case of invert sugar in the presence of 10 or more grams of sucrose, titrated against 10 ml. of Fehling solution. Lane and Eynon have pointed out that the total time of boiling has a pronounced effect on the reducing power of invert sugar mixed with large amounts of sucrose. The maximum discrepancies occur usually when the titer is very high, close to 50 ml.

An interesting case is presented by lactose, titrated against 10 ml. of Fehling solution. Here the factor, C/10C, found experimentally by Lane and Eynon decreases between 15- and 30-

Table III. Invert Sugar Table for 10 Ml. of Alkaline Ferricyanide Solution, Diluted with 20 Ml. of Water

Invert Sugar	Titer: Invert Sugar Alone		Invert Sugar + 1 Gram of Sucrose		Invert Sugar + 3 Grams of Sucrose		Invert Sugar + 5 Grams of Sucrose		Invert Sugar + 10 Grams of Sucrose	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Mg.										
400	14.30	14.28	14.12	14.11	14.11	14.00	13.89	13.84	13.62	13.64
360	15.93	15.95	15.79	15.76	15.64	15.64	15.52	15.48	15.16	15.15
320	18.00	18.05	17.78	17.83	17.64	17.70	17.56	17.54	17.14	17.17
280	20.83	20.77	20.49	20.51	20.28	20.36	20.12	20.20	19.71	19.79
260	22.45	22.46	22.18	22.16	22.01	22.01	21.78	21.85	21.39	21.41
240	24.50	24.43	24.08	24.10	23.92	23.94	23.85	23.79	23.49	23.32
220	26.70	26.77	26.46	26.40	26.31	26.23	26.01	26.09	25.50	25.58
200	29.60	29.60	29.11	29.18	28.99	28.99	28.91	28.86	28.39	28.31
180	33.08	33.07	32.51	32.60	32.36	32.38	32.25	32.28	31.51	31.67
160	37.41	37.43	36.99	36.87	36.58	36.64	36.56	36.57	35.81	35.89

ml. titer, and then increases again up to 50-ml. titer. This would mean that in the lower range m is greater than unity, but in the higher range smaller than unity, and would explain the unusual discrepancies observed when the entire range is considered to have only one value for m. But it is also possible that the exception is only apparent and caused by experimental difficulties in maintaining a uniform rate of boiling and addition of sugar solution, which affects the results obtained with disaccharides more than it does with monosaccharides.

Jackson and Mathews (*2*) have called attention to the fact that the Lane and Eynon factors found by different operators or with different batches of Fehling solution may vary somewhat from those given by Lane and Eynon, and recommend that each analyst standardize his own analyses with solutions of the pure sugar. This can now be readily done by plotting two or more points on double log paper and drawing a straight line through them.

VOLUMETRIC FERRICYANIDE METHOD

In this method the concentrations of the potassium ferricyanide and potassium hydroxide were increased over those specified by Ionescu and Vargolici, in order that titers between 15 and 50 ml. of sugar solution might correspond to approximately 400 to 100 mg. of invert sugar in 100 ml. of solution, similar to the range of the Lane and Eynon method. A solution containing in 1 liter 56.000 grams each of potassium ferricyanide and potassium hydroxide answered these requirements. Of this solution, 10 ml. were transferred to a 250-ml. Erlenmeyer flask, and diluted with 20 ml. of water. The determinations were then carried out exactly as in the Lane and Eynon method, 5 drops of methylene blue indicator being added toward the end of the titration. In each case the incremental method of titration was used in the first experiment, and in the subsequent experiments almost all of the sugar solution was added at one time, and the titration completed by dropwise addition of the sugar solution. The titers were determined in this manner for solutions containing invert sugar alone, and in the presence of 1, 3, 5, and 10 grams of added sucrose in 100 ml. of solution.

It was found that the precision of the ferricyanide method is not as high as in the Lane and Eynon method. When the titer lay between 35 and 50 ml., duplicate tests often varied by 0.2 to 0.3 ml. It is therefore advisable with this reagent to keep the titer within 15 and 35 ml., as was done by Main (*5*) in his pot method with Soxhlet solution. The titers found in this range for invert solutions, containing 400 to 160 mg. of invert sugar in 100 ml., are shown in Table III.

The values of constants m and log b in Equation 1, calculated from the experimental titers in Table III, are given in Table IV, together with the ratios of m to log b and the average and maximum deviations of the calculated from the found values. The titers calculated from the equations are shown in Table III, next to the found values.

The average deviations of the found from the calculated values are slightly larger than the corresponding figures for the Lane and Eynon method, even though the titer range is only from 15 to 35 ml. The same is true of the maximum deviations except for the mixture of invert sugar with 10 grams of sucrose. It must be considered, however, that Lane and Eynon did not publish their original experimental values, and that those given in their tables are probably taken from smoothed curves. Nevertheless, the lesser precision of the ferricyanide method is indicated by the fact that neither the m nor the log b values in Table IV show a regular trend, contrary to those in the Lane and Eynon method. The ratio of m to log b, however, increases regularly with an increase in added sucrose, whereas in the Lane and Eynon method the trend is downward. On the whole, the Lane and Eynon method appears to be preferable.

Ionescu and Vargolici claim that a solution may contain as much as 30% sucrose in addition to 0.5% glucose without affecting the titer. The figures in Table III show that this is not generally true, but that sucrose does affect the reducing power of invert sugar, as in the Lane and Eynon method.

Table IV. Constants in Equation 1 for Reducing Effect of Invert Sugar upon Alkaline Ferricyanide Reagent in Absence and Presence of Sucrose

	m	log b	$\frac{m}{\log b}$	Deviation: Average	Deviation: Maximum
				Ml.	*Ml.*
Invert sugar alone	1.0520	3.8919	0.2703	0.043	0.07
Invert sugar plus 1 gram of sucrose	1.0481	3.8768	0.2704	0.049	0.12
Invert sugar plus 3 grams of sucrose	1.0497	3.8777	0.2707	0.043	0.11
Invert sugar plus 5 grams of sucrose	1.0603	3.9001	0.2718	0.049	0.08
Invert sugar plus 10 grams of sucrose	1.0639	3.9001	0.2728	0.073	0.16

SUMMARY AND CONCLUSIONS

When the titers, y, found in the determination of reducing sugar by the Lane and Eynon method, or by a similar direct volumetric determination with alkaline ferricyanide solution, are plotted against the concentrations, x, of the reducing sugar, the equation of the resulting curve is $y = bx^{-m}$, or $\log y = \log b - m \log x$, a straight-line equation in which b and m are constants. These constants have been calculated for all sugars and sugar mixtures used by Lane and Eynon, with both 10 and 25 ml. of Fehling solution, as well as for invert sugar and mixtures of invert sugar with sucrose, determined by means of an alkaline ferricyanide solution. The agreement between the titers calculated from the equations and those given in the Lane and Eynon tables is very close. The precision of the alkaline ferricyanide method is somewhat lower; best results are obtained if the titer range is kept within 15 to 35 ml. Sucrose affects the reducing power of invert sugar not only in the Lane and Eynon method, but also in the alkaline ferricyanide method.

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A System of Laboratory Evaluation

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THE increasing use of statistical methods in analytical laboratories is a recognition of the value of having a control on the analytical process, which in turn is a control on a process or material. In the presentation of methods it is now commonplace to include a statement of standard deviations or probable error. Such statistical data are of considerable value, particularly in the selection of methods for particular purposes. However, the practical value of an analytical method in industrial laboratories does not depend so much upon the inherent accuracy and precision of the method as measured in a methods investigative laboratory as it does upon the actual performance of the method in the control or plant laboratory where it is used by available personnel, under conditions which may include special requirements as regards speed, quantity, and other factors.

Many data, including standard deviations, biases, probable errors, or limits of error and precision, are based upon analytical data produced under conditions which do not include the pressure, tensions, and limitations to be noted in most modern industrial plant laboratories. It seems obvious that the best way to measure the practical effectiveness of a method is to evaluate the analytical data when the operators are not conscious that their data on a particular or specific sample will be checked.

Many schemes have been tried out to make such evaluations. The problem is specially important when several laboratories are concerned and it is desirable to have their work maintained on similar levels of efficiency. The circulation of standard samples among laboratories is of limited utility, since the samples are invariably recognized and are given special attention, thus giving little information as to the normal efficiency of the laboratory.

Many other metering or checking schemes have been used and, within limits, all yield useful data. One plan that has worked out successfully in Aluminum Company of America metal plants over a period of years is described in the following paragraphs.

Arrangements are made at each plant maintaining a laboratory to choose an individual not connected with the laboratory to select check samples. This individual goes to the laboratory and selects at random a sample which has been analyzed and reported. The sample which is selected, together with the reported analysis, is sent to the Analytical Division at Aluminum Research Laboratories.

At Aluminum Research Laboratories the sample is assigned for analysis to a chemist who is not informed of the plant laboratory results. When the analysis is completed, the results are compared with the plant results. If there is failure to agree within satisfactory limits, the chemist is told to repeat his analysis in multiple to determine data on an umpire basis. The agreement of results is judged by the permissible deviations given in Table I. The results obtained at Aluminum Research Laboratories are the basis from which permissible deviations are measured.

In considering this table it should be borne in mind that the permissible tolerances which have been set up obviously pertain to only one industry and should not be construed as necessarily or desirably applicable in the case of materials other than aluminum and aluminum alloys.

Table I. Allowable Deviations in Check Analyses Metals

Range of Content %	Allowable Deviation %	Range of Content %	Allowable Deviation %
0.00–0.03	0.01	7.01– 7.50	0.31
0.04–0.10	0.02	7.51– 8.00	0.32
0.11–0.20	0.03	8.01– 8.60	0.33
0.21–0.30	0.04	8.61– 9.20	0.34
0.31–0.40	0.05	9.21– 9.80	0.35
0.41–0.55	0.06	9.81– 10.40	0.36
0.56–0.70	0.07	10.41– 11.00	0.37
0.71–0.85	0.08	11.01– 11.60	0.38
0.86–1.00	0.09	11.61– 12.20	0.39
1.01–1.15	0.10	12.21– 12.80	0.40
1.16–1.30	0.11	12.81– 13.40	0.41
1.31–1.45	0.12	13.41– 14.00	0.42
1.46–1.60	0.13	14.01– 14.75	0.43
1.61–1.80	0.14	14.76– 15.50	0.44
1.81–2.00	0.15	15.51– 16.25	0.45
2.01–2.20	0.16	16.26– 17.00	0.46
2.21–2.40	0.17	17.01– 17.75	0.47
2.41–2.60	0.18	17.76– 18.50	0.48
2.61–2.80	0.19	18.51– 19.25	0.49
2.81–3.00	0.20	19.26– 20.00	0.50
3.01–3.30	0.21		
3.31–3.60	0.22		
3.61–4.00	0.23	And thereafter increasing at	
4.01–4.40	0.24	the rate of 0.01% for each	
4.41–4.80	0.25	additional 1.0% of constit-	
4.81–5.20	0.26	uent, reaching 1.00% at	
5.21–5.60	0.27	70%, and thereafter re-	
5.61–6.00	0.28	maining constant	
6.01–6.50	0.29		
6.51–7.00	0.30	70.00–100.00	1.00

The laboratories are scored in accordance with the percentage of agreements. The allowable deviations were originally set up on more or less an arbitrary basis, but have evolved to their present levels by adjustments based upon the actual records made by laboratories. In general, all permitted deviations are smaller today than when the table was set up more than 20 years ago. The deviations shown are those permitted between a laboratory working under the pressure of plant production and a central laboratory working in the absence of production pressure. The table, however, is used in other ways. If in a given laboratory the work of one analyst under plant conditions is checked by another analyst in the same laboratory, the allowable deviations given in the table are to be divided by 1.5. For duplicate results by the same analyst, the allowable deviations in the table are divided by 2.5.

In Table II a typical tabulation of check results for a 6-month period is shown. Because of the nature of the determinations made, the laboratories are listed in two groups.

Table II. Laboratory Check Analyses

(6-month period)

Laboratory	Determinations	Outside Limits	Percentage Agreement
	Class R Plants		
A	50	0	100.0
B	50	0	100.0
C	47	0	100.0
D	46	0	100.0
E	28	0	100.0
F	51	1	98.0
G	33	1	97.0
	Class FC Plants		
H	272	0	100.0
I	211	0	100.0
J	198	0	100.0
K	212	1	99.5
L	183	1	99.5
M	251	2	99.2
N	115	1	99.1
O	180	2	98.9
P	168	2	98.8
Q	166	2	98.8
R	155	2	98.7
S	148	2	98.6
T	133	2	98.5
U	199	4	98.0
V	255	10	96.1
W	198	11	94.4
X	105	8	92.4
	3454	52	98.5

The determinations checked cover the ordinary impurities and alloying elements met in current metal production. Laboratories V and W are special cases with somewhat more difficult work than that carried out in other laboratories.

The checking system described affords a ready means of comparing the effectiveness of laboratories doing the same type of work. Investigation of failures to check often reveals weaknesses of methods, faulty application of methods, inadequate personnel, or other curable troubles. The main value of the system is that it reveals on a comparative basis the quality of work done in the laboratories.

Anomalous Behavior of Methyl 12-Hydroxy-9,10-Octadecenoates in Rapid Iodine Number Determinations

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The methyl esters of ricinoleic, ricinelaidic, and O-propionylricinoleic acids quantitatively add iodine chloride from Wijs reagent in less than 1 minute. However, if mercuric acetate is present, methyl ricinoleate and ricinelaidate react with additional halogen, thus giving high iodine values, whereas the methyl O-propionylricinoleate behaves normally. This anomalous effect is due to the presence of the free hydroxyl group.

THE use of mercuric acetate catalyst to speed the rate of addition of Wijs reagent to nonconjugated, unsaturated double bonds constituted a decided improvement in the iodine number technique by allowing the attainment of quantitative addition in less than 3 minutes (*2*), in contrast to the standard method for the determination of iodine value (*1*) which requires 30 to 60 minutes. Norris and Buswell (*4*) found that Hanus reagent with mercuric acetate was even more satisfactory than the Wijs reagent for the determination of nonconjugated unsaturation.

Table I. Rate of Reaction with Wijs and Bromine Reagents
(Without Mercuric Acetate)

Time, Min.	Halogen Equivalent[a]	Iodine Value
A. 0.02568 *M* Methyl Ricinoleate, 0.06861 *M* Wijs		
1.0	1.998	81.16
20.0	2.016	81.89
30.0	2.021	82.07
B. 0.02411 *M* Methyl Ricinelaidate, 0.06861 *M* Wijs		
1.0	2.006	81.50
3.0	2.005	81.45
11.0	2.009	81.60
30.0	2.006	81.50
30.0	2.004	81.40
60.0	2.009	81.60
C. 0.02568 *M* Methyl Ricinoleate, 0.07449 *M* Bromine		
1.0	2.030	82.44
1.0	2.035	82.67
10.0	2.021	82.07
20.0	2.024	82.21

[a] Halogen equivalent is number of atoms of halogen absorbed per mole of compound.

