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ANALYTICAL EDITION

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Radioactive Studies

MICROCHEMISTRY

NOTES ON ANALYTICAL PROCEDURES

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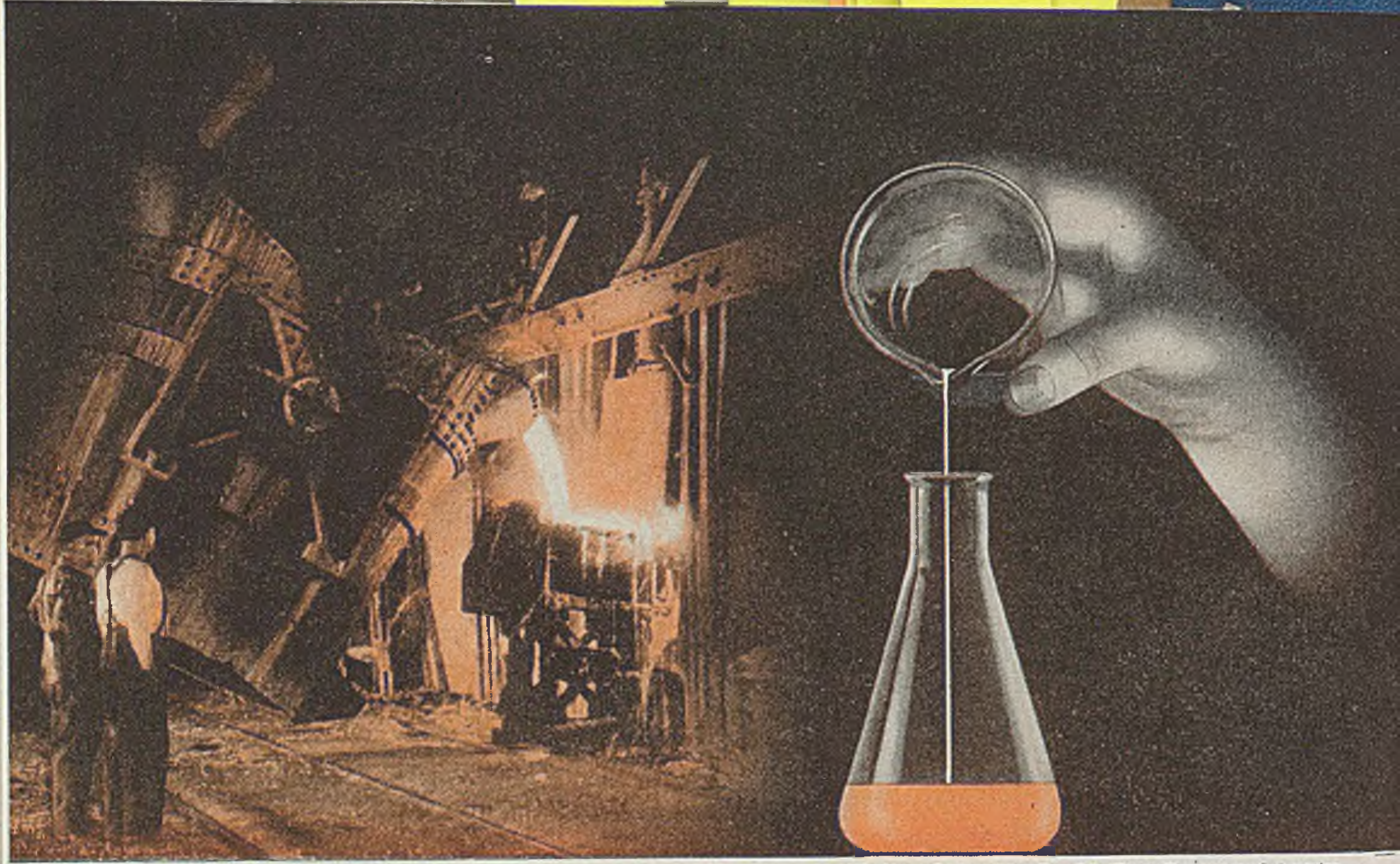

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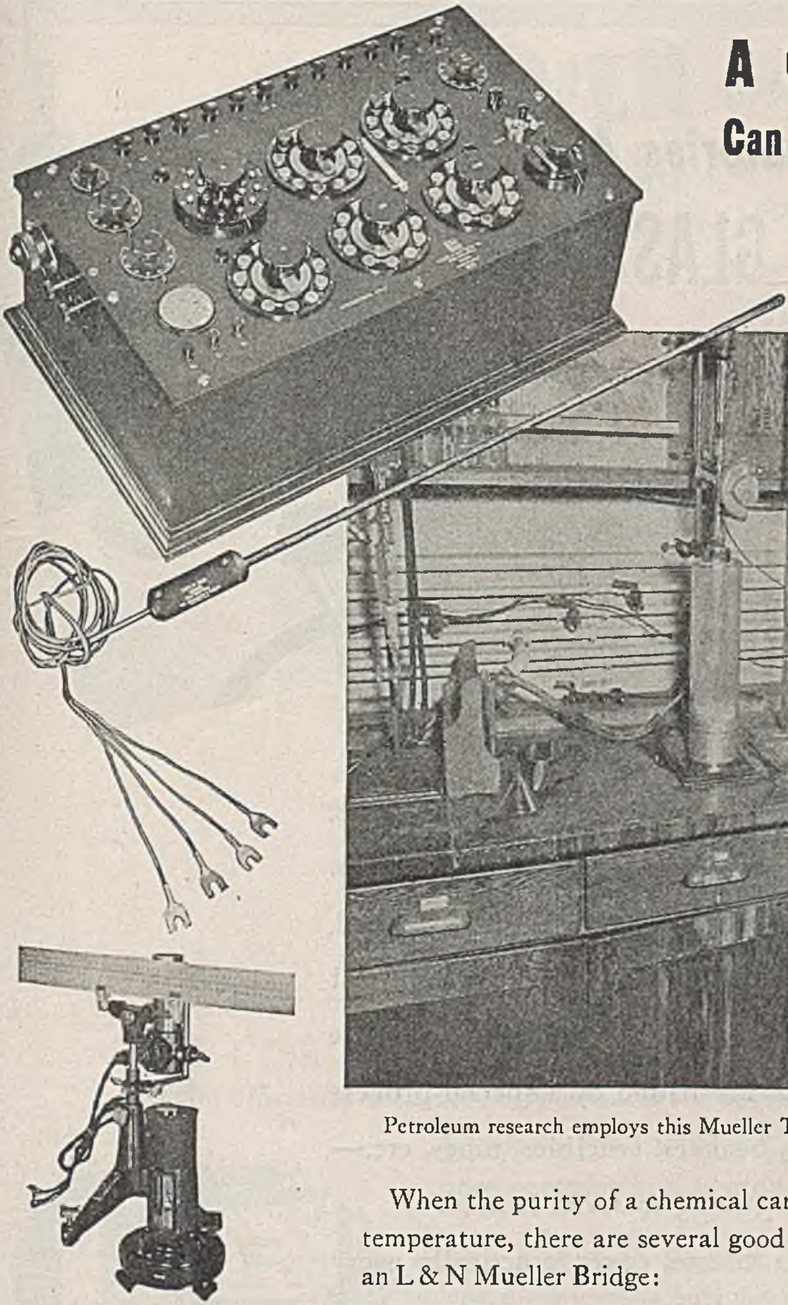

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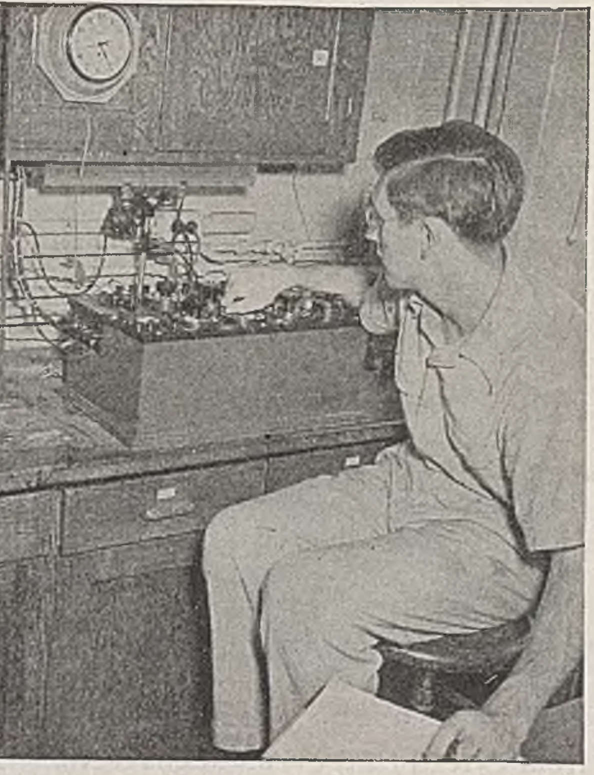

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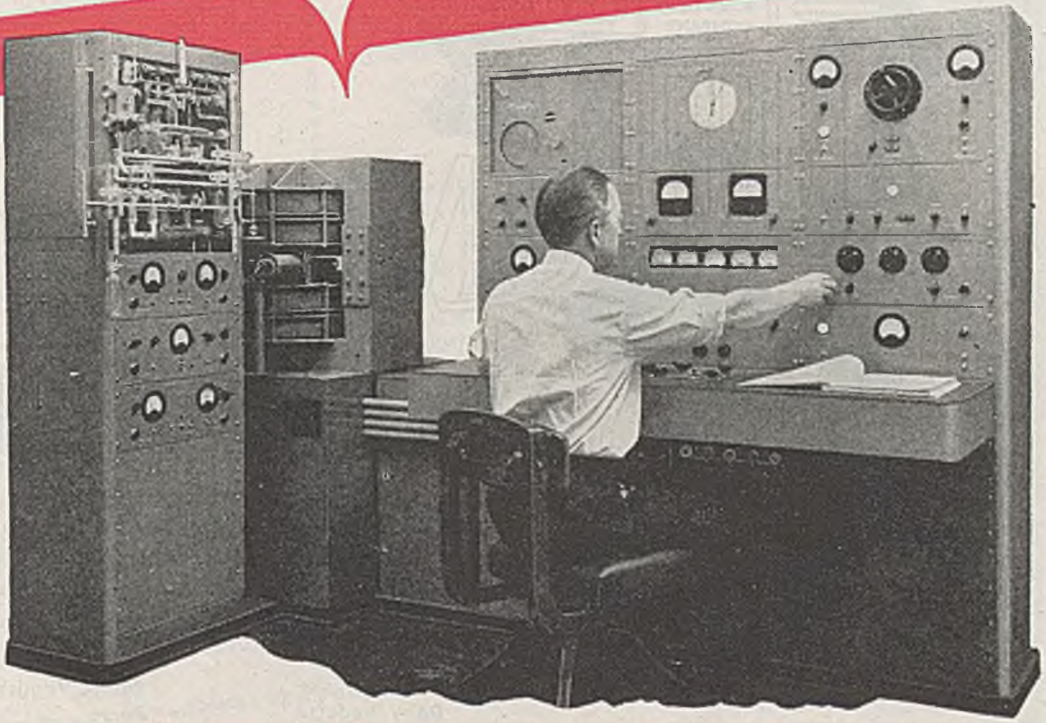

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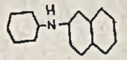

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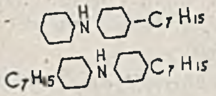

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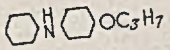

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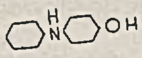

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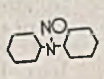

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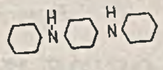

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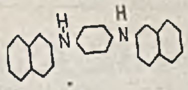

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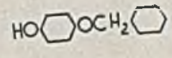

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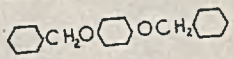

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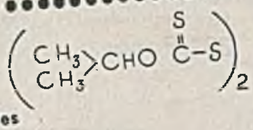

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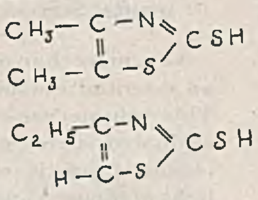

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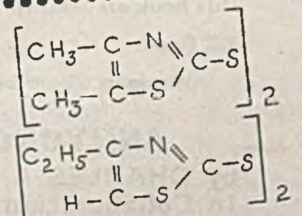

