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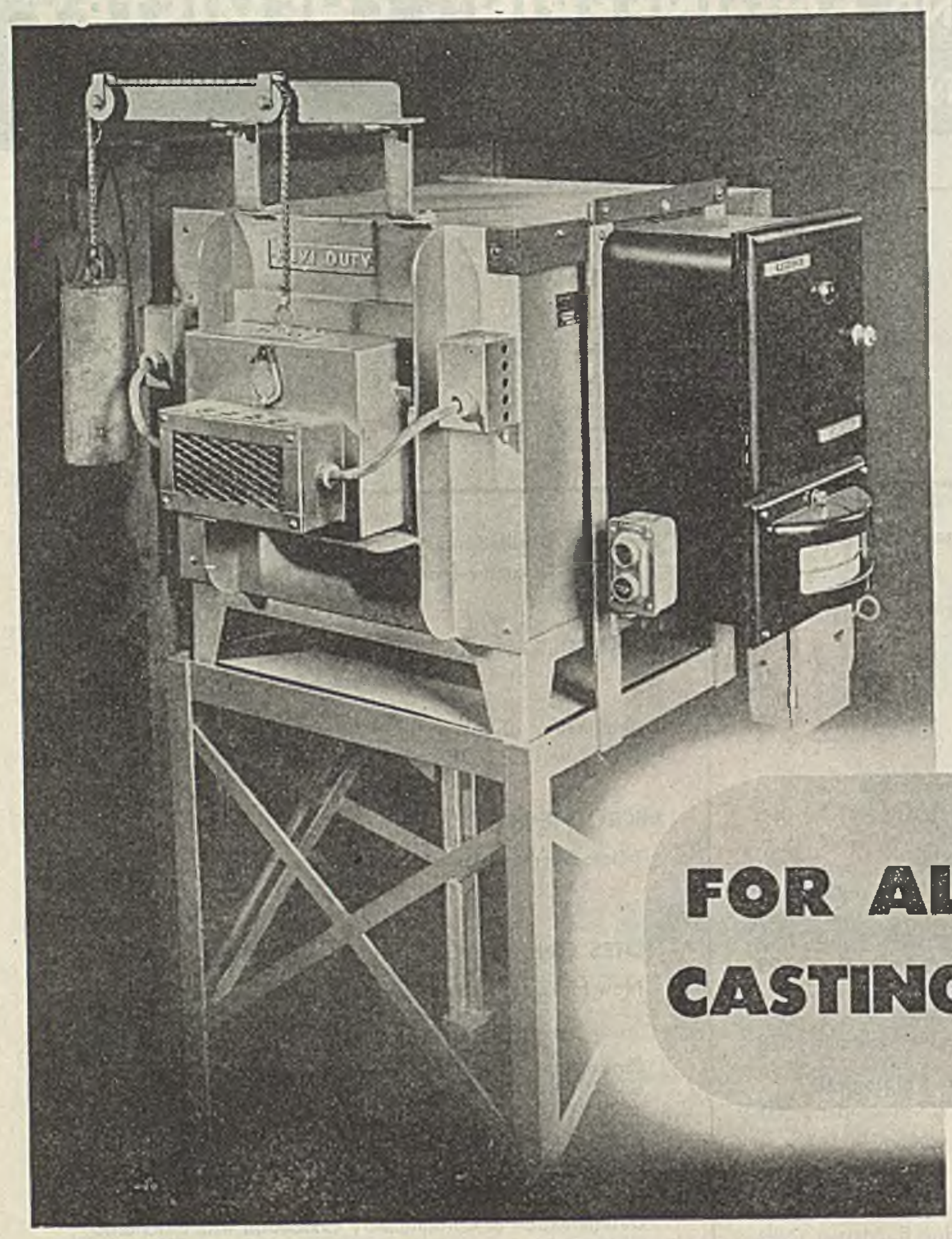
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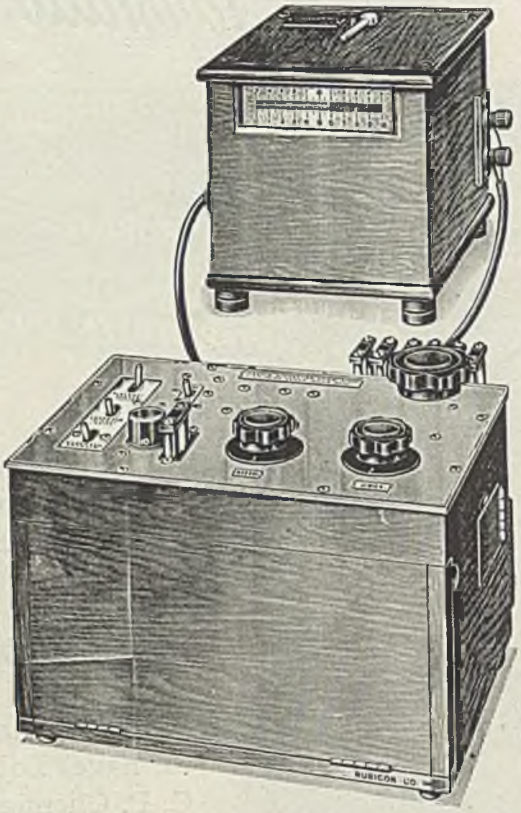

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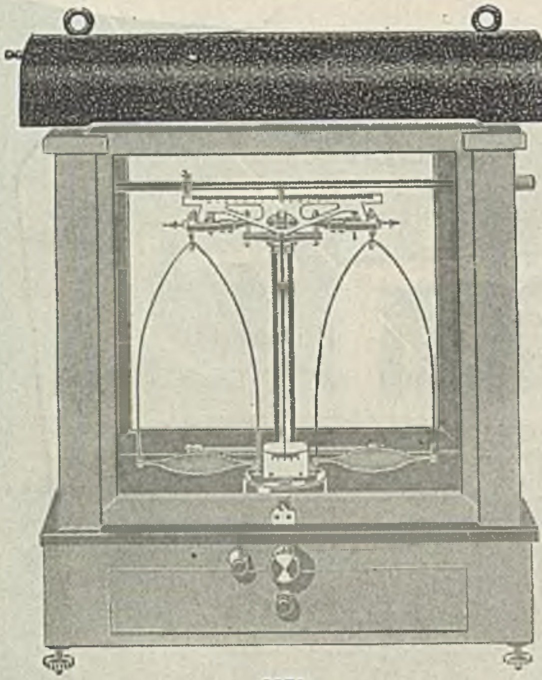
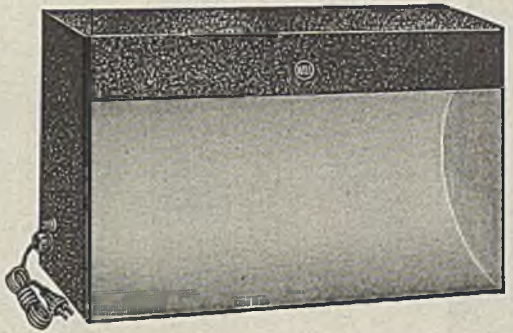


2071



10301

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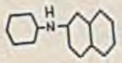

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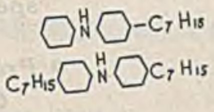

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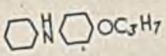

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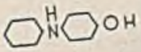

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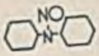

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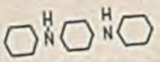

Diphenyl p Phenylene Diamine

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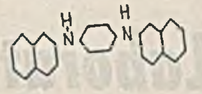

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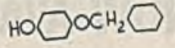
M. P. 230° C
Purity 98%



Monobenzyl Ether of Hydroquinone

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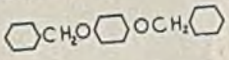

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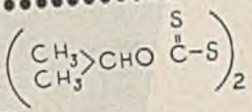
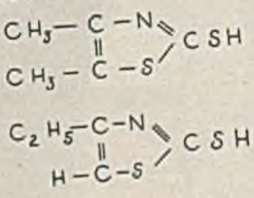


$\left(\begin{matrix}CH_3\\CH_3\end{matrix}>CHO\,\overset{S}{\overset{\|}{C}}-S\right)_2$

Di Isopropyl Dixanthogen

Available in commercial quantities
M. P. 52°
Purity 98%



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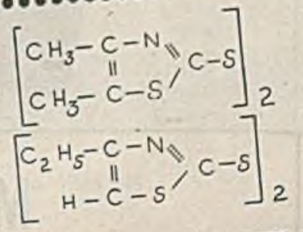

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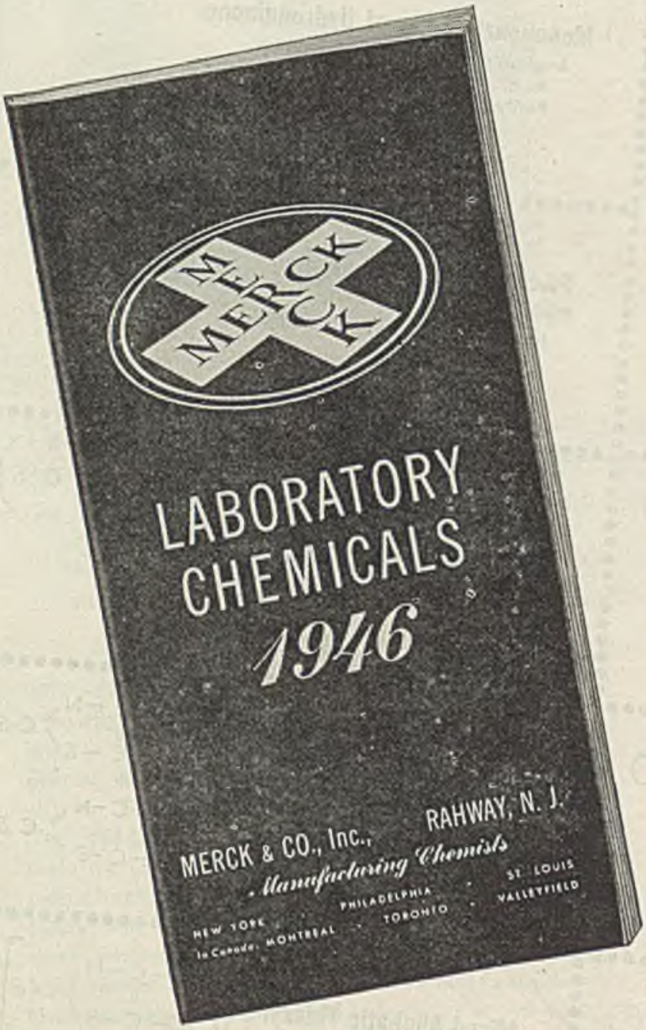
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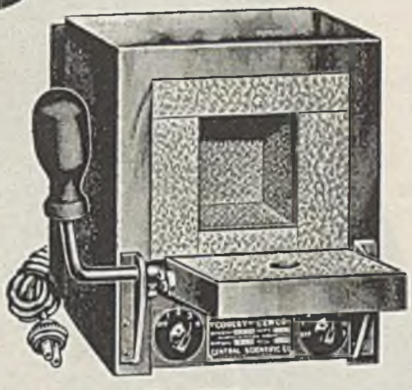

No. 13635-36

No. 13635 Cenco-Cooley Model SM1 Muffle Furnace with Rheostat Control, for ashing, igniting, and other laboratory purposes requiring a temperature of not over 1000°C. (1850°F.) intermittently or 950°C. (1750°F.) continuously.

The furnace is strongly constructed of heavy transite and sheet steel, amply insulated. The muffle consists of five pieces with four separable heating elements mounted in an improved refractory. The hinged door when open acts as a shelf.

Terminals extending through the muffle connect resistances on the outside back of the furnace. The terminal block, wiring and resistances are protected by a ventilated metal guard. Two dials control the resistances and provide temperature settings over a wide range. The dials permit four coarse and seven fine temperature settings for a total of 29. Seven temperatures are obtainable on each of the Off, 1, 2 and 3 positions and one, maximum temperature, on 4. Power required, 6.1 amperes. Dimensions: over-all, 11½ x 12 x 11½ inches. Muffle space: height, 4 inches—width, 3½ inches—depth, 4 inches.

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For volts, A.C. or D.C.	115	230
Each	$55.00	$59.00

No. 13636 Cenco-Cooley Model SM1 Electric Muffle Furnaces with Rheostat, same as No. 13635, but with the addition of a Pyrometer reading to 2000°F. and 1000°C.

No.	A	B
Voltage, A.C. or D.C.	115	230
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No. 13647 Cenco-Cooley Model SM2 Electric Muffle Furnaces with Rheostat, same as 13635 but of larger muffle dimensions. This furnace may be operated continuously at 950°C. or 1750°F. and intermittently as high as 1020°C. or 1850°F. Maximum current required, 19.7 amperes. Dimensions, over-all: 14 x 12 x 20 inches. Muffle space: height, 3 inches—width, 5 inches—depth, 8½ inches.

No.	A	B
For volts, A.C. or D.C.	115	230
Each	$86.50	$86.50

No. 13648 Cenco-Cooley Model SM2 Electric Muffle Furnaces with Rheostat, same as No. 13647, but with the addition of a Pyrometer for indicating muffle temperatures to 2000°F. and 1000°C.

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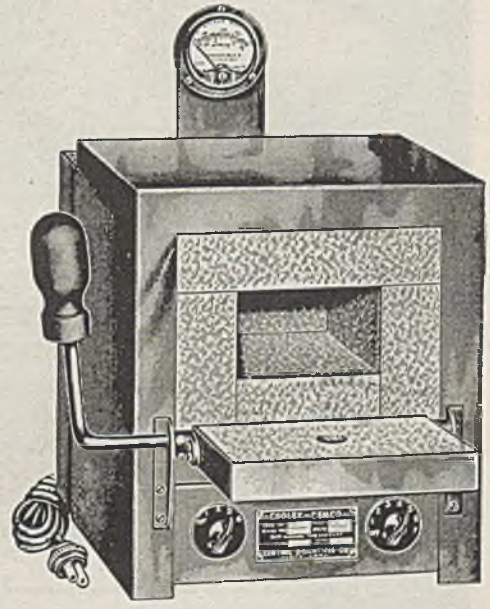

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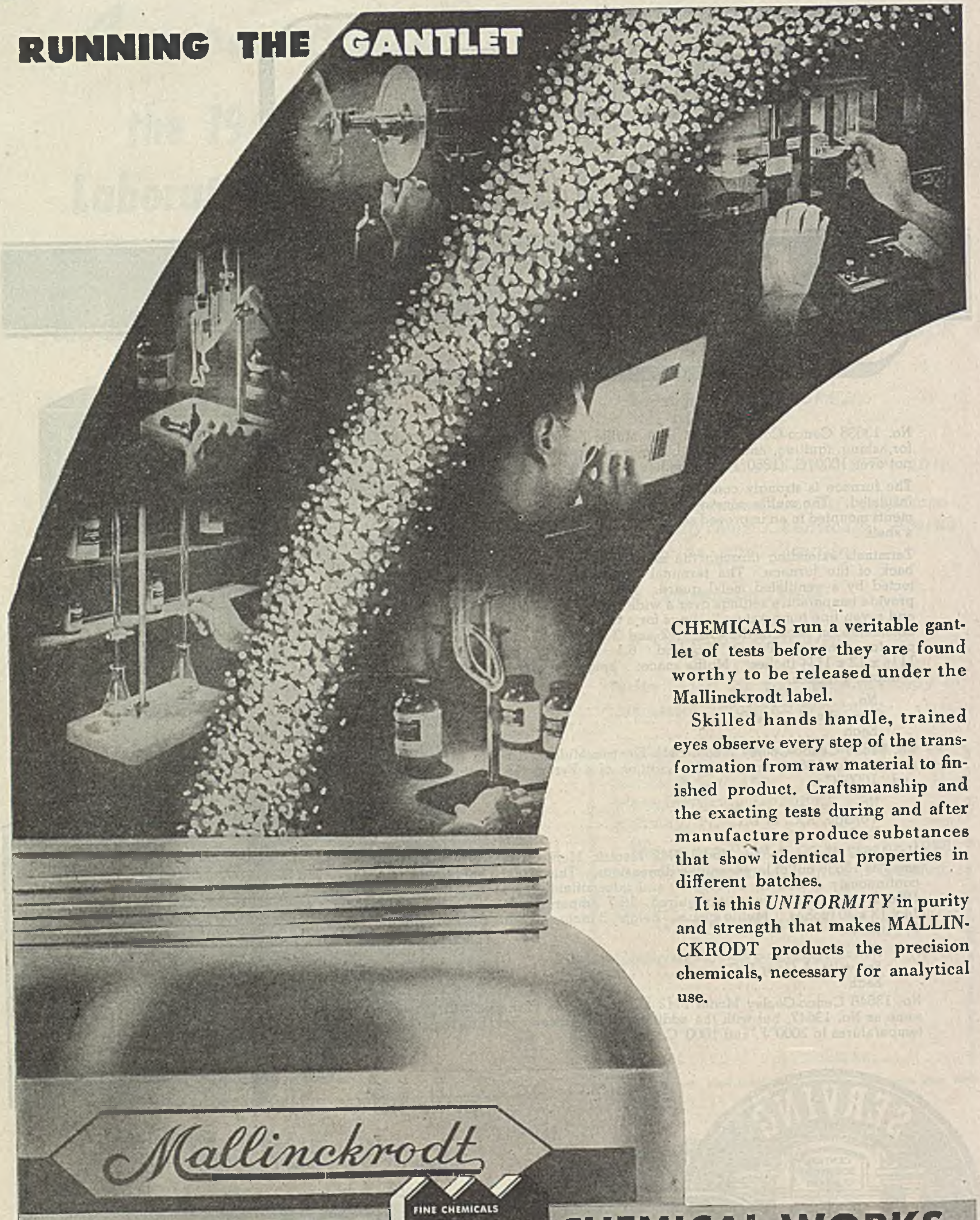
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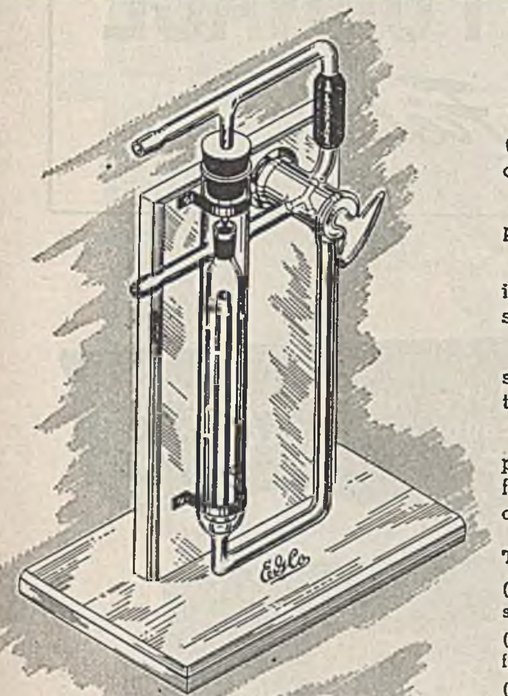

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By increasing the diameter of the float and the float chamber, we have increased the sensitivity to the point where any laboratory system can be held to within one micron of the pressure desired.

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The apparatus consists of three parts:

(1) The "U" tube which is the reservoir for the mercury and has three-way stopcock which connects to the system and central sealed-in tapered tube.

(2) A float which is weighted with glass at the upper portion and has a receptacle at the top into which is fitted a soft rubber disc or diaphragm.

(3) The manifold which has an orifice of correct size at the end of the tube, leads into the "U" tube and centers over the rubber disc on the float.

The principle of assembly and operation are as follows:

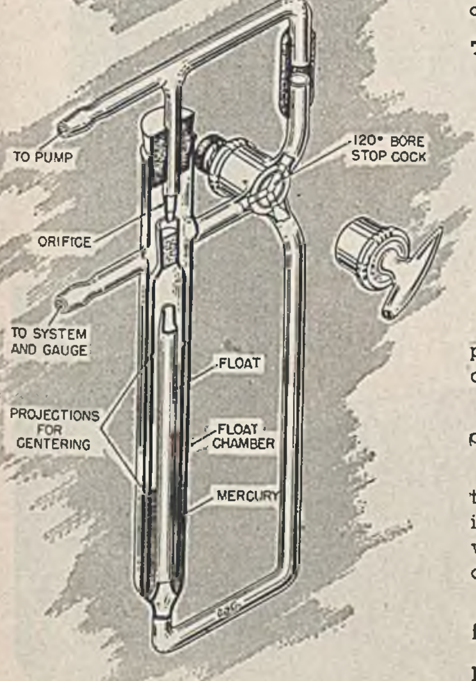
(a) The stopcock is put in "open" position.

(b) Mercury to a height of 2 in. is poured into the reservoir of the "U" tube and the float dropped in.

(c) The manifold is connected by tightly inserting the rubber stopper holding the vertical throttling tube. The tube is centered as nearly as possible over the diaphragm and set so that there is about a millimeter of clearance between the orifice and the disc.

(d) Connect to vacuum pump and system and start suction pump.

(e) When the desired vacuum is reached, close stopcock and system will immediately begin to function. If slightly reduced pressure (within a mm. or so of this setting) is desired, the orifice is pulled up slightly and vice versa, if increased pressure is wanted.



The functioning is explained by the fact that when the pressure is reduced to the desired point in the manostat and system, equal pressure exists within the mercury-sealed bell chamber of the float and outside of it. The mercury therefore is at the same level.

As soon as the stopcock is closed, it is obvious that any evacuation of the system can only be accomplished through the orifice which is now just exactly in contact with the disc.

The leak (not exceeding the capacity of the pump) now causes increased pressure in the system and consequent mercury displacement downward outside the float and upward inside the float. The float then sinks, opening up the orifice and permits unrestricted exhaust which then restores equilibrium as the float rises and pushes the disc in contact with the orifice and throttles the effect of the pump as required.

With properly assembled system, smooth accurate control is obtained with no visible fluctuations.

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Note: E-1853. Cartesian Manostat with two stopcocks, unmounted, still available at........each $19.50

For complete details, see article by Roger Gilmont in the October 1946, Analytical Edition of "Industrial and Engineering Chemistry."

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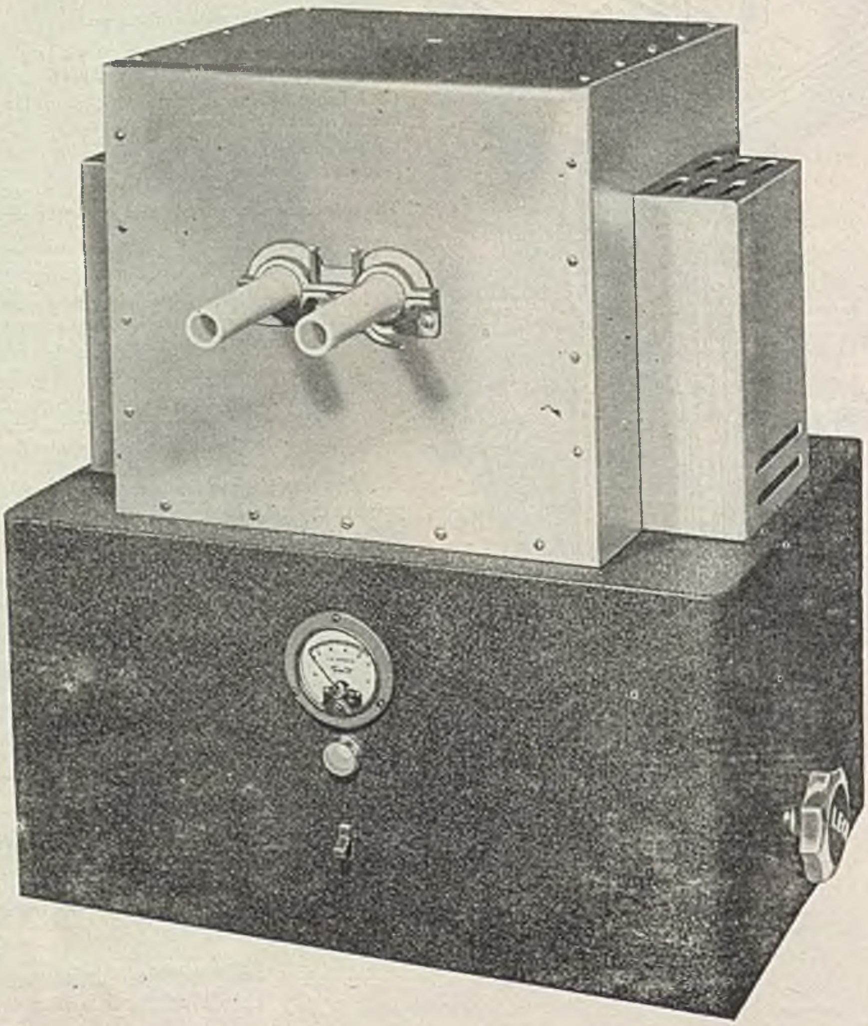

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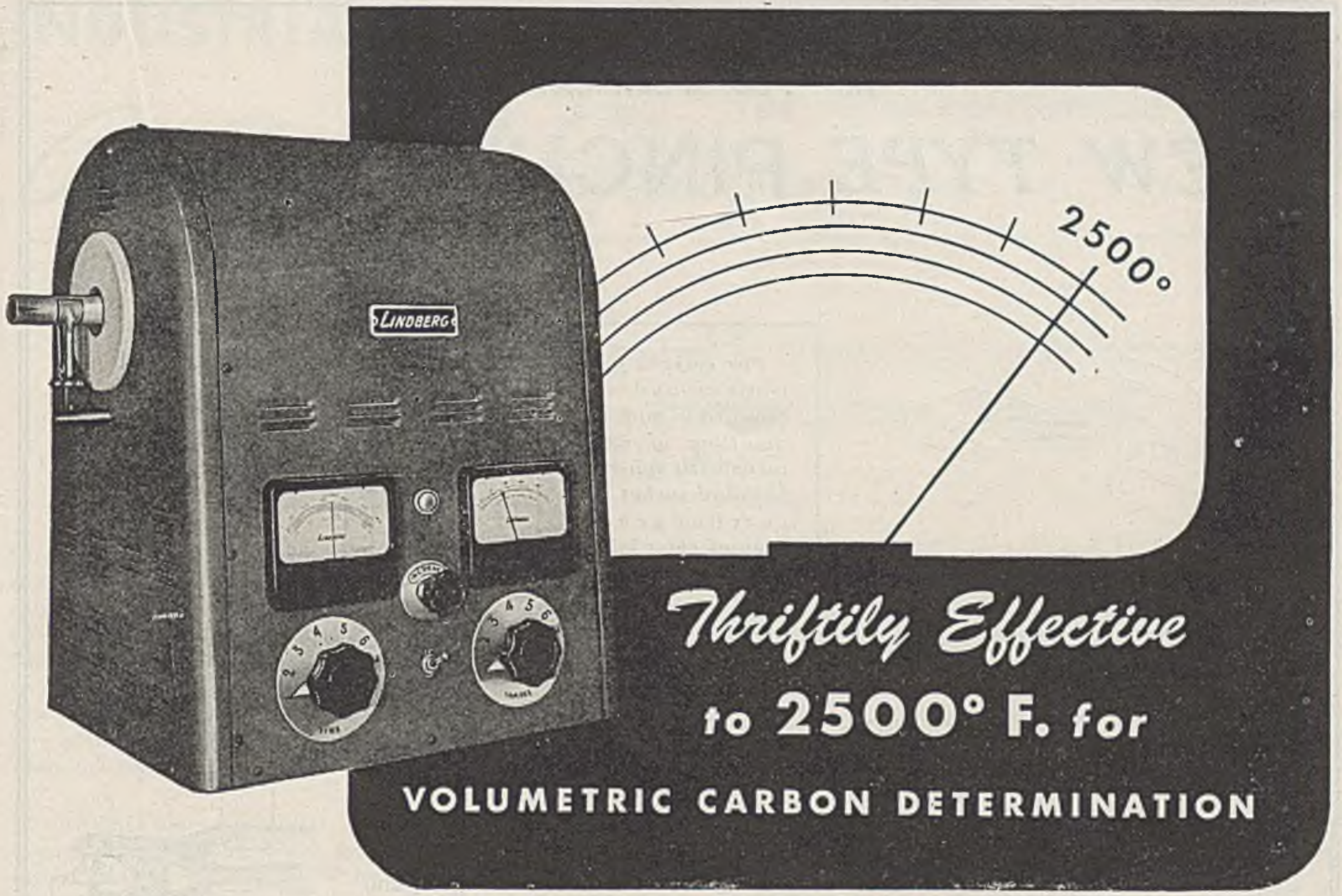

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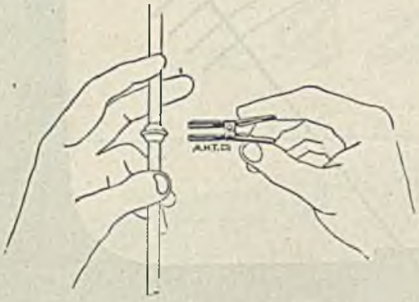


Fig. 1

Showing appearance of Sizes 12 and 18 and method of attaching to joints. Parts held securely by spring upon release of finger pressure.

For quick, convenient and safe mounting and dismantling of apparatus with spherical ball-and-socket interchangeable ground glass joints.

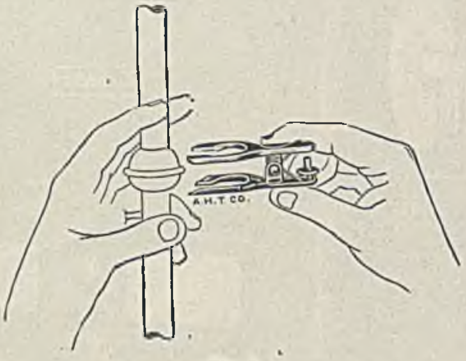
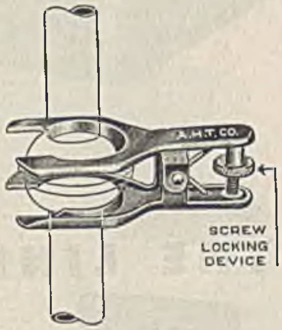


Fig. 2.

Showing appearance of Sizes 28 to 65, incl., and method of attaching to joint. After release of finger pressure, locking device is screwed into position.

3241.

Showing appearance of Sizes 12 and 18. Joint held securely by spring.



3241.

Showing appearance of Sizes 28 to 65, incl., with locking device screwed into position.

PINCH CLAMPS, A.H.T. Co. Specification (Patented), for use on spherical ball-and-socket glass joints. Of brass, with smooth, black, corrosion-resistant finish, and with strong, spring closed, forked jaws. With the two parts of the glass joint held in one hand, and the Clamp held between thumb and forefinger of the other hand, as shown in Fig. 1 and Fig. 2, the Clamp can be quickly slipped over the joint. When pressure is released, the two parts are held securely by the spring.

Sizes 28 to 65, inclusive, are provided with a screw locking device in addition to the spiral spring, so that a considerable load can be suspended from the joint without danger of leakage. However, the Clamps are designed primarily for securing the joint and are not intended to replace the usual clamps, rings, tripods, etc., as ordinarily used for supporting glassware assemblies. The size number indicates the diameter in millimeters of the ball over which the Clamp fits.

The use of these Clamps adds greatly to the convenience and speed of mounting and dismantling glass apparatus with spherical interchangeable ground joints, and reduces the possibility of breakage in handling.

3241. **Pinch Clamps, A.H.T. Co. Specification**, as above described.

Size number	12	18	28	35	50	65
Takes spherical joint No.	12/1 to 12/5, incl.	18/7 and 18/9	28/11 to 28/15, incl.	35/20 and 35/25	50/30	65/40
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Determination of Extinction Corrections in Infrared Analysis of Gaseous Hydrocarbon Mixtures

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Infrared analysis of gaseous hydrocarbon mixtures involves determination of extinctions for the individual components. Experimental data must be corrected for second-order effects due to energy scattered within the instrument, the structure of the absorption band, and intermolecular action. A simple relationship permits correction for these deviations. The method simplifies the work connected with the calibration or recalibration of a spectrophotometer. Use of a reference substance is suggested as a diluting agent in cases where molecular interaction influences absorption.

INFRARED absorption spectrophotometry is slowly acquiring an important position in the routine testing of light hydrocarbon mixtures. Speed is one of the important requirements of these methods, and because much time may be lost in computing the results of infrared analysis, development of abbreviated procedures for such calculations becomes of considerable importance.

In the infrared analysis a certain proportion of time is spent in estimating corrections for second-order effects, the magnitude of which varies with the pressure and composition of the hydrocarbon mixtures. The normal procedure involves the use of several correction factors, but their separate determination and practical application are somewhat tedious because of the absence of a straight-line relationship between the factors involved (*1-6*). The present paper describes a simple method for developing such relationships which has been in successful use for a number of years in these laboratories.

Infrared analysis is based on the law of Beer and Lambert, which is applicable to monochromatic radiation as absorbed by an ideal absorbing medium. The law states that for equal intensities of transmitted light the concentration of the absorbing matter is inversely proportional to the thickness of the absorbent layer. On this basis the following expression gives the relationship between the number of molecules, n, distributed along the path of the radiation and the extinction, E:

$$n = kE \qquad (1)$$

where k is a constant. The extinction is obtained as the logarithm of the ratio of the incident to the transmitted radiation intensities. Radiant energy absorption expressed in this form is useful in infrared analysis because of the near approach in actual practice to the relationship expressed in Equation 1. However, it is frequently necessary to consider a small correction term to bring about linearity.

The extinction contributions of individual absorbing substances are considered numerically additive, subject to certain conditions which are taken into account below. In analyzing mixtures attempts are made to select some specific wave length for each individual component at which interference from the absorption bands of other components present will be negligible. This seldom can be achieved in practice and, as a result, a system of simultaneous equations must be solved in order to establish the effect produced on the observed extinction by the extinction contributions from each of the individual constituents of the mixture, so that they may be subtracted in effect. Either before proceeding with or during the course of these calculations the values of the observed extinctions must be corrected for the following sources of error in their measurements:

1. Correction for the energy scattered within the instrument and reaching the recording device by a circuitous path. This correction is regarded as an instrumental factor. Various methods are in use for making this correction, such as subtracting a small numerical value from the energy readings (*1, 3, 4*).
2. Correction for the energy received by the recording device from bands other than the one under investigation. This correction is for that energy portion of the optical beam which is not materially affected by the sample. It is exhibited in the case of an absorption band of the narrow or line type of structure and is the so-called error of band shape and finite slit widths (*3, 5*). The emphasis here on the energy consideration is that from the energy viewpoint this source of error can be treated in a manner similar to that in the case of the first type of error.
3. Correction necessitated by the unique absorption response exhibited by certain molecules in the presence of other molecules. This effect comes under the heading of pressure broadening of a band (*5*).

The proposed correction method outlined below makes it clear that carefully planned auxiliary experiments will be required to distinguish and identify the type of effect being corrected, since the effects themselves are of dissimilar origin and are yet corrected in a similar manner. For simplicity all these corrections may be regarded as a single correction for a particular curve. This can be considered as part of the simplification introduced by the present method.

By plotting observed extinction, E_o, for an individual hydrocarbon against partial pressure a curve is obtained. A difference, ΔE, will be exhibited between the observed extinction and the theoretical extinction. This is demonstrated in Figure 1.

Inspection of a large number of curves of the above type shows that for a particular curve:

1. Deviations from the theoretical tangent increase with increase in magnitude of the observed extinction.
2. The magnitude of the deviation or correction depends on the magnitude of the extinction and is independent of the nature and the pressure of the other hydrocarbons present, subject to the establishment of certain experimental conditions.
3. Corrections to be applied to the observed extinctions are proportional to the square of these values. Mathematically this relationship may be expressed as follows:

$$E_c = E_o\,(1 + \alpha E_o) \qquad (2)$$

where E_c is the corrected extinction.

The numerical value of the coefficient, α, varies with the instrument and instrument setting and should be determined experimentally as described further below.

The simplifications developed in this work involve the direct application of corrections to the observed extinctions. Usually only one curve at a given wave length requires correction. However, in a case where two curves at the same wave length require corrections an approximate correction can be assigned, and after the calculations are carried out, the exact correction may be estimated and applied.

Examples of bands which may be selected for routine inspection of hydrocarbon mixtures and which follow the above rules are shown in Table I. This tabulation is by no means exhaustive with respect to the hydrocarbons enumerated or to other absorption bands associated with the individual hydrocarbons listed.

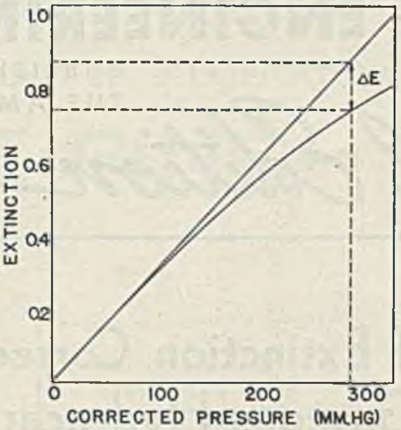

Figure 1. Deviation of Observed and Theoretical Extinctions

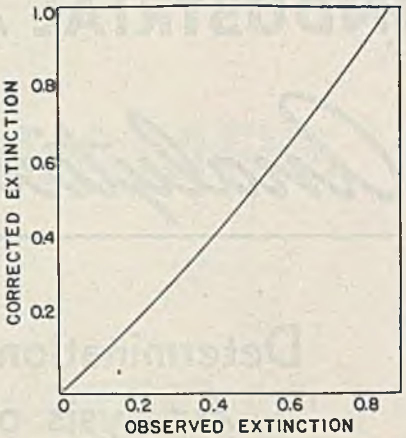

Figure 2. Relation of Corrected Extinction to Observed Extinction

Practical application of the suggested correction method for the observed extinction values may be visualized from the following detailed description of the individual steps in calibrating or recalibrating an instrument.

1. Determine the extinctions at various partial pressures for absorption bands, each of which shows the largest possible deviation from a straight line at the instrument settings to be used. The isobutane band of the approximate wave length 8.4 microns is a suitable example for this purpose. Plot these extinctions against partial pressures reduced to the reference temperature and corrected for differences in deviation from the ideal gas laws (Figure 1).
2. Draw a tangent to the above curve passing through the origin. This tangent represents the theoretical values of the corresponding observed extinctions and the corrected extinctions computed by the use of Equation 2 should fall closely along this tangent.
3. Determine the difference between the theoretical and the observed extinctions at some suitable arbitrary pressure. In order to minimize the error in further calculations the largest difference which corresponds to the highest partial pressure should be selected.

Table I. Absorption Bands of Hydrocarbons Suitable for Use with Proposed Correction Method

Hydrocarbon	Approximate Wave Length, Microns
Methane	7.6
Ethylene	5.2
Ethane	12.0
Propane	13.2
Isobutane	8.4
Butene-1	5.5
Butadiene-1,3	6.3
cis-Butene-2	10.2
n-Butane	10.2
Isopentane	10.2
2-Methylbutene-1	11.0
Dimethylbutane-2,3	8.7

Table II. Comparison of Observed, Corrected, and Theoretical Values of Extinctions for n-Pentane

(Wave length 13.7 microns, various pressures. Corrections for deviations attributed to scattered energy)

Partial Pressure, Mm. Hg	Extinction			Deviation from Theoretical, %	
	Observed	Corrected	Theoretical	Observed	Corrected
50	0.076	0.077	0.076	0.0	1.3
100	0.151	0.154	0.152	0.7	1.3
150	0.222	0.228	0.228	2.6	0.0
200	0.293	0.303	0.304	3.6	0.3
250	0.363	0.379	0.380	4.6	0.3
300	0.453	0.455	0.456	5.0	0.2

As it follows from further description, establishment of the complete curve for observed extinctions at varying pressures is necessary only for locating the position of the tangent. After this position is established one point on the observed extinction curve is sufficient to locate the remainder of the curve. If this method is used, selection of the point and its very exact location become of primary importance.

4. Determine the value of the coefficient, α, in Equation 2 from the data obtained under item 3. Using this value, plot the corrected extinctions against the observed extinctions by employing this equation and substituting different values for E_o (Figure 2). In some instances a plot of observed extinctions against the correction factors is advantageous.

By assuming the validity of Equation 2, a mathematical method may be readily developed by which α may be determined directly from the experimental data.

As a further illustration, the following example is given of a practical application of the developed relationships.

Assume that an extinction corresponding to a certain band representing a hydrocarbon in a mixture under analysis has been determined as E_o, and the extinction as determined for the pure hydrocarbon is E_{op}. Referring to Figure 2, the corresponding corrected extinctions would be E_c and E_{cp}. Therefore, the per cent hydrocarbon in the mixture is equal to

$$\frac{E_c}{E_{cp}} \times 100$$

In the above example no corrections are shown regarding the interferences in the absorption band that may be caused by other hydrocarbons present. These ,corrections are made by solving a series of simultaneous equations as described in standard manuals.

The accuracy of the described correction method may be visualized from the following typical examples.

CORRECTION FOR SCATTERED ENERGY

To illustrate the accuracy of the correction method as applied to scattered energy, measurements were taken with a metal shutter on *n*-pentane at wave length 13.7 microns where sufficient intensity of scattered energy is present for tests. When the *n*-pentane band is tested by means of a transmitting LiF shutter, the measurements give a straight-line relationship. Thus the deviations obtained in the extinctions estimated from measurements made with a metal shutter may be readily attributed to scattered radiation within the instrument. As shown in Table II, the deviations between the corrected and theoretical extinctions are well within the experimental error of such measurements. The value of α as applied in this instance is 0.12.

Table III. Comparison of Observed, Corrected, and Theoretical Values of Extinction for Isobutane

(Wave length 8.4 microns, various pressures. Corrections for deviations attributed to band structure)

Partial Pressure, Mm. Hg	Extinction			Deviation from Theoretical, %	
	Observed	Corrected	Theoretical	Observed	Corrected
50	0.150	0.154	0.154	2.6	0.0
100	0.291	0.307	0.309	5.8	0.6
150	0.427	0.462	0.463	7.8	0.2
200	0.558	0.618	0.618	9.7	0.0
250	0.681	0.769	0.772	11.8	0.4
300	0.794	0.914	0.926	14.2	1.3

CORRECTION FOR BAND STRUCTURE

The deviations shown by isobutane at the wave length 8.4 microns are taken to show the application of the correction method to an instance where band structure is the factor involved. Isobutane does not exhibit pressure broadening of the band at this wave length (*5*) and the deviations are attributed to band shape (*3*). Both the scattered energy of the instrument on which these tests were made and the possibility of pressure broadening were checked in this laboratory for the wave-length setting used and found to be negligible. A value of 0.19 for the coefficient α is applied in this case. Results are shown in Table III.

It is clear that, within the experimental error, the proposed method applies to the correction of effects arising from band structure. This correction is characteristic of the band and therefore subject to experimental restrictions making modification of the calculation procedure necessary in some cases.

CORRECTION FOR MOLECULAR INTERACTION

The complex optical effects observed in the case of certain gases, of which methane is an example, have been repeatedly mentioned in the literature (*5*). It appears from these descriptions that certain absorption bands which fall into this category are not particularly desirable for analytical purposes where exact quantitative information is sought. However, the correction of this type of band is possible.

In cases where band broadening occurs, the absorption for the gas under investigation is influenced not only by the total pressure on the sample, but also by the nature of the molecules present, as is clearly shown in Figure 3. However, in such cases a single calibration curve for the absorber can be made to suffice by using a reference substance such as air as a diluting agent, so that the variations in the deviations due to the foreign substances present are made conveniently small.

Thus, if a sample is appropriately diluted and a fixed total pressure is used, Equation 2 holds for the correction listed under item 3. This may be visualized from the laboratory data shown in Table IV; α in this case is 7.59. The deviations of the corrected values are well within the accuracy of the measurements.

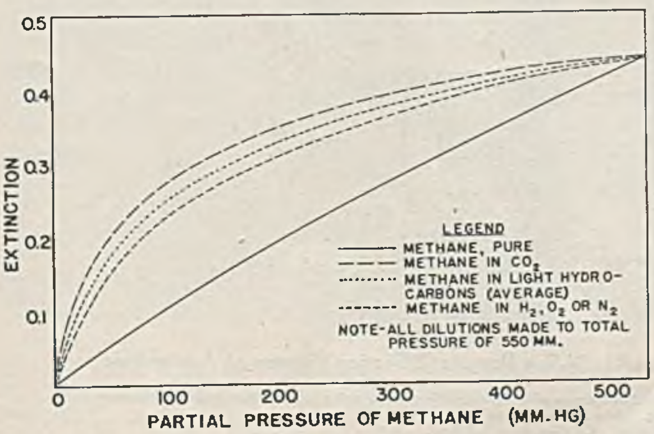

Figure 3. Extinction of Methane in Various Gases

Table IV. Comparison of Observed, Corrected, and Theoretical Values of Extinctions for Methane in Air

(Wave length 7.6 microns, total pressure of 400 mm. Corrections for deviations attributed principally to pressure broadening)

Partial Pressure, Mm. Hg	Extinction			Deviation from Theoretical, %	
	Observed	Corrected	Theoretical	Observed	Corrected
10	0.048	0.063	0.069	30.4	8.4
20	0.084	0.137	0.138	39.1	0.1
30	0.114	0.213	0.206	44.6	1.0
40	0.138	0.282	0.276	50.0	2.2
50	0.160	0.354	0.344	53.5	2.9
60	0.178	0.421	0.413	59.6	1.9
70	0.196	0.484	0.481	59.2	0.6
80	0.212	0.553	0.551	61.4	0.4
90	0.225	0.612	0.620	63.7	1.3

Table V. Comparison of Actual and Determined Compositions of Several Synthetic Blends

	Present, Mole %	Found, Mole %	Deviation, Mole %
	Sample 1		
Air	5.4	5.6	0.2
Methane	85.3	86.3	1.0
Ethylene	0.6	0.0	0.6
Ethane	4.8	5.1	0.3
Propylene	0.0	0.0	0.0
Propane	3.9	3.0	0.9
	Sample 2		
Methane	5.1	5.1	0.0
Ethylene	19.9	18.9	1.0
Ethane	28.4	29.5	1.1
Propylene	21.6	22.7	1.1
Propane	25.0	23.8	1.2
	Sample 3		
Air	11.7	11.7	0.0
Methane	38.2	39.7	1.5
Ethylene	9.9	8.7	1.2
Ethane	17.3	17.5	0.2
Propylene	8.1	7.9	0.2
Propane	14.8	14.5	0.3

ANALYSIS OF SYNTHETIC BLENDS

Table V shows the order of accuracy secured under actual analytical conditions. Synthetic blends were analyzed by diluting with air as described above. The hydrocarbon components were determined directly, while the air content of the original sample was obtained by difference. The deviations between the synthetic and calculated analyses are within the experimental error of the measurements.

ACKNOWLEDGMENT

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Identification of Organic Compounds by Use of Chromium Target X-Ray Diffraction Powder Patterns

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A study was made of the x-ray diffraction powder diagrams of a series of solid derivatives (anilides) of saturated aliphatic acids. It has been found that the use of chromium target x-radiation gives patterns of increased dispersion with the result that each member of the homologous series C_1 to C_{18} can readily be distinguished and identified. Structural isomers within the series may also be identified. Technical details on the use of chromium radiation for powder diffraction work are described. Tables of powder diffraction measurements are given.

THE use of x-ray diffraction patterns for the identification of crystalline material was outlined by Hull (*10*) in 1919 when he showed that a crystalline substance gives a diffraction pattern which is always the same for the same substance, and is sufficiently different from many of its chemical homologs to enable identification to be made. The application of the method has been mainly confined to inorganic compounds and minerals; the number of crystalline organic compounds recorded is relatively small. Of the one thousand patterns listed by Hanawalt, Rinn, and Frevel (*9*), forty-nine are of organic compounds. This is due in part to the complex nature of the powder patterns resulting from crystals of comparatively low symmetry. This condition should be improved if greater dispersion of the pattern were accomplished by the use of radiation of longer wave length and/or larger camera diameter and necessary refinement of collimator design. These difficulties were discussed at a recent meeting in England on the subject of physical methods of identification of materials, reported by Bannister (*2*). At this meeting Bunn suggested the use of larger camera diameter to give greater pattern dispersion.

The use of x-ray powder diffraction patterns for the identification of organic compounds poses certain unique problems. For example, the success or failure of the method in identifying individual members of a homologous series will depend upon the extent to which an additional methylene group affects the powder pattern of a typical member of the series. The differences between the patterns for each adjacent member must be sufficiently clear to establish identification. Similarly, the patterns for structural isomers must be distinctive. Rodgers (*2*) reported that in almost all cases powder patterns have proved exact enough to discriminate unambiguously between different organic compounds, even those of essentially similar chemical structure.

Recent work by McKinley, Nickels, and Sidhu on the identification of phenols (*13*) and by Clarke, Kaye, and Parks (*5*) on the identification of aldehydes and ketones by means of x-ray diffraction powder patterns clearly showed the applicability of the method. No published powder data, however, were available with which to evaluate the ability of the method to distinguish between each member of a homologous series, or of a number of structural isomers.

For the present work, the anilides of the saturated aliphatic acids were chosen. The identity of the anilides could readily be checked, as ample melting point data were available (*11*). These same anilides have been investigated by Robertson (*16*) for the purpose of relating melting point and molecular structure.

X-RAY APPARATUS AND TECHNIQUE

General Electric XRD Type I diffraction equipment was used in recording the powder patterns. Increased pattern dispersion was accomplished by the use of chromium K-α (λ = 2.285 *kX*) radiation. The effect on pattern dispersion of this longer wavelength radiation is illustrated in Figure 1. A very marked improvement in pattern dispersion and definition will be seen in the change from molybdenum K-α (λ = 0.708 *kX*) and copper K-α (λ = 1.537 *kX*). The same pattern dispersion could be accomplished by the use of larger camera diameters but the refinement in the collimator system required to give suitable definition of the pattern, together with the increased target to specimen and specimen to film distances, would require longer exposure times. The source of chromium radiation was a General Electric CA-6 Coolidge type tube with beryllium metal windows. The use of beryllium metal as the window of the tube is reported by Atlee (*1*) to give greatly increased useful intensity for wave length of x-radiation larger than 1.5 *kX*.

The filter used to pass essentially the K-α wave length was made from vanadium pentoxide (c.p., supplied by Eimer and Amend, New York, N. Y.) ground in cellulose acetate or nitrate cement (*14*). (Duco Household cement was found very satisfactory.) The mixture was thinned with amyl acetate and spread on glass to give a uniform film. After evaporation of the solvent, the film was stripped from the glass plate under water. The concentration found to give satisfactory removal of the Cr K-β lines was 15 mg. of vanadium pentoxide per square centimeter. This figure was determined by a series of powder photographs of sodium chloride taken with a range of concentrations of vanadium pentoxide in the filter. The concentration at which the (200) reflection due to K-β was barely detectable was considered satisfactory. The powder camera used was that of the General Electric XRD unit, the diameter being 143.2 mm. The specimen was mounted in a wedge, which was adjusted in the camera by sighting through the pinhole collimator to intercept one half of the beam. The tube was operated at a potential of 35 kv. and a current of 15 ma. Using Eastman Type K radiographic film the exposure time required was about 4 hours.

The relative intensities of the lines of the powder diffraction pattern should refer to randomly oriented powders. In the case of organic compounds which crystallize in needles or plates, this condition is experimentally difficult to obtain particularly in the case of wedge specimen mounts. The samples used were carefully ground in an agate mortar. In the case of one particularly plate-like material, propionanilide, a second sample was ground with Pyrex. No significant variation in relative line intensity was noted when compared to the previous photograph. The Pyrex adds considerably to the absorption in the specimen.

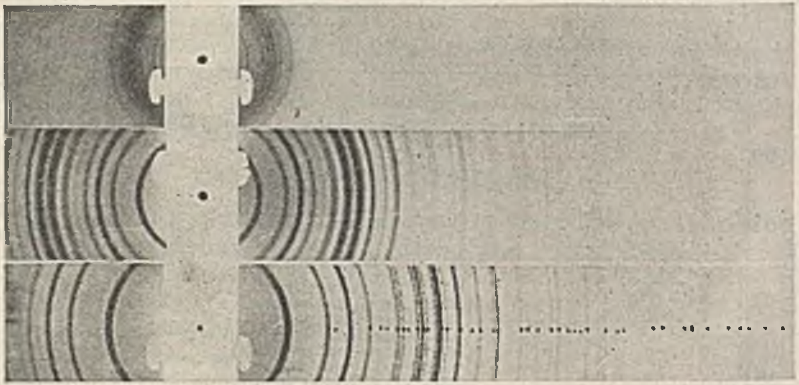

Figure 1. X-Ray Powder Diffraction Patterns of Acetanilide

Effect of change of x-ray wave length on pattern dispersion and resolution
Top. Mo K-α radiation, λ = 0.71 kX
Middle. Cu K-α, λ = 1.54 kX
Bottom. Chromium radiation, λ = 2.29 kX
Camera diameter 143.2 mm.

Table I. Melting Points of Anilides of Aliphatic Acids

Acid	No. of Carbon Atoms in Acid	Melting Point, ° C. (This Research)	Melting Point, ° C. (*11*)
Formic	1	47.6	50
Acetic	2	113.6	114.1
Propionic	3	104	104–104.5, 105.6
n-Butyric	4	93.5	92, 96, 97
Isobutyric	4	102.5	104–105, 105
n-Valeric	5	63	61–62, 62–63, 63
Isovaleric	5	109	109.5, 109–110, 110
α-Methylbutyric	5	109	105.5–106.5, 108, 110–111
Pivalic	5	132	128, 132–133
n-Caproic	6	94.5	92, 94–5, 96
Isocaproic	6	111	110.5, 111.5, 112
Enanthic	7	64	64, 65, 69
Caprylic	8	54	55, 57
Pelargonic	9	57.5	57
Capric	10	68	70
Undecylic	11	70	71
Lauric	12	78	76.5, 78
Myristic	14	85	80–82, 84
Palmitic	16	91	90.5, 90.6
Stearic	18	95	94, 95.5

Lindemann glass or beryllium metal powder might give improved results.

PREPARATION OF ANILIDES

Formanilide was prepared by boiling an equimolar mixture of 87% formic acid and aniline until the temperature of the mixture reached 280° C. (*18*). The product was recrystallized from low-boiling petroleum ether. By refluxing together equimolar quantities of the acid and freshly distilled aniline for 2 to 3 hours the following anilides were prepared: acetanilide (*19*), propionanilide (*6*), *n*-butyranilide, isobutyranilide, α-methylbutyranilide, pivalanilide, and caproanilide (*12*). The anilides of *n*-valeric, isovaleric, and isocaproic acids were prepared (*7*) by adding aniline to a benzene solution of the corresponding acid chloride in the proportion of 2 moles of aniline to 1 of acid chloride. In each case the mixture was brought to gentle reflux for 10 minutes, then cooled, and the aniline hydrochloride removed by filtration. Evaporation of the filtrate gave the crude crystalline anilide. In the same way the anilides of undecylic, lauric (*4*), myristic, palmitic (*7*), and stearic acids were prepared (*8*). The anilides of enanthic, caprylic, pelargonic, and capric acids were obtained by heating equimolar proportions of the acid and aniline in sealed tubes at a temperature of 160° to 190° C. for 2 hours (*15*). In general it was found that the anilides of lower members of the series (C_2 to C_5) could be crystallized readily from ethanol-water mixtures, the intermediate members (C_6 to C_{11}) could be crystallized from petroleum ether, and the higher members (C_{12} to C_{18}) could be crystallized from benzene.

The melting points of the prepared anilides, as well as the values given in the literature, are given in Table I.

DISCUSSION OF POWDER DIFFRACTION DATA

The powder diffraction data for the anilides of the normal aliphatic acids from C_1 to C_{12}, inclusive, and of the even-numbered carbon acids C_{14} to C_{18} as well as for the iso acids C_4, C_5, and C_6 and of two other structural isomers of the C_5 aliphatic acid are listed in Table II (p. 664). The intensities recorded were estimated from a visual examination of the film. The most intense lines of the patterns are listed in Table III and in Table IV the compounds are listed in order of the strongest line of the patterns.

Examination of the powder diffraction data for unique characteristics by which identity of the compounds can be established shows that the patterns of the anilides of the normal acids C_1 to C_8 are readily distinguished. The patterns of the even numbers of the series C_8 to C_{18} show a marked similarity, suggesting a uniformity of crystal structure which may be described as "isostructural". Each pattern, however, has unique characteristics by which it can be distinguished; this is particularly true of the longest *d* spacing recorded, which shows a measurable stepwise change with increasing chain length of the acid. Only two acids with an odd number of carbon atoms greater than C_8 were examined. These indicated that a separate isostructural series is formed by these compounds. These results are in agreement with the findings of Slagle and Ott (*17*) in their x-ray investigation of the fatty acids.

A graphic representation of the melting point *vs.* carbon chain length of the compounds as given by Robertson (*17*) (see Figure 2) shows no regular relationship up to C_8. From C_8 to C_{18} the data show regularly increasing melting points with increasing carbon chain length. This result is in conformity with the isostructural relationship found in the examination of the powder data.

The effect of structural isomerism on the powder diffraction pattern was examined in the case of the normal and isoisomers of butyric, valeric, and caproic acids. The pattern of the straight-chain derivative could be readily distinguished from that of its structural isomer. In the case of the C_5 acid four structural isomers were examined: *n*-valeric, isovaleric, α-methylbutyric, and pivalic acids. The diffraction patterns of the anilides of these acids could be readily distinguished.