These authors noted, however, that, although castor oil yielded the expected iodine number of 84.0 with the usual Hanus reagent, the addition of mercuric acetate resulted in an iodine number of 90.7. They attributed this anomaly to ricinoleic glycerides, since a similar result was obtained with petroleum ether–extracted castor oil acids.

In connection with other work, the authors had prepared pure methyl esters of ricinoleic and ricinelaidic acids (the *cis* and *trans* isomers of 12-hydroxy-9,10-octadecenoic acid), and had independently observed an analogous effect while determining their iodine numbers by the Wijs mercuric acetate technique. They further observed that Wijs reagent alone adds quantitatively to methyl ricinoleate and methyl ricinelaidate. Despite the absence of mercuric acetate catalyst, the reaction occurred with surprising speed, being essentially complete in less than 1 minute. To determine whether Wijs reagent was unique in its ability to add rapidly to these unsaturated compounds, a standard solution of bromine in glacial acetic acid (*5*) was also tested. It was found to react with equivalent speed.

In Table I, data are given which indicate the rate of reaction of methyl ricinoleate and methyl ricinelaidate with Wijs and bromine reagents. Aliquot portions from a standard solution of each of the esters in glacial acetic acid were used to obtain samples of equal weight. The molar concentration listed in the tables are the values calculated for the solutions obtained by mixing the reagents.

To determine the effect of mercuric acetate on the course of the reaction, the halogenating agent was mixed with the esters and the mixture then treated with mercuric acetate solution. The time was recorded from the addition of the latter. Examination of the data from these experiments (see Table II) demonstrates that the addition of mercuric acetate to solutions of dihalogenated ricinoleates or ricinelaidates in Wijs or bromine in acetic acid solutions results in a further utilization of the excess free halogen present.

Since the ricinoleates and ricinelaidates differ from the normal unsaturated fatty acids only by the possession of the 12-hydroxyl group, it is reasonable to conclude that the further utilization of halogens in the presence of mercuric acetate takes place at the hydroxyl group, probably involving an oxidation of the secondary alcohol group, or a substitution activated by the hydroxyl group.

In another series of experiments, three samples of methyl ricinoleate were allowed to react with Wijs solution for 30 minutes. One of the samples was titrated, and the iodine value was determined to be 82.1. To the other two samples, mercuric acetate was added, and at the end of 3 more minutes, the iodine value had risen to 88.8, and finally after 15 minutes, to 100.4.

Table II. Effect of 0.0147 *M* Mercuric Acetate on Iodine Values

Time, Min.	Halogen Equivalent	Iodine Value
A. 0.01968 *M* Methyl Ricinoleate, 0.05257 *M* Wijs		
1.0	2.054	83.44
3.0	2.188	88.91
3.0	2.187	88.82
9.0	2.368	96.21
15.0	2.470	100.31
15.0	2.473	100.45
B. 0.01847 *M* Methyl Ricinelaidate, 0.05257 *M* Wijs		
1.0	2.051	83.30
3.0	2.116	85.97
10.0	2.193	89.08
15.0	2.206	89.61
C. 0.01968 *M* Methyl Ricinoleate, 0.05644 *M* Bromine		
1.0	2.032	82.53
3.0	2.071	84.12
10.0	2.123	86.22
20.0	2.172	88.23
60.0	2.318	94.16
D. 0.02991 *M* Methyl *O*-Propionylricinoleate, 0.05246 *M* Wijs		
1.0	1.989	68.52
3.0	1.983	68.29
15.0	1.993	68.65

To prove conclusively that the excessive utilization of the halogen reagents was due to the free hydroxyl group, methyl *O*-propionylricinoleate was prepared and examined as above. The behavior of this ester was entirely normal as shown in Table II, thus demonstrating that the anomalous behavior of the ricinoleate and ricinelaidate is due to its free hydroxyl group.

From a practical point of view, the results of Wijs mercuric

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acetate iodine number determinations should be critically examined if the presence of free hydroxyl groups is suspected.

EXPERIMENTAL

PREPARATION OF METHYL RICINOLEATE (*3*). Castor oil was converted to castor oil methyl esters by saponification, isolation of the acids, and esterification with 2 to 4% sulfuric acid in absolute methanol. The esters (650 grams) were fractionally distilled through a 60-cm. (24-inch) Vigreux column, and methyl ricinoleate was collected at 157° to 158° C. at 1-mm. pressure. The yield was 474 grams of material having the following constants: n_D^{30} = 1.4596, iodine value, 82.0 (theory, 81.2).

PREPARATION OF METHYL RICINELAIDATE (*3*). From 2000 grams of castor oil, 530 grams of crude ricinelaidic acid were obtained by elaidinization of the acids with oxides of nitrogen (*3*). The acids were converted to the methyl esters by refluxing with 2 to 4% sulfuric acid in absolute methanol and separated from nonvolatile material by distillation from a Claisen flask at 1-mm. pressure. There was obtained 465 grams of impure product. This was then fractionally distilled as above, and the main fraction collected, b.p. 181° at 2 mm., and recrystallized twice from a mixture of Skellysolve F and diethyl ether. The yield was 290 grams of pure methyl ricinelaidate, m.p. 30° to 31° C., n_D^{30} = 1.4582, iodine value, 81.5 (theory, 81.2).

PREPARATION OF METHYL *O*-PROPIONYLRICINOLEATE (*6*). Castor oil methyl esters, prepared as above, were heated rapidly and briefly to 180° C. with two-thirds their weight of propionic anhydride. The mixture was fractionally distilled to obtain the pure ester which had the following constants: b.p. 186° at 1 mm., n_D^{30} = 1.4510, saponification equivalent, 185.6 (theory, 184.3), acid value, 0.0, and iodine value, 68.5 (theory, 68.9).

PROCEDURE. Automatic pipets were used to obtain aliquots of all standard solutions. An aliquot portion (10.96 ml.) of the compound and 24.98 ml. of the halogen reagent were mixed and allowed to react for the stated time interval, and the excess reagent was then titrated to obtain the results given in Table I. To determine the effect of mercuric acetate shown in Table II, the ester and halogen reagent were mixed, and immediately treated with 10.0 ml. of 2.5% mercuric acetate in glacial acetic acid, and allowed to react for the intervals recorded, beginning with the addition of mercuric acetate. Blank experiments, without the presence of the unsaturated compound, were performed in all the series to eliminate corrections necessitated by the presence of small amounts of oxidizable materials in the mercuric acetate solution.

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Improved Device for Decomposition of Grease

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IN THE laboratories of the Rock Island Arsenal, where the number of grease samples to be analyzed and the time available are determining factors, the standard method of the American Society for Testing Materials (*1*) for decomposing the soap in the grease was too time-consuming when a 30-gram sample was used, the time varying from 20 minutes with a light grease to 2 hours with some of the heavier greases. This method of soap decomposition consists essentially of shaking 8 to 30 grams of the sample, depending on the consistency of the grease, in a separatory funnel at room temperature with petroleum ether and 10% hydrochloric acid.

Since the "boiling method" is used in many grease testing laboratories, its suitability for the Arsenal needs was looked into. Briefly, this method consists in placing about 30 grams of grease in a 400-ml. beaker, adding about 200 ml. of 10% hydrochloric acid solution, and then heating the mixture to the boiling point of the hydrochloric acid solution to accelerate the decomposition. It was found that the time required to break down the grease could be reduced to from 5 to 10 minutes for the average grade to 20 minutes for the heavier grades. This method does not require the undivided attention of the analyst; however, unless the mixture is constantly stirred, steam has a tendency to build up pressure beneath the floating grease layer. In the case of the heavier grades of greases especially, this steam pressure may cause violent bumping with subsequent loss of material due to splattering.

To overcome this, several procedures were tried but only two proved effective. The first, which was very effective but cumbersome, consists in placing a slow-speed motor on a rack over the hot plate and stirring the mixture as it boils. The second procedure is the percolator method.

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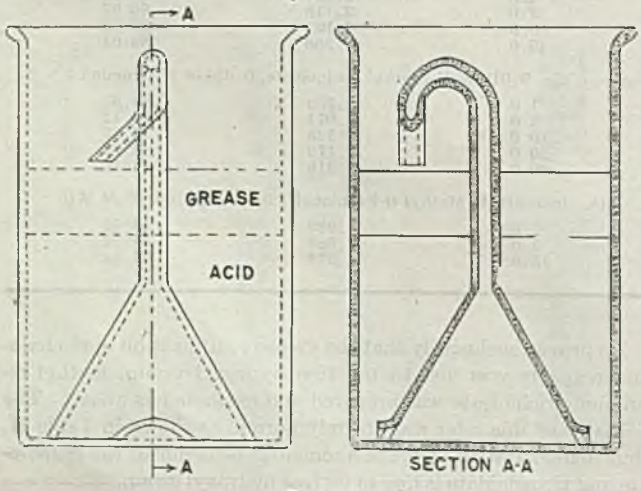

Figure 1

When the grease percolator, as shown in Figure 1, is placed in the beaker with the grease sample and the hydrochloric acid solution, the steam is provided with an outlet, thereby preventing excessive bumping due to the pressure buildup. The percolator serves a twofold purpose. Primarily, it serves to prevent violent bumping with its subsequent loss of sample and, secondly, it is used to agitate the grease, thus accelerating the decomposition by exposing more surface to the acid solution. This secondary effect is accomplished by means of the twist in the steam tube (see diagram). When the mixture reaches the boiling point of the hydrochloric acid solution, steam and hydrochloric acid solution "boil up" through the percolator out of the tube and are forced back into the surface of the grease layer by their own pressure. By placing the exit tube at an angle, the steam and hydrochloric acid solution which spurt out with some force tend to agitate the grease layer, causing it to revolve on the surface of the hydrochloric acid solution.

The percolator can be readily made in the laboratory from an ordinary 2.5-inch diameter 60-degree angle soft-glass funnel. Two or more venting grooves are bent in the lip of the funnel. The stem is then bent in the manner shown by the diagram.

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Distillation Trap for Determining Moisture in Relatively Dry Materials

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A COMMON method for rapid determination of moisture is distillation of the material with a solvent immiscible with water and collection of the water in a suitable trap where its volume may be measured. Several types of distillation traps are described in the literature (*1, 3–10, 12*), the earliest being that of Bidwell and Sterling. These traps have been designed to use solvents with densities both heavier and lighter than water. Liquids heavier than water have several advantages, other than their usual nonflammability. Since most samples float on the heavy solvent, scorching on the bottom of the flask and excessive bumping are eliminated. The vapor and condensate are at all times in the path of continuous flow, with no stagnant pockets in the condensed solvent or water where individual droplets form and remain isolated.

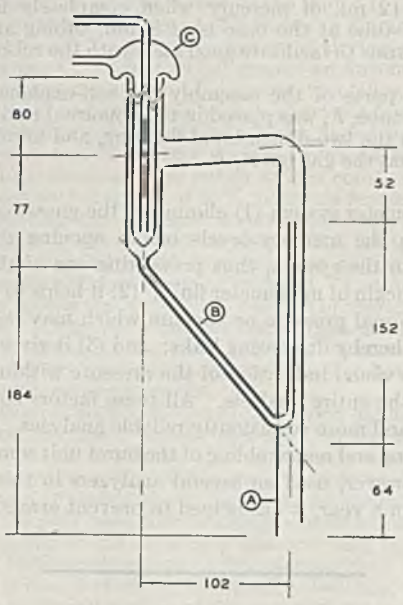

Figure 1. Diagram of Trap

Dimensions in mm.

The usual trap is graduated in 0.1 ml., and the volume of water collected may be estimated to 0.01 or 0.02 ml. For products of low moisture content, a large sample must be taken to obtain the usual 5 or 10 ml. of water. Many products are too bulky for an adequate sample weight, and in many instances only small quantities are available for analysis. For these reasons a trap designed particularly for small amounts of moisture has been desired. Attempts to modify existing heavy solvent traps by decreasing the diameter of the usual graduated tube to secure smaller unit volumes were not satisfactory because the solvent did not fall dropwise through the water layer, and the water was swept out of the trap. As a result, a new type of tilt trap (Figure 1) using a heavy solvent was designed to allow precise measurement of small volumes of water.

DESCRIPTION OF TRAP

Tube *A* (17 mm. in diameter) is connected to the boiling flask with a cork or ground-glass joint. Vapors from the boiling flask pass through *A* into the 25-mm. diameter section of the trap containing an immersion condenser, *C*, the shoulder of which rests loosely on the top of the trap, and positions the tip of the condenser near the graduated arm, *B*. It is important that the condenser be immersed in the condensed water and solvent. *B* was made of a 1-ml. Pyrex pipet with 0.01-ml. divisions. The portion of the return line inside tube *A* was made of 6-mm. tubing. The height of the open end of this tube was adjusted to cause the condensed water layer to remain in the 25-mm. diameter tube above the constricted section. When the trap is tilted to bring *B* into a vertical position, the water layer falls into this graduated tube, where the water volume can be read directly to 0.01 ml. and estimated to 0.001 ml. As the zero graduation mark will not necessarily coincide with a meniscus, the volume is determined by taking the difference between the meniscus readings. The trap was designed for use with perchloroethylene $\left(d = 1.63\frac{15}{4}\right)$; other solvents may be used if their density is near that of perchloroethylene.

OPERATION OF TRAP

The sample is weighed into a 250-ml. boiling flask containing 150 ml. of perchloroethylene, the trap is connected, and cold water is circulated through the condenser. It is important to fill the return line of the trap with solvent before distillation starts, in order to prevent water from entering the small diameter tubing. The content of the flask is quickly brought to boiling, and maintained at a vigorous boil. It is necessary to have a large flow of condensed solvent through the return line. If the flow is small, the solvent in the portion of the return line inside tube *A* may boil and the water layer may fall into the return line and completely upset the correct operation of the trap.

Small droplets that sometimes remain on the condenser and glass surface of the trap at the completion of the distillation will unite with the condensed liquids if the condenser is lifted and touched with a small rod (1 mm. in diameter) wetted with Tergitol 4 or 7. An excess of wetting agent will make it difficult to read the meniscus between the solvent and water, because of formation of a cloudy layer. When the condenser is replaced and the contents of the trap are gently swished, the glass surfaces will drain. Since the condenser maintains the water layer and condensed solvent near room temperature, the water volume may be read as soon as boiling has ceased, thereby shortening by several minutes the total time of the determination.

The trap was tested for water recovery by placing 0.50 ml. of water in the boiling flask with 150 ml. of perchloroethylene and boiling for 30 minutes. The water recovery was 0.48 ml. Cause for the discrepancy of 0.02 ml. was not determined, but is probably water held on the surfaces of the trap and condenser. When determining the moisture content of a foodstuff, the incomplete recovery of water may be neglected, because decomposition of the sample at the high temperature of the boiling solvent requires an arbitrary adjustment of the total distillation time to produce agreement between the distillation method and a reference method. For whole egg powder, with perchloroethylene as the solvent, a distillation time of 25 minutes was found to give results comparable to those obtained by the A.O.A.C. (*2*) and the faster high-vacuum methods (*11*).