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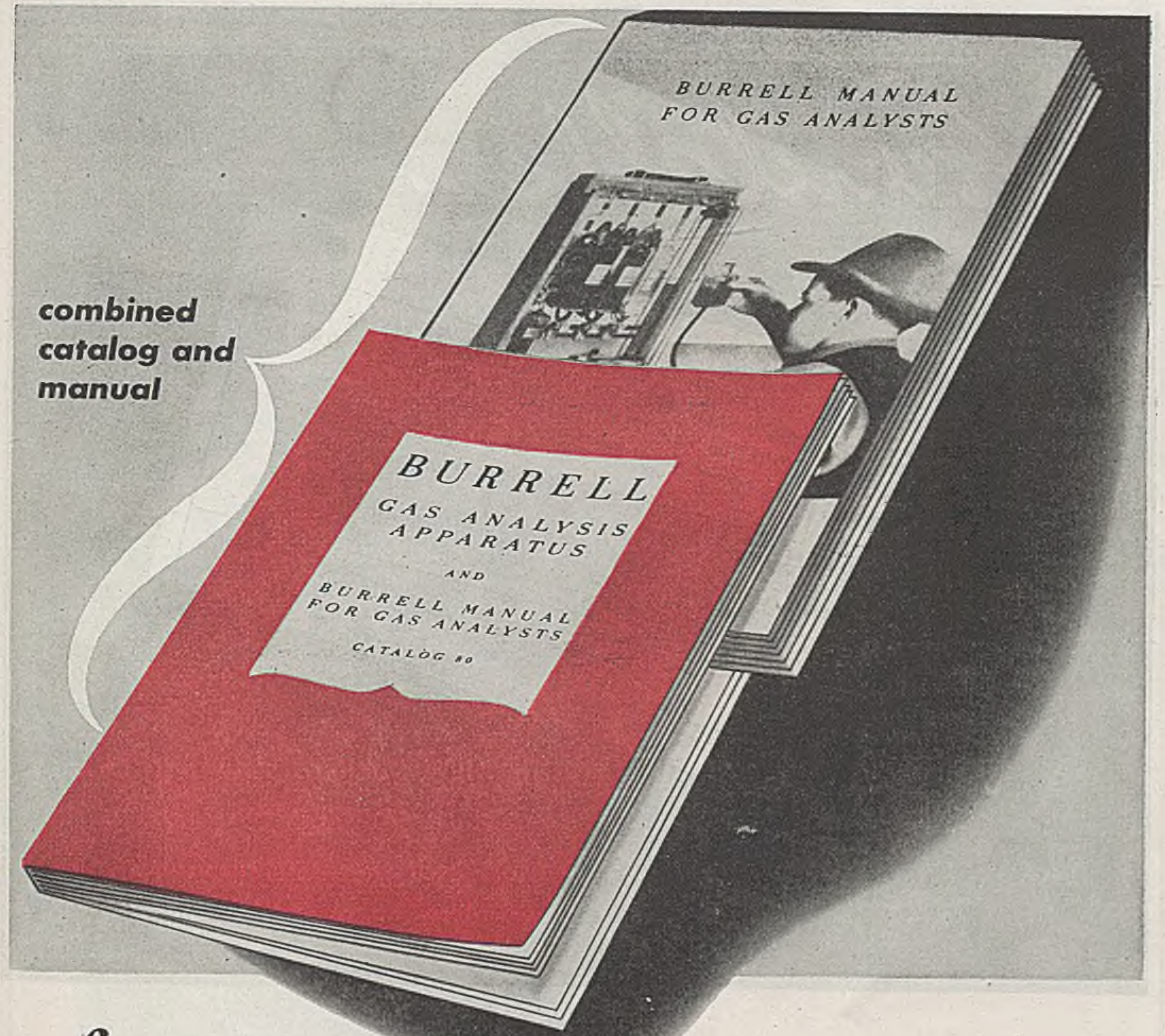
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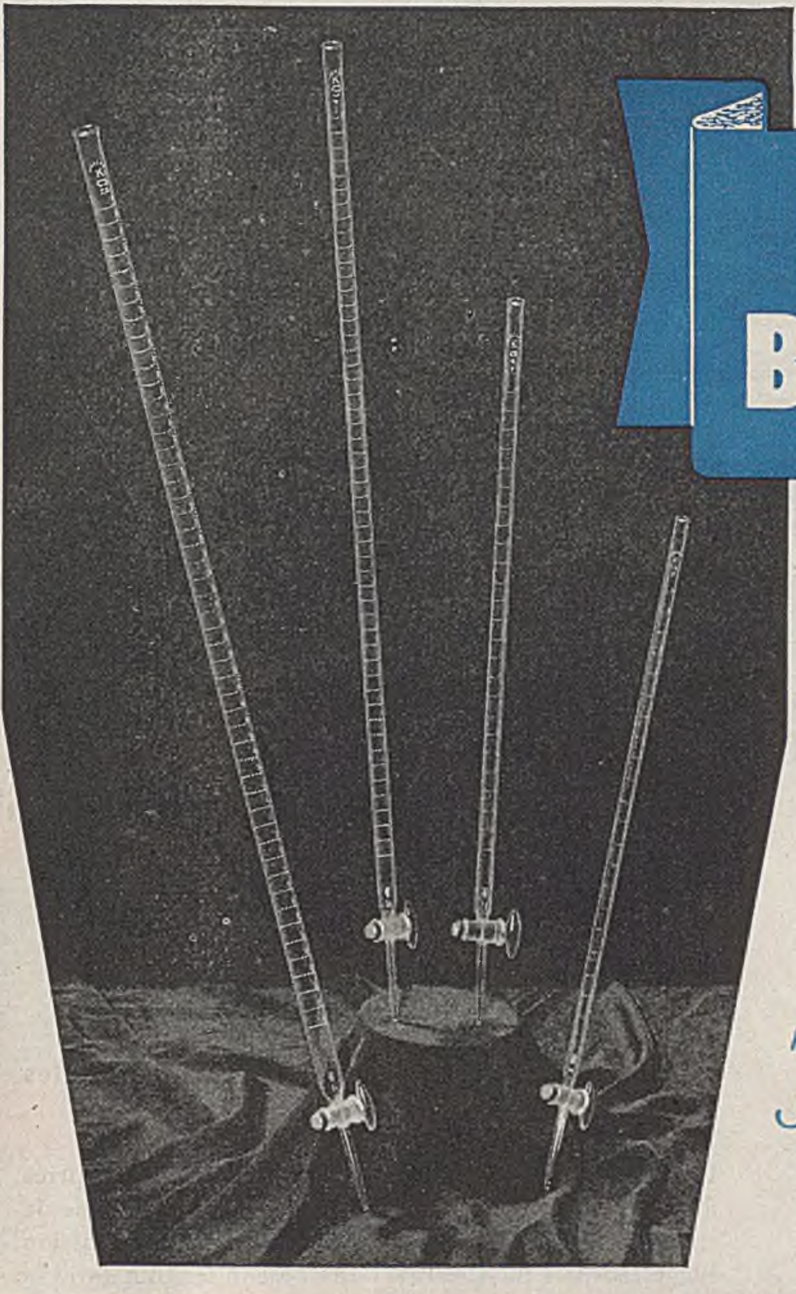

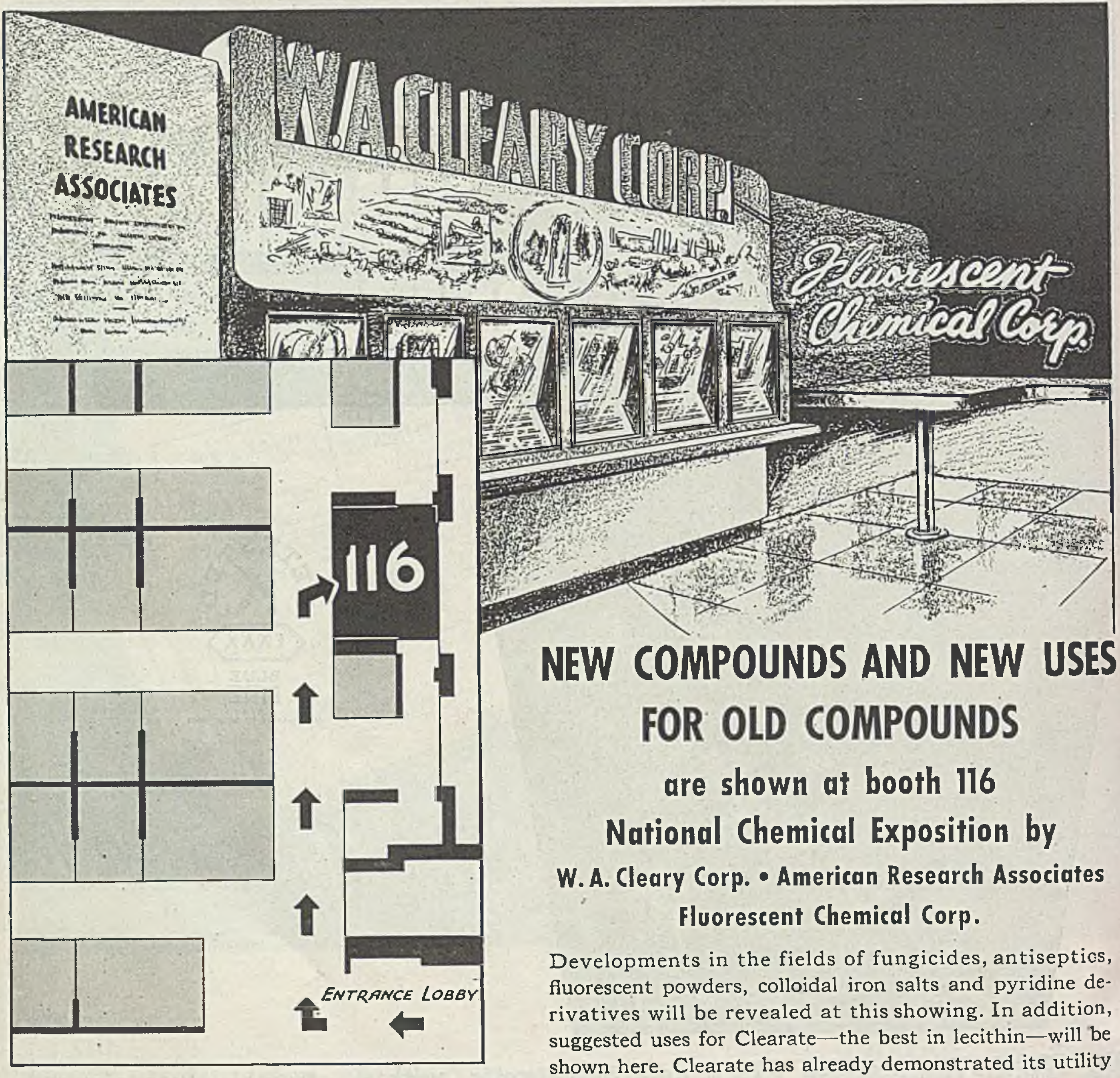

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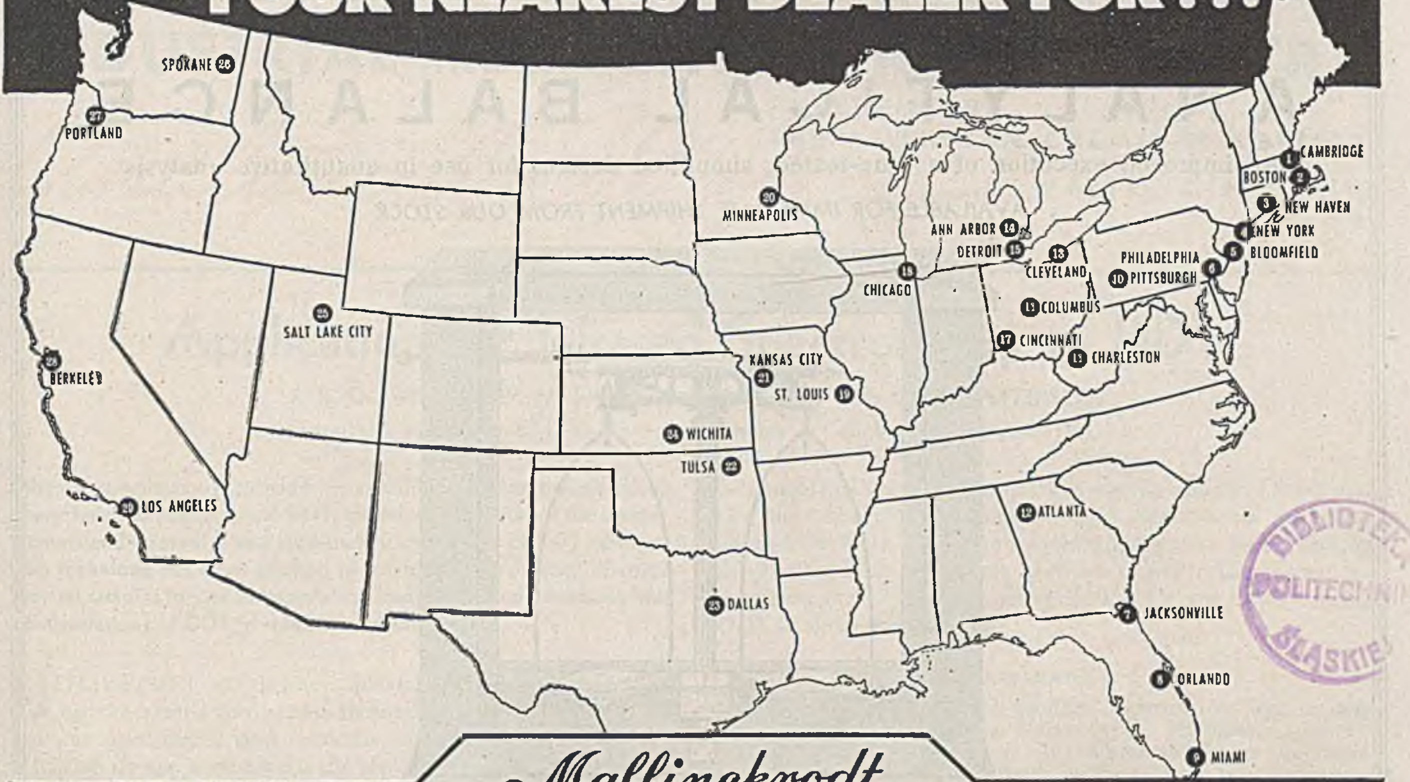

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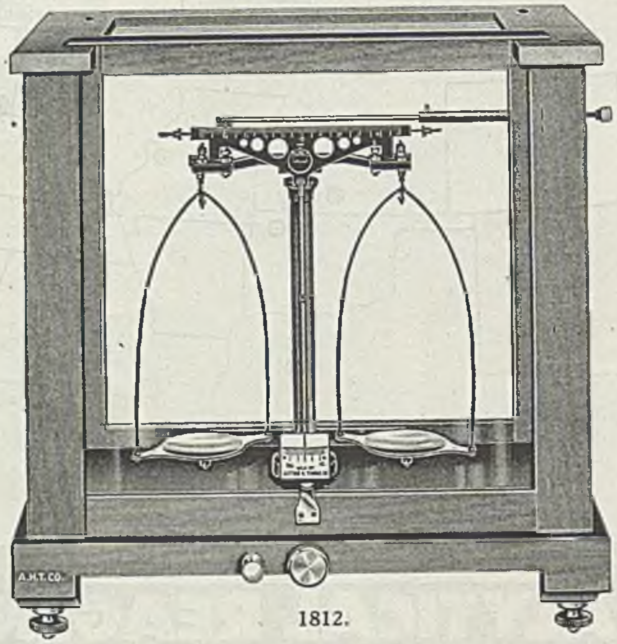

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Applications of Infrared Spectroscopy to DDT

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Infrared spectroscopy provides a valuable tool for the chemical characterization of technical DDT, including detection of the several isomers and impurities and quantitative estimation of DDT content. This technique has been applied in establishing the purity of commercial samples for use in formulation studies and in determining low concentrations of DDT in residues and dispersions.

UTILIZATION of dichlorodiphenyltrichloroethane (DDT) by the armed forces and increasing interest in potential postwar agricultural and domestic applications have focused attention on new methods for the identification and quantitative estimation of DDT. Various analytical methods have been devised for the quantitative determination of *p,p'*-DDT together with its isomers. Winter (*10*), Hall *et al.* (*5*), and Fahey (*3*) have employed methods of analysis depending upon the determination of halogens in organic compounds. Neal *et al.* (*7*) and Gunther (*4*) have described methods for determining DDT based upon dehydrohalogenation with alcoholic alkali and determination of the resulting HCl. Colorimetric methods have been reported by Schechter *et al.* (*8, 9*) and Bailes (*1*). Cristol, Hayes, and Haller (*2*) have described a method for the determination of *p,p'*-DDT in technical DDT by recrystallization from saturated solutions of pure *p,p'*-DDT in aqueous ethanol.

Such methods are very useful but there is still a recognized need for a technique which will identify the several isomers of DDT and avoid complications arising when DDT is associated with other chlorine-containing compounds.

The term DDT is employed here in accordance with terminology in common usage in current literature publications: "The symbol 'DDT' is a contraction for dichloro-diphenyl-trichloroethane, the generic name of the active insecticidal principle. Theoretically there are forty-five possible dichlorodiphenyltrichloroethanes. However, the term 'DDT' is confined to the product obtained on condensation of chloral (or its alcoholate or hydrate) with chlorobenzene in the presence of sulfuric acid" (*6*). When referring to specific isomers of DDT, for example, *p,p'*-DDT is used to designate 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)-ethane and *o,p'*-DDT for 1,1,1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane.

In this laboratory, absorption spectroscopy has been successfully applied to the chemical characterization of DDT in connection with the development of special formulations for use by the armed forces. It has been shown that infrared spectroscopy provides a means of determining both the purity of DDT and the presence of relative proportions of the isomers and impurities which may occur along with *p,p'*-DDT.

It is well known that certain chemical structural units possess characteristic, isolated, infrared absorption frequencies. By study of reference samples of DDT and selected isomers, absorption bands may be assigned to the DDT molecule and to the isomers and by-products associated with commercial DDT. Critical examination of the absorption spectrum makes it possible to determine qualitatively the purity of a given sample of DDT and also the nature of the impurities. A quantitative analytical method for DDT purity and concentration may be devised on this basis. Both procedures have been used in the current research for characterizing commercial DDT's and for estimating DDT in spray compositions.

APPARATUS

The infrared spectrograph used in this work was built in 1940 in the physics shops of the University of Michigan under the supervision of H. M. Randall. It is a rock salt prism spectrometer of conventional optical design, using a 15-cm. rock salt prism and an off-axis parabolic mirror of 1-meter focal length. A record of per cent transmission versus wave length is recorded directly by means of a periscopic beam-splitting device and a recording potentiometer.

The spectrograph is calibrated in terms of wave lengths by running the spectra of standard substances such as ammonia (Figure 1), carbon dioxide, and water vapor. The instrumental quality permits a precision in measuring wave lengths of absorption bands of ±0.01 micron or better, although the practical accuracy in assigning wave lengths in routine work is usually not greater than ±0.1 micron. All wave lengths except those in Figure 1 are therefore expressed in the nearest 0.1 micron.