Since the x-ray diffraction powder pattern is specific for each polymorphic form of a substance, the possible existence of such forms should be considered. From the x-ray diffraction examination no evidence was observed of polymorphic changes in these compounds. All samples were crystallized from solvents, at room temperature. These conditions would tend to give a product stable at room temperature. Patterns taken at intervals of several months on the same specimen showed no change. The

Table III. Four Strongest Lines of Powder Diffraction Patterns of Anilides of Some Saturated Aliphatic Acids

Name	No. of Carbon Atoms in Aliphatic Acid	1st Line	2nd Line	3rd Line	4th Line
Formanilide	1	3.61	3.75	3.09	5.16
Acetanilide	2	9.44	5.92	3.64	3.41
Propionanilide	3	3.75	6.17	8.59	4.46
n-Butyranilide	4	4.05	5.05	5.65	3.55
Isobutyranilide	4	7.09	4.05	5.72	4.47
n-Valeranilide	5	4.77	3.64	10.25	5.50
Isovaleranilide	5	7.41	4.13	9.95	5.00
d,l-α-Methylbutyranilide	5	7.28	4.17	3.28	5.17
Pivalanilide	5	7.14	4.20	4.62	5.00
n-Caproanilide	6	3.82	3.55	5.55	4.77
Isocaproanilide	6	4.21	7.51	4.80	3.53
Enanthanilide	7	4.70	4.15	4.00	3.78
Caprylanilide	8	16.4	4.03	3.94	8.06
Pelargonanilide	9	17.0	8.46	4.49	3.95
Capranilide	10	19.1	4.05	9.12	3.93
Undecylanilide	11	4.05	4.25	3.64	17.4
Lauranilide	12	3.86	20.7	3.75	3.61
Myristanilide	14	4.36	3.85	11.6	3.73
Palmitanilide	16	4.40	3.85	3.75	3.63
Stearanilide	18	4.41	3.85	3.74	3.65

Table IV. Data Arranged in Order of Strongest Line of Diffraction Pattern

1st Line	2nd Line	3rd Line	4th Line	No. of Carbon Atoms in Aliphatic Acid	Name
3.61	3.75	3.09	5.15	1	Formanilide
3.75	6.17	8.59	4.46	3	Propionanilide
3.92	3.55	5.55	4.77	6	*n*-Caproanilide
3.86	20.7	3.75	3.61	12	Lauranilide
4.05	5.05	5.65	3.55	4	*n*-Butyranilide
4.05	4.25	3.64	17.4	11	Undecylanilide
4.21	7.51	4.80	3.53	6	Isocaproanilide
4.36	3.85	11.6	3.73	14	Myristanilide
4.40	3.85	3.75	3.63	16	Palmitanilide
4.41	3.85	3.74	3.65	18	Stearanilide
4.70	4.15	4.00	3.78	7	Enanthanilide
4.77	3.64	10.25	5.50	5	*n*-Valeranilide
7.09	4.05	5.72	4.47	4	Isobutyranilide
7.14	4.20	4.62	5.00	5	Pivalanilide
7.28	4.17	3.28	5.17	5	*d,l*-α-Methylbutyranilide
7.41	4.13	9.95	5.00	5	Isovaleranilide
9.44	5.92	3.66	3.41	2	Acetanilide
16.4	4.03	3.94	8.06	8	Caprylanilide
17.0	8.46	4.49	3.95	9	Pelargonanilide
19.1	4.05	9.12	3.93	10	Capranilide

Table II. X-Ray Diffraction Data

Formanilide, C_1

d	I/I_1
14.0	0.50
7.28	0.15
7.03	0.20
6.19	0.05
5.94	0.10
5.61	0.25
5.32	0.40
5.16	0.70
4.86	0.40
4.69	0.70
4.33	0.70
4.13	0.10
3.81	0.50
3.75	0.80
3.61	1.00
3.52	0.02
3.45	0.05
3.25	0.40
3.09	0.80
2.99	0.10
2.93	0.05
2.81	0.15
2.65	0.05
2.55	0.05
2.52	0.05
2.38	0.05
2.34	0.05
2.30	0.05
2.24	0.05
2.18	0.05
2.04	0.05
2.01	0.05

Acetanilide, C_2

d	I/I_1
9.44	1.00
6.66	0.50
6.33	0.05
5.92	0.80
5.09	0.50
4.83	0.05
4.67	0.10
4.40	0.30
4.28	0.30
4.23	0.02
4.03	0.20
3.95	0.30
3.86	0.20
3.66	0.60
3.58	0.30
3.41	0.60
3.26	0.15
3.17	0.20
3.02	0.05
2.99	0.25
2.79	0.15
2.74	0.05
2.65	0.10
2.56	0.15
2.51	0.15
2.46	0.10
2.42	0.05
2.38	0.02
2.35	0.20
2.25	0.20
2.19	0.05
2.16	0.10
2.04	0.10
2.01	0.10
1.93	0.10
1.90	0.10

Propionanilide, C_3

d	I/I_1
8.59	0.60
6.17	0.80
4.86	0.40
4.46	0.60
3.75	1.00
3.21	0.60
3.08	0.02
2.82	0.10
2.70	0.10
2.59	0.05
2.56	0.10
2.40	0.05
2.26	0.05
2.20	0.10
2.16	0.10
1.93	0.05

n-Butyranilide, C_4

d	I/I_1
10.25	0.05
8.64	0.05
7.73	0.05
6.94	0.05
5.65	0.30
5.05	0.50
4.78	0.10
4.67	0.10
4.45	0.07
4.05	1.00
3.92	0.15
3.73	0.15
3.47	0.10
3.35	0.30
3.09	0.20
3.00	0.07
2.64	0.02
2.47	0.05
2.04	0.10

Isobutyranilide, C_4

d	I/I_1
9.94	0.40
7.09	1.00
5.72	0.60
5.00	0.50
4.77	0.50
4.47	0.60
4.20	0.10
4.05	0.80
3.86	0.20
3.62	0.05
3.47	0.02
3.35	0.30
3.18	0.20
3.11	0.15
2.99	0.02
2.29	0.05
2.25	0.02
2.05	0.07

d,l-α-Methylbutyranilide, C_5

d	I/I_1
10.27	0.20
7.28	1.00
6.58	0.05
5.80	0.60
5.17	0.70
4.93	0.30
4.77	0.30
4.63	0.70
4.55	0.20
4.46	0.05
4.33	0.05
4.17	1.00
3.95	0.30
3.70	0.30
3.43	0.60
3.28	0.80
3.12	0.40
3.01	0.15
2.95	0.10
2.89	0.15
2.71	0.10
2.61	0.10
2.46	0.10
2.33	0.15
2.22	0.05
2.20	0.05
2.09	0.10

Isovaleranilide, C_5

d	I/I_1
9.95	0.80
7.41	1.00
7.00	0.02
5.85	0.50
5.00	0.70
4.75	0.70
4.59	0.05
4.13	1.00
3.88	0.20
3.70	0.20
3.47	0.20
3.34	0.70
3.19	0.70
3.07	0.20
2.66	0.30
2.45	0.05
2.29	0.05
2.11	0.05
2.04	0.10

n-Valeranilide, C_5

d	I/I_1
10.25	0.60
6.48	0.50
5.50	0.60
5.25	0.60
4.77	1.00
4.59	0.05
4.44	0.05
4.25	0.10
3.78	0.15
3.64	1.00
3.50	0.20
3.39	0.30
3.33	0.10
3.00	0.05
2.88	0.05
2.38	0.10
2.04	0.10

Pivalanilide, C_5

d	I/I_1
7.14	1.00
6.10	0.01
5.83	0.20
5.21	0.20
5.00	0.50
4.62	0.60
4.51	0.30
4.41	0.15
4.20	1.00
4.04	0.10
3.37	0.20
3.29	0.20
3.13	0.10
2.98	0.02
2.91	0.05
2.85	0.02
2.74	0.02
2.65	0.02
2.44	0.02
2.39	0.02
2.33	0.05
2.26	0.02
2.23	0.05

n-Caproanilide, C_6

d	I/I_1
10.8	0.15
7.57	0.05
6.85	0.20
5.92	0.05
5.55	0.60
4.77	0.60
4.67	0.10
4.31	0.10
3.82	1.00
3.55	0.80
3.46	0.10
3.22	0.10
2.98	0.10
2.89	0.10
2.51	0.10
2.45	0.10
2.17	0.10
2.04	0.10

Isocaproanilide, C_6

d	I/I_1
14.8	0.20
7.51	0.80
5.92	0.30
5.59	0.05
5.16	0.30
4.80	0.80
4.36	0.30
4.21	1.00
4.05	0.10
3.80	0.10
3.53	0.50
3.45	0.10
3.31	0.50
3.12	0.15
2.93	0.02
2.89	0.02
2.83	0.05
2.78	0.05
2.72	0.02
2.56	0.05
2.53	0.05
2.45	0.10
2.36	0.10
2.29	0.05
2.25	0.05
2.19	0.10
2.13	0.15
1.99	0.10
1.94	0.05
1.91	0.05

Enanthanilide, C_7

d	I/I_1
8.13	0.20
7.21	0.30
5.88	0.60
5.72	0.10
5.59	0.10
5.16	0.02
4.70	1.00
4.47	0.02
4.15	0.80
4.00	0.80
3.78	0.80
3.59	0.60
2.27	0.10
2.21	0.10

n-Caprylanilide, C_8

d	I/I_1
16.4	1.00
12.9	0.20
11.1	0.20
10.2	0.20
8.06	0.50
6.65	0.10
5.59	0.20
4.77	0.10
4.38	0.20
4.22	0.20
4.03	0.60
3.94	0.60
3.82	0.20
3.66	0.20
3.22	0.05
3.14	0.15
3.06	0.10
2.89	0.05
2.57	0.05
2.39	0.05
2.10	0.05

Pelargonanilide, C_9

d	I/I_1
17.0	1.00
11.5	0.10
10.6	0.05
8.46	0.80
5.92	0.20
4.49	0.50
4.40	0.20
4.25	0.10
4.05	0.40
3.95	0.50
3.78	0.05
3.68	0.05
3.14	0.10
2.05	0.15

Capranilide, C_{10}

d	I/I_1
19.1	1.00
16.1	0.02
12.4	0.10
10.8	0.05
9.12	0.80
6.40	0.15
4.86	0.30
4.45	0.50
4.23	0.50
4.05	1.00
3.93	0.60
3.81	0.40
3.67	0.30
3.50	0.10
3.14	0.30
2.98	0.10

Undecylanilide, C_{11}

d	I/I_1
17.4	0.20
8.89	0.20
5.98	0.15
4.66	0.02
4.44	0.05
4.36	0.05
4.25	0.50
4.05	1.00
3.89	0.20
3.64	0.30
3.42	0.15
3.29	0.02
3.21	0.10
3.14	0.05
3.06	0.05
3.02	0.05
2.81	0.05
2.45	0.10
2.35	0.02
2.30	0.02
2.29	0.02
2.24	0.05
2.18	0.05
2.07	0.02
2.04	0.05
2.00	0.05

Lauranilide, C_{12}

d	I/I_1
20.7	0.60
10.30	0.15
9.27	0.30
8.13	0.30
6.94	0.02
5.37	0.15
5.17	0.10
4.52	0.10
4.38	0.40
4.05	0.30
3.86	1.00
3.75	0.50
3.61	0.50
3.14	0.20
3.07	0.02
2.33	0.05
2.30	0.05

Myristanilide, C_{14}

d	I/I_1
23.4	0.30
12.8	0.05
11.6	0.50
9.94	0.30
8.78	0.05
7.65	0.30
7.14	0.10
6.01	0.20
4.86	0.30
4.61	0.05
4.36	1.00
4.03	0.40
3.85	1.00
3.73	0.50
3.62	0.50
3.37	0.02
3.14	0.20
2.43	0.10
2.31	0.05
2.18	0.02

Palmitanilide, C_{16}

d	I/I_1
12.6	0.50
10.3	0.10
9.12	0.02
8.21	0.30
7.34	0.05
6.55	0.15
5.31	0.15
4.86	0.20
4.56	0.05
4.40	1.00
4.23	0.10
4.13	0.05
4.00	0.15
3.85	1.00
3.75	0.60
3.63	0.60
3.14	0.10
3.06	0.02
2.42	0.10
2.35	0.02
2.30	0.05
2.11	0.02
2.07	0.02
2.04	0.02

Stearanilide, C_{18}

d	I/I_1
16.4	0.20
14.0	0.20
12.2	0.02
10.9	0.02
9.49	0.05
8.78	0.05
7.79	0.02
7.09	0.02
6.75	0.01
5.74	0.01
5.25	0.01
4.81	0.05
4.41	1.00
4.01	0.20
3.85	1.00
3.74	0.50
3.65	0.50
3.14	0.10
2.43	0.10
2.08	0.02
2.05	0.10

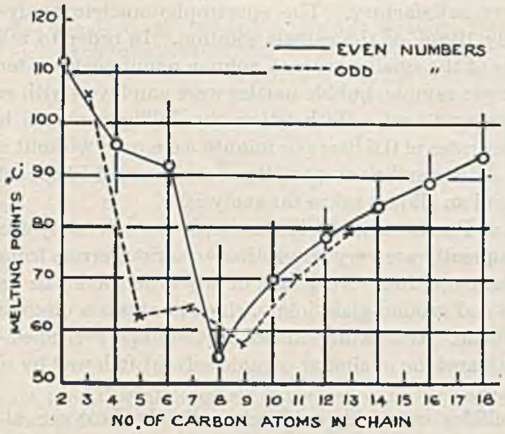

Figure 2. Effect of Chain Length on Melting Point of Anilides of Aliphatic Acids

Data from Robertson (*16*)

optical studies of Bryant (*3*) on the *p*-bromoanilides of the aliphatic acids showed metastable-polymorphic forms which, however, were evident only in crystallizations from melt.

It was noted that extreme purity of the crystalline samples was not necessary in obtaining distinctive diffraction patterns. For instance, a crude sample of acetanilide, melting 5° below that of National Bureau of Standards microanalytical acetanilide, gave a pattern identical with that of the purer sample. This is an indication that great care in recrystallizing a derivative until a constant melting point is reached may not always be necessary for identifications when the x-ray diffraction method is employed. This observation is in agreement with the authors' experience in the wider application of the method.

SUMMARY

Using chromium target x-radiation, the powder diffraction patterns for the anilides of the normal saturated fatty acids (C_1 to C_{18}) were shown to be sufficiently characteristic to enable individual identification. The anilides of structural isomers of several of the fatty acids gave distinctive diffraction patterns. Extreme purity of the crystalline derivatives was found to be unnecessary in obtaining characteristic patterns.

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Determination of Hydrogen Sulfide in Gases

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Two colorimetric methods have been developed for the analysis of traces of hydrogen sulfide in gases. The hydrogen sulfide is first absorbed in a caustic solution, and in the more sensitive method is converted to bismuth sulfide. The concentration of the resulting suspension is determined by means of a spectrophotometric measurement. In the absence of a spectrophotometer the sulfide is made to react with a uranyl-cadmium reagent and analyzed by visual comparison in a chromometer. With the spectrophotometric method as little as 7 micrograms of hydrogen sulfide may be determined with a precision of ±10%. For larger samples the precision improves to ±3%. The chromometer technique requires five times as much sulfide for equal precision, but still is far more sensitive than titration.

THE sensitivity of even the elaborate titration technique described by Shaw (*3*) for the determination of hydrogen sulfide is inadequate for such special applications as the study of catalyst poisons, particularly where the lack of sensitivity cannot conveniently be overcome by increasing the size of the sample to be analyzed. In a more effective procedure for the determination of traces of hydrogen sulfide, presented by Moses and Jilk (*2*), a photoelectric cell measures the degree of darkening of a lead acetate–impregnated tape through which the gases are passed. The present paper describes another approach to the problem whereby as little as 1.4 micrograms of hydrogen sulfide in aqueous solution can be detected optically. Two procedures were developed specifically to meet the problems of the identification and determination of organic sulfur compounds present as impurities in commercial gases and solvents. Their application to the solution of these problems will be described in succeeding papers.

Both of the analytical methods described employ a solution of the hydrogen sulfide in 6% aqueous sodium hydroxide. For the applications under consideration this involves scrubbing the sulfide-bearing gas with caustic. In the more sensitive of the two analytical methods the sulfide in solution is converted to bismuth sulfide and the concentration of the resulting suspension is determined by measuring the transmission of monochromatic light with a spectrophotometer. The precision of the analysis is determined by the amount of hydrogen sulfide collected in the absorbing solution. The precision is ±10% when 7 micrograms of hydrogen sulfide are collected. This corresponds to the amount of sulfur in 0.1 cubic foot of gas containing sulfur in a concentration of 0.11 grain per 100 cubic feet (1 grain per 100 cubic feet = 22.9 micrograms per liter). With larger concentrations of sulfur or a larger sample, a precision of ±3% can be achieved.

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The second method is useful when a spectrophotometer is not available. In this case cadmium sulfide is precipitated in the presence of uranyl ion and the sulfide concentration is then determined by matching of color and opacity against a blank in a visual comparometer. The sensitivity is approximately one fifth that of the spectrophotometric method, but is still far superior to that experienced in titration methods.

GENERAL PROCEDURE

Reagents. The following solutions are required.

Caustic Solution, 6% by weight. Dissolve 1130 grams of reagent grade sodium hydroxide in 10 liters of distilled oxygen-free water and dilute to 18 liters.

Bismuth Reagent. Dissolve 42.8 grams of c.p. bismuth nitrate pentahydrate in 3 liters of glacial acetic acid and dilute with 15 liters of distilled water.

Uranyl-Cadmium Reagent. Dissolve 44.4 grams of uranyl nitrate hexahydrate and 31.4 grams of cadmium acetate dihydrate in 20 liters of distilled water plus 4 liters of glacial acetic acid (all c.p.).

Standard Sulfide Solutions for Calibration Purposes. Prepare fresh each day by dissolving approximately 3 grams of c.p. sodium sulfide nonahydrate in 1 liter of the 6% caustic solution. Determine concentration by iodometric titration *(3)*. Dilute aliquots with 6% caustic to provide solutions of known concentrations for the calibrations.

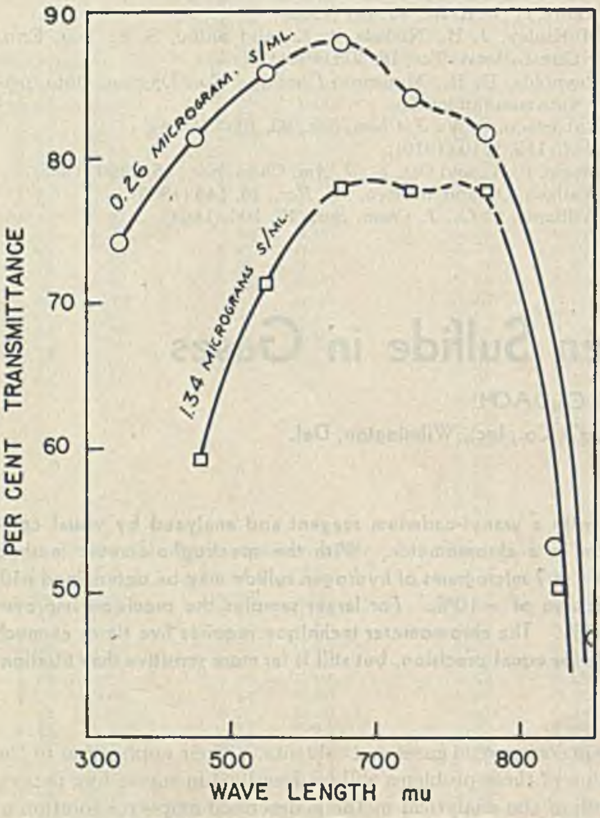

Figure 1. Light Absorption by Bismuth Sulfide Suspension

Scrubbing Hydrogen Sulfide from a Gas Stream. Both procedures employ a caustic solution of sulfide ion obtained by scrubbing the gas to be analyzed. To avoid oxidation of the sulfide ion the gas must be free of oxygen, but hydrogen, nitrogen, carbon monoxide, methane, ethylene, and up to 2% carbon dioxide do not interfere. Up to 1% oxygen in the gas to be analyzed is automatically removed by the procedure for converting organic sulfur compounds to hydrogen sulfide *(1)*. Hydrogen sulfide is readily and completely absorbed from a gas by bubbling through a 6% caustic solution. For the chromometer method a Milligan gas-washing bottle containing 100 ml. of 6% caustic has been found very satisfactory. The spectrophotometric analysis requires only 10 ml. of the caustic solution. In order to take full advantage of the smaller reagent volume requirement in terms of minimum gas sample, bubble bottles were employed with capacities as low as 10 ml. With either the Milligan or the bubble bottles, gas rates of 0.6 liter per minute were used without sulfide leakage. After a sufficient quantity of gas is scrubbed the solution is mixed and an aliquot taken for analysis.

General Precautions. The methods are extremely sensitive and consequently are very susceptible to serious errors from accidental contamination. No grease of any type should be used on stopcocks and ground-glass joints, since it causes a discoloration of the caustic. Glassware should be thoroughly cleaned, preferably with acetone or similar organic solvent followed by several water rinses.

Since sulfides are readily oxidized by dissolved oxygen, all solutions are deoxidized and transferred where possible under a blanket of nitrogen. The short time of exposure in the final mixing of reagents has a negligible effect.

The analysis requires the addition of either the bismuth or the uranyl reagent to the caustic solution of the sulfide. The order of mixing and the time of standing between preparation and analysis must be rigidly standardized. When the reagents are mixed, heat of neutralization is evolved, effervescence may occur, and crystal growth or agglomeration begins. These changes are rapid at first but become slow after 3 to 5 minutes. Despite the heat of reaction it was not found necessary to thermostat the solution. In the course of several hundred determinations by each method, no tendency for the precipitate to settle could be observed during the 10 minutes necessary for the analysis. (A private communication from J. K. Fogo, who was kind enough to check the spectrophotometric procedure, states that difficulty was encountered from a tendency of the bismuth sulfide to precipitate before the light transmittance could be measured. His suggestion that all trouble from this source may be avoided by adding 0.2% clear Knox gelatin to the bismuth reagent appears to have real value.)

The exact concentration of reagents is not critical; however, they must be so balanced that the final solution is weakly acid.

SPECTROPHOTOMETRIC METHOD

Equipment. A Coleman Model 10S double monochromator spectrophotometer was employed, in conjunction with a Coleman 310 electrometer. The cuvettes were cylindrical Pyrex tubes 16 mm. in inside diameter.

Procedure. To the 6% sodium hydroxide solution containing the sulfide, an equal volume of the bismuth nitrate–acetic acid reagent is added. The product is weakly acid, so that carbon dioxide is liberated from any carbonate present. The solution is mixed by bubbling deoxidized nitrogen (purchased as such in standard cylinders from Air Reduction Sales Co.) through it for 30 seconds and then is allowed to stand for exactly 5 minutes. A portion of this sample (10 ml.) is poured into the spectrophotometer cuvette. The spectrophotometer is balanced at an arbitrary 100% light transmission in the absence of the cuvette, and 7 minutes from the time of precipitation the per cent transmittance of sample is determined with the cuvette in place. The sulfide concentration is then read directly from a calibration chart.

When sampling a gas containing a very low concentration of hydrogen sulfide it is necessary to pass enough gas through the

Table I. Sample Calibration Data for Spectrophotometric Method

Micrograms/Ml.[a]	% Transmittance
0	84.1
0.292	69.6
0.292	68.8
0.292	68.0
0.73	52.7
0.73	51.1
0.73	51.1
1.47	31.5
1.47	32.4

[a] Diluted from standard solution containing 1.47 grams of sulfur per ml. as determined iodometrically.

Table II. Analysis of Hydrogen Sulfide–Bearing Gas by the Spectrophotometric and Colorimetric Methods

Run No.	H_2S Concentration (Arbitrary Units) Spectrophotometer	Colorimeter
1	17.1	17.7
2	18.0	17.7
3	20.6	22.9
4	20.6	21.2
5	22.4	20.5
6	20.6	20.5
7	20.6	20.5
7A	2.5	2.4
8	22.2	21.2
9	18.6	18.3
10	12.0	11.0
11	13.2	12.0

minimum quantity of caustic (10 ml.) to give between 6 and 40 micrograms of sulfur. When more concentrated gases are being analyzed, larger volumes of caustic solution can be employed or the sample can be diluted with fresh caustic, so that the final 10-ml. sample contains the amount of sulfur specified above.

Calibration. The calibration chart is made initially by repeating the above determinations on solutions of 6% sodium hydroxide containing known sulfide concentrations prepared from the standard solution. When the sulfide concentration of these solutions is plotted against the logarithm of the per cent transmittance the relationship is linear. A typical set of calibration data is shown in Table I. The slope of the line remains the same from day to day but the intercept at zero sulfide concentration shifts slightly from 85% transmittance, presumably because of changes in the reagents and photometric system. Once the slope is established, therefore, it is sufficient to calibrate the unit by mixing equal volumes of the sulfide-free caustic and bismuth reagents and measuring per cent transmittance to determine the zero point.

Selection of Reagent and Light Wave Length. Cadmium, lead, and bismuth were examined as reagents for the sulfide precipitation. Of these, bismuth sulfide produced the greatest changes in per cent transmittance of light for a given change in sulfide concentration. Consequently bismuth was selected for further study. The variation in transmittance of light as a function of wave length for aqueous suspensions of bismuth sulfide of two different concentrations is shown in Figure 1. It is seen that the greatest sensitivity is obtained at the shortest wave length which could be reached with the spectrophotometer employed, 350 millimicrons. All analyses were therefore performed with light of this wave length (actually 350 to 355 mμ). It is possible that even shorter wave lengths would have given greater sensitivity.

VISUAL METHOD

Equipment. During a period when the spectrophotometer was not available, visual comparisons were made by means of a Saybolt Standard universal chromometer No. 2895. A standard chromometer comparator tube was used for the blank, while the second tube was of special design with a leveling tube and plunger (Figure 2, an adaptation of the principle employed in the Kennicott, Campbell and Hurley colorimeter, Eimer & Amend Catalog No. 7-155). The light source was a G.E. Type H-3 mercury vapor lamp mounted in a Bausch & Lomb Type B adjustable microscope lamp housing. Polished standard thickness Corning filters 30 and 512, 5 cm. (2 inches) square, were mounted between the light source and the chromometer. A scale 10 units high (40 cm.) is mounted behind the tubes to measure the liquid height.

Procedure. A blank solution is prepared by mixing equal volumes of the 6% caustic and the uranyl-cadmium reagent. A sufficient quantity of this solution is put into the blank tube to fill it just to the "10" mark on the scale (approximately 120 ml.). An aliquot of the standard sulfide solution containing 30 to 200 micrograms of sulfur is diluted with 6% sodium hydroxide to 70 ml. and mixed by means of a stream of nitrogen. After mixing, 70 ml. of the uranyl reagent are added and again the solution is agitated with nitrogen. The solution is then poured into the special comparator tube and allowed to stand 3 minutes before balancing. The analysis is completed by adjusting the balancing plunger in the side arm of the comparator tube until the color and intensity of the sulfide solution match those in the blank as nearly as possible. The procedure is repeated with sulfide aliquots of different sizes.

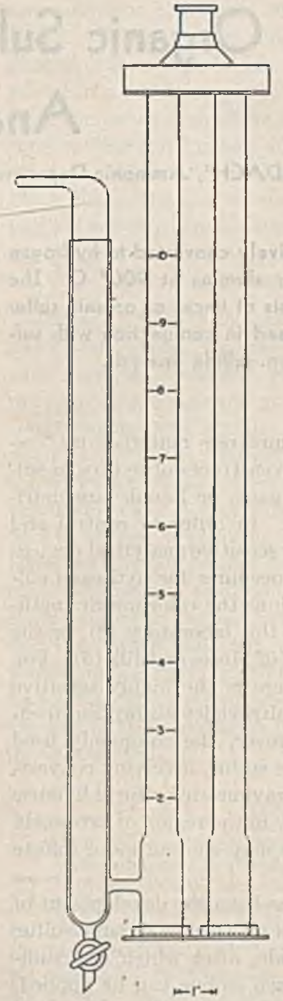

Figure 2. Chromometer Comparison Tube

If the logarithm of the balancing height is plotted against the sulfide content, a straight line is obtained except for a gentle curve near the origin. A new curve must be prepared each day because of uncontrollable variations. Unknown sulfide solutions are analyzed by the same technique. When collecting a sample sufficient gas must be passed through the minimum volume of caustic (70 ml.) to give at least 30 micrograms of sulfur in order to fall in the range of the chromometer. If more than 200 micrograms of sulfur is collected, an aliquot is taken.

Although the balance point is readily reproducible, a personal factor is definitely present. For maximum precision each operator should prepare his own calibration curves. Eye fatigue is a problem if a large number of analyses are involved.

A comparison of analyses by the spectrophotometric and the colorimetric methods is shown in Table II where the off gas from an experiment was analyzed simultaneously by both methods.

Discussion of Visual Technique. The function of the uranyl ion in the solution is not clear, but it greatly improves the accuracy of visual comparison over that with cadmium sulfide alone. The advantage gained by the use of the uranyl-cadmium reagent is limited to measurements in the chromometer and does not appear in spectrophotometer studies. The two filters mounted on the mercury lamp transmit only the green and blue components of the light, both of which are partially transmitted by the sulfide-free solution. When sulfide is added, the green transmission is unaffected but some blue is absorbed. The degree of absorption is a function of the concentration and height of the column of sulfide solution. A nearly exact color balance can be obtained between a sulfide-free and a sulfide-containing solution by adjusting the height of the latter.

The specially designed comparator tube with a plunger to balance the heights of liquid is more convenient to use and permits higher precision than comparators which depend upon stopcocks for establishing liquid levels. Very little extra liquid is required and the plunger permits approaching balance from either side until the operator is certain that the best match has been achieved.

ACKNOWLEDGMENT

The authors are indebted to numerous members of the laboratory staff for assistance in carrying out the work and in the preparation of this paper.

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Conversion of Organic Sulfur to Hydrogen Sulfide for Analysis

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Organic sulfur compounds are quantitatively converted to hydrogen sulfide by passing with hydrogen over alumina at 900° C. The technique has made possible the analysis of traces of organic sulfur compounds in gases or liquids when used in conjunction with sufficiently sensitive methods for hydrogen sulfide analysis.

MODERN catalytic processes require raw materials possessing a high degree of purity. Even traces of hydrogen sulfide or organic sulfur compounds in gases or liquids are detrimental to many catalytic reactions. In order to control and eliminate these catalyst poisons, highly sensitive analytical devices are essential. Several satisfactory procedures for hydrogen sulfide determinations are available, such as the colorimetric methods described in a recent paper from this laboratory (*2*), or the lead acetate-impregnated tape method of Moses and Jilk (*5*). For specific organic sulfur compounds there is the highly sensitive isatin test for thiophene (*1*) and the ultraviolet absorption technique for carbon disulfide (*7*). However, the commonly used combustion technique for total organic sulfur, involving converting the sulfur to sulfate followed by gravimetric or turbidimetric analysis (*3*, *6*), is very difficult to apply in the region of extremely low sulfur content where the reagents may contain more sulfate than the sample being analyzed.

The purpose of the present study has been the development of a technique for complete conversion of all volatile organic sulfur compounds present to hydrogen sulfide, after which any sufficiently sensitive procedure for hydrogen sulfide can be applied. A modification of the method presented by Jilk (*4*) was selected after a survey of various alternative procedures. In Jilk's method the gas containing organic sulfur compounds is freed from oxygen, humidified, and passed over activated alumina at 500° C. By raising the catalyst temperature from 500° to 900° C. as much as 1% oxygen in the gas was found to have no effect on the results. Humidification of the gas was not necessary, and complete conversion of methyl mercaptan and thiophene to hydrogen sulfide was obtained, whereas at 500° C. only 60 and 20% conversions were obtained, respectively. At 900° C. carbonyl sulfide, carbon disulfide, methyl mercaptan, thiophene, methyl thiocyanate, and sulfur dioxide were tested and found to be completely converted to hydrogen sulfide when passed over activated alumina in the presence of excess hydrogen. No other sulfur compounds were tested.

PROCEDURE FOR GASES

The gases, containing organic sulfur and excess hydrogen, are passed over 6 ml. of 14- to 20-mesh alumina (desulfurized Alorco Grade A, or gel prepared by precipitation from aluminum nitrate solution with ammonia) in a 10-mm. inside diameter quartz or Vycor tube heated to 900° in a vertically mounted split electric furnace. All connecting lines are glass; rubber joints, where unavoidable, are boiled in caustic to remove sulfur, and a minimum of rubber surface is exposed since rubber reversibly absorbs sulfur compounds. Gas rates up to 0.6 liter per minute were found permissible. To avoid errors caused by absorption on the catalyst, it is desirable to equilibrate the catalyst with the gas for at least 30 minutes; with small samples the catalyst may be purged with pure hydrogen for one hour before the analysis, and the adsorbed sulfur removed by another 1-hour purge to conclude the analysis. The hydrogen sulfide-bearing gas from the converter passes through a Milligan bubbler containing 6% caustic solution. The hydrogen sulfide absorbed is analyzed colorimetrically as described in an earlier paper from this laboratory (*2*).

PROCEDURE FOR LIQUIDS

The liquid to be analyzed is placed in a suitable bubbler and sulfur-free hydrogen is passed through it at a rate of approximately 0.6 liter per minute. The volume of liquid is adjusted to give a suitable quantity of hydrogen sulfide for subsequent analysis. The temperature of the bubbler is chosen to give a convenient rate of evaporation, and hydrogen is passed through it until the sample is completely volatilized. The gas stream is passed over alumina at 900° C. and the hydrogen sulfide collected in caustic, just as in the procedure for gases. The hydrogen stream is continued for another hour to flush the system and recover all sulfur adsorbed by the catalyst. Alternatively, nonvolatile or high-boiling liquids can be stripped of their volatile sulfur content with hydrogen by prolonged bubbling without complete vaporization of the liquid. In this case the analysis would necessarily be for volatile sulfur only. The time required is best determined by experiment, since it depends on the volatility of the sulfur compounds present.

Some vapors—for instance, benzene—deposit carbon on the catalyst. If the deposit becomes heavy the activity of the catalyst is lowered. Should this tendency exist, a very small sample must be analyzed or the catalyst must be regenerated periodically during the determination. Carbon deposits also increase the adsorption of sulfur on the catalyst and make necessary prolonged purging with hydrogen at the end of the analysis. Complete regeneration is accomplished by passing air over the catalyst for 5 minutes at 900° C. The catalyst is purged of sulfur before each regeneration. The regenerating air is by-passed around the absorbing solution to avoid oxidation of sulfide.

DEMONSTRATION OF CONVERSION TO HYDROGEN SULFIDE

Activated alumina (Alorco Grade A) or precipitated aluminum oxide when charged as 14- to 20-mesh granules in a quartz tube was found to give complete conversion at 900° C. at a space velocity of 3000 hours^{-1}. The hydrogenation was demonstrated for carbonyl sulfide, carbon disulfide, methyl mercaptan, methyl thiocyanate, thiophene, and sulfur dioxide, as shown in Table I. The determinations were made by introducing a measured volume of the gas or a weighed amount of the liquid into the gas stream. The actual concentration was therefore indefinite. It was found impractical to make up homogeneous gas samples for this purpose

Table I. Conversion of Organic Sulfur to Hydrogen Sulfide over Alumina at 900° C.

Sulfur Compound	Space Velocity	Average Sulfur Concentration		Carrier Gas	Converted[a] to H_2S
	Hours^{-1}	*Micrograms/liter*	*Grains/100 cu. ft.*		%
COS	2800	1260	55.7	H_2	97
	2800	1260	55.7	33CO-67H_2	96
	2800	500	21.9	H_2	104
	17,000	96	4.2	33CO-67H_2	100
	Empty tube	440	19.4	33CO-67H_2	100
CS_2	3000	530	23.0	H_2	96
CH_3SH	3000	1010	44.5	33CO-67H_2	109
	3000	1260	55.7	H_2	100
CH_3SCN	3000	343	15.0	H_2	100
C_4H_4S	3000	457	20.0	H_2	100
	2500	171	7.5	33CO-67H_2	97

[a] Deviations from 100% are considered within precision of experiments.

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Table II. Determination of Sulfur Content of Liquids

Solvent	Sample *Ml.*	Sulfur Compound	Sulfur *Micrograms/ ml.*	Found[a] %
No. 30 white oil	25	COS	13.7	92, 92
	25	CH_3SH	14.2	96
	25	C_4H_4S	110	102, 97
Benzene	5	CS_2	640	98, 101, 99
	2	C_4H_4S	8.3	99, 98, 100

[a] Deviations from 100% are considered within precision of experiments.

because the sulfur content dropped fairly rapidly with time when stored either in a water-sealed holder or in a metal cylinder.

Carbonyl sulfide is most readily converted to hydrogen sulfide. As shown in Table I, conversion is completed at 900° C. even in the absence of a catalyst. In the presence of alumina a temperature of 500° C. is sufficiently high to assure complete conversion of carbonyl sulfide and carbon disulfide, provided oxygen is absent from the gas. (Oxygen is automatically converted to water by the catalyst when operated at 900° C.) However, even in the absence of oxygen, thiophene and mercaptans are not completely converted to hydrogen sulfide at 500° C.

Examples of sulfur determinations in liquids are shown in Table II. In the case of the white oil solutions the oil was not vaporized over the catalyst; instead, the volatile sulfur was removed by stripping. Some of the sulfur solutions were unstable, as evidenced by a decrease in volatile sulfur with time. The benzene solutions were completely vaporized and passed over freshly regenerated catalyst. The carbon formation from a single analysis was not sufficient to interfere with the analysis.

ADSORPTION OF SULFUR ON CATALYST

Even at 900° C. some sulfur is retained by the alumina catalyst. The amount retained represents an equilibrium value for a given concentration and does not affect conversion. In analyzing a continuous gas sample of fairly uniform composition it is therefore sufficient to operate the catalyst until equilibrium is established (0.5 hour), after which a sample can be analyzed without danger of error due to adsorption. In case sulfur is to be determined in a batch sample of liquid or in a gas of varying composition, the catalyst must be completely purged with hydrogen before starting the analysis and again after all the sample has been treated. With 6 ml. of 8 to 14-mesh alumina at 900° C., complete desulfurization of the catalyst is achieved by passing 28 liters of pure hydrogen over it.

GENERAL APPLICATION

The analytical technique can be applied to a wide variety of gases and liquids. Successful analyses have been carried out on such gases as hydrogen, carbon monoxide, methane, ethylene, nitrogen, and coke-oven gas, and such liquids as methanol, benzene, cyclohexane, tetralin, and white oil. No tests have been made in which the hydrogen content of the vapors passing over the hydrogenation catalyst was less than 30%. The presence of water vapor is not necessary but it is helpful in some cases in reducing carbon deposition. Carbon dioxide does not interfere, provided it is not present in quantities sufficient to neutralize the caustic scrubbing solution. Unsaturated compounds, either initially present or formed over the catalyst, do not interfere. Oils and tars which collected in the scrubber may cause trouble if present in quantity. Should this occur, the scrubber solution can be acidified and the hydrogen sulfide stripped out and reabsorbed. Oxygen in concentrations up to 1% in the gas stream has been found harmless.

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Identification of Sulfur Compounds in Gas Mixtures

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A sensitive method for identification and quantitative determination of sulfur compounds present in gas mixtures depends on differences in solubility of the sulfur compounds in an inert solvent. A complete analysis usually involves both an absorption and a stripping run in a multiple-plate saturator. The total sulfur content of the gas leaving the saturator is plotted against gas volume. A stepwise curve results, wherein the gas volume at which the sulfur concentration changes abruptly is characteristic of a specific sulfur compound and the magnitude of the change is a measure of the concentration of that compound. As yet an exhaustive evaluation of the method to determine its accuracy has not been made, but identification runs on partially purified manufactured gas and coke-oven gas are presented, the results of which are in general agreement with previous industrial experience.

THE problem of completely removing sulfur compounds from gases is frequently encountered, particularly in catalytic processes. The most suitable means for effecting sulfur removal depends on the types present. Hydrogen sulfide is the most common form of sulfur encountered, but it is usually accompanied by relatively small concentrations of such organic sulfur compounds as carbonyl sulfide, carbon disulfide, and mercaptans. A new method has been developed for identifying and determining the concentration of these organic sulfur compounds when present in concentrations of a few parts per million. The technique is based on differences in solubility in an inert solvent used in conjunction with a highly sensitive analytical method (*1, 2*). It is applicable not only to sulfur compounds but to any other class of compounds for which a sufficiently sensitive analytical method is available.

The accuracy and reliability of this method of identification have not been demonstrated on gases of known composition. Because of time limitations, the plant tests were made after only qualitative evaluation of the method on known gas mixtures. However, the results obtained on partially purified manufactured gas and coke-oven gas are in sufficient agreement with previous experience in the industry (*4*) to justify presentation at this time.

THEORY

The successful method herein presented is based on the following theory:

Henry's law generally applies to the solubility of gases in inert liquid at low concentrations. This law states that at equilibrium

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the concentration of a gas which will dissolve in a solvent is directly proportional to the partial pressure of the gas over the solvent.

$$p = H_T x$$

where p = partial pressure of solute over solution
H_T = proportionality constant at temperature T
x = mole fraction of solute in solvent

In the present application the sulfur compounds studied follow closely Raoult's law, which is a special case of Henry's law in which the proportionality constant is equal to the vapor pressure of the pure solute:

$$p = p_T x \qquad (1)$$

where p_T = vapor pressure of pure solute at temperature T

Since the partial pressure of a component in a gas mixture is equal to the product of its mole fraction and the total pressure,

$$p = Py \qquad (2)$$

where P = total pressure
y = mole fraction of solute in gas phase

Combining Equations 1 and 2, at equilibrium one mole of solvent will contain

$$x = \frac{Py}{p_T} \text{ moles of solute} \qquad (3)$$

Let n equal the number of moles of gas of composition, y, containing this number $\frac{Py}{p_T}$, of moles of solute.

Then

$$ny = \frac{Py}{p_T} \text{ moles of solute in } n \text{ moles of gas} \qquad (4)$$

or

$$n = \frac{P}{p_T} \text{ moles of gas} \qquad (5)$$

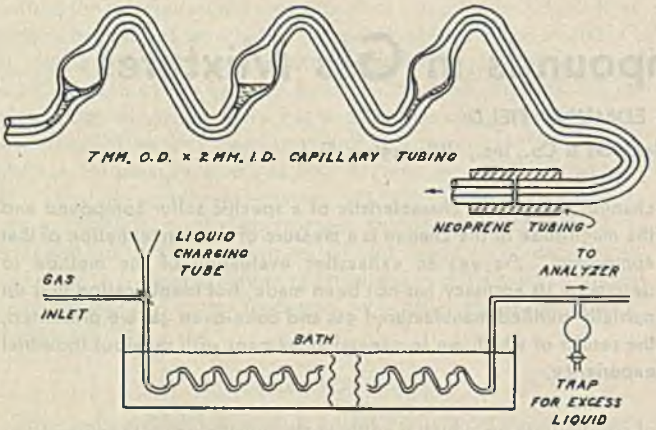

Figure 1. Diagram of Saturator

Thus the quantity of gas, n, which contains as much solute as one mole of liquid in equilibrium with it is dependent only on the ratio of the total pressure to the solubility coefficient or in this case the vapor pressure of the pure solute at the temperature in question. On the basis of a material balance, n is therefore the minimum quantity of the gas sample which could be used to saturate one mole of liquid with the solute and is a unique function of the solubility of this solute in the liquid. Hence an experimental determination of n reveals the solubility (or vapor pressure) of the solute. In the case of organic sulfur compounds this is usually sufficient to identify them. The relationships are the same, regardless of whether a liquid is being saturated by absorption of a component from a gas, or a gas is being saturated by stripping a component from a liquid.

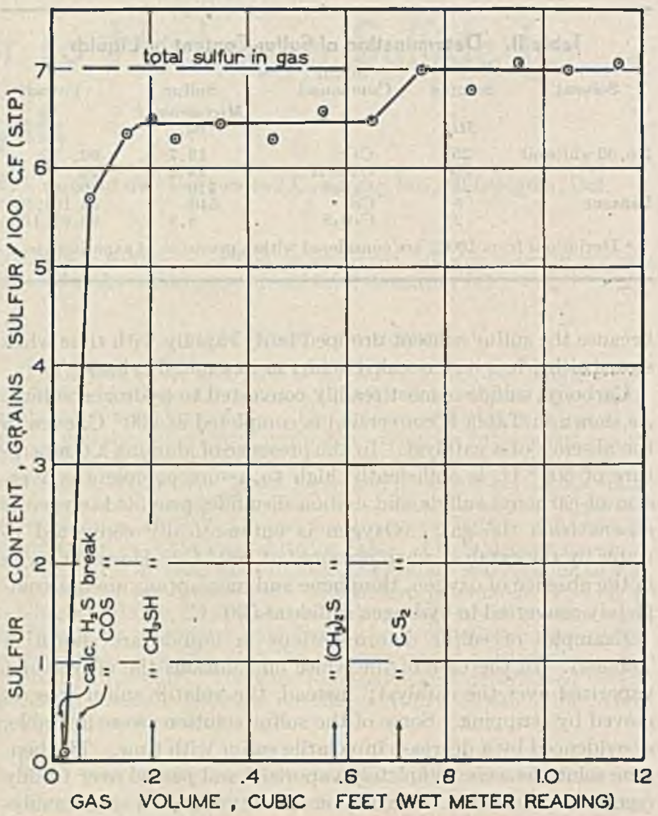

Figure 2. Composition of Blow Run Gas, Absorption Run

To determine these minimum gas quantities experimentally, it is necessary to have an efficient apparatus for contacting the liquid and gas, so that when absorbing the sulfur from a gas at least 80 to 90% of the liquid in the saturator can be saturated with the sulfur compound at the inlet gas composition before any of that compound appears in the exit gas, or when stripping sulfur from a liquid 80 to 90% of the saturated liquid will be stripped of a given sulfur compound before the sulfur concentration in the exit gas drops below the original saturation value. Such an apparatus is described below.

EQUIPMENT

A highly efficient saturator was constructed from twenty 60-cm. (2-foot) lengths of 2 × 7 mm. capillary tubing containing a total of 200 enlargements as illustrated in Figure 1. The sections are connected by butt joints with neoprene tubing. The scrubbing liquid, No. 30 white oil obtained from L. Sonneborn Sons, Inc., is introduced at the inlet end of the saturator (through the liquid charging tube) and distributed by passing a stream of hydrogen through the saturator. A very small quantity of liquid is retained in each enlargement, thereby providing 200 static pools of solvent. The entire unit is immersed in a liquid bath thermostated to ±0.5° C. A trap is provided at the exit end to catch any excess liquid carried out of the saturator.

The exit gases were analyzed by converting the sulfur compounds to hydrogen sulfide over alumina at 900° C. followed by spectrophotometric determination (*1*, *2*).

SAMPLE PROCEDURE AND CALCULATION FOR AN ABSORPTION RUN

The saturator was charged with 48 ml. of sulfur-free No. 30 white oil. The oil was distributed through the cells by means of cylinder hydrogen and the temperature adjusted to 14° C. Blow run gas from the generators was sampled after hydrogen sulfide removal in a Thylox unit by filling a stainless steel cylinder under pressure, and the analysis was started immediately. The gas was passed through the saturator at a rate of 0.005 cubic foot per minute and led directly to the analyzer previously described (*2*); total sulfur content was determined at frequent intervals. The

Table I. Vapor Pressure of Common Sulfur Compounds, Atmospheres

Compound	Temperature, ° C. −20°	−10°	0°	+10°	+20°	+30°	+40°	Reference
Hydrogen sulfide	5.39	7.53	10.2	13.6	17.7	22.6	28.3	(*3*)
Carbonyl sulfide	3	4.3	6	8.2	11	14	18	(*3*)
Methyl mercaptan	0.33	0.52	0.78	1.16	1.68	2.36	3.22	(*3*)
Ethyl mercaptan	0.095	0.158	0.251	0.398	0.602	0.890	1.284	(*9*)
Dimethyl sulfide	0.082	0.138	0.226	0.362	0.552	0.812	1.15	(*5*)
Carbon disulfide	0.061	0.101	0.132	0.263	0.392	0.550	0.816	(*5*)
Thiophene	0.008	0.016	0.029	0.050	0.082	0.13	0.20	(*7*)

volume of treated gas was plotted against its sulfur content (Figure 2). The total sulfur content of the unscrubbed gas was also determined and is shown by the dotted line.

Identification of the sulfur compounds present depends on the volume of gas corresponding to each "break" in the curve. For convenience in calculating the break volume, the vapor pressures of several common organic sulfur compounds have been collected in Table I. These values have been interpolated, extrapolated, or calculated where necessary to put the data in the form presented. The calculated break volumes for possible sulfur compounds are indicated by the arrows on Figure 2. When an increase in the sulfur content of the gas leaving the saturator occurs at a volume corresponding to the calculated break volume for one of the sulfur compounds it indicates the presence of that sulfur compound and the magnitude of the increase in sulfur content gives the concentration of that compound in the gas.

The break volume for carbon disulfide, for example, is calculated as follows:

$$n = \frac{P}{p_T} \tag{5}$$

p_T = 0.308 atmosphere for CS_2 at 14° C.
P = 1 atmosphere

giving n = 3.25 moles of gas to saturate 1 mole of oil with carbon disulfide.

But 48 ml. of oil were used (density 0.77, average molecular weight 154); so the amount of oil was $\frac{48 \times 0.77}{154 \times 454} = 0.000529$ pound mole. The amount of gas required to saturate the oil in the absorber is therefore $3.25 \times 0.000529 = 0.00172$ pound mole of gas. Under the wet meter conditions this gives a calculated break volume of $0.00172 \times 359 \times \frac{295}{273} \times \frac{760}{741} + 0.02$ cubic foot of free space in absorber = 0.70 cubic foot. The presence of carbon disulfide in the gas is shown in Figure 2 by the sudden rise in total sulfur at approximately the predicted 0.70 cubic foot break point. The amount of carbon disulfide is represented by the increase in sulfur corresponding to the break, or 0.6 grain of sulfur per 100 cubic feet (1 grain per 100 cubic feet = 22.9 micrograms per liter) at standard temperature and pressure.

The similarity in vapor pressure of hydrogen sulfide and carbonyl sulfide makes it difficult to distinguish between their break points. Hydrogen sulfide was therefore determined independently (1 grain of sulfur per 100 cubic feet) by absorption in cadmium acetate, made acid with acetic acid, followed by iodometric titration (*8*). Since the analysis of the gas at the end of the absorption run was 7 ± 0.3 grains of sulfur per 100 cubic feet, it was not possible to detect the presence of small concentrations of any sulfur compounds less volatile than carbon disulfide. However, by making a stripping run it was possible to determine the presence of any less volatile sulfur compounds because as the sulfur concentration in the gas drops below 1 grain per 100 cubic feet, the precision of the analysis becomes better than ±0.1 grain per 100 cubic feet as illustrated below.

EXAMPLE OF STRIPPING RUN

A 100-ml. sample of white oil was saturated with the same gas in the preceding example by bubbling the gas through the oil at a rate of 70 cubic feet per hour for 2 hours at −5° C. in a flask fitted with a sintered-glass sparger. About 50 ml. of this oil were transferred into the saturator and distributed by means of a slow stream of hydrogen, avoiding all contact with air. The saturated oil was stripped at 19.4° C. by bubbling a stream of hydrogen through it at a rate of 0.007 cubic foot per minute. The exit gas was analyzed for total sulfur and the sulfur content plotted against gas volume as before.

The break points for the different sulfur compounds were calculated exactly as in the preceding example. Because of the difference in temperature for the saturation and stripping, the concentration of sulfur in the absorber of gas did not correspond to that in the original sample. The correction was made by means of Raoult's law, as shown in the following example for carbon disulfide.

$$Py = xp_T \tag{3}$$

In this case,

P = 1
p_T = 0.416 atmosphere at 19.4° C.
p_T = 0.135 atmosphere at −5° C.

giving $y_{19.4°} = 0.416\,x$

and $y_{-5°} = 0.135\,x$

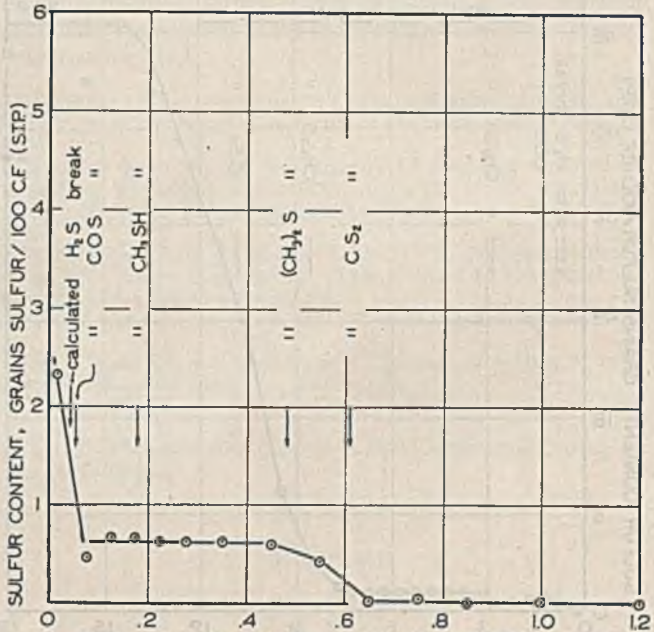

Figure 3. Composition of Blow Run Gas, Stripping Run

Since x, the concentration of gas in the solvent, is not changed when the saturated oil is warmed before stripping, it can be eliminated from the two equations to give

$$y_{-5°} = 0.33\,y_{19.4°}$$

Consequently, the concentration of carbon disulfide found in the stripping hydrogen must be multiplied by 0.33 to give the corresponding concentration in the original gas. A similar correction was made for each component present.

The volume of gas is shown plotted against sulfur content in Figure 3. For convenience in comparing with the absorption run on the same gas (Figure 2), the sulfur concentrations were corrected for temperature before plotting. As may be seen from the curve, most of the hydrogen sulfide and carbonyl sulfide was stripped from the oil before good total sulfur analyses were obtained. It is for the less volatile sulfur compounds that the stripping run is most accurate. The absorption and stripping runs therefore supplement each other and a complete analysis usually requires both determinations.

Figure 4 is included to illustrate the behavior of a gas more concentrated in sulfur. In this case the gas is coke-oven gas partially purified by scrubbing with water, light oil, and ammonium carbonate solution. This preliminary treatment removed essentially all of the hydrogen sulfide and high-boiling sulfur compounds, leaving primarily carbon disulfide and a little carbonyl sulfide.

TECHNIQUE AND SOURCES OF ERROR

Certain organic sulfur compounds have been demonstrated (*2*) to be relatively unstable even in an inert solvent such as white oil. Exposure to oxygen or to metal walls can also affect the sulfur content of a gas or solution. For this reason analyses are completed as rapidly as possible and the procedures for sampling are arranged to minimize such losses. The equipment itself is of glass and quartz with neoprene-connected butt joints where required.

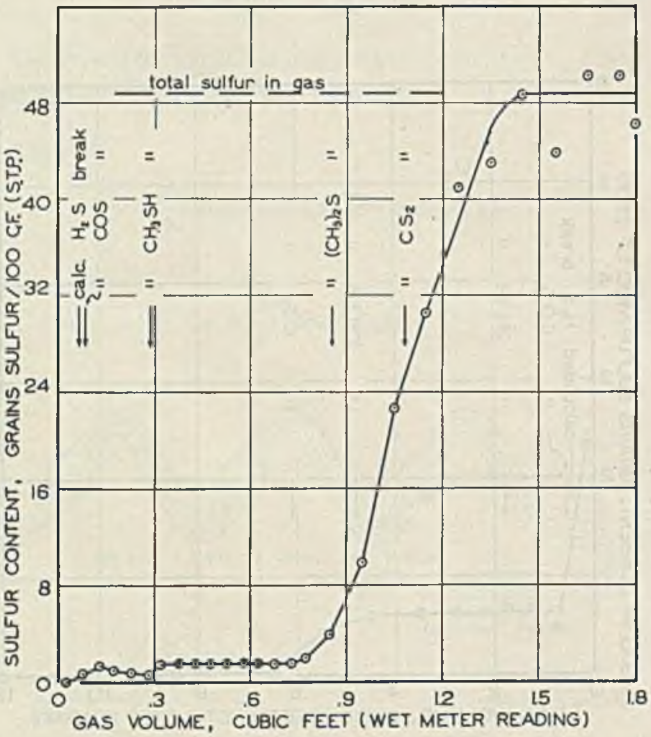

Figure 4. Composition of Coke-Oven Gas after Preliminary Scrubbing, Absorption Run

White oil was selected as the scrubbing liquid because it combines to an unusual degree the desirable properties of inertness, low volatility, and low viscosity. Other solvents can be used, provided they do not react with the sulfur compounds and are not volatilized to any large extent during the analysis. A more viscous solvent might require more plates in the saturator in order to give satisfactorily sharp breaks. The greater the number of plates the sharper the breaks but also the more solvent holdup, and hence the larger gas samples required for an analysis.

Since the volume of gas required for an identification run is directly proportional to the solubility of the sulfur compounds and the volume of solvent used, it is possible to separate the break points of two sulfur compounds of similar solubilities by increasing the quantity of solvent or lowering the temperature of the solvent to increase the solubility of the sulfur compounds.

Table II. Sulfur Content of Plant Gases

Gas Analyzed	Grains of Sulfur per 100 Cubic Feet (S.T.P.)					
	H_2S	COS	CH_3SH	CS_2	Higher boiling	Total
Coke-oven gas after removal of benzene, NH_3, H_2S, CO_2	0	0.7	0.8	46.5	0.5	48.5
Water gas from coke[a]						
Blue gas	0.5	3.6	0.25	0.35	0.02	4.7
Blow run gas	1.0	5.5	0	0.6	0.02	7.1

[a] After partial H_2S removal.

The absorption of appreciable quantities of any component of the gas being analyzed will complicate the determination, since the net effect is to change the quantity and quality of the solvent medium. Analysis for the sulfur compounds present in a "wet" natural gas would offer this type of difficulty, since it might contain about 100 grains of gasoline per cubic foot of gas. Corrections for this type of interference can be made by measuring the increase in solvent volume and determining the solubility of the sulfur compounds in the resultant solvent.

Usually both an absorption and a stripping run are required for a complete analysis of a gas. If desired, the stripping run can be performed directly on the oil saturated in the absorption run. However, the length of time required for complete saturation may lead to errors arising from instability of the solution. The saturating technique described using a simple scrubbing bottle has the dual advantage of rapid saturation and convenient use of a low absorption temperature. Low-temperature saturation followed by higher temperature stripping increases the sulfur concentration in the stripping gas and therefore the accuracy of the determination.

The organic sulfur is converted to hydrogen sulfide for analysis as previously described (*2*), except that only 1 ml. instead of 6 ml. of alumina catalyst is employed. The smaller quantity of catalyst minimizes the adsorption of sulfur and hence gives a quicker response to changes in composition. The hydrogen sulfide may be determined by any sufficiently sensitive procedure, such as the spectrophotometric method (*1*) or the lead acetate-impregnated tape technique of Moses and Jilk (*6*). The sensitivity of the analyses for hydrogen sulfide is of paramount importance since, as can be seen from Figures 2, 3, and 4, it is necessary to obtain gas analyses at frequent intervals in order to detect sharp break points.

RESULTS

The results obtained with this method on three common commercial gases are summarized in Table II.

In coke-oven gas the major impurity remaining after the usual procedures for by-product recovery is carbon disulfide, although significant amounts of carbonyl sulfide, methyl mercaptan, and high-boiling sulfur compounds are also present. In water gas, on the other hand, carbonyl sulfide is the major impurity. Similar analyses following attempted purification are especially useful in revealing which types of compounds escape treatment.

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Evaluation of Laboratory Distillation Apparatus

Improved Oldershaw Glass Bubble Plate Columns, Automatic Still Heads, and Accessories

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Novel test methods have been developed for evaluating laboratory distillation apparatus under conditions approximating actual operation rather than under ideal conditions for maximum separation. In particular, the effect of reflux ratio on efficiency and separation has been studied. Test methods for evaluating the other principal characteristics of distillation apparatus are also described in detail. The Oldershaw glass bubble plate column has been improved and studied, using the test methods described. The column has been found highly satisfactory for analytical distillations of hydrocarbon mixtures because of uniformity of its operating characteristics. Automatic still heads and other accessory equipment have been developed which contribute to the uniformity of the performance of the column.

ANALYTICAL distillations are of increasing importance as a control and specification test for petroleum products and as a general research tool. In consequence, the comparative performance of the several types of distillation apparatus in general use is of considerable interest. However, data obtained for the operating variables of any given distillation apparatus may depend to a large degree upon the methods of measurement used. While Ward (*10*) has discussed in a comprehensive manner the interrelation of the principal variables in column performance, there is no generally accepted system of test methods for experimentally evaluating the significant variables of distillation apparatus performance. The usual practice has been to evaluate distillation apparatus under idealized conditions of total reflux, long equilibration time, etc. However, the extrapolation of such data to actual operation at finite reflux ratios may lead to questionable results in the case of small-scale laboratory columns. It has been found for such columns that actual separations obtainable at finite reflux ratios are generally appreciably lower than would be predicted from column efficiencies measured at total reflux.

A series of test methods has been devised for measuring the principal variables affecting column operation under conditions approximating actual operation. In particular, test procedures have been devised for evaluating column efficiency at finite reflux ratios, for measuring feed rates to the column, operating holdup, static holdup, heat loss, pressure drop, and the actual reflux ratios provided by automatic still heads.

This article includes a detailed description of test methods and an example of their application to an improved form of the Oldershaw bubble plate column (*6*).

Among the columns in common use in various laboratories for analytical distillations are the glass helices packed column (*11*), the Podbielniak Heligrid (*7*), the Stedman screen cone column (*9*), and the Oldershaw bubble plate column (*6*). Preliminary comparisons made on these columns indicated that the Oldershaw column has exceptionally high throughput capacity and a low operating holdup per theoretical plate relative to other columns. These facts, together with the fact that the fractionating efficiency of the column is nearly independent of the throughput rate and shows no significant variation with time or from column to column, make the bubble plate column an excellent tool for analytical distillations, especially in commercial laboratories where high fractionating efficiency for a given length of column is a secondary consideration compared with reproducibility of results and length of distillation time. The bubble plate column as originally described by Oldershaw has been improved by making the plates more uniform and by increasing the number of holes per plate, thus materially increasing the throughput capacity of the column. Auxiliary equipment, such as automatic still heads, timers, and product receivers, has been developed which has contributed to the reproducibility of the data obtainable with the glass bubble plate column. (The columns and other equipment tested were manufactured by the Glass Engineering Laboratories, San Carlos, Calif.)

DEFINITIONS

Because of the appreciable heat loss in laboratory batch distillations, the standard nomenclature used in large-scale continuous distillation is not readily applicable. The following definitions of terms used in the present article are given to avoid possible ambiguities.

Feed Rate (F, ml. per hour). The rate of entry of vapor into the bottom of the column, in terms of the equivalent volume of liquid.

Overhead Rate (O, ml. per hour). The rate of removal of vapor from the top of the column, in terms of the equivalent volume of liquid. This is equal to the reflux rate plus the product rate.

Condensation Rate (C, ml. per hour). The condensation rate due to heat loss in the column. This is equal to the difference between the feed and overhead rates.

Product Rate (P, ml. per hour). The liquid distillate take-off rate.

Reflux Rate (R, ml. per hour). The rate of return of condensed overhead to the top of the column.

Reflux Ratio (R/P). The reflux rate divided by the product rate.

The following relations hold for a batch column operating at constant feed rate.

$$F = O + C$$

$$O = P + R$$

$$P = \frac{F - C}{\frac{R}{P} + 1}$$

Number of Theoretical Plates. The number of successive infinitesimal vaporizations at equilibrium required to give the measured separation. The qualification "infinitesimal" requires measurements to be made at total reflux (or to be corrected for the effect of reflux ratio as described by McCabe and Thiele, *5*).

Plate Equivalents. A quantity numerically equal to the number of theoretical plates operating at total reflux which would give the separation obtained when the column is operating at a finite reflux ratio.

CRITERIA AND TEST METHODS

The following characteristics of column performance were studied:

1. Fractionating efficiency and its variation with feed rate.
2. Actual separation obtained at various reflux ratios.
3. Flood point or feed capacity with liquids of various surface tensions.

4. Pressure drop of the column and its variation with feed rate using liquids of various surface tensions.
5. Operating holdup and its variation with feed rate.
6. Drainage or static holdup.
7. Accuracy of the reflux ratios provided by the two types of still heads and the variation of reflux ratio with overhead rate.
8. Condensation in the column due to heat loss through the Dewar jacket and variation of heat loss from column to column.

All efficiency measurements were made with the *n*-heptane–methylcyclohexane binary using the equilibrium composition of Beatty and Calingaert (*2*) and the refractive index data of Bromiley and Quiggle (*3*). The refractive indices of the test samples were measured with a Pulfrich refractometer with a precision of 0.0001 unit which corresponds to about 0.13 theoretical plate in the 0.3 to 0.4 mole per cent region of the McCabe-Thiele diagram for *n*-heptane–methylcyclohexane. The refractive indices obtained for the pure materials are compared with the values given by Bromiley and Quiggle (*3*) in Table I.

Table I. Refractive Indices of Materials Used for Column Testing

Material	Boiling Point, ° C.	Observed Refractive Index, n_D^{20}	Literature[a] Refractive Index, n_D^{20}
n-Heptane	98.4	1.3878	1.3877
Methylcyclohexane	100.8	1.4229	1.4231

[a] Bromiley and Quiggle (*3*).

In making measurements at total reflux, the samples of the distillate and the reflux to the flask were collected as described by Oldershaw (*6*) after equilibrating the column for 1.5 hours. In the efficiency measurements at finite reflux ratios, the distillate was continuously returned to the flask through a U-tube, as diagrammatically shown in Figure 1, thus operating the column essentially as a continuous still. The separation efficiencies at finite reflux ratios were calculated in terms of theoretical plates by the method of McCabe and Thiele (*5*) and as "plate equivalents" as suggested by Baker *et al.* (*1*) by using the McCabe and Thiele diagram with the same operating line as at total reflux.

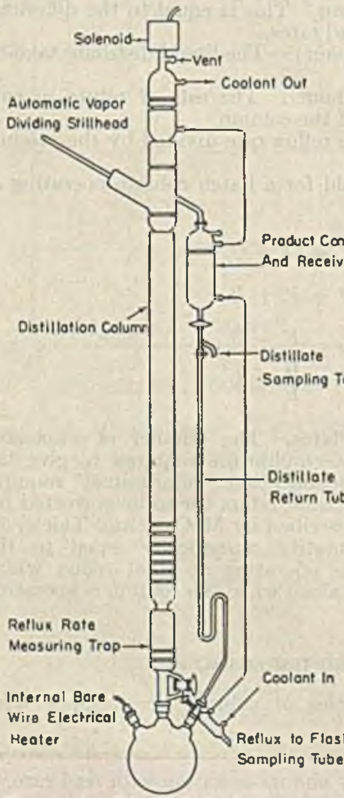

Figure 1. Distillation Column and Accessories Arranged for Fractionating Efficiency Tests

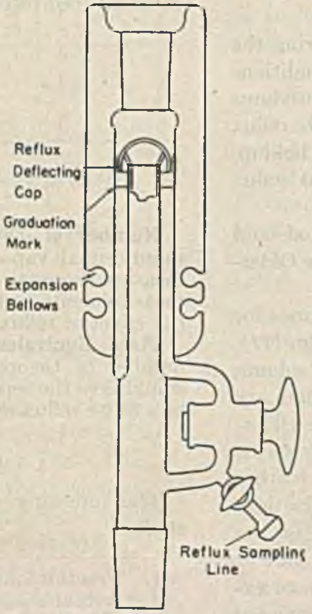

Figure 2. Trap for Measuring Feed Rate

The overhead rate could not be conveniently measured directly, since operating the column at total takeoff upsets the operating conditions because of the absence of reflux. Accordingly the column operating rates were determined in terms of the reflux to flask rate at total reflux (corresponding to the feed rate) which was measured with the reflux trap shown in Figure 2. The overhead rate differs from the feed rate by the condensation rate due to heat loss in the column and accordingly may be estimated from the feed rate if the heat loss of the column is known.

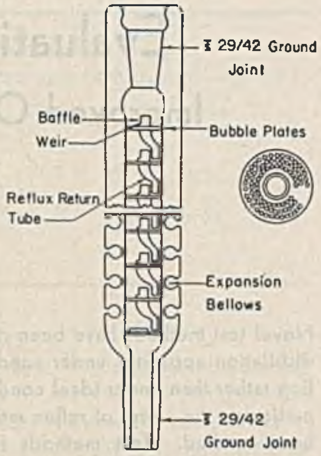

Figure 3. Improved Oldershaw Bubble Plate Column with Detail View of One Plate

The column heat loss was determined by measuring the reflux to flask when operating the column at a rate barely sufficient to produce reflux in the still-head condenser. The measured rate thus approximated the condensation rate of the column. It was established by other means that, as might be expected, the condensation rate of the column due to heat loss is substantially independent of the feed rate.

The pressure drop of the column was determined by measuring the difference in levels of the liquid in the U-tube connecting the flask and the still head. The feed capacity or flood point was determined by visual observation as the feed rate was slowly increased.

The operating holdup was measured by cutting off the current to the bare-wire immersion-heater and simultaneously closing the stopcock of the reflux trap, Figure 2. The liquid collecting in the trap was drained through a suitable cooler and was measured volumetrically.

The electrical timer was first calibrated by measurement of the off-on time ratios by means of a chronograph. The distillate rates delivered by the types of still heads at various nominal reflux ratios and overhead rates were then measured and the actual reflux ratios calculated. The overhead rates were measured without the column by mounting the still head directly on the reflux trap.

DISTILLATION APPARATUS

The items of distillation apparatus evaluated by the present test methods are described in detail below.