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Manometric System for Volumetric Gas Analyzers

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THE use of nonscientific personnel in operation of the so-called precision model volumetric gas analyzer has presented many difficulties in this laboratory, which has to analyze several hundred gas samples a week. The two most troublesome are blowing out or sucking in of manometer fluid by the operator, and the development of a leak in the middle of an analysis.

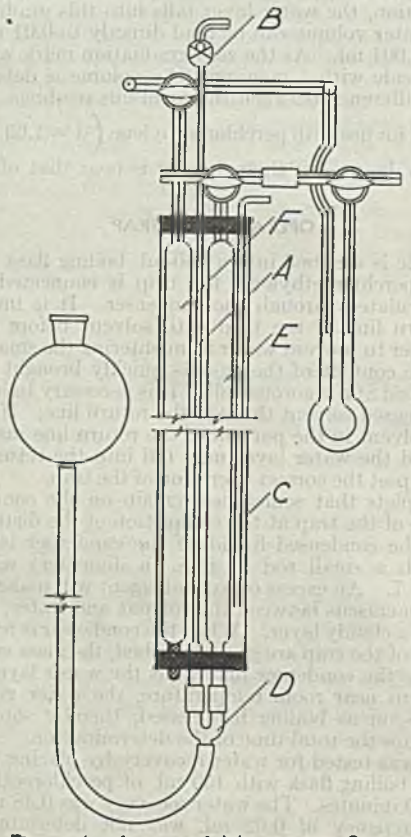

Figure 1. Improved Manometric System as Installed in a Regular Gas-Measuring Unit

The first difficulty is frequent with beginners but occasionally happens during fast operation to the most experienced gas analyst. With standard apparatus this is usually due to difficulty in obtaining accurate equalization of the mercury levels in the leveling bulb and the gas buret, particularly in the lower portions of the system, or failure to close the manometer stopcock before starting the flow of gas. The second difficulty is usually due to excess positive or negative pressure in the system.

These difficulties and the time lost in dismantling, cleaning, and reassembling apparatus, refilling the manometer, and repeating analyses, prompted the design of the system described below.

Nearly all commercial models of volumetric gas analyzers contain one ordinary U-type manometer with one arm attached to the compensating tube and the other to the manifold or to the buret itself. The system described here consists of two manometers, one for rough preliminary equalizing of the gas pressure and the second for sensitive and accurate final pressure balance. For the latter, the manometer contained in the original apparatus serves very well when filled with a slightly acidified aqueous solution.

For the first manometer, a design was worked out which roughly equalizes the gas pressure before opening the sensitive manometer to the system, gives a continuous visual indication of the pressure within the system, and compensates partially any abnormal pressure or vacuum developed in the system during the analysis. This manometer is built into the water jacket and makes use of the gas buret for one arm of the U. The other arm is a small-diameter glass tube which connects to the gas buret at the base by means of a small glass Y.

The system is shown in Figure 1 as it was built into the regular buret manometer-compensator assembly.

The left arm, *A*, of the built-in manometer is constructed of 6- and 8-mm. tubing, the base being 8-mm. tubing to correspond with the gas buret outlet. The main body of the arm is of 6-mm. tubing and has a small ground-glass, ball check valve, *B*, sealed to the top. The over-all length of this tube for a 77.5-cm. (31-inch) water jacket, *C*, is 100 cm. (40 inches) and it contains approximately 12 ml. of mercury when completely filled. The connecting Y-tube at the base is of 8-mm. tubing and has 2.5-cm. (1-inch) arms to facilitate good seals with the rubber connecting tubing.

The other parts of the assembly are self-explanatory. The compensator tube, *F*, was placed in the abnormal position shown, for clarity on the two-dimensional drawing, and normally occurs directly behind the gas buret, *E*.

This manometer system (1) eliminates the guesswork involved in equalizing the mercury levels before opening the sensitive manometer to the system, thus preventing one of the causes of blowout or suckin of manometer fluid; (2) it helps to compensate for any abnormal pressure or vacuum which may be exerted on the system, thereby decreasing leaks; and (3) it gives the analyst a continuous visual indication of the pressure within the system throughout the entire analysis. All these factors contribute toward faster and more consistently reliable analyses. The system makes cleaning and reassembling of the buret unit somewhat more difficult; however, used on several analyzers in this laboratory for more than a year, it has helped to prevent errors.

Lubricant Reservoir for Stirrer Shaft

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IN ORDER to avoid liquid-sealed stirrers, the author has been using stirrers of the type described by Fieser (*1*). The stirrer bearing is equipped with a 2-cm. section of rubber tubing which projects above the end of the bearing and makes a tight fit on the stirrer shaft. This rubber bearing requires frequent lubrication to prevent heating and consequent impairment of the seal.

A very satisfactory lubricant reservoir can be made by cutting off the closed end of a medicine dropper bulb and fitting the decapitated bulb over the rubber bearing. This device has been found serviceable over long periods of time, requiring only a few drops of glycerol or heavy mineral oil once a day.

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Experimental Dryer for Pre-Pilot Plant Studies

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IN DESIGNING pilot-plant equipment with which to study the factors involved in large-scale processing of various products developed in the laboratory, experimental drying apparatus is frequently needed capable of determining the drying characteristics of different materials under widely varying conditions and of yielding data translatable to larger scale operations. Such a machine should require a small quantity of material.

In recent years, drying techniques have been aimed at achieving the most rapid rate of drying possible without introducing deleterious effects on the product and consistent with the most economical methods for handling the material. This has been accomplished in many cases by employing a through-air circulation method of drying, by which heated air is forced at high velocity through a porous bed of the material supported on a perforated-metal or screen surface. An experimental unit which meets these requirements is here described.

EQUIPMENT

Figure 1 shows a general layout of the unit. It consists essentially of a centrifugal blower, *A*, 7.5 inches in diameter with a V-belt drive from a 0.5-horsepower motor; a drying cabinet, *B;* a torsion balance, *C*, reading to 0.2 gram; an automatic wet and dry-bulb recorder-controller, *D*, having throttling control and automatic reset and equipped with a chart reading to 300° F.; an air-conditioning cabinet having a 2-row finned-tube steam coil with 39 square feet of heating surface; plus ductwork, control valves, and accessories. The entire unit is constructed of sheet metal covered with 2 inches of 85% magnesia insulation.

For supporting the material several stainless steel pans are provided, each 1 square foot in area. The bottoms are constructed of perforated metal or wire screen having apertures of various sizes for different kinds of material. Pan inserts are also provided to reduce the area of the bottom or increase the height of the walls. Nichrome wires suspended from an aluminum rod and clamped to the drying pan at its four corners pass through the roof of the drying cabinet (Figure 2). The holes in the roof are sealed with rubber stoppers.

The inside cross-sectional area of the drying cabinet is 4 square feet and the distance from the pan shelf to the roof is 2 feet. Thus when the air enters the drying cabinet, its velocity is reduced to a very low value. When the pan is elevated by the wires approximately 10 inches above the shelf and suspended from the balance on the roof, accurate weighings can be made very rapidly without shutting off the air supply and upsetting the control conditions. A further advantage of this plenum chamber above the drying pan is that it produces uniformity of air flow through the 1 square foot of drying surface of the pan without baffles or vanes.

Starting at the blower, the air flows through the upper duct to the drying cabinet. At location 1, Figure 1, is a manually operated volume-control damper, by means of which the total flow of air is regulated. The air next passes through an orifice nozzle, 2. Centrally located in the nozzle is a Pitot tube, which is connected to the upper inclined manometer on the cabinet and gives a reading of velocity head in inches of water; from this and from the temperature the volume-flow of the air is calculated. The air now enters the drying cabinet and passes down through the material in the pan. The pan rests on a shelf which forms an orifice in the drying cabinet. Static pressure openings above and below the shelf and connected to the lower inclined manometer indicate the loss in pressure as the air passes through the material and the pan. This information is vital to the design of a blower for larger equipment.

Mounted just above and behind the drying pan are the dry and wet bulbs of the air-operated temperature recorder-controller (Figure 2), by which the temperature and humidity of the air blowing on the wet material are controlled. A slight error in the wet-bulb temperature of the drying air is introduced here, since the evaporation from the wick is included in the air passing through the pan. Also entering the drying cabinet just above the pan is an iron-constantan thermocouple, connected to a potentiometer. The thermocouple lead wires are coiled, so that when the point is injected into the wet material, the pan can be raised and lowered for weighing and the additional tare due to the thermocouple will be practically constant.

As the air leaves the bottom of the pan, it passes over the sensitive portion of an industrial thermometer and then enters the return duct. Here the amount of spent air vented at 4 is automatically controlled by damper, 3, operated by a diaphragm motor which functions from the wet bulb of the controller. An equal amount of fresh air enters at 5. The recirculated air plus the fresh air then enters the conditioning cabinet.

In the conditioning cabinet the air first passes through the steam heater. The supply of steam is automatically controlled by a diaphragm valve which functions from the dry bulb of the instrument. If necessary, the heated air is then humidified by spraying steam or a fine mist of water through nozzles facing against the path of air flow. The quantity sprayed is automatically controlled by a diaphragm valve which functions from the wet bulb of the instrument. Either water or steam can be supplied to the humidifying control valve, the choice being determined by the wet-bulb temperature required.

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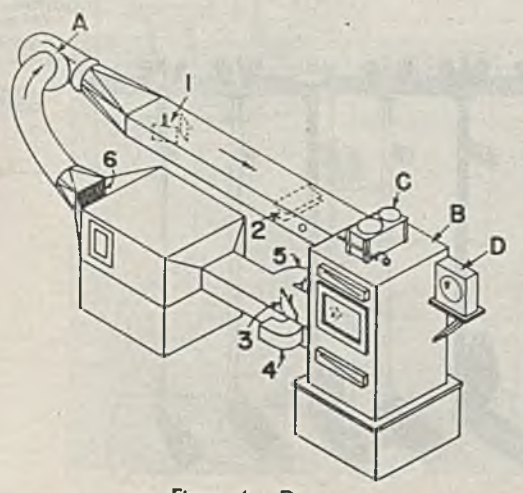


Figure 1. Dryer

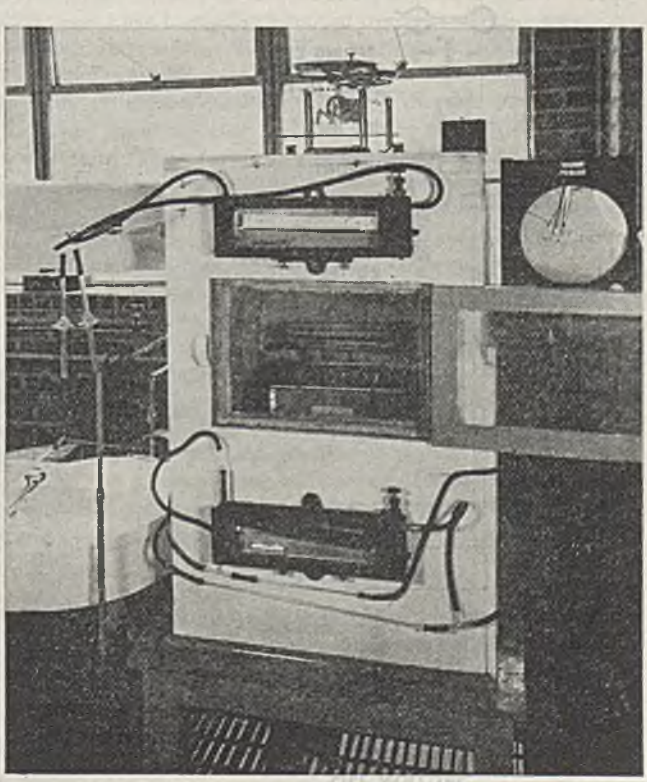
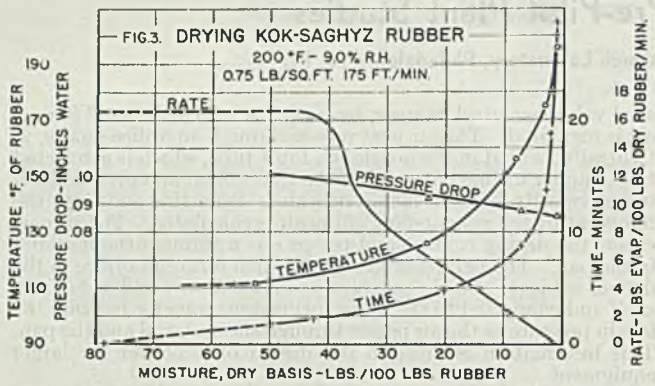


Figure 2



The conditioned air finally passes through a copper diffusing screen, 6, which eliminates any droplets of water. If the humidifying nozzles were located in the duct leading to the heater, the diffusing screen would be unnecessary. The air now returns to the blower for another cycle.

EXAMPLE OF USE

The utility of such an experimental dryer was demonstrated during the development of a pilot-plant process for extracting rubber from the Russian dandelion.

The purified rubber as extracted from the root was in the form of small discrete particles which floated in water. This material was first dewatered on a centrifuge, then spread into a drying pan having a perforated metal bottom. Studies were made to determine the optimum air temperature, velocity, depth of loading, etc. Samples from each test were checked by compounding the rubber and subjecting it to physical tests. The type of drying data obtained from a single test is illustrated in Figure 3. Air at 200° F. and 9% relative humidity was circulated at a rate of 175 c.f.m. per square foot of pan area; the tray was loaded with 0.75 pound (dry weight) of rubber per square foot.

It was demonstrated that such a heat-sensitive material could be dried very rapidly at an elevated temperature with better results and more economically than by a conventional method for drying rubber, such as vacuum drying. The data obtained made possible the operation of a pilot-plant dryer under conditions which yielded the best quality of dried rubber.

Pycnometer Holder

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SINCE the publication by Lipkin, Davison, Harvey, and Kurtz (*1*) of a new design of pycnometer especially suited to the precise determination of the densities of volatile liquids, routine use of this instrument has indicated the need for a multiple holder assembly with which to support two or more pycnometers at one time in a glass jar thermostat. A simple and satisfactory type of holder which has been in use in this laboratory for several years is illustrated and described herewith.

Figure 1 shows the structural details of the holder proper.