In studying DDT, carbon disulfide was used as the solvent. Rock salt cells, 5 or 20 mils thick, were used to hold the DDT solutions.

The volume of DDT solution prepared was usually about 5.0 ml., but less than 0.2 ml. is required to fill the absorption cell. The infrared absorption spectrum can be obtained from as little as 1 mg. of DDT if the volume of the solution is restricted to 0.2 ml.

About 45 minutes are required to record the complete spectrum over the range 1 to 15 microns. If only the range 7 to 12 microns is examined, a record can be made in about 10 minutes.

SOURCE OF REFERENCE COMPOUNDS

PURE *p,p'*-DDT (m.p. 108.6–109.5° C. corrected). U. S. Public Health Service; a sample purified by Merck & Co. for the Insect Control Committee of the Office of Scientific Research and Development.

o,p'-DDT (m.p. 73–74° C.). Grasselli Chemicals Department, E. I. du Pont de Nemours & Company, Cleveland, Ohio.

m,p'-DDT (liquid at room temperature). Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Beltsville, Md.; a sample furnished by M. S. Newman, Ohio State University.

1,1-DICHLORO-2,2-BIS(*p*-CHLOROPHENYL)ETHYLENE (m.p. 88–89° C. corrected). Prepared in this laboratory.

BIS(*p*-CHLOROPHENYL)SULFONE (m.p. 148–149° C. corrected). Prepared in this laboratory.

2,2,2-TRICHLORO-1-(*o*-CHLOROPHENYL)ETHYL-*p*-CHLOROBENZENESULFONATE (m.p. 105–106° C.). Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Beltsville, Md.; a sample from P. D. Bartlett, Harvard University.

1,1-DICHLORO-2,2-BIS(*p*-CHLOROPHENYL)ETHANE (*p,p'*-DDD) (m.p. 108–109.5° C.). Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Beltsville, Md.; a sample furnished by H. S. Mosher, Pennsylvania State College.

These reference compounds were studied without purifying to constancy of infrared spectrum.

Table I. Key Infrared Absorption Bands for DDT and Related Materials

Figure	Compound	Wave Length, Microns
1	*p,p'*-DDT	9.1, 9.8, 12.9
2	*o,p'*-DDT	9.6, 13.3
3	*m,p'*-DDT	10.9
4	1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethylene	10.2
5	Bis(*p*-chlorophenyl)sulfone	8.6
6	2,2,2-Trichloro-1-(*o*-chlorophenyl)ethyl-*p*-chlorobenzenesulfonate	8.4, 10.1
11	*p*-Chlorophenyl group	9.0, 9.1
12	*o*-Chlorophenyl group	9.4, 9.6

SPECTROSCOPIC STUDIES OF DDT AND RELATED COMPOUNDS

The characterization of absorption bands by assignment to structural units frequently occurring in commercial DDT was accomplished by the study of a group of reference compounds structurally related to DDT. The spectra of pure *p,p'*-DDT, the *o,p'*- and *m,p'*-isomers, and by-products encountered in commercial DDT are discussed in the following sections. A summary tabulation of key absorption bands for each compound is given in Table I.

PURE *p,p'*-DDT. A sample of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, purified by recrystallization by Merck and Co. and selected by the Insect Control Committee as a comparison standard for purity, was examined spectrographically. The infrared absorption curve from 7 to 14.5 microns is shown by the tracing of the original record in Figure 1. The spectrum of the solvent, carbon disulfide, and the position of the ammonia absorption bands are also included for reference. Intense absorption bands were recorded at 9.1 and 9.8 microns which were later found to be bands common to the DDT isomers and impurities containing a *p*-chloro substituted phenyl grouping. The bands at 9.1 and 9.8 microns were assigned to the *p*-chlorophenyl groups by comparison with *p*-chlorotoluene (Figure 11). A third intense band at 12.9, when resolved at low concentrations, proved to be a doublet.

o,p'-ISOMER OF DDT. The absorption spectrum of 1,1,1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane is shown in Figure 2. In addition to strong absorption bands at 9.1 and 9.8 microns, there is a band of similar intensity at 9.6 which is not present in pure *p,p'*-DDT. This band is assigned to the *o*-chlorophenyl group by comparison with *o*-chlorotoluene (Figure

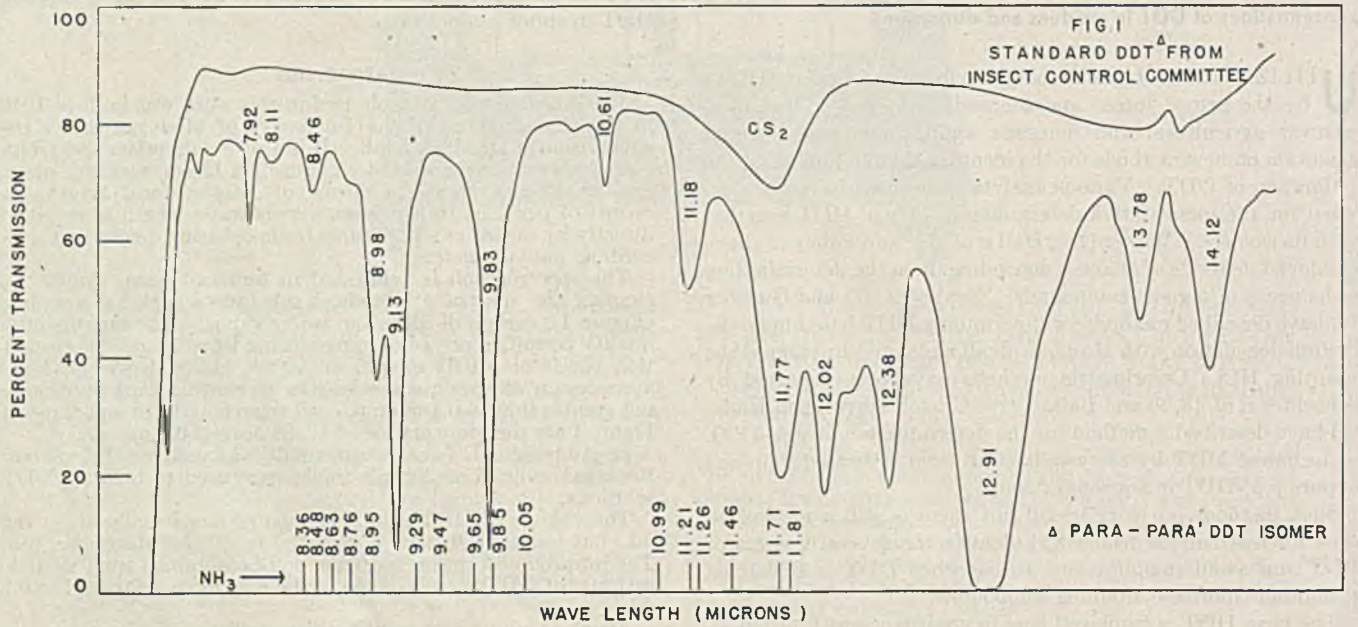
FIG 1
STANDARD DDT^Δ FROM INSECT CONTROL COMMITTEE

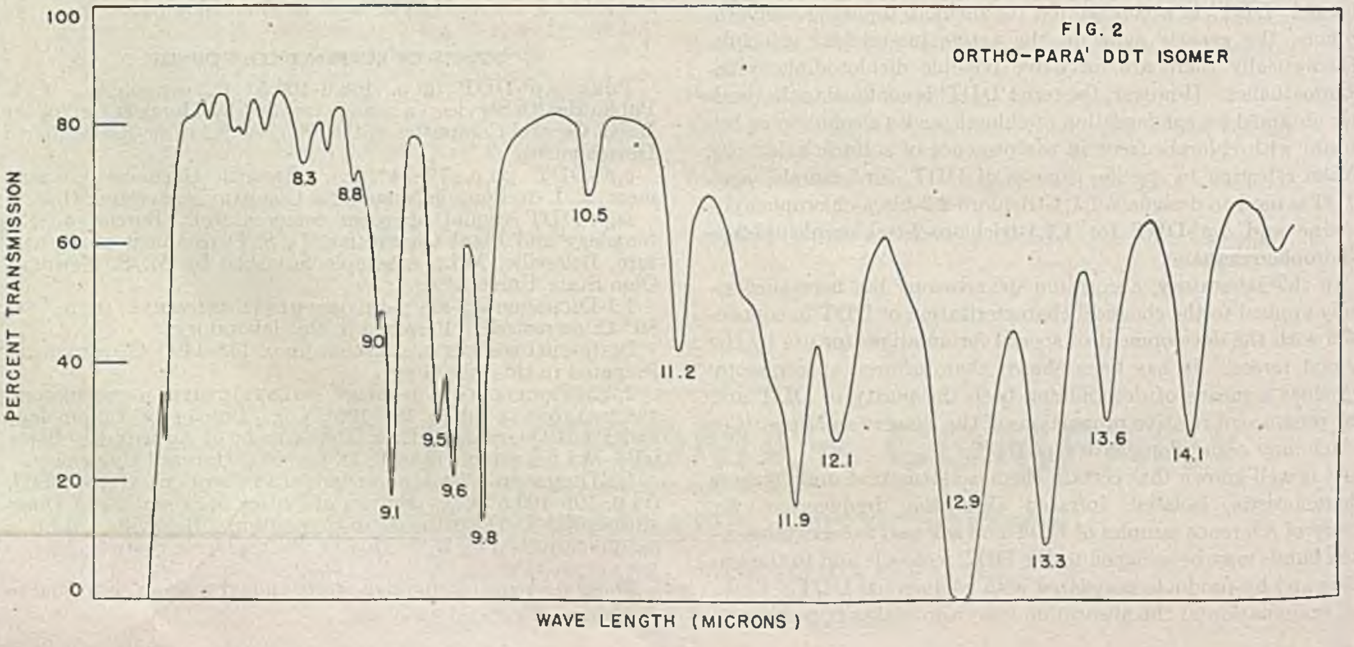
FIG. 2
ORTHO-PARA' DDT ISOMER

12). A strong band at 13.3 microns also characterizes this compound.

m,p'-Isomer of DDT. Strong absorption at 10.9 microns was the outstanding characteristic of 1,1,1-trichloro-2-*m*-chlorophenyl-2-*p*-chlorophenylethane (Figure 3). Major absorption bands for the *p*-chlorophenyl group occurred at 9.1 and 9.8 microns. Bands at 9.6 and 13.3 suggest the presence of some ortho isomer as an impurity in this sample.

Ethylene Analog of DDT. One of the more probable products of degradation of p,p'-DDT is the dehydrohalogenation compound, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene. The infrared absorption spectrum of this material (Figure 4) showed an intense band at 10.2 microns in addition to the bands at 9.1 and 9.8 microns.

Commercial By-products of DDT. An impurity found in commercial DDT which arises as a by-product in the manufacturing process is bis(*p*-chlorophenyl)sulfone. The infrared spectrum of this material (Figure 5) showed intense bands at 7.5 and 8.6 microns and an absorption band of lesser intensity at 7.8 microns. Minima at 9.1 and 9.8 were also present.

The absorption curve of 2,2,2-trichloro-1-(*o*-chlorophenyl)-ethyl-*p*-chlorobenzenesulfonate, another by-product in DDT manufacture, showed minima at 9.1, 9.6, and 9.8 microns (Figure 6). Other absorption bands are at 8.4 and 10.1 microns.

The spectrum of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (p,p'-DDD) was very similar to that of pure p,p'-DDT except for displacements of some of the bands (Figure 7).

BASIS FOR ASSIGNMENTS

The designation of certain strong absorption bands as key absorption bands for the compounds involved was made on the basis of a direct comparison of the spectra of the compounds. The assignment of the band at 9.1 microns to the *p*-chlorophenyl group and the band at 9.6 microns to the *o*-chlorophenyl group is based solely on the spectra of *p*-chlorotoluene and *o*-chlorotoluene. Although these assignments seem reasonable and consistent, they are tentative and should be restricted to the DDT system and not applied to para and ortho configurations generally without further evidence.

SENSITIVITY

The limiting sensitivity of the method to *p*- and *o*-chlorophenyl groups is about 0.5 mole per cent under the conditions used—namely, 1-gram sample in 5 cc. of carbon bisulfide in a 5-mil cell. If higher sensitivity for the determination of o,p'- or p,p'-isomers

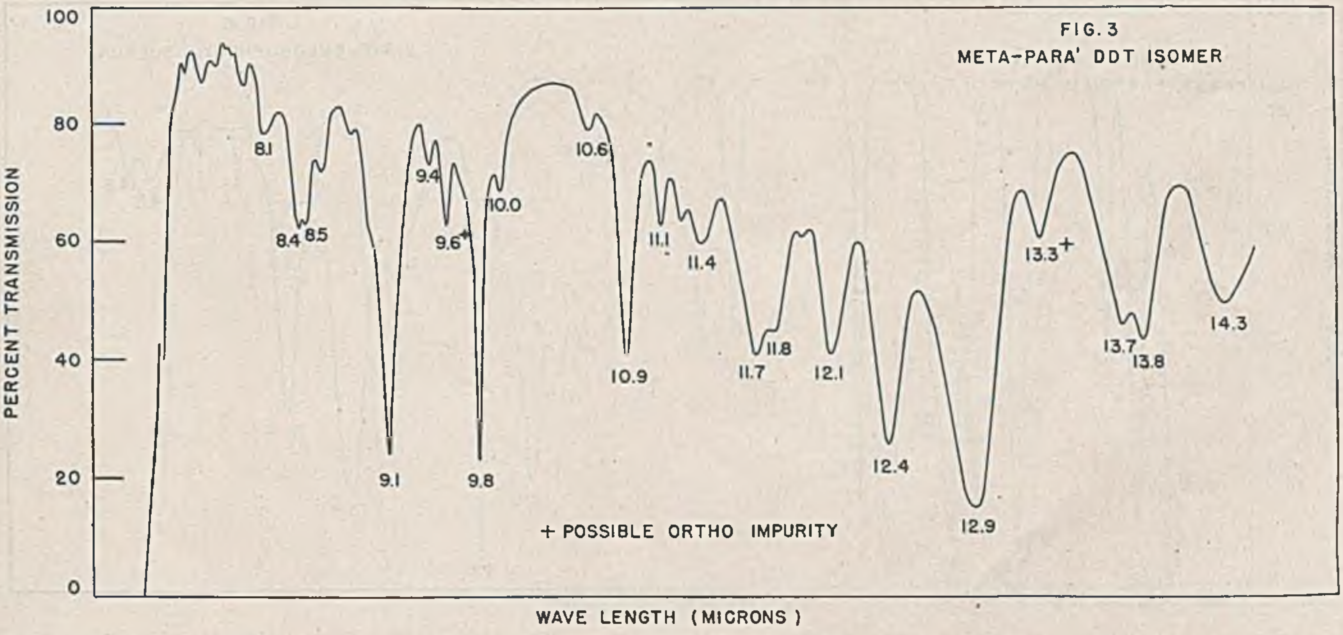
FIG. 3
META-PARA' DDT ISOMER

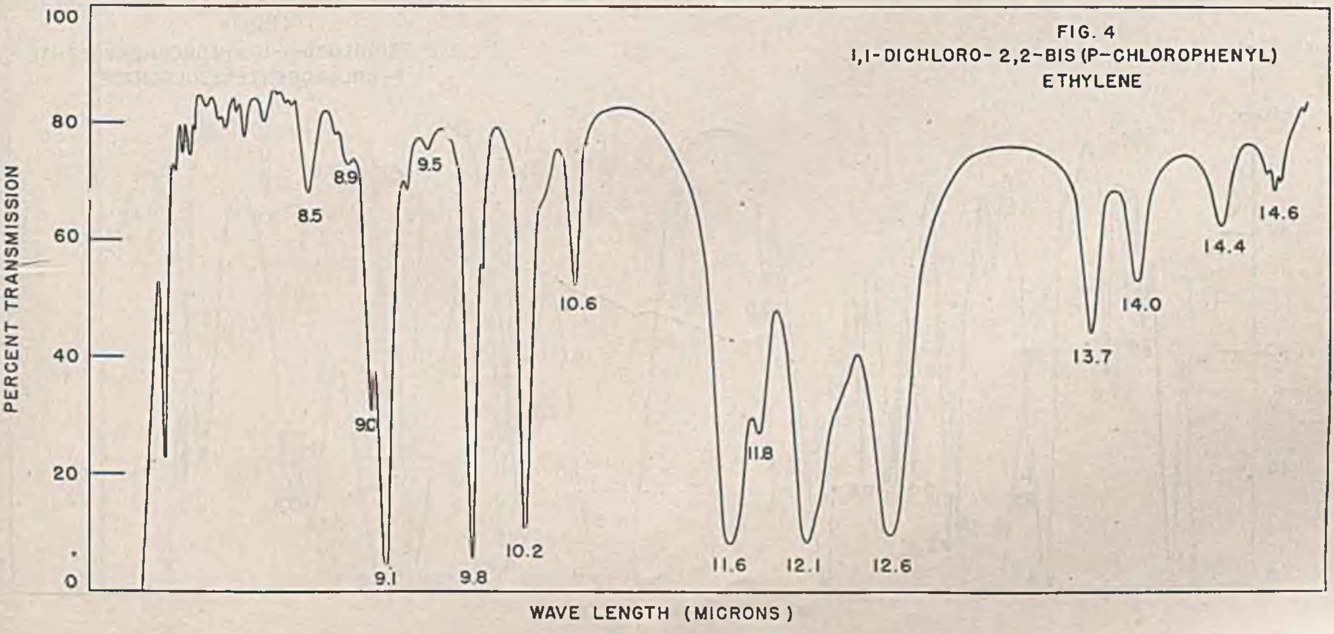
FIG. 4
1,1-DICHLORO-2,2-BIS (P-CHLOROPHENYL) ETHYLENE

is desired, it can readily be attained by using a thicker cell or by using the bands at 12.9 and 13.3 microns.