The improved Oldershaw column (Figure 3) consists of a series of perforated glass plates sealed into a tube. Each plate is equipped with a baffle to direct the flow of liquid, a weir to maintain the proper liquid level on the plate, and a reflux return tube. The inner diameter of the standard column is 26 to 28 mm. The holes in the plates are drilled with a red-hot tungsten wire of 0.89-mm. (0.035-inch) diameter. The number of holes per plate has been increased to 82 from the 42 described by Oldershaw (*6*). The ascending vapor stream flows through the holes in the plates and bubbles through the liquid reflux. The lowermost plate in the column serves as a small reservoir which is necessary to maintain a liquid seal for the drain tube from the first regular plate. The column is provided with an integral Dewar jacket with expansion bellows, permitting use of a 30-plate column to 250° C. The details of the method of construction have been described by Oldershaw (*6*).

The automatic vapor-dividing still head (Figure 4) includes a glass valve plunger which is arranged to direct the vapor stream selectively to the re-

Table II. Fractionating Efficiency and Operating Holdup of Improved Bubble Plate Column

(Column dimensions: 27 to 28 mm. inside diameter, 30 actual plates, 80 holes per plate, 0.9-mm. diameter holes, 25-mm. spacing between plates)

Column Operating Rate		Reflux Ratio (to 1)	Fractionating Efficiency			Operating Holdup	
Feed	Overhead		Theoretical plates	Plate efficiency	Plate equivalents	Total	Holdup quotient[a] (× 10³)
Ml./hour	*Ml./hour*			%		*Ml.*	
1500	1300	∞	17.2	57	..	47	1.82
2500	2300	∞	18.8	63	..	50.5	1.07
3000	2800	∞	19.4	65	..	53	0.91
3500	3300	∞	18.2	61	..	55.5	0.87
4000	3800	∞	16.7	56	..	59	0.88
1500	1300	27	17.1	57	12.6	47	1.83
2500	2300	27	17.4	58	12.7	50.5	1.06
3000	2800	27	18.0	60	12.7	53	0.98
3500	3300	27	17.0	57	12.6	55.5	0.93
4000	3800	27	16.6	55	12.3	59	0.89
3000	2800	64	18.2	61	15.5	53	0.97
3000	2800	42	18.0	60	14.4	53	0.98
3000	2800	13	14.9	50	9.1	53	1.18

[a] Ml. holdup per theoretical plate per ml. per hour feed.

flux condenser or to the product condenser. A direct current solenoid operates the plunger at timed intervals. The still-head temperature is measured by a partial immersion thermometer provided with a standard-taper joint. The still head is completely Dewar-jacketed to improve the accuracy of the temperature measurements, to prevent heat losses from upsetting the accuracy of the reflux ratio, and to permit use of the still head with liquids that boil below room temperature. The countercurrent relation of the vapor and reflux streams in the reflux condenser minimizes supercooling of the reflux. The reflux condenser is preferably also Dewar-jacketed as shown to prevent frosting when low-boiling materials are distilled.

The alternative liquid-dividing still head (Figure 5) has a tilting funnel which receives the liquid stream from the reflux condenser and normally returns it to the column. The funnel is tipped at timed intervals by a solenoid to deliver the liquid to the product receiver. The liquid-dividing still head is otherwise similar to the vapor-dividing still head.

The reflux ratio controller consists of a time switch driven by a small synchronous motor and is of conventional design. It is adapted to deliver periodic currents of 3 seconds' duration and is adjustable to provide nominal reflux ratios in the range of 2/1 to 100/1.

The combined condenser and product receiver (Figure 6) consists of a liquid-jacketed graduated tube with a coiled vent line enclosed in the liquid jacket. For distillations of low-boiling liquids it is desirable to provide an external Dewar jacket as shown to prevent frosting.

A satisfactory flask and heater for analytical distillations should combine safety, low heat capacity, high potential heat input, and ability to distill the charge to negligible residue without excessive charring. No completely satisfactory flask and heater has been tested to date. For the purposes of column evaluation a 500-watt bare Chromel A wire immersion heater was used. It has the advantage of low heat capacity and immediate response to regulation.

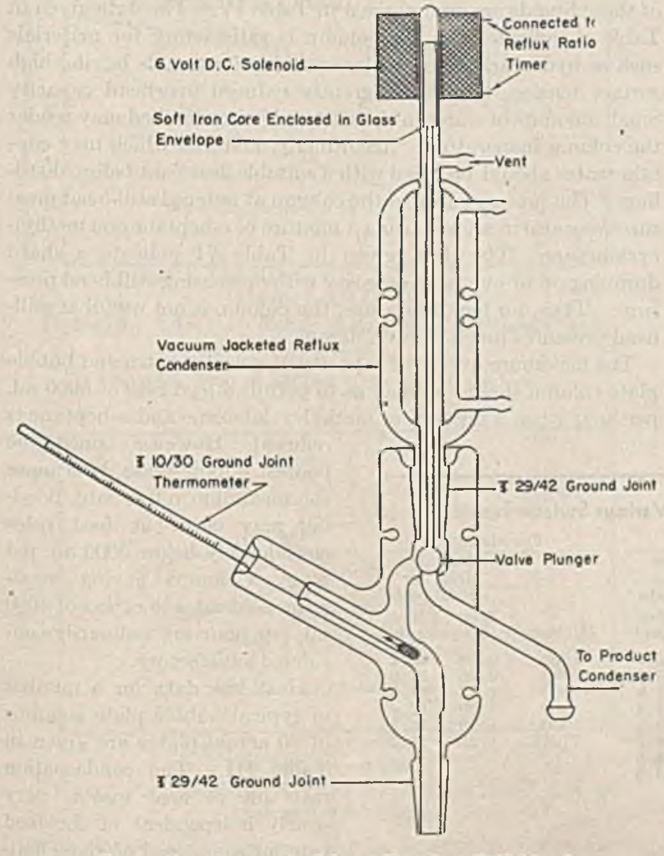

Figure 4. Automatic Vapor-Dividing Still Head

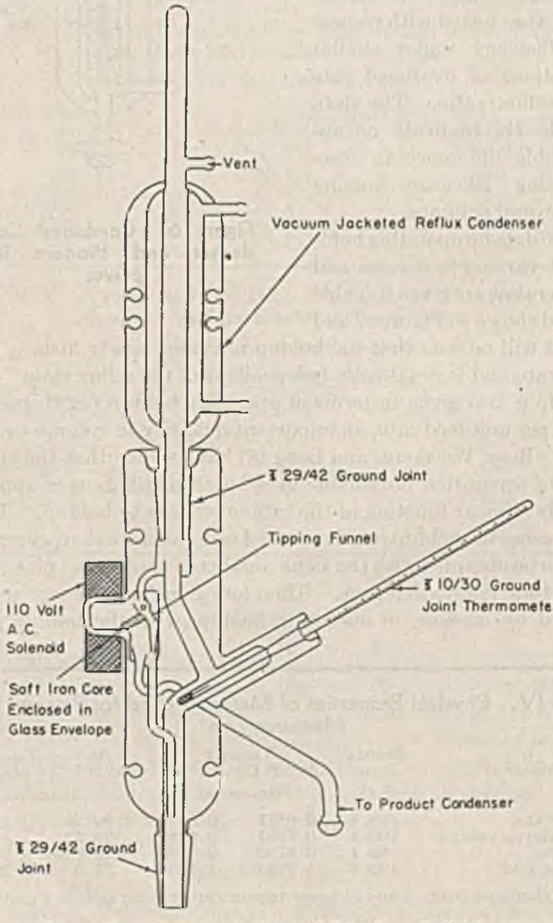

Figure 5. Automatic Liquid-Dividing Still Head

EXPERIMENTAL

Tests were conducted on a typical bubble plate column at infinite reflux ratio and at a nominal reflux ratio of 20 to 1 using various feed rates. Tests were also made at various reflux ratios using a constant feed rate of 3000 ml. per hour. The data given in Table II and presented graphically in Figures 7 and 8 show the effects of feed rate and reflux ratio upon column efficiency to be evident although not large. The fractionating efficiency has a peak value at a feed rate in the neighborhood of 3000 ml. per hour. However, optimum separation is obtained at a given product rate by operating the column at a somewhat higher feed rate and a higher reflux ratio. This may be seen from Figure 9 in which

Table III. Comparative Fractionating Efficiencies and Heat Losses of Sample Bubble Plate Columns

Column No.	Maximum Feed Rate	Fractionating Efficiency[a]		Condensation Rate of *n*-Heptane Due to Heat Loss
		Theoretical plates	Plate efficiency	
	Ml./hour		%	*Ml./hour*
1	5200	19.4	65	200
2	5150	19.1	64	260
3	5200	19.3	64	170
4	4730	19.9	66	180
5	4500	20.8	69	190
6	4250	19.8	66	230

[a] At 3000 ml. per hour feed and infinite reflux ratio.

separation expressed in plate equivalents is plotted against feed rate, the reflux ratio being varied to provide a constant product rate.

A number of bubble plate columns of identical dimensions were tested with respect to efficiency under similar conditions of overhead rate and reflux ratio. The data (Table III) indicate no appreciable difference in fractionating efficiency among the several columns.

The data on operating holdup at various feed rates and reflux ratios are given in Table II and shown in Figures 7 and 8. It will be seen that the holdup increases nearly linearly with feed rate and is practically independent of the reflux ratio. The holdup is also given in terms of operating holdup per theoretical plate per unit feed rate, an important quantity in column evaluation. Rose, Welshans, and Long (8) have shown that the sharpness of separation obtainable in a batch distillation is approximately a linear function of the ratio of charge to holdup. Thus, decreasing the holdup relative to feed rate enables a sharper separation to be obtained with the same number of theoretical plates and same total distillation time. Therefore gains in efficiency accompanied by increase in operating holdup as in the bubble plate column of Langdon and Tobin (4) may lead to an actual decrease in the sharpness of separation in a given batch distillation.

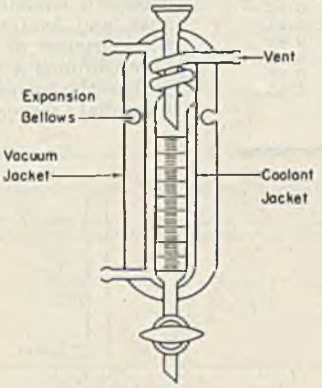

Figure 6. Combined Condenser and Product Receiver

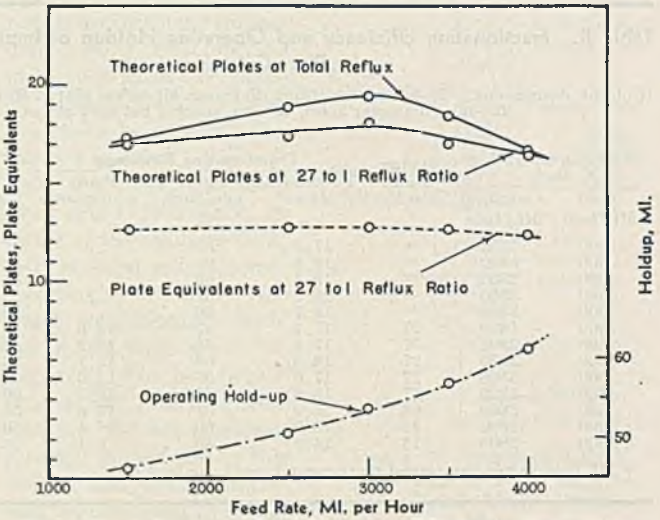

Figure 7. Influence of Feed Rate upon Efficiency, Separation, and Operating Holdup

30-actual-plate column

The residual drainage or static holdup of the column after draining 10 minutes is 0.6 ml. total or 0.02 ml. per plate when distilling *n*-heptane. Longer drainage time does not reduce the static holdup. The static holdup does not vary significantly with the viscosity in the case of light hydrocarbon distillates.

The pressure drop and feed capacity of the bubble plate column are largely dependent upon the surface tension of the liquid being distilled, because of the capillarity of the bubble plate holes. The pressure drop of the column was measured at various rates using several different liquids. The relevant physical properties of these liquids are summarized in Table IV. The data given in Table V indicate that the column is satisfactory for materials such as hydrocarbons but is less suitable for liquids having high surface tension, because of greatly reduced overhead capacity Small amounts of water in the material being distilled may render the column inoperative. Accordingly, material which may contain water should be dried with a suitable desiccant before distilling. The pressure drop of the column at reduced still-head pressures was also measured using a mixture of *n*-heptane and methylcyclohexane. The data given in Table VI indicate a sharp dropping off of overhead capacity with decreasing still-head pressure. Thus, for high feed rates, the column is not useful at still-head pressures much below 250 mm.

Table IV. Physical Properties of Materials Used for Pressure Drop Measurements

Material	Boiling Point	Density		Surface Tension	
		At 20° C.	At b.p.	At 20° C.	At b.p.[a]
	° *C.*	*Grams/ml.*		*Dynes/cm.*	
n-Heptane	98.4	0.6837	0.6180	20.26	12.5
Methylcyclohexane	100.8	0.7691	0.6989	23.73	15.7
Benzene	80.1	0.8790	0.8153	29.02	21.3
Formic acid	100.8	1.220	1.170	37.6	29.0

[a] Calculated from values at lower temperatures using Eötvös equation.

The maximum overhead capacity of a well-constructed bubble plate column should be such as to permit a feed rate of 5000 ml. per hour when a mixture of methylcyclohexane and *n*-heptane is refluxed. However, since the poorest bubble plate determines the maximum reflux rate, flooding may occur at feed rates considerably below 5000 ml. per hour. Columns having maximum feed rates in excess of 4000 ml. per hour are ordinarily considered satisfactory.

Heat loss data for a number of typical bubble plate columns of 30 actual plates are given in Table III. The condensation rate due to heat loss is very nearly independent of the feed rate for a material of given boiling point and heat of vaporiza-

Table V. Pressure Drop of Bubble Plate Column with Liquids of Various Surface Tensions

n-Heptane			Methylcyclohexane			Benzene			Formic Acid		
Feed rate	Pressure drop per actual plate			Pressure drop per actual plate			Pressure drop per actual plate			Pressure drop per actual plate	
Ml./hour	*Mm. Hg*	*Mm. liquid*[a]	*Ml./hour*	*Mm. Hg*	*Mm. liquid*[a]	*Ml./hour*	*Mm. Hg*	*Mm. liquid*[a]	*Ml./hour*	*Mm. Hg*	*Mm. liquid*[a]
1000	..	..	1000	..	..	1000	0.76	12.7	200	0.88	10.2
1500	0.50	11.1	1500	0.62	12.1	1500	0.82	13.6	400	0.95	11.0
2000	0.53	11.6	2000	0.63	12.3	2000	0.84	13.9	600	1.02	11.8
2500	0.55	12.0	2500	0.65	12.6	2500	0.87	14.4	800	1.09	12.7
3000	0.57	12.5	3000	0.67	13.0	3000	0.91	15.2	1000	1.18	13.7
3500	0.60	13.1	3500	0.71	13.8	3500	1.00	16.7	1125[b]	1.23	14.3
4000	0.64	14.1	4000	0.77	15.0	4000	1.11	18.5	...	..	..
4500	0.70	15.4	4500	0.85	16.5	4280[b]	1.17	19.5	...	..	..
5000	0.77	16.9	5000	0.93	18.1	...	..	..	...	..	..
5230[b]	0.80	17.6	5230[b]	0.97	18.9	...	..	..	...	..	..

[a] Mm. of refluxing liquid at boiling point.
[b] Flood point of column with given liquid.

Table VI. Pressure Drop of Bubble Plate Column at Various Still-Head Pressures

(Material refluxed: mixture of *n*-heptane and methylcyclohexane, surface tension at 100° C. = 13.2 dynes per cm.)

Feed Rate	Still-Head Pressure Drop per Actual Plate					
	760 Mm. Hg		500 Mm. Hg		250 Mm. Hg	
Ml./hour	*Mm. Hg*	*Mm. liquid*[a]	*Mm. Hg*	*Mm. liquid*[a]	*Mm. Hg*	*Mm. liquid*[a]
1500	..	..	..	..	0.668	13.1
2000	0.598	12.3	0.624	12.6	0.724	14.2
2500	0.612	12.6	0.649	13.1	0.852	16.7
3000	0.632	13.0	0.718	14.5	Floods	
3500	0.675	13.9	0.802	16.2		
4000	0.719	14.8	Floods			

[a] Based upon total pressure drop as measured at U-tube in distillate return tube (see Figure 1).

tion. The heat loss may vary considerably from column to column. A well-constructed vacuum jacket, however, should allow a condensation rate of only about 200 ml. per hour of *n*-heptane.

Two types of completely vacuum-jacketed automatic still heads have been used with the bubble plate column—i.e., the vapor-dividing and the liquid-dividing types (Figures 2 and 3). While both types are satisfactory with respect to providing accurately reproducible reflux ratios, the vapor-dividing type is believed to be preferable for the following reasons: A well-constructed vapor-dividing still head provides less product leakage at total reflux than the liquid-dividing type. The fragile moving parts are more easily removed and repaired in the vapor-dividing than in the liquid-dividing type. The vapor-dividing type tends to provide actual reflux ratios which are closer to the off-on ratio of the electrical timer than does the liquid-dividing type. The liquid-dividing type is disadvantageous in that it permits loss of reflux to the product take-off in the event of flooding of the still head. This is an important consideration if the still head is to be used in conjunction with a packed column, because proper technique calls for the preliminary flooding of the column to wet the column packing thoroughly before commencing distillation.

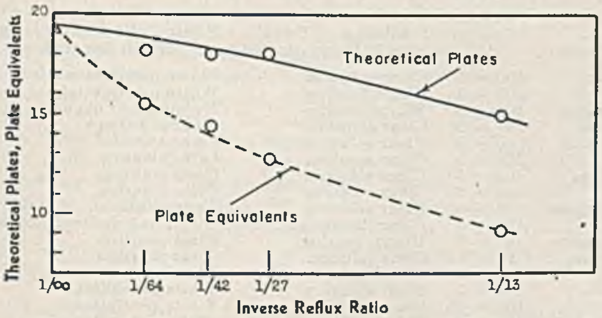

Figure 8. Effect of Reflux Ratio upon Efficiency and Separation

Feed rate, 3000 ml. per hour. 30-actual-plate column

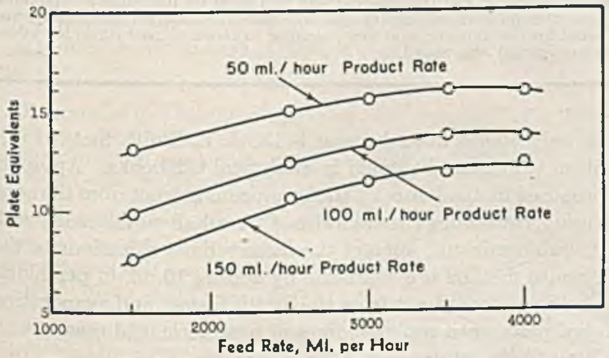

Figure 9. Influence of Feed Rate upon Separation at Constant Product Rate

Reflux ratio increased with increasing feed rate to provide constant product take-off rate. 30-actual-plate column

Data for the actual reflux ratios provided by particular still heads of the two types at various overhead rates and nominal reflux ratios are given in Tables VII and VIII. It will be noted that, in all cases, the actual reflux ratios provided by the still heads are higher than the off-on time ratios provided by the electrical timer. This can be compensated for by setting the timer to a ratio slightly lower than that which it is desired to maintain. The reflux ratio provided by either of the two types of still head appears to be nearly independent of the overhead rate.

The actual reflux ratio provided by a given still head will depend upon such considerations as distance of travel of the valve plunger or tipping funnel, adjustment of solenoid with respect to its armature, and amount of condensation produced in the lower portion of the still head by the supercooled reflux stream.

The present evaluation of the operating characteristics of the Oldershaw bubble column, the automatic still heads herein described, and other accessories shows the apparatus to be well suited to requirements of analytical distillations of hydrocarbons.

Table VII. Effect of Overhead Rate upon Actual Reflux Ratios of Automatic Still Heads of Two Types

(Electrical timer ratio: 24.1 to 1)

Overhead Rate, Ml./Hour	Actual Reflux Ratio (to 1)	
	Vapor-dividing still head	Liquid-dividing still head
2000	28.4	31.1
2500	27.8	30.0
3000	27.4	29.4
3500	27.0	29.1
4000	26.7	28.9

Table VIII. Actual Reflux Ratios Provided by Automatic Still Heads at Various Electrical Timer Ratios

(Overhead rate: 3500 ml. per hour)

Electrical Timer Ratio (to 1)	Actual Reflux Ratio (to 1)	
	Vapor-dividing still head	Liquid-dividing still head
3.7	4.3	4.1
6.3	7.3	8.0
11.6	13.0	14.0
24.1	26.9	28.9
43.3	42.2	50.0
66.5	63.8	77.3

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Determination of Sodium and Potassium in Silicates

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Upon the addition of a 20% solution of hydrogen chloride in anhydrous *n*-butyl alcohol (Willard and Smith reagent) to a butyl alcohol solution of the perchlorates of sodium and potassium, the two alkali metals are precipitated quantitatively as a mixture of sodium chloride, potassium chloride, and potassium perchlorate. This precipitation can be carried out in the presence of most elements commonly found or occasionally encountered in silicates and is proposed as basis of a new method for the determination of sodium and potassium.

WILLARD and Smith (*8*) introduced a solution of hydrogen chloride in anhydrous *n*-butyl alcohol as a reagent for the quantitative separation of sodium from lithium, and Kallmann (*4*), making use of the difference in solubility of the perchlorates and chlorides of the three alkali metals in butyl alcohol containing the same reagent, described a method for the quantitative separation of lithium from both sodium and potassium.

It was shown that lithium perchlorate and chloride are very soluble, that potassium is precipitated as a mixture of perchlorate and chloride, and that sodium perchlorate which is only sparingly soluble in butyl alcohol is quantitatively converted into the insoluble chloride.

As sodium and potassium are quantitatively precipitated by the solution of hydrogen chloride in butyl alcohol (Willard and Smith reagent), this solution suggested itself as the logical precipitant for sodium and potassium for their quantitative separation from the nonalkali constituents of silicates.

Preliminary work, recorded in Table I, indicated that the perchlorates of aluminum, calcium, magnesium, and iron which are all very soluble in butyl alcohol, are not precipitated by the Willard and Smith reagent. Manganese perchlorate, which decomposes upon heating and forms a residue in butyl alcohol, is soluble as chloride in butyl alcohol containing the Willard and Smith reagent.

When fuming large amounts of titanium salts with perchloric acid, some decomposition takes place. Any precipitate thus formed can be conveniently filtered off, however, after diluting with water. Since soluble titanium perchlorate is not precipitated by the Willard and Smith reagent, moderate amounts of this element do not interfere in the method suggested below.

More serious is the behavior of barium, strontium, and lead from silicates containing these elements in an acid-soluble form. The perchlorates of barium, strontium, and lead are very soluble in both water and butyl alcohol. Like sodium, they are precipitated, presumably quantitatively, by the Willard and Smith reagent. Certain precautions requiring hardly any additional work and obviating the difficulties just described, have been incorporated in the method described below.

About 2.7 kg. (6 pounds) of the Willard and Smith reagent, used in this investigation, were prepared by passing dry hydrogen chloride from a tank into a beaker containing 2.26 kg. (5 pounds) of anhydrous *n*-butyl alcohol. The beaker was externally cooled and the gassing interrupted several times, until the butyl alcohol was nearly saturated with hydrogen chloride at room temperature and showed a specific gravity of about 0.905, indicating an approximately 20% solution of hydrogen chloride in butyl alcohol.

PROCEDURE

DECOMPOSITION OF SAMPLE. Transfer 0.5 to 1.0 gram or more, depending on the alkali metal content, of the finely ground sample to a 50- to 100-ml. platinum dish, moisten with water, and add 20 ml. of 47% hydrofluoric acid and 15 ml. of 72% perchloric acid. Stir well with a platinum wire or the rubber end of a policeman and evaporate with moderate heat on a hot plate until copious white fumes of perchloric acid escape. Remove from the hot plate, wash down the sides of the dish with a little water, and again heat until fumes of perchloric acid escape freely and about half of the acid has been expelled. Do not fume to dryness, since this may cause thermal decomposition of perchlorates.

When cool, take up with 20 ml. of hot water and warm until all salts have dissolved. A residue at this stage denotes incomplete decomposition of the sample or presence of large amounts of titanium or of barium sulfate.

Filter through a small paper into a 250-ml. beaker and wash 8 to 10 times with hot water. If there is any doubt as to whether the sample was completely decomposed, ignite the paper in the original platinum dish, again treat with small portions of hydrofluoric and perchloric acids, evaporate to near dryness, take up with water, and filter into the main solution.

Evaporate on a hot plate to fumes of perchloric acid, finally expelling the excess of acid. To prevent decomposition of perchlorates, particularly of aluminum perchlorate, which would render subsequent separations more difficult, moderate heat only should be used, and expulsion of the perchloric acid must not be carried too far. The resulting perchlorates should not be bone-dry, but a small amount of perchloric acid, indicated by the escape of white fumes, should be left.

A limited number of silicates particularly highly aluminous minerals, yield incompletely to the action of hydrofluoric acid. Others may be high in titanium, barium, or lead. For such samples and additional complex inorganic compounds an alternative way of decomposition is desirable.

Table I. Solubility of Perchlorates in *n*-Butyl Alcohol and in Butyl Alcohol Containing Willard and Smith Reagent

Element	Weight Taken, Mg.	Solubility of Perchlorates in Butyl Alcohol	Effect of Willard and Smith Reagent
Sodium	100 ± 5	Clear solution	White precipitate
	500 ± 5	White residue	White precipitate
Potassium	100 ± 5	White residue	No apparent change
Lithium	300 ± 10	Clear solution	Clear solution
Aluminum	100 ± 5	Clear solution	Clear solution
	500 ± 5	Clear solution	Clear solution
Calcium	100 ± 5	Clear solution	Clear solution
	500 ± 5	Clear solution	Clear solution
Magnesium	200 ± 10	Clear solution	Clear solution
Iron	100 ± 5	Clear, brown solution	Clear, pale yellow solution
Manganese	100 ± 5	Brown residue	Clear solution
Titanium	10 ± 1	Clear solution	Clear solution
	100 ± 10	Cloudiness	Cloudiness
Barium	100 ± 5	Clear solution	White precipitate
Strontium	100 ± 10	Clear solution	White precipitate
Lead	100 ± 5	Clear solution	White precipitate
Zirconium	50 ± 5	Clear solution	Clear solution
Vanadium	50 ± 10	Clear solution	Clear soluton
Chromium	10 ± 2	Clear solution	Clear solution

The chlorides of the elements listed were fumed to near dryness with an excess of perchloric acid. The perchlorates were heated to boiling with 25 ml. of butyl alcohol and the solution was examined for insoluble compounds: 11 ml. of the Willard and Smith reagent were then added, the boiling was continued for one minute, and after cooling to room temperature, the effect of the precipitant was noted.

The only choice in such cases is the J. L. Smith method (*7*), details of which can be found in analytical textbooks. Applying the proposed method directly to the aqueous extract from the original fusion, containing the chlorides of the alkali metals along with considerable calcium, some of the more serious objections to the J. L. Smith method are overcome by adding 10 ml. of perchloric acid to the water extract from the Smith fusion, and evaporating on a hot plate until copious fumes of perchloric acid escape, and finally until almost dry.

PRECIPITATION OF SODIUM AND POTASSIUM. To the cold perchlorates add 25 ml. of anhydrous *n*-butyl alcohol and heat the solution to boiling. (A precipitate at this stage consists of potassium perchlorate, and with a little experience, it is not difficult to estimate the approximate potassium content of the sample, a fact which is most valuable to the analyst who intends to confine his work to the determination of only one of the two alkali metals. The potassium perchlorate can be filtered off on a Gooch crucible, converted to the chloride by ignition, dissolved in water, and finally determined as potassium perchlorate.)

Add dropwise to the boiling solution 3 ml. of the Willard and Smith reagent and then 8 ml. more. (A white precipitate formed at this point denotes the presence of sodium which can be observed even in the presence of large amounts of potassium.)

Allow to simmer for 3 minutes, cool to room temperature, decant the supernatant liquid into a dry Gooch crucible, transfer the bulk of the precipitate onto the crucible without policing the beaker, and wash 8 to 10 times with 1- to 2-ml. portions of a 6 to 7% solution of hydrogen chloride in butyl alcohol, made by diluting 40 ml. of the Willard and Smith reagent with 100 ml. of butyl alcohol. Discard filtrate and washings, unless wanted for the determination of a nonalkali constituent of the sample.

SEPARATION OF SODIUM AND POTASSIUM. Dry the beaker and Gooch crucible for about 15 minutes on a hot plate or in an electric drying oven. Then dissolve the precipitate on the Gooch, and also any particles adhering to the sides of the beaker, in a minimum amount of hot water. For this purpose it is desirable to arrange the filtering apparatus so that the filtrate can be directly caught in a 250-ml. beaker.

Add 5 ml. of perchloric acid and evaporate on a hot plate nearly to dryness. Since small amounts of nonalkali elements may have escaped the preceding separation, it is not advisable as suggested in the Smith and Ross procedure (*6*) to expel all perchloric acid at this stage. This is done, however, during the reprecipitation of the potassium perchlorate.

Cool, add 15 to 20 ml., depending on the alkali metal content, of a mixture of equal parts per volume of butyl alcohol and ethyl acetate, digest near boiling for 2 to 3 minutes, cool, and decant the supernatant liquid into a dry but unweighed Gooch crucible. Again the filtering apparatus should be arranged so that the filtrate can be caught directly in a small beaker. Wash the potassium perchlorate three times by decantation with 3-ml. portions of the mixed solvent. Reserve filtrate and washings.

Dissolve the residue in the crucible in a minimum amount of hot water, catching the solution in the original beaker, add 1 ml. of perchloric acid, evaporate to dryness, and expel any acid condensed on the side walls of the beaker by brushing with a free flame. Cool, dissolve salts in 3 to 5 ml. of water, and again evaporate to dryness. Cool, add 10 to 15 ml. of the mixed solvent, digest near boiling as before, cool to room temperature, and filter through the original crucible which in the meantime has been dried, ignited, cooled, and weighed. Transfer the residue to the Gooch crucible, police the beaker, and wash the crucible 8 to 10 times with 1-ml. portions of the mixed solvent. Reserve filtrate and washings which have been caught in the original beaker containing the bulk of the sodium. Dry the precipitating beaker for a few minutes on a hot plate and brush any unremoved particles of potassium perchlorate into the Gooch crucible. Dry the crucible for 1 hour at 110° C. and finally, while covered with a watch glass, for 15 minutes at 350° C. Cool and weigh as potassium perchlorate.

DETERMINATION OF SODIUM. The subsequent treatment of the butyl alcohol–ethyl acetate solution containing the sodium depends largely on the amount of sodium present.

If the Willard and Smith reagent, as precipitant for sodium and potassium in their separation from the nonalkali constituents of the sample, caused little or no apparent precipitation of sodium, the logical choice should be one of the two triple acetate methods (*1*, *2*).

Evaporate the combined filtrates and washings, after diluting with one third their volume of water, on the water bath in such a way as to avoid condensation on the upper part of the beaker.

When completely dry, add 10 ml. of water, 1 ml. of nitric acid, and 1 ml. of sulfuric acid and evaporate on a hot plate to strong fumes of sulfuric acid. This treatment is usually sufficient to destroy any brown coloration due to organic matter. If not, a few drops of nitric acid should be added and the fuming resumed. Finally, fume to complete dryness, dissolve salts in a few milliliters of hot water, filter off any insolubles if necessary, evaporate to 1 ml., cool, and precipitate the sodium with triple acetate reagent, directions for which can be found in analytical textbooks.

If the Willard and Smith reagent caused considerable precipitation of sodium chloride, sodium should finally be precipitated and determined as the chloride.

Table II. Separation of Sodium and Potassium from a Number of Elements

				Regular Method		Rapid Routine Method, Combined Chlorides Found
Element or Compound	Weight Taken	NaCl Used	KCl Used	NaCl found	KCl found	
	Mg.	Mg.	Mg.	Mg.	Mg	Mg.
....	...	50.0	50.0	50.4	50.2	....
....	...	10.0	100.0	9.7^a	100.9	....
....	...	100.0	100.0	....	....	199.2
Al	150	100.0	100.0	99.8	101.1	....
	300	100.0	100.0	....	....	200.5
Ca	50	100.0	50.0	100.8	50.4	....
	300	3.0	100.0	3.3^a	101.3	....
Mg	100	50.0	50.0	.....	....	100.8
	300	100.0	100.0	100.2	100.4	....
Fe	20	50.0	50.0	.....	....	99.9
Mn	20	5.0	50.0	5.0^a	49.7	....
Ti	20	50.0	50.0	49.3	49.6	....
Ba	25	50.0	50.0	49.5^b	50.6	....
	20	50.0	50.0	51.0^c	49.8	....
Pb	20	50.0	50.0	50.3^b	50.7	....
	20	50.0	50.0	51.8^c	49.7	....
As	10	50.0	50.0	50.6	49.8	....
V	10	50.0	50.0	.....	....	100.4
H_3PO_4	32	10.0	50.0	9.6	50.8	....
	32	100.0	100.0	.....	....	201.2
H_3BO_3	40	50.0	50.0	.....	....	99.3
	200	50.0	50.0	.....	....	100.7
CHOHCOOH | CHOHCOOH	250	50.0	50.0	48.7	48.9	....
	1000	10.0	50.0	7.8^a	48.2	....
Mixture of Al 150 Ca 50 Mg 50 Fe 5 Ti 10 H_3PO_4 32		50.0	50.0	.....	....	100.2
		6.0	50.0	6.0^a	50.4	....
		100.0	100.0	100.8	101.0	....

[a] Sodium determined as triple acetate.
[b] Sodium determined as chloride after removal of Ba or Pb as carbonates.
[c] Sodium determined as sulfate after removal of Ba or Pb as sulfates.

Evaporate the combined filtrates and washings from the potassium determination, after diluting with water, in the same way as for the triple acetate method. When completely dry, add 10 ml. of water and 3 ml. of perchloric acid and evaporate slowly, with a cover glass on, to strong fumes of perchloric acid. Increase the heat until all organic matter is destroyed. Finally evaporate to near dryness.

Add 15 to 20 ml. of butyl alcohol and heat the solution to boiling. Add 7 or 9 ml., respectively, of the Willard and Smith reagent, the first 2 ml. dropwise, allow to simmer for one minute to facilitate coagulation of the sodium chloride, cool to room temperature, collect the precipitate on a dry Gooch crucible, and wash 5 times with 1- to 2-ml. portions of the 6 to 7% solution of hydrogen chloride in butyl alcohol.

Dry the crucible for half an hour at 110° C., then ignite for 5 minutes in a muffle at 600° C. Cool in a desiccator, then weigh the crucible plus sodium chloride. Dissolve the precipitate in hot water, collecting and reserving the washings in a small beaker, dry the crucible for one hour at 110° C., cool, and weigh. The loss in weight represents sodium chloride.

The sodium chloride solution can be tested for possible presence of barium or lead by one of two procedures.

1. Add 1 gram of ammonium carbonate, heat to boiling, and allow to stand for one hour. The solution should remain clear. If it contains any precipitate, filter it off, evaporate the filtrate to dryness, transfer with hot water to a weighed platinum dish, add a few drops of hydrochloric acid, evaporate to dryness, heat as usual to expel any ammonium chloride, and weigh as pure sodium chloride.
2. Precipitate any barium or lead present by adding 1 ml. of sulfuric acid and determine the sodium in the filtrate as sodium sulfate.

RAPID ROUTINE METHOD. Collect the mixture of alkali chlorides and potassium perchlorate, obtained as described above, on a dry Gooch crucible, policing the beaker in which the precipitation was carried out. Special attention should be paid to the amount of potassium perchlorate present, prior to the addition of the Willard and Smith reagent, and also to the amount of sodium chloride precipitated.

Dry the crucible for one hour at 110° C., then increase the heat of the muffle gradually to 650° C., at which temperature the crucible is kept for half an hour, while covered with a watch glass or platinum cover. Cool and weigh, and dissolve chlorides of sodium and potassium in hot water, receiving filtrate and washings directly in a small beaker. Dry the crucible for one hour at 110° C., cool, and weigh. The loss in weight represents the combined chlorides of sodium and potassium.

Depending on the relative amounts of sodium and potassium present, based largely on observations made during the precipitation with the Willard and Smith reagent, precipitate either the sodium as triple acetate or the potassium as perchlorate or chloroplatinate and calculate the other alkali metal from the weight of the combined chlorides.

Acid-soluble barium or lead salts would accompany the sodium and potassium. In such cases, the aqueous solution of the combined chlorides should be treated with a small amount of ammonium carbonate and the chlorides of sodium and potassium recovered in the filtrate of the lead or barium carbonate.

Corroboration and Verification. Both methods described above were applied to the quantitative separation and determination of sodium and potassium in the presence of elements which form the main constituents of silicates or may occasionally be encountered.

Table III. Effect of Sulfate Ion

NaCl Used	KCl Used	0.1 *N* H_2SO_4 Used	Equivalent to Sulfur	Sulfur Found: Combined chlorides	Sulfur Found: NaCl	Sulfur Found: $KClO_4$ + KCl	Sulfur Found: 6% solution of HCl in butanol
Mg.	*Mg.*	*Ml.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
50	..	1	1.6	..	..	..	1.4
50	..	4	6.4	..	0.1	..	6.6
100	..	8	12.8	..	0.2	..	12.2
100	..	10	16.0	..	0.4	..	15.5
100	..	15	24.0	..	0.8	..	22.0
..	50	1	1.6	..	..	..	0.8
..	100	8	12.8	..	..	0.4	12.8
..	100	15	24.0	..	..	0.6	23.8
100	100	5	8.0	0.3	..	..	8.1
100	100	15	24.0	1.2	..	..	23.2

The solution of sodium and/or potassium chloride to which varying amounts of 0.1 *N* sulfuric acid were added, was fumed to near dryness with perchloric acid and treated with butyl alcohol and the Willard and Smith reagent, and the sulfate ion determined in the resulting fractions.

Table IV. Determination of Sodium and Potassium in Standard Samples

B. of S. Sample No.	Type of Sample	Weight of Sample	Certificate Value: Combined chlorides	Certificate Value: Na_2O	Certificate Value: K_2O	By Analysis: Combined chlorides	By Analysis: Na_2O	By Analysis: K_2O
		Grams	*Gram*	%	%	*Gram*	%	%
70	K_2O - feldspar	1.0000	0.2439	2.38	12.58	0.2433[a]	2.27[b]	12.66
		1.0000	0.2439	2.38	12.58	0.2440[a]	....	...
		1.0000	0.2439	2.38	12.58	......	2.35	12.68
		1.0000	0.2439	2.38	12.58	......	2.41	12.53
		0.5000[c]	0.1220	2.38	12.58	0.1224[a]	....	...
99	Na_2O - feldspar	1.0000	0.2088	10.73	0.41	0.2100[a]	10.82[b]	0.38
		1.0000	0.2088	10.73	0.41	......	10.75	0.44
		1.0000	0.2088	10.73	0.41	......	10.68	0.37
		0.5000[c]	0.1044	10.73	0.41	0.1049[a]	....	...
		0.5000	0.1044	10.73	0.41	......	10.74	0.44
91	Opal glass	1.0000	0.2112	8.48	3.25	0.2118[a]	....	...
		1.0000	0.2112	8.48	3.25	......	8.50	3.25
		1.0000	0.2112	8.48	3.25	......	8.52	3.32
		0.5000[c]	0.1056	8.48	3.25	0.1065[a]	....	...
		0.5000[c]	0.1056	8.48	3.25	......	8.44	3.22
80	Soda-lime glass	1.0000	0.3145	16.65	0.04	0.3149[a]	16.70	0.02
		1.0000	0.3145	16.65	0.04	......	16.65	0.00
		0.5000[c]	0.1572	16.65	0.04	0.1570[a]	....	...
98	Plastic clay	1.0000	0.0554	0.28	3.17	0.0557[a]	....	...
		1.0000	0.0554	0.28	3.17	0.0560[a]	0.26[d]	3.21
		1.0000	0.0554	0.28	3.17	......	0.30[d]	3.15
		1.0000	0.0554	0.28	3.17	......	0.30[d]	3.14
		0.5000[c]	0.0277	0.28	3.17	0.0285[a]	0.28[d]	3.17
89	Pb-Ba glass	1.0000	0.2405	5.70	8.40	0.2415[a,e]	....	...
		1.0000	0.2405	5.70	8.40	......	5.72[f]	8.42
		1.0000	0.2405	5.70	8.40	......	5.81[g]	8.40
		0.5000[c]	0.1203	5.70	8.40	......	5.73	8.46
		0.5000[c]	0.1203	5.70	8.40	0.1200[a,e]	5.67[b]	8.48
1[a]	Limestone	1.0000[i]	0.0186	0.39	0.71	......	0.43[d]	0.74
		2.0000[i]	0.0372	0.39	0.71	......	0.36	0.72

[a] Combined chlorides by rapid routine method.
[b] Na_2O calculated by difference from weight of combined chlorides.
[c] J. L. Smith fusion applied.
[d] Sodium determined as triple acetate.
[e] Pb and Ba previously removed with ammonium carbonate.
[f] Sodium determined as chloride after removal of Pb and Ba with $(NH_4)_2CO_3$.
[g] Sodium determined as sulfate.
[i] Sample decomposed with $HClO_4$ in covered dish, prior to addition of HF.

All nonalkali elements and compounds used in these tests were specially prepared or tested to be alkali-free. In order to duplicate as much as possible all operations that a sample of silicate has to go through, the hydrochloric or nitric acid solution of these elements and the aqueous solution of acids were evaporated to dryness in a platinum dish. Hydrofluoric and perchloric acids were then added and the methods, described in the preceding paragraphs, applied. The results, presented in Table II, show that in the proposed method direct precipitation of sodium and potassium in the presence of large amounts of other elements is possible.

An attractive feature is the fact that the method provides at an early stage of the analysis definite indications as to the relative amounts of sodium and potassium present.

In contrast to the J. L. Smith method (*7*), no solid reagents are used if the sample can be decomposed by acid treatment. No ammonium salts are used. They would interfere because of the small solubility of ammonium perchlorate in butyl alcohol containing the Willard and Smith reagent and in the mixture of butyl alcohol and ethyl acetate.

Another advantage lies in the removal of lithium at an early stage of the analysis, thus obviating one of the major objections inherent in the Smith and Berzelius methods.

While magnesium may interfere in the Smith method, and definitely does interfere in the Berzelius method (*3*), and causes the use of 8-hydroxyquinoline in the more recent method of Marvin and Woodlaver (*5*), it causes no difficulty in the proposed method.

Moderate amounts of phosphoric, boric, and even tartaric acids do not interfere. The effect of the sulfate ion was investigated (Table III).

Any sulfate ion remaining after the fuming with perchloric acid will cause formation of sodium sulfate, and to a lesser degree, of potassium sulfate, both insoluble in butyl alcohol. The data in Table III indicate that the Willard and Smith reagent causes considerable conversion of these sulfates into the equally insoluble and noninterfering chlorides:

$$Na_2SO_4 + 2HCl \longrightarrow 2NaCl + H_2SO_4$$
$$K_2SO_4 + 2HCl \longrightarrow 2KCl + H_2SO_4$$

As much as 15 mg. of sulfur in form of sulfates apparently is quantitatively converted into chlorides and does not interfere. For larger quantities of sulfates, the writer would suggest either reprecipitation of the mixture of alkali chlorides and potassium perchlorate, or, preferably, treatment of the aqueous solution of these alkali salts with a few drops of barium chloride, after converting them to the chlorides by ignition, and simultaneous removal of the excess reagent with ammonium carbonate.

The method discussed above was applied in the determination of sodium and potassium in a number of representative standard samples of silicates and related products (Table IV).

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Polarographic Determination of Tin in Foods and Biological Materials

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A rapid and precise polarographic method for the determination of tin in foods and biological materials has been developed, which is applicable to the determination of tin in concentrations as low as 0.5 part per million. The accuracy is of the order of ±5% for concentrations in excess of 10 parts per million and somewhat less for smaller amounts. It has been demonstrated that moderate amounts of iron, copper, bismuth, cadmium, mercury, cobalt, and zinc may be present without interference. Lead leads to high results and a procedure in case lead is present is outlined.

THE accurate determination of traces of tin in foods is of considerable interest and has many limitations. The method adopted by the Association of Official Agricultural Chemists (*2*) has been widely used for many years, but while it is very reliable it is subject to a number of disadvantages. In order to obtain satisfactory precision it is necessary to handle large samples, usually 50 to 100 grams, and the wet digestion of such large samples is time-consuming and requires large quantities of oxidizing acids. The hydrogen sulfide separation is also objectionable, from the standpoint of both the toxicity of the hydrogen sulfide and the tedious filtration of the slimy precipitate.

The polarographic procedure described permits the determination of tin on a much smaller sample with the elimination of the sulfide separation. Greater sensitivity is obtained and the precision in the lower range is greatly enhanced.

At the time this study was instigated the behavior of solutions of tin at the dropping mercury electrode was not completely understood. Lingane (*6*) found that stannous tin in tartrate solutions yielded a well-defined anodic wave due to the oxidation of stannous to stannic tin and a well-defined cathodic wave corresponding to the reduction of stannous tin. No wave was obtained for stannic tin. The same author (*4*) reported a similar composite wave for stannous tin in sodium hydroxide solution and a rather poorly defined double wave for the reduction of stannic tin in hydrochloric acid solution. Smrz (*8*) obtained well-defined waves for the reduction of stannous tin in hydrochloric acid. Lingane and Scott (*3*) reported that stannous tin was not reducible in perchloric acid, but that well-defined waves were obtained on addition of chloride ion. A similar behavior was found for stannic tin in perchloric acid. In the presence of added chloride a double wave was obtained. Alimarin (*1*) reported an application of the polarograph to the determination on tin in ores in which stannic tin was reduced in a supporting electrolyte of hydrochloric acid and sulfuric acid.

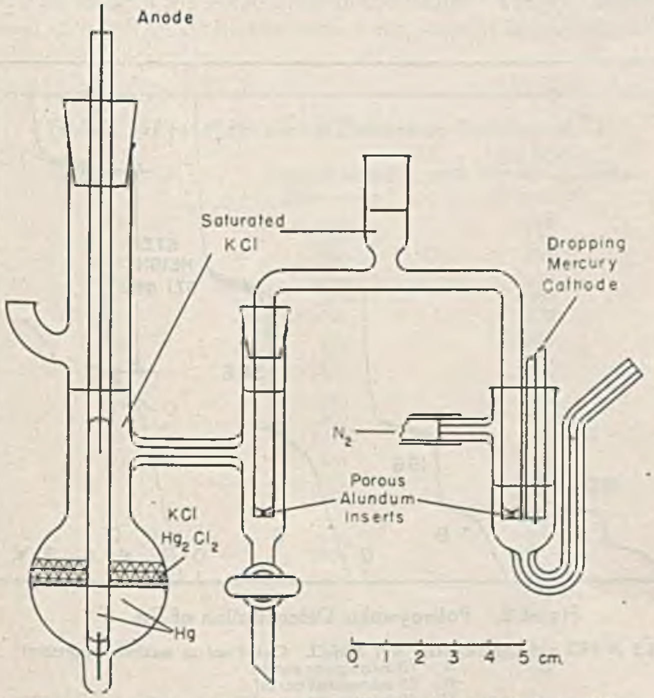

Figure 1. Calomel Electrode and Electrolysis Cell Assembly

A very complete discussion of the theoretical considerations of the polarography of stannic tin in halide solutions was presented by Lingane (*7*) while this investigation was in progress. Lingane, working with pure solutions, recommended a supporting electrolyte of ammonium chloride in hydrochloric acid with a trace of gelatin to suppress maxima. After the present paper had been submitted for publication, a polarographic procedure for the determination of tin and lead in copper base alloys was described (*5*).

APPARATUS

The usual polarograph electrolysis cell of the simple Heyrovský type is not applicable to the determination of tin, since the anode pool effects some reduction of stannic tin. For this reason it is necessary to use an external reference anode. In the work under discussion a saturated calomel cell was used, the construction of which is shown in detail in Figure 1.

The cell is made of heavy-walled Pyrex and is designed to minimize concentration polarization by virtue of the relatively large area of mercury exposed. Connection to the electrolysis vessel is made through an inverted U-tube salt bridge filled with a saturated solution of potassium chloride. Small pieces of porous Alundum are fused into the tips of the bridge. The electrical resistance of the bridge is low, and the potassium chloride diffuses at such a low rate that the sample is not measurably diluted.

The electrolysis vessel (Figure 1) is of very simple construction. Dissolved oxygen is swept out of the solution by passing a current of nitrogen through the capillary tube. When this flow is stopped and diverted to the side arm, a blanketing atmosphere of nitrogen is maintained over the solution in the cell. A manifold system permits the simultaneous deaeration of several samples, preventing any loss of time at this point of the procedure. The cell described not only permits the increased sensitivity associated with the use of a relatively small volume of solution (3 to 4 ml.), but in conjunction with the use of the external electrode permits a maximum economy of mercury. Only a few tenths of a gram are used per determination and this is completely recoverable.

A Heyrovský-type polarograph manufactured by E. H. Sargent & Co. was used throughout the course of this investigation. The full-scale galvanometer sensitivity was 0.0028 microampere per millimeter. A 60- to 65-mm. length of marine barometer tubing was used as the cathode capillary and under an applied pressure of 75 cm. of mercury the drop time was approximately 3.3 seconds with the capillary immersed in distilled water. Under these conditions 1.94 mg. of mercury were delivered per second. Although it would be desirable to work under constant-temperature conditions, the measurements reported were made at room temperature and are subject to a small error which under normal operating conditions probably does not exceed 5%.

EXPERIMENTAL

Although very satisfactory anodic waves can be obtained for the oxidation of stannous tin (*3*, *4*), it was felt that considerable difficulty would be associated with obtaining and maintaining the tin in a completely reduced state, and that it would be preferable to work with solutions of stannic tin. In preliminary experiments it was shown that well-defined waves suitable for analytical purposes could be obtained in a medium of dilute sulfuric acid containing a soluble chloride such as ammonium chloride, sodium chloride, potassium chloride, or hydrochloric acid and a trace of certain organic substances such as gelatin, methyl red, or cresol red which act as maximum suppressors. It was shown that the reduction of tin occurred in two very definite steps, first a reduction of the tetravalent tin, supposedly existing as the anion of the acid H_2SnCl_6 to the divalent state; then, in the second step, the subsequent reduction to metallic tin. With increasing concentrations of chloride ion the two waves became more widely separated and more sharply defined. The second wave marking the reduction of divalent tin to metallic tin approximated the form of a typical reversible reaction, while the shape of the first wave indicated that the current in this step of the reduction was limited by factors other than diffusion, probably by the dissociation of the aquo-stannic ion. In concentrated chloride solutions the increase in diffusion current due to the second step of the reduction is approximately equal to one half of the total diffusion current. It was further demonstrated that the second portion of the reduction wave was well suited to analytical measurement, since the diffusion current could readily be measured and was directly proportional to tin concentration. These experimental results and conclusions are in substantial agreement with those of Lingane (7).

Some difficulty was encountered in attempts to apply the procedure outlined above to the determination of tin in the sulfuric acid residues resulting from the acid digestion of food products. Results in most instances were completely satisfactory but extremely abnormal curves were obtained for occasional samples. The current in these instances would increase rapidly and almost linearly with increasing applied voltage. Similar curves were obtained on solutions yielding normal curves to which were added small amounts of nitric acid containing oxides of nitrogen. The same behavior could also be induced by passing a small amount of nitric oxide into the solution prior to electrolysis. It was inferred that the occasional abnormal curves were due to incomplete decomposition and removal of nitrosyl sulfuric acid formed during the digestion step. It was observed that when solutions giving these abnormal curves were boiled vigorously and again diluted to volume the polarograms were usually normal and recovery determinations were fairly satisfactory. Even when this procedure was followed, an occasional failure was noted, especially during the analysis of such products as evaporated milk, sardines, and shrimp.

In order to eliminate entirely the occurrence of these troublesome failures, methods of separation and concentration were studied. It was shown that tin could be completely precipitated as the hydroxide and, in the presence of added aluminum, the precipitated hydroxides could readily be separated by centrifuging. The supernatant liquid was removed by decantation, and the precipitate dissolved in hydrochloric acid and diluted to volume with a saturated solution of ammonium chloride. The solutions so prepared produced uniformly consistent and well-defined curves entirely free of the abnormality noted previously. In addition, the separation step permitted a reduction in volume with an accompanying increase in sensitivity.

DETAILS OF PROCEDURE

REAGENTS. A. Ammonium chloride. Saturated solution in distilled water.

B. Hydrochloric acid (1 + 1). Dilute C.P. acid with an equal volume of distilled water.

C. Aluminum chloride. Dissolve 4.65 grams of aluminum chloride nonahydrate in distilled water and dilute to 250 ml. 1 ml. = 2 mg. of Al.

D. Standard tin solution. Dissolve 0.500 gram of pure tin in 250 ml. of hydrochloric acid and dilute to 500 ml. with distilled water. For use dilute 25 ml. to 250 ml. with dilute hydrochloric acid (reagent B). 1 ml. = 0.1 mg. of Sn.

E. Cresol red. Saturated solution of *o*-cresolsulfonphthalein in distilled water.

PREPARATION OF SAMPLES. Transfer a 5- to 10-gram sample of the food product to a 250-ml. Erlenmeyer flask and add 10 to 15 ml. of nitric acid and 2 to 3 ml. of sulfuric acid. Heat slowly to begin the oxidation. As charring occurs add nitric acid in small increments. When sulfur trioxide fumes are evolved with no further charring or darkening, add 1 ml. of perchloric acid and continue heating until the perchloric acid is volatilized and sulfuric acid is refluxing freely on the walls of the flask. Allow to cool and add 10 to 15 ml. of distilled water.

SEPARATION OF TIN. Transfer the digested sample to a 50-ml. conical centrifuge tube. A long-taper tube accurately graduated at 10 ml. is most desirable. Rinse the flask with a small volume of water and finally dilute to approximately 20 ml. Add 1 ml. of aluminum chloride solution (reagent C) and one drop of methyl red indicator. Make alkaline with concentrated ammonium hydroxide and add 0.1 to 0.2 ml. in excess. A large excess of ammonium hydroxide is to be avoided, since tin and aluminum hydroxides become somewhat soluble. Centrifuge at high speed until the precipitate has been well packed in the tip of the tube. A trunnion-head centrifuge was found to be somewhat more satisfactory than a fixed-angle machine, since the precipitate is packed more firmly into the tip of the tube and the supernatant liquid may be poured off with less danger of disturbing the precipitate. Decant the clear supernatant liquid as completely as possible. To the residue in the tube add 2.5 ml. of hydrochloric acid (reagent B) and shake to effect solution. Add sufficient solution (reagent A) to bring the final volume to 10.0 ml.

POLAROGRAPHY. Transfer a 4- to 5-ml. portion of the prepared solution to a clean dry electrolysis cell and add one drop of cresol red solution (reagent E). Bubble nitrogen through the solution for 10 minutes, then divert the flow of gas to provide a blanketing flow over the surface of the solution. Record the polarogram between 0 and 0.8 volt at the highest galvanometer sensitivity which will permit the recording of the complete curve. Measure the height of the second tin wave in the manner illustrated in Figure 2 and calculate the tin content of the sample, using the appropriate sensitivity factor and the calibration constant obtained from standard samples.

CALIBRATION. Transfer accurately measured aliquots of the standard tin solution (reagent D) to centrifuge tubes, dilute with distilled water, and precipitate the tin as directed above. Record the polarograms and measure the wave height, then plot

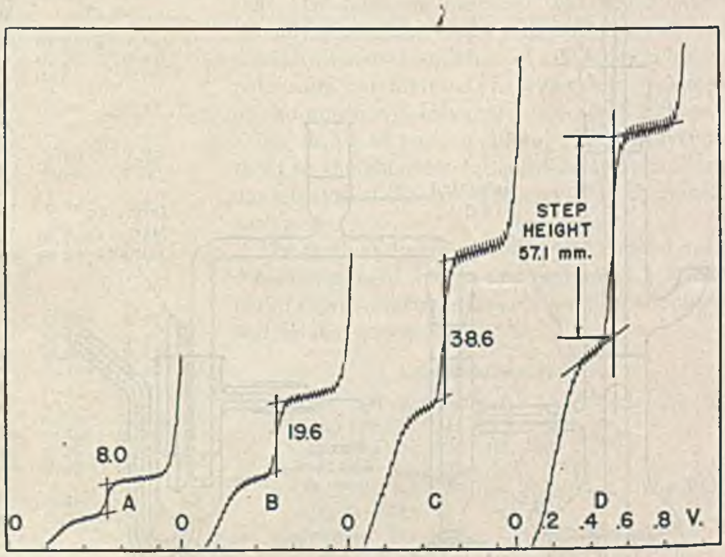

Figure 2. Polarographic Determination of Tin

In 1.5 *N* HCl and approximately 4 *N* NH_4Cl. Cresol red as maxima suppressant
A. 10 micrograms per ml.
B. 25 micrograms per ml.
C. 50 micrograms per ml.
D. 75 micrograms per ml.
Recorded at $^1/_{20}$ full-scale sensitivity, 1 mm. = 0.056 microampere

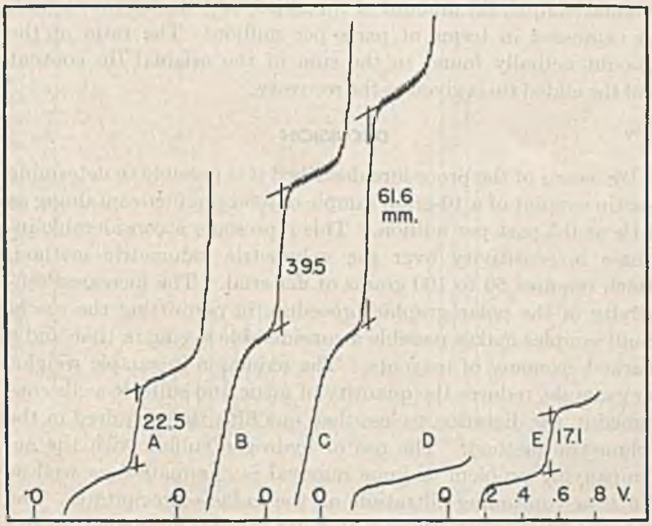

Figure 3. Determination of Tin in Presence of Lead

A. 200 micrograms of Pb in 10 ml. of acid medium
B. 200 micrograms of Sn in 10 ml. of acid medium
C. 200 micrograms of Pb + 200 micrograms of Sn in 10 ml. of acid medium
D. 200 micrograms of Sn in 13 ml. of alkaline medium
E. 200 micrograms of Sn + 200 micrograms of Pb in 13 ml. of alkaline medium
Recorded at $^1/_{10}$ full-scale sensitivity, 1 mm. = 0.028 microampere

the wave height against tin concentration, multiplying the measured heights by the appropriate sensitivity factor. Draw a straight line through the points and from the slope of the line compute the conversion factor relating wave height to tin concentration. Each capillary must be calibrated, and additional standards should be run at intervals. With proper care a capillary will last almost indefinitely.

INTERFERING ELEMENTS

The behavior of a number of potential interfering elements was studied in order to determine their effect on the determination of tin by the method described. Some of these elements are eliminated to a certain extent in the ammonium hydroxide separation. It was demonstrated that iron, copper, bismuth, cadmium, mercury, antimony, nickel, cobalt, and zinc could be present in concentrations equal to or slightly greater than that of the tin without noticeable effect on the results. The presence of lead, however, may lead to some error, since it is precipitated with the tin and is reduced at a voltage too near that of the second tin wave to be resolved. The results of these determinations are shown in Table I.

Table I. Effect of Extraneous Elements on Recovery of Tin

Added Metal	Amount Added *Micrograms*	Tin Found (200 Micrograms Added) *Micrograms*
Fe	200	204
	500	200
	1000	200
Cu	200	200
	500	200
	1000	200
Bi	200	200
	500	200
	1000	200
Cd	200	200
	500	200
	1000	202
Hg	200	204
	500	202
	1000	202
Sb	200	200
	500	202
	1000	202
Ni	200	200
	500	202
	1000	202
Co	200	200
	500	200
	1000	202
Pb	200	324

Table II. Recovery of Tin in Presence of Lead by Modified Procedure

Amount of Lead Added *Micrograms*	Tin Found (400 Micrograms Added) *Micrograms*
0	400
200	405
500	391
1000	409

The potential error due to lead interference is not regarded as a serious disadvantage in the application of the method to the determination of tin in foods, since lead, if present, usually occurs in relatively minor concentrations. In the event that the presence of significant quantities of lead is suspected, it is possible to overcome the interference as outlined below. This modified procedure involves recording the polarogram on the solution in the usual manner, then making a portion of the acid solution strongly alkaline by the addition of a measured amount of ammonia and ammonium citrate, and recording a second polarogram. In the ammoniacal citrate solution the lead wave is well defined and the tin wave is completely suppressed.

POLAROGRAPHY OF TIN IN THE PRESENCE OF LEAD. Record the polarogram as usual on the ammonium chloride–hydrochloric acid solution and determine the combined wave height due to tin and lead. To a 5.0-ml. aliquot of the solution add 1.0 ml. of concentrated ammonium hydroxide and 0.5 ml. of ammonium citrate (50% w/v). Record the polarogram of this solution and measure the height of the lead wave. Prepare solutions containing no tin and varying amounts of lead as directed in the section on calibration. Precipitate the aluminum and lead and dissolve in the hydrochloric acid–ammonium chloride supporting electrolyte. Record the polarogram on the acid solution and on the ammoniacal citrate solution prepared as directed above. Measure the heights of the lead waves and plot the wave heights in the acid medium against those of the corresponding solutions in the alkaline medium. It is unnecessary to correct the diffusion current in the alkaline medium for the dilution, since the same dilution factor is introduced in both standards and unknowns. The slope of this line is determined by the dilution factor and by the relative diffusion rates of the lead ions in the two media and hence should remain constant as long as the composition of the two solutions is unchanged. Using this curve, convert the height of the lead wave obtained for the unknown in alkaline medium to the equivalent wave height for the same amount of lead in acid medium. Deduct this computed wave height from the combined wave height of the tin and lead in acid medium to obtain the net diffusion current due to tin.

Figure 3 shows a series of polarograms illustrating the method of correcting for lead interference. Polarogram D shows a very small inflection due to the trace of lead in the reagents used. For very precise determinations of minute concentrations added precautions would be required in order to free the reagents from traces of tin and lead.

Results of a series of determinations of tin in the presence of varying amounts of lead are shown in Table II. Recoveries are satisfactory even though the concentrations of lead may exceed that of tin by a ratio of 2.5 to 1. The method would obviously not be applicable to the determination of a trace of tin in a relatively gross amount of lead.

RECOVERY DETERMINATIONS

A considerable number of samples representing a wide variety of food products have been analyzed both before and after the addition of measured amounts of tin. Most of these samples originally contained considerable tin; consequently, the results of the recovery determinations in these cases must be regarded as only circumstantial evidence of the precision of the method, since compensating errors might still exist. In a few cases, the

Table III. Results of Recovery Determinations

Product	A Original Tin Content *P.p.m.*	B Tin Added *P.p.m.*	C[a] Tin Present *P.p.m.*	D Tin Found *P.p.m.*	E Recovery[b] %
Evaporated milk	25.8	25.0	50.8	52.3	103
	27.0	25.0	52.0	53.0	102
	39.1	25.0	64.1	63.9	100
	41.5	50.0	91.5	90.8	99
	46.7	25.0	71.7	72.4	101
	58.4	25.0	83.4	83.1	100
	62.3	25.0	87.3	88.0	101
	69.3	25.0	94.3	92.2	98
	82.6	25.0	107.6	107.6	100
Whole milk	0.4	5.0	5.4	5.4	100
Grapefruit juice	83.4	25.0	108.4	108.0	100
	98.0	25.0	123.0	122.0	99
Prunes	23.8	50.0	73.8	72.0	98
	21.2	15.0	36.2	36.0	101
	24.2	15.0	39.2	39.0	99
	2.1	10.0	12.1	12.0	99
Apricot preserves	1.4	10.0	11.4	11.4	100
Beans with pork	8.9	10.0	18.9	18.7	99
Beets	2.1	10.0	12.1	12.0	99
Mixed vegetable juices	15.6	15.0	30.6	31.8	104
	6.2	25.0	31.2	31.0	99
	3.1	25.0	28.1	27.8	99
Mixed vegetables	0.8	10.0	10.8	10.8	100
Black eyed peas	8.7	10.0	18.7	18.0	96
	6.0	10.0	16.0	16.5	103
Green peas	0.0	25.0	25.0	24.2	97
	0.0	25.0	25.0	23.9	96

[a] Values in C are equal to the sum of those in A and B.