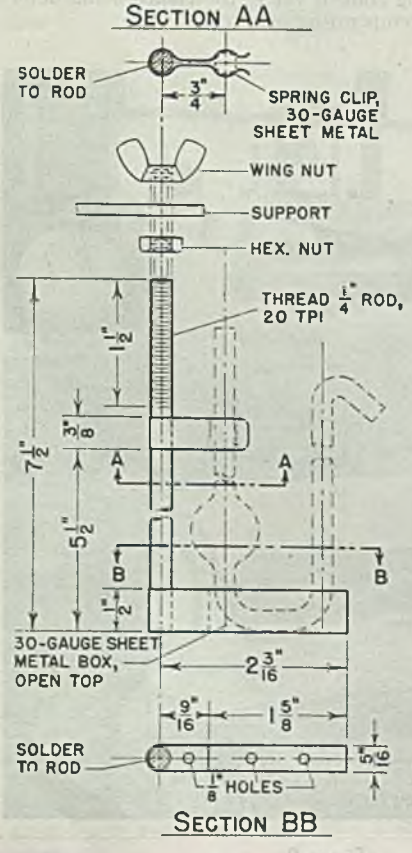

Figure 1. Pycnometer Holder Detail

It may be made of brass or any other available metal which can be hard- or soft-soldered and will not corrode in the thermostat liquid.

Figure 2 illustrates a convenient mounting for suspending the holders in the thermostat. It consists of a brass bar 0.125 inch thick, 1 inch wide, and 12 inches long with seven $^{9}/_{32}$ inch holes drilled 1.5 inches apart to accommodate the threaded ends of the holders. Two nuts support each holder and permit regulation of the depth of immersion of the pycnometers. A total of six holders with pycnometers may be conveniently suspended in a 12-inch diameter jar with this mounting. The ends of the mounting as illustrated are drilled to fit over posts clamped to the sides of the thermostat. However, the posts need not be used, the bar simply being allowed to rest on the edges of the jar. Individual mountings for each holder which can be hooked or clamped to the edge of the jar may be used if desired.

Wing nuts provide a convenient means for rotating the holders to the best position for reading the levels of the menisci. Pycnometers may be placed in or removed from the thermostat without removing the assembly from the bath or disturbing other pycnometers mounted in it.

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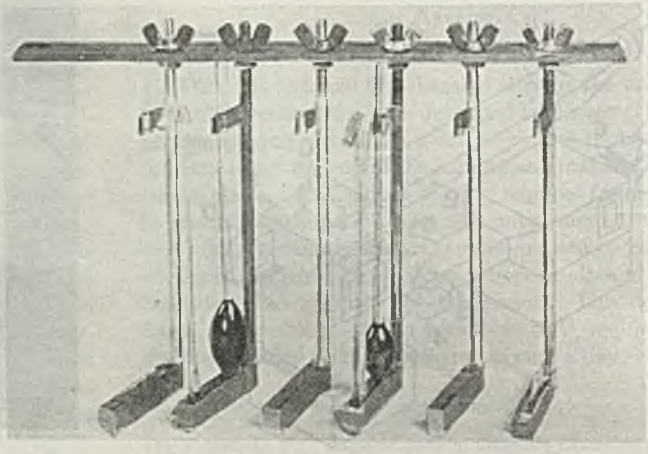

Figure 2. Multiple Holder Assembly

A Combination Glass Soxhlet Extractor and Vapor Degreaser for General Laboratory Use

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IN CONNECTION with investigations of certain types of insulating materials, such as capacitor dielectrics (impregnated paper, mica, ceramics, and plastics), extraction procedures and suitable techniques for proper cleansing of instruments and test specimens are of basic importance. The usual type of glass Soxhlet extractor and various modifications (the literature is voluminous in this connection), including metal and earthenware types designed particularly for use in biochemical and nutrition laboratories (*1*, *2*, *3*), have this in common, that the condenser is made the top (cover) section of the extraction compartment or is adapted to it. This necessitates removal of the condenser when introducing and withdrawing the parts to be treated. Frequently, operations of the sort referred to above must be performed with dispatch, requiring minimum manipulation. Furthermore, it is often desirable to treat instruments and complete or partial test assemblies whose geometric shapes, particularly as regards their length, are such that commercially available equipment will not accommodate them.

To overcome these limitations a combination extractor and degreaser has been designed and constructed in which the water condensers are integral with the liquid (extraction) and vapor (degreasing) compartments, so that there is direct access to these compartments without manipulation of the apparatus.

As shown in Figure 1, the apparatus consists of two parts: a solvent container (flask) and an extractor and degreaser unit, both of Pyrex. The flask is fitted with a female section of a $\frac{45}{50}$ T ground-glass joint. The male section of this joint is attached to the lower end of the extractor and degreaser unit. Vapor ducts leading from the flask to the extraction and degreaser unit, as well as the degreaser compartment itself, are wrapped with asbestos tape to reduce condensation on the walls of these components. Approximate over-all dimensions of the apparatus are 62.5 cm. (25 inches) high × 20 cm. (8 inches) wide × 16.25 cm. (6.5 inches) deep. The flask is charged with a volume (1200 cc.) of solvent approximately three times the minimum required to operate the extractor. The heating is controlled to provide distillation at a mild rate. Under these conditions the data in Table I have been obtained on the rate of solvent loss by evaporation.

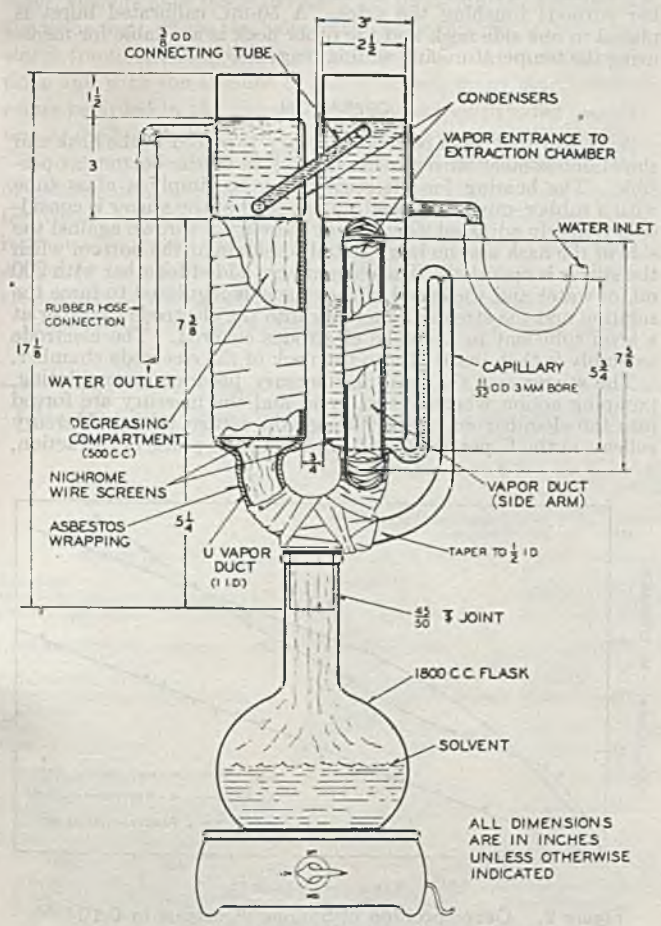

Figure 1. Soxhlet Extractor and Vapor Degreaser

Table I. Performance of Apparatus

Solvent	Rate of Evaporation Loss *Cc./hour*	Extraction Cycle *Min.*
Benzene	5	45
Acetone	10	40
Ether	24	25
Trichloroethylene (Permachlor)	2	60

Some reduction in the consumption rate may be effected by providing caps for the tops of the compartments. However, experience has shown that without caps the loss in most cases is sufficiently low, so that the equipment is well adapted to protracted extraction treatments. Virtually all the vapor condenses on the lower third of the condenser surface. Additional solvent may be introduced through the degreaser compartment to replace solvent lost during operation. Because of the open-top feature, the equipment should be located under a hood or where the escaping vapor can be readily removed from the working area.

Without interrupting the boiling and condensation of the solvent, samples to be treated are inserted and withdrawn through the wide cylindrical mouth at the top of each compartment. The vapor phase chamber is distinct from the liquid extraction compartment, thus permitting vapor cleansing of laboratory appliances without contaminating test specimens in the extraction section. Thorough cleansing is often expedited by subjecting the work to a short treatment in the liquid phase followed by a dip in the vapor to remove last traces of contamination.

Because of its flexibility, this apparatus has served well as a general laboratory utility. The equipment may be constructed of metal or part metal, part glass. (In a modification of the all-glass unit the condensers have been constructed of metal in such a manner that the cooling liquid is in direct contact with the glass surface of the compartments. These condenser shells are firmly secured in proper position on the extraction and degreasing columns.) A proportionate increase or decrease in the dimensions of the component parts (with the exception of the capillary) should provide a unit which will satisfy specific requuirements.

ACKNOWLEDGMENT

The author wishes to acknowledge suggestions as to design details given by H. W. Weinhart, his colleague at these laboratories, who also supervised the construction of the apparatus.

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Reaction Vessel for Maintaining Constant pH by Continuous Electrometric Titration during Sodium Amalgam Reductions

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A NUMBER of chemical reactions occur at definite optimum pH but liberate substances which alter the pH. In order to maintain the desired pH it is therefore necessary to add controlled amounts of acid or base to the system during the course of the reaction. Such control has been accomplished by use of indicators, buffers, or electrometric instruments. The first method is not practical where the reaction medium is turbid or colored, or the pH of the solution is changing rapidly; the second is limited by questions of buffer capacity and the isolation of the product.

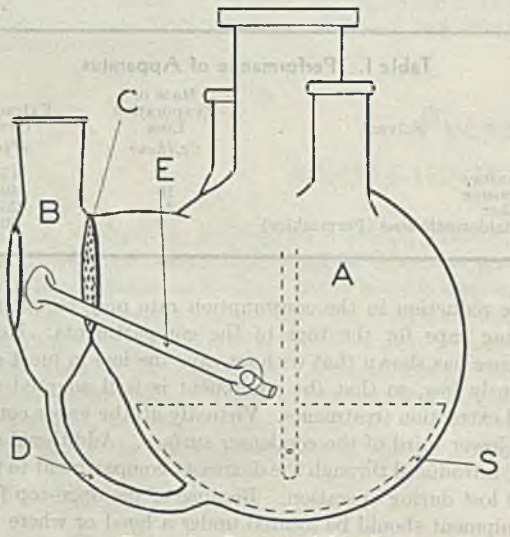

Figure 1. Reaction Vessel

Electrometric control can be maintained in large-scale reactions by the use of automatic potentiometric equipment. On a smaller scale it is possible to use an external centrifugal pump and electrode chamber with manual control of the addition of acid or base required to hold the pH constant, but this system requires fairly large volumes of liquid and may result in corrosion in the pump chamber. A number of micro and semimicro control techniques have been devised, but these methods are not readily adapted to the usual laboratory preparation (*1*).

A simple, all-glass vessel is needed to accomplish this purpose without the use of external circulating pumps and expensive automatic control instruments—i.e., one suited for laboratory use. The authors have devised such a vessel for use in studies of the sodium amalgam reduction of aldonolactones to aldoses where the reduction was studied at several pH ranges. With slight modification this vessel may be employed for many other types of reactions where pH control is necessary.

APPARATUS

The reaction vessel (Figure 1) consists of a 1-liter, three-necked Pyrex flask, *A*, with a small electrode chamber, *B*, sealed on just above the middle of the flask. Larger or smaller flasks may be used just as readily. A stainless-steel stirrer, *S*, having a hinged blade, which is a circular segment of the cross section of the flask and fitting to within 1 to 2 mm. of the bottom, furnishes the pumping action (*2*). The stirring motor should be both fast and powerful. A motor controlled by a centrifugal governor is preferable to one with a rheostat control.

The flask and the electrode chamber are separated by a perforated glass disk, *C*, 3 cm. in diameter, containing a large number of 1- to 2-mm. holes. The perforations serve to diminish the impact of the solution against the electrodes, especially when mercury is used in the reaction mixture. The neck of the electrode chamber is large enough to accommodate a No. 6 rubber stopper. The main portion of the electrode chamber is a flat cylinder 2.5 cm. deep on its horizontal axis, one base of which is the perforated disk. A conical taper, 2 cm. deep, connects the bottom side of this cylinder to the lower side of the flask at a point vertically about 1 cm. from the bottom of the flask by means of an 8-mm. glass tube, *D*, which has a slight U-bend. This tube serves as the main path for the return of the mercury from the electrode chamber to the flask. Another glass tube, *E*, connects the center of the electrode chamber to the lower third of the flask. This tube is joined to the flask by an inner seal just above the point where the stirrer blade moves along the wall of the flask and opens within the flask as a spout which points in the direction of movement of the blade along the wall. The tube acts as a siphon and keeps constant the level of the aqueous solution in the chamber; it also provides for a rapid change of the liquid in the electrode chamber.

The pH changes occurring in the electrode chamber can be most accurately followed when a direct-reading pH meter is employed, but the ballistic type of instrument may be used almost as readily. The electrodes may be constructed to fit the dimensions of the cell, or any of the long electrodes furnished commercially can be adapted to fit the cell. An agar–potassium chloride bridge was found to be superior to the capillary glass type, but a commercial calomel cell with a flexible rubber tip containing a pinhole was satisfactory.

The electrodes are inserted in a two-holed rubber stopper and are adjusted to fit into the lower portion of the electrode chamber without touching the sides. A 50-ml. calibrated buret is placed in one side neck and the other neck is available for measuring the temperature and adding reagents.

OPERATION

A 10- to 15-ml. pool of clean mercury is placed in the flask and the stainless-steel stirrer is fitted as close to the bottom as possible. The bearing for the stirrer may be simply a glass tube with a rubber–mineral oil seal. The speed of the stirrer is considered properly adjusted when all the mercury is thrown against the side of the flask and no large globules remain at the bottom when the stirrer is operated. The reagents are added together with 200 ml. of water and the speed of the stirrer is regulated to force the solution and the stream of mercury into the electrode chamber at a level sufficient to keep the electrodes covered. The electrode assembly is then inserted into the neck of the electrode chamber.

The stirrer and the whirling mercury produce an oscillating, pumping action whereby the liquid and the mercury are forced into the chamber and back through the return tubes. Mercury collects in the U-portion of tube *D* during one phase of the action,

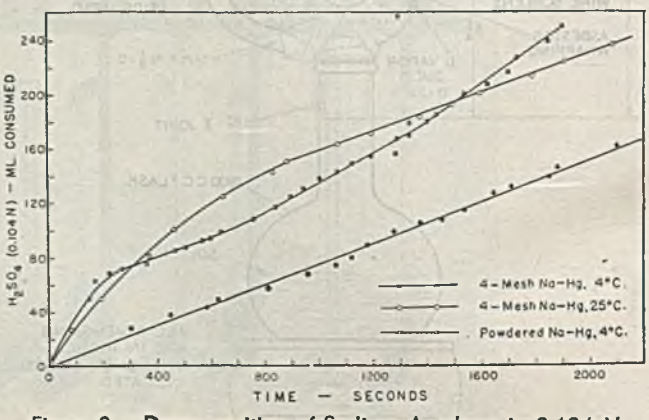

Figure 2. Decomposition of Sodium Amalgam in 0.104 *N* Sulfuric Acid

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and when the oscillating solution moves away from the opening, a stream of mercury and liquid pours back into the flask. The whirling solution creates a suction on the siphon tube, *E*, and keeps the liquid in the electrode chamber at a constant level. The stream of mercury mixes the contents of the chamber, so that the pH readings are representative of the whole sample.