APPLICATIONS OF INFRARED TECHNIQUE

The practical value of the infrared absorption method for the study of DDT is illustrated by several applications.

The purity of laboratory recrystallized DDT has been confirmed by the use of the infrared absorption technique. Comparison of the spectra of this material and the standard DDT showed by the absence of bands at 9.6 and 13.3 microns that the recrystallized material was free of *o*-isomer (Figure 8).

Two commercial DDT samples of a special grade from the same manufacturer gave melting points of 106–107° and 102.5–104.5° C. The higher melting sample, when subjected to a high-temperature test for caking tendency, stood up under these conditions while the lower melting DDT in the same system failed completely. The question arose as to whether the caking tendency of the latter was due to residual solvent, the presence of which was indicated by strong odor, or to other impurities in the DDT. Spectrographic examination requiring less than 30 minutes showed the presence of the *o,p'*-isomer. The presence of the *o,p'*-isomer in the low melting sample (Figure 10) is shown by definite absorption at 9.6 and 13.3 microns, while the higher melting sample (Figure 9) shows only trace absorption at these wave lengths.

The application of the infrared absorption method of determining qualitatively the purity of DDT was further demonstrated by examination of a group of commercially available DDT samples discussed in the following section. The transmission curves of these samples, on the basis of the absorption bands assigned to the isomers and by-products, indicate the relative prominence of the known impurities.

COMMERCIAL DDT SAMPLES

As an illustration of the applicability of the method in assaying the purity of commercial samples, absorption coefficients taken from the recorded spectra of a number of commercial samples are tabulated in Table II. The isomers and impurities

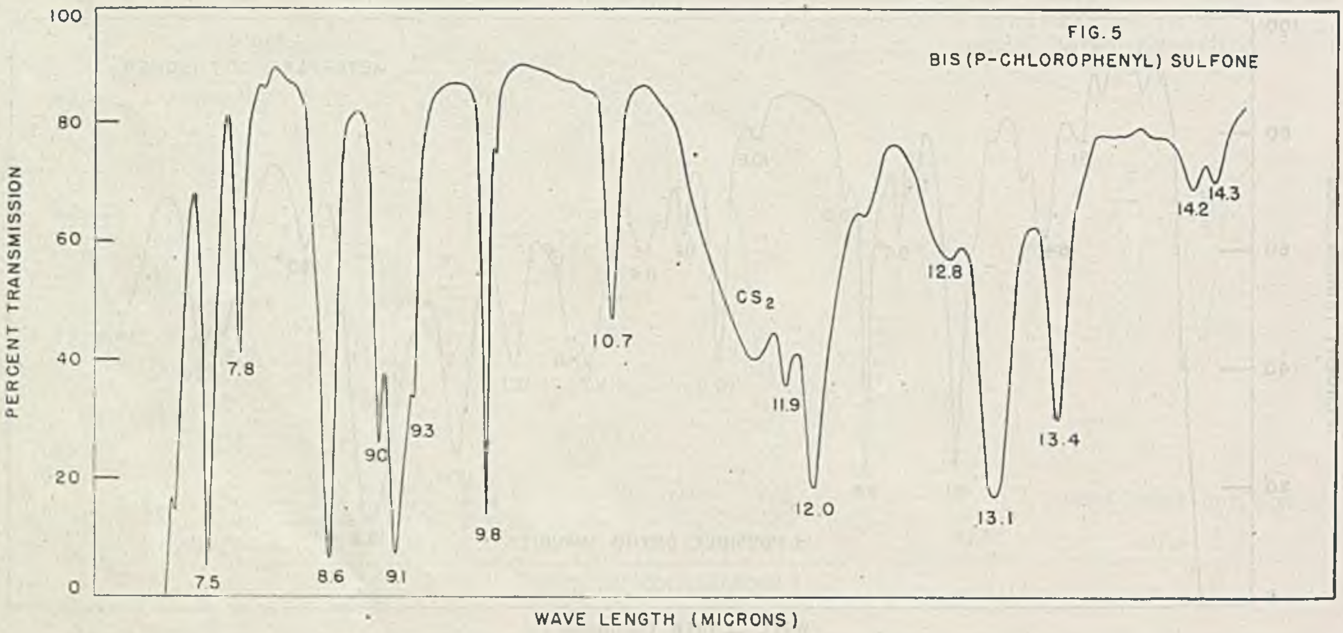
FIG. 5
BIS (P-CHLOROPHENYL) SULFONE

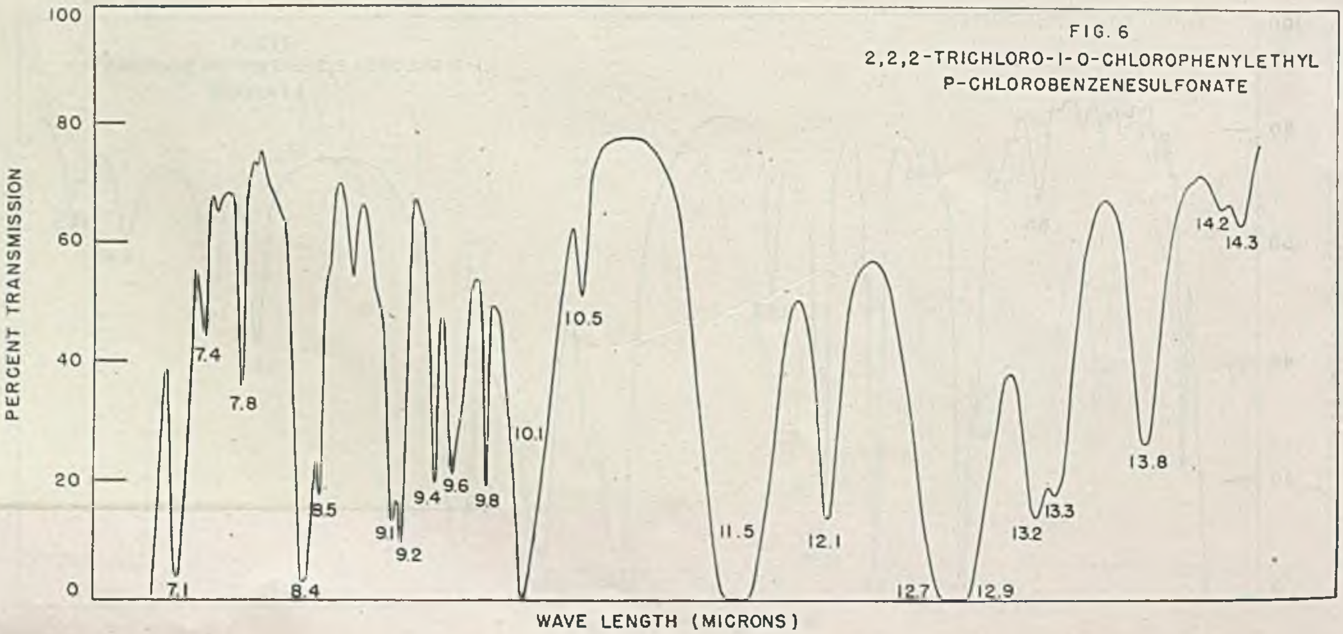
FIG. 6
2,2,2-TRICHLORO-1-O-CHLOROPHENYLETHYL P-CHLOROBENZENESULFONATE

Table II. Absorption Coefficients for Impurities in Commercial Samples of DDT

Sample[a]	o,p'-DDT 9.6	 13.3	2,2,2-Trichloro-1-(o-chlorophenyl)ethyl-p-chlorobenzenesulfonate, 8.4	Bis(p-chlorophenyl)-sulfone, 8.6
A	0.15	..	0.05	0.06
B	0.17	..	0.11	0.01
C	0.15	..	0.09	0.01
D	0.01	..	0.00	0.00
I	0.14	..	0.08	0.02
II	0.14	..	0.09	0.02
IIIA	..	0.04	0.03	0.00
IIIB	0.03	0.20	0.04	0.00
IV	0.15	..	0.09	0.00
V	0.15	..	0.07	0.01
VI	0.06	..	0.06	0.12
VII	0.12	..	0.06	0.03
VIII	0.15	..	0.16	0.02
IX	0.11	..	0.09	0.00
X	0.14	..	0.07	0.02
XI	0.13	..	0.18	0.03

[a] From various manufacturers. D, IIIA, and IIIB are different lots of a special grade from one producer; A and VII, B and V, and C and XI represent pairs from three different producers.

most commonly encountered in technical DDT, in addition to p,p'-DDT, are (1) the o,p-isomer, (2) bis(p-chlorophenyl)sulfone, and (3) 2,2,2-trichloro-1-(o-chlorophenyl)ethyl-p-chlorobenzenesulfonate, with a trace of the m,p'-isomer in some samples.

The absorption coefficient, expressed in Table II as $\log_{10} I_0/I$ where I_0 = transmitted radiation at zero concentration and I = transmitted radiation of the sample at the given wave length, is a linear measure of the concentration of the impurities present and may be calibrated in terms of mole per cent by studying known mixtures.

An examination of these data shows that there are obvious differences, apparent from a qualitative study of the original records, in the relative concentrations of the various impurities in the several samples. For example, samples D and IIIA appear to have the least amounts of the three impurities listed above. Sample XI has a high content of 2,2,2-trichloro-1-(o-chlorophenyl)ethyl-p-chlorobenzenesulfonate, while sample VI is high in bis(p-chlorophenyl)sulfone content. For a finer distinction between samples low in o-isomer, such as IIIA and IIIB, the band at 13.3 microns was used.

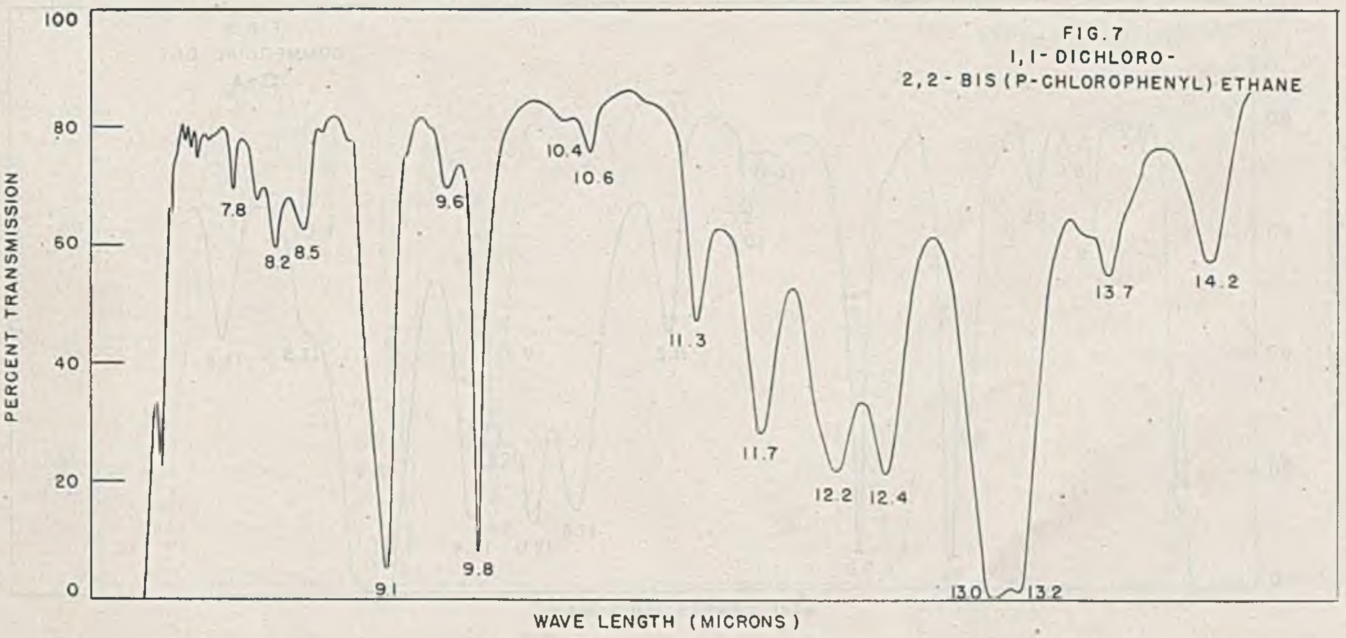

FIG. 7
1,1-DICHLORO-2,2-BIS(P-CHLOROPHENYL) ETHANE

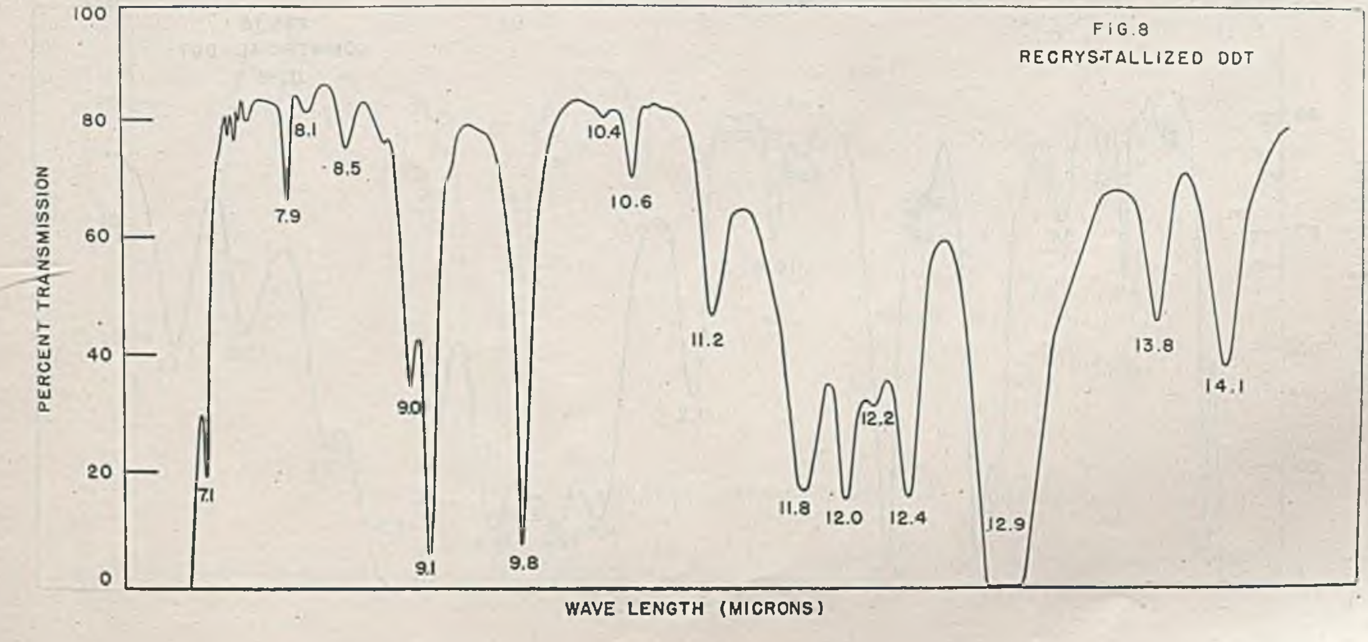

FIG. 8
RECRYSTALLIZED DDT

QUANTITATIVE DETERMINATION OF DDT

Infrared absorption provides the basis for an analytical procedure for determining concentration of DDT, which has the following advantages: (a) rapidity of analysis, results available in less than 30 minutes; (b) analysis of samples too small for gravimetric or volumetric methods; (c) preservation of sample.