[b] Recovery percentages are obtained from the ratio of figures shown in D to corresponding values in C.

initial tin content of the product was negligible and the fact that results of recovery determinations on these samples were uniformly acceptable more clearly indicates the precision which may be expected. Satisfactory recoveries have been obtained on samples containing as much as 400 parts per million of tin.

The data presented in Table III show the tin content in the original sample, the amount of tin added, and the amount found, all expressed in terms of parts per million. The ratio of the amount actually found to the sum of the original tin content and the added tin is given as the recovery.

DISCUSSION

By means of the procedure described it is possible to determine the tin content of a 10-gram sample of food product containing as little as 0.5 part per million. This represents a considerable increase in sensitivity over the volumetric iodometric method, which requires 50 to 100 grams of material. The increased sensitivity of the polarographic procedure in permitting the use of small samples makes possible a considerable saving in time and a marked economy of reagents. The reduction in sample weight, for example, reduces the quantity of nitric and sulfuric acids consumed in the digestion to less than one fifth that required in the volumetric method. The use of hydrogen sulfide with the accompanying problem of fume removal is eliminated, as well as the time-consuming filtration of the sulfide precipitate. The reduction in sample size also permits the use of smaller vessels and enables the operator to handle three to four times as many determinations concurrently.

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RAW SUGAR

Sampling, Mixing, and Testing

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New practices relating to the sampling, mixing, and testing of undamaged raw sugar imported in bags became effective in the Bureau of Customs in 1943. At the same time a new procedure for controlling the mixing and testing was introduced. The new practices include reduction in the sampling ratio from 100% to one bag in seven and the optional use of a new method of mixing. Experimental work on which the new practices are based is described. Data on the efficacy of the mixing and testing, as revealed by the new control procedure, are given.

THE customs duty on imported raw sugar is based on the direct polarization. In the case of raw sugar in bags, the samples for analysis are obtained from mixtures of portions taken by means of a trier (*6*) inserted into the bags. The Customs Regulations of 1907, 1923, 1931, and 1937 provided that 100% of the bags be sampled.

In 1942, as the result of requests of several government agencies that all possible steps be taken to conserve jute bags because of war conditions, W. R. Johnson, Commissioner of Customs, initiated a systematic study of the sampling, mixing, and testing of raw sugar to ascertain if the percentage of bags sampled per cargo could be reduced without jeopardy to the revenue and the number of bags damaged by customs samplers thereby lessened. The study was developed and conducted by the bureau's Division of Laboratories under the direction of H. J. Wollner (then consulting chemist to the Secretary of the Treasury). The evaluation of the results was made by the application of statistical principles employing standard methods (*1*).

SAMPLING

Precision Using Customs Trier. The preliminary study involved the determination of the degree of variability of the sugar, from bag to bag, in two different cargoes, A and B. Similar information was subsequently obtained on a third cargo, C. The study was designed to reveal information regarding the number of bags which would have to be sampled to ensure that the maximum gain or loss in revenue per cargo due to sampling errors, with a given degree of probability, would not be excessive.

Cargo A appeared to contain a considerable amount of sugar which had been stored for some time prior to export; it was not very uniform in appearance. The sugar in cargo B was generally uniform in appearance. The sugar in cargo C appeared to represent an abnormal case, varying from moist dark brown to dry almost-white sugar.

The three cargoes were sampled and tested by customs officers at Philadelphia, the samples being taken with the customs short trier (*6*) and the tests being made by the customs laboratory method (*8*). One core was taken from each bag sampled and placed in a 2-ounce glass container, which was then sealed with Scotch tape. The cores were taken at regular intervals from

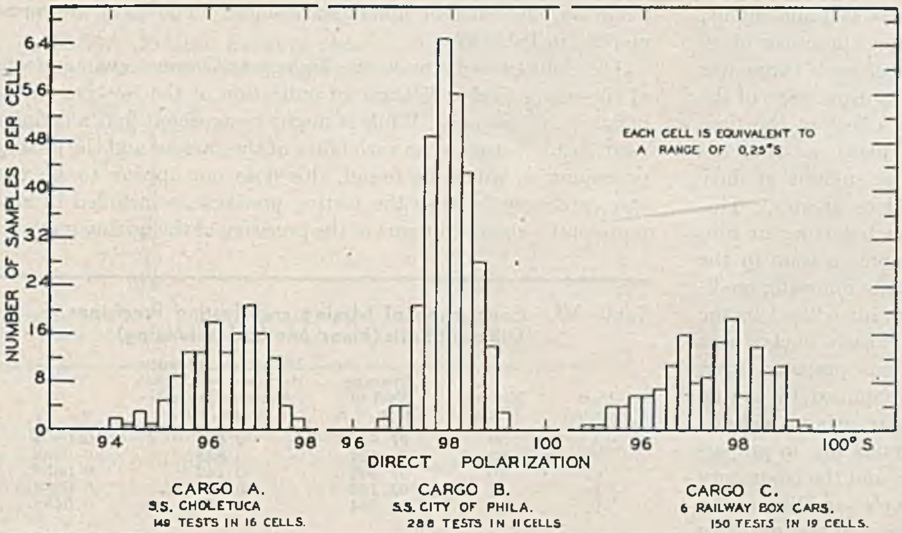

Figure 1. Histograms of Frequency Distribution in Sampling

Table I. Summary of Sampling Data for Three Different Cargoes Using Customs Short Trier

Cargo	No. of Bags	No. of Cores[a]	No. of Groups	Average Test, ° S.	σ', ° S.	Difference Between Highest and Lowest Individual Test, ° S. Actual	Statistical[b]
A	8,996	149	17	97.360	0.718	3.82	4.31
B	19,530	288	32	98.025	0.474	2.47	2.84
C	1,800	150	30	97.157	1.059	4.36	6.35

[a] Also number of tests.

[b] Based on ± $3\sigma'$.

Table II. Summary of Sampling Data for Cargo C Using Three Different Types of Triers

Trier	No. of Cores[a]	Average Test, ° S.	σ', ° S.
Customs short form	150	97.157	1.059
Modified customs short form	150	97.136	1.022
Canadian	150	97.141	1.053

[a] Also number of tests.

different parts of the bags, and each sample was thoroughly mixed before testing. The data are summarized in Table I. Histograms, showing frequency distributions, appear in Figure 1.

The universe standard deviations, σ', shown in Table I represent the variation of the sugar in each cargo and are referred to as sampling precisions. A relatively minor part of the indicated variation is incidental to the testing (see Table IX).

Precision Using Different Triers. The data for cargo C were obtained in a study of the relative efficiency of three different types of triers, the customs short trier, a modified customs short trier, and a Canadian sugar trier. The modification of the customs trier consisted of building up one of its sides by welding on a strip of sheet metal, in the hope of obtaining a more representative sample. The Canadian trier was furnished to the bureau by one of the government war agencies interested in the conservation of jute. It had a solid pointed tip, was longer and narrower than the customs trier, and was said to cause less damage to the bags during sampling. In this study one trier was assigned to a sampler and three cores were taken from each bag sampled—one core for each trier. In terms of sampling precision, the three triers appeared to be about equal (Table II).

While the Canadian trier caused less damage to the bags, it was found unsuitable for use in sampling hard, gummy sugar, which was being imported in quantity at the time. An endeavor to eliminate this objection was made by cutting off the solid tip. While cores could be obtained from all types of raw sugar, using the modified Canadian trier, dry sugar had a tendency to slip off when the trier was removed from the bag, and some sugars caked in the spoon of the trier and were rather difficult to detach. Accordingly this phase of the sampling study was terminated, and all subsequent tests were made with the customs short trier.

Maximum Precision. The maximum universe standard deviation found in the study of cargoes A, B, and C was 1.059° S. The cargo for which this figure was obtained undoubtedly comprised abnormally nonuniform sugars. In view of this, and since customs experience over a period of years indicates that cargoes of raw sugar in normal times are generally more uniform, 1.1° S. is considered a conservatively high figure for the variation among bags in a cargo of undamaged raw sugar. The only published information on this subject which has come to the attention of the writer is that developed by Vondrak (*11*) and by Browne and Zerban (*2*).

Probable Effects of Reduced Sampling. A universe standard deviation of 1.1° S. was used in calculating the number of bags of undamaged raw sugar which would have to be sampled at random (one core per bag) to ensure that the maximum sampling error, with a given degree of probability, would not exceed certain figures. The calculated values appear in Table III.

Table III indicates that in order to ensure a sampling error of not more than 0.05° S. in 99 cases out of 100, at least 3212 bags should be sampled, one core per bag. For an average cargo of 20,000 bags this would require the sampling of about one bag in seven. If we assume that the cargo consisted of 20,000 bags of 96° S. Cuban sugar, containing 325 pounds per bag, a sampling error of 0.05° S. would be equivalent to about $37 at the present rate of duty (*10*), or about 0.075% of the total duty involved. According to Table III, if the same cargo were sampled 100%, the sampling error would not exceed 0.02° S. in 99 cases out of 100. This would be equivalent to about $15 at the present rate or about 0.03% of the total duty involved.

The possibility of applying a sampling ratio of one bag in seven to all cargoes of undamaged raw sugar was considered. In this connection the maximum gain or loss in revenue for different sized cargoes of 96° S. Cuban raw sugar due to sampling errors, assuming a sampling ratio of one bag in seven and a probability of 0.99, was calculated (Table IV).

Actual Effects of Reduced Sampling. The customs duties which would result from 100% sampling and reduced sampling of Cuban raw sugar in bags were determined from tests made of actual samples from five different cargoes. The sampling, mix-

Table III. Relation between Maximum Sampling Error and Number of Bags to Be Sampled, One Core per Bag[a]

Maximum Sampling Error, ° S.	No. of Bags to Be Sampled (Cores)[b]
0.5	32
0.2	201
0.1	803
0.05	3,212
0.02	20,073
0.01	80,293

[a] Based on σ' of 1.1° S. and probability of 0.99.

[b] Calculated by use of formula: $n = \frac{t^2 \times \sigma'^2}{E^2}$

where n is number of bags to be sampled (cores), t is factor for probability, σ' is universe standard deviation, and E is maximum sampling error.

ing, and testing were done by customs officers at Philadelphia. In the case of 100% sampling, the usual customs practices (*3*, *8*) were followed, except that the average test of each cargo was calculated on a weight basis rather than on the usual basis of the number of bags. If the mixing practices in effect at the time were applied to the sugar obtained in the reduced sampling experiments, fewer mixes would result and the amount of duty represented by each mix consequently would be greater. This indicated the importance of ensuring thorough mixing in connection with reduced sampling practices—more so than in the case of 100% sampling. With this in mind, the following modifications in the existing practices (*3*, *8*) were introduced in the case of the reduced sampling experiments: each bucket was mixed separately; one laboratory sample was prepared from each bucket; each laboratory sample was obtained by taking portions from different parts of the mixed sugar, using a measuring spoon; the quantity of sugar in each sample was in proportion to the quantity of sugar in each bucket; and the laboratory mixed together the samples from the half-day's sampling of the cargo and, with one exception, made ten tests on the resulting mixture. The results obtained for the five cargoes appear in Table V.

Sampling Ratio Recommended. It was decided to recommend that for customs purposes the sampling of one bag in seven, using the customs short trier, be authorized in the case of undamaged raw sugar. This recommendation was based primarily on the data derived from the statistical study (Table IV) and on actual cargoes (Table V). Data were subsequently obtained on a sixth cargo, sampling 100% and one bag in seven, but were not included in Table V.

MIXING

The over-all error in the average test for a cargo of raw sugar includes, in addition to the sampling error, errors incidental to the mixing and testing operations. Effects of sampling errors have previously been discussed. With regard to mixing and testing errors, for practical reasons these are considered as a combined error in the following discussion.

Precision of Hand Mixing Method. The first step in the study of mixing consisted of determining the precision of the hand method of mixing (*5*) which was in effect at the time. Five cargoes of Cuban raw sugar were involved, one each at Baltimore, New Orleans, New York, Philadelphia, and Savannah. The sampling, mixing, and testing were done by customs officers in the usual manner, except that five tests instead of two were made on each mix of undamaged sugar. The data are summarized in Table VI.

Table IV. Relation between Maximum Sampling Error and Maximum Gain or Loss in Revenue for Different Sized Cargoes of 96° S. Cuban Raw Sugar (Sampling Ratio 1 in 7)[a]

No. of Bags in Cargo	No. of Bags Sampled (Cores)	Total Revenue, $	Maximum Sampling Error[b], ° S.	Maximum Gain or Loss in Revenue $	%
50,000	7,143	121,875	0.034	61	0.05
20,000	2,857	48,750	0.053	39	0.08
10,000	1,429	24,375	0.075	27	0.11
5,000	714	12,188	0.106	19	0.16
2,000	286	4,875	0.168	12	0.25
1,000	143	2,438	0.237	9	0.37
500	71	1,219	0.335	6	0.49
300	43	731	0.433	5	0.68

[a] Based on σ of 1.1° S., probability of 0.99 and 325 pounds of sugar per bag dutiable at $0.0075 per pound.

[b] Calculated by use of formula appearing under Table III.

Table V. Comparison of Revenue for Five Cargoes Based on Actual Tests

Cargo	No. of Bags in Cargo	100% Sampling: No. of tests	Average test, ° S.[a]	1 Revenue	Reduced Sampling: Sampling ratio	No. of tests	Average test, ° S.[b]	2 Revenue	Difference in Revenue, 1 − 2: $	%
1	7043	24	96.92028	$ 17,578	3 in 7	40	96.913	$ 17,576	+ 2	0.01
2	15709	48	97.31611	39,397	2 in 7	63	97.342	39,412	−15	0.04
3	24993	74	97.10752	62,557	1 in 7	80	97.106	62,555	+ 2	0.00
4	7124	24	97.01166	17,864	3 in 7	50	96.999	17,861	+ 3	0.02
5	49483	138	97.18038	124,038	1 in 7	80	97.218	124,106	−68	0.05

[a] Calculated to 5 decimals in accordance with practice in effect at the time.

[b] Calculated to 3 decimals in accordance with present practice.

The differences between the highest and lowest average tests of the mixes (Table VI) are an indication of the relative variability of the cargoes. While it might be expected that a definite relationship between the variability of the cargoes and the mixing precisions, σ, would be found, this does not appear to be the case, probably because the testing precision is included in and represents a significant part of the precision of the mixing method.

Table VI. Comparison of Mixing and Testing Precisions, σ, for Different Ports (Hand Method of Mixing)

Port Symbol	No. of Mixes	Average Test of Cargo, ° S.	Difference between Highest and Lowest Average Tests of Mixes, ° S.	σ, ° S.
A	36	97.528	0.484	0.0409
B	33	97.324	0.828	0.0658
C	20	97.549	0.142	0.0536
D	21	97.188	0.484	0.0479
E	15	96.864	0.160	0.0438

Precision of New Mixing Method. The customs regulations in effect at the time (*6*) required that the average test be determined for the sugar represented by each half-day's sampling of a cargo and that not more than 3 full buckets of sugar should be mixed together (*7*). This meant that under 100% sampling a number of mixes were generally necessary for each half-day's sampling of a cargo. It was anticipated that a similar condition might also apply when one bag in seven was sampled. Since by limiting the number of mixes per cargo to one each half-day the over-all work would be simplified, it was decided to develop a method of mixing which would serve this purpose in most cases and yet be sufficiently precise.

While the modifications in existing practices referred to in connection with Table V resulted in one mix per half-day, it was believed practicable to devise a simpler method. Accordingly, a number of mixing experiments were subsequently conducted by customs officers at Philadelphia. These experiments culminated in the development of special equipment and a new method of mixing, which was called the box and screen method (*5*). (The method employs a 0.375-inch mesh wire screen, fitted over a 4-box receiver, each box being detachable. With the aid of a similar receiver all the sugar is screened and quartered three times.) The most important experiment is described in the following:

> Two abnormal mixtures, each consisting of about 37.5 pounds of low test raw sugar (95° S.) and about 37.5 pounds of high test raw sugar (97.7° S.) were used. In each case 5 bucketfuls (about 75 pounds) were prepared, each containing approximately equal layers of the low and high test sugar. Each lot was mixed by the box and screen method, with the exception that one lot was screened twice instead of three times. In each case 30 groups of samples, each group consisting of one sample from each of the four boxes, were taken from the final mixture. The four samples in each group were taken at the same time. Each sample consisted of about 2 ounces. All the samples in each mixture were tested as a unit, without mixing, by the same chemist, under the same conditions. In the case of two screenings the elapsed time for the mixing was 3.33 minutes and the mixing precision, σ, was 0.1701. In the accepted mixing procedure involving three screenings 5.67 minutes were consumed and the precision was found to be 0.1102.

The precision, σ, of 0.1102 for the box and screen method of mixing represents an extreme condition. In view of this and the results obtained in the study of the hand method of mixing, 0.11° S. may be considered a conservatively high figure for the

Table VII. Relation between Number of Tests per Mix and Maximum Mixing and Testing Error per Mix[a]

No. of Tests per Mix	Maximum Mixing and Testing Error per Mix, ° S.[b]
2	0.200
4	0.142
6	0.116
8	0.100
16	0.071
32	0.050
64	0.035
128	0.025
256	0.018

[a] Based on σ of 0.11 and probability of 0.99.

[b] Calculated by use of formula appearing under Table III.

combined mixing and testing precision, σ, when either method is properly used on undamaged raw sugar. An idea of the relative efficiency of the two methods can be obtained by reference to Table X.

TESTING

MIXING AND TESTING ERRORS. Using 0.11 as the mixing and testing precision, the maximum mixing and testing errors per mix for different numbers of tests per mix, for a probability of 0.99, were calculated (Table VII).

NEW CUSTOMS METHOD

SAMPLING AND MIXING PROCEDURES. Detailed instructions on new procedures for the sampling and mixing of raw sugar for customs purposes were prepared as an amendment to the Bureau of Customs Sampling Guide. This amendment (*5*), in the form of method 17, entitled "Raw Sugar", became effective July 14, 1943.

INSTRUCTIONS ON TESTING. The maximum gain or loss in revenue for a cargo of raw sugar due to the mixing and testing error depends in part on the number of mixes, the quantity of sugar in each mix, and the number of tests per mix. In view of this, and since the amount of revenue represented by a cargo depends partly on the quantity of sugar involved, it was deemed impractical to require that the number of tests per mix or per cargo be such that the maximum mixing and testing error, with a given degree of probability, would not exceed a specified figure. The instructions (*9*) finally issued in this connection were based on a practical application of statistical principles. The pertinent part of these instructions is as follows:

> The sample submitted to the laboratory for a mix may consist of four full cans, two full cans, one full can, or even one partially full can, depending upon the quantity of sugar present in the mix. Two tests shall be made on each can submitted from each mix of undamaged raw sugar, except that in the case of mixes representing 5000 or more bags, four tests shall be made on each can.
>
> Inasmuch as it is desired to obtain data on the efficacy of the previous mixing of the sample, special care shall be taken to avoid mixing the sugar in the can either before or when removing a portion for test. All reasonable efforts shall be made to take each test portion from a different position in the can. For example, after the upper surface layer has been discarded, the first test portion shall be taken from the resulting exposed surface. The succeeding surface layer shall then be discarded before the next portion is removed for weighing.

The requirement as to the number of tests per can was designed to keep the errors incidental to the mixing and testing as low as practicable. For this purpose it was desirable that each test portion come from a different part of the mix, preferably by having the number of cans sent to the laboratory for each mix correspond to the number of tests to be made on each mix. It was deemed impractical at the time to submit one can per test because of the difficulty in getting proper containers. In order to accomplish the desired purpose and at the same time permit a study of the efficiency of the routine mixing and testing operations, instructions regarding the nonmixing of the samples in the laboratory were included.

ESTIMATED OVER-ALL PRECISION. It was anticipated that, following the practical application of method 17, the mixing and testing error for an average cargo generally would not exceed the maximum sampling error for the cargo. For example, according to Table IV, the sampling error for a 20,000-bag cargo, sampling ratio one bag in seven, would not be expected to exceed 0.053° S. in 99 cases out of 100. Assuming five as the average number of mixes, each representing 4000 bags, and eight tests per mix, the mixing and testing error for the cargo would not be expected to exceed 0.045° S. in 99 cases out of 100. This figure is obtained by dividing the maximum mixing and testing error per mix (from Table VII) by the square root of the number of mixes. It may also be assumed that the sampling, mixing, and testing error for the cargo would not exceed 0.069° S. in 99 cases out of 100. This figure is obtained by taking the square root of the sum of the squares of the maximum sampling error and the maximum mixing and testing error.

In view of the foregoing, it would appear reasonable to assume that the maximum sampling, mixing, and testing errors due to chance, when method 17 is followed, generally will not be excessive.

CONTROL OF MIXING AND TESTING

CONTROL PROCEDURE. Under the reduced sampling procedure authorized by method 17 each mix represents a greater proportion of the cargo and the total number of mixes required for the cargo are materially less than when 100% sampling is practiced. This indicated the desirability of maintaining some kind of statistical control in connection therewith. Accordingly a procedure designed to reveal inadequacies in the routine mixing and testing of each importation of undamaged raw sugar was devised (*4*), and made official for customs purposes on July 14, 1943. The following are the pertinent portions of the procedure:

> When imported raw sugar is sampled for test at each port, the appraiser forwards to the director of the National Bureau of Standards a duplicate of one of the samples sent to the customs laboratory.
>
> Only one sample is submitted to the National Bureau of Standards for each importation. It is taken from one of the regular mixes of undamaged sugar and consists of the same number of cans as the regular laboratory sample from that mix.
>
> The samples sent to the customs laboratory and the National Bureau of Standards are tested immediately on receipt. The average tests and the individual tests obtained on the duplicate samples are forwarded to the U. S. Customs Laboratory, Baltimore, Md., where they are studied by statistical methods.

The customs laboratories do not know which mixes are being studied until after their reports have been submitted to the appraisers. Accordingly, their results represent routine conditions for the testing.

DATA, CRITERIA, AND CONCLUSIONS. The more important of the statistical values derived from the control procedure will be found in Tables VIII, IX, and X.

Some of the criteria which were set up in connection with the study of the data and the conclusions which were drawn from the study are as follows:

> If the standard deviation, σ, for both the customs and the National Bureau of Standards tests for a given sample are out of control, existence of disturbing factors outside the laboratory, presumably in the mixing operation, is indicated. Only three such cases were noted among the 399 samples which could be considered.
>
> If the difference between the average tests (customs and N.B.S.) on the same sample exceeds the range of the control limits for averages, $2A\sigma$, an assignable cause in the nature of a constant testing error or a change in the moisture content is indicated. In determining the range of the control limits for averages the higher of the two σ's was used. Assignable causes were indicated in 28% of the cases when the hand method of mixing was involved, and

Table VIII. Comparison of Average Tests for Individual Customs Chemists and Individual Customs Laboratories with Those for N.B.S.[a]

Customs Laboratory Symbol	Customs Chemist Symbol	No. of Samples	Average Test, ° S.		
			1 Customs	2 N.B.S.	Difference 1 − 2
A		57	97.158	97.185	−0.027
	H	8	97.404	97.345	+0.059
	I	49	97.118	97.159	−0.041
F		99	97.401	97.343	+0.058
	J	86	97.403	97.334	+0.069
	K	2	97.000	96.936	+0.064
	L	11	97.460	97.487	−0.027
B		128[b]	97.138	97.139	−0.001
	M	6	96.754	96.738	+0.016
	N	46	97.296	97.284	+0.012
	O	76	97.073	97.082	−0.009
C		120	97.218	97.149	+0.069
	P	14	97.058	96.941	+0.117
	Q	106	97.239	97.177	+0.062
D		150	97.369	97.356	+0.013
	R	144	97.370	97.358	+0.012
	S	6	97.353	97.298	+0.055
G		7	98.576	98.710	−0.134
	T	6	98.556	98.705	−0.149
	U	1	98.696	98.738	−0.042
E		64	96.997	96.940	+0.057
	V	21	96.934	96.857	+0.077
	W	24	96.962	96.904	+0.058
	X	19	97.112	97.078	+0.034
Total		625			
Averages			97.254	97.227	+0.027

[a] Table is based on data for samples obtained by both methods of mixing. Number of tests per sample varies from 2 to 8.

[b] Includes samples from 2 ports.

in 34% of the cases when the box and screen method was involved. For these, 70% of the differences were 0.2° S. or less, 95% were 0.3° S. or less, 98% were 0.4° S. or less, 99% were 0.5° S. or less, and none exceeded 0.583° S.

The following conclusions can be drawn from Table X: There is little difference in the precision of the mixing by customs officers at the several ports; and in terms of mixing precision there is little difference between the two methods of mixing as practiced by customs officers.

The $\dot{\sigma}$'s in Tables IX and X can be used in calculating the maximum mixing and testing error per mix for a given probability. However, since the $\dot{\sigma}$'s are based on two tests per can per sample, there may be some question as to the reliability of the error thus determined. Accordingly, a number of the $\dot{\sigma}$'s in Table IX were recalculated, using the data for the first test on each can per sample. Table XI indicates that, as anticipated, the effect of making two tests per can under the prescribed conditions is equivalent to that of making one test on each of two cans.

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Table IX. Comparison of Mixing and Testing Precisions, $\dot{\sigma}$, for Each Method of Mixing Based on Tests by N.B.S. and Customs[a]

Laboratory Symbol	Customs Chemist Symbol	Hand Method		Box and Screen Method	
		No. of samples	$\dot{\sigma}$	No. of samples	$\dot{\sigma}$
A	I	32	0.064	..	...
N.B.S.		32	0.039	..	...
F	J	76	0.060	..	...
N.B.S.		76	0.040	..	...
F	L	30	0.064	..	...
B	O	..	...	41	0.061
N.B.S.		..	...	41	0.050
B	O	..	...	58[b]	0.060
N.B.S.		..	...	58[b]	0.049
B	N	..	...	34[b]	0.044
N.B.S.		..	...	34[b]	0.042
C	Q	..	...	106	0.065
N.B.S.		..	...	106	0.046
C	P	..	...	37	0.088
D	R	41	0.047	103	0.044
N.B.S.		41	0.043	103	0.042
D	S	...	...	30	0.055
G	T	34	0.041	..	...
E	V	..	...	34	0.041
	W	..	...	47	0.051
	X	..	...	49	0.066

[a] Same samples used in each case where N.B.S. data are given. In such cases, each sample came from a different cargo. Where no N.B.S. data are given, all samples were not tested by N.B.S. and more than one sample may have come from the same cargo.

[b] Includes samples from 2 ports.

Table X. Comparison of Mixing and Testing Precisions, $\dot{\sigma}$, for Each Method of Mixing Based on N.B.S. Tests

Port	Hand Method		Box and Screen Method	
	No. of samples	N.B.S., $\dot{\sigma}$	No. of samples	N.B.S., $\dot{\sigma}$
A	38	0.038	...	...
F	87	0.040	...	...
Y	...	...	33	0.045
B	...	...	63	0.049
C	...	...	120	0.046
D	43	0.043	107	0.041
E	...	...	63	0.047
All	202	0.040	423	0.044

Table XI. Comparison of Mixing and Testing Precisions, $\dot{\sigma}$, for Each Method of Mixing Based on Customs Tests

(2 tests per can and one test per can per sample)

Laboratory Symbol	Customs Chemist Symbol	No. of Tests per Can	Hand Method		Box and Screen Method	
			No. of samples	$\dot{\sigma}$	No. of samples	$\dot{\sigma}$
A	I	2	32	0.064	..	...
A	I	1	32	0.056	..	...
F	J	2	76	0.060	..	...
F	J	1	76	0.063	..	...
B	O	2	..	...	41	0.061
B	O	1	..	...	41	0.063
B	O	2	..	...	58[a]	0.060
B	O	1	..	...	58[a]	0.062
B	N	2	..	...	34[a]	0.044
B	N	1	..	...	34[a]	0.045
C	Q	2	..	...	106	0.065
C	Q	1	..	...	106	0.069
D	R	2	41	0.047	103	0.044
D	R	1	41	0.055	103	0.049

[a] Includes samples from 2 ports.

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Picric Acid Method for Determination of Aromatic Content of Aviation Gasoline

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Dobryanskii and Tikhonov-Dubrovskii utilized the difference in solubility of picric acid in aromatic and nonaromatic hydrocarbons to develop a method for determining the aromatic content of aviation gasoline. The method has been modified to increase its accuracy, precision, and rapidity. The solubility of the picric acid in gasoline is determined at some temperature between 20° and 30° C. Applying a temperature correction to obtain the solubility at 25° C., the percentage of aromatics is obtained by reference to a standard curve. The presence of olefins and naphthenes necessitates a slight correction: −1.4% for each 10% of olefin and −0.6% for each 10% of naphthenes. The method is accurate to ±1% in the range of 0 to 25% of aromatics.

A METHOD for determining the aromatic content of aviation gasoline by utilizing the difference in solubility of picric acid in aromatic and nonaromatic hydrocarbons was reported by Dobryanskiĭ and Tikhonov-Dubrovskiĭ (*2*). Their method for determining the dissolved picric acid was tedious, and they did not consider the effect of variations in temperature on the solubility. The authors have developed a more accurate, more precise, and more rapid method for determining the dissolved picric acid. By making a temperature correction, the solubility of the acid may be determined at any convenient temperature between 20° and 30° C. (a wider range may be used if needed). The per cent of aromatics in the gasoline is then obtained directly from a curve of aromatic content versus solubility.

The procedure is most accurate in the determination of a single aromatic hydrocarbon in paraffin hydrocarbons, but is satisfactory for those mixtures of aromatics which may be found in aviation gasoline. The presence of olefins and naphthenes in gasoline necessitates a slight correction: −1.4% for each 10% of olefins and −0.6% for each 10% of naphthenes. For high accuracy, therefore, the bromine number of cracked gasolines should be determined and the appropriate correction made.

METHOD

A 60-ml. sample of the gasoline is measured into a 125-ml. Squibb-type separatory funnel containing 1 gram of pure picric acid. Commercially available C.P. or reagent quality picric acid containing up to 10% water gives precise results, but for a large number of determinations the dry picric acid is more convenient. The sample is brought to room temperature, which should be between 20° and 30° C., and is shaken for 5 minutes, either by hand or by means of a mechanical shaker. If shaken by hand, the flask is held in the finger tips, so that the heat from the hand will not cause a change in temperature during the shaking period. The temperature of the sample is then recorded and the sample is filtered into a 125-ml. Erlenmeyer flask through a Whatman No. 1 or other fast filter paper. A 50-ml. sample of the filtrate is pipetted into a 250-ml. iodine flask containing 40 ml. of distilled water. Three drops of *m*-cresol purple indicator are added, and 0.05 *N* alkali is added to the sample from a buret, while the flask is swirled gently, until the color of the indicator is changed to purple and approximately 1-ml. excess of alkali has been added. The mixture is then shaken vigorously for one minute. The two layers are allowed to separate, after which the excess alkali is titrated with 0.01 *N* hydrochloric acid to the complete disappearance of the reddish-purple color of the indicator as viewed under a tungsten filament lamp.

The dissolved picric acid in 100 ml. of a saturated solution of picric acid in the gasoline is expressed by the equation:

$$\frac{\text{Mg. of picric acid}}{100\text{ ml.}} = 458.2 \times (\text{ml. of NaOH} \times N\ \text{NaOH} - \text{ml. of HCl} \times N\ \text{HCl})$$

The measured solubility is corrected to the value for 25° C. by the equation:

$$\text{Solubility at } 25^\circ\text{ C.} = \frac{\text{mg. of picric acid}}{100\text{ ml.}}[1 + 0.035(25^\circ\text{ C.} - t)]$$

where *t* is the observed temperature in degrees Centigrade. The percentage of aromatics in the gasoline is then read from one of the curves presented with this report, as discussed below.

EXPERIMENTAL

The development of the method included the following investigation:

Titration of the picric acid dissolved in the gasoline.
Effect of temperature on the solubility of picric acid.
Satisfactory shaking time to saturate gasoline with picric acid.
Effect of purity of picric acid on its solubility in gasoline.
Solubility of picric acid in blends of aromatics with iso-octane (2,2,4-trimethylpentane, Rohm and Haas).
Effect of olefins and naphthenes upon the solubility of picric acid.

SELECTION OF TITRATION METHOD. In this portion of the work the following points were studied:

The most suitable indicator for the titration.
Direct titration of the picric acid compared with back-titration of an excess alkali.
Size of the gasoline sample.
Concentration of alkali.

A blend of 10% benzene in iso-octane was prepared and 500 ml. were shaken with 5 grams of picric acid for 30 minutes. Samples of 10 to 15 ml. of this gasoline, saturated with picric acid, were pipetted into 125-ml. iodine flasks containing water and the acid was titrated: (1) by adding 0.01 or 0.05 *N* alkali with long shaking until an end point was reached with phenolphthalein indicator, or (2) by adding an excess of alkali as evidenced by the color change of thymol blue, bromothymol blue, phenolphthalein, or *m*-cresol purple, and back-titrating with 0.01 *N* acid.

These tests showed that thymol blue did not give a satisfactory end point, probably because it was soluble in the gasoline; that bromothymol blue had a green to yellow end point that was very difficult to detect in the picric acid solution; and that a higher solubility was obtained by using phenolphthalein than by using *m*-cresol purple. This difference may be attributed to differences in the pH range of the two indicators, to the fact that more carbon dioxide may be titrated as picric acid by using phenolphthalein, and that the *m*-cresol purple end point was more easily detected than the phenolphthalein end point. The selection of *m*-cresol purple made it necessary to use the back-titration procedure, since it was impossible to extract all the picric acid from the gasoline phase at the alkaline pH range of this indicator (pH 7.4 to 9.0). The back-titration procedure had a further advantage in that the solution required less shaking to reach the end point.

In varying the size of the gasoline sample for titration from 10 to 50 ml., it was noted that the larger the sample the lower the apparent solubility of picric acid. This effect was attributed to interference by small amounts of carbon dioxide dissolved in the water. Although it would be possible to correct for this aliquot error empirically, it seemed advisable to use the larger gasoline sample.

In comparing results obtained by using 0.01 *N* and 0.05 *N* alkali, it was found that the more concentrated alkali gave re-

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sults of higher precision. It is probable that the 0.01 N alkali contained sufficient carbonate to cause the poorer results. Therefore, 0.05 N alkali is recommended.

DETERMINATION OF TEMPERATURE COEFFICIENT. Measurements of the solubility of picric acid were made at room temperature and at approximately 0° C., in blends of aromatics with technical grade iso-octane and in Houdry process gasoline. These solubilities were inserted into the ideal solubility equation to obtain a constant by which solubilities determined near 25° C. may be corrected to give the solubility at 25° C.

In using ideal solubility Equation 1, weights W_1 and W_2 in milligrams of picric acid per 100 ml. of gasoline have been substituted for mole per cents n_1 and n_2, since

$$\log \frac{n_1}{n_2} = \frac{\Delta H(T_1 - T_2)}{2.303R(T_1T_2)} \qquad (1)$$

the solubilities are low. The constant, $\Delta H/2.303R$, has been designated by S, giving the equation the following form:

$$\log \frac{W_1}{W_2} = S\,\frac{(T_1 - T_2)}{(T_1 - T_2)} \qquad (2)$$

After solving for S in Equation 2, using the experimental values from Table I, the fractional increase in solubility per degree at 25° C., $\frac{w}{W}$, has been calculated from Equation 3,

$$\log \left(1 + \frac{w}{W}\right) = \frac{S}{298^2} \qquad (3)$$

Since the variation of solubility with temperature over a restricted range will be practically linear, solubilities determined between 20° and 30° C. may be corrected to 25° C. by the relation:

$$\text{Solubility at 25° C.} = \text{observed solubility}\left[1 + \frac{w}{W}(25 - t)\right] \qquad (4)$$

where t is the observed temperature in degrees Centigrade.

Table I gives the data obtained and the calculated values of w/W.

A value of 0.035 for w/W is recommended for correcting solubilities to 25° C., but should not be used for solubilities measured outside the range of 20° to 30° C. For work of high accuracy it is recommended that the temperature be maintained at 25° C. by means of a constant-temperature bath.

DETERMINATION OF SHAKING TIME. A study was made to determine the minimum shaking time in which a solution of picric acid in gasoline would reach equilibrium. It was found that for a fuel high in aromatics, such as Houdry process fuel, the amount of picric acid dissolved in the gasoline was almost at a maximum after 5 minutes of shaking, being only 1 to 2% greater after 20 minutes. For the iso-octane (0% aromatics), however, a 2-minute shaking period was as adequate as 5 minutes; only a slight increase in solubility was noted after a longer shaking period. A 5-minute period has been selected as the most satisfactory.

Table I. Temperature Coefficient Data

Gasoline	Temperature, ° C., T_1	Solubility, Mg., W_1	Temperature, ° C., T_2	Solubility, Mg., W_2	Temperature Coefficient, Equation 3, $\left(1 + \frac{w}{W}\right)$
Iso-octane	23.6	10.9	1.4	4.7	1.035
Benzene and iso-octane blend					
10% benzene	26.6	59.1	0.5	22.0	1.036
25% benzene	26.0	262.3	0.7	119.3	1.029
Xylene and iso-octane blend					
10% xylene	26.6	74.2	0.5	29.2	1.034
25% xylene	26.2	334.6	0.5	167.4	1.025
Houdry gasoline	25.5	167.1	0.5	43.8	1.051

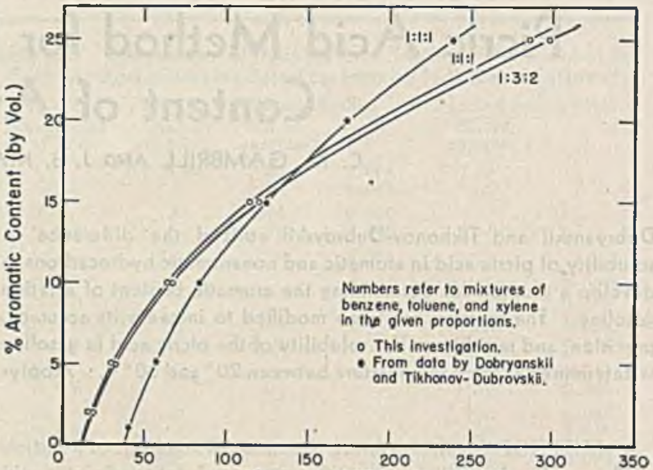

Figure 1. Solubility of Picric Acid

EFFECT OF PURITY OF PICRIC ACID ON ITS SOLUBILITY. Various stocks of picric acid were found to differ in solubility in the same gasoline. Recrystallization increased the solubility of impure samples, but did not change that of the reagent grade material. The solubility of the picric acid is thus a function of its purity.

As shown in Table II, drying the acid has no significant effect on the determination.

SOLUBILITY OF PICRIC ACID IN BLENDS OF AROMATICS. Blends of aromatics with iso-octane were prepared and the solubility of picric acid in these blends was determined by the method described above. The results of these determinations are given in Table III, and are plotted in Figures 1 and 2. All compositions given in this paper are reported on a volume per cent basis.

Table II. Effect of Drying Picric Acid on Its Solubility in Hydrocarbon Blends

Blend	Solubility of Picric Acid Undried	 Dried
	Mg./100 ml.	
A	63.2	63.5
	61.4	62.1
B	297.1	299.2
	301.4	298.9
	301.5	298.2

Table III. Determination of Aromatics in Blends

Aromatic Blends with Iso-octane		Solubility of Picric Acid, 25° C.
	%	*Mg./100 ml.*
Aromatics	0	11.0
Benzene	5	26.9
	10	55.8
	20	163.0
	25	253.1
Toluene	3	23.1
	10	69.3
	20	198.8
Xylene (commercial)	3	24.0
	10	70.2
	20	206.5
	25	320.5
1:1:1 mix[a]	2	17.3
	5	31.5
	10	64.0
	15	115.4
	25	286.2
1:3:2 mix[a]	2	18.5
	5	32.8
	10	67.3
	15	119.8
	25	297.8

[a] A mixture of benzene, toluene, and commercial xylene in given proportions.

Table IV. Solubility of Picric Acid in 10% Blends of Aromatics in Iso-octane

Aromatic Compound	Solubility of Picric Acid *Mg./100 ml.*	Aromatics (1:3:2 Curve) %	B.P. (Theoretical) ° *C.*
Possible aviation gasoline constituents			
Benzene	56	8.7	80.1
Toluene	69	10.4	110.8
Xylene (commercial)	70	10.5	...
o-Xylene	82	11.8	144
m-Xylene	81	11.7	138.8
m,*p*-Xylene (mixture)	78	11.3	...
Ethylbenzene	48	7.6	136.2
Cumene	36	5.7	153
Improbable aviation gasoline constituents			
Mesitylene	99	13.4	164.8
Diethylbenzene	41	6.5	182
Triethylbenzene	41	6.5	218
m-Diisopropylbenzene	22	3.0	204
p-Cymene	29	4.4	176
n-Butylbenzene	33	5.1	180
sec-Butylbenzene	26	3.9	174
tert-Butylbenzene	27	4.1	169
sec-Amylbenzene	20	2.6	189
tert-Amylbenzene	24	3.5	190

A plot of the values obtained by Dobryanskiĭ and Tikhonov-Dubrovskiĭ is included in Figure 2 for the sake of comparison. It is believed that the differences in intercept and in slope between their curve and the authors' are due to (1) the presence of olefins or naphthenes in their base stock; (2) the presence in their xylene of some impurity, such as ethylbenzene, in which picric acid is less soluble, and (3) the fact that their determinations were made at temperatures some 10° lower than the authors'.

Besides the three aromatics for which solubility values are reported in Table III, a number of other aromatics were tested in 10% blends with iso-octane. These results are given in Table IV.

EFFECT OF OLEFINS AND NAPHTHENES. Blends of iso-octane were prepared with cyclohexane and its methyl and *o*-dimethyl derivatives and with amylene, diamylene, diisobutylene, and cyclohexane. Various aromatics were added to these blends, and the solubility of picric acid in the mixture was determined. The apparent content of the aromatic compound or mixture used was then calculated from the curve given by that aromatic in mixture with only iso-octane. The results of these tests, given in Table V, show that both naphthenes and olefins cause a small increase in the apparent aromatic content, the effect of the olefins being greater. The error in terms of per cent aromatics is approximately +1.4% for each 10% of olefins and not more than +0.6% for each 10% naphthenes.

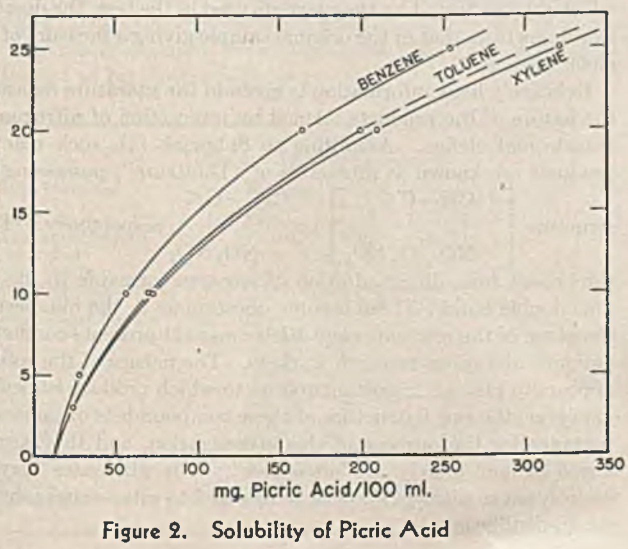

Figure 2. Solubility of Picric Acid

Table V. Effect of Olefins and Naphthenes on Solubility of Picric Acid in Gasoline

	Solubility of Picric Acid *Mg./100 ml.*	Aromatics Calculated from Picric Acid Solubility %
A. Naphthenes present		
10% benzene, 9% methylcyclohexane, 81% iso-octane	59.1	10.4
10% toluene, 9% methylcyclohexane, 81% iso-octane	73.3	10.5
10% xylene, 9% methylcyclohexane, 81% iso-octane	77.7	10.6
10% 1:1:1[a], 9% methylcyclohexane, 81% iso-octane	69.7	10.5
10% 1:3:2[a], 9% methylcyclohexane, 81% iso-octane	71.7	10.5
10% benzene, 45% methylcyclohexane, 45% iso-octane	85.8	13.8
10% toluene, 45% methylcyclohexane, 45% iso-octane	98.8	13.0
10% xylene, 45% methylcyclohexane, 45% iso-octane	106.4	13.4
10% 1:1:1[a], 45% methylcyclohexane, 45% iso-octane	94.5	13.2
0% aromatics, 50% methylcyclohexane, 50% iso-octane	23.1	3.0
0% aromatics, 25% cyclohexane	11.3	0
0% aromatics, 25% *o*-dimethylcyclohexane	12.6	0.3
B. Olefins present		
10% 1:1:1[a], 10% amylene, 80% iso-octane	76.0	11.4
10% 1:1:1[a], 25% amylene, 65% iso-octane	100.8	13.7
10% 1:1:1[a], 10% diamylene, 80% iso-octane	77.7	11.5
10% 1:1:1[a], 25% diamylene, 65% iso-octane	97.1	13.4
10% 1:3:2[a], 10% amylene, 80% iso-octane	82.9	11.8
10% 1:3:2[a], 25% amylene, 65% iso-octane	102.3	13.6
10% 1:3:2[a], 10% diamylene, 80% iso-octane	79.3	11.4
10% 1:3:2[a], 25% diamylene, 65% iso-octane	98.7	13.3
0% aromatics, 10% cyclohexene	13.5	0.6
0% aromatics, 25% cyclohexene	22.2	2.9
C. Naphthenes and olefins present		
10% 1:1:1[a], 25% methylcyclohexane, 10% diamylene, 55% iso-octane	94.8	13.2
10% 1:3:2[a], 25% methylcyclohexane, 10% diamylene, 55% iso-octane	99.0	13.3

[a] A mixture of benzene, toluene, and commercial xylene in given proportions.

SOLUBILITY OF PICRIC ACID IN PURE AROMATICS. The results of measurements of the solubility of picric acid in undiluted aromatics, not especially purified, are given in Table VI.

ANALYSIS OF AVIATION GASOLINES. Since the different aromatic compounds give slightly different solubility curves, it is necessary in applying the picric acid method to gasoline to make some assumption regarding the composition of the aromatics in the gasoline. The authors have assumed that a 1 to 3 to 2 mixture of benzene, toluene, and xylene gives a good average representation of the aromatics in most aviation gasoline, and have

Table VI. Solubility of Picric Acid in Undiluted Aromatics

Aromatic	Solubility of Picric Acid *G./100 ml. aromatic*	Temperature ° *C.*
Benzene	7.550	22.4
Toluene	8.950	22.3
Xylene (commercial)	9.810	22.8

Table VII. Determination of Aromatics in Aviation Gasoline

Gasoline	Per Cent Aromatics Picric acid method	Ultraviolet absorption (*1*)	Sulfonation (*5*)
A	0	0.2	
B	0	< 1	
C	25.0	24	
D	10.6	11	
E	0	< 1	
F	20.6[a]	21.0	21[a]
G	25.2[a]	23.4	24
H	0.8	1.5	2

[a] Corrected for olefin content.

used the curves for this mixture as a standard in determining the aromatic content of a number of typical fuels. Table VII compares results with those obtained on the same gasolines by other workers using ultraviolet absorption and acid absorption methods. Agreement between the different methods is seen to be satisfactory.

DISCUSSION

The chief error in the picric acid method lies not in the reproducibility of the determinations, which is about ±0.2%, but in the difference of solubility of the acid in the various individual aromatic compounds. The solubilities in benzene, toluene, and xylene are sufficiently similar so that no great error is committed by assuming them to be present in the ratio of 1 to 3 to 2, and in the gasolines examined the results appear to be accurate to better than 1%. To obtain more accurate results for the low-boiling constituents, it is only necessary to fractionate the gasoline and determine the benzene and toluene contents separately on the appropriate fractions. However, for the higher-boiling compounds, such as ethylbenzene and cumene, the solubility is low, and in so far as these compounds are present the aromatic content of the gasoline will be underestimated.

LITERATURE CITED

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(2) Dobryanskiĭ, A. F., and Tikhonov-Dubrovskiĭ, N. T., *Azerbaidzhanskoe Neftyanoe Khoz.*, No. 5, 84 (1935).
(3) Kurtz, S. S., Jr., private communications.

Determination of Olefinic Unsaturation

Nitrogen Tetroxide Method as Applied to Petroleum Hydrocarbons in the Gasoline Boiling Range

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A radically new method has been developed for determining the olefinic unsaturation of petroleum hydrocarbons lying in the gasoline boiling range. It is based on the reaction of nitrogen tetroxide with olefinic materials to convert them into oily addition products, or nitrosates. Separation of the unreacted material, including paraffins, naphthenes, and aromatics, may be effected by steam-distillation or by reaction and solution of the nitrosates in alcoholic potassium hydroxide and potassium sulfide. The change in volume of the sample gives a measure of the olefinic unsaturation.

THE determination of olefinic unsaturation in hydrocarbons has long been a controversial subject in the petroleum industry. Calculations based on the bromine number or iodine number have been accepted generally as the only feasible means of determining such unsaturation. That such methods are not entirely satisfactory is generally realized, as evidenced by the large number of bromine or iodine number procedures which have been proposed; almost every major oil company has its own modification which may give results differing appreciably from those of another company. The nature of the solvent used, temperature, time of contact, excess of halogen present, and many other factors affect the results which are obtained. The nature of the unsaturate itself also is an important factor. In conjugated diolefins, halogenation of both double bonds is usually incomplete and this same uncertainty applies to aromatics with an olefinic side chain. Extensive substitution, rather than simple addition of halogen, also may occur.

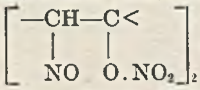
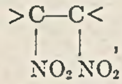
The difficulty of translating the bromine or iodine number into per cent olefinic unsaturation likewise is an important factor, due to lack of knowledge, in general, of the average molecular weight of the olefins involved or their distribution throughout the sample. In the case of whole gasoline samples, particularly those which are thermally cracked and may contain a mixture of olefins and diolefins as well as aromatics or even acetylenes, the problem becomes most acute.

A method that will give a direct volumetric measure of the olefinic unsaturation of the hydrocarbon sample, regardless of the type of olefin present, and is without effect on paraffins, naphthenes, or aromatics, would present an almost ideal solution to this problem. Such a method has been developed at this laboratory and has given most promising results on a wide variety of the most difficult and complex types of samples, both synthetic and natural. It also has the additional advantage that it can be used on dark-colored samples.

DESCRIPTION OF METHOD

The author has recently noted that nitrogen tetroxide will react rapidly and completely with all commonly available olefinic materials in the temperature range 104° to 410° F., converting them into heavy, oily addition products, the majority of which are of very low volatility, and from which any unreacted components of the mixture can be removed readily by a simple steam-distillation. The possibility of using nitrogen tetroxide as an analytical tool for resolving complex olefinic-aromatic mixtures at once became apparent and an extended investigation was undertaken.

Two methods finally resulted from this investigation, the distillation method mentioned in the preceding paragraph and a rapid method based on the discovery that the olefin nitrosates will react with alcoholic potassium hydroxide and potassium sulfide to form products soluble in 50% alcohol. It thus becomes possible to measure the volume of the paraffins, naphthenes, and aromatics, which are unaffected by the reagents used in the test, the decrease in volume from that of the original sample giving a measure of the olefin content.

Relatively little information is given in the literature regarding the nature of the products formed by interaction of nitrogen tetroxide and olefins. According to Sidgwick (*4*), such reaction products are known as nitrosates or "Dinitrüre", possessing the structure  $\left[\begin{array}{cc}-\mathrm{CH}- & \mathrm{C}< \\ | & | \\ \mathrm{NO} & \mathrm{O.NO_2}\end{array}\right]_2$ or  $\begin{array}{cc}>\mathrm{C}- & \mathrm{C}< \\ | & | \\ \mathrm{NO_2} & \mathrm{NO_2}\end{array}$, respectively. They thus result from direct addition of nitrogen tetroxide to the olefinic double bond. There is some question as to the bimolecular structure of the nitrosates and Riebsomer (*3*) presents conflicting opinions of various research workers. The nature of the solvent appears to play an important role as to which product is formed. However, the exact structure of these compounds is of minor importance for the purpose of this investigation, and they are referred to here merely as "nitrosates". The nitrosates may be hydrolyzed to nitro-alcohols or rearranged to nitro-oximes during steam-distillation.

APPARATUS

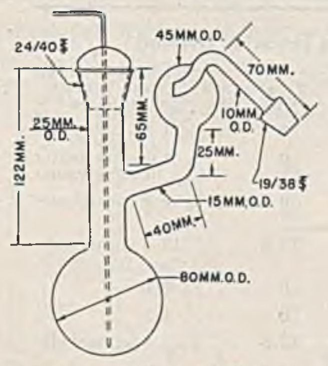


Figure 1. Treating Flask

A 200- to 250-ml. treating-distillation flask with a spray trap on the outlet and a steam inlet tube, as illustrated in Figure 1. Ground-glass connections are recommended.

Product receiver assembly, consisting of a curved glass adapter (Figure 2) with an extension of 4-mm. glass tubing which will nearly reach the bottom of the 150- to 250-ml. separatory funnel used as a receiver. A short length of 2-mm. capillary glass tubing is sealed in the upper wall of the large end of the adapter as an air inlet. The purpose of this adapter is to cause the drops of distilled oil to issue below the surface of the water in the separatory funnel, thus making evident the point at which these drops of oil become heavier than water. This receiver assembly is not designed for very volatile samples, which may require a more adequate condensing system.

Reaction Bottle. A modified Babcock bottle (*1*).

REAGENTS

Sulfamic Acid Solution. Dissolve 20 grams of sulfamic acid ($H_2NSO_2.OH$) in water and dilute to 200 ml. (a 25% solution of urea may be used instead, if desired).

Alcoholic Potassium Hydroxide Solution, 10%. Dissolve 20 grams of potassium hydroxide in methanol and dilute with methanol to 200 ml.

Alcoholic Potassium Sulfide Solution. Dissolve 50 grams of potassium hydroxide in about 130 ml. of methanol, cool, and dilute to 160 to 175 ml. Pass hydrogen sulfide into this solution until the weight has increased 15.0 grams (about 18 ml. increase in volume), cool, and dilute to 200 ml. with methanol.

Nitrogen Tetroxide (obtainable in 10-lb. cylinders from Du Pont Co.).

Alkaline Sodium Sulfide Solution. Dissolve 100 grams of sodium hydroxide and 150 grams of sodium sulfide crystals in 800 ml. of water, cool, and add 200 ml. of acetone.

Alcoholic Potassium Hydroxide Solution, 25%. Dissolve 50 grams of potassium hydroxide in methanol and dilute with methanol to 200 ml.

Dilute alcoholic sodium hydroxide solution. Dissolve 40 grams of sodium hydroxide in water, dilute to 100 ml. with water, and add 100 ml. of methanol.

Note. Methanol is used in preparing these reagents in preference to ethanol, as solutions prepared with the latter soon turn dark red.

DEVELOPMENT OF THE METHOD

To be of value for determining the olefin content of a gasoline sample, it must be shown that nitrogen tetroxide is without effect on the other components of the sample. Accordingly, a series of known mixtures was prepared, containing various paraffins, naphthenes, olefins, diolefins, acetylenes, aromatics, etc., in the boiling range of gasoline or approximately 104° to 410° F. Most of the materials used were of a commercial grade without any attempt at purification (Table I).

Table I. Test Components

Mixed heptanes	Phillips Petroleum commercial grade (2% soluble in concentrated H_2SO_4)
Cyclopentane	Phillips Petroleum technical
Methylcyclohexane	Dow Chemical Co. technical
Cyclohexene	Dow Chemical Co. technical
Pure *n*-heptane	Westvaco (Bureau of Standards certificate)
2-Methylpentadiene	Commercial Solvents Corp.
Diisobutylene	Eastman Kodak Co. practical
Dicyclopentadiene	Koppers Co.
α-Methylstyrene + cumene	Crude mixture
Dipentene	Hercules Powder Co. (commercial)
p-Cymene	Claflin Co.
Mesitylene	Eastman Kodak Co.
Xylene	General Chemical Co. reagent
Iso-octane	Knock test standard
C_{10} aromatics	Isolated from Houdry gasoline
Phenylacetylene	Eastman Kodak Co.
Phenol	Reagent grade
Benzene	Barrett Co. "pure"
2-Methylpentane	140° F. cut, acid-treated gasoline

This first series of blends was analyzed by a rather crude procedure which subsequently was improved to reduce handling losses. The chilled sample was saturated with gaseous nitrogen tetroxide, washed with water to remove any excess nitrogen tetroxide, transferred to a flask, and steam-distilled into a chilled receiver until the portions of oil coming over were heavier than water. After removal of the water layer, the distilled oil was extracted with 10% sodium hydroxide solution to remove any nitrosate reaction product carried over and the volume of the unreacted hydrocarbon was then measured, applying a correction factor for handling losses. The decrease in volume represented the olefinic unsaturation of the sample. Any aromatics in the treated hydrocarbon could readily be determined by the usual sulfuric acid treating procedure and corrected to the basis of the original sample.

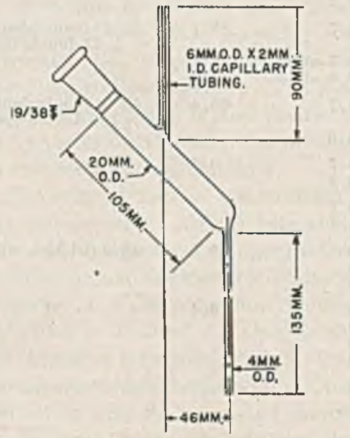


Figure 2. Adapter

In Table II are shown the various blends analyzed by the original nitrogen tetroxide method. As the commercial mixed heptanes used in preparing most of these blends contained 1.8% of material reacting with nitrogen tetroxide, values on such blends were corrected on the basis of the amount of this heptane used. The bromine numbers of most of the blends were determined and calculated as mono-olefin. The "total olefin" value is based on the volume per cent of added olefin, regardless of its actual purity. In the case of dipentene, results indicated the dipentene to have a purity of 88%, and the figure on the α-methylstyrene blend was based on the result of a polymerization test.

Considering the lack of refinements in this original distillation procedure, surprisingly good agreement was shown between the amounts of olefin assumed to be present and those determined, most of the discrepancies probably being due to impurities in the added material. Where diolefins were present, the results obtained were definitely superior to those calculated from the bromine number. It is evident that nitrogen tetroxide is without appreciable action on paraffins, naphthenes, and aromatics boiling in the range 120° to 410° F. As phenol reacts with nitrogen tetroxide, phenolic constituents, if present in appreciable amounts in a sample, should be removed prior to the analysis by a caustic wash. The majority of such phenols as occur in gasoline are soluble in aqueous caustic solution.

PROCEDURE

Method A. This method is intended for the volumetric determination of the total olefinic unsaturation of hydrocarbons boiling between 120° and 410° F.

Immerse the clean, dry, treating flask (Figure 1) in an ice bath extending well up around the neck of the flask. Record the temperature of the sample and pipet 50 ml. into the flask. Place the bath and flask under the hood. Place a suitable thermometer covering the range 30° to 120° F. in the sample and introduce nitrogen tetroxide gas well below the surface of the sample through a glass tube drawn out to a long slender 1-mm. capillary, controlling the flow of gas to maintain the temperature of the sample at 80° to 100° F. (Saran or a short length of Tygon tubing has been found satisfactory for connecting the glass delivery tube to copper tubing from the cylinder of nitrogen tetroxide. Rubber should not be used. The cylinder should be maintained at a temperature above 71° F. to facilitate vaporization of the nitrogen tetroxide.) Completion of reaction is indicated by a definite drop in sample temperature to about 70° F., even though the flow of gas is increased, and by marked formation of brown fumes

Table II. Analysis of Known Mixtures by Original Nitrogen Tetroxide Method

Test	Blend	%	Bromine No. of Blend	Calculated Mono-olefin Equivalent, %	Total Added Olefin, %	% Olefin Content from Volume Decrease
1	Commercial heptane	100	0.6	......	0	1.8
2	Heptane Cyclopentane	66.7 33.3	0.3	......	0	0.6 (corrected for heptane value)
3	Heptane Methylcyclohexane	66.7 33.3	....	......	0	0.4 (corrected)
4	Heptane Cyclohexene	86.7 13.3	27.2	14.0	13.3	13.2 (corrected)
5	Pure *n*-heptane	100	0	......	0	0.0
6	Isohexane	100	0	......	0	1.2
7	Heptane 2-Methylpentadiene	86.7 13.3	29.3	15.4 (equivalent to 1.14 double bonds)	13.3	13.6 (corrected)
8	Heptane Diisobutylene	66.7 33.3	47.4	33.2	33.3	33.4 (corrected)
9	Heptane Dicyclopentadiene	86.7 13.3	33.2	27.4	13.3	13.6 (corrected)
10	Heptane α-Methylstyrene Cumene	66.7 23.7 ± 0.3 9.6 ± 0.3	38.1	28.1 (equivalent to 1.17 double bonds)	23.7 ± 0.3	24.6 (corrected)
11	Heptane Dipentene	66.7 33.3	65.4	49.5 (equivalent to 1.5 double bonds)	33.3 (?)	29.2 (corrected)
12	Heptane *p*-Cymene	66.7 33.3	0.4	......	0.0	0.2 (corrected)
13	Heptane Mesitylene	86.7 13.3	....	......	0.0	0.0 (corrected)
14	Heptane Cyclohexene Diisobutylene	50 25 25	92.2	48.2 (94 Mol. wt.)	50	48.7 (corrected)
15	Heptane Cyclohexene 2-Methylpentadiene Xylene	50 20 10 20	60.4	31	30	29.7 (corrected)
16	Heptane C_{10} aromatics (330°–380° F.)	75 25	....	......	0.0	0.0 (corrected)
17	Iso-octane	100	....	......	...	1.0
18	Iso-octane Phenylacetylene	96 4	....	......	4.0	4.6 (uncorrected)
19	Heptane Benzene Phenol	86.7 8.0 5.3	....	......	...	6.2

above the surface of the sample. (Samples of low olefin content may produce only a slight rise in temperature.) Remove the thermometer and delivery tube, flushing each with small portions of water to prevent loss of sample.

Add sulfamic acid (or urea) solution slowly to the chilled sample, with continuous agitation, until the brown fumes disappear, taking care to avoid loss due to foaming. The sample usually assumes a green or blue color at this point. Connect the flask to an efficient condenser and the receiver assembly and insert the steam inlet tube. Put 10 to 20 ml. of water in the receiver to cover the end of the adapter extension and surround the assembly with an ice bath. Immerse the distillation flask in a beaker of hot water and place a heater under the beaker to bring the water to boiling, then introduce steam into the sample, slowly at first, and adjust the rate as distillation proceeds. The side tube on the adapter should be closed off at the start to prevent loss of vapors and then opened if the water in the receiver starts to suck back. Continue distillation until the distillate becomes heavier than water and sinks to the bottom. (Occasionally a sample is encountered, such as triisobutylene or some polymer gasolines, where the nitrosate distillate is partly lighter than water. In this case, distillation is stopped when the ratio of oil to water in fresh portions of the distillate decreases to about 1 to 4.)