The pH control is effected as follows: One hand is used to operate the buret which contains the standard acid or base while the other hand taps the electrometer key. Thus, if base is liberated during the experiment and the desired range is 3.5 to 4.5, the dial of the pH meter is set at pH 4 and standard acid is added at a rate which causes minimum deflection of the needle. With a little experience the operator can maintain the pH of the reaction mixture within 0.5 to 1.0 pH units in a continuously changing system.

EXAMPLE. The precision of the method can be demonstrated by a study made on the rate of decomposition of 25-gram samples of 2.5% sodium amalgams of different particle size and at various temperatures in contact with an aqueous phase maintained in the pH range of 3.5 to 4.5. The deviation of the points from the smooth curve in Figure 2 may be taken as a measure of the degree of control attained. The entire reaction vessel may be submerged in a constant-temperature bath when it is desirable to control the temperature at which the reaction is allowed to proceed.

ACKNOWLEDGMENTS

The authors wish to thank Harold E. Zaugg of the Abbott Laboratories, North Chicago, Ill., for furnishing the stainless-steel stirrer and for helpful advice during the course of the work.

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Estimation of Iodine Color of Starches and Starch Fractions

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STARCHES and starch fractions are usually characterized in part through the color produced by addition of iodine to their solutions. Exact comparison of these solutions can be made only by means of the spectrophotometer (*1*, *3*, *4*, *5*, *9*), but in many instances, and for routine testing, visual estimation of color is useful. Heretofore, however, no standard method for comparing starch-iodine colors has been employed, and, in most cases, authors have failed to record the procedure used in making the color test. Since the color with iodine of some starches and starch fractions changes with the concentration of the starch solutions and with the amount of iodine added, many starch-iodine colors recorded in the literature without accompanying description of the test method are not suitable for comparative work.

In order to facilitate and standardize the designation of color of starch-iodine solutions, the following method has been devised for visual comparison of these solutions. The method gives reproducible results and is sensitive to small differences in color. All colors are referred to standard color charts (*7*, *8*) and hence are capable of direct comparison in different laboratories

Color names have been chosen with a view to keeping the nomenclature as simple as possible. In general, comparisons have been made with standard colors or with common color names. It is recognized that the designation of color by name is inexact to the extent that most names may properly describe a number of colors within a given small range. Hence, for more exact designation of color, the more precise notation devised by Munsell (*7*) has also been used. The results obtained in applying the test method to several starches and starch fractions are shown in Table I.

The method is particularly useful in determining the purity of amylopectin fractions. The presence in amylopectin of amylose in quantities so low as to be scarcely evident on potentiometric iodine titration (*2*) is readily shown by the blue color produced on addition of 0.1 ml. of iodine to the starch dispersion, while more iodine up to 0.5 ml. brings out the typical amylopectin color. The persistence of the blue color and its influence on the final color may serve as a rough indication of the amount of amylose present. With appreciable amounts of amylose in the amylopectin, the blue color of the amylose-iodine complex masks the color of the amylopectin with iodine and prevents its visual detection. This method, therefore, does not serve to detect amylopectin in mixtures where amylose constitutes more than 6 to 8% of the total carbohydrate present. In the latter solutions the amylose-iodine complex usually precipitates.

Under the controlled conditions of test employed here, the color produced by iodine on waxy cornstarch is true purple and not red as has often been reported. The red (sometimes called reddish-brown) color frequently associated with waxy cornstarch is observed only in the presence of an excess of iodine and is in part due to the color of the free iodine in the solution. A number of intermediate stages of color can be observed (*6*) in waxy

Table I. Colors Produced by Iodine on 0.03% Dispersions of Starches, Starch Fractions, and Starch Derivatives

	Colors Observed with Various Amounts of 0.01 *N* Iodine on 10-Ml. Starch Dispersions			
	Color Comparison Made with Ridgeway Color Charts (*8*)		Color Notation from Munsell Color Charts (*7*)	
Starch Sample	0.10 ml. (2 drops)	0.50 ml. (10 drops)	0.10 ml. (2 drops)	0.50 ml. (10 drops)
Amylose	Spectrum blue	Deep blue precipitate	5PB 4/12	5PB 3/12
Whole cornstarch (disintegrated)	Spectrum blue	Deep blue precipitate	5PB 4/12	5PB 3/12
Corn amylopectin (not purified)[a]	Light spectrum blue (49b)[b]	Spectrum violet	5PB 5/10	3P 4/10
Corn amylopectin (cotton treated, *1*)[c]	Light blue-violet	Amethyst-violet to violet-purple	9PB 5/8	4P 3/10
Potato amylopectin[c]	Light purple (65b)	Magenta	10P 5/10	5RP 4/12
Waxy cornstarch (hand-pollinated)	Light amethyst-violet (61b)	True purple to magenta	5P 5/8	4RP 4/10
Waxy rice	Light pink (67f)	Reddish magenta (69')	5RP 7/8	7RP 4/12
Waxy barley starch	Light spectrum violet (59b)	Violet-purple	10P 5/10	10P 4/10
β-Amylase limit dextrin (cornstarch)	Spectrum blue	Spectrum violet	5PB 4/12	3P 3/10
Wheat dextrin (roasted 6 hours at 180° C.)	Light amethyst-violet (61b)	True purple	5P 5/8	4RP 4/10
Wheat dextrin (roasted 6 hours at 190° C.)	Pale pink (3'f)	Light jasper red to light coral red	8RP 7/8	4R 6/10

[a] Iodine absorption (*2*) 16 mg. per gram; approximate amylose content 8.0%.
[b] Numbers refer to plates whose color nomenclature has been simplified.
[c] Approximate amylose content 0%.

starch dispersions as the amount of iodine is increased toward an excess. Under identical conditions of test the waxy starches seem to differ in the color produced by iodine as one proceeds from type to type. Listed in order of decreasing red and increasing violet contents the starch-iodine dispersions may be arranged as follows: waxy rice, waxy corn, and waxy barley. To this series may be added in order potato amylopectin and corn amylopectin. This order coincides with the arrangement of Baldwin, Bear, and Rundle (*1*) who have suggested that it is also the order of increasing length of chain ends for the respective starch molecules.

METHOD

Thirty milligrams of starch are dispersed in 10 ml. of 1 *N* potassium hydroxide by allowing the mixture to stand with occasional shaking at 0° C. for 1 to 2 hours. For starch in the whole-granule state, 20 ml. of 0.5 *N* potassium hydroxide are used for the dispersion. The dispersion is neutralized with 1 *N* hydrochloric acid to a phenolphthalein end point and 1 drop of acid added in excess. The solution (pH 4 to 6) is then made up to 100-ml. volume, giving a starch concentration of 0.03%. By proceeding in this fashion, a constant amount of salt is introduced into each sample. Large amounts of salt, which produce changes in the iodine color, are to be avoided. To 10 ml. of the solution in a 16- by 150-mm. test tube is added 0.5 ml. (10 drops) of 0.01 *N* iodine solution (KI = 0.014 *M*) dropwise, with shaking. After 0.1 ml. (2 drops) has been added, the color of the solution is observed. At this point, the presence of small amounts of amylose in amylopectin will be evidenced by a blue color. The remainder of the 0.5 ml. of iodine is then slowly added and the color again observed. Further addition of iodine is unnecessary and in some cases may vitiate the color test by superimposing the color of free iodine on the starch-iodine color. All observations of color are made by transmitted daylight or a daylight fluorescent lamp and colors compared to the standard color chart.

SUMMARY

Starch-iodine color tests, to evidence small differences between starches or starch fractions and to be comparable among different laboratories, must be performed under uniform conditions in the absence of a large excess of iodine. A procedure is outlined for the rapid determination of starch-iodine colors. It is especially satisfactory for rapid estimation of the purity of amylopectin when contaminated with less than 6 to 8% amylose.

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A Versatile Arc-Spark Stand

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AN arc-spark stand combining the adjustments of the pin-type stand and the versatility of the Petrey stand (*1*) has been developed which is capable of supporting heavy weights and does not place any strain on the optical bar or the spectrograph. The size, shape, and vertical adjustments of the stand simplify nondestructive spectrographic analyses on relatively massive parts. In many laboratories this stand will broaden the scope of adaptability of the spectrograph, as either the pin technique (using fixtures) or the flat technique (*2*, *3*) may be used.

DESCRIPTION

A steel plate, 30 cm. (12 inches) square and 0.5 cm. ($^3/_{16}$ inch) thick, is used as the sample-supporting table. In the center of the edge of the sample plate towards the spectrograph slit a notch is cut, 2.5 cm. (1 inch) wide and 2.5 cm. (1 inch) deep, similar to the cut-out portion of the Petrey stand. The sample lying on the sample plate can easily be excited from the bottom, using the sample as one electrode and a graphite rod as the other (*2*, *3*). The notch must be large enough so that the excitation will be between the sample and the graphite rod and not between the sample plate and graphite rod. Notches of various size may be placed on the edges of the sample plate and the correct size found by trial. In this case, extra plate-holding screw holes are made in the top of the plate, in order that the plate may be turned to bring the proper notch toward the spectrograph slit.

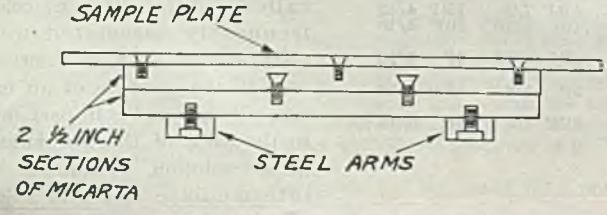

Figure 1. Method of Insulating Sample Plate

The sample plate is insulated from the remainder of the stand by two 1.8-cm. (0.5-inch) thick sections of micarta (Figure 1). All screws which fasten the micarta to the sample plate, etc., are offset from each other at least 2.5 cm. (1 inch). By this means at least 2.5 cm. (1 inch) of air or micarta insulate the sample plate from the remainder of the stand. The micarta is fastened to two

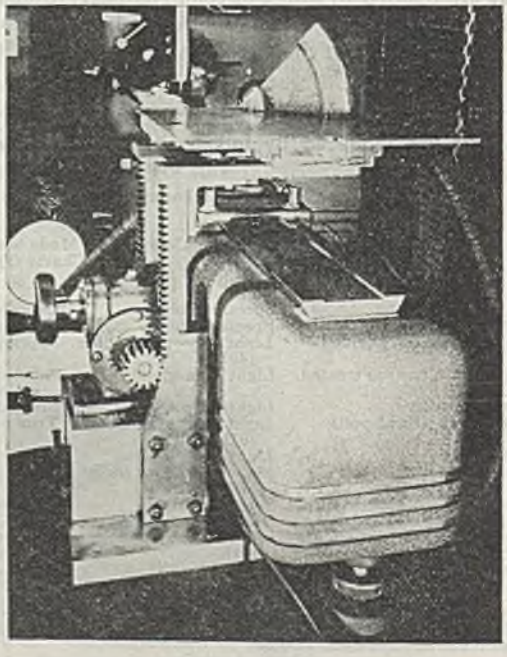

Figure 2. Arc-Spark Stand

solid pieces of steel which lead to one side of the optical bar, where they are attached to two bars of steel with teeth on the outer side which act as a rack for a rack and pinion motion.

A commercial-type speed reducer (15 to 1) with a reducer arm extending from each side was purchased and placed on a heavy steel platform about 10 cm. (4 inches) above the base of the stand (Figure 2). A pinion was attached to each reducer arm in such a manner as to contact the rack part of the uprights. On the motor extension part of the speed reducer a micarta knob was attached, to control the vertical motion of the sample plate.

The base, 28.5 cm. (11.25 inches) square and 2.5 cm. (1 inch) thick, rests on the table which supports the spectrograph (Bausch & Lomb large Littrow). Thus, the entire weight of the stand and sample is supported with no strain on the optical bar or the spectrograph.

All parts of the stand are of heavy, sturdy steel, to ensure rigidity. Although the stand is heavy (35 to 40 kg.), it is not cumbersome or bulky. It has supported over 50 kg. (100 pounds) without bending or twisting. With weights of this size, however, a thumb-type setscrew is placed on the side to contact one of the movable uprights. With smaller samples (5 to 10 kg.) this setscrew is not necessary, as the sample plate will remain in the position in which it is placed by the rack and pinion movement.

This stand is so constructed that the center of the notch in the center of the edge of the sample plate towards the spectrograph slit is exactly on the optical axis when the stand is placed firmly against the optical bar (Figure 2). In some instances, where the optical bar is of different design (Hilger, etc.), two slots in the base of the stand are advisable. Bolts can then be placed through these slots and through the supporting table. The stand can then be adjusted until it is properly aligned and the bolts tightened to give the same effect as at the author's laboratory, where the weight and position of the stand against the optical bar are used to hold the stand in proper alignment. Once the stand is in position, it is no longer necessary to move or adjust it, except with the rack and pinion motion.

The base of the stand is grounded to eliminate slight shocks due to induction from the sample plate, although the stand is usually adjusted by a gage before the sample is excited and it is not necessary to touch the stand during excitation.

Small fixtures to hold pins, etc., can easily be made to clip or screw onto the sample plate. Thus, the stand is used for many and varied types of samples, as either an upper or lower electrode holder as desired.

One lead from the source is attached to the sample plate by a countersunk screw, and the other lead to the portion of the regular B. & L. arc-spark stand which is used. The source leads are connected through a switch to convert from arc to spark as necessary. The stand is used at all times (with or without fixtures as necessary) as one pole of the source used.

The stand described has been in use over a year and can be recommended for various sizes, shapes, and weights of samples, either arc or spark. The direct current arc has been used for over an hour (arcing solutions with a fixture attached to the stand) with less than 1-minute interruptions every 5 minutes, without undue heating of the sample plate or stand.

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to the Drafting and Tool Departments. He is particularly obliged to H. P. Conrad, senior chemist, for his active help.

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Apparatus for Vacuum Distillation of Volatile High-Melting Solids

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THE vacuum distillation of volatile high-melting solids necessitates laboratory apparatus of special design. In ordinary apparatus, the distilling solid soon clogs the narrow passage between the distilling vessel and the receiving vessel, particularly in the inaccessible places underneath stoppers and in the interior of the receiving vessel.