The method has been used experimentally in this research in analyzing dilute aqueous suspensions of DDT used in tests against insects. The suspensions were prepared in such a manner that calculation of composition was not possible; the infrared method was therefore utilized. A quantity of suspension sufficient to yield 10 to 100 mg. of DDT was evaporated to dryness. The residue was dissolved in sufficient carbon bisulfide to give a solution containing from 0.2 to 1.2% DDT. The concentration of DDT in the carbon bisulfide was determined accurately by infrared absorption, and from this figure the concentration of DDT in the original water suspension was calculated. It is necessary, of course, in such cases to prepare a standard curve of transmission versus concentration by which transmission of the unknown sample can be related to its concentration.

The same procedure can be used to analyze spray residues recovered from leaf surfaces, fruits, etc. Thus, in this investigation, concentration of residual spray on walls has been determined by washing DDT from the surface and analyzing for DDT spectroscopically. In such cases it is desirable to run a "blank" consisting of the solvent extract of unsprayed surfaces like those being examined to ensure that interfering substances are not being extracted from these surfaces.

In carrying out these analyses, a DDT of predetermined composition was used and its treatment and exposure were such that the composition was not altered. The only object was to learn the amount of such DDT present in a given sample. For such work, the 9.8-micron band was used and only the transmission at this single band was required for analysis of the samples.

A more complicated situation will be met in some cases. DDT of unknown history or material subjected to conditions possibly causing chemical change may be submitted. The quantitative determination of such materials will require more time and results will be less accurate than in the simple case cited above. It is necessary first to obtain the infrared absorption spectrum of the sample in order to determine whether impurities—e.g., isomers, by-products, or degradation products—are present. It has been shown previously that these extraneous materials have characteristic absorption bands. By means of standard transmission versus concentration curves prepared for the extraneous materials, their concentration in a particular sample can be determined. Likewise the total concentration of material showing absorption at 9.8 microns can be measured. The concentration of p,p'-DDT in the sample can be determined by dif-

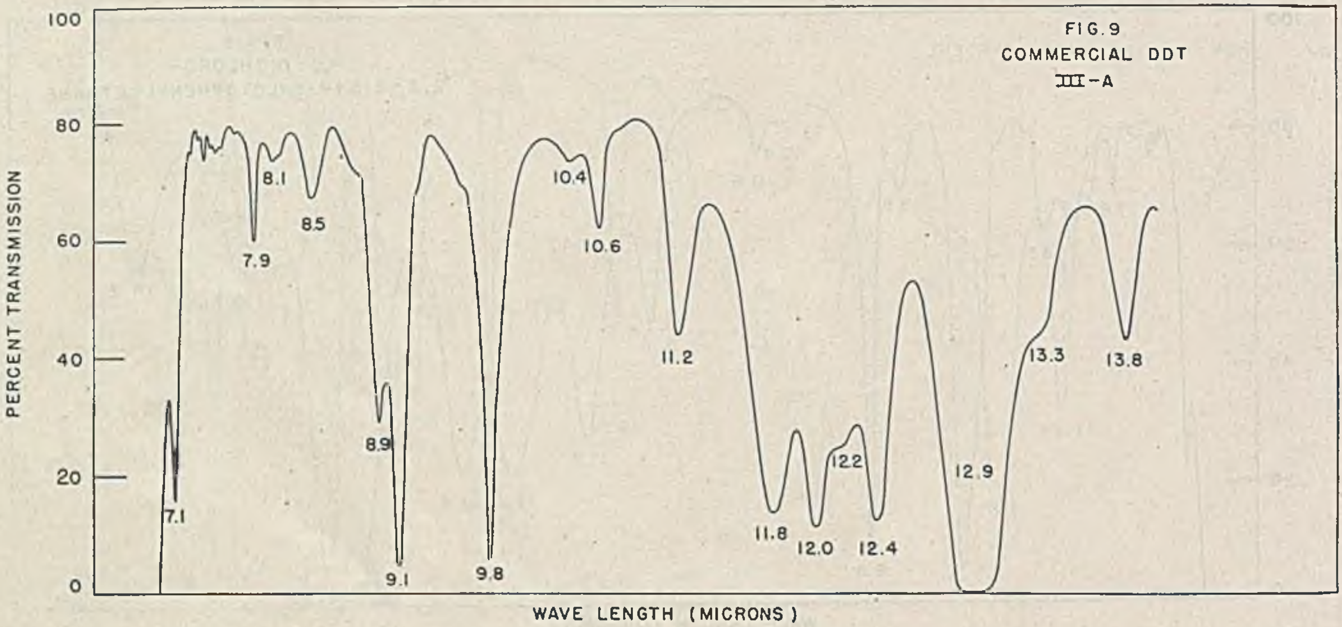
FIG. 9
COMMERCIAL DDT
III-A

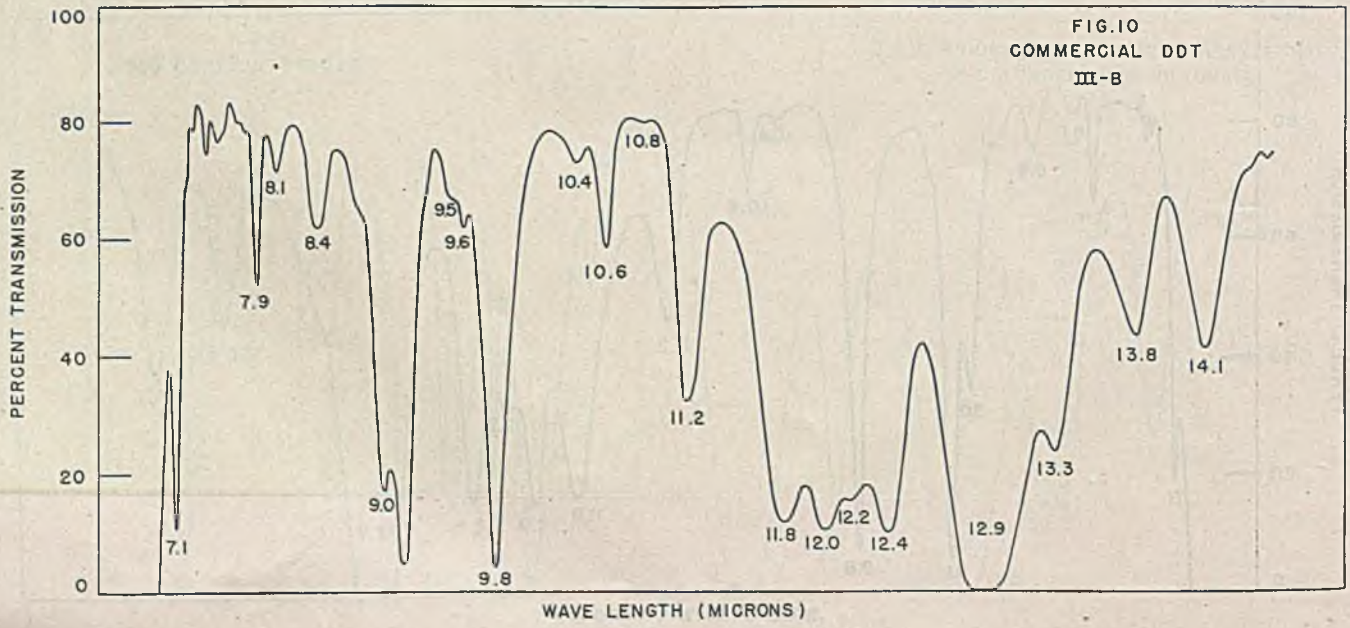
FIG. 10
COMMERCIAL DDT
III-B

ference. The same procedure is useful for determining the proportions of the several isomers in DDT. By use of standard curves prepared from pure samples of the isomers, the concentration of m,p'-DDT or o,p'-DDT in the sample can be measured. The concentration of the p,p'-isomer will then be calculated by difference, using the 9.8-micron band for determining total DDT in the sample.

STATUS

Although methods based on infrared absorption have proved valuable for research purposes in this investigation, their development has not been carried to the point of setting up detailed procedures which can be applied directly in control. It is believed that the basis for development of such procedures has been laid by the work described above.

ACKNOWLEDGMENTS

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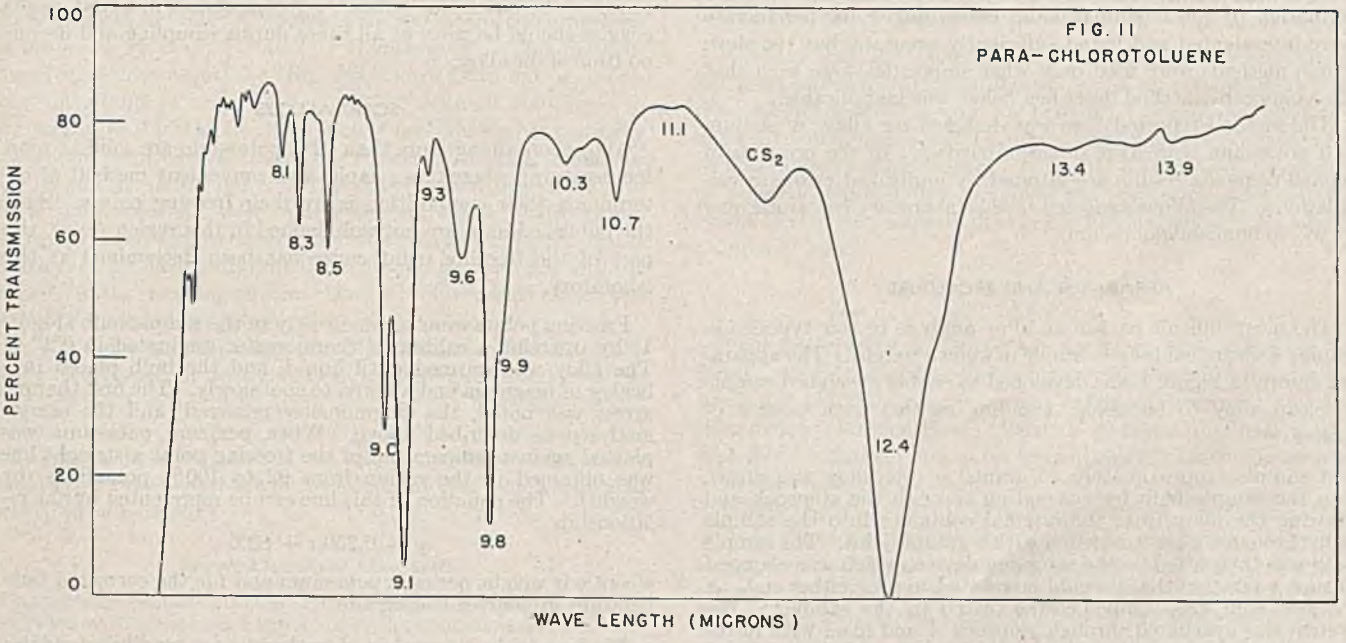
FIG. 11
PARA-CHLOROTOLUENE

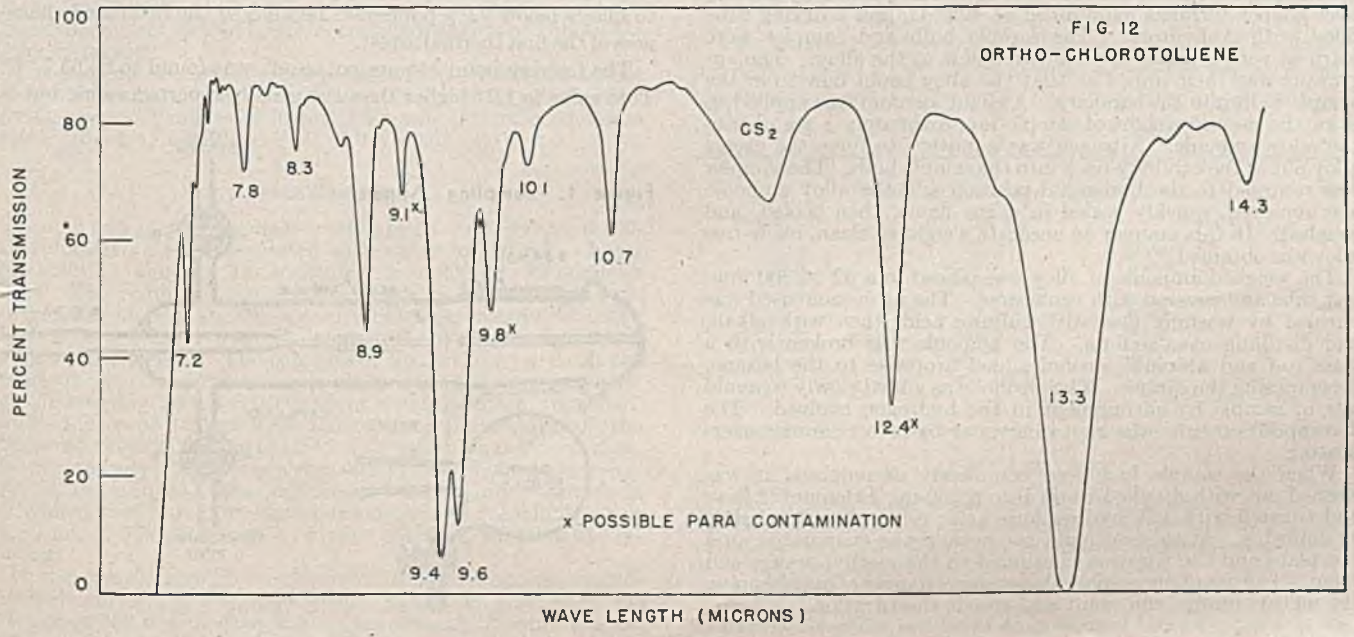
FIG. 12
ORTHO-CHLOROTOLUENE

Routine Analysis of Sodium-Potassium Alloys

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A volumetric method for the determination of potassium in sodium-potassium alloys is described. A sample of the alloy is obtained in an ampoule in such a way that contact with moisture and oxygen is prevented. The sample thus obtained is reacted with absolute alcohol under neohexane and subsequently titrated with standard acid. Alloys of higher than 92% potassium content are solid at room temperature and are analyzed by means of their freezing points. An equation is given for the freezing point curve. Accuracy of ±0.1% potassium is readily obtainable. Liquid alloys can be analyzed in less than 1 hour and solid alloys in about 5 minutes.