Remove the receiver and carefully draw off any heavy nitrosate and the water. Add 10 ml. of the 10% alcoholic potassium hydroxide to the remaining hydrocarbon, stopper the funnel, and shake vigorously a few moments. Add 25 ml. of water, again shake vigorously, and allow to settle, keeping the funnel cold. Draw off the aqueous layer carefully, add 15 ml. of the alcoholic potassium sulfide to the hydrocarbon, and shake vigorously for 4 minutes. Add 50 ml. of water, shake, and allow to settle as before. Draw off the aqueous layer. Wash the hydrocarbon once more with 50 ml. of water. Drain the hydrocarbon layer into a 50-ml. buret which has been cleaned with chromic-sulfuric acid mixture and well rinsed with water. Rinse the separatory funnel with several small portions of water, thus bringing the hydrocarbon layer well within the graduations of the buret. Immerse the buret for 5 minutes in a suitable water bath (such as a section of 50-mm. glass tubing closed at one end and filled with water) maintained within 2° F. of the temperature at which the test sample was measured. Read the volume of hydrocarbon to the nearest 0.1 ml. and record as volume of unreacted material. If desired, this material may be used, after drying, for determination of density, refractive index, or acid absorption to ascertain the content of aromatics.

As a check on the completeness of olefin removal, it may be advisable to make a duplicate determination. React the residue in the distillation flask with an equal volume of alkaline sodium sulfide solution and discard. To determine the distillation and handling loss, repeat the procedure given above on another 50-ml. portion of the original sample, omitting the treatment with nitrogen tetroxide.

CALCULATION. Calculate the percentage of olefinic unsaturation by means of the following equation:

$$U = \frac{50.0 - (V + C)}{50.0} \times 100$$

where

U = per cent olefins by volume
V = volume of unreacted hydrocarbon, ml.
C = loss correction, ml.

When analyzing samples of polymer gasoline, tri-, or tetraisobutylene, after saturation with nitrogen tetroxide the mixture should be allowed to stand for about 5 minutes before destroying the excess nitrogen tetroxide, since the reaction is slower than in the case of most olefins.

METHOD B. This method is intended for the determination of the total olefinic unsaturation of hydrocarbons boiling between 104° and 410° F. It is directly applicable to samples containing not more than 50% by volume of olefin, and is applicable to samples containing over 50% by volume of olefin, providing they have been diluted with a suitable measured amount of nonolefinic hydrocarbon and the determination is made on the diluted sample.

Immerse the clean dry Babcock reaction bottle in an ice-water bath to about the 60% mark, record the temperature of the sample, and pipet 10.00 ml. into the bottle. Place the bath and bottle under the hood near the nitrogen tetroxide cylinder. Place the thermometer and capillary end of the nitrogen tetroxide delivery tube in the sample and introduce a stream of the gas at such rate that the temperature of the sample is held between 80° and 100° F. Completion of the reaction is indicated by a definite drop in sample temperature to about 70° F., even though the flow of gas is increased, and by the marked appearance of brown fumes above the surface of the sample. (Samples of low olefin content may produce only a slight rise in temperature.) Stop the flow of gas and remove the delivery tube, touching it to the inside of the neck of the bottle to drain off any sample.

Raise the thermometer and flush with 1 ml. of the dilute alcoholic sodium hydroxide solution before withdrawing, to prevent loss of sample.

Table III. Comparison of Analytical Methods on Samples Containing Diolefins

	Usual Method				Nitrogen Tetroxide Method			
	Olefins by bromine no.	Aromatics by specific dispersion	Sum	Acid treat on original	Olefins by volume decrease	Aromatics by acid treat	Sum	Acid treat on original
			Sample 818 AL					
Cut 4 (150–205)	52	0	52	46	46	2	48	46
Cut 5 (205–250)	46	11	57	49	36	11	47	49
Cut 6 (250–302)	40	23	63	57	28	27	55	57
Cut 7 (302–347)	28	39	67	61	20	39	59	61
Cut 8 (347–396)	22	44	66	61	17	45	62	61
			Sample 806 AL					
Cut 5	56	16	72	63	46	18	64	63
Cut 6	45	37	82	71	29	43	72	71
Cut 7	25	56	81	77	17	51	78	77
Cut 8	19	60	79	75	18	59	77	75

Agitate the bottle in the ice bath with a swirling motion and gradually add 1 ml. more of the sodium hydroxide solution to decompose excess nitrogen tetroxide. In a similar manner gradually add 8 ml. of the 25% alcoholic potassium hydroxide solution, causing the sample to turn dark brown. Moisten the glass stopper of the bottle with a drop of the potassium hydroxide solution, insert, and shake the bottle vigorously for 30 seconds. Release any gas pressure carefully to avoid loss of sample. Gradually add 15 ml. of the alcoholic potassium sulfide with agitation and cooling. Stopper the bottle and shake a few moments, release any gas pressure, then continue vigorous shaking for 4 minutes. Dilute the mixture gradually with water (25 to 27 ml.) to bring the unreacted hydrocarbon within the graduations on the neck of the bottle, mix well, release any gas pressure, and centrifuge at 1000 r.p.m. for 2 to 3 minutes.

Immerse the bottle for 3 minutes in a water bath maintained within 2° F. of the temperature at which the test sample was measured. Read the volume of the hydrocarbon to the nearest 1% (0.1 ml.) and record as the volume per cent of unreacted sample.

CALCULATION. $U = 100 - V$, where U = per cent olefins by volume and V = per cent of unreacted sample.

SAFETY PRECAUTIONS

Vapors of nitrogen tetroxide are toxic (concentrations as low as 300 parts per million may prove fatal); so all operations involving its use should be carried out under an efficient hood.

Nitrogen tetroxide may react with certain organic compounds to form products which are violently explosive. The higher-boiling hydrocarbons, including higher aromatics, are much more susceptible to oxidation or nitration than are those in the gasoline boiling range and the nitrosates of some of the terpenes (reaction products with turpentine) have been found to decompose spontaneously. Therefore, prolonged contact of oils or greases with excess nitrogen tetroxide, which might lead to nitration or peroxide formation, should be avoided. Graphite is recommended as a lubricant on any valves or pipe connections which may be in contact with the gas.

No serious decomposition of the nitrosates of olefins in the gasoline boiling range has been observed at temperatures up to 212° F., with the exception of high concentrations of certain terpenes, although many of them show very gradual evolution of fumes on long standing, even at room temperature. Most severe tests, including the use of detonators, have failed to explode them. They exert a pronounced, although temporary, irritating action if permitted to come in contact with the mucous membrane or sensitive skin surfaces.

It is felt that petroleum hydrocarbons in the gasoline boiling range, when handled as specified in this method, present no hazard and this is substantiated by several hundred analyses in various laboratories. However, the use of a safety shield or at least a face mask is advised.

This method was applied with marked success to a number of laboratory samples evidently containing diolefins, where a marked difference had been found to exist between the total unsaturation determined by acid-treating (*1*) and the sum of the apparent olefin content calculated from the bromine number and the apparent aromatic content calculated from the specific dispersion (*2*). A comparison of these methods on two such samples appears in Table III.

It is at once evident that far better agreement is found between the sum of aromatics plus olefins determined by the nitrogen tetroxide procedure and the total acid absorption than by the usual method of analysis.

The method has likewise shown its value for the determination of aromatics in polymer gasoline or highly cracked naphthas. Removal of the olefins is readily effected by their conversion to nitrosates and steam-distillation of the unchanged aromatics, paraffins, and naphthenes. The aromatics in the distillate may be then determined in any desired manner or actually isolated, as by preferential adsorption on silica gel or by sulfonation and hydrolysis of the sulfonic acid.

The original method was substantially improved by saturating the sample with nitrogen tetroxide in the distillation flask itself, destroying excess nitrogen tetroxide by the addition of urea or sulfamic acid solution, steam-distilling, and washing the distillate with alcoholic potassium hydroxide and potassium sulfide as described in Method A. Caustic should not be used to destroy the nitrogen tetroxide, since it may react with the nitrosates during steam-distillation to form more volatile oils, which would come over with the unreacted components of the sample and not be removed by the washing step, leading to low results for the olefin content.

This analytical procedure is limited at present to samples lying in the gasoline boiling range: (1) inclusion of lower-boiling fractions would increase and make more uncertain the handling losses, (2) inclusion of material boiling above 410° F. requires the use of excessive amounts of steam for distillation and lessens the sharpness of the split between unreacted hydrocarbon and nitrosate, and (3) certain of the higher-boiling aromatics, such as naphthalene and acenaphthene, may be nitrated or oxidized to an appreciable extent, leading to high results for the olefin content.

Desiring to develop a more rapid procedure which could be used for routine testing without involving the elaborate distillation setup, it was discovered that the oily nitrosates would react with alcoholic potassium sulfide to give compounds which were soluble in 50% alcohol. The reaction could thus be carried out in a Babcock-type bottle, such as is used in determining the acid absorption of gasoline, the nitrosate dissolved by the addition of alcoholic potassium sulfide, and the volume of unreacted sample read in the neck of the bottle after centrifuging. Handling losses were thus reduced to a minimum, only 10 ml. (or 5 ml.) of sample were required, and an average single determination could be made in 20 minutes or less. However, the accuracy of reading was limited to 1% by virtue of the small sample size and design of the bottle, and the maximum olefin content which could be determined was limited by the amount of absorbing reagent which could be used.

Table IV gives a comparison of this rapid procedure with the distillation procedure on several samples.

It was found that blends with triisobutylene and with decene-1 in acid-treated naphtha did not give theoretical results by this rapid procedure; the decene-1 gave rise to an intermediate dark red oil layer and low results were obtained with the triisobutylene. The latter compound also gave trouble in the distillation procedure, because early portions of the distillate of the nitrosate

Table IV. Comparison of Rapid and Distillation Methods

Sample	% Olefins (Rapid Method)	% Olefins (Distillation Method)
Impure heptane-cyclopentane	2	1.8
Heptane-2-methylpentadiene	15	15.2
Heptane-diisobutylene	34	34.2
100° to 150° F. gasoline cut	20	20 (by bromine No.)
Crude benzene	7	8
B-1	25	25.4
B-2	34	34.3
B-3	28	27.5
B-4	28	27.7

were lighter than water, contrary to the behavior of the nitrosate distillate of most olefins.

By shaking this light nitrosate distillate with alcoholic potassium sulfide for 3 minutes, it was rendered soluble in 50% alcohol, this minimum time factor being required for complete reaction. It was also discovered that the nitrosate of decene-1 reacted completely with alcoholic potassium hydroxide to give a compound soluble in 50% alcohol. Therefore, to take care of any type of sample, the rapid method was modified to include treatment with alcoholic potassium hydroxide prior to the addition of alcoholic potassium sulfide and the shaking time with the latter reagent was increased to 4 minutes as described in Method B. This method gives results which compare very favorably with those of Method A, and has a marked advantage in simplicity and rapidity where only the volume per cent olefin is desired. However, Method A should be used where additional work is to be done on the unreacted portion of the sample, such as determination of aromatic content, density, or refractive index.

Cooperative results obtained by Sub-Committee XXV of A.S.T.M. Committee D-2 on a considerable number of synthetic and natural samples, using both Methods A and B, will appear in a later paper.

ACKNOWLEDGMENT

The author wishes to express his thanks to A. H. A. Heyn of the Sun Oil Co. for the suggested design of adapter, which makes more convenient observation of the point at which the oily distillate in Method A becomes heavier than water.

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Analysis of Furfural-Water Solutions

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Rapid and accurate analyses have been developed for determination of water in furfural by a cloud-point method, and for furfural in water by an electrometric titration with bromine.

SIMPLE, dependable analyses of furfural-water solutions are needed in connection with furfural solvent refining and extractive distillation processes. Current methods for analyzing water in the furfural phase include titration with the Karl Fischer reagent, toluene distillation, and centrifuge, refractive index, and cloud-point (saturation temperature) determinations. Methods for analyzing furfural in the water phase include ultraviolet absorption (spectrometric), colorimetric determinations with fuchsin-sulfite and with aniline reagents, titration with hydroxylamine hydrochloride, and gravimetric determinations with special reagents such as phloroglucinol. None of the above methods has superseded the others to the extent of being specified for standard or reference analyses. The methods given here are based on calibrations of known quantities of furfural and of water, and are of sufficient speed and accuracy for general use.

Water in furfural is determined by observation of the cloud point of equal volumes of furfural and a cloud-point reagent consisting of a mixture of 1-hexanol and cottonseed oil. Cloud points with cottonseed oil alone occur at undesirably high temperatures, and are lowered by the presence of the alcohol; by adjusting the ratio of oil to alcohol, the cloud point may be brought to an optimum temperature level.

This procedure and the cloud-point behavior resemble the determination of water in aniline with the cottonseed oil–mineral oil reagent developed by Seaman, Norton, and Hugonet (*5*). Using dry furfural, the method should be adaptable to the determination of water in any other organic liquid that does not react with furfural merely by substituting it for 1-hexanol.

Hughes and Acree (*3*, *4*) reported that furfural reacts with bromine to equimolar proportions rapidly and with a second mole or more of bromine slowly at 20° to 30° C. The first mole of bromine (reacted at 0° C.) yielded 2 moles of hydrogen bromide. The same authors developed a satisfactory bromometric analysis for furfural that consists essentially of providing excess bromine with bromide-bromate reagent, reacting at 0° C. in a 3% hydrochloric acid solution, replacing the excess bromine with iodine using potassium iodide, and then titrating the free iodine with standard thiosulfate and starch indicator. The method specifies 0.1 *N* reagents and is not well adapted to samples containing only a few milligrams of furfural.

In this laboratory, attempts at direct titration of furfural using bromide-bromate reagent showed that the rate of the first

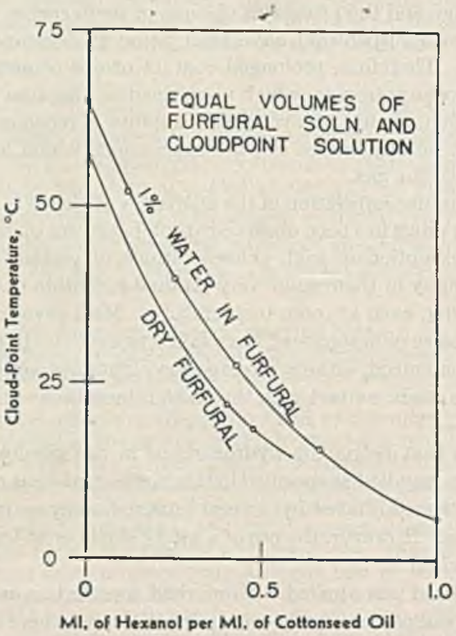

Figure 1. Effect of Hexanol–Cottonseed Oil Ratio on Cloud Point

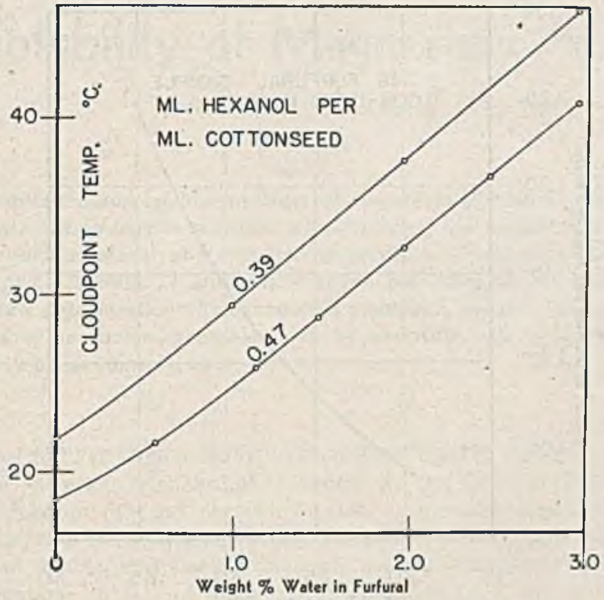

Figure 2. Effect of Water Concentration on Cloud Point of Furfural Solutions with Hexanol–Cottonseed Oil Mixtures

reaction was far too slow to be satisfactory, but that in the presence of hydrochloric acid and mercuric chloride, free bromine in aqueous solution reacts rapidly as far as equimolar proportions. This permits observation of an end point when free bromine persists in the solution. The end point is conveniently observed as e.m.f. (or pH) of a calomel electrode. The e.m.f. rises sharply from about 250 to over 800 millivolts (0.25 to 0.8 volt) and persists for a limited time when the end point is reached. A certain excess of bromine is consumed over the stoichiometric equivalent. But with proper precautions and attention to detail, the end point is reproducible. Plots of stoichiometric bromine against bromine to "potentiometric end points" gave straight lines for any given concentration of bromine water, so the reagent may be standardized by titration against pure furfural in terms of its "potentiometric normality".

CLOUD-POINT DETERMINATION OF WATER

Materials and Equipment. The 1-hexanol may be obtained from Carbide and Carbon Chemicals Corp., and is dried by distilling off the water before use. The cottonseed oil may be commercial Wesson oil. The furfural may be obtained from Quaker Oats Co. and is dried and purified by redistillation under reduced pressure, rejecting the first 25% of distillate.

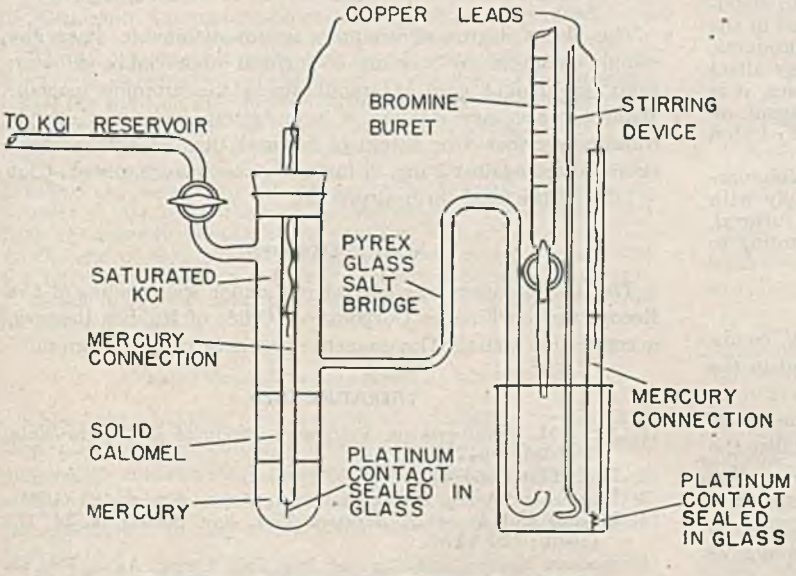

Figure 3. Potentiometric Titration Assembly

The cloud-point apparatus is a 2.5 × 10 cm. (1 × 4 inch) test tube mounted in a water bath consisting of a 250-ml. beaker warmed by a Bunsen burner. The test tube contains an A.S.T.M. titer test thermometer extending to about 1.25 cm. from the bottom. A wire bent to form a loop encircling the thermometer is used as the stirrer. The thermometer is mounted in a cork with an off-center hole for the wire stirrer. The A.S.T.M. aniline point apparatus (*1*) may be used with equal satisfaction.

Procedure. The cloud-point reagent is made up of about 0.4 ml. of dry hexanol per ml. of cottonseed oil and is kept in a glass-stoppered flask.

The cloud-point apparatus is charged with 10 ml. of furfural and 10 ml. of cloud-point reagent. The mixture is warmed with stirring until it is perfectly clear and transparent, then cooled slowly with stirring until the cloud point is observed. A haze appears as the cloud point is approached, and the solution becomes suddenly opaque at about 0.75° C. lower. The "opaque point" is reproducible to ±0.1° C., and is taken as the cloud point. The reagents are calibrated against samples of wet furfural made up with known amounts of water. Sample calibration tests are plotted in Figures 1 and 2.

It is recommended that samples containing more than 3% water be mixed with 1, 2, or 3 parts of dry furfural for testing. For samples containing less than 1% water, a slight improvement in accuracy and convenience is obtained by using a cloud-point reagent of about 0.3 ml. of hexanol per ml. of cottonseed oil.

BROMOMETRIC TITRATION OF FURFURAL

Materials and Equipment. The titration cell consists of a 250-ml. beaker marked at the 100-ml. level and equipped with a stirrer, a thermometer, a normal calomel electrode, and a reference electrode of a spiral of platinum wire sealed in a glass tube (Figure 3). The standard bromine reagent is delivered from a 50-ml. buret.

The cell is mounted in a water bath, such as a 1-liter beaker, since the temperature must be constant to ±1° C. or less during a titration.

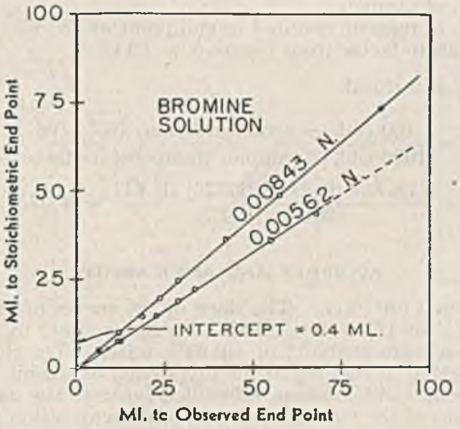

Figure 4. Potentiometric Titration of Furfural in Water at Room Temperature

The e.m.f. (or pH) is observed by a sensitive potentiometer, an electronic voltmeter, or a pH meter of the proper range (0 to 1 volt), such as is specified for the A.S.T.M. acid and base numbers electrometric titration apparatus (*2*).

The bromine reagent is made up approximately 0.005 molal (0.005 *N*) in bromine, 0.01 molal (0.01 *N*) in potassium bromide, and with 10 ml. of concentrated hydrochloric acid per 100 ml. of distilled water. It should be made up fresh daily and standardized against furfural.

Mercuric chloride as saturated solution in distilled water is run through the electrode into the cell for each titration.

Procedure. The bromine reagent is calibrated against 5-mg. samples of furfural, using the same titration procedure as for unknowns. At any constant temperature, the volume of reagent plots as a straight line against amount of furfural with an intercept of −0.4 ml. of 0.005 *N* bromine (Figure 4). After subtraction of 0.4 ml. from the buret reading at the end point, a "potentiometric normality" of the reagent may be used (sample calculations).

A "temperature factor" read from Figure 5 is used when the bromine calibration is made at a different temperature from that at which samples are tested.

In general, two titrations are run on an unknown sample, the first to determine the approximate furfural concentration, and the second on a size of sample that contains approximately 5 mg. of furfural.

For the second titration, the titration beaker is charged with the sample and diluted with distilled water to the 100-ml. mark; 3 ml. of the mercuric chloride solution are added and the stirrer is started. When the temperature is constant, bromine reagent equivalent to about 95% of the end point is run in from the buret as fast as it will drain, or within 60 seconds. This will cause a temporary or false end-point potential. As soon as the e.m.f. has fallen below 0.75 volt, bromine reagent is added in increments of approximately 1% of the expected total until the e.m.f. remains above 750 millivolts for 90 seconds. This is taken as the end point.

Titration of Furfural in Water. Sample Calculations.

Molecular weight of furfural = 96.1

Specific gravity of aqueous solutions = 1.00

Standardization of bromine reagent: 1.000 gram of dry furfural made up to 1 liter with distilled water. 1 ml. = 1 mg. of furfural.

Titrate 5.0 ml. with bromine reagent. 17.0 ml. required at 21° C. From Figure 5, temperature factor = 1.040.

Potentiometric normality

$$\text{Normality factor} = \frac{(\text{mg. of furfural})\ (\text{temperature factor})}{(\text{molecular weight})\ (\text{ml.} - \text{zero correction})}$$

$$= \frac{(5.0)\ (1.040)}{(96.1)\ (17.0 - 0.4)} = 0.00326$$

Titration of Sample. For second (final) titration of an unknown, take a size of sample that will consume approximately the same volume of bromine reagent as required for the standardization.

20.0 ml. of sample
18.8 ml. of reagent required to end point at 28° C.
Temperature factor from Figure 5 = 1.115

Weight % of furfural

$$= \frac{100\ (\text{ml.} - \text{zero correction})\ (\text{n.f.})\ (96.1)}{1000\ (\text{ml. of sample})\ (\text{temperature factor})}$$

$$= \frac{(18.8 - 0.4)\ (0.00326)\ (9.61)}{(20.0)\ (1.115)} = 0.0259$$

ACCURACY AND APPLICABILITY

Water in Furfural. The slope of the curves of Figure 2 is about 8° C. for 1% water. A cloud point accurate to ±0.1° C. then gives a reproducibility of ±0.01% water. The cloud point is not sensitive to changes in the proportion of sample to cloud-point reagent. While clean, redistilled furfural was used in the development of the method, polymer or decomposition products, acidity, and hydrocarbons present in plant samples may affect the cloud point. For determinations on impure samples, it is recommended that calibrations of the cloud-point reagent on pure furfural be checked against a calibration using dehydrated plant furfural to avoid possible error from impurities.

Furfural in Water. As discussed earlier, the bromine reaction is neither instantaneous nor does it stop completely with the consumption of the first mole of bromine per mole of furfural. Furthermore, aqueous bromine tends to hydrolyze according to the equation

$$Br_2 + H_2O \rightleftharpoons HBr + HBrO$$

To avoid errors introduced by the above phenomena, conditions must be rigidly standardized in the respects noted in the procedure.

The use of hydrochloric acid, potassium bromide, and mercuric chloride has two effects: The first two compounds stabilize the bromine reagent, greatly reducing the rate of hydrolysis. Hydrolyzed material does not give reproducible end points; hence the reagent must be made up fresh daily. All three halides appear to act catalytically, speeding the reaction of the first mole of bromine without a corresponding effect on further bromine consumption. The end point is not appreciably affected by wide variations in acid or salt concentrations.

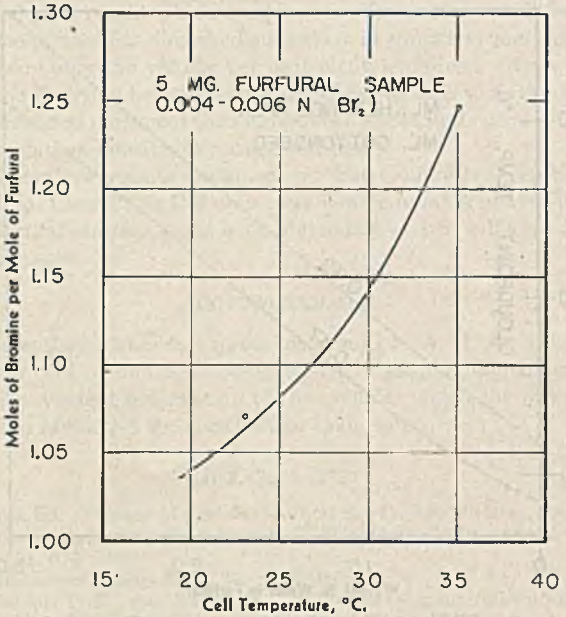

Figure 5. Effect of Temperature on Bromine Requirement

Electrometric titration of furfural in water

The bromine required for the end point depends upon the rate of bromine addition, and to a great extent upon temperature. The use of the temperature factor (Figure 5) may be eliminated and a slight improvement of accuracy gained by thermostating the water bath, so that bromine standardization and the determinations are both made at the same temperature. The method will obviously give high results on a sample containing impurities that react with bromine.

Bromine concentration of 0.005 *N* and sample size of 5 mg. of furfural were selected somewhat arbitrarily for accuracy and convenience. With proper care and attention to detail, a titration is reproducible to ±0.5% of the total furfural in a 5-mg. sample. The absolute accuracy as per cent furfural in water then depends upon the concentration and sample size:

Furfural Concentration %	Sample (Containing 5 Mg. of Furfural) *Ml.*	Accuracy *% Furfural in water*
0.01	50	±0.00005
0.1	5	0.0005
1.0	0.5	0.005
5.0	0.1	0.02

The above degree of accuracy is not attainable when the sample contains an amount of furfural appreciably different from the amount used in standardizing the bromine reagent. While the accuracy relation is incompletely known, a sample containing either 4 or 6 mg. of furfural titrated with reagent standardized against 5 mg. of furfural gives an accuracy of about ±1.0% of the total furfural present.

ACKNOWLEDGMENT

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Solubility of Magnesium Ammonium Phosphate Hexahydrate

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Despite the appreciable solubility of magnesium ammonium phosphate hexahydrate in solutions of electrolytes, the composition of the solution of analysis is such as to render the salt almost completely insoluble therein. If the recommended procedure for the gravimetric determination of magnesium is employed, recovery as magnesium ammonium phosphate will be complete well within the limits of experimental error.

DESPITE its universal application as the basis of the accepted quantitative analytical procedures for the determination of magnesium (*4*) and phosphorus (*10*), magnesium ammonium phosphate hexahydrate is widely recognized as being one of the most soluble precipitates extensively used in gravimetric determinations (*5*, *21*). A number of investigators (*1*, *3*, *15*, *19*, *20*) have reported solubility data for magnesium ammonium phosphate, but a comparison of the various data reveals a definite lack of agreement among the published results. Further, the effect of the presence of ammonium hydroxide on the solubility of magnesium ammonium phosphate in solutions containing various added salts has received but little attention. This latter is of the greatest practical importance, since the standard analytical procedures call for the addition of considerable quantities of ammonium hydroxide to the solution of analysis.

This contradictory and incomplete nature of the existing data reflects an obvious need for an accurate and comprehensive determination of the solubility of magnesium ammonium phosphate in various concentrations of aqueous and ammoniacal salt solutions likely to be encountered in analytical practice. The present investigation was undertaken to provide this necessary information.

PREPARATION OF SATURATED SOLUTIONS

Magnesium ammonium phosphate hexahydrate was prepared by the reaction of diammonium phosphate and magnesium chloride in aqueous solution. The precipitate was thoroughly washed with distilled water, anhydrous ethanol, and anhydrous ether. Analysis by igniting weighed samples to magnesium pyrophosphate in tared silica crucibles at 1000° to 1050° C. in a muffle furnace indicated an average purity of 99.88%.

Standard solutions of the various salts in which the solubility of magnesium ammonium phosphate was to be determined were prepared in the accepted manner of diluting a weighed quantity of the salt, the highest grade reagent of commerce, to a definite volume in volumetric equipment of proved accuracy. In many cases, the solution medium for these standard salt solutions was ammonium hydroxide of known normality, prepared by dilution of the concentrated C.P. reagent and checked by analysis.

The saturated solutions of magnesium ammonium phosphate hexahydrate were prepared by agitating 1 gram of the hexahydrate in 200 ml. of the required salt solution for 24 hours in a flask immersed in a constant-temperature bath at 25° ± 0.05° C. At the end of this period, the solution was rapidly filtered, and the filtrate set aside in a tightly stoppered bottle for analysis. A sample of the salt solution before saturation was also set aside for use as a blank.

ANALYSIS OF SATURATED SOLUTIONS

This comprehensive investigation of solubilities, involving a large number of magnesium determinations in solutions whose magnesium content would necessarily be very low, demanded a method of analysis which would allow the rapid, as well as accurate, estimation of very small quantities of magnesium. Colorimetric methods were considered as being most likely to satisfy the requirements of speed and precision.

A number of reagents are known to give color reactions which are characteristic for magnesium (*2*, *6*, *9*, *11*, *12*). Of these, titan yellow has probably received the most intensive study, and it was evident from a careful consideration of the literature references describing colorimetric methods for the determination of magnesium (*7*, *14*, *16*, *18*) that titan yellow offered an excellent possibility of successful application in the present investigation. When magnesium hydroxide is precipitated in the presence of titan yellow by sodium hydroxide, the yellow color of the reagent changes to red or orange red at a pH of 12.5. According to Ludwig and Johnson (*14*), the lake which is formed with dilute magnesium solutions remains dispersed for rather long periods, particularly in the presence of protective colloids such as starch, agar, or dextrose. In the absence of such materials, flocculation occurs readily and the results are not reproducible. Gillam (*7*) advised the addition of hydroxylamine hydrochloride to retard the fading of the color produced, an observation which was fully substantiated in the present work. Stross (*18*) emphasized the necessity of rigid adherence to an established technique, especially during the development of color, if reproducible results are to be obtained. The magnesium-titan yellow complex appears to be of colloid nature, and it is well known that the properties of colloids are influenced by the conditions of their formation.

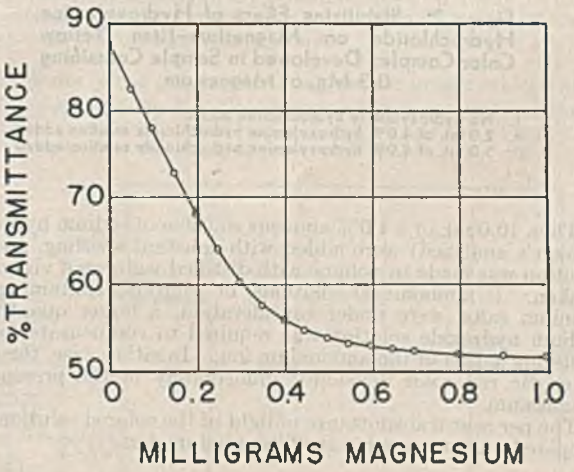

Figure 1. Per Cent Transmittance Versus Magnesium Content of Solution in Which Magnesium-Titan Yellow Complex Has Been Developed

After considerable preliminary experimentation, the colorimetric method developed for use in the present investigation was substantially that proposed by Gillam (*7*):

A carefully measured volume of the saturated solution of magnesium ammonium phosphate was pipetted into a 100-ml. volumetric flask. The sample should contain a maximum of 0.3 mg. of magnesium. This permits a transmittance of at least 60% through the colored solution subsequently developed, as measured in a filter photometer of standard design, employing light filters allowing maximum transmittance of light of a wave length of 524 millimicrons—the approximate region of maximum absorption of light by the color complex. The reason for this limit of sample size is at once apparent upon consideration of Figure 1. Up to a magnesium content of about 0.3 mg., the curve is practically linear and of steep slope. This agrees well with the experience of others (*7*, *8*, *13*, *18*).

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To the sample were then added 10.0 ml. of a 1.0% aqueous solution of gelatin (Eastman Kodak No. 1099). This will effectively prevent flocculation in solutions containing as high as 1.0 mg. of magnesium.

Next, 5.0 ml. of a 4.0% aqueous solution of hydroxylamine hydrochloride (Merck reagent) were added, followed by dilution to approximately 70 ml. with distilled water. The effectiveness of this quantity of hydroxylamine hydrochloride in preventing the fading of the color complex for a period of time sufficient to permit its quantitative determination in the filter photometer is graphically shown in Figure 2.

One milliliter of dye solution (0.15 gram of Eastman Kodak No. P4454 titan yellow in 75 ml. of 95% ethanol and 25 ml. of distilled water) was then added.

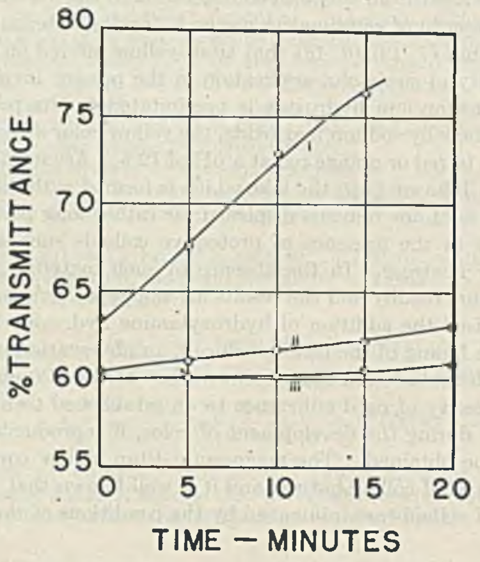

Figure 2. Stabilizing Effect of Hydroxylamine Hydrochloride on Magnesium–Titan Yellow Color Complex Developed in Sample Containing 0.3 Mg. of Magnesium

I. No hydroxylamine hydrochloride added
II. 2.0 ml. of 4.0% hydroxylamine hydrochloride solution added
III. 5.0 ml. of 4.0% hydroxylamine hydrochloride solution added

Then 10.0 ml. of a 4.0% aqueous solution of sodium hydroxide (Baker's analyzed) were added with constant swirling, and the solution was made to volume with distilled water and vigorously shaken. If ammoniacal solutions, or solutions containing ammonium salts, were under consideration, a larger quantity of sodium hydroxide solution was required to compensate for the buffering action of the ammonium ion. In either case, the characteristic red color developed immediately in the presence of magnesium.

The per cent transmittance of light of the colored solution thus prepared was measured in the filter photometer.

In this manner, three analyses were made of each of the duplicate saturated solutions of magnesium ammonium phosphate hexahydrate in the specified solution of electrolyte, thus giving six replicate analyses for each solution investigated. The arithmetic mean of the six photometer readings was calculated, and its equivalent in terms of milligrams of magnesium determined by means of a calibration curve. This curve was prepared by developing the magnesium–titan yellow color complex in solutions of the given electrolyte to which had been added measured quantities of a standard magnesium sulfate solution, determining the per cent transmittance of light, and averaging the results for each magnesium concentration to allow a graphical representation of milligrams of magnesium versus photometer reading. It was not found advisable to construct a single calibration curve which would apply throughout the entire investigation. The use of freshly prepared reagents, particularly the gelatin solution, and the amount of caustic solution used to develop the color complex, contributed to slight displacements of the photometer readings for a given magnesium concentration. It was found expedient to analyze all the samples relating to a given added electrolyte in one continuous series of operations and to collect the data required for a calibration curve at the same time.

SOLUBILITY DATA

In Tables I, II, III, and IV, the solubility data are recorded in terms of milligrams of magnesium per liter of solution at 25° C. The data have been grouped in general relation to the magnitude of the normality ranges of the added electrolytes and in several instances are repeated for greater ease of comparison. The data were submitted to a statistical analysis which revealed that in the majority of cases the standard deviation of the average solubility determined for each solution amounted to less than 1% of the average solubility value.

In water, the solubility of magnesium ammonium phosphate hexahydrate was found to be equivalent to 13.6 mg. of magnesium per liter of solution at 25° C.

Selections of solubility curves, representing the extreme effects of added electrolytes, are presented in Figures 3 and 4. These allow a convenient orientation of the relative solubilities of magnesium ammonium phosphate in the several solution media investigated.

Table I. Solubility of Magnesium Ammonium Phosphate Hexahydrate

Salt Solution	Normality of Salt Solution 0.001	0.005	0.010	0.025	0.050	0.075	0.100
	Mg. of magnesium per liter of solution						
NH_4OH	9.60	3.42	1.39	...	0.70	...	0.53
$(NH_4)_2HPO_4$	12.7	8.10	4.68	2.29	1.26	1.12	1.00
Na_2HPO_4	13.1	9.93	8.95	...	8.14	...	7.66

Table II. Solubility of Magnesium Ammonium Phosphate Hexahydrate

Salt Solution	Normality of Salt Solution 0.05	0.10	0.20	0.30	0.40	0.50
	Mg. of magnesium per liter of solution					
$(NH_4)_2C_2O_4$						
Aqueous solution	38.8	57.0	89.5	121.0	152.0	180.0
In 0.01 *N* NH_4OH	22.5	...	64.5	...	112.0	...
In 0.10 *N* NH_4OH	8.76	...	27.1	...	47.7	...
In 1.00 *N* NH_4OH	2.63	...	8.32	...	14.4	...
$Na_2C_2O_4$						
Aqueous solution	43.5	68.5	106.0	138.0	166.0	191.0
In 0.01 *N* NH_4OH	22.1	...	60.5	...	109.0	...
In 0.10 *N* NH_4OH	6.57	...	21.3	...	39.4	...
In 1.00 *N* NH_4OH	2.40	...	7.00	...	11.9	...
$(NH_4)_2MoO_4$						
Aqueous solution	340.0	493.0	730.0	...	...	...
In 0.05 *N* NH_4OH	...	...	404.0	...	...	...
In 0.20 *N* NH_4OH	...	...	2.5	...	...	...

Table III. Solubility of Magnesium Ammonium Phosphate Hexahydrate

Salt Solution	Normality of Salt Solution 0.10	0.50	1.00
	Mg. of magnesium per liter of solution		
NH_4Cl	19.1	38.0	53.0
$NaCl$	22.3	32.0	37.0
KCl	18.8	26.4	29.8
NH_4NO_3	19.3	35.0	46.5
$NaNO_3$	20.0	30.5	35.0
KNO_3	17.9	24.6	26.0
$(NH_4)_2SO_4$	24.1	52.2	73.0
Na_2SO_4	25.0	38.6	46.0
K_2SO_4	21.9	34.2	39.2
$CaCl_2$			
Aqueous solution	296	499	622
In 0.1 *N* NH_4OH	131	311	416
In 1.0 *N* NH_4OH	18.3	26.9	27.9
In 2.0 *N* NH_4OH	6.6	12.1	12.9
$BaCl_2$			
Aqueous solution	125	184	199
In 0.1 *N* NH_4OH	70	140	155
In 1.0 *N* NH_4OH	15.3	26.0	27.6

Table IV. Solubility of Magnesium Ammonium Phosphate Hexahydrate

Salt Solution	0.10	0.25	0.50	0.75	1.00	1.50	2.00	3.00	5.00
	Mg. magnesium per liter of solution								
NH_4OH	0.53	..	0.44	..	0.55	..	...	0.70	0.80
$(NH_4)_2HPO_4$	1.00	..	0.76	..	0.50	..	...	...	...
NH_4Cl									
Aqueous solution	19.1	25.9	38.0	46.0	53.0	61.5	67.0	79.0	86.0
In 0.01 *N* NH_4OH	7.24	..	16.5	..	22.0	..	30.0	...	...
In 0.10 *N* NH_4OH	2.11	..	5.53	..	7.46	..	9.30	...	...
In 1.00 *N* NH_4OH	1.20	..	2.96	..	4.20	..	5.60	...	...
NH_4NO_3									
Aqueous solution	19.3	24.6	35.0	42.0	46.5	52.0	54.0	56.5	59.0
In 0.01 *N* NH_4OH	6.80	..	14.4	..	19.1	..	26.0	...	...
In 0.10 *N* NH_4OH	1.71	..	4.50	..	5.90	..	7.65	...	...
In 1.00 *N* NH_4OH	1.22	..	2.80	..	4.00	..	5.30	...	...
$(NH_4)_2SO_4$									
Aqueous solution	24.1	35.8	52.2	64.0	73.0	87.0	97.5	119.0	148.0
In 0.01 *N* NH_4OH	9.24	..	22.7	..	35.0	..	56.0	...	...
In 0.10 *N* NH_4OH	3.07	..	8.85	..	13.8	..	21.0	...	...
In 1.00 *N* NH_4OH	1.25	..	3.70	..	5.90	..	10.0	...	...
NaCl									
Aqueous solution	22.3	27.2	32.0	35.0	37.0	39.4	40.2	39.6	36.2
In 0.01 *N* NH_4OH	6.30	..	11.7	..	15.1	..	16.6	...	...
In 0.10 *N* NH_4OH	1.75	..	3.78	..	4.76	..	5.66	...	...
$NaNO_3$									
Aqueous solution	20.0	25.4	30.5	33.4	35.0	37.4	38.2	37.0	29.0
In 0.01 *N* NH_4OH	6.00	..	11.4	..	13.8	..	14.7	...	...
In 0.10 *N* NH_4OH	2.70	..	6.35	..	8.86	..	12.7	...	...
Na_2SO_4									
Aqueous solution	25.0	32.0	38.6	42.8	46.0	51.0	54.0	...	...
In 0.01 *N* NH_4OH	8.53	..	19.6	..	27.4	..	34.5	...	...
In 0.10 *N* NH_4OH	2.70	..	6.35	..	8.86	..	12.7	...	...
In 1.00 *N* NH_4OH	0.80	..	2.40	..	3.64	..	4.80	...	...

Normality of Salt Solution

SOLUBILITY OF MAGNESIUM AMMONIUM PHOSPHATE IN THE SOLUTION OF ANALYSIS

The quantitative determination of magnesium by precipitation as magnesium ammonium phosphate followed by ignition to magnesium pyrophosphate has been investigated by Epperson (*4*). Analysis of aliquots of a standard solution of magnesium chloride gave closely checking true results even in the presence of large excesses of added salts. In no case was there evidence of loss of magnesium ammonium phosphate by solution.

The problem of the solubility of magnesium ammonium phosphate in the solution of analysis of both phosphate and magnesium was further investigated by Hoffman and Lundell (*10*). In the case of phosphate analysis, they found the loss of magnesium ammonium phosphate by solution to amount to the equivalent of about 0.02 mg. of magnesium for each precipitation. Concerning the solubility of magnesium ammonium phosphate under the conditions which exist in the determination of magnesium by the standard procedure, they state that its direct determination is difficult, but by an indirect method they estimated a loss of 0.01 mg. of magnesium by solution of magnesium ammonium phosphate for each precipitation.

This insignificant solubility of magnesium ammonium phosphate in the solutions of analysis as reported by Hoffman and Lundell was confirmed by the direct determination of the magnesium remaining in solution by the colorimetric method of analysis herein described, after precipitation as magnesium ammonium phosphate by the recommended procedure.

A standard solution of magnesium sulfate heptahydrate (Baker's analyzed) was prepared to contain 12.25 grams of the salt in 2 liters. Aliquots of this stock solution containing the equivalent of 0.2771 gram of magnesium pyrophosphate were analyzed for magnesium by the method of Epperson (*4*). The filtrates and wash liquors of each of the four determinations made were combined, and the volumes were reduced by evaporation, transferred to 100-ml. volumetric flasks, and made to volume with distilled water. Aliquots of each solution were analyzed colorimetrically for magnesium. Further determinations were made in which additions of ammonium salts to the sample solutions preceded the gravimetric analysis. The filtrates and wash liquors were treated as outlined above.

The results of the gravimetric analyses are presented in Table V. It is evident from the close agreement of the actual and theo-

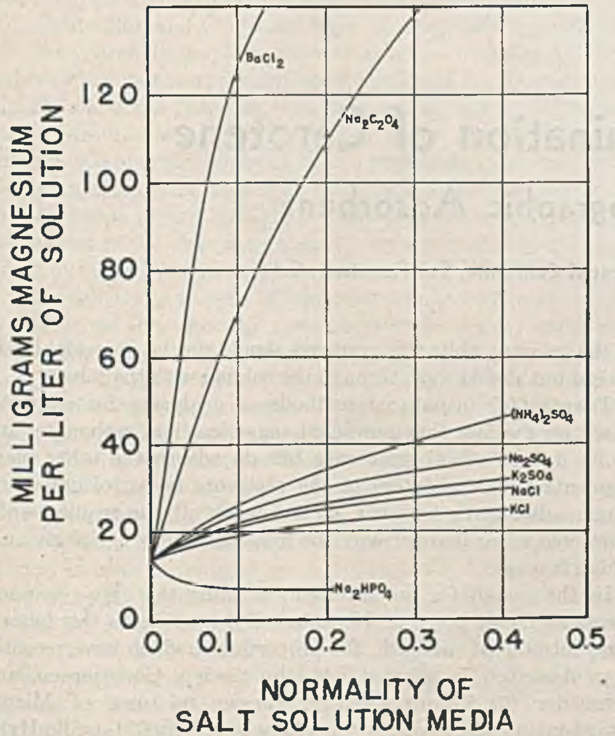

Figure 3. Solubility of Magnesium Ammonium Phosphate Hexahydrate in Salt Solutions

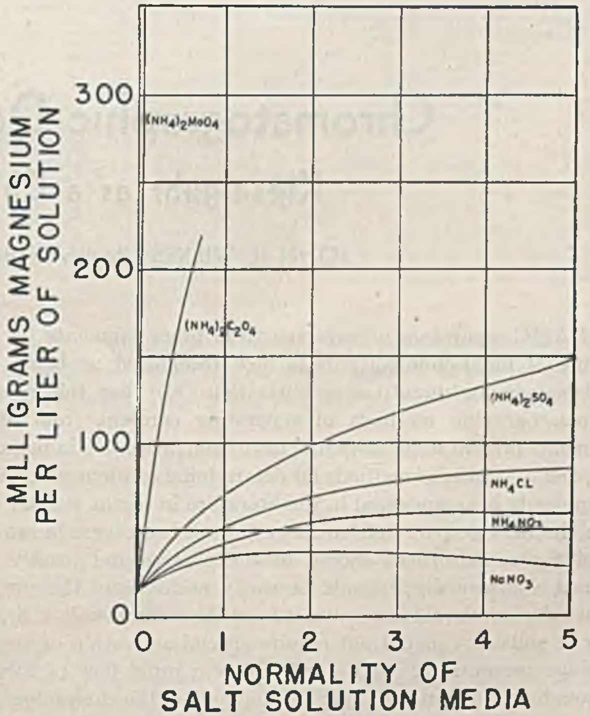

Figure 4. Solubility of Magnesium Ammonium Phosphate Hexahydrate in Salt Solutions

Table V. Gravimetric Analyses for Magnesium

Variation in Standard Procedure	$Mg_2P_2O_7$ or Equivalent	
	Taken	Found
	Gram	*Gram*
No variation	0.2771	0.2772
	0.2771	0.2767
	0.2771	0.2770
Solution of analysis 2.0 *N* with respect to ammonium chloride	0.2771	0.2773
	0.2771	0.2769
	0.2771	0.2771
Solution of analysis 2.0 *N* with respect to ammonium sulfate	0.2771	0.2770
	0.2771	0.2771
	0.2771	0.2766
Solution of analysis 0.3 *N* with respect to ammonium oxalate	0.2771	0.2769
	0.2771	0.2773
	0.2771	0.2769

retical values for magnesium pyrophosphate, that little if any loss of magnesium ammonium phosphate resulted. Further, a statistical analysis of variance (*17*) of these four groups of data indicated that the addition of ammonium salts had no effect on the analytical results.

The photometric analyses of the combined filtrates and wash liquors indicated a maximum magnesium content of 0.003 mg. in the aliquot taken in all cases. The colorimetric method herein described allows the detection of as little as 0.005 mg. of magnesium with a fair degree of accuracy, but below this range the results must be expressed as an estimated maximum. Larger aliquots led to erratic results due to the high salt concentrations in the evaporated solutions. However, the maximum of 0.003 mg. of magnesium in the aliquot taken (10.0 ml.) represents a loss of 0.03 mg. of magnesium in the total filtrate and wash liquors of an analysis involving two precipitations, or approximately 0.015 mg. of magnesium per precipitation. This is in excellent agreement with the value of 0.01 mg. of magnesium per precipitation reported by Hoffman and Lundell.

DISCUSSION OF RESULTS

In general, the presence of added salts effects a considerable increase in the solubility of magnesium ammonium phosphate hexahydrate. Ammonium salts exert a greater influence in this respect than do the corresponding salts of sodium or potassium in equivalent concentrations. Molybdate and oxalate anions have an unusually high solubilizing effect, indicating the probable formation of complex ions. The cations calcium and barium also exhibit exceptional behavior.

However, the addition of relatively small quantities of ammonium hydroxide substantially reduced the solubility of magnesium ammonium phosphate in every salt solution investigated, and with increasing additions of ammonium hydroxide the solubility approached an insignificant figure. This effect is of greatest importance in relation to the use of magnesium ammonium phosphate as a quantitative gravimetric precipitate of analysis.

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Chromatographic Determination of Carotene

Kieselguhr as a Chromatographic Adsorbent

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PHASIC separation of carotene from other pigments by the use of immiscible solvents is now recognized as being unsatisfactory for quantitative separation (*9*). For this reason, chromatographic methods of separating carotene from other pigments present in plant tissues have been increasing in popularity, and a number of methods for determining carotene chromatographically have appeared in the literature in recent years. For the chromatographic determination of total carotenes in routine analysis, an adsorbent should be inexpensive and readily obtained commercially; should be easily packed into the adsorption column; should not contract from the column walls if drawn dry of solvent; should not require special activation or special storage precautions; and should allow a rapid flow of solvent through the column and rapid development of the chromatogram. All noncarotene pigments should be adsorbed and firmly held in the column, while the carotenes should not be appreciably absorbed but should wash through the column with the solvent.

Tswett (*15*) introduced methods of analyzing for carotene, based on the fact that powdered sugar, calcium carbonate, and inulin do not adsorb carotenes but do adsorb the other plant pigments from a solution of the pigments in petroleum ether. These adsorbents, however, do not meet all the requirements. Powdered sugar is reportedly the most satisfactory, lacking only a high flow rate.

In the search for an adsorbent meeting the above requirements as far as possible, Kernohan (*7*), working in this laboratory, introduced soda ash, the properties of which have recently been described in greater detail by Cooley, Christiansen, and Schroeder (*5*). More recently, various mixtures of Micron Brand magnesium oxide with soda ash or Johns-Manville Hyflo Super-Cel have been introduced which have many of the desired properties (*4*, *10*, *16*). These mixtures do not, however,

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Heat-treated diatomaceous earths, which have been widely used as filter aids and diluents in preparing adsorbents for chromatographic purposes, possess in themselves a large number of the desired properties of adsorbents for the chromatographic determination of carotene. Hyflo Super-Cel can also be used in the determination of cryptoxanthin and probably in some types of vitamin A analysis. Some methods of extracting carotene from dehydrated alfalfa meal are compared.

meet all requirements, as it is necessary to mix the two materials before use, and, for the development of the chromatogram, to moisten the adsorbent in the column with petroether, then to add the solution of plant pigments in petroleum ether and to adsorb the pigments on the column, and finally to elute the carotenes from the column with a solution of acetone in petroleum ether.

Soda ash has the advantages of low cost and of being used without mixing or other preliminary treatment. The solution of plant pigments in petroleum ether or similar solvent may be poured directly onto the dry column, and, as soda ash has almost no adsorptive power for carotenes, the carotenes are washed directly through the column with petroleum ether without the necessity of using special solvent mixtures to elute the carotenes after adsorption or of separating the pigment-free solvent from the pigment solution, as is required when eluting carotenes from mixtures of magnesium oxide and Hyflo Super-Cel. The adsorption bands of noncarotene pigments are not, however, as sharply defined on soda ash chromatographic columns as is sometimes desired. The adsorbent must be protected from atmospheric moisture, and only one technical grade of soda ash, (Wyandotte light soda ash, Wyandotte Chemical Corp., Michigan Alkali Division, Wyandotte, Mich.) has been found to have the proper adsorptive properties.

Experiments in this laboratory have shown that heat-treated siliceous earths possess to a large degree the requisite properties of an adsorbent for routine determination of carotene, and this adsorbent has been used in this laboratory for the past six years. The commercial brands of Johns-Manville Hyflo Super-Cel, Celite 501, Celite 535, and Celite 545 have all been found satisfactory for the chromatographic determination of carotene. Hyflo Super-Cel is, however, the strongest adsorbent for the carotenoid pigments and has therefore been adopted for use in this laboratory. Strain *et al.* (*14*), found that Celite 501 adsorbed the chlorophylls and xanthophylls from a petroleum ether solution of plant pigments, and used this heat-treated siliceous earth for the separation of xanthophylls. They found this adsorbent useful because of the clear separation of pigment bands and the high filtration rate of the columns.

Although Hyflo Super-Cel has been widely used as a diluent and filter aid for other chromatographic adsorbents, apparently little use has been made of its adsorptive properties, though these have been known for some time (*11, 18*). Used in an adsorption column in proper amounts, it separates almost all noncarotene pigments from a petroleum ether solution of plant pigments, while allowing the carotenes to pass through the column almost unadsorbed (*17*). Lycopene, however, cannot be separated from carotenes with this adsorbent. Hyflo Super-Cel is inexpensive, uniform in properties, and exceptionally stable. After storage in open sacks for 5 years it was found to be as active as newly manufactured material. Its rapid flow rate and other desirable properties when used in an adsorbent column are well known to workers in this field. As the heat-treated siliceous earths are comparatively weak adsorbents, they are more strongly affected by traces of polar solvents, such as acetone or methanol, than are the mixtures of magnesium oxide with Hyflo Super-Cel.

Preparation of the pigment solution for chromatographing depends on the nature of the material under consideration. Any of the well-known methods of obtaining a solution of plant pigments in hydrocarbon solvent may be used, as indicated by the circumstances. The method of saponification with alcoholic potassium hydroxide and extraction of the pigments from the alcoholic solution with petroleum ether is widely applicable, though this method is generally being superseded by less drastic methods of extraction. When polar solvents are used in the extraction of carotene from the material, special care must be taken to remove entirely the polar solvents from the petroleum ether solution, as they will otherwise elute the adsorbed pigments from the chromatographic column. Hyflo Super-Cel is especially well adapted to the separation of cryptoxanthin from carotene by the method of Buxton (*3*); the cryptoxanthin does not pass through the chromatographic column, but forms a band on the column at some distance from any xanthophylls, thus permitting ready separation and elution of the cryptoxanthin.

PROCEDURE

Extraction of Carotene. In the determination of the carotene content of dehydrated alfalfa meal, the pigment solution may conveniently be prepared by the method of Wall and Kelley (*16*), in which the meal is refluxed for 30 minutes with a mixture of acetone and petroleum ether (Skellysolve B), or by the method of Silker, Schrenk, and King (*10*), in which the finely divided sample is allowed to stand overnight in the dark in a mixture of acetone and Skellysolve B. When low-boiling petroleum ether (boiling range 30° to 60° C.) is used in place of Skellysolve B, a somewhat modified procedure is necessary to remove all the acetone by volatilization prior to chromatographing the solution. Filtration of the sample before heating is, however, unnecessary. The modified procedure used in this case is as follows:

One or 2 grams of finely ground alfalfa meal (preferably through a 40-mesh screen) are weighed into a 125-ml. Erlenmeyer flask and covered with 60 ml. of a mixture of 1 part of redistilled acetone to 2 parts of petroleum ether. The tightly stoppered containers are then set aside in the dark for at least 16 to 18 hours, usually overnight, though an extraction period up to 70 hours may be used if desired. The solutions are decanted into 300-ml. tall-form beakers, the flasks are rinsed twice with two 50-ml. portions of petroleum ether, the beakers are placed on the water bath, and the solutions are evaporated to a volume of 10 to 15 ml. The solutions must not be allowed to evaporate to dryness, or loss of carotene will occur. Fifty milliliters of fresh petroleum ether are then added to the beakers, and the solution is again evaporated to a volume of 10 to 15 ml. Forty milliliters of fresh petroleum ether are added, and the solution is ready for chromatographing. The entire procedure of removing the acetone requires about 15 minutes.

For routine control work, the method of Kernohan (*7*) may often be of use. A 1-gram sample of finely ground alfalfa meal (passes a 40-mesh screen) is weighed into a 125-ml. Erlenmeyer flask, 100 ml. of low boiling petroleum ether are added, and the flask is tightly stoppered and allowed to stand in the dark for at least 16 hours, though it may be allowed to stand for as long as 70 hours without changing the results.

The solution is immediately ready for chromatographing after standing the proper length of time. Results by this method are somewhat lower than by the methods given above, as explained below.

The solution of pigments may be prepared by other methods for materials to which these methods cannot be applied, depending on the nature of the material. Crude carotene solutions obtained by the method of the Association of Official Agricultural Chemists (*1*) or by similar methods may be purified chromatographically. Care must be taken to wash all traces of alcohol from the solution of the pigments.

Chromatographic Separation of Carotene. The chromatographic column is prepared by packing the adsorbent (Hyflo Super-Cel) into a glass column 3.3 cm. in diameter to a height of from 15 to 25 cm. The adsorbent packs readily into the tube. When only total carotenes are to be determined, it is convenient to pack the column by placing a plug of cotton or glass wool in the bottom of the tube and forcing the tube into a container of the adsorbent. When enough adsorbent is in the tube, it is pressed firmly down into the tube with a plunger. This method of preparing the adsorption column is unusually rapid and gives sufficiently uniform packing to permit separation of the carotenes from the noncarotene pigments. When it is desired to remove some of the adsorbed pigment bands, such as cryptoxanthin or vitamin A, from the column more uniform packing of the adsorbent into the tube may be obtained by adding successive small portions of the adsorbent to the tube, and pressing the material firmly and smoothly into place with a plunger.

The chromatogram is developed by placing the column under suction and pouring the solution of the pigments, including the sample in the case of dehydrated alfalfa meals extracted by the methods of Silker, Schrenk, and King or of Kernohan, onto the top of the column, allowing the solution to be drawn down to the top of the column, and washing the carotene through the column with fresh petroleum ether until the petroleum ether comes out colorless. It is unnecessary to filter the sample from the petroleum ether solution, as the adsorbent in the column acts as an excellent rapid filter. The carotenes pass through the column with the petroleum ether, are removed from the receiving vessel, and are made up to a volume of 200 ml., and the concentration of carotene is determined colorimetrically. A photoelectric colorimeter is used in this laboratory. The total adsorptive power of the column can be varied by varying the amount of adsorbent in the column.

When dehydrated alfalfa meal is analyzed by this method, most of the noncarotene pigments are adsorbed in the first 1 or 2 inches of the column. The additional length of the column is used to separate certain noncarotene pigments which are occasionally present in dehydrated alfalfa and are weakly adsorbed. These weakly adsorbed pigments behave as carotene in the immiscible solvents method (*1*, *2*). When appreciable quantities of fats are present in the solution, the noncarotene pigments are less adsorbed than normally, and the longer column is required to give complete separation of carotene.

DISCUSSION

Hyflo Super-Cel used in the method outlined above readily separates carotene from the noncarotene pigments which are separated from the carotenes by the immiscible solvents method. It also separates carotene from cryptoxanthin, xanthophyll esters, and acid decomposition products of xanthophylls, none of which are extracted from petroleum ether by 90% aqueous methanol, although saponification transforms the xanthophyll esters to the free xanthophyll, which is extracted by the 90% aqueous methanol. Hyflo Super-Cel is useful for the determination of carotene in ensilage, but cannot be used to determine carotene in tomatoes as it does not separate the carotenes from lycopene. If a petroleum ether solution of crude carotene is prepared from tomatoes by the immiscible solvents method (*1*, *2*), and the pigment solution is poured upon a column of Hyflo Super-Cel 3.3 cm. in diameter by 60 cm. in length, and washed with fresh petroleum ether, an upper red band of lycopene will separate from a lower band of carotene, both pigments being slightly adsorbed. However, the bands are too close together to permit quantitative separation of the pigments. The adsorptive power of different lots of Hyflo Super-Cel varies slightly. In most instances, Hyflo Super-Cel will slightly adsorb carotene, and the first few milliliters of petroleum ether passing through the column are colorless. In some lots, however, there is no indication of any tendency to adsorb carotene.

Hyflo Super-Cel has only slight adsorptive power for vitamin A esters, and so may be used in place of soda ash for the determination of vitamin A in mixed feeds by the method of Cooley, Christiansen, and Schroeder. Strain (*12*) has observed that vitamin A is moderately adsorbed on Celite 501. A similar condition exists with Hyflo Super-Cel. The action of Hyflo Super-Cel on vitamin A and vitamin A esters is shown by the following experiments:

A 0.1-ml. portion of fish oil containing approximately 150,000 I.U. of vitamin A per gram was dissolved in 15 ml. of petroleum ether. This solution was adsorbed in a column of Hyflo Super-Cel 3.3 cm. in diameter by 25 cm. in length, and the column washed with petroleum ether. When the first drops of petroleum ether passed through the column, the column was examined by an ultraviolet light, and showed a narrow, green-fluorescing band 2 to 3 cm. from the bottom of the column. The first portion of the petroleum ether passing through the column was tested with Superfiltrol, and failed to give the characteristic color reaction for vitamin A (*8*, *19*). The adsorbent was removed from the tube and the portion containing the fluorescing band cut from the column. This portion when added to Super-Filtrol with additional petroleum ether gave a strong blue color indicative of the presence of vitamin A. This is presumably vitamin A ester, as it is known that vitamin A exists in fish oils primarily as the ester. Repetition of this test, with continued washing of the column with petroleum ether, showed that the vitamin A ester was rapidly washed through the column with petroleum ether.