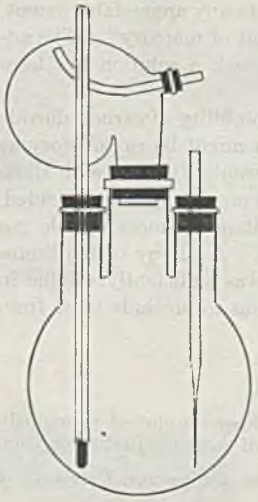
Two methods are used to overcome this difficulty. The first consists in heating the narrow parts to a temperature above the solidifying point of the distilling solid. Haehn (*3*) accomplished this by a hot oil jacket, Steinkopf (*8*) by an electrically heated wire coil. Hauschild (*4*) used a specially designed still head which could be flamed directly. The second method consists in using specially designed flasks in which inaccessible narrow passages between the still and the receiver are eliminated. The most important apparatus of this type is the sword flask designed by Anschuetz (*6*), or its variations by Baer (*1*), Muencke (*6*), and others (*5*, *7*). Another has been described by Bolstad and Dunbar (*2*).

However, none of this equipment is readily available or available in sizes large enough to be practical for the handling of fairly large quantities of chemicals. A simple method was devised for this purpose, utilizing standard laboratory glassware (Pyrex).

The apparatus consists of a large three-necked flask (5 liters), and a retort (0.5 or 1 liter), the neck of which has been cut off conveniently. The shortened neck of the retort is inserted into the center neck of the flask (see figure). The other two necks of the flask hold a thermometer and a capillary tube. The vacuum connection is made through an upward-curved glass tube inserted into the tubulature of the retort. Heating is best carried out by inserting the flask deep into a suitable bath. Before charging, the flask should be tested for its ability to withstand a vacuum, taking adequate precautions. (Specially hand-picked flasks are available from Corning Glass Works. Caution must be used in all cases.)

The vacuum attachment clogged only when too much air was allowed to enter the apparatus through the capillary tube, and drops or particles of the distilland were carried up beyond the receiver. It was also found helpful to suspend, near the end of a distillation, a large test tube inside the center neck of the flask. This was done by means of a hook of noncorroding wire which was inserted through the neck of the retort and anchored to the sharp edge inside. By suspending the test tube within the center neck of the flask, the path of the distilling vapors is greatly shortened. Otherwise it would be necessary to overheat the contents of the flask to force the distillate up to the receiver.

An apparatus like the one described is available in large sizes, is comparatively inexpensive, and has operated satisfactorily in distilling fairly large amounts of material with only few interruptions.



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Apparatus for Trapping Ammonia in the Kjeldahl Method for Nitrogen

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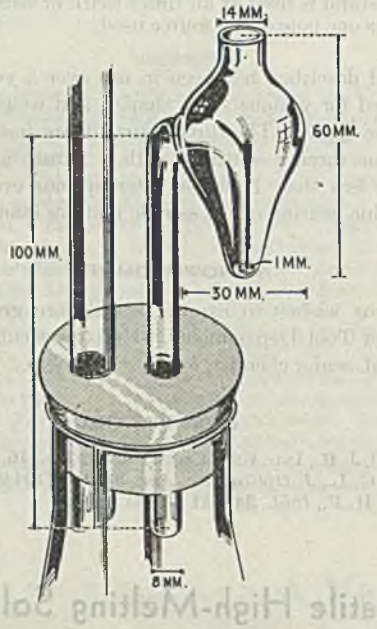
THE apparatus described below has been used satisfactorily in this laboratory for 20 years, to seal the receiver used in catching the ammonia distillate in the determination of nitrogen.



Used in analytical laboratories where nitrogen or protein is determined as a regular routine, the trap automatically catches the ammonia in the distillation step, eliminating the necessity of dipping the delivery tube into the standard acid. It offers several advantages: It does not require a delivery tube that must be removed from the solution before turning off the heat; a smaller quantity of solution may be used in the receiving flask; the action of the trap is automatic; its dependability has been proved by the laboratory's record in various collaborative check samples; and it can be easily made by anyone experienced in working glass.

The block-tin delivery tube from the condenser and the tube from the trap extend through a No. 10 rubber stopper into a 500-ml. wide-necked Erlenmeyer flask used as the receiver. In operation about 2.5 cm. (1 inch) of water are put into the trap; more water is undesirable because of the danger of siphoning it out of the trap before completion of the distillation.

The apparatus will trap any ammonia vapors that are driven through the condenser by retaining them in solution. When the distillation is complete and the heat is turned off, the lower pressure inside the system will cause the solution in the trap to siphon into the receiving flask. The concentration of ammonia in the trap is very low. Experience has shown that it is not necessary to rinse the trap with water at the end of the distillation.

Using the trap and C.P. ammonium sulfate as a standard, recoveries have been found quantitative with amounts of nitrogen as high as 140 mg. per determination. The acid used is standardized according to the procedure of the Association of Official Agricultural Chemists (*1*).

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Aqueous Solutions of Alcohols as Confining Liquids for Gas Analysis

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THE use of solutions of alcohols, particularly glycerol, as confining liquids for gas analysis has been mentioned in numerous papers since it was first reported by Burgess and Wheeler (*1*). Using a solution of equal parts of glycerol and water previously saturated with coal gas, they reported that "the gases do not dissolve in such a mixture to any appreciable extent, and its use is more convenient than that of mercury". The advantage of the low freezing point of such a solution has been mentioned.

The authors have investigated the solubility of carbon dioxide in aqueous solutions of alcohols which might be satisfactory as confining liquids and compared these solubility data with those obtained for solutions of inorganic salts previously recommended. Carbon dioxide was selected because it is the most soluble gas commonly encountered in gas analysis. A survey of the literature (*4*) showed that carbon dioxide was sufficiently soluble in aqueous solutions of monohydric alcohols to preclude them from further consideration.

EXPERIMENTAL

The apparatus and technique are those employed previously (*2*, *3*). The organic compounds were of reagent quality or were vacuum-distilled. Dissolved gases were removed from the water and the compounds (except glycerol and dihydroxy diethyl ether) by refluxing for 20 minutes or by vacuum distillation. The absorption bulb and gas buret were maintained at 25° ± 0.1° C. The carbon dioxide (99.8% purity) was saturated with water vapor from the solution by passage through a spiral-type bubbler maintained at 25° C. Values of the vapor pressure of the water in the solution were taken from the literature or calculated from

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Table I. Solubility of Carbon Dioxide in Aqueous Alcohol Solutions

(Temperature 25° C., partial pressure of CO_2 760 mm.)

Compound Used	Concentration	Solution Used	Gas Absorbed	Solubility of CO_2	
	Wt. %	*Ml.*	*Ml.*	*Ml.*[a]	α[b]
None	0.0	24.99	20.57	0.823	0.754
Glycerol	40.0	50.00	29.62	0.592	0.542
Glycerol	50.0	50.00	25.55	0.512	0.468
Glycerol	50.0	50.00	23.10	0.462	0.423
Sulfuric acid	5.0				
Ethylene glycol	60.0	49.99	31.36	0.627	0.574
Ethylene glycol	40.0	50.00	32.68	0.654	0.599
Ethylene glycol	20.0	50.00	36.31	0.726	0.666
Dioxane[c]	60.0	50.00	76.13	1.523	1.395
β-β'-Dihydroxy ethyl ether[c]	60.0	24.99	15.80	0.633	0.579
Tetrahydrofurfuryl alcohol[c]	75.0	50.00	55.66	1.113	1.020

[a] Ml. of CO_2 at 25° C. and 760 mm. dissolved per ml. of solution.
[b] Ml. of CO_2 calculated to 0° C. and 760 mm. dissolved per ml. of solution.
[c] This solution reacted with mercury.

Raoult's law. The total pressure maintained in the apparatus was 760 mm. of carbon dioxide plus the vapor pressure of the solution at 25° C.

The solubility data are given as milliliters of carbon dioxide at 760 mm. and 25° C. dissolved in 1 ml. of solution. From this is calculated the Bunsen coefficient, α, which is the milliliters of carbon dioxide, calculated to 760 mm. and 0° C., dissolved in 1 ml. of solution (*4*). Although the precision of the results is 0.002, it can be considered that the accuracy of α is 0.005. The data are given in Table I.

DISCUSSION

The Bunsen coefficient for an acidified 50% glycerol solution (0.423) is almost twice that found for the 20% sodium sulfate plus 5% sulfuric acid solution (0.247) previously recommended (*2, 3*). Although sodium sulfate decahydrate will crystallize from the acidified sodium sulfate solution below 16° C., this solution will continue to dissolve less gas than the acidified glycerol solution. Only at temperatures below the cryohydric point would the acidified glycerol solution have advantages. The cryohydric temperature of saturated aqueous sodium sulfate solution is −1.10° and of sodium chloride is −21.1° C. An acidified aqueous solution of sodium chloride is recommended for use at temperatures to −20° C. (−4° F.).

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Third paper in series; for Nos. 1 and 2 see (*2, 3*).

Electronic Timer

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Washington, D. C.

RECENT work in the physical chemistry laboratory of this bureau involved the use of a solenoid-operated, enclosed glass pump. The electronic timing device described by Bechtold (*1*) appeared particularly well suited for controlling this solenoid because of its simplicity, ease of construction, and readily controllable pulse rate. However, this timer proved unsatisfactory in operation since, under the conditions which obtained, the gas-filled triode (885) had an average service life of only about 12 hours. No current-limiting element was included in the triode plate circuit. Thus, the charging surge supplied to capacitor C_2 (Bechtold's designation) was, upon breakdown of the triode, in excess of the rated peak current for the tube. This overload caused the tube to fail prematurely. Insertion of resistance to limit the peak current to the specified maximum (300 milliamperes) resulted in feeble actuation of the relay. Satisfactory operation required the use of a more sensitive relay, or of a tube having a higher peak current rating.

In the improved circuit given in Figure 1 the type 885 tube has been replaced by a type 2050 gas-filled tetrode and a current-limiting resistor has been inserted. This resistor, R_6, has a value of about 170 ohms and limits the charging surge of C_2 to less than the rated maximum (1 ampere) of the 2050 tube. Resistor R_5 has been added to limit grid current and rheostat R_7 to reduce arcing of the relay contacts on an inductive load, such as a direct current solenoid.

The modified circuit has proved highly satisfactory as evidenced by over 200 hours of operation, including continuous periods of as long as 60 hours, with no evidence of tube failure. Its readily adjustable pulse rate, obtained by manipulation of potentiometer R_1 and the adjustability of the range of rates depending upon the values of R_1, R_2, and C_1, make it applicable to a wide variety of timing operations.

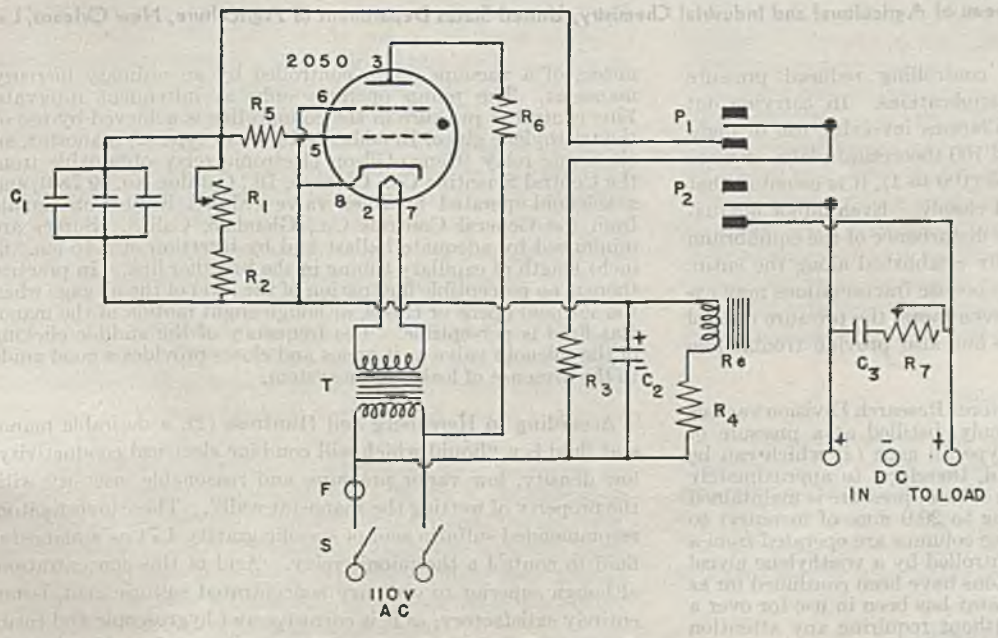

Figure 1. Circuit for Electronic Timer

C_1, 3 paper condensers, 400 wv, 2 μfd. each; C_2, 250 wv. electrolytic condenser, 8 μfd.; C_3, paper condenser, 450 wv., 1 μfd.; R_1, 1-megohm potentiometer, No. 6 taper; R_2, 50,000 Ω, 1-watt carbon; R_3, R_4, 10,000 Ω, 1-watt carbon; R_5, 1-megohm, 1-watt carbon; R_6, 150 Ω 5-watt wire-wound; R_7, 100 Ω, 2-ampere rheostat; T, 6.3-volt 3-ampere filament transformer; Re, double-pole, double-throw relay, 2000 Ω coil; F, 2.0-ampere fuse; S, double-pole, single-throw toggle switch; 2050, RCA type 2050 gas-filled tetrode; P_1, P_2 relay contact points

ACKNOWLEDGMENT

Suggestions made by P. J. Franklin in connection with the design of this circuit are gratefully acknowledged.

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Gage for Preparation of Laboratory Solutions

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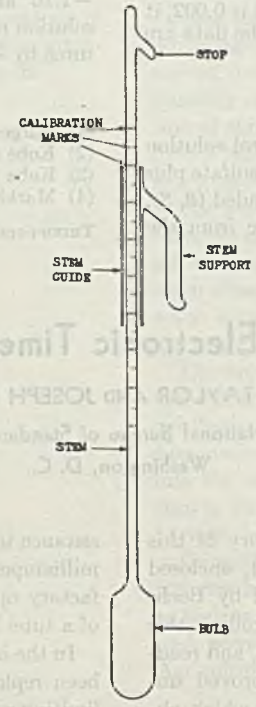
THE use of a 1- or 2-liter volumetric flask for making large quantities of standard solutions up to 19 liters (5 gallons) is somewhat tedious and time-consuming. While clear-glass bottles can be calibrated by placing a mark at the desired point, this method cannot be used for opaque bottles and has the additional disadvantage that the bottle must be level.

A bottle gage embodying the float principle is presented in the diagram and furnishes a simple, rapid, and accurate method for making up solutions in large bottles.



The gage consists of a hollow bulb on the end of a stem, together with a guide and support for the stem. The bulb must be of such size and shape that it will pass through the mouths and necks of all bottles to be used and at the same time float in distilled water. The stem support must have enough clearance between it and the guide tube to accommodate all bottles.

The gage for 2-, 3-, and 5-gallon bottles used in this laboratory has the following dimensions:

Bulb. Length, 5.5 cm.; greatest width, 2.3 cm.; volume displacement, 14.0 cc.