IN A problem involving the production of metallic potassium, an urgent need arose for a method of determining potassium when alloyed with sodium, which could be used for routine control analyses. The usual gravimetric methods involving the formation of the chloroplatinate, cobaltinitrite, or perchlorate were investigated and found sufficiently accurate, but too slow. These methods were used only when impurities were such that the volumetric method described below was inapplicable.

The method reported here was designed for alloys of sodium and potassium with little or no impurities. In the presence of foreign elements results are vitiated by multiplied errors in calculations. The alloys analyzed in this laboratory contained over 99.9% sodium and potassium.

APPARATUS AND PROCEDURE

The most difficult part of an alloy analysis of this type is obtaining a clean, oxide-free sample of known weight. The apparatus shown in Figure 1 was developed to enable a weighed sample of clean alloy to be taken, avoiding contact with oxygen or moisture.

A sample (approximately 30 grams) of the alloy was drawn into the sample bulb by evacuating through the stopcock and drawing the alloy from the original container into the sample bulb through a glass tube fitted with a ground joint. The sample bulb was then fitted to the sampling device, which was clamped in such a position that it could be rotated to raise either end. A weighed thin glass ampoule was placed in the sampler; the system was evacuated through stopcock *A* and filled with nitrogen through stopcock *B*. The nitrogen was purified by passing over copper turnings maintained at 425° C. and a drying tube filled with Anhydrone. The sample bulb and sampler were warmed with a flame to permit free flow of the alloy. The apparatus was then tipped so that the alloy could flow from the sample bulb into the capillary. A slight vacuum was applied to draw the desired weight of sample (approximately 1 gram) into the alloy ampoule. Nitrogen was admitted to force the excess alloy out of the capillary back into the sample bulb. The sampler was returned to the horizontal position and the alloy ampoule was removed, quickly sealed in a gas flame, then cooled, and weighed. In this manner an accurate weight of clean, oxide-free alloy was obtained.

The weighed ampoule of alloy was placed in a 32 × 300 mm. test tube and covered with neohexane. The neohexane used was purified by washing first with sulfuric acid, then with alkali, and distilling over sodium. The ampoule was broken with a glass rod and absolute alcohol added dropwise to the hexane, decomposing the sample. The alcohol was added slowly to avoid loss of sample by entrainment in the hydrogen evolved. The decomposition tube was kept in a water bath to minimize overheating.

When the sample had been completely decomposed it was washed out with distilled water into a 250-ml. Erlenmeyer flask and titrated with 1 *N* hydrochloric acid, using phenolphthalein as indicator. At the end point the hexane was evaporated on a hot plate and the titration continued to the methyl orange end point. The use of phenolphthalein reduces danger of overstepping the methyl orange end point and speeds the titration.

CALCULATIONS

Calculations were made in the following manner:

Let
x = weight of potassium in sample in grams
w = weight of sample in grams
ME = milliequivalents of hydrochloric acid

$$ME/1000 = x/39.1 + (w - x)/23$$

Solving the equation for x gave

$$x = 2.43\,w - 0.0559\,ME$$

An operator with a little practice can analyze an alloy in less than an hour with an accuracy of ±0.1% potassium. Considerable care must be exercised in following the procedure to obtain this precision. The most frequent errors are those caused by impure hexane, oxide film, and loss of sample in transferring. Because of the hazardous nature of the materials involved, safety goggles should be worn at all times during sampling and decomposition of the alloy.

SOLID ALLOYS

Alloys containing more than 92% potassium are solid at room temperature; therefore a rapid and convenient method of determining their composition is by their freezing points. Since the published data are not well defined in this region (*2, 3*), this part of the freezing point curve has been determined at this laboratory.

Freezing points were taken directly in the sample bulb (Figure 1) by inserting a calibrated thermometer graduated in 0.2° C. The alloy was warmed until liquid, and the bulb placed in a beaker of magnesia and allowed to cool slowly. The first thermal arrest was noted, the thermometer removed, and the sample analyzed as described above. When per cent potassium was plotted against temperature of the freezing point a straight line was obtained in the region from 92 to 100% potassium (by weight). The equation of this line can be represented by the relationship

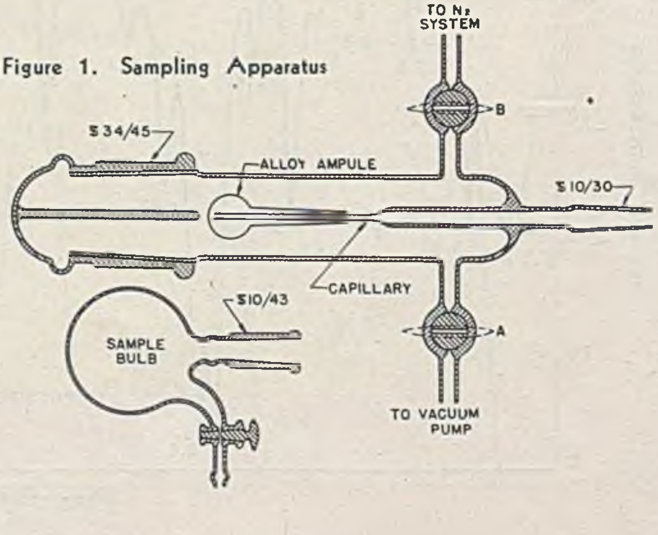
$$y = 0.259\,t + 83.5$$

where y is weight per cent potassium and t is the corrected temperature in degrees Centigrade.

The freezing point method of analysis is not readily extendable to alloys below 92% potassium because of the decreased sharpness of the first thermal arrest.

The freezing point of pure potassium was found to be 63.7° C. This value is 1.2° higher than the usually reported value, but is

Figure 1. Sampling Apparatus



in good agreement with the value of 63.65° reported by Edmondson and Egerton (*1*). A considerable amount of potassium has been made in this laboratory which analyzed 99.9+% potassium and gave a corrected freezing point of 63.7° C.

SUMMARY

A rapid method for the routine analysis of alloys of sodium and potassium is presented. Alloys of greater than 92% potassium can be analyzed in less than 5 minutes while those under 92% can be analyzed in less than an hour. With the exercise of reasonable care results should be accurate to within ±0.1% potassium. The freezing point of molten potassium has been determined as 63.7° C.

ACKNOWLEDGMENT

The authors gratefully acknowledge the services of C. A. Kraus of Brown University, from whose original work this method was developed, and A. Spencer Lehmann and C. R. Witschonke of Brown University and later this laboratory, who contributed by both suggestions and much of the work on the production of the alloys.

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Determination of Ethylene Chlorohydrin

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A CONVENIENT method for determining ethylene chlorohydrin in binary mixtures is the refractometric procedure as proposed by Berry (*1*) and by Gomberg (*2*). This method, however, is not specific for ethylene chlorohydrin and is, therefore, unsuitable in certain cases. Other methods mentioned in the literature, such as the colorimetric procedure of Sapadinsky (*4*) or one mentioned in Berry's (*1*) paper without reference or details and involving reflux of the sample with silver nitrate in nitric acid solution, were found too unreliable. Miller and Denny (*3*) used a method in which the ethylene chlorohydrin is hydrolyzed by barium hydroxide on standing overnight, and the chlorine in the resulting barium chloride is determined as an indication of the ethylene chlorohydrin concentration.

It is a well-established fact that ethylene chlorohydrin can be easily hydrolyzed by refluxing with caustic, and it was thought that this reaction might be made the basis of a more specific and reliable method. While it was not possible to make the caustic consumed a direct measure of the ethylene chlorohydrin, determination of the chloride ion of the alkali chloride which is formed proved to be successful.

APPARATUS AND REAGENTS

Apparatus required includes an electric (or other) hot plate provided with a rack for support of reflux condensers, reflux condensers with standard-taper ground-glass joints, 300-ml. Erlenmeyer flasks with standard-taper ground glass joints to fit the above condensers, a 50-ml. buret, and assortments of volumetric flasks and pipets.

The reagents are 5% aqueous potassium hydroxide, C.P. nitric acid, 0.1 *N* ammonium thiocyanate, 0.1 *N* silver nitrate, and ferric ammonium sulfate indicator (3.5 grams of ferric ammonium sulfate, 10 ml. of water, and 2 ml. of 6 *N* nitric acid).

PROCEDURE

From 3 to 5 grams of sample are weighed accurately into a 100-ml. volumetric flask and diluted with water to 100 ml. From this solution aliquots are measured into 300-ml. Erlenmeyer flasks. The volume of the aliquots should be such that they do not contain more than 350 mg. of ethylene chlorohydrin. The aliquots are refluxed with 50 ml. of 5% potassium hydroxide solution for one hour. The contents of the Erlenmeyer flasks are then cooled to room temperature, and 10 ml. of concentrated nitric acid, followed by 50 ml. of 0.1 *N* silver nitrate solution, are added. After addition of 2 ml. of ferric ammonium sulfate indicator, the unreacted silver nitrate is titrated with ammonium thiocyanate. The reacted silver nitrate is a measure of the ethylene chlorohydrin in the aliquot. One milliliter of 0.1 *N* silver nitrate is equivalent to 8.05 mg. of ethylene chlorohydrin. A blank is run on 50 ml. of 5% potassium hydroxide solution, omitting the refluxing.

If the sample should be dissolved in a nonaqueous, water-insoluble solvent, the sample weight should be such that not more than 350 mg. of chlorohydrin are actually present and the entire sample should be refluxed. This amount of ethylene chlorohydrin (350 mg.) is the safe maximum amount which can be determined with 50 ml. of 0.1 *N* silver nitrate.

Solvents and compounds which contain loosely combined halogens interfere with the determination of chlorohydrin. In case any of these compounds are present, it is suggested that the chlorohydrin be extracted with two equal volumes of water and be determined in each extract. If X_1 and X_2 represent the grams of ethylene chlorohydrin found in the respective extracts, the grams of ethylene chlorohydrin in the original sample, X, can be calculated from

$$X = \frac{X_1^2}{X_1 - X_2}$$

Some chlorinated solvents have an appreciable solubility in water. Since these are usually highly chlorinated, even a relatively low solubility may introduce considerable errors. Chloroform belongs in this class. In such instances distillation will probably be the best means for separating ethylene chlorohydrin from the interfering substances.

If ethylene chlorohydrin is to be determined in presence of inorganic chlorides, distillation will also be the most convenient means for separation. Care must be taken that sufficient water be present or be added, so that the constant-boiling mixture (42.5% ethylene chlorohydrin, 57.5% water; boiling point 96° C. at 760 mm.) will carry over the ethylene chlorohydrin with the first portions of the distillate.

The accuracy and reproducibility of the method described are evidenced by Table I, which shows a few of the many results obtained on aqueous and nonaqueous solutions of ethylene chlorohydrin.

Table I. Ethylene Chlorohydrin

Found, Mg.	Present, Mg.	Solvent
26.4	27.0	Water
59.5	59.4	Water
117.3	118.3	Water
177.7	178.0	Water
235.5	237.0	Water
357.8	357.6	Water
196.3	195.9	Xylene
322.5	324.0	Xylene
355.9	359.0	Carbon tetrachloride plus xylene 1 to 1

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Colorimetric Determination of Local Anesthetic Compounds

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A NUMBER of esters of *p*-aminobenzoic acid are employed in therapeutics as local anesthetic agents. Since these compounds contain a diazotizable aryl amine group, the authors have adapted the Bratton and Marshall method (*2*) of determining sulfanilamide derivatives to the colorimetric determination of these anesthetic agents. In this method, the primary aryl amine is diazotized and coupled with *N*-(1-naphthyl) ethylenediamine to yield a colored azo dye. Use of this coupling component results in a simpler and more sensitive method than when β-naphthol is employed as described by Willstadt (*7*) and Eissner (*3*). Although the method is not specific when two or more primary aryl amines are present as a mixture, such mixtures are seldom encountered in practice, and the diazotization procedure is generally more specific and simpler than the bromination methods used for assay of local anesthetic agents (*1*, *5*, *6*).

The official U.S.P. XII drugs, benzocaine, procaine hydrochloride, butacaine sulfate, and butyl aminobenzoate were chosen for investigation, although other local anesthetic agents, such as larocaine, tutocaine, monocaine, and panthesine may be determined in a similar manner. Cocaine, metycaine, alypine, stovaine, diothane, nupercaine, and phenacaine do not yield azo dyes and hence do not interfere in the determination. Likewise, epinephrine and ephedrine, which are often used in conjunction with local anesthetic agents, do not interfere.

REAGENTS

Standard solutions of anesthetic compounds.

0.001% solutions of benzocaine, procaine hydrochloride, butyn sulfate, and butesin in distilled water were prepared with the aid of a minimal quantity of dilute hydrochloric acid if necessary.

10% ammonium hydroxide solution.

4 *N* sulfuric acid.

Chloroform, reagent grade.

All other reagents necessary were prepared according to the specifications of Bratton and Marshall (*2*) with the exception of ammonium sulfamate which was replaced with undenatured 95% per cent ethanol as recommended by Lee, Hannay, and Hand (*4*).

DEVELOPMENT OF COLOR

Pipet 1, 2, 3, 4, and 5 cc. of the respective standard solutions of the anesthetic compounds into 50-cc. volumetric flasks each containing 5 cc. of 4 *N* sulfuric acid. Add 1 cc. of 0.1% sodium nitrite solution to each flask and allow to stand 3 minutes, then add 5 cc. of 95% ethanol and allow to stand for 2 minutes. Add 1 cc. of 0.1% *N*-(1-naphthyl) ethylenediamine solution, shaking after each addition, and make up to volume with distilled water. The color is developed rapidly and may be read in a photoelectric colorimeter after several minutes.

PHOTOMETRIC MEASUREMENTS

Absorption curves with a single peak absorption at 545 mμ, using a Coleman Model 10-S spectrophotometer, were noted.

Per cent transmittances of the solutions were determined with an electrophotometer (Fisher Electrophotometer, Fisher Scientific Co., Pittsburgh, Pa.), using a filter transmitting at 525 mμ and plotted against concentration on semilog paper. A plot of the per cent transmission thus obtained resulted in a smooth curve which was essentially a straight line in conformity with Beer's law.

AQUEOUS AND INJECTABLE SOLUTIONS

Dilute the solution with distilled water so that the final dilution contains approximately 10 micrograms of *p*-aminobenzoic acid ester per cc. Use a 5-cc. aliquot of this dilution for the development of color. Read the per cent transmittance on a photoelectric colorimeter and determine the concentration from the standard curve.

OINTMENTS

Weigh accurately a sample of ointment calculated to contain approximately 0.1 gram of *p*-aminobenzoic acid ester. Dissolve in 50 cc. of petroleum ether and extract with five 10-cc. portions of 1% sulfuric acid. Filter the combined acid extracts through a moistened filter paper into a 100-cc. volumetric flask and add sufficient distilled water through the filter to bring the volume to 100 cc. Transfer 5 cc. of this solution to a 500-cc. volumetric flask and make up to volume with distilled water. Use a 5-cc. aliquot of this dilution for the development of color. Read the per cent transmittance on a photoelectric colorimeter and determine the concentrations from the standard curve.