One milliliter of the oil previously used was saponified, and an aliquot approximately equivalent to that used in the previous test was taken and similarly chromatographed on a column of Hyflo Super-Cel. When the first drops of petroleum ether passed through the column, examination by ultraviolet light showed a green-fluorescing band only 6 cm. from the top of the column. This portion of the column gave a positive test for vitamin A with Superfiltrol. A narrow band which fluoresced green was adsorbed near the top of the column, but failed to give a positive test for vitamin A with Superfiltrol.

To test the ability of Hyflo Super-Cel to separate vitamin A from its ester, 0.1 ml. of the oil dissolved in 15 ml. of petroleum ether containing an aliquot of saponified fish oil was chromatographed on a column of Hyflo Super-Cel 3.3 cm. in diameter by 25 cm. long. When the first petroleum ether passed through the column, examination by ultraviolet light showed two distinct green-fluorescing bands, separated from each other by a distance of about 5 cm. The lower band, presumably of vitamin A ester, was readily washed through the column, leaving the free vitamin A in the column. When a mixture of fish oil, saponified fish oil, and carotene was chromatographed on a column of Hyflo Super-Cel 60 cm. long by 3.3 cm. in diameter, it was possible to observe separate bands of vitamin A, vitamin A ester, and carotene. However, the bands of vitamin A ester and carotene were so close together as to prevent ready separation.

Table I. Comparison of Chromatographic and Immiscible Solvents Method of Determining Carotene in Dehydrated Alfalfa

(Hyflo Super-Cel adsorbent)

Sample No.	Brooke, Tyler, Baker Method *Mg./100 g.*	BTB Method Followed by Adsorption *Mg./100 g.*	Chromatographic Method *Mg./100 g.*
1	4.9	4.3	5.0
2	4.1	3.6	3.3
3	8.2	7.0	7.1
4	9.7	8.9	9.2
6	14.1	12.0	12.3
7	24.0	21.7	23.0
8	11.0	10.4	10.7

Table II. Comparison of Petroleum Ether and Petroleum Ether–Acetone Extraction Methods, Impure Acetone Solvent

Carotene, Mg. per 100 grams

Sample No.	Petroleum, Ether, Super-Cel Column, Extracted 16 Hours	Petroleum, Ether, Super-Cel Column, Extracted 64 Hours	Petroleum Ether–Acetone Super-Cel Column, Extracted 16 Hours	Petroleum Ether–Acetone, MgO Super-Cel Column, Extracted 64 Hours
23	7.6	7.9	6.2	1.0
	7.6		6.7	3.7
			7.0[a]	
24	6.0	6.2	3.9	0.8
	6.0		6.2	2.8
			5.7[a]	
25	3.7	3.5	2.8	0.6
	3.7		2.8	1.0
			3.9[a]	
39	22.0	21.7	16.6	6.7
	22.0		18.4	12.3
			17.7[a]	
41	24.1	24.1	17.7	5.4
	23.8		19.5	11.0
			19.0[a]	
42	25.2	25.8	21.7	4.6
	25.8		19.2	11.0
			20.7[a]	

[a] Petroleum ether–acetone extracted samples not filtered before adding with solvent to chromatographic column.

Although no attempt has been made to develop a method for using these heat-treated siliceous earths for the determination of vitamin A, the tests described above indicate the possibility of such methods. A possible mode of application to the determination of vitamin A in mixed feeds would be the preparation of a solution of carotene and vitamin A ester by the method of Cooley, Christiansen, and Schroeder (*5*), substituting one of the siliceous earths for the soda ash adsorbent in their method, followed by saponification and separation of the vitamin A and carotene by chromatographing on Hyflo Super-Cel or Celite 501. Because of the speed with which complete development of a chromatogram can be carried out with these siliceous earths, the requirement of two chromatographic procedures should not be unduly burdensome.

COMPARISON OF EXTRACTION METHODS

The method originally used in this laboratory for the extraction of carotenes from dehydrated alfalfa meal preparatory to chromatographing is that of Kernohan (*7*), described above Results are very reproducible. The results obtained by this method, using Hyflo Super-Cel as an adsorbent, and by the immiscible solvents method as modified by Brooke, Tyler, and Baker (*2*), are compared in Table I.

A number of authors have shown that much of the pigment determined as carotene in the immiscible solvents method is without vitamin A activity. Kemmerer and Fraps (*6*) compared a number of methods of determining crude carotene, and found significant variations in the amount of crude carotene and in the amount of the components possessing vitamin A activity present in the crude carotene solutions prepared by each method. As can be seen from Table I, results obtained by the chromatographic method using the extraction method of Kernohan may be either higher or lower than those obtained by the immiscible solvents method.

According to Silker, Schrenk, and King (*10*), it is not possible to extract all the carotene from finely divided dehydrated alfalfa meal by allowing the sample to stand in petroleum ether as recommended by Kernohan (*7*), but all the carotene can be extracted by allowing the sample to stand in a mixture of Skellysolve B and acetone for 16 to 18 hours. No data, however, are given to confirm this. Comparative tests of the two methods, and re-extraction tests on the alfalfa residue remaining after extraction with petroleum ether alone by the method of Kernohan, have confirmed the claim that extraction with petroleum ether alone by the method of Kernohan is incomplete, and that higher results are obtained by extraction with a mixture of petroleum ether and acetone as recommended by Silker, Schrenk, and King or by Wall and Kelley (*16*).

Experiments were also conducted to determine whether the extraction time of 16 to 18 hours used by Silker, Schrenk, and King (*10*) could be lengthened to 70 hours without loss of carotene. It was found that this longer extraction time is satisfactory; thus this extraction method can be used even when laboratory work is not conducted on the day following the placing of the samples in the solvent, if special precautions are taken to ensure the purity of the acetone.

In the first series of tests, somewhat higher results were obtained in some instances by the extraction method of Silker *et al.* than by the method of Kernohan, but these were found to be due to certain impurities which had passed through the adsorption columns. On more thorough chromatographic purification, higher results were obtained with petroleum ether extraction than by extraction for 16 hours at room temperature with a mixture of 20 ml. of acetone and 40 ml. of petroleum ether. When this test was repeated, allowing the samples to stand in contact with the solvents for 64 hours, similar amounts of carotene as in the 16-hour extraction were found with petroleum ether, but much lower and erratic results were obtained with the mixed solvents, as shown in Table II. Loss by oxidation rather than incomplete extraction appears to cause the low results by the latter method.

The acetone used in these tests was commercial c.p. acetone. As this seemed the probable source of oxidation, steps were taken to purify the acetone. Distillation of a similar batch of acetone from an ordinary distilling flask showed it to have a boiling range of from 50° to 70° C. The fraction boiling from 56.5° to 57.3° C., about half the total acetone, was taken for all further tests. Strain and Manning (*13*) recommend the addition of 0.5% redistilled dimethyl aniline to solvents used in extracting carotenoids from plant material in order to neutralize plant acids during extractions, to counteract acidity which might otherwise develop upon the adsorption columns, and to minimize pigment oxidation. As dimethyl aniline was not readily available, tests of an antioxidant were conducted by adding 0.200 gram of hydroquinone to some of the samples extracted by mixtures of acetone and petroleum ether.

Table III. Comparison of Hyflo Super-Cel with Magnesia–Hyflo Super-Cel Mixture as Chromatographic Adsorbents

Carotene, Mg. per 100 Grams

Sample No.	Extracted with Petroleum Ether		Extracted with Acetone and Petroleum Ether		Extracted with Acetone, Petroleum Ether, and Hydroquinone	
	MgO	Super-Cel	MgO	Super-Cel	MgO	Super-Cel
2	3.0	3.3 3.4 3.2	4.3	4.4 4.4	4.3	....
3	6.7	6.7 6.7	7.6	7.4	7.6 7.0	7.9 7.4
4	8.9	8.9 9.2	9.2	9.2	9.5 8.9	9.2 9.7
5	12.3	12.0 12.7	14.1	12.5	14.1	14.1 14.1
6	12.3	12.3 12.3	13.9	15.5	13.6	13.3 14.1

The use of hydroquinone to diminish oxidation of carotene is well known. Because of its acid properties hydroquinone cannot be considered a complete substitute for dimethyl aniline, and its use would be inadvisable with any but dehydrated materials. As hydroquinone is insoluble in petroleum ether, it precipitates upon evaporation of the acetone, and thus is removed from the solution. If the hydroquinone were not removed, it would tend to elute the adsorbed pigments from the chromatogram, making separation of the carotene from the noncarotene pigments difficult. This effect was somewhat noticeable when the magnesia adsorbent was used and the carotene eluted with a mixture of 4% acetone in petroleum ether.

Some of the results obtained by extracting with mixtures of petroleum ether and acetone containing added hydroquinone as compared to extracting with mixtures lacking the hydroquinone are shown in Tables III and IV. These results are inconclusive, and show no particular advantage to be gained from the use of hydroquinone. Unfortunately, the lot of acetone believed to have caused the oxidation of carotene was entirely used in the preliminary determinations, and further lots of acetone which were not redistilled failed to show low results when used in extracting dehydrated alfalfa meal. The addition of hydroquinone, dimethyl aniline, or other suitable antioxidant should, however, be a useful precaution against oxidation when plant pigment is extracted by allowing plant material to stand in contact with the solvents for a considerable period of time. Redistilled dimethyl aniline as recommended by Strain and Manning should be preferable to hydroquinone, as the dangers of an acid reaction would be lacking.

Tests with the redistilled acetone in the various extraction methods were again conducted (Tables III and IV). These results show clearly that higher results are obtained with the extraction method of Silker, Schrenk, and King than with the method of Kernohan. Table III also shows that comparable results are obtained using Hyflo Super-Cel as an adsorbent in the place of the more complicated Hyflo Super-Cel–magnesium oxide mixture. Table IV shows the results of tests of other methods of extraction and different times of extraction. The results in Table IV were obtained over a period of approximately 3 weeks, during which time the samples were stored in the dark at room temperature, so that some of the differences in carotene content shown are due to loss of carotene in the samples during storage. In the method of Wall and Kelley (*16*), 1-gram samples of dehydrated alfalfa meal were refluxed for 45 minutes with a mixture of 30 ml. of acetone and 70 ml. of low-boiling petroleum ether. The time of refluxing was 15 minutes more than that recommended by Wall and Kelley, and was increased by this amount to compensate for the lower boiling temperature caused by using low-boiling petroleum ether in place of Skellysolve B in the mixed solvent. Results obtained by this method were very similar to those obtained by the method of Silker, Schrenk, and King.

Table IV. Effect of Extraction Methods on Carotene Content of Dehydrated Alfalfa Meals Determined Chromatographically with Hyflo Super-Cel Adsorbent

		Carotene, Mg. per 100 Grams				
		No. 2	No. 3	No. 4	No. 5	No. 6
1	90 hours with petroleum ether at room temperature	... ...	6.7 6.7	8.9 8.9	13.0 13.3	14.1 14.1
2	Petroleum ether, 20 hours at room temperature	3.3 3.3	6.7 6.7	9.2 9.2	12.0 12.7	12.3 12.3
3	Acetone–petroleum ether mixture, 20 hours at room temperature	4.4 4.4	8.9 8.2	9.7 10.0	15.2 15.7	15.0 15.5
4	Acetone–petroleum ether mixture, 90 hours at room temperature	... ...	7.6 7.6	9.2 9.2	14.1 14.7	14.7 15.7
5	Acetone–petroleum ether–hydroquinone, 90 hours at room temperature	... ...	7.6 7.6	9.7 9.7	15.2 16.3	16.3 16.3
6	Wall and Kelley method, reflux with acetone–petroleum ether	4.4 4.4	8.2 8.9	10.0	15.5	15.2
7	Residue from petroleum ether extraction by immiscible solvents method	0.72	0.96	0.80	1.32	1.24
8	Method 7 followed by adsorption on Hyflo Super-Cel	0.32	0.40	0.28	0.80	0.96
9	Sum of methods 2 and 7	4.02	7.66	10.0	13.67	13.53

To test for the completeness of extraction by the method of Kernohan, 2.5-gram samples of dehydrated alfalfa meal were extracted for 20 hours at room temperature with 150 ml. of low-boiling petroleum ether in a 250-ml. Erlenmeyer flask. The samples were filtered off into Gooch crucibles, and thoroughly washed with petroleum ether. The remaining sample was then treated by hot saponification and the carotene content determined by the immiscible solvents method of Brooke, Tyler, and Baker (*2*). A portion of the crude carotene solution so obtained was chromatographed on a column of Hyflo Super-Cel 3.3 cm. in diameter by 15 cm. in height to remove noncarotene pigments.

Table IV shows that carotene was not completely extracted by petroleum ether, thus confirming the results obtained in comparing carotene determinations made by this method with those made with other, more recently developed extraction methods. However, in view of the fact that approximately 10 to 25% of the carotene determined by the various abridged chromatographic methods has no vitamin A activity (*6*), the extraction method of Kernohan may be useful under certain conditions for routine control work on dehydrated alfalfa meals, as it enables rapid estimation of the vitamin A activity of this material, often with an accuracy comparable to other methods of determining the vitamin A activity from the carotene content.

EFFECT OF POLAR SOLVENTS

In preliminary experiments in the comparison of the extraction methods of Kernohan and of Silker, Schrenk, and King, using acetone that was not redistilled, the petroleum ether–acetone extraction gave higher results than petroleum ether extraction for the old samples of alfalfa, and slightly lower results for the newly dehydrated samples. During the analysis, part of a gray-colored band was observed to pass into the solution of carotenes obtained by chromatographing the solution from the petroleum ether–acetone extraction. This band had an orange-red fluorescence under the light from a General Electric mercury projector spotlight which was equipped with a filter to transmit primarily ultraviolet light. Comparison of the appearance under this light of the carotene solutions prepared by chromatographing the solutions from the petroleum ether extraction and the petroleum ether–acetone extraction showed that the latter had a faint reddish fluorescence not present in the solution prepared from samples extracted by petroleum ether alone.

To analyze solutions obtained by extraction with the mixed solvents, special care was given to removing all the acetone from the solutions before chromatographing, and the columns of Hyflo Super-Cel used were 25 cm. long. Under these conditions, none of the gray band passed through the column, and, upon following the progress of the bands through the adsorption column with ultraviolet light, it was found that a colorless, orange-red fluorescing band was adsorbed below the gray band and did not pass through the column. The final carotene solutions did not fluoresce red after this treatment of the extract. The colorless band showing the orange-red fluorescence was removed from the chromatographic column and eluted with acetone. The material when concentrated was found to be slightly yellow in color. The pigment was transferred to petroleum ether which was washed free from acetone. It was then found that this material could not be extracted from petroleum ether with 90% aqueous methanol solution.

Further experiments with modifications of the method of removing the acetone from the petroleum ether and acetone mixture led to the development of the method recommended under Procedure. With this method, the fluorescent band remains firmly held near the top of a column of Hyflo Super-Cel only 15 cm. long, and no danger of contamination of the solution of carotenes exists. In this case, several extremely narrow bands of yellow pigment often appear below the fluorescent band. It is recommended, however, as a matter of routine precaution, that all carotene solutions prepared when acetone is used as a solvent and Hyflo Super-Cel as an adsorbent be checked for fluorescence.

The effects of a solution of 4% acetone in petroleum ether in eluting carotenoid pigments from a chromatographic column of Hyflo Super-Cel were tested, using a chromatogram which had been developed from a petroleum ether extract of high-grade alfalfa meal. In this instance, all visible and fluorescent pigments were firmly adsorbed in the top 5 cm. of a 25-cm. column. On percolating the petroleum ether–acetone mixture through the column, the chlorophylls and some yellow pigments remained firmly adsorbed in the column, moving downward only slightly. Three bands separated from these strongly adsorbed pigments and moved down the column rapidly: a lower yellow band, an intermediate gray, and an upper yellow. The mixed pigments contained in the two lower bands were separated from the upper yellow band. The mixed pigments of the lower yellow band and the gray band were not extracted from petroleum ether by 90% aqueous methanol solution. The solution fluoresced red in ultraviolet light. The pigment solution was allowed to stand overnight in contact with a methanolic sodium hydroxide solution, the pigment was extracted from the methanol with petroleum ether, and the petroleum ether solution was extracted with 90% methanol. The remaining petroleum ether solution was a clear yellow color, and showed no fluorescence in ultraviolet light. It therefore appears that this pigment is one of the interfering pigments in the method of immiscible solvents. The upper yellow band from the chromatogram was readily extracted from petroleum ether solution by 90% aqueous methanol, and was probably a xanthophyll.

These preliminary experiments indicate that the use of dilute solution of polar solvent in petroleum ether offers a rapid method of separating small quantities of noncarotene pigments having solubility relations similar to those of carotene.

SUMMARY

Heat-treated kieselguhr, especially Johns-Manville Hyflo Super-Cel, is an excellent chromatographic adsorbent for the routine determination of total carotenes, and can also be used in the separation of cryptoxanthin from carotene. Preliminary tests indicate that this adsorbent may be applicable to the separation of vitamin A from carotenoids, and so may be useful in the determination of vitamin A in certain instances.

Tests have confirmed claims that extraction of carotene from dehydrated alfalfa meal with mixtures of petroleum ether and acetone gives more complete extraction than extraction by allowing the meal to stand in contact with petroleum ether for 16 hours or more. The latter method, however, gives consistent results and should frequently be useful for routine control work on dehydrated alfalfa meal.

The chromatographic method described is unusually rapid and requires minimum manipulation, thus reducing chances for error and enabling easy training of operators. As the adsorbent does not shrink from the walls of a chromatographic column if drawn dry of solvent, it is especially convenient when batteries of chromatographic columns are used.

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Molecular Distillation as a Step in the Chemical Determination of Total and Gamma-Tocopherols

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A METHOD for quantitatively concentrating tocopherols from lipides is much needed in the vitamin E analysis of many natural products. Such a procedure is desirable especially for fats and oils of low tocopherol content, to enable the use of ethanol as the solvent in the colorimetric measurement of tocopherols and to avoid the possible inhibiting effect (*7*) of fats on the color development in the Emmerie-Engel reaction. The authors have found that distillation of the extracted lipide under low pressure in a simple molecular still effects quantitative separation of as little as 60 micrograms of tocopherols from 1 gram of fat. The distillate, usually 15 to 20 mg. in total weight, contains the tocopherols in a sufficiently concentrated form for colorimetric assay purposes. In addition, all of the chlorophyll and much of the carotenoids remain in the residue.

Dam and associates (*2*, *4*) have reported quantitative recoveries by molecular distillation of α-tocopherol added to nonsaponifiable matter at a level about 3%. Their standardized distillation conditions were 100° C. at 1μ pressure for 30 minutes. However, in the authors' laboratory, in order to avoid saponification it was necessary to distill fats containing only 0.006 to 0.2% tocopherols. For this concentration range quantitative separation is achieved in the apparatus described below by distilling at 215° to 220° C. at 1μ or less for 30 minutes.

Saponification, which would appear to be the proper procedure for concentrating tocopherols from lipides, has not proved satisfactory for fats of low tocopherol content. Tocopherols at levels comparable to those occurring in animal fats—e.g., 60 micrograms per gram—have been recovered to the extent of only 60 to 70%. Saponification has been conducted in a closed system under nitrogen, according to directions given by Chipault *et al.* (*1*) with the use of pyrogallol as an antioxidant, or with a minimum of alkali and exposure to heat, without affording full recoveries. Separation by adsorption of tocopherols on alumina Al_2O_3 has also failed to give quantitative results in preliminary trials. On the other hand, complete recovery has been obtained by the method described here.

EXPERIMENTAL

A diagram of the distillation apparatus is shown in Figure 1.

Procedure. The fat sample, 1 gram or less, is weighed into the aluminum cup, melted if necessary to form a thin film, and placed in the still. Aluminum strips are attached to the cup merely for ease of handling. The sample is degassed by closing the still with a large rubber stopper and reducing the pressure to less than 1μ at room temperature. This minimizes splashing of the sample in the subsequent distillation. The pressure is restored to atmospheric, and without delay the condenser is inserted and the pressure reduced again to 1μ. The condenser is then filled with acetone and dry ice. The surface of the oil in the bath is adjusted level with the bottom of the condenser. The temperature of the bath is raised rapidly to 220° C. and maintained at 215° to 220° C. for 30 minutes while distillation takes place. Then the oil bath is removed and the still is allowed to cool to room temperature under vacuum. The condenser is removed carefully from the still and the distillate washed off quantitatively with chloroform and transferred, by means of evaporation under nitrogen, to a known volume of absolute ethanol. Separate portions of the sample are used for the analyses of total tocopherols and γ-tocopherol.

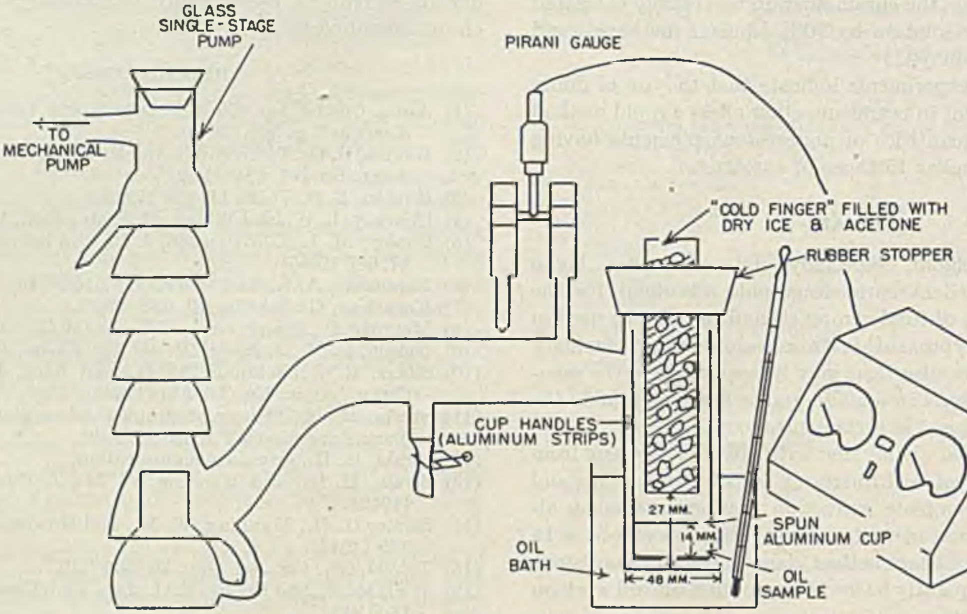

Figure 1. Diagram of Distillation Apparatus

RESULTS AND CONCLUSIONS

Recovery experiments were performed in which γ-tocopherol was added to lard in amounts varying from 0.06 to 2.0 mg. per gram. The base values of the lard, given in Table II, were 27 micrograms per gram of total tocopherols and less than 4 micrograms per gram of γ-tocopherol. No further tocopherols were found with exhaustive distillation for 3 hours or on raising the temperature to 230° C. The values shown in Table I are the results of duplicate distillations and analyses. The range of recovery values is between 92 and 102%. Gamma-tocopherol values are shown because of their specificity; however, Emmerie-Engel results for total tocopherols also show excellent recoveries. Gamma-tocopherol was measured by use of the Quaife method (*8*) as modified by Weisler (*11*). This procedure involves coupling of γ-tocopherol with a diazo compound to form a red dye; α- and β-tocopherols do not react. Total tocopherols were determined colorimetrically by the Emmerie-Engel reaction (*3*) according to the technique previously described (*10*).

Table I. Recovery of γ-Tocopherol by Molecular Distillation

γ-Tocopherol Added to 1 Gram of Lard[a]	Recovery after Distillation
Mg.	%
0.06	92
0.12	95
0.25	101
0.50	99
1.00	93
2.00	102
Av. recovery	97

[a] This contained 27 micrograms per gram of total tocopherols and < 4 micrograms per gram of γ-tocopherol according to distillation analysis.

Table II. Tocopherol Content of Fats Determined on Molecular Distillates of Samples of 1 Gram or Less[a]

Material Distilled	Tocopherol Content Total	Gamma
	γ/gram	
Margarine, clarified[b]	544	260
Lard	27	< 4
Carrot oil (from fresh carrot 0.3% oil)	1,620	0
Cottonseed oil, refined		
Sample 1	726	313
Sample 2	901	345
Egg lipide (from whole egg, 11.5% lipide)	130	44
Olive oil	69	..

[a] No attempt has been made to use samples larger than 1 gram. A larger sample in the present apparatus might form too thick an oil film for molecular distillation. The still could be enlarged to accommodate a larger sample.

[b] Bioassayed for vitamin E activity.

The procedure has been applied to a variety of food fats, a representative selection of which is shown in Table II. Distillates in which carotenoids were known to be present were hydrogenated (*9*) before assaying for tocopherols. The lard distillates were found to be free of substances which inhibit color development of the Emmerie-Engel reaction (*7*). The clarified margarine sample was bioassayed (Miss Marion Ludwig performed the bioassay) and found to contain vitamin E activity equivalent to 0.32 mg. of *d*,α-tocopherol per gram. Chemical determination showed 0.544 mg. per gram of total tocopherols, of which 48% is γ-tocopherol and the remainder probably α-tocopherol. This is in good agreement with the bioassay result. Previous findings (*5*, *6*) relative to the sparing action of γ-tocopherol on α-tocopherol in bioassay tests suggest that this mixture of 0.284 mg. of α-tocopherol plus 0.260 mg. of γ-tocopherol would give the same biological response as 0.3 to 0.4 mg. of *d*,α-tocopherol alone.

Experience with the method described leads to the belief that most naturally occurring fats and lipide extracts can be analyzed for tocopherols using the intermediate step of distillation. It is planned to survey common foods for total tocopherol and for γ-tocopherol content and to compare the results with bioassays in selected cases.

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Kjeldahl Determination of Nitrogen

Elimination of the Distillation

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An acidimetric macroprocedure is described for determining nitrogen without a distillation. The ammonium ion is titrated with standard sodium hydroxide in the presence of formaldehyde.

ARTMANN and Skrabal (*1*) and Rupp and Rossler (*7*) have shown that ammonia can be accurately determined by oxidation to nitrogen in alkaline solution by means of standard hypobromite solution, the excess of the latter being determined by adding potassium iodide and acid and titrating the liberated iodine with thiosulfate. Willard and Cake (*8*) and more recently Haanappl (*3*) have used this method to eliminate the distillation in the Kjeldahl determination. This procedure has one serious disadvantage: The alkaline hypobromite solution employed to oxidize the ammonia must be kept between 0° and 5°, since it is unstable at room temperature.

Ammonia reacts rapidly with formaldehyde to form hexamethylenetetramine, which has very weakly basic properties (*6*) ($K_b = 8.0 \times 10^{-10}$). Therefore ammonium salts may be sharply titrated in the presence of formaldehyde with sodium hydroxide and phenolphthalein indicator. Kolthoff (*5*) has found that the reaction between ammonia and an excess of formaldehyde goes so rapidly that the titration may be made directly—i.e., without excess of alkali. This reaction has been employed in the present modification of the Kjeldahl procedure.

The proposed method consists essentially of three steps: (1) The usual destruction of the organic matter by oxidation with hot concentrated sulfuric acid in the presence of potassium sulfate and a mercury catalyst. (2) Neutralization of the excess sulfuric acid with approximately 10 *N* alkali to the methyl red end point. Sodium bromide is present during the neutralization to form a complex and thus prevent the precipitation of mercury compounds.

$$Hg^{++} + 4Br^- \longrightarrow HgBr_4^{--}$$

(3) Titration of the ammonium salt with standard 0.1 *N* sodium hydroxide to the phenolphthalein end point in the presence of formaldehyde.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$$

$$4NH_3 + 6CH_2O \longrightarrow (CH_2)_6N_4 + 6H_2O$$

REAGENTS

Sodium Hydroxide Solution, 50%. Dissolve 600 grams of sodium hydroxide (Baker's C.P. pellets, 0.004% silica) in 600 ml. of water. Let the solution stand several days in a paraffin-lined rubber-stoppered bottle and decant the clear supernatant liquid.

Standard Sodium Hydroxide Solution, 0.1 *N*. Dilute approximately 8 grams of concentrated (50%) carbonate-free sodium hydroxide solution to 1 liter with equilibrium water. Standardize against potassium biphthalate. Store in an alkali-resistant glass container protected from the atmosphere with an Ascarite tube.

Sodium Hydroxide Solution, approximately 10 *N*. Dilute about 800 grams of concentrated (50%) carbonate-free sodium hydroxide solution to 1 liter with equilibrium water. Store in an alkali-resistant glass container protected from the atmosphere by an Ascarite tube.

Concentrated Sulfuric Acid, C.P., specific gravity 1.84.

Potassium Sulfate Crystals, Baker's C.P.

Methyl Red, 0.004 *M* (0.1%). Dissolve 0.25 gram of indicator in 250 ml. of alcohol.

Phenolphthalein, 0.03 *M* (1%). Dissolve 2.5 grams of indicator in 250 ml. of alcohol.

Neutral Formaldehyde Solution, approximately 18%. Dilute 45 ml. of Merck's reagent-grade formaldehyde (36 to 38%) with an equal volume of water. Add 2 drops of 0.03 *M* phenolphthalein and neutralize with 0.1 *N* sodium hydroxide to the first detectable pink color. This solution should be prepared just before it is used.

Sodium Bromide Solution, 60%. Dissolve 150 grams of Merck's reagent chemical in water and dilute to 250 ml.

Mercuric Oxide, reagent grade.

Eleven organic compounds were purified by repeated crystallization till a constant sharp melting point was obtained. The compounds were dried to constant weight in vacuo in an Abderhalden dryer containing phosphorus pentoxide in the bulb.

PROCEDURE

Weigh accurately a sample that will yield approximately 4 milliequivalents of nitrogen and transfer directly into a 500-ml. 29/42 standard-taper round-bottomed Pyrex flask. This flask is fitted with a 20-cm. (8-inch) removable neck and serves for both digestion and titration. Add 10 grams of anhydrous potassium sulfate, 0.6 to 0.7 gram of mercuric oxide, and 15 ml. of concentrated sulfuric acid. Put the neck of the flask in place, shake the mixture, and heat it in a fume chamber below the boiling point until frothing ceases. Then increase the heat so that the solution boils gently. If necessary, replace the sulfuric acid that has boiled off, but take care that the quantity of acid in the flask at the end of the digestion does not exceed 15 ml. Continue the heating with sulfuric acid until the solution turns colorless and then 20 minutes longer. Cool the flask to at least 50°, carefully add 50 ml. of water, and swirl the flask until the solid material has dissolved completely. Add 10 ml. of 60% sodium bromide, then 2 drops of methyl red. Neutralize the excess sulfuric acid with 10 *N* sodium hydroxide till the methyl red begins to change color. Now boil the solution gently for 3 minutes to expel carbon dioxide, cool to room temperature, and add 10 *N* alkali dropwise till the solution is just yellow. Next add *N* sulfuric acid dropwise till the pink color is restored. Then add the standard 0.1 *N* sodium hydroxide from a buret to the methyl red end point. Read the buret.

Add 30 ml. of 18% formaldehyde solution. At this point, the solution may become slightly pink. Disregard this, and continue the titration till the solution is yellow again. Add 8 drops of phenolphthalein and complete the titration to the first distinct pink color. The alkali used between the methyl red and phenolphthalein end points is equivalent to the nitrogen present.

When more than 17 ml. of concentrated sulfuric acid must be neutralized before titration of the ammonium salt, sufficient silica is introduced as an impurity in the sodium hydroxide to buffer the solution at the phenolphthalein end point and thus prevent a sharp color change. Therefore it is suggested that no more

Table I. Determination of Nitrogen

Compound	% N Theory	Recommended Procedure: No. of determinations	Recommended Procedure: % N mean	Recommended Procedure: Mean deviation	Standard Procedure: No. of determinations	Standard Procedure: % N mean	Standard Procedure: Mean deviation
Acetanilide	10.36	2	10.30	0.03	2	10.33	0.01
Anthranilic acid	10.22	2	10.24	0.02	..	...	...
Benzamide	11.57	2	11.56	0.04	..	...	...
p-Chloroaniline	10.97	3	10.92	0.00	..	...	...
Cysteine	11.57	4	11.53	0.01	..	...	...
Dicyandiamide	66.64	6	66.51	0.01	6	66.54	0.02
p-Dimethylaminobenzaldehyde	9.40	2	9.34	0.01	..	...	...
Diphenylamine	8.28	3	8.23	0.00	4	8.23	0.04
Diphenylcarbamine chloride	6.04	2	6.02	0.01	..	...	...
sym-Diphenylurea	13.21	3	13.17	0.06	..	...	...
Sulfanilic acid	8.08	4	8.07	0.02	..	...	...

than approximately 15 ml. of sulfuric acid be present at the end of the digestion.

Determine and apply a blank correction, which is usually between 0.20 and 0.30 ml.

The results of analyses of eleven organic compounds are indicated in Table I.

DISCUSSION

As shown in Table I, the described method yields results with an average error of −0.04% nitrogen. Even this small difference may be due in part to failure to obtain perfectly pure organic compounds. The results compare very favorably with those of the standard Kjeldahl method with compounds of both high and low nitrogen content.

The disadvantage of the method is the fact that elements such as calcium, barium, copper, and iron interfere by forming precipitates which obscure the end point. Phosphorus also interferes because primary phosphate is titrated to secondary phosphate between the two end points. This renders the procedure inapplicable to fertilizers and many biological samples. The method is applicable to samples containing organic and nitrate nitrogen when the usual sulfuric-salicylic acid modification is applied previous to digestion (*2*, *4*).

With the elimination of the distillation, approximately 20 minutes are saved in each determination.

Work is in progress to adapt the described procedure to the micro scale.

ACKNOWLEDGMENT

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Determination of Carbon and Hydrogen by Combustion

Unitized Dual Apparatus and Improved Procedure

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A dual unitized combustion apparatus and improved procedure are described for the determination of carbon and hydrogen in macrosize samples. The dual feature, absence of rubber connections, provisions for adequate combustion control, and well-defined procedure all combine to give accurate results in the minimum of time. Other noteworthy features are control and indication of all gas flow rates, adequate and convenient pyrometer temperature indication, addition of extra oxygen between the sample and catalyst, use of carefully determined combustion and operating conditions, and a method for accurate analyses of volatile samples. Using the long, precision procedure, a skilled operator can make two determinations in an 8-hour day with a precision of ±0.008% hydrogen and ±0.009% carbon and a probable accuracy of 0.011% hydrogen and 0.015% carbon. Using the short, routine procedure, one experienced operator can make as many as eight determinations daily with a precision of ±0.02% hydrogen and ±0.05% carbon and with a probable accuracy of 0.05% for each element. Both procedures are applicable in presence of sulfur, halogens, nitrogen.

MOST of the progress made in recent years in the determination of carbon and hydrogen has been in the field of microchemistry. Excellent methods and apparatus (*1*, *2*, *5–9*) have been developed which possess the desired attributes of speed, convenience, and accuracy when properly applied, but which too frequently produce results of only moderate accuracy when used on a routine basis (*9*). In this, as in many other laboratories, there has been a definite need for a method which is accurate, precise, and rapid under normal industrial operating conditions. Because macromethods are less susceptible to variations in technique and are thus more suitable for industrial service analysis, it was decided that further development of the macromethod, along lines followed by the microchemists, offered the best possibilities of success.

Wagman and Rossini (*10*) have obtained very precise and accurate results on benzoic acid using large samples (1.8 grams) and improved techniques and apparatus developed at the National Bureau of Standards. In their work on the atomic weight of carbon, Baxter and Hale (*1*) also obtained excellent results using various hydrocarbons and even larger amounts (3 grams) of sample. These investigators had for their prime objective the greatest possible accuracy without regard for time required for analysis. In the present method, accuracy and precision have been achieved by adopting features of the Baxter and Hale apparatus particularly suitable for routine work; speed has been secured by providing a dual apparatus which permits the simultaneous combustion of two samples, by providing convenient and adequate control of the combustion, and by carefully determining the minimum time required for each phase in the analysis.

The conventional combustion method and apparatus for determination of carbon and hydrogen are not generally suitable for industrial use where speed is a consideration, and where analysts may be frequently replaced, and for applications where the greatest precision and accuracy are important. Using the simple apparatus and procedure given in the numerous references on the subject, one usually encounters the following difficulties: (1) loss of much time and effort in establishing the essential conditions, (2) nonsuitability of the apparatus for continuous use, (3) inadequate indications and control of flow rates, (4) inadequate control of furnace temperature, (5) lack of assurance of excess oxygen in combustion tube, (6) errors caused by use of rubber connections, (7) inadequacy of the combustion tube filling for materials containing elements other than carbon, hydrogen, and oxygen, (8) requirement of 4 or more hours per analysis, (9) lack of qualitative evidence of complete oxidation of the carbon and hydrogen, and (10) lack of suitable technique for handling volatile samples. The method described here is a result of a study made to overcome or minimize these difficulties.

The combustion apparatus was unitized in a compact assembly to increase the convenience of use and to allow standardization of technique and procedure; and since it was found that two determinations could easily be made simultaneously, a dual unit

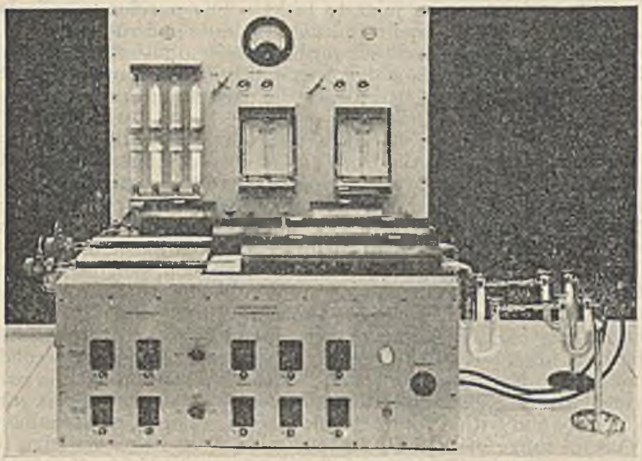


Figure 1. Front View of Dual Combustion Apparatus

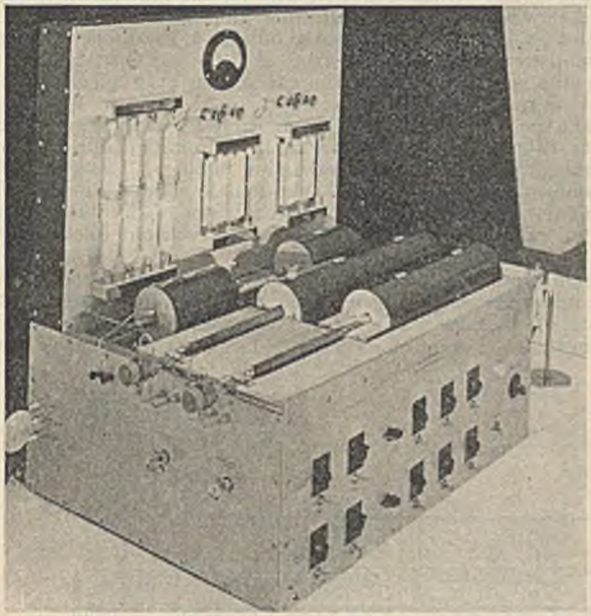


Figure 2. Side View of Dual Combustion Apparatus

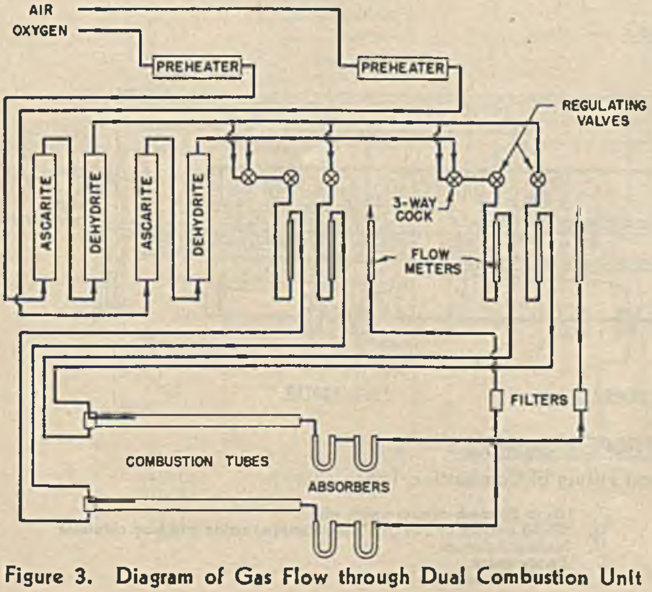


Figure 3. Diagram of Gas Flow through Dual Combustion Unit

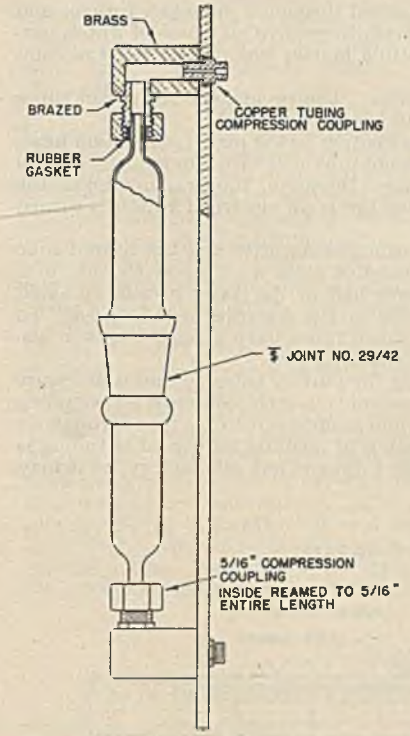


Figure 4. Detail of Purifier Tube and Mounting

was designed to increase the number of analyses per unit time. Proper control and indication of the gas mixture in the combustion tube were achieved by use of microrotameters (0 to 50 ml. per minute) to indicate continuously the rate of flow of air, oxygen, and exit gases and by the use of needle valves to adjust the flow of the air and oxygen. Proper adjustment of furnace temperature was made possible by use of thermocouples and a sensitive direct indicating meter supplied with a suitable selector switch. Excess oxygen in the gases passing over the catalysts was ensured by provision to admit oxygen in the zone between the sample and the catalyst (*3*). Contamination from rubber connections was avoided by use of commercial compression metal fittings, a special metal-to-glass fitting, and standard-taper glass joints. Complete retention of sulfur, halogen, and nitrogen acidic gases was obtained by proper use of lead chromate, silver gauze, and lead peroxide in the combustion tube. Sensitive and immediate control of the rate of volatilization of the sample was obtained by an electric wire heater wound directly on the combustion tube. Errors from contamination of the air and oxygen used were obviated by passing these gases over heated copper oxide in permanently connected heaters.

Permanent connections and mountings were used to allow movement of the apparatus without seriously disrupting its period of usefulness. Special all-glass counterpoises for the absorbers were constructed (having approximately the same net volume, weight, and surface as the actual absorbers) to minimize weighing errors and facilitate correction to a vacuum basis.

APPARATUS

The dual arrangement and general construction of the apparatus are shown in the first two figures. Figure 1 is a front view giving some detail of the absorption train and Figure 2 is a side view showing the gas-inlet and tube-closure assembly arrangement. A diagram of the air and oxygen flow through the apparatus and a schematic arrangement are given in Figure 3. The constructional details of the combustion tube and filling are shown in Figure 6, the electrical wiring diagram in Figure 7, and the arrangement of the absorption train in Figure 8.

The two combustion heaters are mounted one behind the other with their centers about 12.5 cm. (5 inches) apart. Behind and parallel to these are located two preheaters. The panels in front and below the heaters contain control knobs for regulating the temperatures of the various furnaces. The large panel behind and above the furnaces supports the gas purifiers, flowmeters, gas control valves, and pyrometer.

Provision is made for supplying either oxygen or air to the combustion tube. Oxygen is used for combustion of the sample and air for purging out the combustion products, so that the absorbers will be filled with air during the weighing operations.

Both oxygen and air are passed through a preheater furnace and then through a purifying train to remove all traces of water, carbon dioxide, and combustible matter before entering the combustion tube.

Preheater and Purifier. The preheaters are nickel tubes filled with copper oxide and heated to 700° C.

They are similar in construction to the main combustion heaters described below but are not provided with temperature control or with individual switches; therefore, they rapidly reach the operating temperature after the main electrical switch is turned on.

The first purifier tube contains Ascarite and the second tube Dehydrite. A twisted strand of glass wool about the size of a pencil is placed in the lower half of the Ascarite tube to avoid plugging caused by swelling of the Ascarite as it is used. To facilitate cleaning, the purifier tubes have ground joints in the center which are sealed with sealing wax.

The method of mounting the purifier tubes is shown in Figure 4. The mounting consists of $^5/_{16}$-inch compression coupling soldered into brass blocks and reamed out to $^5/_{16}$ inch throughout their length. A short section of medium hard rubber tubing is used as gasket (soft rubber tubing is not satisfactory, as it may wrinkle and cause the joint to leak). The purifier tube is installed in the mount by first placing the nuts and rubber gaskets on the narrow tubes and then pushing one end into the mounting block far enough to allow the other end to enter its mount. This connection is gas tight, yet allows the parts to be easily removed for servicing.

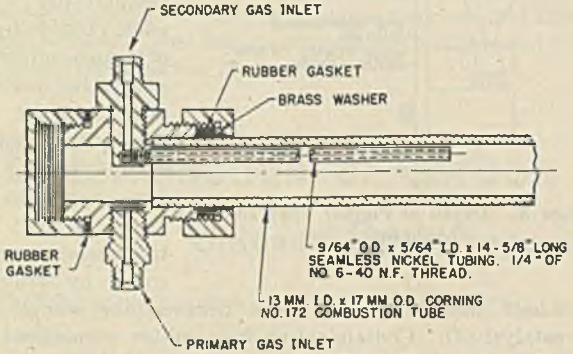


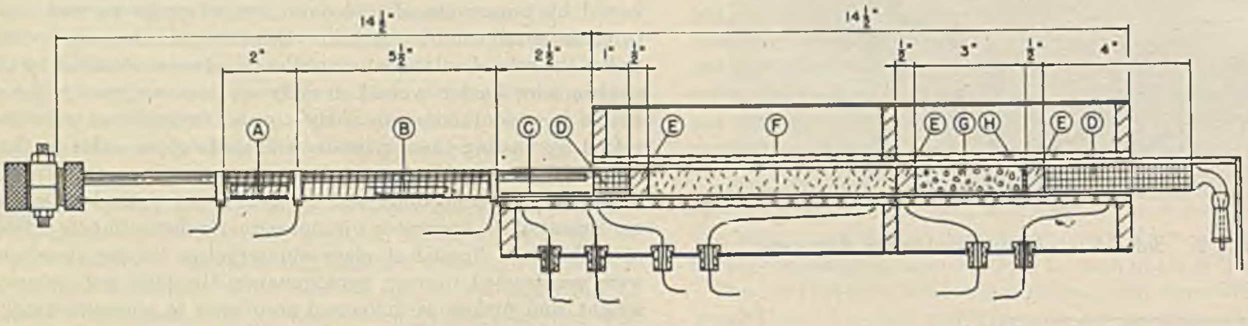
Figure 5. Detail of Gas-Inlet and Tube-Closure Assembly

Combustion Tube. A metal gas-inlet and tube-closure assembly is attached to the front end of each combustion tube; it has a screw cap to provide an opening into the combustion tube and has two gas inlets. The "primary" gas inlet allows gas to enter the front of the combustion tube; the "secondary" inlet conducts the gas, by means of a small-diameter nickel or platinum tube, to a point just in front of the main catalyst section. Figure 5 shows the construction of the gas-inlet and tube-closure assembly and the method of connecting it to the combustion tube. By means of a 3-way cock, either air or oxygen can be passed through the primary inlet, but only oxygen can be passed through the secondary inlet. Each gas line leading to the combustion tube is provided with a packless needle valve for close control of the gas-flow rate and with a rotameter flowmeter. The flowmeters have a useful range of 0 to 60 ml. per minute, and are sensitive to changes of 5 to 10% of the gas flow in the range of 5 to 60 ml. per minute. The mountings for the flowmeters are similar to those for the purifiers.

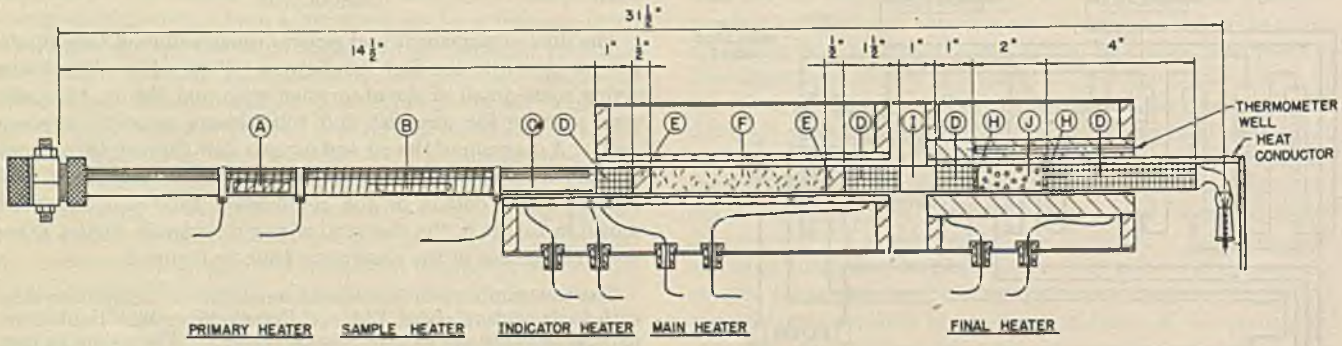
All the gas lines before the combustion tube are constructed of metal tubing. Rubber is used only for the gaskets on the purifiers, flowmeters, and gas-inlet and tube-closure assembly. The rubber gaskets are always on the outside of the tubes where only a small area of the rubber is exposed to the gas flow; in each case the area is separated from the gas stream by a narrow annular dead air space.

The special combustion tube, shown in Figure 6, is constructed from 13-mm. inside diameter and 17 mm. outside diameter. Corning No. 172 Pyrex combustion tubing. The exit end is fitted with a $^7/_{25}$ standard-taper female joint. A thin-walled capillary tube is sealed through the center of the joint to carry water vapor directly into the absorber without allowing it to come in contact with the connection.

Two types of combustion tube fillings are used: lead peroxide for materials containing nitrogen, and lead chromate for other materials because it is more easily prepared and more desirable from the standpoint of accuracy and ease of operation. Figure 6



STANDARD FILLING



SPECIAL FILLING FOR NITROGEN SAMPLES

Figure 6. Detail of Construction and Filling of Combustion Tubes

A. 1.5-inch roll of 40-mesh copper gauze
B. Sample Boat
C. Indicator, 2.5 × 0.5 inch rectangular strip of 40-mesh copper gauze
D. Roll of 20-mesh silver gauze
E. Roll of 40-mesh copper gauze
F. 10- to 20-mesh copper oxide wire
G. 50-50 mixture of 10- to 20-mesh copper oxide and lead chromate
H. Ignited Asbestos
I. Empty space
J. 10- to 20-mesh lead peroxide

shows the arrangement of both types of fillings. As indicated, a 1-inch section containing a Pyrex rod separator is provided between the lead peroxide and the copper oxide sections of the filling. This construction reduces the heat transfer between these two sections and allows more accurate control of the temperature of the lead peroxide. In preparing the combustion tube fillings, the copper gauze and the silver gauze are heated in a Bunsen flame before rolling in order to burn off all organic matter and to anneal the gauze, thus simplifying the rolling operation.

COMBUSTION TUBE HEATERS. The temperature of each combustion tube is regulated by means of five independently controlled heaters. Figure 7 is the wiring diagram of the five heaters and Figure 6 shows their position relative to the combustion tube filling. The "primary" heater and the "sample" heater consist of coils of resistance wire wound directly on the combustion tube as described elsewhere (*4*). The resistance wire is wound on a standard combustion tube and this is then sealed to the exit end from a previously used tube; in this way, the ground joint is used over and over again.

The temperature of the primary heater is controlled by a rheostat placed in series with the heater. The sample-heater temperature is controlled by a variable-voltage autotransformer and two fixed resistances, either of which may be connected in series with the heater by means of a 3-way switch. As shown in Figure 7, these two heaters have a common connection that eliminates a possible cold spot between the two sections. This arrangement requires the use of an autotransformer which has a common lead from input to output. The maximum temperature obtainable with the sample heater is approximately 725° C. A chart is prepared to show the temperatures obtainable with the various combinations of the autotransformer and the 3-way switch settings. Such a chart is very useful in controlling the combustion of the sample.

The indicator heater, main heater, and final heater are all in the main combustion furnace housing. The last two heaters are constructed of resistance wire wound on $1^1/_{16}$-inch inside diameter Alundum tubing. The Alundum tubing is supported in a section of 4-inch steel tubing by means of Transite disks; the space between the Alundum tube and the steel tube is filled with shredded magnesia pipe lagging for insulation. The element for the indicator heater consists of small coils of resistance wire placed in a grooved refractory half-sleeve that is placed under the lower half of the split Alundum tube. The upper half of the Alundum tube is attached to a removable unheated section to permit observation of this part of the combustion tube. The indicator heater element operates from a 50-volt transformer to permit use of heavier wire in the winding.

Two different final heaters are required, the one used in a given combustion depending on the combustion tube filling employed (Figure 6). The heater used with the lead chromate filling is built as an integral part of the standard combustion furnace and is similar to the main heater. The heater used with the lead peroxide filling is constructed as a unit separate from the indicator heater and the main heater, and is constructed of insulated resistance wire wound on a cylindrical block of Duraluminum. Otherwise in construction and insulation this heater is similar to

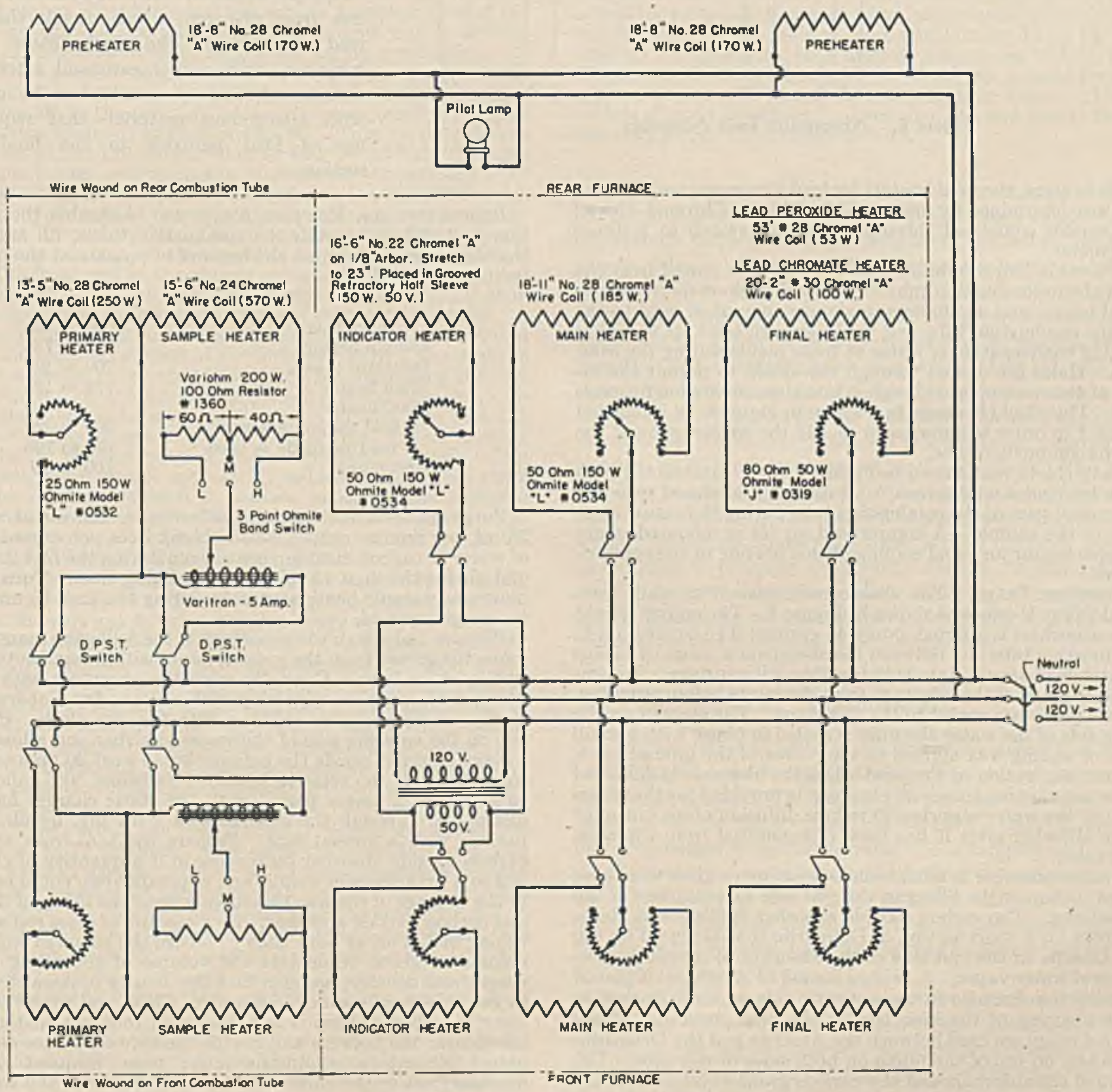


Figure 7. Electrical Wiring Diagram of Dual Combustion Apparatus

the other heaters. The Duraluminum block is fitted with a removable Duraluminum half-sleeve which fits closely around the upper part of the combustion tube as an aid in maintaining close temperature control, yet provides a means of inserting the combustion tube with the resistance winding in place on the front end. The temperature of the three heaters in the main combustion furnace is controlled by means of rheostats connected in series with each heater.

The heaters, as described, are designed to operate on 120 volts. A slight modification of the resistance windings is required when operating at significantly different voltages.

The temperature of the heater for the lead peroxide is determined by means of a short-stemmed thermometer placed in the well in the end of the Duraluminum block. The temperatures of the main heaters, the final heaters for lead chromate, and the preheaters are determined by means of No. 22 gage Chromel-Alumel thermocouples connected through a selector switch to a direct reading meter.

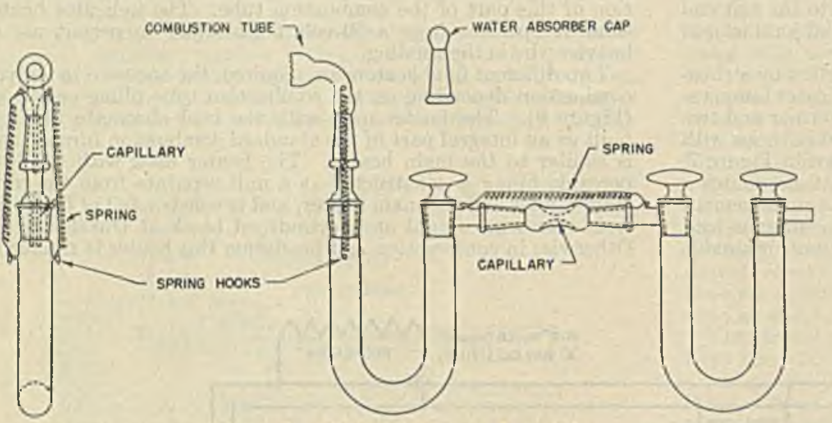


Figure 8. Absorption Train Assembly

A removable Duraluminum heat conductor is placed over the exit end of the combustion tube. It extends a short distance into the final heater and conducts a moderate amount of heat to the end of the combustion tube and to the ground joint, as an aid in preventing condensation of water at these points during the combustion. Holes are drilled through the shield to permit the insertion of thermocouples through it into the combustion furnaces beyond. This shield is shown in position in Figure 6; it is omitted in Figure 1 in order to show more clearly the construction of the end of the combustion tube.

A safety shield (not shown in Figure 1 or 2), constructed with a Pyrex top and a wire screen front and end, is placed over the front exposed part of the combustion tube during the actual combustion of the sample. A compressed air jet is mounted under the sample heater for rapid cooling of this portion of the combustion tube.

Absorption Train. The absorbers consist of specially constructed Pyrex U-tubes as shown in Figure 8. The empty weight of these absorbers is approximately 45 grams. The connection to the combustion tube and between the absorbers is made by means of $^7/_{15}$ standard-taper joints held together with springs. To simplify the removal of the lubricant from the joints before weighing, only male joints are sealed to the absorbers. The stopper on the entering side of the water absorber is sealed in place, with a small amount of sealing wax applied to the center of the ground joint to prevent separation of the joint when the absorber is detached from the combustion tube. A glass cap is provided for the entering side of the water absorber to reduce diffusion of air out of or into the absorber after it has been disconnected from the combustion tube.

The water absorber is filled with Dehydrite; a glass wool plug is placed on top of the filling in the exit side to avoid loss of the finer particles. The carbon dioxide absorber is filled with Ascarite, except for a short section of Dehydrite that is placed on top of the Ascarite in the exit side of the absorber to prevent a possible loss of water vapor. A twisted strand of glass wool is placed along with the Ascarite in the entering side of the absorber to prevent plugging of the absorber by the used Ascarite. Small glass wool plugs are used between the Ascarite and the Dehydrite sections and on top of the filling on both sides of the tube. The stoppers of the absorbers and the various ground connections are lubricated by a soft hydrocarbon grease such as Cello-Grease. The exit side of the carbon dioxide absorbers are connected to the exit-gas flowmeters by means of a short piece of rubber tubing. These flowmeters measure the excess oxygen from the combustion. Glass wool filters are placed immediately before the exit-gas flowmeters to remove foreign materials originating from the rubber tubing which might otherwise cause the bobs to stick.

ANALYTICAL PROCEDURE

Two procedures have been developed for use with the described apparatus. The routine procedure is used with samples that require only ordinary precision and accuracy and that must be analyzed in a short period of time. The precision procedure is used for the analysis of samples that require the best possible precision and accuracy. The chief differences in the two procedures are that the precision procedure requires use of a balance sensitive to 0.00001 gram, greater care in preparing and handling the absorbers, and more careful combustion technique along with the use of a larger sample.

Generally, the precision procedure is applied only to the analysis of materials that are mainly made up of carbon, hydrogen, and oxygen and that contain a relatively small proportion of ash, nitrogen, chlorine, sulfur, etc. Best results are obtained with materials, relatively free from nitrogen, which permit the use of lead chromate in the final heater section; however, with proper care and attention to details, satisfactory results can be obtained with nitrogenous materials that require the use of lead peroxide in the final heater section.

Procedure for Routine Analysis. Assemble the combustion unit, fill and install the combustion tubes, fill and attach the absorbers, and adjust the heaters to operate at the following temperatures (° C.):

Primary heater	650 ± 25
Sample heater	700 to 725
Indicator heater	700 ± 25
Main heater	775 ± 25
Final heater	
If lead chromate is used	600 ± 25
If lead peroxide is used	190 to 195
Preheaters	700 ± 50

Purge the combustion train with oxygen and air at a rate of 35 ml. per minute until a 3-hour blank does not exceed 0.3 mg. of water or carbon dioxide; use oxygen during the first 2.75 hours and air for the final 15 minutes of purging time. Turn the primary and sample heaters on only during the first 15 minutes of the purging period.