Stem. Length, 32.0 cm.; diameter, 0.5 cm.

Stem Guide. Length, 9.0 cm.; inside diameter, 0.6 cm.

Support. Clearance between support and guide, 1.5 cm.

The gage is calibrated by measuring the desired quantity of distilled water into a bottle of suitable size, placing the gage in position, and making a mark on the stem even with the top of the guide tube. This process is repeated for other quantities and bottles as desired. However, the calibrations for bottles of any given size may be used for all bottles of the same size, provided that they are of approximately the same diameter and height.

In general, to make up a chemical solution the calculated amount of chemical or chemicals is put in the empty bottle, the gage is placed in position, and distilled water is added to the proper mark. The solution is mixed well and then standardized, adjustments being made when necessary.

Since the gage operates near the center of the solution with respect to the circumference of the bottle, its accuracy is not affected if the bottle is not exactly level. The slight difference between the specific gravity of the unmixed solution and that of distilled water does not materially affect its accuracy.

A suitable holder for the gage is made by placing a small piece of cotton in a 500-cc. graduate.

ACKNOWLEDGMENT

The author is indebted to J. H. Jordan for making the gage as well as for suggestions concerning details.

Di- and Triethylene Glycols as Manostat Fluids

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DEVICES for automatically controlling reduced pressure have numerous laboratory applications. In carrying out exacting laboratory vacuum distillations involving use of high-efficiency fractionating columns of 100 theoretical plates or more and operating at high reflux ratios (100 to 1), it is essential that the column pressure be controlled closely. Even minor fluctuations in pressure will cause serious disturbance of the equilibrium between liquid and vapor carefully established along the entire length of the column. Since such precise fractionations may extend over periods of a month or even more, the pressure control should not only be very precise but also provide trouble-free operations.

In the laboratory of the Naval Stores Research Division various terpene hydrocarbons are commonly distilled at a pressure of 20 mm. of mercury. A Palkin-type oil gage (*4*) which can be easily read to 0.5 mm. of oil (and, therefore, to approximately 0.03 mm. of mercury) is used, and column pressure is maintained at 293.0 mm. of oil (corresponding to 20.0 mm. of mercury) to approximately this precision. Five columns are operated from a single "column line" manifold controlled by a triethylene glycol manostat, and individual distillations have been continued for as long as 5 weeks. The same manostat has been in use for over a year without replacement and without requiring any attention other than resetting.

A dual system of pressure control involving an automatically controlled gas leak from the higher pressure column line to the lower pressure vacuum pump line is used. The low pressure pump line is maintained at approximately 10 mm. of mercury by means of a vacuum pump controlled by an ordinary mercury manostat. The pump operates only at infrequent intervals. Fine control of pressure in the column line is achieved by use of the triethylene glycol Hershberg-Huntress-type (*2*) manostat, an electronic relay (Cenco-Gilson electronic relay obtainable from the Central Scientific Co., Chicago, Ill., Catalog No. 99,780), and a solenoid-operated breather valve (Model K-20-1 obtainable from the General Controls Co., Glendale, Calif.). Surges are minimized by adequate ballast and by insertion of a 15-cm. (6-inch) length of capillary tubing in the breather line. In practice there is no perceptible fluctuation of the level of the oil gage when the solenoid opens or closes, although slight motion of the manostat fluid is perceptible. The frequency of the audible clicking of the solenoid valve as it opens and closes provides a good guide to the presence of leaks in the system.

According to Hershberg and Huntress (*2*), a desirable manostat fluid is a "liquid which will combine electrical conductivity, low density, low vapor pressure, and reasonable viscosity with the property of wetting the manostat wall". These investigators recommended sulfuric acid of specific gravity 1.71 as a manostat fluid to control a thermionic relay. Acid of this concentration, although superior to ordinary concentrated sulfuric acid, is not entirely satisfactory, as it is corrosive and hygroscopic and easily becomes fouled with grease from the stopcocks. In addition, some electrolysis occurs and the electrodes become pitted.

The Cenco-Gilson electronic relay, which is reported to operate on as little as 0.5 microampere, permits the use of a practically

Table I. Comparative Properties of Manostat Fluids

Substance	Specific Gravity at 20° C.	Viscosity at 20° C. Centipoises	Boiling Point at 760 Mm. ° C.	Vapor Pressure at 25° C. Mm.
Mercury	13.55 (3)	1.547 (3)	357.9 (3)	0.0018 (3)
80% H_2SO_4	1.7272 (3)	20.3 (3) (at 25° C.)	202 (3)	0.124 (3)
75% H_2SO_4	1.6692 (3)	14.0 (3) (at 25° C.)	182 (3)	0.408 (3)
Diethylene glycol	1.1184 (3)	35.7 (1)	244.8 (1)	0.1 (1) (0.1 at 45° C.)
Triethylene glycol	1.1254 (1)	47.8 (1)	287.3 (1)	0.01 (1) (0.1 at 80° C.)

nonconducting manostat fluid, therefore materially enlarging the field from which a suitable fluid may be selected. Both diethylene glycol and triethylene glycol, which are readily available commercially, have been found superior to sulfuric acid for use as manostat fluids. Both these glycols have sufficient electrical conductivity to operate the Cenco-Gilson electronic relay, but when they are used with the thermionic relay suggested by Hershberg and Huntress, a drop of concentrated sulfuric acid must be added to provide sufficient conductivity.

The significant properties of the substances discussed above as possible manostat fluids are compared in Table I.

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A Rapid-Filling Capillary Polarimeter Tube

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IN THE course of an extended study of the optical rotations of several scarce materials, the limited quantities of sample available necessitated the use of capillary polarimeter tubes. The ordinary polarimeter tubes which are generally used in sugar analysis (*1*) and are readily available have an inside diameter of about 9 mm. With a tube of this bore, it would have been necessary either to reduce the length to a few millimeters or to use extremely dilute solutions. Since the rotation is a function of the length of tube and concentration of the solution, neither alternative was feasible. Compared with the usual 9-mm. diameter tube, the 2-mm. bore tube employed by the authors requires only 5% of the solution volume for an equal tube length.

Many investigators have employed capillary tubes such as the Fischer microtube (*2*) the Naumann tube (*3*) or various modifications of them. The filling of small-bore tubes of these types presents definite difficulties. It is impossible to pour the liquid into the vertically held tube while one of the cover glasses is fastened to the lower end. If any air bubbles are trapped in the course of the filling, it is generally necessary to empty the entire sample before attempting to refill free of air bubbles.

This difficulty is usually overcome by introducing the solution from a long thin dropper which will extend to the bottom of the capillary (*2*). Withdrawing the dropper as the liquid enters the tube permits filling with a fair degree of success. However, the fragility of the long dropper and the ever-present danger of losing the sample if the dropper is broken are disadvantages.

The "halo" caused by light scattered from the inside walls of small-bore tubes makes it difficult to obtain a well-defined balance of the photometric field. Naumann (*3*) overcomes this difficulty by employing black glass capillary tubes with etched inside walls, but admits that proper cleaning of the etched tube is a problem in itself.

The authors have reduced this halo effect to a minimum by limiting the field of the polarimeter. When a diaphragm is mounted in the threaded end cap of the tube nearest the analyzer, with its hole diameter so selected that it subtends a smaller angle to the observer than does the end of the capillary bore nearest the polarizer, the halo is eliminated at the expense of a small reduction in the diameter of the photometric field.

In order to obtain satisfactory tubes for their investigation, the authors have devised a new type of capillary tube by the simple expedient of introducing into an ordinary straight-bore, 100-mm. polarimeter tube a piece of capillary whose outside diameter makes a rather snug sliding fit (about 0.01-mm. clearance) in the inside of the regular tube. These sections of capillary are optically polished on both ends. Their total length is made approximately 0.5 mm. shorter than that of the regular tube, so that the original tube length still remains effective when rotation measurements are made.

While using these assembled capillary tubes it became apparent that they can be filled easily, rapidly, and safely by putting the necessary amount of solution into the large tube and then slowly lowering the capillary into it. The lowering of the capillary displaces the solution, which rises into the bore completely free of bubbles. The solution also rises in the annular space between the tube and the capillary, but this does not interfere, nor does it use much of the solution. For a tube of the dimensions stated, the annular volume is about 0.015 ml.

If the solution does not come all the way to the top, when the capillary is lowered in the tube, a small amount may easily be added from a short dropper.

In many laboratories it is necessary to have a large number of polarimeter tubes of different bore size to accommodate the various quantities of solutions to be measured on the polarimeter. By means of a series of different-size capillaries which may be readily constructed, a single observation tube may be quickly converted into a capillary tube of the proper bore. Water-jacketed tubes without tubulatures may be similarly converted to capillary tubes, bearing in mind, of course, that the time required for attaining temperature equilibrium will be greatly increased because of the increased thickness of tube wall.

SUMMARY

Polarimetric measurements on small amounts of the sample require the use of capillary tubes. As a result of optical rotation studies on several small samples, a rapid-filling capillary polarimeter tube has been developed. For small volumes of solutions, this tube gives the maximum tube length which is concomitant with a sufficiently large field to permit photometric matching.

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Electrolyte Solution Heating Element for Steam Microbath

ALEXANDER P. MARION, Queens College, Flushing, N. Y.

A SIMPLE, rapid, and efficient heating device particularly adapted for use as an electrically operated steam bath can be constructed by immersing two wire electrodes in a solution of an electrolyte of proper concentration. The apparatus (Figure 1) has an automatic cutoff feature and requires no external transformer or resistance control.

The apparatus is a vessel of about 200-ml. capacity covered by a metal water bath adapter through which the electrodes pass. The electrodes are two pieces of No. 12 copper wire bared for a length of 4 cm. and insulated from the adapter by Lucite bushings. The wires fit snugly into holes drilled through the Lucite. One of the bushings is cut to permit the electrode to be partially raised out of the solution, thereby altering the effective size of the electrode. Two parallel grooves, each the thickness of the metal plate and 1 cm. apart, are cut in a 2.5-cm. length of 0.94-cm. (0.375-inch) diameter Lucite rod. The section below the uppermost groove is then filed to have two parallel flat faces, the material down to the depth of the groove being removed. The opening in the metal plate is made by drilling a hole and filing until the lower end of this bushing will pass through. Then by raising the bushing to the level of the lower groove and rotating it 90° the area of the electrode is reduced, thereby decreasing rate of heating.

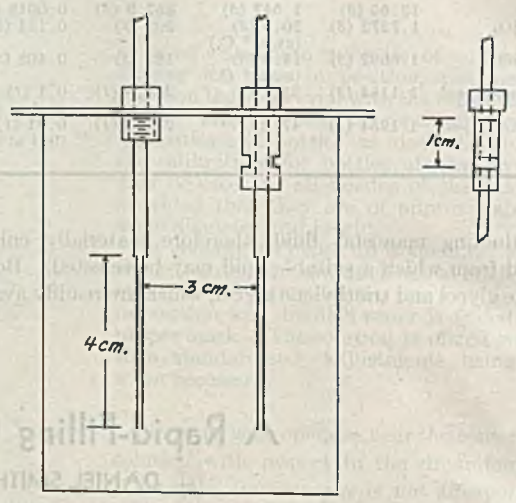

Figure 1. Details of Apparatus, Including Side View of Special Bushing

A 1% copper sulfate solution proved satisfactory as the electrolyte. Some idea of the time to reach the boiling point may be useful: 100 ml. of solution produced steam in less than 1.5 minutes after the unit was plugged into the commercial power lines.

The automatic cutoff is obtained by suspending the electrodes so that they do not touch the bottom of the vessel. Then as the level of the solution drops below the lower edge of the electrodes the circuit is broken. As the electrolyte remains in the residue, the addition of water will recharge the apparatus.

Semimicro Ion-Exchange Column

NORMAN APPLEZWEIG

American Home Products Corporation, Products Development Laboratory, 254 West 31st St., New York, N. Y.

IN RECENT months the writer has had an opportunity to study the ion-exchange adsorption of a large number of organic compounds. In order to obtain basic facts as to adsorption capacity of exchangers and recovery data it was found expedient to use small quantities of exchange materials.

The ion-exchange columns recommended by investigators in the water-conditioning field (*1–4*) were found to be oversized (200- to 1000-ml. exchanger beds) and cumbersome to operate. A need was felt for a column which would hold from 5 to 20 ml. of exchanger and could easily be assembled, backwashed, or connected in series with another column.

Such an apparatus was constructed by using a 9-mm. standard Kimble condenser tube measuring 42.5 cm. long when the beveled end had been cut off. A plug of glass wool was inserted at the bottom and a three-way stopcock was attached by means of a rubber stopper.

A complete assembly of two columns is shown in Figure 1. The solution to be run enters C^1 by means of a funnel and constant-head device. After flowing through the exchange bed in the first column it passes to the second by means of a tube leading from B^1 to C^2. Samples from the first column may be taken at any time through A^1 by turning the stopcock.

The effluent passes out of the second column through A^2 and its flow rate may be adjusted by means of the stopcock.

The columns may be backwashed by attaching a tube from a raised water bottle to B^2 as illustrated or to A^1 for the first column and providing an overflow tube.

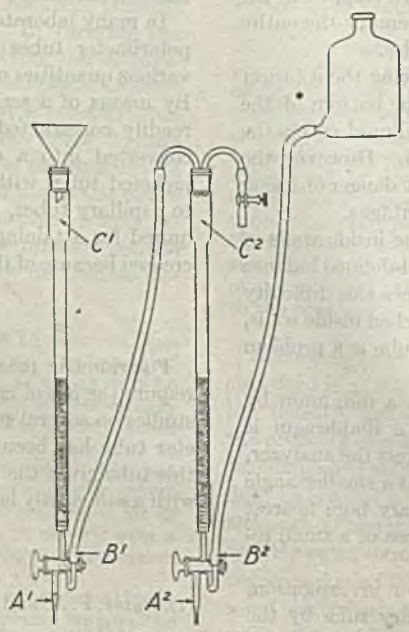

Figure 1

Even at moderately rapid backwash rates the exchangers remained suspended in the wide part of the tube at C^1C^2 and showed no tendency to be spilled over. No trouble was caused by entrapped air, as is usual in larger columns. Flow rates could be adjusted with fair accuracy over a wide range. Where necessary, the tube may be calibrated to study bed volume changes.

This apparatus has been found useful in studies on the ion-exchange adsorption and recovery of alkaloids, amino acids, and other organic compounds.