COMPRESSED TABLETS

Reduce 10 or 20 tablets, whichever is most convenient, to a fine powder by grinding in a mortar. Accurately weigh a portion of this powder calculated to contain approximately 0.1 gram of the *p*-aminobenzoic acid ester. Suspend or dissolve the powder in 50 cc. of distilled water in a separatory funnel, make slightly alkaline with 10% ammonium hydroxide, and extract with five 10-cc. portions of chloroform. Pass the combined chloroform extractions through a funnel containing a small pledget of cotton previously moistened with chloroform and wash the funnel and cotton with an additional 10 cc. of chloroform. Evaporate the chloroform on a water bath with the aid of a gentle air blast impinged on the surface of the solution. When the chloroform solution has reached a volume of 5 cc., add 5 cc. of ethyl alcohol and evaporate to dryness at a temperature not exceeding 50° C. To the dry residue add 5 cc. of alcohol and then 50 cc. of 1% sulfuric acid and warm on a water bath to 50° C. Transfer to a 100-cc. volumetric flask with the aid of distilled water and make up to volume with distilled water. Transfer 5 cc. of this solution to a 500-cc. volumetric flask and make up to volume with distilled water. Use a 5-cc. aliquot of this dilution for the development of color. Read the per cent transmittance on a photoelectric colorimeter and determine the concentration from the standard curve.

BLOOD AND SPINAL FLUID

To 4 cc. of trichloroacetic acid in a 15-cc. centrifuge tube, add 1 cc. of blood, serum, plasma, or spinal fluid dropwise, shaking after the addition of each drop. Centrifuge for 3 minutes and transfer 1 cc. of the clear, supernatant liquid to a 100-cc. volumetric flask. Make up to volume with distilled water and use a 5-cc. aliquot of this dilution for the development of color. Read the per cent transmittance on a photoelectric colorimeter and determine the concentration from the standard curve. If higher concentrations are expected, other suitable dilutions may be used.

This method cannot be used if sulfonamides are present, since they will interfere by giving the same color reaction.

DISCUSSION

The color produced in this reaction develops rapidly and reaches its full intensity in from 1 to 2 minutes. It is stable for at least 4 hours, with the exception of butyn sulfate, in which case it begins to fade in about one hour. Exposure of the colored solutions to strong light should be avoided, since this causes fading.

The best working range for this method was found to be from 10 to 50 micrograms for the electrophotometer used.

A number of determinations carried out on known amounts of the compounds investigated indicate that a maximum error of about 2% may be expected in the recommended working range.

The efficiency of the method for pharmaceutical preparations depends upon the thoroughness of extraction and the complexity of the mixture. As pointed out above, diazotizable aryl amines interfere, and the possibility of their presence in complex mixtures must be considered.

SUMMARY

A rapid colorimetric method for the determination of local anesthetics of the *p*-aminobenzoic acid ester type consists of

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diazotizing the amino group and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride. Data resulting from determinations of procaine hydrochloride, benzocaine, butyn sulfate, and butesin indicate a maximum error within 2%.

Procedures for the determination of these compounds in pure systems, in biological fluid, and in various pharmaceutical preparations are given. Aromatic amino compounds, notably sulfonamides, interfere.

ACKNOWLEDGMENT

The authors wish to thank Miss Vivian Treakle for performing the many routine analyses required for this paper.

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Molecular Weight and Mercaptan Content of Mixtures of Primary Mercaptans

Gravimetric Determination

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The mercaptan sulfur content of a mixture of primary mercaptans is determined by titration with silver nitrate, and the weight of silver mercaptide formed during the titration is determined. From these data the average molecular weight of the mercaptans and the percentage of mercaptans are calculated. The percentage of nonmercaptan material is found by difference.

COMMERCIAL mixtures of primary mercaptans may contain varying amounts of alkyl disulfides, alkyl halides, alcohols, etc., as impurities. A method was desired for determining the average molecular weight of the mercaptan fraction of the mixture, rather than the average molecular weight of the whole mixture as would be determined by cryoscopic measurements. The percentage of nonmercaptan material is often of interest in following the fractionation of mixtures.

Knowing the weight of silver mercaptide formed from a known number of moles of mercaptan (determined by silver nitrate titration), the molecular weight of the mercaptan fraction can be calculated.

PROCEDURE

Dissolve an accurately weighed sample of 0.3 to 0.5 gram of mercaptan in 400 ml. of absolute ethanol in a 600-ml. beaker. Add 6 ml. of concentrated ammonium hydroxide, and titrate with 0.1 N aqueous silver nitrate to an amperometric end point (*1*), adding the reagent dropwise with efficient stirring. If more than 0.1 ml. of reagent in excess is added, it is advisable to back-titrate with a very dilute solution of mercaptan in alcohol.

After allowing the precipitate to settle, pour the clear supernatant liquid through a weighed fritted-glass crucible. Do not transfer any precipitate. Pour the suspension of precipitate into centrifuge tubes and centrifuge at high speed for 3 minutes. Wash the precipitate quantitatively into the centrifuge tubes with absolute ethanol, loosening the precipitate with the aid of a rubber policeman. Stir up the precipitate in the centrifuge tubes and centrifuge again. Repeat the operation of adding ethanol, stirring, and centrifuging until the precipitate has been washed three times. Transfer the precipitate into the crucible using a minimum quantity of ethanol and allow to drain.

Dry the precipitate for 2 hours at 60° to 70° in a vacuum oven and weigh.

CALCULATIONS

$$M = \frac{1000\,W}{A \times N} - 106.9$$

$$\text{Per cent RSH} = \frac{A \times N \times M}{S} \times \frac{1}{10}$$

Per cent nonmercaptan materials = 100 − per cent RSH

where M = average molecular weight of mercaptans in mixture
W = weight of silver mercaptide
A = ml. of silver nitrate used
N = normality of silver nitrate
S = weight of sample

DISCUSSION

Because of the difficulty of washing the precipitated silver mercaptides, the precipitation is carried out with an exactly equivalent amount of silver nitrate. The amperometric method of Kolthoff and Harris (*1*), in which aqueous silver nitrate is added to an ammoniacal alcoholic solution of mercaptan, was found convenient. The potentiometric method of Tamele and Ryland (*2*), using alcoholic silver nitrate, could also be used. An accidental excess of silver can easily be removed by adding a very dilute alcoholic solution of mercaptan of known concentration.

In order to prevent occlusion of mercaptan with the silver mercaptide it was found necessary to use sufficient alcohol and to titrate with silver nitrate of such concentration that the final composition of the solvents was 95% alcohol. To prevent local excess of water, the silver nitrate should be added slowly with efficient stirring. The use of alcoholic silver nitrate (*2*) might be advantageous.

Considerable difficulty was encountered in filtering the silver mercaptide. The mercaptide settled readily, leaving a clear supernatant liquid, but the precipitate clogged the pores of the filter. The best filtering medium found was a fine fritted-glass crucible under efficient suction. Since washing the precipitate on the filter was too slow to be practical, centrifuging and decantation were used.

The precipitate was found to decompose when dried at 100° C., but at temperatures up to 70° C. no change in weight upon prolonged heating was observed, even though the color darkened to a deep orange. Mercaptides containing an excess of silver nitrate were less stable than carefully washed samples.

The procedure given above is intended for mixtures of primary mercaptans. When applied to tertiary mercaptan mixtures, two difficulties were encountered. The silver mercaptides of mixed tertiary mercaptans were found to be soluble in alcoholic solution. By adding enough water after the addition of silver nitrate to make the final solution 75 to 85% alcohol, the mercaptides were precipitated. However, the mercaptides were liquid at room temperature, making the filtering and washing operations very difficult. By carrying out the titration at 0° to −15° C., the

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Table I. Molecular Weight of Primary Mercaptans

Mercaptan	Mercaptan Sulfur Calcd. %	Mercaptan Sulfur Found %	Molecular Weight Calcd.	Molecular Weight Found	RSH %
$C_8H_{17}SH$	21.91	21.00	146.3	146.5	96.0
$C_{10}H_{21}SH$	18.39	18.15	174.3	175.2	99.2
$C_{12}H_{25}SH$	15.84	15.74	202.4	202.3	99.3
$C_{14}H_{29}SH$	13.91	13.80	230.4	232.8	100.2
$C_{16}H_{33}SH$	12.40	12.35	258.5	260.5	100.4

mercaptides were precipitated as solids which could be filtered and washed (with 70% alcohol) without centrifuging. Unfortunately, even the low-temperature technique did not permit filtration without centrifuging when applied to primary mercaptans. The accuracy of the modified method for tertiary mercaptans was not established, although the precision was comparable to that of the primary mercaptan method.

ACCURACY AND PRECISION

A series of straight-chain primary mercaptans containing eight to sixteen carbon atoms per molecule was analyzed. The mercaptans were prepared from carefully fractionated alkyl bromides which were obtained from alcohols derived from fats. The samples were believed to be of the correct molecular weight, but it was suspected that they contained small amounts of nonmercaptan impurities.

The results are given in Table I. Each result is the average of at least three determinations.

From the results in Table I it is concluded that the method yields the correct molecular weight to an accuracy of 1 to 2 units of molecular weight (0.5 to 1%).

Duplicate determinations in general were reproducible to ±1 unit of molecular weight.

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Determination of Acid in the Presence of Aluminum

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Of the methods proposed for estimation of free acid in aluminum salts, probably the most satisfactory are those in which the acid is titrated with standard alkali after conversion of the aluminum into a stable complex ion. From the Craig procedure, which involves the fluoride complex, an accurate method has been developed for the determination of acid in solutions in which the concentration of acid is high with respect to that of aluminum. A volumetric method for the analysis of hydrous alumina, embodying the improved procedure, is described.

LITERATURE and data relative to the determination of acid in the presence of aluminum salts have been in existence for nearly a hundred years. [References to much of the early literature on the subject are given by Beilstein and Grosset (*1*), Ivanov (*10*), and Kolthoff and Furman (*12*).] Because of the industrial importance of aluminum sulfate, most of the work has been devoted to the study of methods of determining free acid in samples of this salt.

The direct titration of the free acid in aluminum sulfate by means of standard base has been widely advocated. Indicators that have been recommended as suitable for use in such a titration in the presence of the salt include Congo red (*21*), methyl orange (alone, *2*, and with Martius yellow, *19*), thymol blue (*3*), sodium alizarin sulfonate (*17*), and the coloring matter of peonies (*17*). Procedures employing differential back-titrations for the determination of both aluminum and free acid in aluminum sulfate have also been suggested (*2*, *6*). In some of the methods the use of titration reference standards containing pure aluminum sulfate at the appropriate concentration is recommended; such a procedure should be regarded as essential because the pH of a solution of a pure aluminum salt is dependent on the concentration (and on the temperature and on the nature of the anion). The outstanding disadvantage of methods involving a titration in the presence of the aluminum salt is that, because of hydrolysis of the aluminum ion, the indicator does not undergo a sharp color change.

Other procedures, in which the aluminum is precipitated before the titration of the free acid, have been proposed. In particular, methods based on the insolubility of ammonium alum in ethyl alcohol (*1*, *11*) and on the precipitation of aluminum by potassium ferrocyanide (*10*, *25*) have been recommended. In some of these procedures the acid is titrated in the presence of the precipitated aluminum; in others the precipitate is first removed by filtration. The precipitation methods are troublesome and rather inaccurate.

Certain other methods that have been studied (*13*, *14*, *15*, *23*) are, like the foregoing ones, subject to criticism on one ground or another.

The most satisfactory methods for this determination, and the ones that have wide applicability to aluminum salts in general, achieve removal of the interference of aluminum by combining it in the form of a complex ion. The free acid may then be determined by titration with standard alkali; the iodometric method has also been proposed (*8*). Complexes that have been suggested as sufficiently stable to prevent significant hydrolysis of the aluminum ion are those formed with oxalate (*8*, *9*) and fluoride ions [a method has been investigated (*24*) that depends on the prevention, by the use of the citrate complex, of one third of the hydrolysis normally arising from aluminum on titration with hydroxide]. The technique involving the formation of a fluoride complex is recommended by, among others, Scott (*18*), Rosin (*16*), and Thorpe (*22*).

The fluoride method for the determination of free acid was probably first proposed by Craig (*5*). The aluminum salt is dissolved in water, potassium (*5*, *18*), or sodium fluoride (*16*, *22*) solution (previously adjusted to be neutral to phenolphthalein), is added in sufficient excess to convert the aluminum into the hexafluoaluminate complex, and the free acid is then titrated by means of standard alkali to a phenolphthalein end point. Bromothymol blue has also been used (*7*) as an indicator in connection with the fluoride method. A method for the simultaneous determination of free acid and aluminum ion, making use of the fluoride complex, has been proposed recently (*20*).

MODIFICATION OF FLUORIDE METHOD

In the course of a study of the reactivity of hydrous alumina toward acids, it was necessary to determine the decrease in the normality of a number of acid solutions that had been in contact with hydrous alumina for various periods of time. The aluminum concentration of the solutions to be analyzed varied from 0 to a maximum value of approximately 0.03 *M*, whereas the acid

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Table I. Accuracy of Conventional[a] Fluoride Method

Concn. of Al^{+++}, Moles/Liter $\times 10^4$	Concn. of F^-, Moles/Liter $\times 10^2$	Molar ratio, F^-/Al^{+++}	Titer of HCl ($\pm$0.0001 *N*)	Recovery of Acid ($\pm$0.1%)
42	12.5	30	0.0939	98.0
83	25	30	0.0936	97.7
100	30	30	0.0921	96.1

[a] "Conventional" means a method in which the fluoride is added before the start of the titration. Details of such a method—e.g., concentration of base employed for the titration—vary from one worker to another (*5, 16, 18*)

Table II. Accuracy of Improved Fluoride Method

Concn. of Al^{+++}, Moles/Liter $\times 10^4$	Molar Ratio. F^-/Al^{+++}	Extent of Neutralization When KF Added ($\pm$0.1%)	Titer of HCl ($\pm$0.0001 *N*)	Recovery of Acid ($\pm$0.1%)
111	30	97.0	0.0947	98.9
111	30	98.5	0.0953	99.5
111	30	99.5	0.0959	100.1
67	60	99.5	0.0959	100.1
67	30	99.5	0.0958	100.0
67	15	99.5	0.0959	100.1

concentration, in general, ranged from initial values of 0.2 or 0.1 *N* to normalities little more than half of these figures. Thus, although qualitatively the problem was similar to that of determining free acid in aluminum salts, the concentration ratios of acid to aluminum encountered in this work were relatively high.

Experiments using sulfuric, hydrochloric, nitric, or oxalic acid, together with dissolved aluminum chloride, showed that the conventional fluoride method (in which the fluoride is added before the alkalimetric titration) is not quantitatively accurate when the concentration of acid is high with respect to that of aluminum. For example, with an acid concentration of 0.07 *N*, an aluminum concentration of 5.6×10^{-3} *M*, and a potassium fluoride concentration of 1.7×10^{-1} *M*, the acid recovery was found with these acids to vary from 97.6 to 98.6%. The data in Table I further illustrate the degree of inaccuracy encountered. (The mole ratio of acid to aluminum in these experiments was several hundred times that encountered in aluminum salts where the mole ratio of free acid to aluminum may be of the order of 0.01.)

The solutions used in these titrations were prepared by adding to 20.00 ml. of standard hydrochloric acid solution sufficient aluminum chloride hexahydrate (recrystallized from an analyzed grade salt) and 1 *M* potassium fluoride solution (previously adjusted so as to give a very faint pink shade in the presence of phenolphthalein—i.e., neutral to phenolphthalein—and then stored in a wax-lined bottle) to give the concentrations noted in the table. The solutions were titrated in a paraffined beaker by means of standard 0.1 *N* sodium hydroxide solution to a phenolphthalein end point. The indicator blanks on water, potassium fluoride, and aluminum chloride plus potassium fluoride were identical. The concentration of hydrochloric acid in the 20.00-ml. sample (determined in both the absence and presence of potassium fluoride) was 0.0958 ± 0.0001 *N*.

Although the molar ratio F^-/Al^{+++} was constant in these experiments, the percentage of acid recovered decreased with increasing concentration of aluminum. This effect is very possibly due to increased occlusion of acid by the larger amount of alkali fluoaluminate precipitate at the higher aluminum concentrations. That the percentage recovery of acid is also a function of the molar ratio F^-/Al^{+++} was shown in a series of similar experiments; with this ratio varying from 7 to 30, and with the concentration of aluminum 0.01 *M*, the recovery varied from 99.1 to 96.1%.