Prepare and weigh the absorbers in the following manner: Remove the grease from the ground joints with a small cotton swab wet in chloroform. Carefully wipe the absorbers with a clean damp cloth and then wipe over with a clean, dry, lint-free cotton cloth; avoid excessive rubbing with the dry cloth. Place the cap on the entering side of the water absorber and allow the absorbers to stand beside the balance for at least 20 minutes before weighing. (If the relative humidity is below 50%, allow them to stand for a longer period until the static charges have been dissipated.) Weigh the absorbers to ±0.1 mg. by direct comparison with a special tare. Prepare the tare from an empty carbon dioxide absorber by placing in it a quantity of glass that is 2 to 3 grams less in weight and approximately equal in volume to the average of the weight and volume of the filling of the water and carbon dioxide absorber; use a mixture of glass rod and glass tubing sealed off at both ends to secure the required weight and volume of glass. Calculate the volume of the filling from its weight and density; assume that the density of Ascarite is equal to the density of sodium hydroxide. Clean and wipe the tare as described above; keep it in a dustproof (but not air-tight) container near the balance and rewipe the tare only once each week unless laboratory conditions make more frequent attention necessary. Use the same tare for weighing both the water and carbon dioxide absorber. Remove the cap from the water absorber before weighing. Open the stopcock on the exit side of the carbon dioxide absorber for a few seconds before weighing to equalize the air pressure inside and outside the absorber. Leave the stopper on the tare open at all times. Always weigh absorbers with their gas-space filled with air rather than oxygen.

Take a sample of approximately 0.2 gram, weighed to ±0.1 mg., for the analysis. Weigh solid or heavy liquid samples in nickel or platinum boats and weigh light liquid samples in sample tubes made from 40-mm. sections of 7-mm. outside diameter Pyrex tubing sealed at one end. Weigh volatile samples in similar sample tubes sealed at one end and drawn out to a fine capillary at the other end. To fill the sample tube, warm the tube in a small flame and then allow it to cool with the capillary immersed in the sample. After filling, warm the capillary to expel all the liquid from it and then bend the capillary back along side the sample tube, but do not seal the capillary at any point.

Make sure that the primary heater and sample heater are off and the combustion tube in these sections is cool. Attach the weighed absorbers to the combustion tube using a small amount of stopcock lubricant placed at the outer edge of each connection, and connect the exit side of the carbon dioxide absorber to the exit gas flowmeter. Remove the indicator heater cover, place the safety shield in position, shut off the secondary gas flow, and adjust the primary gas flow to 15 to 30 ml. per minute of air to prevent diffusion of room air into the combustion tube. Open the combustion tube, take out the removable copper spiral and, with the aid of a wire hook, insert the sample to a point just beyond the center of the sample heater. Place the glass sample tube in a nickel boat with the open end or capillary toward the catalyst. Replace the copper spiral in the center of the primary heater and close the combustion tube. If the sample is extremely volatile, use solid carbon dioxide to cool the sample heater section of the combustion tube before introducing the sample and to control the rate of vaporization of the sample during the combustion.

Adjust the gas flow to give 10 ml. of oxygen per minute in the primary inlet and 25 ml. of oxygen per minute in the secondary inlet. Use air in the primary inlet only when burning samples which have a tendency to flash or explode. Turn on the primary heater and adjust the temperature to 650° ± 25° C. Turn on the sample heater and gradually increase its temperature until the sample begins to vaporize and reduces the indicator strip. (The vapors are carried over the copper oxide indicator strip by the gas flow from the primary inlet. As soon as the primary gas flow contains an insufficient amount of oxygen for complete oxidation, the front end of the copper oxide indicator strip will become reduced up to the point where the oxygen coming from the secondary inlet builds up an excess of oxygen in the tube. A sharp line of demarcation is thus established between the reduced portion and oxidized portion of the indicator strip. The position of this line serves as an immediate guide for controlling the rate of vaporization of the sample, provided a correlation has previously been made between the position of the line and the amount of excess oxygen in the gas issuing from the combustion tube. Highly volatile samples, and samples that contain sulfur or halogens, often do not appreciably reduce the indicator strip. When the sample is known to contain halogens, the indicator strip should be removed before beginning the combustion to avoid the formation of a black deposit on the glass which makes observation of following determinations difficult.)

Regulate the rate of volatilization of the sample to maintain always an excess of 10 to 20 ml. of oxygen per minute as indicated by the exit gas flowmeter. Gradually raise the temperature of the sample heater to 700° to 725° C.; remove the safety shield and replace the cover over the indicator section to aid in burning out any carbon residue. Readjust the gas flow rates to 20 ml. of oxygen per minute in the primary inlet and 15 ml. of oxygen per minute in the secondary inlet. If the capillary sample tube has been used, alternately allow the sample tube to cool and then reheat several times to remove any sample vapors and combustion products remaining in the sample tube and to burn any carbon residue.

After all the carbon has been burned, continue the above flow rates for 10 to 12 minutes; then close the secondary gas inlet and purge for 15 minutes with air admitted through the primary inlet at a rate of 30 to 35 ml. per minute. After starting to purge with air, allow the primary heater and sample heater to cool in preparation for the next determination. Before terminating the purging period, make certain that all water has been purged into the absorber and that no small droplets remain in the vertical male joint of the absorber. Remove the absorbers and weigh as before.

To avoid contamination of tube by materials in the air, always attach a fresh set of absorbers to the combustion tube before allowing the furnaces to cool. Before beginning an analysis, turn on the furnaces, purge the combustion tube for at least 15 minutes with both oxygen and air after all the furnaces, except the primary heater and the sample heater, have come to operating temperatures.

Procedure for Precision Analysis. Assemble the apparatus and adjust the temperature of the heaters as directed above in the procedure for routine analysis. Purge the combustion train with oxygen and air at a rate of 25 ml. per minute until a 5-hour blank does not exceed 0.3 mg. of water or carbon dioxide; use oxygen during the first 4.5 hours and air for the final 30 minutes of purging time.

Prepare the absorbers as directed under the previous procedure, but allow them to stand 45 minutes or more before weighing them. When weighing the water and carbon dioxide absorbers, use a separate specially prepared tare for each type of absorber. Construct the tares from empty water and carbon dioxide absorbers and prepare them for use in weighing as directed for the preparation of the single tare. Weigh the absorbers by direct comparison with the tare and record the weights to ±0.01 mg. Just before weighing the carbon dioxide absorber, open one of the stopcocks on the absorber and on the tare for a few seconds, but have the stopcocks closed during the weighing operation. Weigh the water absorber with the cap removed from it and its tare, but replace the caps as soon as possible.

Take a 0.5-gram sample for the analysis; weigh the sample, contained in an appropriate container, to 0.01 mg. Connect the absorbers, insert the sample, and make the combustion exactly as directed in the procedure for routine analysis, but use an oxygen flow rate of only 5 ml. per minute in the primary inlet and 15 ml. per minute in the secondary. Burn the sample at such a rate as to maintain the excess oxygen flow rate at 5 to 10 ml. per minute until combustion is essentially complete. Readjust the oxygen flow rates to 10 ml. per minute in each inlet while burning any carbon residue, and continue for 10 to 15 minutes after all the carbon has been burned; then purge with air through the primary inlet at a rate of 20 to 25 ml. per minute for 30 minutes. Remove the absorbers and weigh as before. Use fresh carbon dioxide absorbers for each analysis and renew the water absorber before it is one half used up.

Calculation of Results. The possible accuracy of both the routine and precision procedures is good enough to justify applying vacuum corrections to the weights of the sample, water, and carbon dioxide. When volatile samples are being analyzed, the correction to the sample weight must include the weight of air displaced by both the liquid and the vapor (errors introduced by neglecting the correction for the vapor may be as great as 0.1%). Based on the calculations by Baxter and Hale (*1*), the volume change of Ascarite on absorbing carbon dioxide is taken at 0.44 ml. per gram of carbon dioxide absorbed. On the basis of similar calculations, the volume change of Dehydrite on absorbing water is taken at 0.76 ml. per gram of water absorbed. This value is based on the assumption that only magnesium perchlorate hexahydrate is formed by the reaction of magnesium perchlorate and water. Although some trihydrate is also formed, the above assumption is probably sufficiently correct for the purpose of making vacuum corrections. In calculating the results reported in this paper, the atomic weights of hydrogen and carbon were assumed to be 1.0080 and 12.010, respectively.

EXPERIMENTAL

A considerable number of experimental determinations and variations were made during the development of the apparatus and the procedures. Throughout this experimental work, the precision procedure was used, so that the results could be applied to both procedures whenever possible. The samples and absorbers for the precision method were weighed by the method of swings on a Troemner balance with a sensitivity of 0.3 mg. per scale division. Weighings for the routine method were made on a Becker, chain-o-matic, magnetic-damped balance with a sensitivity of 0.3 mg. per scale division.

Time Required for Equilibration of Absorbers before Weighing. The two main factors which govern the time required for the wiped absorbers to reach a constant weight are: (1) equilibration of the outside surface of the glass by dissipation of static charges placed on the glass during the wiping operation and by equilibration of the glass surface and the moist air;

Table I. Precision of Weighing of Absorbers

Expt. No.	Date	No. 1 Dehydrite	No. 1 Ascarite	No. 2 Dehydrite	No. 2 Ascarite
1	1–4	1.10820	3.38472	4.97148	4.56806
2	1–4	1.10809	3.38460	4.97115	4.56798
3	1–4	1.10813	3.38468	4.97121	4.56805
4	1–5	1.10830	3.38468	4.97129	4.56802
5	1–5	1.10826	3.38469	4.97144	4.56799
6	1–5	1.10832	3.38467	4.97144	4.56806
7	1–5	1.10833	3.38461	4.97136	4.56793
8	1–8	1.10854	3.38469	4.97170	4.56792
9	1–8	1.10859	3.38461	4.97177	4.56797
10	1–8	1.10861	3.38465	4.97167	4.56790
11	1–8	1.10889	3.38463	4.97178	4.56789

Table II. Time Required for Removal of Combustion Products during Purging

		Gain in Weight of Absorbers after Purging with Air at a Rate of 20 Ml. per Minute									
		Up to 10 Minutes		10 to 30 Minutes		30 to 60 Minutes		60 to 180 Minutes		Up to 300 Minutes	
Detn. No.	Benzoic Acid	H_2O	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O	CO_2
	Gram	*Gram*	*Gram*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
1	0.2345	0.1045	0.5929	0.11	0.00	0.13	−0.04	0.13	−0.03	...	...
2	0.2272	0.0999	0.5689	0.10	0.04	−0.02	0.01	0.01	0.01	...	...
3	0.2561	0.1144	0.6478	0.09	0.06	0.16	0.07	0.26	0.10	...	...
4	0.2470	0.1108	0.6224	0.14	0.11	0.12	0.06	0.13	0.04	...	...
5	0.00	...	...	...	...	...	...	...	...	0.28	0.17
6	0.00	...	...	...	...	...	...	...	...	0.39	0.24

(2) equilibration of the gas inside the absorber to room temperature and pressure. The effects of these two factors on the final weight of the absorber were determined independently.

The time required for the equilibration of the outside of the absorber was studied by observing the rate of change of weight of an empty carbon dioxide absorber after it had been wiped by several different methods; the absorber was weighed by direct comparison with a tare that consisted of a similar empty carbon dioxide absorber that had been wiped several hours before it was used. Both the absorber and the tare were weighed with the stoppers closed in order to eliminate any effect of temperature on the gas density inside the absorber. A small amount of radium bromide was present in the balance case during the experiment as a possible aid in dispelling static charges. The tests were made at 23° to 27° C. and at a relative humidity of approximately 70%.

The rate of equilibration of the air temperature and resulting gas density inside the absorber was determined by heating or cooling an empty carbon dioxide absorber to a temperature 10° to 15° C. different from the room temperature and observing the rate of change of weight by weighing as before. The stopcocks on both the absorber and the tare were left open during the experiments. The absorber was wiped at least one hour before beginning the test, so that the static charges would have been dissipated.

The details of the various experiments are given in the following list and the results are plotted in Figure 9.

Experiments. 1. The absorber was first wiped with a damp cotton cloth and then with an air-dry cotton cloth. Rubbing with the dry cloth was kept at a minimum. After the absorber had been wiped, the fingers were passed lightly over the surface of the glass as a possible aid in removing static charges.

2. The conditions were the same as those in 1 except that the absorber was rubbed for approximately 2 minutes with the dry cloth.

3. The conditions were the same as those in 2 except that the absorber was not touched with the fingers after wiping.

4. Experiment 3 was repeated except that an oven-dried cotton cloth was substituted for the air-dry cloth. This cloth left a great deal of lint on the absorber.

5. The conditions were the same as those in 3 except that a dry wool flannel cloth was used in place of the dry cotton cloth.

6. The absorber was cooled to approximately 10° C. in a refrigerator.

7. The absorber was heated in the oven to approximately 35° C.

These experiments indicate that with proper wiping and with the absorbers at room temperature, the weight of the absorber will be within 0.1 mg. of the final weight after standing 20 minutes and the difference will be less than 0.05 mg. after standing 45 minutes. In localities where the relative humidity is much lower, longer time of standing will probably be required for proper equilibration.

Precision of Weighing of Absorbers. By repeated wiping and weighing of four typical absorbers, it was shown that these operations can generally be carried out with a precision of 0.05 to 0.10 mg.; in a few cases deviations as great as 0.3 mg. are encountered. A summation of these trials is given in Table I.

Purging the Combustion Train. The time required for purging the combustion train was determined, using samples of benzoic acid, by changing and weighing the absorbers at appropriate intervals after the combustion had been judged complete as shown by absence of any residue in the sample heater section. The results, given in Table II, show that only negligible quantities of water and carbon dioxide remain after purging for 10 minutes at a rate of 20 ml. per minute after the combustion is complete. A longer purging time has been specified in both procedures in order to provide a desirable safety factor and to allow sufficient time for the oxygen in the combustion train and the absorbers

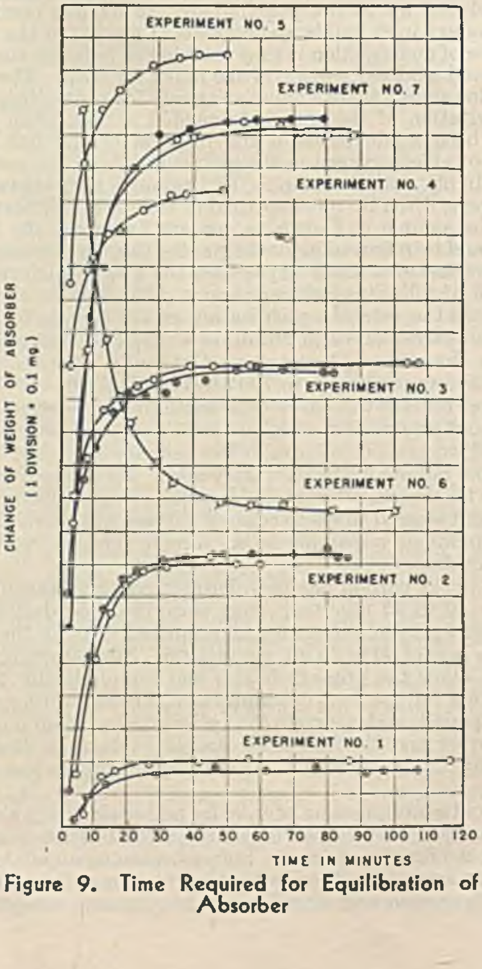


Figure 9. Time Required for Equilibration of Absorber

Table III. Effect of Oxygen Flow Rate and Copper Oxide Catalyst Temperature upon Completeness of Combustion

Material	Detn. No.	Sample	Oxygen Flow Rate Primary	Oxygen Flow Rate Secondary	Oxygen Flow Rate Total	Excess Oxygen Flow Rate Average	Excess Oxygen Flow Rate Minimum	Time for Combustion	Catalyst Temp.	Hydrogen	Carbon
		Gram	*Ml./min.*	*Ml./min.*	*Ml./min.*	*Ml./min.*	*Ml./min.*	*Hours*	° C.	%	%
Neutral oil	1	0.51710	5	10	15	8	2	2	710	13.658	86.324
	2	0.55591	5	10	15	6	2	3	750	13.657	86.300
	3	0.62633	5	10	15	5	1	3	750	13.654	86.278
	4	0.60760	10	35	45	25	8	1.5	675	13.463	85.497
	5	0.57113	10	35	45	27	20	1.25	700	13.576	85.900
	6	0.55941	10	35	45	25	18	1.25	700	13.469	85.335
	7	0.60889	10	35	45	25	7	1.25	725	13.638	86.242
	8	0.52830	10	35	45	25	17	1.25	725.	13.634	86.206
	9	0.58596	5	40	45	23	15	1	750	13.660	86.279
	10	0.59493	15	30	45	20	13	1.25	750	13.660	86.299
p-Phenyl phenol	11	0.56564	15	30	45	22	18	1	750	5.946	84.723
	12	0.55395	5	10	15	5	2	2	750	5.929	84.732
								Min.			
Anthracene	13	0.16620	5	10	15	6	2	40	750	5.705	94.221
	14	0.17016	15	30	45	20	19	15	750	5.705	94.224
Chrysene	15	0.20829	5	10	15	7	1	55	750	5.468	94.090
	16	0.26275	15	30	45	20	13	25	750	5.458	94.074

Table IV. Reproducibility of Routine and Precision Procedures

Detn. No.	Precision Procedure Neutral oil	Precision Procedure Hydrogen	Precision Procedure Carbon	Routine Procedure Neutral oil	Routine Procedure Hydrogen	Routine Procedure Carbon
	Gram	*% by wt.*	*% by wt.*	*Gram*	*% by wt.*	*% by wt*
1	0.54308	13.653	86.308	0.2057	13.66	86.42
2	0.51775	13.670	86.322	0.2239	13.75	86.18
3	0.61875	13.657	86.306	0.2050	13.67	86.36
4	0.63619	13.667	86.173	0.1757	13.70	86.28
5	0.55575	13.650	86.311	0.1918	13.65	86.34
6	0.51726	13.640	86.304	0.2033	13.66	86.37
7	0.57089	13.652	86.317	0.2050	13.68	86.41
8	0.56751	13.642	86.304	0.2045	13.66	86.41
9	0.49913	13.654	86.312	0.1969	13.66	86.35
10	0.45472	13.647	86.331	0.2089	13.68	86.36
11	0.40530	13.656	86.327	0.2100	13.64	86.35
12	0.45003	13.646	86.329	0.2083	13.66	86.31
13	0.51944	13.656	86.319			
Average		13.652[a]	86.316[a]		13.67[b]	86.36[b]
Standard deviation		±0.008[a]	±0.009[a]		±0.02[b]	±0.05[b]

[a] Does not include No. 4. [b] Does not include No. 2.

The following blanks were taken before and after the above determinations; a correction was not applied to the results.

Time, Hours		Front Tube, Mg. H_2O	Front Tube, Mg. CO_2	Rear Tube, Mg. H_2O	Rear Tube, Mg. CO_2
Before	3.5	0.09	0.00	0.07	0.02
After	4.5	0.11	0.07	0.35	0.07

to be displaced completely by air. In the routine procedure, the period of purging may be used advantageously for weighing a new set of absorbers and samples.

Effect of Catalyst Temperature and Oxygen Flow Rate upon Completeness of Combustion. Several different types of compounds were burned at various copper oxide catalyst temperatures and at different oxygen flow rates; the results of these tests are given in Table III. The samples used were commercially available materials of unknown purity. For the purpose of these comparisons, it was assumed that the combustion was complete when duplicate results were obtained at two widely different oxygen flow rates. The results obtained indicate that the copper oxide catalyst must be maintained above 750° C. unless low oxygen flow rates and, consequently, longer combustion times are used. However, temperatures above 800° C. must be avoided, since Corning No. 172 Pyrex generally is not satisfactory at such temperatures, even when well supported.

Precision and Accuracy. The precision of both procedures was determined by repeated analysis of a sample of neutral oil; the results are given in Table IV. The probable deviation is ±0.02% hydrogen and ±0.05% carbon for the routine procedure, and is ±0.008% hydrogen and ±0.009% carbon for the precision procedure. It is believed that the precision of the method is determined to a great extent by the accuracy of the weighings. The precision of the precision method could probably be further improved by the use of larger samples. The accuracy of the routine method has been determined by analysis of several Bureau of Standard samples issued as standards for the microdetermination of carbon and hydrogen and of several compounds of better than ordinary purity. The results of these tests (Table V) indicate that the accuracy is in the order of 0.05% for both elements. The naphthalene, toluene, nitrobenzene, and *p*-nitrophenol were purified by several sublimations, crystallizations, or fractional distillations, as the case may be, of ordinary c.p. or high purity chemicals. The benzoic acid and ammonium thiocyanate were Mallinckrodt's analytical quality. The Bureau of Standards sample of benzoic acid was also analyzed according to the precision procedure. The results, given in Table VI, show an accuracy of 0.011% for hydrogen and 0.015% for carbon.

Time Required for Analysis. Table VII gives the average time required for the various operations necessary for two simultaneous determinations by the routine procedure and the precision procedure. The over-all working time can be slightly decreased from the value given by using the weighed absorbers from one analysis for alternate subsequent determinations. Approximately 5 years of experience indicate that six to eight determinations can be made in an 8-hour day by the routine procedure, provided the furnaces are at the operating temperature at the beginning of the day.

DISCUSSION

The merits of the described apparatus and procedures are principally due to the adaptation of previously known practices and to the emphasis placed on adequate control of the combustion operations rather than to the development of new ideas and techniques. The principle of introducing oxygen at two points in the combustion tube was successfully used by Dennstedt (*3*), but this idea has not usually been incorporated in the classical methods. In the present apparatus, the double oxygen inlet is advantageously used in combination with the indicator strip and the sensitive flowmeters for instant indication of the entering and excess oxygen flow rates. This system provides a convenient and safe means of controlling the combustion so that the combustion can be made at the maximum possible rate while still maintaining the proper conditions to ensure complete oxidation. With the catalyst temperature and flow rates employed, experience has shown that excess oxygen must be present at all times in the catalyst section in order to ensure complete combustion of materials that crack easily to form methane, etc. There is also some indication that the use of the double oxygen inlet materially reduces the possibility of explosion when burning inflammable materials.

The rotameter-type flowmeter is a decided improvement over the conventional bubble-counter-type flowmeter. The rotameter flowmeter acts instantly, continuously indicates the prevailing rate of flow, and becomes more sensitive as the flow rate is decreased. The gas flow rates employed in the authors' procedures are higher than rates at which bubbles can be counted and thus

Table V. Accuracy of Routine Procedure

Material		Carbon[a]	Hydrogen[a]
		% by weight	
Naphthalene		93.75 93.83 93.64 93.66	6.40 6.35 6.30 6.30
	Average	93.72	6.34
	Theory	93.71	6.29
Toluene		91.05 91.12 91.15 91.18	8.84 8.85 8.82 8.84
	Average	91.12	8.84
	Theory	91.25	8.75
Benzoic acid (Mallinckrodt's analytical reagent quality)		68.84 68.90 68.87 68.84	5.08 4.99 4.98 4.98
	Average	68.86	5.01
	Theory	68.84	4.95
Nitrobenzene		58.58 58.53 58.53	4.08 4.08 4.07
	Average	58.55	4.08
	Theory	58.53	4.09
p-Nitrophenol		51.89 51.88 51.78	3.61 3.60 3.61
	Average	51.85	3.61
	Theory	51.80	3.62
Ammonium thiocyanate		15.95 15.99	5.32 5.37
	Average	15.97	5.34
	Theory	15.78	5.30
Acetanilide (NBS standard sample 141)		71.13 71.10 71.06	6.80 6.72 6.77
	Average	71.10	6.76
	Theory	71.09	6.71
Cystine (NBS standard sample 143)		29.89 29.95 29.95	5.10 5.08 5.09
	Average	29.93	5.09
	Theory	29.99	5.04
Benzoic acid (NBS sample 39f)		68.79 68.78 68.76	5.01 5.02 5.00
	Average	68.78	5.01
	Theory	68.84	4.95

[a] Corrected to a vacuum basis.

give a reliable indication of the flow rate. Furthermore, when bubble counters are used, there is always a possibility of contaminating the gases or connecting lines with the liquid used in the counter.

The use of resistance wire wound directly on the combustion tube to heat the sample section was used successfully by Baxter and Hale (*1*). The low heat capacity of this type of sample heater makes possible a rapid change in heating rate by the simple process of adjusting a rheostat or a variable transformer. It provides complete visibility of the sample during combustion, adequate control at all times, and quick cooling after the combustion is complete. An attempt was made to control the combustion of the sample by the use of a fully heated furnace section which was slowly moved forward over the sample by means of a crank and screw arrangement similar to that used for microcombustions (*5, 8*) except that it was operated manually. This arrangement was moderately successful, but it required considerably more attention from the operator than the resistance wire wound directly on the glass tube. When the described heater is used, the combustion proceeds with very little attention once the proper rate has been established.

Table VI. Accuracy of Precision Procedure

Material		Carbon[a]	Hydrogen[a]
		% by weight	
Benzoic acid (NBS standard sample 39f)		68.830 68.830 68.828	4.963 4.966 4.962
	Average	68.829	4.964
	Theory	68.843	4.953

[a] Corrected to a vacuum basis.

Table VII. Time Required for Two Simultaneous Analyses by Routine and Precision Procedures

Operation	Time in Minutes: Routine procedure	Time in Minutes: Precision procedure
Weigh absorbers (4)	8	45
Weigh samples (2)	8	35
Connect absorbers, insert samples	7	7
Make combustion	55	155
Purge with air	15	30
Prepare absorbers for weighing	7	7
Equilibrate absorbers	20	45
Weigh absorbers (4)	8	45
Calculate results	3	10
Total elapsed time for 2 analyses	131	379
Total working time for 2 analyses	96	304

The ground joint with sealed-in capillary used on the end of the combustion tube is similar to that employed by Baxter and Hale (*1*). This design, together with the Duraluminum heat transfer block, has eliminated any trouble arising from the condensation of water in the exit end of the combustion tube.

During 5 years, approximately 6500 carbon and hydrogen determinations have been made with the aid of one dual unit. During this time, the apparatus and procedure have given satisfactory results in the routine analysis of the following materials:

(1) Hydrocarbons, such as paraffins, aromatics, naphthenes, aviation gasoline and other low-boiling materials.
(2) Oxygen-containing materials, such as alcohols, phenols, glycols, ethers, esters, ketones, aldehydes, and acids.
(3) Sulfur-containing materials, such as mercaptans, sulfides, disulfides, and thiophenes.
(4) Nitrogen-containing materials, such as amines, amides, cyanides, cyanates, hydrazines, pyridines, and nitro compounds.
(5) Halogen-containing materials, such as alkyl mono- and dichlorides, and alkyl bromides.
(6) Various mixtures of the above-mentioned elements.
(7) Esters of iron, aluminum, and copper.

ACKNOWLEDGMENT

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Microdetermination of Halogens and Sulfur

Using the Grote Combustion Apparatus

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Automatic combustion methods for the determination of sulfur, chlorine, bromine, and iodine are described. By the use of a modified Grote combustion tube in combination with volumetric procedures, satisfactory micromethods have been developed. The indicators used are dipotassium rhodizonate for sulfur, dichlorofluorescein for chlorine and bromine, and starch solution for iodine. The largest standard deviation for these methods was found to be ±0.14% for sulfur, ±0.10% for chlorine, ±0.17% for bromine, and ±0.15% for iodine in the group of compounds analyzed. Methods are also described for the acid-base titration of sulfur (in the absence of acid-forming elements other than carbon) and for the determination of traces of chlorine employing a turbidimetric estimation of the chloride ion.

COMBUSTION methods for the determination of halogens and sulfur were among the first microchemical procedures suggested by Pregl. Other methods for the decomposition of the sample, such as the micro-Carius and the Parr microbomb, have been described by Niederl and Niederl (*9*). Huffman (*7*) has described a combustion method for sulfur in which the sulfur oxides are adsorbed on metallic silver. Hallett and Kuipers (*6*) have described a combustion and titration procedure for sulfur similar to that used in this laboratory and have summarized the literature on the sulfur determination. Another modified combustion method originally developed on the macro scale for halogens and sulfur by Grote and Krekeler (*4*) and later on a micro scale for sulfur by Schoberl (*13*) has been described and used in Germany. (Reference is made in this paper only to Grote, in order to conform with the original Jena literature describing the apparatus.) Wurzschmitt and Zimmerman (*15*) modified the original Grote combustion tube and used it in the macrodetermination of halogens, sulfur, mercury, and selenium in organic compounds; sulfur in volatile inorganic materials such as iron pyrites; and carbon by the absorption of the carbon dioxide in alkali followed by a modified Winkler titration technique.

Previous to the war, a Grote microapparatus was obtained from Germany and was used in this laboratory for a number of years. During the past few years, Grote combustion tubes made from fused quartz and also from Vycor silica glass No. 790 have been used. The apparatus is now available from domestic sources (Arthur H. Thomas, Philadelphia, Pa.; Corning Glass Works, Corning, New York; Thermal Syndicate, Ltd., New York, N. Y.).

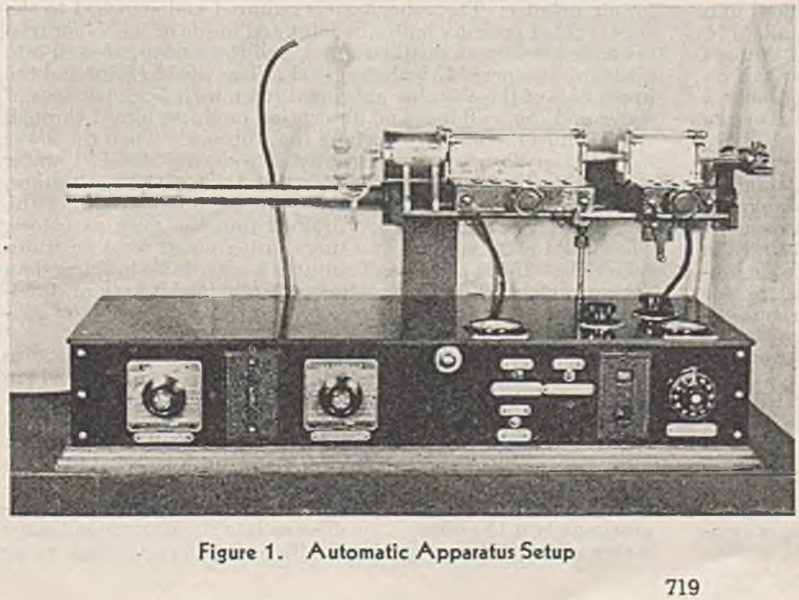

Figure 1. Automatic Apparatus Setup

COMBUSTION FURNACE

Electrical units have been found to be the most satisfactory means for heating the combustion tube. Figure 1 shows an automatic apparatus as set up in this laboratory. It is similar in construction to that previously described (*11*) for the determination of nitrogen by combustion, but other designs, such as those of Hallett (*5*), Clarke and Stillson (*2*), and another design described by the authors (*12*) would also be suitable.

Three furnaces are used, as can be seen in Figure 1. One is a short movable furnace (8.5 cm. long) heated to 750° C., which is used for the combustion of the sample. The speed and temperature of the movable furnace may be varied to suit the rate of combustion of the material being burned. This is followed by a long stationary furnace (18.5 cm. long) also at 750° C., which heats the portion of the combustion tube containing the sintered frits. The function of the third short furnace (8.5 cm. long), which is heated to 350° C., is to prevent condensation of vapor in the exit end of the combustion tube and in the ground-glass joint which connects the two pieces of apparatus. Details on construction have been amply described in the references given.

COMBUSTION TRAIN AND AUXILIARY EQUIPMENT

The combustion train consists of a Grote combustion tube and a Grote absorber through which oxygen is drawn by means of a slight vacuum. An aspirator pump or house vacuum is satisfactory. Before entering the combustion tube, the oxygen passes through a pressure regulator filled with concentrated sulfuric acid, a safety trap, and a U-tube containing Ascarite to remove any sulfuric acid mist. Figure 2 shows the Grote combustion tube with specifications, and Figure 3 the Grote absorber. Figure 1 shows them assembled in the authors' setup.

The combustion tube may be made of fused quartz containing sintered-quartz frits or of Vycor silica glass No. 790, in which case the frits are of the corresponding material. Glass is not satisfactory because of the high temperatures required in the sintered-frit portions of the combustion tube. A satisfactory porosity of the frit in the absorber is such that 0.5 ml. of water per minute will flow through the frit at atmospheric pressure. Similar measurements of the two frits in the combustion tube gave a flow rate of 1.33 ml. of water per minute. It is felt that the porosity of the frits in the combustion tube should not be greater than that indicated above.

REAGENTS

Combustion is carried out in an atmosphere of oxygen. The oxygen need not necessarily be free of water, but must not contain halogen or sulfur. The following reagents are required:

FOR DETERMINATION OF SULFUR. Barium chloride, 0.01 *N* (standardized gravimetrically by barium sulfate method).

Bromine, saturated water solution.
Sodium hydroxide, 0.1 *N*.
Hydrochloric acid, 0.05 *N*.

Phenolphthalein indicator solution.
Alcohol, 95% (3A grade).
Sulfuric acid, 0.01 *N* (standardized by acid-base titration against sodium hydroxide which has been standardized against Bureau of Standards potassium acid phthalate).
Dipotassium rhodizonate indicator, made by dry grinding 0.5 gram of dipotassium rhodizonate with 49.5 grams of cane sugar.

FOR DETERMINATION OF CHLORINE AND BROMINE. Hydrogen peroxide (reagent grade), 3%, made by diluting 30% Superoxol.
Silver nitrate, 0.01 *N*.
Sodium acetate, saturated water solution.
Acetone, C.P.
Dichlorofluorescein indicator prepared by dissolving 0.01 gram of dichlorofluorescein in 100 ml. of 60% alcohol to which are added 2.5 ml. of 0.01 *N* sodium hydroxide.
Hydrazine sulfate, saturated water solution (bromine determination only).

FOR DETERMINATION OF IODINE. Sodium hydroxide, 5%.
Sodium acetate, 20%.
Solution of sodium acetate in glacial acetic acid, 10%.
Bromine, free from iodine.
Formic acid, 90%.
Potassium iodide.
Sodium thiosulfate, 0.01 *N*.
Sulfuric acid, 1 to 2.
Starch indicator solution.
Potassium biiodate for standardization of the sodium thiosulfate solution.

PROCEDURE FOR COMBUSTION

The absorbing solution used in the Grote absorber depends on the nature of the analysis. Sodium hydroxide solutions, 0.1 *N* and 5%, are used in the determination of sulfur and iodine, respectively, while 3% hydrogen peroxide is used in the determination of chlorine and bromine. Dilute hydrogen peroxide cannot be used as the absorbing medium for sulfur determinations where dipotassium rhodizonate is used. Apparently even traces of hydrogen peroxide remaining in solution after attempts to destroy it by boiling in acid solution tend to destroy the color of this indicator. This has also been noted by Hallett and Kuipers (*6*).

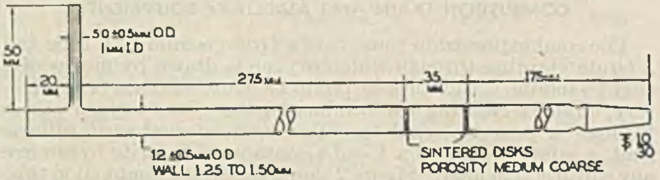

Figure 2. Grote Combustion Tube

Five milliliters of the appropriate solution are introduced into the top of the absorber. By means of a rubber pressure bulb (5 × 7 cm.), approximately one half of the solution is forced through the frit into the U-portion of the absorber while the other half remains above the frit. The absorber, previously heated over a flame to remove moisture from the joint, is connected to the ground joint of the combustion tube in the 350° C. furnace. Since the thermal coefficients of expansion of the combustion tube and the absorber are different, the joint must be disconnected while the apparatus is still hot. The exit end of the absorber is connected to the vacuum line, the vapor trap being inserted between the absorber and the source of vacuum. It has been found that the rate of oxygen flow through the tube can vary between wide limits. In general, a fairly rapid stream of oxygen, about 60 ml. per minute, should be maintained. This rate of flow corresponds to about 70 bubbles of oxygen per minute passing through the U-portion of the Grote absorber which serves as flowmeter or bubble counter.

The platinum boat containing the weighed sample which may vary from 4 to 20 mg., depending upon the per cent halogen or sulfur in the compound, is inserted into the combustion tube at a distance of about 3 cm. from the stationary furnace. The combustion tube is then closed with a rubber stopper, the movable furnace brought to within about 5 cm. of the stationary furnace, and the automatic time switch set for a 20-minute period of combustion. In the authors' apparatus, this switch starts the motion of the movable furnace and also turns on the current to heat the furnace to the required temperature of about 750° C. During this 20 minutes the furnace will have moved over the sample and the combustion will be complete.

Some difficulty has been experienced with back-firing. The original Grote combustion tube has a one-hole disk fused inside the tube about 5 cm. in front of the first sintered frit. As originally designed, the function of this disk was to prevent back-firing during the combustion. On the basis of a large number of determinations, it was felt that this disk was not desirable. It was thought that the tendency of low-melting compounds to back-fire was apparently due to the abnormal concentration of vapors and liquid distillate collecting in front of this disk, thus causing the formation of explosive mixtures. A modified Grote combustion tube was constructed without this disk. In the use of this tube, a roll of platinum gauze about 6 cm. long is inserted in front of the first frit so that about 2 cm. extends out of the stationary furnace. Using this procedure, the back-firing has been greatly reduced.

Table I. Determination of Efficiency of Grote Absorber

Sulfur Taken, Mg.	0.01 *N* NaOH Required, Ml.	Sulfur Found, %
5.032	31.45	100.2
4.138	25.88	100.3

DETERMINATION OF SULFUR

COMPOUNDS CONTAINING ONLY CARBON, HYDROGEN, OXYGEN, AND SULFUR. It is obvious that if the compound contains only carbon, hydrogen, oxygen, and sulfur, the sulfur determination can be carried out as an acid-base titration. In this case, the oxidation products are absorbed in neutralized 3% hydrogen peroxide solution, and after any carbon dioxide has been expelled by boiling, the sulfuric acid is titrated with 0.01 *N* sodium hydroxide in the presence of methyl red indicator.

The efficiency of the Grote absorber was checked by combustion of C.P. sulfur (Table I).

COMPOUNDS CONTAINING CARBON, HYDROGEN, OXYGEN, SULFUR, NITROGEN, ALKALI METALS, AND HALOGENS. Sulfur in the presence of halogens and nitrogen cannot be determined by acid-base titration, but it can be determined volumetrically, using standard barium chloride.

The oxidation products which have been absorbed in the 0.1 *N* sodium hydroxide are washed from the Grote absorber in the following manner: The vapor trap is removed and attached to the small rubber pressure bulb, the joint and inside of the vapor trap are rinsed once with distilled water, and the washings forced into a 125-ml. stoppered Erlenmeyer flask. The vertical joint and the upper half of the absorber are rinsed twice with 5-ml. portions of water and the washings and absorption products forced through the frit into the flask by opening the stopcock. Then the lower half of the absorber is rinsed by introducing distilled water through the horizontal joint, shaking, and inverting the absorber, so that the wash water reaches all parts of the lower half of the absorber. The washings are drained into the flask as before. This washing is repeated two times, using about 5 ml. of water each time. If the per cent of sulfur is known to be low, less than approximately 7%, a better titration is obtained if 5 ml. of standardized 0.01 *N* sulfuric acid are added at this point and later subtracted from the total titration.

Five milliliters of saturated bromine water are added to oxidize any sulfite to sulfate. Then 5 ml. of 0.1 *N* hydrochloric acid are added and the solution is boiled on the acid side to expel any excess bromine and to concentrate the volume to approximately 20 ml. It is then cooled in ice water, and 2 drops of phenolphthalein solution are added and enough 0.1 *N* sodium hydroxide to make the solution alkaline. The acidity is adjusted with 0.05 *N* hydrochloric acid until the pink color just disappears. One dipper (approximately 0.15 gram) of the dipotassium rhodizonate indicator is then added; followed by 25 ml. of 95% alcohol and enough water to make the volume to 50 ml. (±5 ml.). The amber-colored solution is then slowly titrated with 0.01 *N* barium chloride. At the first appearance of a reddish color, the titration should be stopped and the flask vigorously shaken. With continued titration, the reddish brown color deepens and, on addition of 1 to 2 drops of 0.01 *N* barium chloride, changes to a deep cherry red. A premature end point will disappear on shaking in 15 to 30 seconds, while the real end point is stable and will persist even after 10 minutes of shaking.

The detection of this end point has been open to much discussion. The use of light filters first suggested by Hallett (*6*) has been adopted in this laboratory in a modified form.

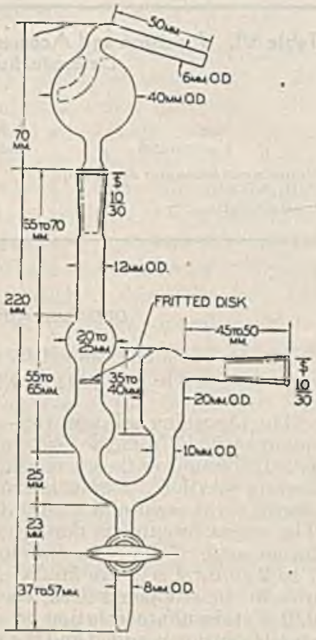

Figure 3. Grote Absorber

This light filter, which is a Wratten filter No. 21 (Eastman Kodak Co., Rochester, N. Y.), is mounted on an opal glass window, 10 × 12.5 cm. (4 × 5 inches) of a small box, 18.75 × 15 × 12.5 cm. (7.5 × 6 × 5 inches), containing a 40-watt blue frosted bulb for illumination. The opal glass area is divided into three parts. The upper third is left uncovered and the lower two thirds are covered, respectively, with one and two thicknesses of the filter material. Thus the flask in which the titration is being carried out can be illuminated by the clear portion and its color, viewed at eye level by transmitted light, compared with the color of one and two layers of the filter. The amber color of the solution being titrated corresponds roughly to a single layer of the filter and persists to within 1 to 2 ml. of the theoretical end point. During the remaining 1 to 2 ml. the color of the solution gradually becomes redder and approximates that of two layers of the filter. The only function of the filters is to indicate the progress of the titration, for as long as the color of the solution corresponds roughly to two layers of No. 21 Wratten filter, the titration should be continued. The end point is a deep cherry red which can be detected without relying on any predetermined exact color match.

In low concentrations of sulfate ion the solubility relation seems to favor the formation of the barium salt of rhodizonic acid, as is apparent from the reddish color of the solution. In concentrations of sulfate less than 5 ml. of 0.01 *N* sulfuric acid, more time and shaking are required to establish equilibrium conditions than in the case of higher concentrations. If the barium chloride solution is run in fairly rapidly with gentle shaking, a red color indicates that an end point is obtained below the stoichiometrical amount required. If allowed to stand for a few minutes, the red color disappears and the original amber color of the solution reappears. The disappearance of the premature end point and the establishment of the equilibrium can be hastened by vigorous shaking. Since the red color produced is due to the formation of the highly colored barium salt of rhodizonic acid, its premature appearance in the presence of excess sulfate ions indicates that the rhodizonic ion is extremely sensitive to barium ions, or that barium rhodizonate forms more rapidly than barium sulfate.

When the end point has been reached, the amount of 0.01 *N* barium chloride used is noted. From this a titration correction value is subtracted. In this laboratory it has been found to be 0.35 ml. by the method described. This correction value is apparently due to the masking of the red color of the barium rhodizonate by the yellow color of the dipotassium salt. It is determined by titrating a known quantity of 0.01 *N* sulfuric acid with 0.01 *N* barium chloride and noting the value to be subtracted to give the correct titration. A considerable amount of gravimetric work has shown that sufuric acid standardized as 0.01 *N* as an acid will serve within the experimental error of this method as 0.01 *N* in regard to the sulfate ion.

In the case of alkali sulfonates or in the combustion of compounds which may leave an ash that would hold back sulfate, the platinum boat containing the weighed sample is placed in a platinum sleeve to prevent any loss of ash by spattering. If desired, the nonvolatile sulfur (as alkali sulfate) may be titrated separately, after dissolving in water, or the alkali sulfate solution may be combined with the volatile sulfur and the two titrated together. The method is applicable to organic sulfur compounds, organic alkali sulfonates, salts of heavy metals of sulfonic acids (except those forming insoluble sulfates in which case some of the sulfur is retained in the ash), and mixtures of organic sulfur compounds with alkali sulfates.

The per cent sulfur is calculated from the following formula:

$$\% \text{S} = \frac{\text{ml. of } 0.01\ N\ \text{BaCl}_2 \times 0.1603}{\text{sample (mg.)}} \times 100$$

Since it has been found desirable for best results to have as constant a titration volume as possible, the sample size is usually chosen to give a titration of about 10 ml. Table II relates the per cent sulfur with the sample size to give this titration with 0.01 *N* barium chloride.

The precision and accuracy of the method can be shown from the results of a series of analyses on six purified sulfur compounds, the purity of which was established by complete elementary analysis and by a sulfur determination by the gravimetric Parr bomb macroprocedure. A variety of sulfur compounds was included in this work in order to determine whether the method was independent of the chemical structure. No difficulty was observed in the case of the compounds investigated. The results are listed in Table III.

In the special case of ionizable water-soluble organic sulfates, preliminary work has indicated that the sulfate ion may be titrated directly with barium chloride under the conditions described above.

DETERMINATION OF CHLORINE AND BROMINE

The titration of chloride and bromide with silver nitrate in the presence of adsorption indicators has been described by Fajans and Wolff (*3*), Kolthoff *et al.* (*8*), and Bullock and Kirk (*1*).

Table II. Relation of Sample Size and Sulfur Content

S, %	Weight of Sample, Mg.
0–7[a]	15.0
10	12.0
15	9.0
20	7.0
25	6.0
30	5.0

[a] For the range of 0 to 7% sulfur, 5 ml. of 0.01 *N* sulfuric acid are added and later subtracted from the total milliliters of barium chloride used.

Table III. Precision and Accuracy of the Volumetric Micromethod for Determination of Sulfur

Empirical Formula	No. of Analyses	Per Cent Sulfur: Theory	Per Cent Sulfur: Parr bomb	Per Cent Sulfur: Micro volumetric	Standard Deviation
$C_6H_8N_2S$	18	22.86	22.90	22.97	±0.14
$C_{10}H_{17}O_7N_3S$	7	9.90	9.86	10.08	±0.14
$C_9H_{12}O_4N_2S$	7	13.12	13.21	13.16	±0.10
$C_{19}H_{34}O_5N_2S$	7	7.97	7.87	8.07	±0.06
$C_{11}H_{16}O_2N_2S$	7	13.33	13.54	13.41	±0.10
$C_{20}H_{13}O_4N_2SK$	9	7.69	7.61	7.64	±0.07
$C_{12}H_{10}O_2S$	2	14.68	14.86	14.77	...

Table IV. Precision and Accuracy of Volumetric Micromethod for Determination of Chlorine

Compound	No. of Analyses	% Chlorine Theory	% Chlorine Micro volumetric	Standard Deviation
2,4-Dinitrochlorobenzene	6	17.53	17.64	±0.09
1,8-Dichloroanthraquinone	6	25.63	25.61	±0.07
$C_{11}H_{16}NOCl$	6	16.59	16.69	±0.10

Table V. Comparison of the Parr Bomb Macromethod and the Volumetric Micromethod for Determination of Chlorine

Compound	No. of Analyses	% Chlorine Parr Bomb	% Chlorine Micro volumetric	Absolute % Difference
Trianthrimide A	2	1.30	1.08	0.28
Trianthrimide B	2	0.99	1.07	0.08
Trianthrimide C	2	1.05	0.99	0.06
Trianthrimide D	2	1.17	1.18	0.01
Indonaphthol blue A	2	2.26	2.38	0.12
Indonaphthol blue B	2	3.62	3.66	0.04
Indonaphthol blue C	2	8.71	8.89	0.18
Indonaphthol blue D	2	9.88	10.04	0.16

The absorbing solution (3% hydrogen peroxide, reagent grade) is transferred quantitatively from the Grote absorber into a 125-ml. Erlenmeyer flask and concentrated to approximately 10 to 20 ml. Three drops of saturated sodium acetate and 20 drops of the dichlorofluorescein indicator are then added, followed by 10 ml. of acetone. Since dichlorofluorescein tends to become colorless in acid solution, it may be necessary to add more than 3 drops of saturated sodium acetate solution in the analysis of compounds containing several different acid-forming elements. In the case of the bromine determination, it is advisable to add 2 drops of saturated hydrazine sulfate solution to ensure the reduction of any bromate which may have formed during the combustion. The halogen is then titrated with 0.01 *N* silver nitrate. For both the chlorine and the bromine determinations, the indicator used is dichlorofluorescein which gives a rosy pink end point. No correction value is required for this titration.

In the special case of ionizable water-soluble organic chlorides or bromides (except reducing substances), the halide can be titrated directly with silver nitrate after addition of the buffer, dichlorofluorescein indicator, and acetone as described above.

Water-soluble organic iodides may also be titrated directly with silver nitrate, but this procedure is not too satisfactory because of the unfavorable factor inherent in the high atomic weight of iodine.

The per cent halogen is calculated as follows:

$$\% \text{ halogen} = \frac{\text{ml. of } 0.01\ N\ AgNO_3 \times \text{milliequivalent} \times 100}{\text{sample (mg.)}}$$

in which the milliequivalents have the values 0.355 and 0.799 for chlorine and bromine, respectively.

For low concentrations of chlorine and bromine, it is advisable to add a known volume—i.e., 5 ml.—of a 0.01 *N* halide solution before starting the titration. This is necessary in order to obtain a sharp end point, since the mechanism of the indicator requires a definite minimum quantity of the colloidal precipitate on which the color reaction takes place.

The precision and accuracy of this method have been checked by the analysis of pure compounds and also by comparison with results by the gravimetric Parr bomb macroprocedure on impure compounds in which chlorine was present as either a major constituent or an impurity. Tables IV and V show typical results for chlorine.

In a similar manner the precision and accuracy of the method with regard to the determination of bromine were checked by the analysis of pure bromine compounds. The results are listed in Table VI.

Table VI. Precision and Accuracy of Volumetric Micromethod for Determination of Bromine

Compound	No. of Analyses	% Bromine Theory	% Bromine Micro volumetric	Standard Deviation
Benzalacetophenone dibromide	6	43.45	43.57	±0.10
$C_5H_{11}NO_3SBr_2$	6	49.20	49.28	±0.10
$C_{16}H_6O_2N_2Br_4$	6	55.34	55.48	±0.17

DETERMINATION OF IODINE

The iodine is determined by an iodometric method similar to that described by Niederl and Niederl (*9*).

The absorbing solution (5% sodium hydroxide) is transferred quantitatively from the Grote absorber into a 125-ml. glass-stoppered Erlenmeyer flask containing 5 ml. of 20% aqueous sodium acetate solution. A solution of 5 ml. of 10% sodium acetate in glacial acetic acid and 4 to 6 drops of bromine are then added. The excess bromine is destroyed by the addition of 20 drops of formic acid. Solid potassium iodide, 1 to 1.5 grams, and 3 ml. of 1 to 2 sulfuric acid are finally added. After standing for 5 minutes in the stoppered flask, the liberated iodine is titrated with 0.01 *N* thiosulfate solution to a pale yellow color, after which starch solution is added and the titration completed.

During the combustion, some iodine vapor may crystallize out on the cool portion of the Grote absorber. In such cases, an auxiliary heating device should be used, such as a suitably constructed copper shield, or some other method of heat transference.

The precision and accuracy of the method were checked by the analysis of purified iodine compounds (Table VII).

Table VII. Precision and Accuracy of Volumetric Micromethod for Determination of Iodine

Compound	No. of Analyses	% Iodine Theory	% Iodine Micro volumetric	Standard Deviation
4-Iodo-2-nitroanisole	8	45.50	45.42	±0.13
4-Iodo-2-nitroaniline	8	48.09	47.87	±0.11
1-(2-Chloro-4-iodobenzeneazo-2-naphthol)	6	31.07	30.90	±0.15

TRACES OF CHLORINE

Small quantities of chlorine have been determined by a combination of combustion in the Grote apparatus and the estimation of the chloride ion by turbidimetry.

The combustion tube is cleaned with hot dilute nitric acid to remove traces of inorganic chlorides which may have remained in the tube from previous combustions and which tend to volatilize slowly at high temperatures. It is also advisable to treat a new tube in a similar manner. The tube is then tested by a trial run to ensure the absence of any blank. The sample sizes have varied from 20 to 130 mg., depending upon the amount of chlorine present. Three per cent hydrogen peroxide (reagent grade) is used for absorbing the oxidation products. The absorbing solution is transferred to a test tube for turbidimetric comparison with standards prepared from known quantities of 0.01 *N* hydrochloric acid. Three drops of dilute nitric acid, one drop of 20% silver nitrate solution, and water to make the volume up to 20 ml. are added. The turbidity of the sample is compared with standards against a dull black background, preferably under fluorescent lighting. The per cent chlorine is calculated as follows:

$$\% \text{ Cl} = \frac{0.355 \times \text{ml. of } 0.01\ N\ HCl \times 100}{\text{sample (mg.)}}$$

The standard deviation was found to be ±0.01% chlorine when the amount of chlorine was in the range of 0.1 to 0.2% and samples of 20 to 130 mg. were used for the combustion. With a sample weight of approximately 100 mg. the sensitivity was found to be about 0.007% chlorine.

DISCUSSION

Tetrahydroxyquinone (THQ sold by Betz & Company, Philadelphia, Pa.) has been suggested by several authors (*6*) as the indicator to be used in the volumetric sulfur procedure. The literature indicates that this material is the disodium salt of tetrahydroxyquinone diluted with some inert material (*14*). It has been shown by Preisler (*10*) that tetrahydroxyquinone is a misnomer and that the compound is in reality a salt of rhodizonic acid. A sample of the dipotassium salt of rhodizonic acid (kindly furnished by P. W. Preisler of Washington University Medical School, St. Louis, Mo.) was analyzed in this laboratory and found by determinations of carbon, hydrogen, and potassium to be dipotassium rhodizonate. Spectrophotometric curves of solutions of commercial tetrahydroxyquinone (THQ obtained from Betz and Company) and a solution of the dipotassium rhodizonate were found to be similar. In the recent work reported in this paper, the dipotassium rhodizonate has been prepared by the procedure described by Preisler, but in much of their earlier work the authors used the so-called THQ which they now believe was a salt of rhodizonic acid.

In order to determine the most favorable concentration of the system, water–organic diluent, various concentrations of water-alcohol and water-acetone mixtures were tried in titrating a constant volume of 0.01 *N* sulfuric acid. The organic diluents investigated were methyl, ethyl, and isopropyl alcohols and acetone. In one case, the organic diluent was varied from 0 to 45 ml. and in the remaining cases from 5 to 25 ml. The initial volume before titrating was 50 ml. (±1).

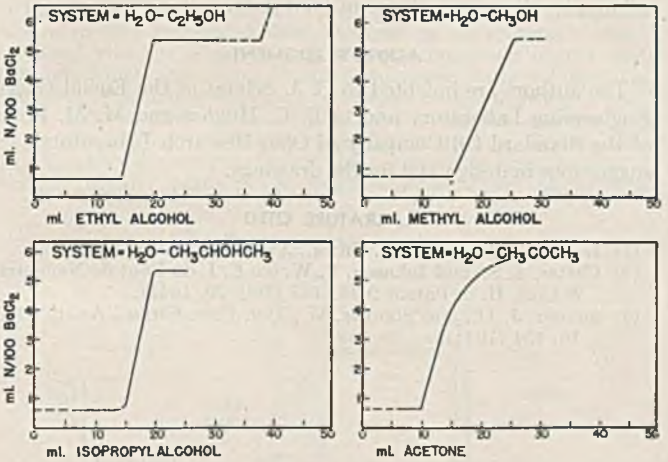

Figure 4. Titrations of Organic Diluents

Titration of 5 ml. of 0.01 *N* sulfuric acid with 0.01 *N* barium chloride. Total volume in each case made up to 50 ml. with water

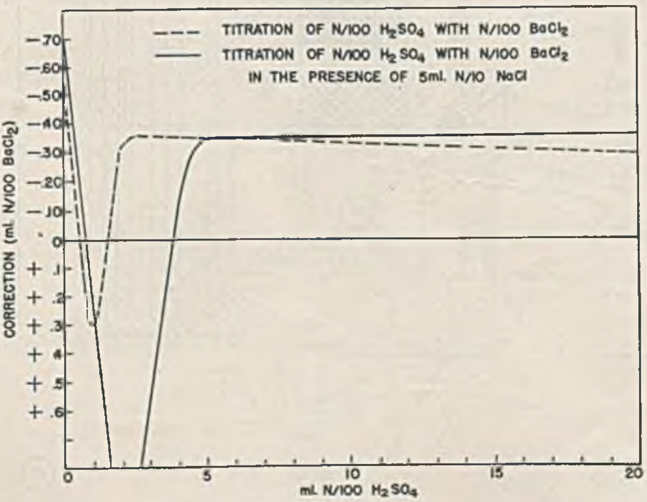

Figure 5. Titration Correction Value

The following data were obtained (shown graphically in Figure 4):

The titration cannot be performed in a wholly aqueous medium.

The most favorable composition of the system, water–organic diluent, is 25 ml. of water to 25 ml. of an organic diluent.

The effect produced by increasing the concentration of the organic diluent from 0 to 25 ml. is striking. In each case a sudden break is observed within very narrow limits.

C.P. ethyl, methyl, and isopropyl alcohols were found to be satisfactory diluents. Because of an obscure end point, acetone was not a satisfactory diluent.

At the very beginning of this work it was observed that a titration correction value existed. It became necessary, therefore, to determine this value at various concentrations of sulfate—that is, from 0.00 to 20.00 ml. of 0.01 *N* sulfuric acid. Two cases were considered: (1) the titration of 0.01 *N* sulfuric acid with 0.01 *N* barium chloride, and (2) the same series of titrations in the presence of 5 ml. of 0.10 *N* sodium chloride. The latter case is important because it represents the conditions of an actual analysis.

The following conclusions were drawn from the data obtained:

In both cases, by using the method of titration described, a fairly constant titration correction value existed in the range 5.00 to 20.00 ml. of 0.01 *N* sulfuric acid. The correction value taken was −0.35 ml. of 0.01 *N* barium chloride.

The presence of 5 ml. of 0.10 *N* sodium chloride does not interfere with the titration in the range 5.00 to 20.00 ml. of 0.01 *N* sulfuric acid.

In the absence of 5 ml. of 0.10 *N* sodium chloride, the lowest concentration of sulfate that can be titrated is about 2.00 ml. of 0.01 *N* sulfuric acid, and in the presence of the salt the lowest concentration is about 5.00 ml. of 0.01 *N* sulfuric acid.

In actual practice, the minimum sulfate concentration should not be less than 5.00 ml. of 0.01 *N* sulfuric acid.

The unusual behavior of the system in the range 0.00 to 2.00 ml. of 0.01 *N* sulfuric acid may be due to unfavorable equilibrium conditions. In the presence of 5 ml. of 0.10 *N* sodium chloride this behavior is enhanced and extends through the range 0.00 to 5.00 ml. of 0.01 *N* sulfuric acid.

The data are shown graphically in Figure 5.

ACKNOWLEDGMENT

The authors wish to acknowledge the suggestions received from the many people who were kind enough to review this paper. Appreciation is also expressed to H. K. Alber of the Arthur H. Thomas Company for the drawings of the apparatus, and to the Corning Glass Works for the several Grote absorbers and combustion tubes furnished during this investigation.

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NOTES ON ANALYTICAL PROCEDURES

New Head for Laboratory Fractionating Columns

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IN DISTILLATION systems, take-off heads which are capable of maintaining a constant reflux ratio regardless of variations in distillation rate and other factors have been described by Bruun (*1*) using a two-way valve, by Carter and Johnson (*2*) using a magnetically operated funnel, and by Snyder and Steuber (*3*) using a U-shaped take-off tube and pressurized receiver which is intermittently vented to the still pressure. None of these devices is satisfactory for the routine laboratory distillation of petroleum products in which appreciable amounts of condensed butane hydrocarbons are to be measured. These low-boiling components tend to vaporize in the take-off line and re-enter the column. The take-off device described here overcomes this difficulty and has the further advantages of high throughput and low holdup.

The feature of this take-off, which is designed for a totally condensing head, is a steel ball bearing encased in glass. This assembly is seated by a joint ground into the throat of a glass funnel leading to the receiver. For alternate use with the head, a double-type condenser utilizing dry ice cooling in addition to the conventional type is described. This condenser gives efficient and complete condensation of C_4 fractions. It avoids the troublesome change from dry ice to liquid coolant, which is encountered in the operation of the usual dry ice head, and eliminates the need for expensive cooling systems.

CONSTRUCTION AND OPERATION

Figure 1 (left) shows the side view of the head, with the take-off mechanism enlarged at center. The steel ball, *A*, encased in glass is shown in position for total reflux, and illustrates the small vapor volume-free space and liquid holdup. The glass funnel, *B*, forms a tight seal for total reflux, the condensate from the drip tip, *C*, flowing over the valve and returning to the column. During take-off a cycle timer connected to an electromagnet, *D* (heavy duty-220-volt alternating current coil 900 ~ resistance), operates to pull the steel ball up to the position of the dotted line and all condensate flows into the receiver. At the end of the take-off period, the valve reseats by gravity and condensate again returns to the column. It has been found desirable, for best operation, to have an indentation blown into the head as shown at *E* to allow closer approach of the magnet core to the valve. Figure 1 (right) shows an alternate type of condenser *F* permitting the use of coolant in center core and in outer jacket. Replaceable attachment *G* on center core facilitates addition of dry ice to the condenser, necessary for condensation of volatile distillates.

Advantages found during operation are: (1) simplicity of operation due to automatic take-off with variable setting for reflux ratio; (2) ruggedness of construction; (3) protection of the steel ball from corrosion and of the distillate from contamination; (4) usefulness for high-temperature distillation because of a small surface area and vapor volume; (5) usefulness for low-temperature distillation because of a positive closure and a variable coolant; (6) high-capacity take-off valve permitting rapid distillation of large volumes; and (7) adaptability to vacuum distillations.

The construction of the apparatus requires glass-blowing skill. However, it can be made readily by a professional glass blower or obtained at a reasonable cost from the Euclid Glass Engineering Laboratory, 6 East 242nd St., Euclid, Ohio. This type of distillation head may be made to fit any size of fractionating column by the proper choice of joint sizes.

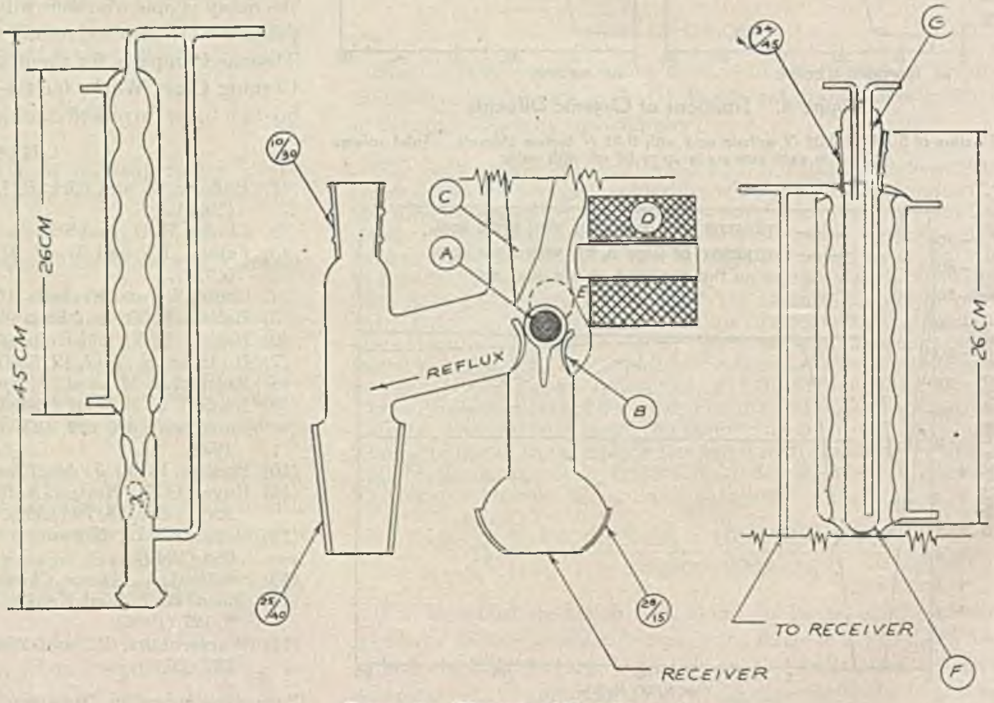

Figure 1. Diagram of Head

ACKNOWLEDGMENT

The authors are indebted to C. J. Schugt of the Euclid Glass Engineering Laboratory and to E. C. Hughes and M. M. Fink of the Standard Oil Company of Ohio Research Laboratory for suggestions in design and for the drawings.