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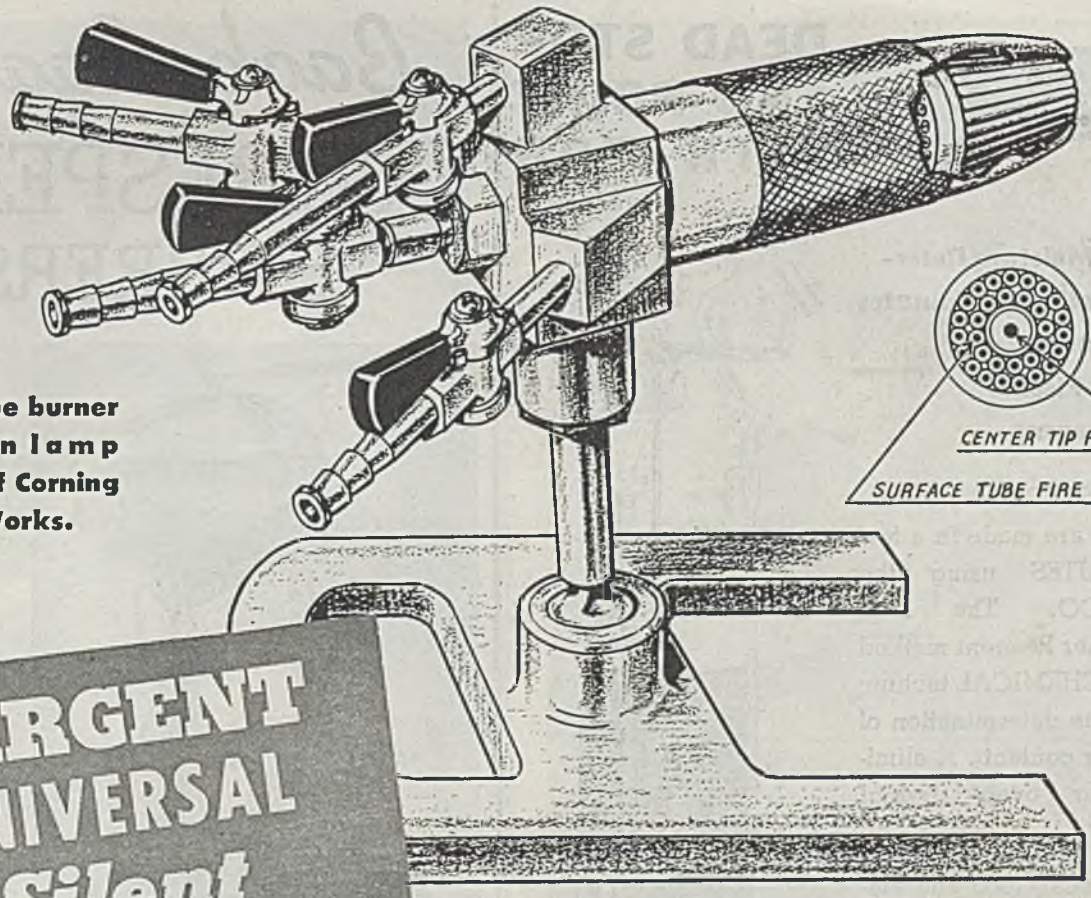

This type burner used in lamp shops of Corning Glass Works.

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Current Developments in

INSTRUMENTATION IN ANALYSIS

Discussed by Ralph H. Müller

INSTRUMENTATION is on the threshold of a new era and the problems of analytical chemistry afford one of its most fertile fields of application. Wartime production demands produced some impressive developments in analysis and control, but it seems more likely that radical changes will result from the technical revelations of the two major war projects—radar and atomic energy. M.I.T. has publicly announced the preparation of twenty-five volumes on the technical history of radar by its Radiation Laboratory staff. This work has been under way since late summer. It is safe to predict that 10% of this material, dealing with circuitry, will find wide application in many branches of science. Most of it renders prewar electronics obsolete. The revelations of the Smyth report on Atomic Energy for Military Purposes state or imply extensive developments in instrumentation. Specifically, production at the Hanford plant was largely automatic and required manipulation at considerable distances, to meet the radiation hazards. The release of these details is less certain, and most likely will have to await military, legislative, and international deliberation. It is generally agreed in Chicago, Oak Ridge, Hanford, and Los Alamos that the immediate benefits will appear in the general availability of radioactive materials for research. It is very unlikely that applications in the field of analysis will be confined to the familiar "tracer" techniques. The nuclear physicists have made, incidentally and of necessity, great strides in the construction and use of Geiger-Müller counters, scaling and recording circuits, and related techniques. Analysts for some time have been feeling their way with these devices in spectroscopy and x-rays.

It is a commonplace to note that war produces great technical advances but, in general, impoverishes and depletes our store of fundamental knowledge. We are doubly discouraged when we recall that "incubation period" which has so strangely affected analytical chemistry. Among the well-established methods and techniques such as emission spectroscopy, infrared, mass spectrometry, polarography, x-rays, electrode potentials, electron diffraction, electronics, it is easy to show that intervals of from 10 to 50 years or more have elapsed between their discovery or development and their widespread use in industry. There may be some acceleration in recent years, but we hesitate to compute second derivatives. It must be admitted that a time delay factor must still be added to any fundamental work which we are now in a position to resume.

Recent Publications

Speaking of fundamentals, we have read and reread J. J. Lingane's paper in the November, 1945, *J.A.C.S.* on coulometric analysis. Shades of Michael Faraday—and a century of incubation! Although others have entertained the enticing notion of measuring electrodeposition in terms of the total charge transported, and achieved limited success, Lingane is providing the basic information and techniques for the practical realization of quantitative separations and determinations. His paper includes an interesting and necessary digression on the precision of the oxygen-hydrogen coulometer. Two factors contributing to the success of this method are the automatic maintenance of constant potential during the electrolysis and the use of the mercury cathode. (The device for potential control was described in the May, 1945, issue of the ANALYTICAL EDITION.) These present intriguing possibilities for instrumental developments, but the author is properly concerned with fundamental inquiry, for without it elaboration in technique would be premature and ill advised.

Some time ago we were prompted to remark, "When a survey of modern analytical chemistry requires the description of instruments ranging from hydrometers to cyclotrons and it can be shown that these devices are all eminently practical and paying their way, one instinctively wonders how the modern analyst is to be appraised. It is evident from the contemporary scene that his former slogan, 'dry-ignite and weigh', no longer carries him through the day's work. He must become familiar with a bewildering array of techniques and at least moderately acquainted with the dialect of the physicist and engineer." We have had ample evidence recently that industry is seriously, though belatedly, concerned about this situation, particularly with the dearth of adequately trained personnel. To the best of our knowledge there is nothing to indicate that the situation has passed the "ho-hum" stage in administrative academic circles.

Ralph H. Müller

We note the launching of another but welcome offensive, by progressive young physicists, who have discovered that chemistry is one of the exact sciences and that analysis has many uses for their special talents. It is increasingly evident that the journals of the American Institute of Physics are becoming required reading for the analyst. Three preprints have become available to this column which should be of interest to our readers. Since they are destined for publication elsewhere, it will be necessary to limit discussion to their main purpose. F. G. Brockman and C. H. Schlesman of the North American Philips Co. and Socony-Vacuum Oil Co., respectively, presented a paper before the Optical Society of America in October, dealing with their researches on an "Alternating Current Bolometer for Infrared Spectroscopy". One of the limitations of older recording infrared spectrometers was the necessity of photographically recording galvanometer deflections. The A.C. bolometer represents one means for obtaining the record with commercially available recorders. The authors describe an arrangement in which a twin filament nickel bolometer element is connected in a bridge circuit excited by a 1000-cycle source. The ratio of the resistances of the filaments should be constant and independent of ambient temperature or changes in bridge current. One of the strips is exposed to the radiant energy to be measured, which results in a change in the resistance ratio. It is very difficult to construct two filaments of identical resistance, and second-order fluctuations are minimized by the addition of corrective networks in the bridge. Bridge unbalance is amplified by a bridged T inverse feedback circuit because it is necessary to discriminate against the harmonies of the fundamental 1000 cycles. In order to drive a D.C. recorder, the signal must be rectified, and this is followed by a degenerative D.C. amplifier for impedance matching purposes. A vacuum tube fork generator is used as the bridge source with a highly degenerative amplifier. This combination provides a 1000-cycle source of harmonic content less than 0.5%

Instrumentation

and a short-term (5 to 10 minutes) stability of about 0.01%. The complete bolometer assembly in an infrared spectrometer can produce a permanent record of the spectrum from 2 to 14 microns in 40 minutes. For the study of hydrocarbon mixtures, the useful region of 7 to 14 microns is recorded in less than 24 minutes. The present useful sensitivity for full scale of the recorder corresponds to a change of bolometer temperature of $11° \times 10^{-4}$ C., and assuming that $\frac{1}{100}$ of full scale can be read, the minimal detectable temperature is 11 micro °C. The response time of the over-all bolometer system is about 0.8 second to attain $1/e$ times the full deflection.

A second paper presented by Brockman at the same meeting describes the production and properties of nickel bolometers. Most of the difficulties in handling thin metal films are avoided in the ingenious scheme of electroplating nickel on 0.002-inch copper foil which is folded flat around a copper plate. After deposition, the copper foil, with nickel on one side only, is cut into 0.038×5 cm. ribbons with a special double-edged shear. A ribbon is then soldered to a platinum frame at both ends and to a support midway between the ends. Copper is then removed by its preferential solubility in concentrated potassium cyanide solution. For a given area and constant current density, the thickness of the nickel film is shown to be a linear function of plating time. Gravimetric and resistance determinations indicate that the thin films retain the properties of bulk nickel. The receiver elements are coated on one side with bismuth black. For a ribbon of mass 6.6×10^{-6} gram the time constant turns out to be 5×10^{-3} second, which is confirmed by its behavior as a harmonic generator when excited by a 1000-cycle source.

"The Geiger-Müller X-ray Spectrometer" is the title of a paper presented by F. G. Firth of the North American Philips Co. at the annual meeting of the American Industrial Radium and X-Ray Society in November, 1945. Improvements in Geiger-Müller counters have permitted a marked reduction in time required for x-ray analysis. As described by the author the spectrometer of the asymmetric focusing type is used with a counter moving along the arc of the circle containing specimen and focus spot. The counter rotates 2θ degrees for θ degrees rotation of specimen. The radius of the circle changes with the Bragg angle. The x-ray tube is provided with interchangeable targets and operates on unrectified high voltage with voltage stabilization to 1%. The counter pulses are amplified and fed to inverter and limiting stages and then to an integrating stage. The counting rate can be read on a meter in this stage or applied by cathode coupling to a recorder. The recorder chart may be synchronized to the spectrometer drive to coordinate intensities with the Bragg angle. Scanning time can be varied for the 90° interval, between 22 minutes and 6 hours. Appropriate scaling circuits provide for the direct counting of pulses, and this becomes necessary when weak intensities must be measured. The number of counts required for a given precision follows from the law of probability, since the pulses occur with random distribution. The error is proportional to the reciprocals of the square root of the number of counts.

A wide range of practical applications is listed by the author; among them are analyses or measurements of particle size, identification by lattice parameters, effects of hardening and annealing treatment, analysis and identification of vitamins, insecticides, medicinals, fats and waxes, starches, sugars, and explosives.

These researches are characteristic of a trend to bring precision methods and tools out of the research laboratory and make them suitable for rapid, simply executed procedures in routine control work.

For those who may be interested in the background material relating to these papers the following sources are suggested: "The Measurement of Radiant Energy", W. E. Forsythe, Ed., McGraw-Hill, New York, 1937; "Applied X-Rays", G. L. Clark, McGraw-Hill, New York, 1940; "Applied Nuclear Physics", E. C. Pollard and W. L. Davidson, Jr., John Wiley, New York, 1942; "Electrical Counting", W. B. Lewis, Macmillan, New York, 1943; "Time Bases", O. S. Puckle, John Wiley, New York, 1943; "Basic Radio", J. B. Hoag, D. VanNostrand, New York, 1942; "Ultra-High Frequency Techniques", J. G. Brainerd, Ed., D. Van Nostrand, 1942.

We note with pleasure the return to the field of instrumentation of R. L. Garman, M. E. Droz, and D. J. DeCain after three years of research in radar. Garman heads the new laboratory of the General Precision Equipment Corp.

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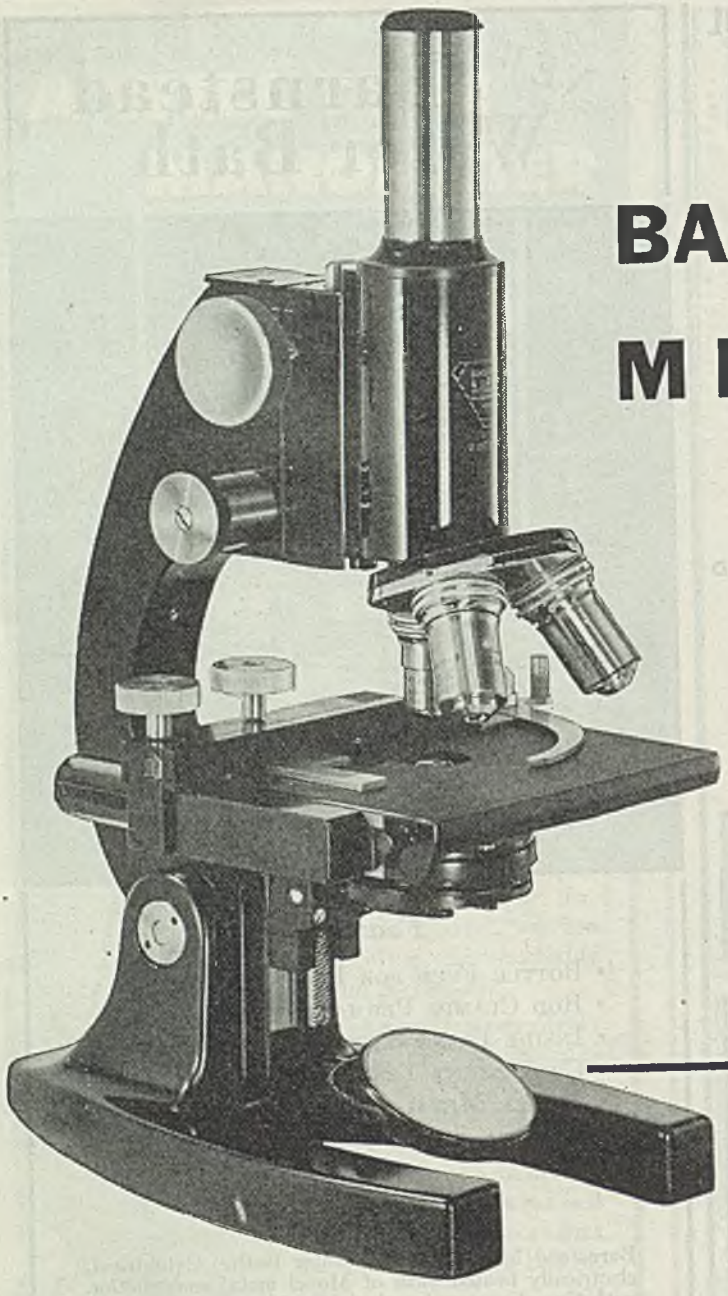

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