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Proportional Flow Controller for Liquids

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A PERENNIAL problem in fractional distillations is the accurate control of reflux ratio with a variable throughput. In the laboratory, manual control guided by visual observation of the flow is usually satisfactory. In pilot-plant and larger installations this method is impractical and hence many contrivances have been devised and described for automatic division of the flow in a given ratio. These generally fall into two classes, the intermittent take-off type and the proportional condensing surface type.

Carter and Johnson (*3*) describe a device employing a funnel moved magnetically; Brunn (*2*) uses a two-way valve and capillaries; Podbielniak (*4*) has an intermittently-opening valve seated in the take-off tube; Berg (*1*) describes a proportional condensing area device. Most reflux ratio controllers are difficult and expensive to build, contain delicate moving parts which get out of order, and are intermittent in operation or of such a nature that the ratio may be varied only by stages.

A proportional flow controller free from these defects has been developed in this laboratory and used successfully on a 5-inch diameter column for one year. It operates on the principle of directing a downflow of liquid into a uniform, free-falling sheet or curtain which is split into two parts by a movable divider.

The device consists of an upper and a lower compartment separated by a horizontal plate, as shown in the schematic cross-sectional views of Figure 1. This plate contains a narrow slot through which the entire liquid condensate flows by gravity, the liquid flow being indicated by arrows on the drawings. Just below and parallel to the slot is fixed a vertical sharp-edged guide plate which collects the liquid as a uniform falling film. The guide plate extends down into a movable tray having a vertical divider plate perpendicular to the guide plate; the arrangement of the slot, the guide plate, and the divider plate is shown schematically in Figure 2. The divider plate has a sharp edge, and is notched to fit closely around the guide plate, so that it cuts the falling film into two separate parts, each of which flows out of one end of the tray into the lower compartment. That compartment in turn is divided on the bottom by a vertical plate, underneath the movable tray, which keeps the two liquid streams separated as they spill from the tray.

The dividing tray, which is supported on horizontal rails as shown, can be moved by a rod projecting through a packing gland in the side of the lower compartment, and its position is indicated by a pointer on the rod. The length of the tray, and the position of the divider plate, may be designed so that the flow can be split into any ratio over the required range, which can be anywhere between zero and total reflux.

The liquid head in the upper compartment is determined by the input rate and the slot dimensions, and the only variable in the liquid sheet leaving the slot is its velocity. Thus the instrument is independent of variations in throughput, within the limit set by the maximum available height above the slot. The upper and lower compartments are connected by vent lines, so that unequal gas pressures cannot develop. The vent from the upper compartment also acts as an overflow line into one end of the overflow compartment, in case the rate of flow becomes greater than the capacity of the slot.

The guide plate below the slot maintains the continuity and uniformity of the falling film, and this constitutes the essential feature which makes the device workable. Without it, the velocity of the liquid will usually be insufficient to form a continuous sheet of its own accord. The slot itself is formed of two V-edged plates as shown in Figure 1. The plates were made as shown because the edges must be parallel and straight, and with the soft brass which was used, this shape appeared to offer the best chance of obtaining these qualities. A thin hardened plate,

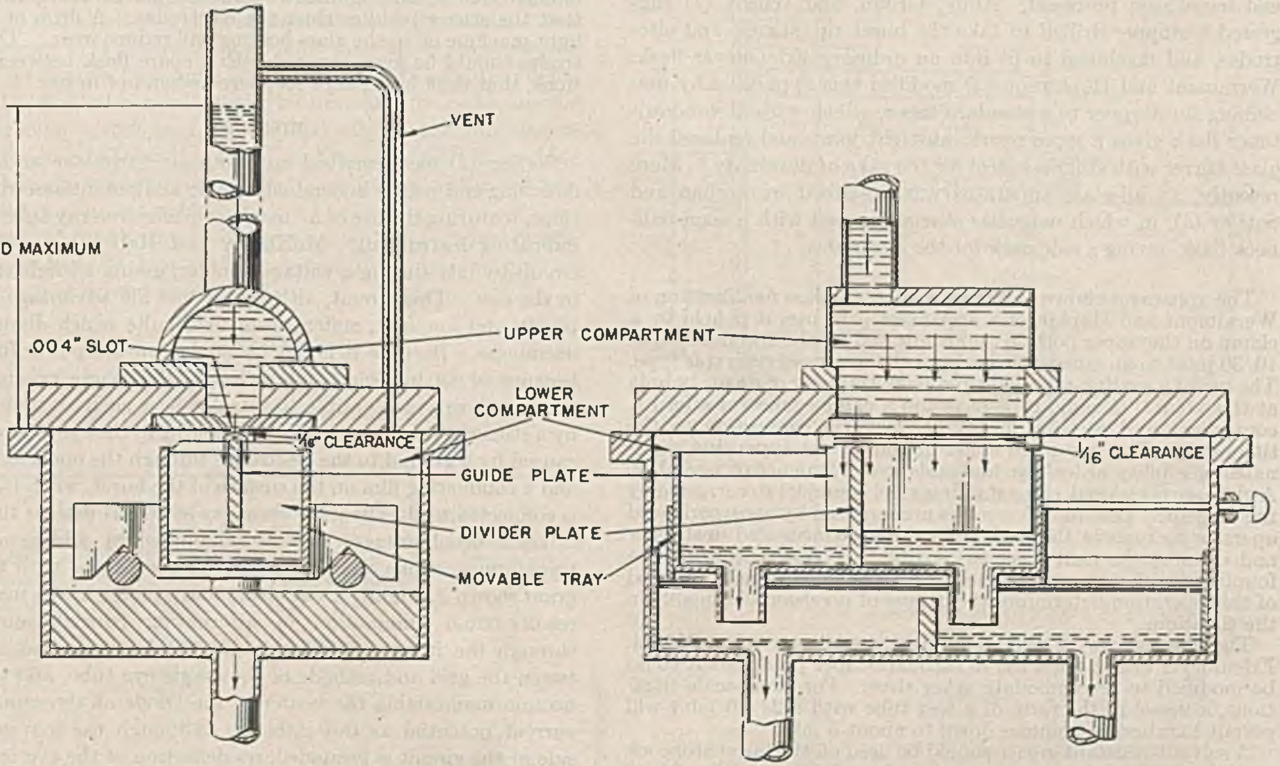

Figure 1. Cross Section of Flow Controller

Left, end view. Right, side view

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[1] Present address, R. T. Vanderbilt Co., East Norwalk, Conn.

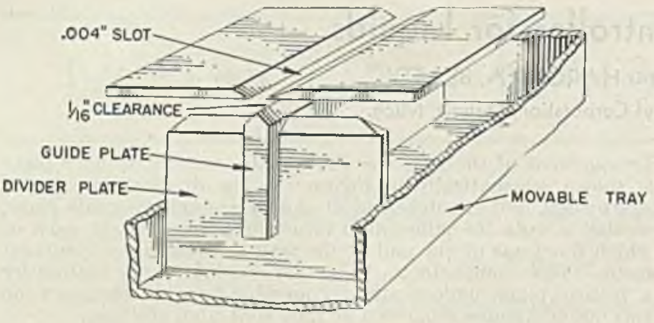

Figure 2. Flow Controller

ground to a sharp edge, would be at least as satisfactory, and probably better than the shape shown in Figure 1. Although the direction of the V as shown does not make the slot self-cleaning, it is necessary to have it as shown in order to feed all the liquid to the guide plate. (A disk-type metal filter with low pressure drop was used on the feed line to remove any scale or sediment from the liquid.) With the exception of the slot, which must be fixed accurately, none of the dimensions are critical, and they may be varied to suit the individual requirements.

The plates are adjustable, so that the liquid head necessary to maintain the proper flow does not become unreasonable. The plates are adjusted at both ends, two feeler gages being used to ensure parallelism. The slot width is determined by the allowable liquid head and the density, viscosity, and surface tension of the liquid. A spacing of 0.0045 inch in a 4-inch long slot is sufficient to carry a flow of 5 to 25 gallons of gasoline per hour at a maximum head of 15 inches, and to provide a continuous sheet of liquid. This slot was tested with gasoline at reflux ratios in the range of 1 to 30. The ratios predicted from the position of the divider were obtained with an accuracy varying from ±1% at a ratio of 1 to ±10% at a ratio of 30, throughout the entire range of 5 to 25 gallons per hour. This degree of precision is entirely adequate for distillation work, but can be further increased by lengthening the slot.

While the present device was designed for reflux control, it is evidently applicable to many installations where it is desired to split a liquid stream into two parts of given, constant ratio. Its advantages include: no moving parts in operation; wide and continuous range of ratios, independent of throughput, pressure, viscosity, etc.; continuous, rather than intermittent, operation with relatively low holdup.

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Improved Apparatus for Karl Fischer Water Determination

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THE need for excluding atmospheric moisture from a Karl Fischer titration is well known; it is equally necessary, for high precision work, to protect the apparatus used from moisture before the titration. Several types of apparatus to accomplish this end have been proposed. Almy, Griffin, and Wilcox (*1*) suggested a stopper drilled to take the buret tip, stirrer, and electrodes, and machined to fit into an ordinary Erlenmeyer flask. Wernimont and Hopkinson (*4*) modified this apparatus by machining the stopper to a standard taper, which with a standard-taper flask gives a more nearly air-tight joint, and replaced the glass stirrer with stainless steel for the sake of durability. More recently, an all-glass apparatus was described by Zerban and Sattler (*5*), in which magnetic stirring is used with a semi-ball-neck flask having a side neck for the electrodes.

The apparatus shown in Figure 1 is an all-glass modification of Wernimont and Hopkinson's apparatus. In use, it is held by a clamp on the upper portion and connected by the standard-taper 10/30 joint to an automatic buret of the overhead reservoir type. The use of a seating-type joint prevents trapping of an air bubble at this point. A radio tube base and a cable connector afford a convenient and positive means of electrical connection to the titrimeter. The one-piece construction of the apparatus eliminates possibility of leakage and adds to convenience of assembly. A glass stirrer is used, since stainless steel is subject to corrosion by the reagent. Less than 5 seconds are required by an experienced operator to remove the flask from the apparatus and unstopper and connect the next flask to be titrated; this feature is also found in the first two types cited. All else being equal, the speed of this operation determines the degree of precision obtainable in the titration.

The dimensions of the apparatus permit use of a 250-ml. Erlenmeyer flask with a 24/40 standard-taper joint, but it could be modified to accommodate other sizes. For small-scale titrations, a vessel in the form of a test tube with a 24/40 joint will permit titration of volumes down to about 5 ml.

A solvent-resistant grease should be used on the buret stopcock and the 10/30 joint, to prevent serious leakage. The 24/40 joint should not be greased, since a slight amount of outward air leakage is necessary to permit addition of the reagent; it is sometimes necessary to grind a slight groove in the male joint to this end. An efficient moisture trap should be used on the air inlet of the buret. (The drying tube usually supplied with the buret is too small to be effective.) The stirrer should be connected to the motor with a short length of soft-rubber tubing to prevent damage due to misalignment. Care should be taken to ensure that the stirrer paddles clear the electrodes. A drop or two of light machine oil in the glass bearing will reduce wear. The electrodes should be kept covered with a spare flask between titrations, that flask being kept stoppered when not in use.

TITRIMETER

Serfass (*3*) has described an electronic titrimeter suitable for detecting end points in conductometric and potentiometric titrations, featuring the use of a "magic eye" electron ray tube for the indicating instrument. McKinney and Hall (*2*) modified the circuit by introducing a voltage doubler, giving a brighter image in the eye. This circuit, although it has the advantage of simplicity and low cost, suffers from two faults which diminish its usefulness. Because it is not isolated from the power line, and because of an inefficient filter circuit, the magic eye image is fuzzy and very susceptible to interferences such as that caused by a stirrer motor. In addition, flickering of the eye is sometimes caused by a ground to the electrodes through the operator's body and a conducting film on the surface of the buret, when the buret is connected to the titration vessel, as in a Karl Fischer titration.

These disadvantages may be eliminated by adding a power transformer, choke, and condenser, in accordance with the diagram shown in Figure 2. A clear, sharp image in the magic eye results from elimination of alternating current component through the improved filter circuit, the by-pass condenser between the grid and cathode of the magic eye tube, and the connection maintaining the heater of the triode at the same direct current potential as the cathode. Although the low potential side of the circuit is grounded, no deflection of the eye is caused by grounding the buret through the operator's body. This effect is eliminated by reduction of the above-ground potential of the

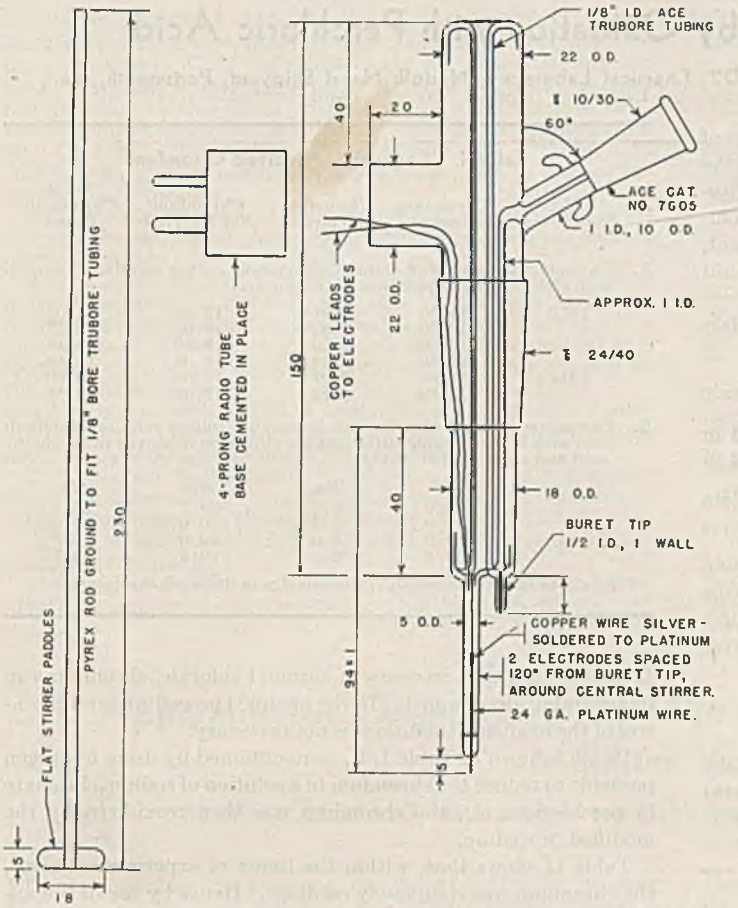

Figure 1. Karl Fischer Electrode-Stirrer-Buret Assembly

amplifier grid to approximately 30 volts, from about 140 in the case of the voltage doubler circuit.

Possibility of greatly increased sensitivity can be introduced by means of the potentiometer in the triode cathode circuit. This is sometimes very desirable in conductometric titrations, where impurities cause a high initial conductivity of the solution being titrated. A similar result could be obtained by replacing the potentiometer with a fixed resistor, and varying the grid bias, as in Serfass' original circuit. However, the desirability of keeping the grid-to-ground potential as low as possible makes the arrangement shown more satisfactory.

Operation of the titrimeter is identical with the original model. Like the voltage doubler model, however, it can be used only on an alternating current power source.

PRECISION

In order to measure the precision obtainable with the apparatus, it was desirable to confine possible deviations to those inherent in the apparatus and the technique involved in its use, as opposed to sampling errors and chemical or physical considerations based on the constitution of the sample. The standardization of Karl Fischer reagent against water was chosen as meeting these requirements.

A solution containing 11.66% by weight of water in methanol was made up in a dropping bottle having a ground-in medicine dropper. This solution, rather than pure water, was used as a standard, to reduce the effect of weighing errors upon precision. Approximately 30 ml. of nearly dry methanol were placed in a 250-ml. standard-taper Erlenmeyer flask, and connected to the titration assembly. The trace of water present was titrated with Karl Fischer reagent until one drop caused the magic eye to remain open for about 30 seconds. (Although this point may be determined with a stop watch, the difference in time required for the eye to close after the next-to-last drop and the last drop is so great as to be readily apparent.) Approximately 1 ml. of the standard water solution was introduced into the flask as rapidly as possible, and titrated as before. The weight of standard solution added was determined by difference.

The results of ten such titrations are given in Table I. The precision is of the same order of magnitude as that obtainable with moderate care in any simple acid-base titration.

Table I. Standardization of Karl Fischer Reagent

Weight of 11.66% Water Solution Grams	Volume of K.F. Reagent Ml.	Water Mg./ml. reagent	Deviation from Mean %
0.8613	30.75	3.266	0.0
0.9231	32.90	3.272	0.2
1.0123	36.22	3.259	0.2
0.8252	29.50	3.262	0.1
0.9138	32.61	3.267	0.1
0.9330	33.33	3.264	0.0
0.9561	34.08	3.271	0.2
0.7196	25.72	3.262	0.1
0.8518	30.39	3.268	0.1
0.8181	29.30	3.256	0.3
	Av.	3.265	0.1

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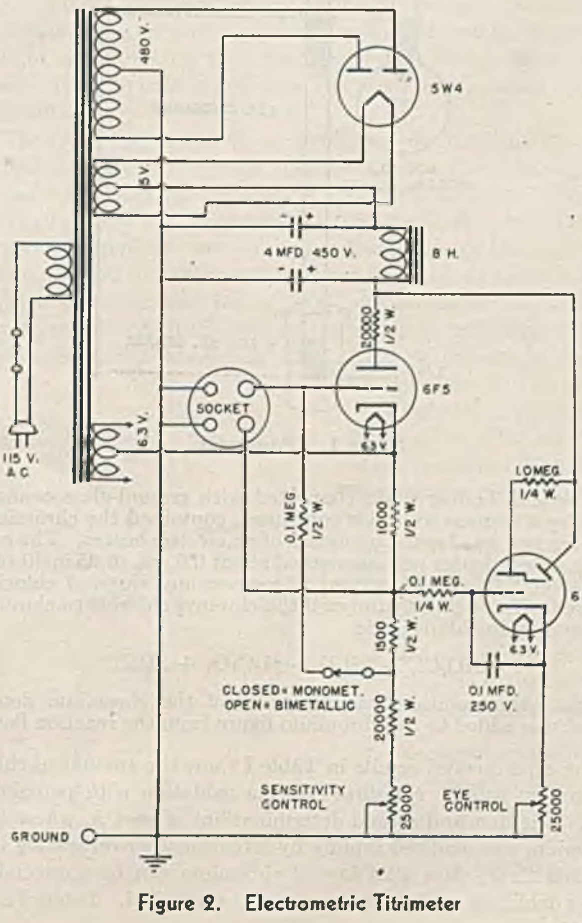

Figure 2. Electrometric Titrimeter

Determination of Chromium by Oxidation with Perchloric Acid

SIGMUND SCHULDINER AND FREDERICK B. CLARDY, Chemical Laboratory, Norfolk Naval Shipyard, Portsmouth, Va.

THE perchloric acid method (*2*, *3*, *4*, *6*) for the determination of chromium essentially consists of oxidation of chromium to the sexivalent state by fuming perchloric acid. The oxidized chromium is titrated with a standard ferrous ammonium sulfate solution to an *o*-phenanthroline end point, an electrometric end point, or a permanganate end point by using an excess of reductant and back-titrating with potassium permanganate solution.

Although the perchloric acid method of oxidation is widely used, the following sources of error have been observed:

1. Loss of chromium by volatilization as chromyl chloride (*1*, *5*).
2. Reduction of chromium by hydrogen peroxide formed in the reaction flask (which can be eliminated by rapid cooling of flask and contents).
3. Incomplete oxidation of the chromium due to incomplete heating (least serious of the three).

Experienced analysts have various methods of overcoming these errors and obtaining consistently accurate results. This paper presents modifications of the conventional procedures which have been satisfactorily used in this laboratory for over two years.

EXPERIMENTAL

After experimenting with vertical air and water condensers, the authors found that the sources of error in the perchloric acid method could be overcome by an arrangement of apparatus as shown in Figure 1.

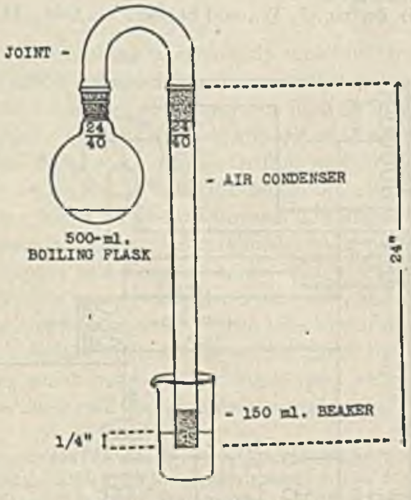

Figure 1. Apparatus

A 500-ml. boiling flask, connected with ground-glass connections by a U-tube to an air condenser, contained the chromium solution and was heated by means of an electric heater. The end of the air condenser was submerged about 0.6 cm. (0.25 inch) in a beaker of water which served to recover any chromyl chloride evolved. The water hydrolyzed the chromyl chloride to chromic acid and hydrochloric acid:

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$$

This water solution was titrated and the chromium determined was added to the chromium figure from the reaction flask.

Table I. Recovery of Evolved Chromium

N.B.S. Sample No.	Chromium Present	Chromium Evolved	Chromium Not Evolved	Total Chromium Found
	%	%	%	%
A. Chromium titrated with ferrous ammonium sulfate solution standardized with potassium permanganate solution				
101B	18.50	1.07[a]	17.45	18.52
	18.50	1.81[a]	16.67	18.48
	18.50	0.12	18.36	18.48
	18.50	0.44	18.05	18.49
121a	18.68	0.07	18.63	18.70
	18.68	0.18	18.58	18.76
B. Chromium titrated with ferrous ammonium sulfate solution standardized with N.B.S. sample 101B (sodium chromate dissolved in perchloric acid and reduced with H_2O_2)				
	Mg.	*Mg.*	*Mg.*	*Mg.*
	30.0	0.1	29.7	29.8
	30.0	0.2	30.0	30.2
	30.0	0.0	30.0	30.
	30.0	0.1	29.6	29.7

[a] Solutions fumed vigorously, intentionally to drive off chromium.

The experimental results in Table I show the amount of chromium that can be volatilized during oxidation with perchloric acid. The first and second determinations of part A, where the chromium was oxidized rapidly by intentionally overheating the reaction flask, show that loss of chromium can be appreciable unless oxidizing conditions are carefully controlled. Tables I and II indicate that, by recovery of chromyl chloride, chromium can be accurately determined. In the modified procedure careful control of the oxidizing conditions is not necessary.

Results shown in Table I, B, were obtained by using hydrogen peroxide to reduce the chromium in a solution of sodium chromate in perchloric acid; the chromium was then reoxidized by the modified procedure.

Table II shows that, within the limits of experimental error, the chromium was completely oxidized. Hence by use of the apparatus and procedure described the chromium factor of the standard ferrous ammonium sulfate solution can be computed stoichiometrically. The chromium results therefore do not depend on an empirical factor but can be derived theoretically.

PROCEDURE FOR HIGH-CHROMIUM STEELS

Place 0.2 gram of sample in a 500-ml. boiling flask with ground-glass connections that can be fitted to an air condenser (Figure 1). Add 10 ml. of hydrochloric acid plus 5 ml. of 1 to 1 nitric acid, and heat until sample is dissolved. Then add 25 ml. of perchloric acid, and heat until the perchloric acid just starts to fume. Connect the reaction flask to the air condenser and place the beaker with about 75 ml. of water in position as in Figure 1. Heat until the reaction flask is cleared of fumes and the perchloric acid refluxes down the sides of the flask. Turn the heater current off and let stand for 2 or 3 minutes. Disconnect the reaction flask and connecting tube from the air condenser and cool the flask rapidly, using first a stream of air and then cold run-

Table II. Results of Chromium Determinations

N.B.S. Sample No.	Weight	Chromium Present	Chromium Found
	Grams	%	%
121a	0.2	18.68	18.66[a]
	0.2	18.68	18.72[a]
	0.2	18.68	18.76[a]
	0.2	18.68	18.76[a]
101a	0.2	18.33	18.37[a]
	0.2	18.33	18.38[a]
101B	0.2	18.50	18.46[a]
	0.2	18.50	18.47[a]
	0.2	18.50	18.55[a]
	0.2	18.50	18.52[a]
111	2.0	0.272	0.274[b]
	2.0	0.272	0.274[b]
72a	2.0	0.655	0.658[b]
	2.0	0.655	0.658[b]
115	1.0	2.16	2.18[b]
	1.0	2.16	2.18[b]

[a] Determined by standardizing ferrous ammonium sulfate solution with standard potassium permanganate solution.

[b] Determined by standardizing ferrous ammonium sulfate solution against N.B.S. samples 101B and 101.

ning tap water. Wash the inside of the connecting tube back into the reaction flask with distilled water and disconnect the tube from the flask. Wash the inside of the air condenser into the beaker of water containing evolved chromium. Pour this solution into the reaction flask. Heat flask and contents until chlorine is completely driven off. Volume should now be about 250 ml. Cool and titrate, following the conventional methods, with standard ferrous ammonium sulfate solution and ferrous *o*-phenanthroline indicator.

The air condenser should be at least 2.5 cm. (1 inch) in diameter and 60 cm. (2 feet) long in order to guard against back-suction of the water into the reaction flask.

After the sample is in solution and the perchloric acid solution is taken to fumes on the hot plate, care should be taken not to oxidize the chromium before the reaction flask is connected to the air condenser as in Figure 1. The solution may be heated to a bright green color but should not turn orange before transfer to the air condenser.

All-glass connections must be used in the oxidizing unit; if fuming perchloric acid comes in contact with organic matter such as rubber, a serious explosion or fire may result.

The reaction flask should be protected from air currents; otherwise the sudden cooling of the flask may cause a suction and some of the water from the water seal may be sprayed into it.

A bank of several oxidizing units can be easily arranged if the work load requires it.

If vanadium is present in the material analyzed, add an excess of ferrous ammonium sulfate solution and then back-titrate with a potassium permanganate solution, omitting the *o*-phenanthroline indicator.

ACKNOWLEDGMENT

The authors wish to express their appreciation to R. S. Gibbs, principal chemist, and Lt. L. D. Wilson, U.S.N.R., laboratory officer, Norfolk Naval Shipyard, for valuable suggestions offered during their review of this paper.

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Apparatus for Quantitative Low-Temperature Vacuum Distillation of Milliliter Volumes

W. MORTON GRANT, Howe Laboratory of Ophthalmology, Harvard Medical School, Boston, Mass.

IT IS frequently desirable to use low-temperature vacuum distillation for quantitative separation of such substances as alcohols, lower fatty acids, and deuterium oxide from nonvolatile materials in small samples. However, this process is inconveniently slow when apparatus incorporates long or complex distillation paths to prevent contamination of the distillate from foaming of viscous solutions, especially those containing protein.

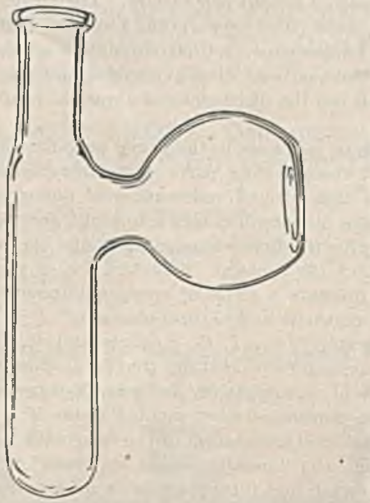
The distillation apparatus shown in the accompanying figure was designed to provide a short distillation path for rapid distillation, while minimizing the chance of contamination from foaming. After trial of several variations in the critical dimensions, this apparatus, which was constructed from parts of a 50-ml. Florence flask and a 25 × 150 mm. test tube, was considered to be of optimum size for the distillation of 1- to 3-ml. samples.

The material to be distilled is introduced into the bulbous side flask by means of a curved-tip pipet. The tube is then closed by a silicone-greased, one-hole rubber stopper carrying a stopcock for connection to a vacuum pump. The side flask is immersed in a dry ice mixture with the tubular portion horizontal. When the contents are frozen, the apparatus is evacuated, sealed by closing the cock, and disconnected from the vacuum line. This whole procedure requires less than a minute. The side flask is then taken from the cold bath and the test-tube portion of the apparatus is immersed in its place, leaving the flask exposed. Distillation is allowed to proceed to completion without artificial heating. Four tubes of the dimensions specified fit conveniently into the mouth of a 0.5-liter Dewar flask.

The apparatus was evacuated by means of a Welch two-stage duo-seal pump which readily reduced the pressure in an empty flask to approximately 1 micron, as judged by the faint blue-gray color produced by a Tesla coil discharge.

With aqueous samples frozen in dry ice, the vacuum appears to be limited by the vapor pressure of the water. During distillation, gases which are trapped in the sample are released and have an appreciable influence on the rate of distillation. Some of this interfering gas can be eliminated by a second evacuation of the apparatus after melting and refreezing the sample. In the case of whole blood the degassing is facilitated by the presence of a small drop of xylene. With a single evacuation, blood, plasma, and urine samples have been distilled at the rate of 0.5 to 1.0 ml. per hour without artificial heating. Comparative distillations made with double evacuation showed an increase in rate of approximately 25% for plasma and saline. Thus, where every saving in time is desirable, the extra manipulation appears warranted.

The quantitative nature of distillation in this apparatus was determined by analysis of distillates from sulfosalicylic acid filtrates of blood to which known amounts of formic acid and methyl alcohol had been added. The distillation of a formaldehyde solution was also studied. Recoveries of formic acid in amounts of 30 to 1000 micrograms per ml. of blood and of methyl alcohol in amounts of 150 to 3000 micrograms per ml. of blood averaged 98 and 101%, respectively, for 9 determinations of each. Solutions containing 1.2 and 3.6 micrograms of formaldehyde per ml. of a mixture of 3% sulfosalicylic acid and 1% sulfuric acid yielded 1.2 and 3.6 micrograms per ml. of distillate. In separate experiments it was found that distillation must be carried to completion in order to obtain the same relative concentrations of volatile constituents in the distillate as in the original sample.



ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Helen E. Pentz in devising and testing this apparatus.

BOOK REVIEWS

Protective and Decorative Coatings. *Joseph J. Mattiello*, Editor. Vol. V. Analysis and Testing Methods. 662 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1946. Price, $7.

In the fifth and latest volume of his series, Dr. Mattiello continues his campaign to place the field of protective and decorative coatings on a firm scientific basis of its own. In answer to the need for systematizing analytical techniques necessitated by the ever-widening variety of new resins and their modifications, he has enlisted the services of several competent author-scientists to contribute to this work.

As with so many other fields of chemical endeavor that have experienced constantly accelerated growth, this industry has amassed data and know-how faster than it could organize and appraise them. Tests that once served as criteria for a given application of a product no longer sufficed to indicate its suitability for a new employment, and so the control chemist gradually lost contact with the firing line of end use. The avalanche of new raw materials and unique applications brought about by the war made it mandatory that the control and research laboratories of the efficient finish company function in close liaison with the actual need. In order to do this, it was necessary to approach the problem from a practical yet academic viewpoint, which is the basic theme of this book.

The first chapter, by R. W. Stafford and E. F. Williams, presents a classification of resins, and means of isolating and studying them by qualitative, physicochemical, and certain special methods. The classification breakdown is: natural resins and their modifications, alkyd resins, aldehyde condensation products, vinyl resins, rubber and rubberlike synthetics, hydrocarbon, and inorganic resins. In addition, the natural and synthetic waxes, carbohydrate, and protein materials are included. A brief discussion of the chemical properties and structure of each member of the above families is given in so far as it bears on their determinations. The second portion of the chapter deals with the analysis of these materials by routine methods and closes with interesting discussion of x-ray radiographic and x-ray diffraction methods of analysis.

Chapter II is concerned with methods for testing and analyzing drying oils. The authors, T. F. Bradley and E. L. Kropa, point out that very few industrial laboratories are concerned with the quantitative determination of a pure fatty acid or its glyceride but rather with the technological values and effectiveness of the material. Viscosity measurements, molecular weight determination, and means for determining the type and degree of unsaturation are discussed, and considerable space is devoted to the use of the thiocyanogen value. The chapter closes with valuable tables of the physical and chemical constants of the commercial fat acids.

A critical appraisal is made in the third chapter of the methods of laboratory testing of metal finishes for outdoor service. The author, S. E. Beck, discusses standardized panel preparation, humidity testing, and the effects of light, temperature, and air circulation on the drying of the films. The sections on statistical evaluation and color are particularly interesting, as are the discussions of abrasion, bending, and flexibility testing.

The spectral characteristics of pigments in the visual and infrared bands are dealt with by V. C. Vesce in three parts: (1) photographic method of measuring visual and infrared reflectances of pigments and pigmented coatings, (2) a spectrophotometric method for the determination of reflectances for the four wave-length bands by the selected ordinate method, and (3) spectral characteristics of pigments. This latter section presents a series of spectrophotometric curves on a large number of synthetic and natural pigments.

The chapter on "Resinography", by T. G. Rochow and R. L. Gilbert, introduces a new approach to resin study that in purpose is related to the analogous fields of metallography and mineralography. Because of the heterogeneous nature of most molded resins it has become useful to study the mode of association of the filler with the embracing resin. In addition, the "metallographic approach" will identify the filler, if it be a metal, and furnish valuable information on the history of fabrication as well. Should the filler be of a mineral nature, either natural or synthetic, a mineralographic approach will yield similar desirable data.

Resinography is also concerned with the structure of the resin or resins involved by studying the resinous phases that may be present and their relationships by difference in refractive index, reflectivity, color, hardness, the effect of polarized light, etc. Indirect methods employing selective staining, selective dissolution, and differential etch patterns are valuable in this respect. The chapter also includes sections on the use of instruments such as the optical microscope and camera and electron microscope in examination of resin specimens.

This book seems to serve well as a clearinghouse and sifting medium for the many diversified but often confusing methods of analysis that have arisen in this field.

Richard L. Demmerle

Spectrographic Analysis of Metallurgical Products

The Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques has published as a 92-page book the proceedings of its fifth congress, which was held January 22 to 24, 1946. In addition to a report of the meeting and a list of members present, the book includes four technical papers, with discussion: Le Dosage Spectrographique des Faibles Teneurs en Aluminium dans les Aciers Ordinaires et Spéciaux, by R. Castro; Causerie sur les Spectrographes, by H. Tardy; Luminosité Comparée du Spectrographe Zeiss Qu 24 et du Spectrographe Zélande de Jobin et Yvon, by E. Loeuille; and Le Dosage des Traces d'Impuretés dans les Alliages de Zinc au Moyen de l'Etincelle Condensée, by P. Croissant. Copies are available through the Centre de Documentation Síderurique, 12 Rue de Madrid, Paris 8, France.

Apparatus for Small-Scale Catalytic Hydrogenation—Correspondence

Sir: The continued interest in the apparatus for small-scale catalytic hydrogenation [Ind. Eng. Chem., Anal. Ed., 14, 907 (1942)], as evidenced by requests for reprints, makes it desirable to describe a modification of the apparatus made shortly after the original article was published. Instead of having the cup and stopcock on the reaction flask, where it caused instability and led to frequent breakage, it was incorporated in the main portion of the apparatus, as indicated in the accompanying diagram. This modification permits the use of any Erlenmeyer flask having an interchangeable ground-glass joint as the reaction vessel.

C. R. Noller

Stanford University,
Calif.

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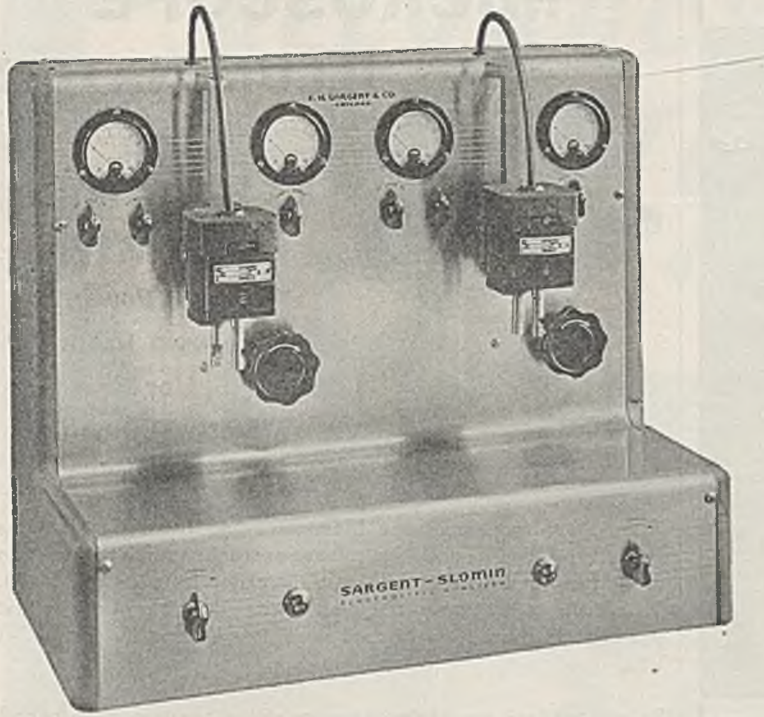

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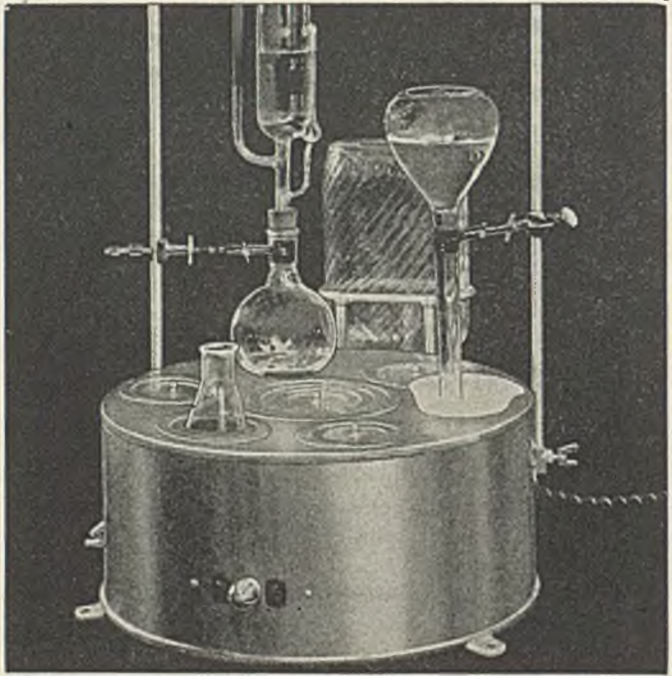

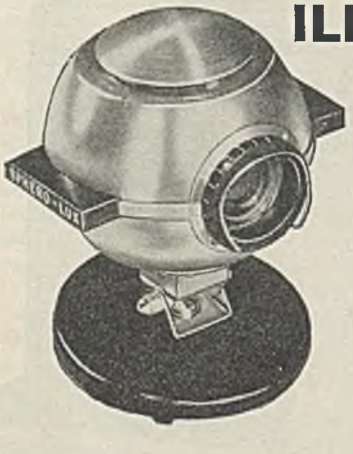
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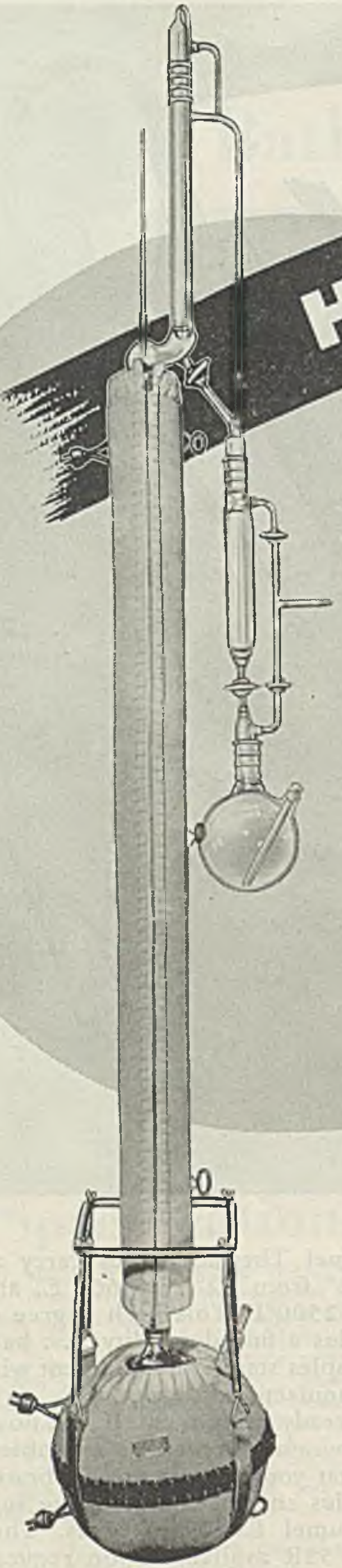

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Current Developments in
INSTRUMENTATION IN ANALYSIS

Discussed by Ralph H. Müller

Optical Filters

Optical methods are widely used in modern analytical chemistry in the visible, ultraviolet, and infrared regions of the spectrum. For general exploratory and research work, the use of single or double monochromators, for the isolation of narrow regions of the spectrum, has found increasing favor; indeed the practice is essential for precise spectrophotometry. The practice has been extended to the relatively simple problems presented by "colorimetric" analysis largely because it affords a high degree of flexibility and convenience in the selection of the appropriate spectral region. Filter photometers may be expected to retain their usefulness, however, especially for those optical procedures which have been carefully standardized and for which a large amount of routine work justifies their limited range. Their use may also be expected to increase in those applications in which the amount or concentration of a definite constituent is to be recorded or monitored.

The selection of filters has always been a difficult matter and usually resulted in a compromise between selectivity and high transmission. Any progress in this field is therefore of considerable value and interest to the analyst.

Interference Filters

Filters of this class are essentially fixed separation Fabry and Perot interferometers and consist of evaporated thin layers of dielectric material between semitransparent metallic films on glass. They are characterized by high transmission and narrow band width. The theory of interference filters is discussed by R. L. Mooney [*J. Optical. Soc. Am.*, **36**, 256 (1946)]. It is shown by this author that the method, which treats the phenomenon of selective reflectivity and transmissivity of surface layers as a problem in electromagnetic theory, is applicable to this type of problem and possesses great advantages over the method involving the superposition of amplitudes resulting from successive reflections. The computational labors are considerable nevertheless, but it is possible, for design purposes, to calculate the specifications for a desired filter. An early description of this class of filters was given by Sanderson and Ueberall in report H-2731 of the Naval Research Laboratory. Dennison and Hadley also reported on related filters at the January, 1946 meeting of the American Physical Society.

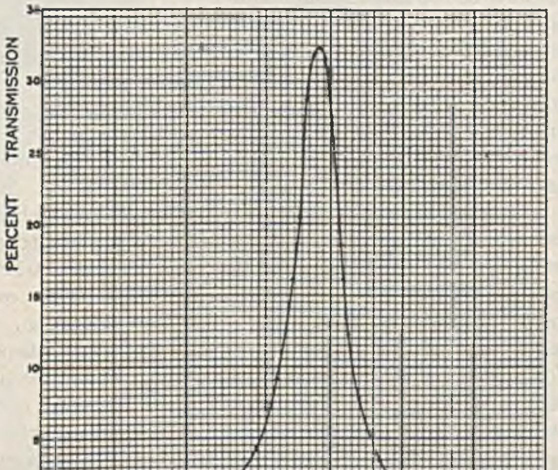


Figure 1

These filters are now made available by Baird Associates of Cambridge, Mass., and the more detailed description which follows describes the types offered by the Farrand Optical Co., Inc., Bronx Blvd. and East 238th St., New York, N. Y.

A typical transmission characteristic of a narrow band interference type filter by Farrand is shown in Figure 1. Some general properties of these filters in parallel light are:

Maximum transmission	20 to 30%
Half width	15 to 20 mμ
Tolerance on wave length for maximum transmission	±10 mμ

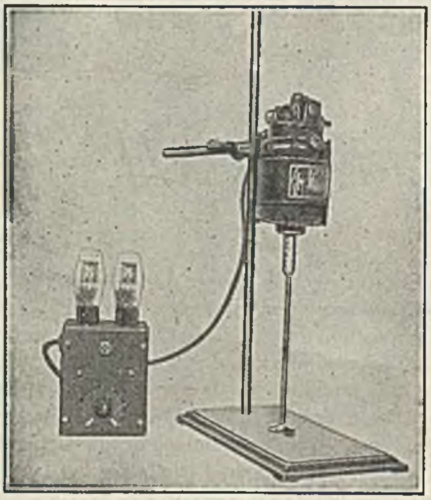
Wave length for maximum transmission is constant over the surface of the filter to within ±3 mμ for a filter of 50-mm. diameter. The peak wave length may be adjusted by rotating the filter around an axis normal to the incident beam.

Individual filters and sets of filters are offered by Farrand in the visual region between 400 and 700 mμ within tolerances of ±10 mμ at peak transmission and 15 to 20 mμ band width at half transmission. These are 50 mm. square, although others are made to special order, and are available at peak wave lengths of 400, 425, 450, 475, 500, 525, 550, 575, 600, 625, 650, 675, and 700 millimicrons. The filters are permanent to normal atmospheric conditions. One interesting property inherent in this class of filter is the fact that excessive heating of the filter is unlikely because radiation which is not transmitted is reflected and not absorbed.

Figure 2 illustrates typical spectral transmission curves for the visible region. Analysts will await with interest the announcement promised by Farrand of other interference filters for the ultraviolet and infrared. These will be concerned with peak transmission under 400 mμ, and in the near infrared from 700 mμ to 2.0 microns and the infrared from 2 to 30 microns.

The instrument designer is provided with a powerful tool by the advent of these filters. Their cost is considerably greater than the crude absorption filters but is far below that of instrumental means for achieving comparable selectivity. In addition, it may be expected that their use with extended sources of radiation will greatly simplify the radiometric and amplifier problems associated with optical measurements.

Particular interest attaches to the promised filters for the ultraviolet and infrared. In the case of the latter we may be provided with a promising alternative to the Pfund technique in which a differential infrared analyzer is sensitized to a given constituent by employing it as a filter in the heterogeneous beam of radiation.



Instrumentation

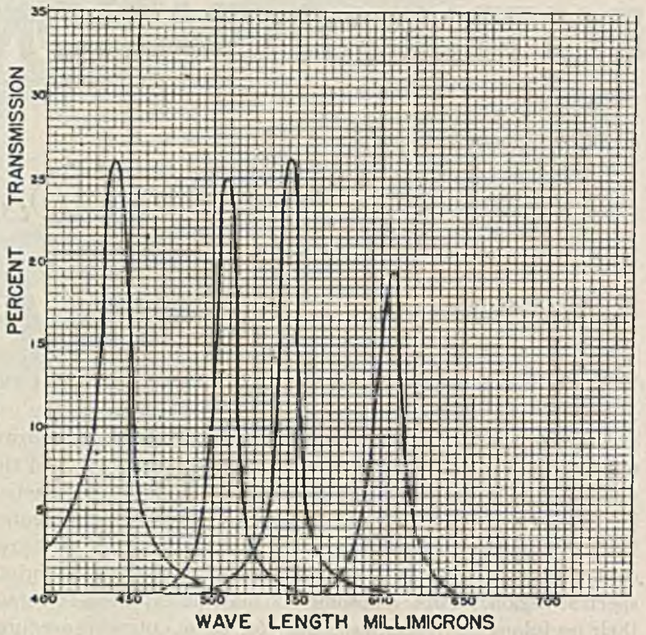


Figure 2

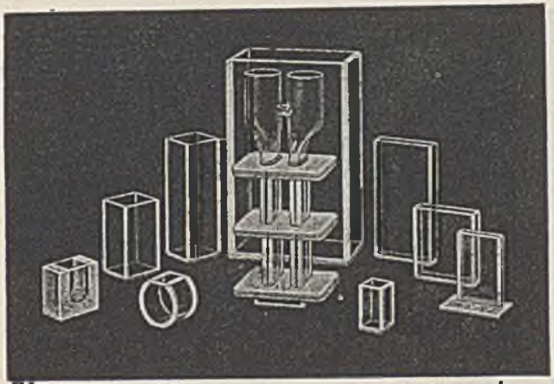
It is an interesting commentary on the interrelation of various techniques to note how the methods for film evaporation and deposition of semitransparent layers have brought an old optical principle to a new and useful application.

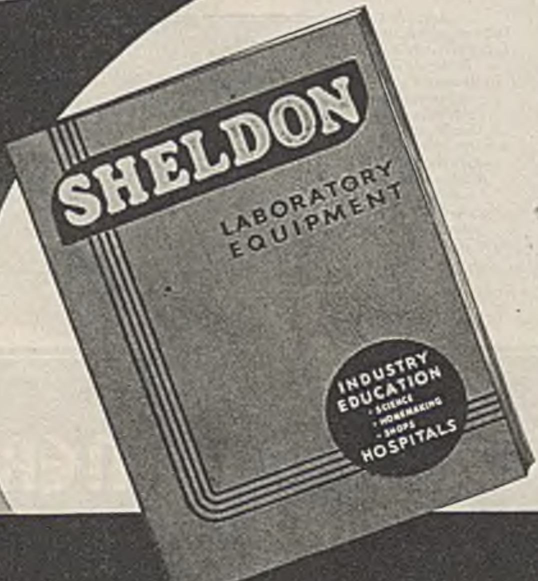
Phototubes

In any photometric problem, increased spectral resolution imposes greater demands upon the means for measuring the radiation. Photomultiplier tubes have found increasing application in a number of instruments, and several types are available, among them RCA 931-A, 1P21, 1P22, 1P28.

The inordinate sensitivity of these tubes simplifies or eliminates the need for subsequent amplification and therefore compensates somewhat for their need of a high voltage supply. Circuits have been described for the stabilization of photomultiplier tubes against line voltage variations and light source fluctuations ("Experimental Electronics", Müller, Garman, and Droz, pp. 74–8, New York, Prentice-Hall, 1942). More recent developments have shown how special requirements can be met including logarithmic response. Two important papers by M. H. Sweet (*Electronics*, March, 1945, p. 102 and Nov., 1946, p. 105) describe several useful procedures for obtaining stable and reliable performance from these tubes. The earlier of these papers describes a compact battery source for the potentials on the dynodes, and the later one some very useful means for improving voltage stabilization by gas-regulator tubes.

A new phototube has been announced by RCA which is not concerned with high sensitivity, but by its special attributes opens up some entirely new fields of application. The RCA-1P42 is a tiny high-vacuum phototube designed particularly for control purposes where space limitation is a prime consideration. It is designed for "end-on" illumination, and the semitransparent cathode surface on the glass window at the large end of the tube is sensitive primarily in the blue region of the spectrum and has negligible sensitivity to the infrared. A few of the characteristics are: dimensions $1^3/_8$ inches by $^1/_4$ inch in diameter; sensitivity 25 microamperes/lumen, d.c. load resistance, 1 megohm. Further details of this tube may be obtained from RCA Commercial Engineering, Section D-6K, Harrison, N. J.

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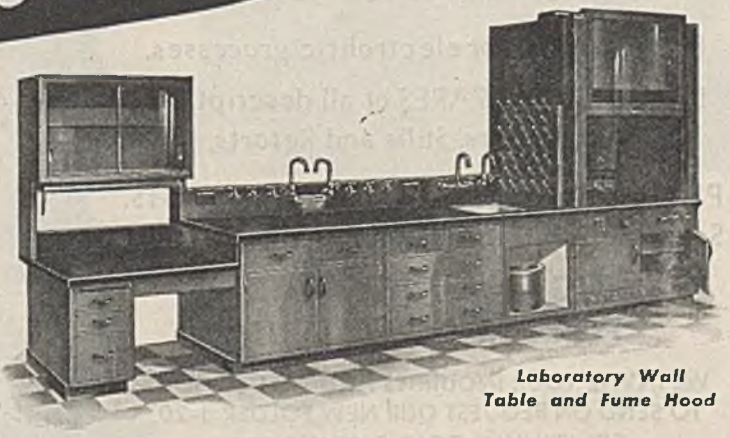

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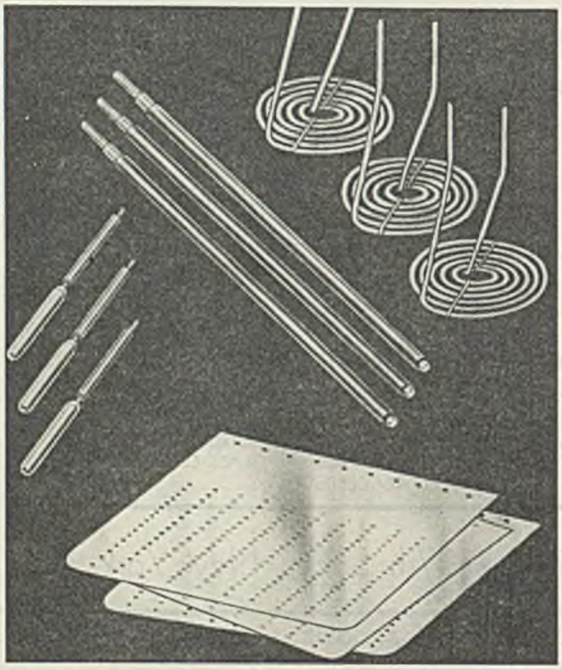

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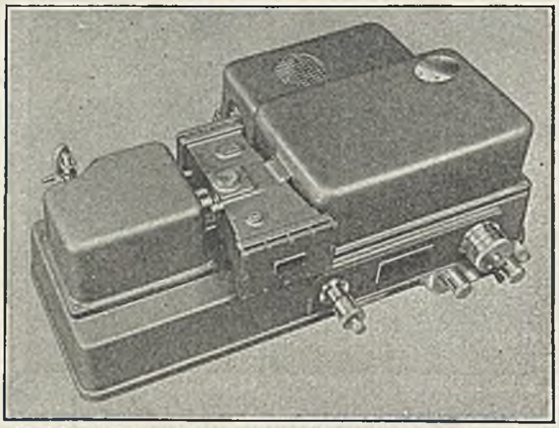

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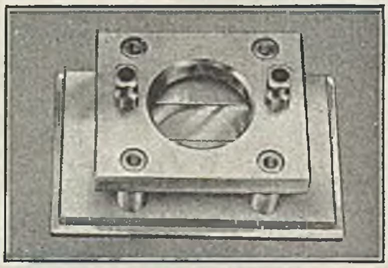

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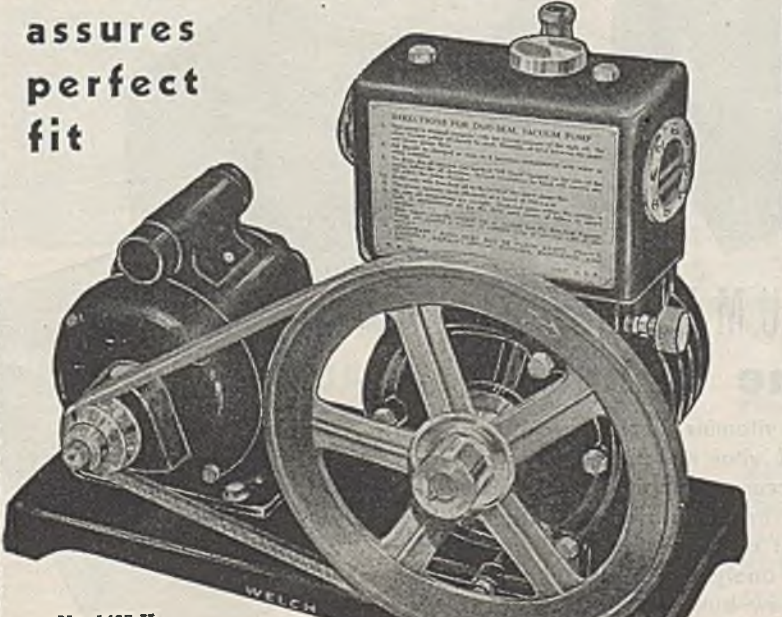
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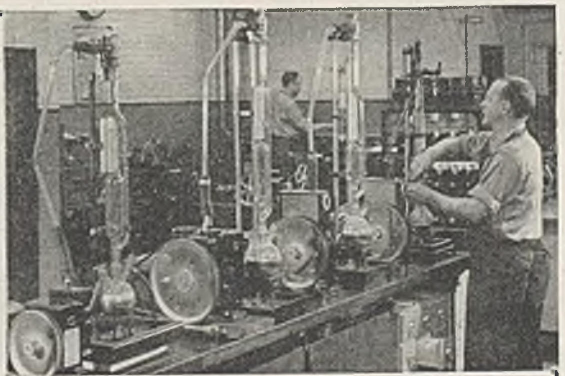


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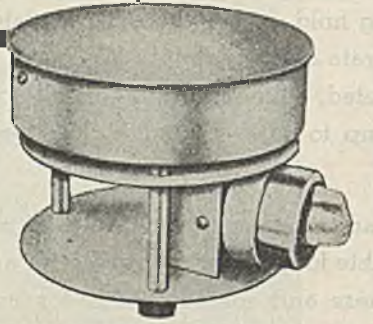


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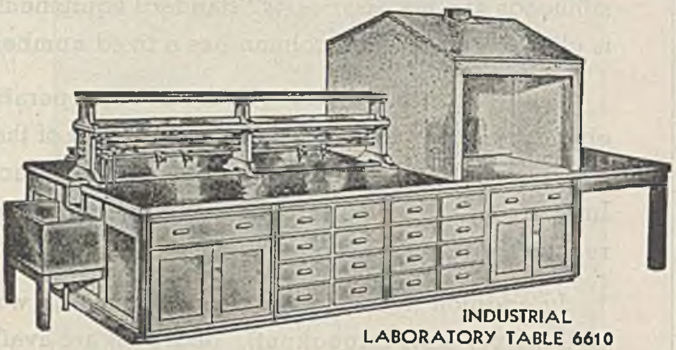

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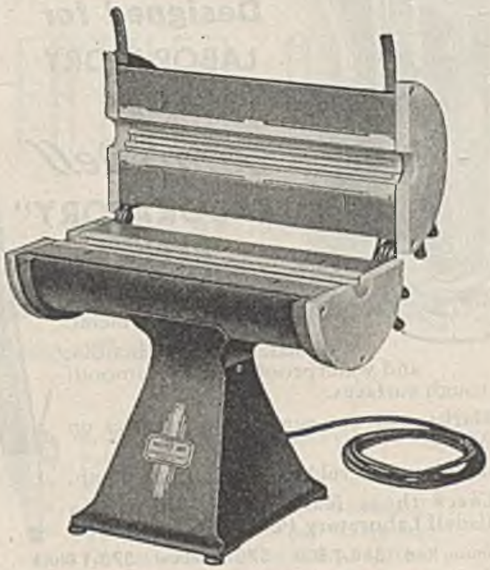

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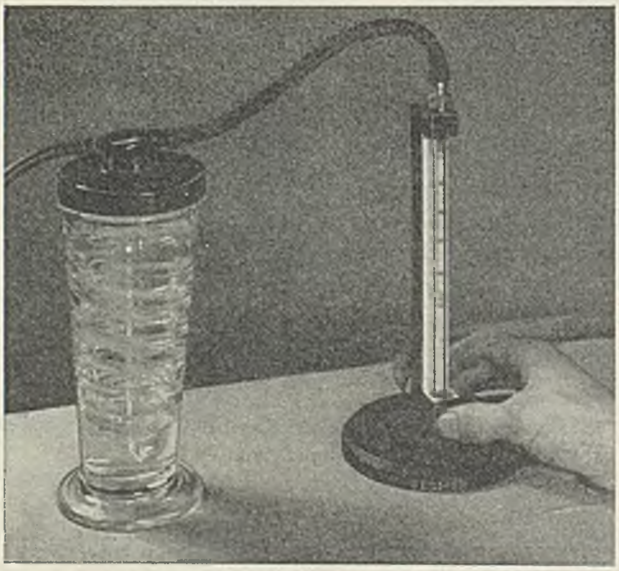

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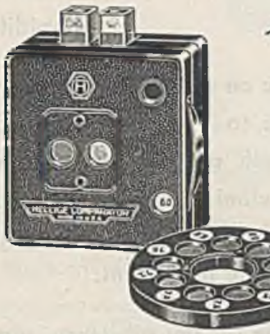

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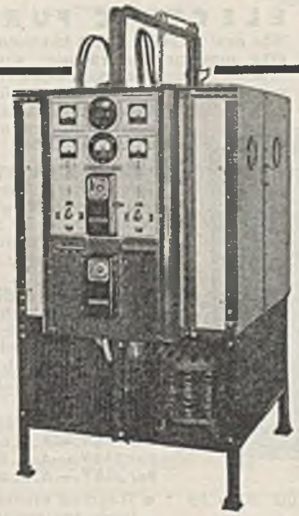

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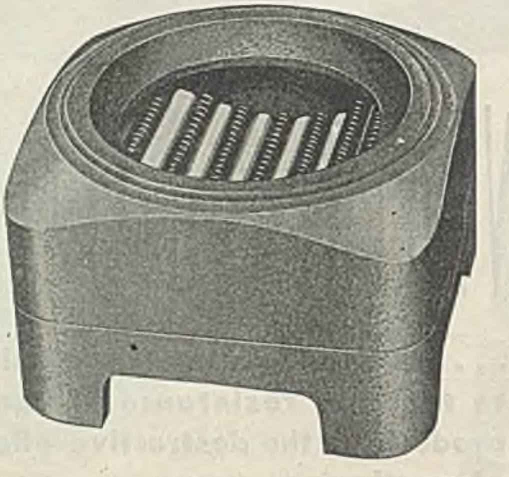

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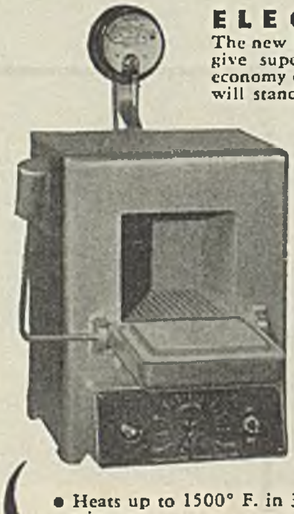

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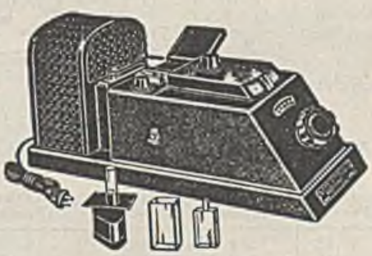

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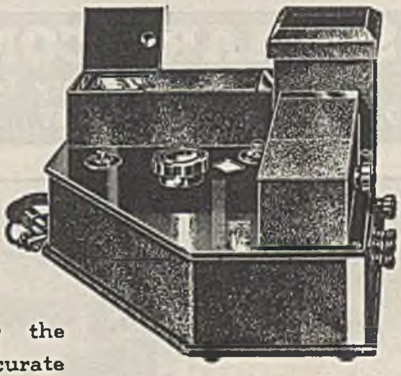

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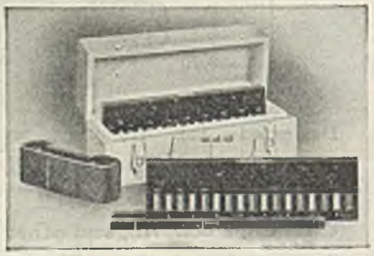


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