If the low values obtained for acid in the presence of aluminum are due to losses by occlusion, this effect should be greatly lessened by adding the potassium fluoride, not at the beginning of the titration, but at a stage corresponding to almost complete neutralization of the acid. This modification of the method leads to accurate determinations of free acid in the presence of aluminum, as shown by the data in Table II.

At least with the concentrations used in the above experiments, the efficiency of the acid recovery is independent of the molar ratio F^-/Al^{+++} when the potassium fluoride is added at a stage of the titration corresponding to 99.5% neutralization. (A minimum molar ratio of 6 is, of course, necessary to convert the aluminum ion to AlF_6^{---}.)

Other experiments—for example, with oxalic acid and aluminum chloride—have confirmed the above finding that quantitative determinations of the acid may be carried out in the presence of aluminum, if addition of the potassium fluoride solution is delayed until neutralization is within a few tenths of 1% of completion.

In practice, one or two trial determinations will be necessary in order to ascertain the point at which the neutral potassium fluoride solution should be added. The writer has found it convenient to add the potassium fluoride at the start of the first trial titration (titrations are carried out in paraffin-lined beakers), and from the value obtained for the acid titer, tentatively assuming it to represent 98% of the true titer, to calculate the volume of alkali corresponding to 99.5% neutralization. The potassium fluoride is added after the addition of this volume of alkali in the titration of the second aliquot, and if the end point is not obtained within 0.5% of this value, the potassium fluoride point of addition is further adjusted before titrating remaining aliquot samples.

VOLUMETRIC ANALYSIS OF HYDROUS ALUMINA

When hydrous alumina is prepared by precipitation from an aluminum salt, it is normally contaminated with the anion of the salt used. No such anion, however, is present in aluminas prepared by the interaction of amalgamated aluminum metal with distilled water. If a weighed quantity of such a pure hydrous alumina is dissolved in an excess of standard acid, and the excess determined using the fluoride method to eliminate the interference of the aluminum, then the equivalents of aluminum present are given by the equivalents of acid neutralized. [For volumetric methods for aluminum, making use of the fluoride complex, see Snyder (*20*) and the references given by him, and the paper by Chernov and Nekrasov (*4*).] From the aluminum content, the composition of the alumina in terms of $Al_2O_3.xH_2O$ is readily determined. The calculation is facilitated by the use of the readily derived relationship:

$$F.W. = \frac{6000\,w}{(x - y)N}$$

where *F.W.* = formula weight of $Al_2O_3.xH_2O$
w = weight of hydrous alumina sample
N = normality of standard alkali used
x = ml. of standard alkali required to titrate volume of acid used for dissolution of sample
y = ml. of standard alkali required to titrate excess acid after complete dissolution

The following procedure was used:

A 0.23-gram sample of powdered pure hydrous alumina was weighed to ±0.1 mg. and transferred to a 125-ml. Erlenmeyer flask, 50.00 ml. of standardized 0.4 *N* sulfuric acid were added, and the mixture was boiled gently until solution was complete. During the dissolution period, which required 2 to 3 hours, the volume of the acid solution was maintained essentially constant (by additions of water), until toward the end when it was allowed

Table III. Sodium Hydroxide Required to Titrate Sulfuric Acid after Various Treatments

Direct Titration	Titration after Boiling		Titration after Addition of	
	2 hours	3 hours	15 ml. of neutral 2 *M* KF	$AlCl_3$ equivalent to 0.15 gram of Al_2O_3 and 15 ml. of 2 *M* KF
32.66	32.65	32.63	32.65	32.68
32.64	32.65	32.63	32.67	32.67
32.66	32.63	...	...	...

to decrease to approximately 25 ml. The solution was cooled to room temperature and the excess sulfuric acid present was titrated by means of standard alkali according to the improved fluoride method, using 15 ml. of 2 *M* potassium fluoride solution (neutral to phenolphthalein).

Table IV. Analyses of Hydrous Aluminas by Volumetric and Gravimetric Methods

	Sample 1		Sample 2	
	Gravimetric	Volumetric	Gravimetric	Volumetric
Formula weights	156.7	157.3	142.7	143.7
	157.1	157.5	142.2	143.7
	156.7	157.4	142.2	143.7
	156.9	...	142.3	143.9
Average formula weight	156.9	157.4	142.4	143.8
Average *x* in $Al_2O_3 \cdot xH_2O$	3.1	3.1	2.2	2.3

Tests showed that quantitative acid recovery was obtained for conditions similar to those of an analysis. In these control experiments, a constant volume of 0.3930 *N* sulfuric acid, diluted to 35 ml., was titrated by means of approximately 0.3 *N* sodium hydroxide after the treatments noted in Table III (the figures in this table refer to the number of milliliters of sodium hydroxide solution required).

A comparison of the results obtained using the volumetric method outlined above with those given by the gravimetric procedure (ignition to constant weight in platinum, using a Fisher blast burner) is given in Table IV. Both alumina samples had been prepared, one (sample 1) at room temperature and the other at an elevated (95° to 100° C.) temperature, by the interaction of amalgamated aluminum with distilled water. The filtered hydrous oxide was allowed to stand for a few days, then pulverized, and finally dried to constant weight in air at 25° C.

The precision of the volumetric method is excellent, and the values obtained are in very good agreement with those given by the standard gravimetric ignition procedure.

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Colorimetric Determination of Cobalt in Metallurgical Products with Nitroso R Salt

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THE routine determination of small quantities of cobalt in metallurgical products by the standard α-nitroso-β-naphthol gravimetric method is unsatisfactory. For materials ranging in cobalt content from 0.005 to 0.2%, the large initial sample and the resulting separations involving several reprecipitations render the gravimetric procedure exceedingly time-consuming and subject to the errors inherent in all lengthy analytical manipulations.

A colorimetric procedure based on the red color formed by nitroso R salt in the presence of cobalt under certain conditions has been used in recent years for determining very small quantities of this element in biological materials (*3*). Haywood and Wood (*1*) have described a photometric method for cobalt in steels, using nitroso R salt. These procedures are based on the fact that the colored complexes formed by most of the common elements with nitroso R salt, except cobalt, are destroyed by nitric acid. The full development of the color with cobalt is attained in the presence of sodium acetate, and such variables as quantity of nitric acid and of nitroso R salt, time of boiling, etc., have an influence on the development of the color.

In this laboratory several important modifications have been introduced to suit the requirements of complex ores and metallurgical products, to widen the applicability of the previous methods, and to save time and material. While the details of this procedure were worked out for final color measurements in a Spekker photoelectric absorptiometer, any other colorimetric means of determining concentrations in solutions, by photoelectric or visual colorimeters or Nessler tubes, can be employed.

PROCEDURE

Reagents. Cobalt sulfate, 0.2385 gram of cobalt sulfate heptahydrate dissolved and made up to 1 liter with water.

Nitroso R salt, 1 gram dissolved in water and made up to 500 ml.

Spekker acid, 150 ml. of phosphoric acid (sp. gr. 1.75) and 150 ml. of sulfuric acid (sp. gr. 1.84) made up to 1 liter with water.

Sodium acetate, 500 grams of sodium acetate trihydrate dissolved and made up to 1 liter with water.

Calibration Graph. To 0, 1, 2, 3, etc., up to 11 ml. of standard cobalt sulfate solution are added 2 ml. of Spekker acid, 10 ml. of nitroso R salt solution, and 10 ml. of sodium acetate solution. A blank is made by adding 2 ml. of Spekker acid and 10 ml. of sodium acetate solution but omitting the nitroso R salt. The blank and the standard solutions are brought to the boil on a hot plate, 5 ml. of nitric acid are added, and the solutions are boiled for at least 1 minute and not more than 2 minutes. The standards and blank are then cooled and diluted to 100 ml. with water.

The absorption of the standards is measured on the Spekker photoelectric absorptiometer using 1-cm. cells and Hilger blue filters No. 6. The blank is set on 1.0 and the differences obtained are plotted against the weights of cobalt taken.

Table I. Comparison of Analytical Procedures

Sample	Standard Gravimetric	Nitroso R salt Operator A	Nitroso R salt Operator B
	% Co	*% Co*	*% Co*
Mill feed	0.14	0.136	0.134
Mill tail	0.06	0.056	0.062
Oxide ore	0.55	0.55	0.55
Cobalt reverberatory slag	0.63	0.66	0.62
Copper concentrate	0.64	0.63	0.60
Copper reverberatory slag	1.47	1.45	1.40
Copper reverberatory matte	1.86	....	1.80
Blister copper	0.0104	0.0102	...
Refined copper	0.0001	0.0001	...

DETERMINATION. For samples containing 0.01 to 0.20% of cobalt use a 0.25-gram sample. With higher grade materials take a 0.5-gram sample and after decomposition dilute to volume and take a suitable aliquot containing 0.01 to 0.5 mg. of cobalt for analysis. For very low cobalt contents, as in refined metals with few impurities, larger aliquots representing 1 to 20 grams may be taken. The maximum quantity of cobalt permissible in a sample is 0.5 mg., as above this concentration the solution no longer appears to obey Beer's law.

Decompose with nitric acid, hydrochloric acid, and bromine, add 5 to 7.5 ml. of 1 to 1 sulfuric acid, and evaporate to strong fumes. Some products will require the use of hydrofluoric acid for complete decomposition. Care should be taken in the addition of reagents, as an excessive concentration of salts in the final solution will increase the absorption.

Cool, dilute to about 30 ml., add 2 ml. of hydrochloric acid, and boil to solution of soluble salts. Pass a brisk current of hydrogen sulfide through the solution for 10 minutes and filter through a Whatman No. 40 filter paper, washing well with acidulated hydrogen sulfide wash water. Boil off hydrogen sulfide, add 5 ml. of nitric acid, and take to fumes of sulfur trioxide. For products like blister or refined copper, determine cobalt on the solution obtained after the electrolysis of copper. Evaporate this solution to fumes of sulfur trioxide, and continue heating until only a small amount of sulfuric acid remains.

Cool, dilute to about 25 ml. with water, and boil to solution of salts. Cool and carefully neutralize with 20% sodium hydroxide to a point where the solution becomes a deep wine red. Should there be little or no iron present, add 2 drops of phenolphthalein and take to the first faint pink. Immediately add 2 ml. of Spekker acid, then 10 ml. of nitroso R salt solution and 10 ml. of sodium acetate solution. Bring to a vigorous boil, add 5 ml. of nitric acid, and boil for at least 1 minute but not more than 2 minutes. Cool and dilute to 100 ml. with water.

At the same time carry out a blank exactly as was done in calibrating the graph. Measure the absorption of the sample in the same manner as were the standards with the blank setting at 1.0. The drum reading obtained for the sample is subtracted from 1.0 and this difference is measured off on the calibration graph to obtain the weight of cobalt present.

RESULTS

Table I compares results obtained by this procedure with those secured by careful work with standard gravimetric methods on specially prepared samples of typical metallurgical products.

For mill feed and tail 0.25-gram samples were used directly; for oxide ore, cobalt reverberatory slag, and copper concentrate, 0.5-gram samples were taken, diluted, and aliquots equivalent to 0.05 gram of original sample were withdrawn. In copper reverberatory slag and copper reverberatory matte 0.5-gram samples and aliquots equivalent to 0.025 gram were taken.

To thirteen 0.25-gram portions of a complex ore containing 4.95% copper and 3.00% iron, which was known to contain very little cobalt, varying quantities of standard cobalt solution were added. These together with another 0.25-gram portion of the ore to which no cobalt had been added were analyzed according to the foregoing procedure. Table II gives the results obtained.

DISCUSSION

INTERFERING ELEMENTS. It was found that even small quantities of copper prevented or masked the full development of the red cobalt complex. This confirms observations made by previous workers on biological materials (*3*), but not brought out by Haywood and Wood working with steels.

As it was necessary to remove copper and all the products on which the authors worked contained this element, a separation with hydrogen sulfide was made on all samples. With this modification, taking the usual precautions, silver, mercury, lead, copper, bismuth, cadmium, arsenic, antimony, tin, molybdenum, selenium, tellurium, gold, platinum, and palladium are removed. To 0.25-gram portions of a sample of known cobalt content (0.18%) the following elements were added as soluble salts: iron, aluminum, zinc, titanium, thorium, uranium, zirconium, tungsten, barium, strontium, calcium, and magnesium. The quantities added were sufficient to give at least 20% of each element relative to the sample; in the case of iron, enough ferric chloride was added to bring the iron content to 50%.

Cobalt was determined as usual and in no case was there observed any significant difference in cobalt recovery. Naturally some of the added elements were removed during the course of the analysis. Barium, for instance, would all be removed as sulfate. Titanium and thorium were troublesome, as hydrolyzed salts continued to be precipitated in the solution after the color had been developed. Filtration through a dry filter paper at this stage removed the turbidity and the cobalt recovery was not affected.

As no pure vanadium salt was available, a vanadium-bearing ore free of cobalt was added to a known cobalt sample, the vanadium content of the final sample being 5%. The cobalt recovery was unaffected. To the same sample varying quantities of manganese were added; up to 10% manganese there was no interference, but quantities above this had to be removed. Likewise chromium and nickel were found to be without effect up to 3 and 5%, respectively, but above these concentrations removal is indicated.

The addition of large quantities of certain of the above elements necessitated slight alterations in procedure which are commented upon in the subsequent sections.

Table II. Recovery of Added Cobalt in Ores

Sample No.	Cobalt Added	Cobalt Found	Recovery
	Mg.	*Mg.*	%
1	Nil	0.01	...
2	0.02	0.03	100
3	0.05	0.06	100
4	0.10	0.11	100
5	0.16	0.165	103
6	0.21	0.225	102
7	0.25	0.26	100
8	0.30	0.315	101
9	0.34	0.35	100
10	0.37	0.385	101
11	0.40	0.41	100
12	0.44	0.45	100
13	0.49	0.50	100
14	0.53	0.54	100

EFFECT OF VARIABLES IN PROCEDURE. Like all colorimetric procedures it is desirable that conditions be standardized as far as practicable and the quantities and directions given in the procedure should be adhered to as closely as possible.

Spekker Acid. Haywood and Wood used Spekker acid for the decomposition of steels. Since their reasons for using this acid did not apply to the authors' procedure, they tried dilute sulfuric acid to acidify the sample after neutralization with sodium hydroxide. They found, however, that when much iron was present low results were obtained, owing to the development of a decided brown tinge in the solution. As phosphoric acid decolorizes iron, an attempt was made to use this acid alone, but it proved unsatisfactory for most metallurgical samples. The familiar combination of phosphoric and sulfuric acids known as Spekker acid was finally tried and found successful. Varying quantities of this acid were added to known ores and to synthetic solutions. It was found that the Spekker acid could be varied from 0.5 to 3.0 ml. without affecting the color development. Any addition above 3 ml. caused a lessening of the depth of color.

Nitroso R Salt. The measurement of nitroso R salt should be accurate, but no appreciable difference was observed with quantities of nitroso R salt varying between 10 and 15 ml. The result was low with less than 10 and high with more than 15 ml. of nitroso R salt solution. The solution is perfectly stable after standing 2 days, but it is probably advisable to make up only sufficient for the day's requirements.

Sodium Acetate. With local ores the essential minimum was 5 ml. of sodium acetate solution. The quantity of sodium acetate necessary would vary with different products and it was decided that a safe addition was 10 ml.

Nitric Acid. It is essential to add sufficient nitric acid to dissolve any precipitate formed with sodium acetate and to destroy color complexes formed with metals other than cobalt. It was found that the nitric acid could be increased to 15 ml. without affecting the color development, when 10 ml. of sodium acetate were used. The presence of certain elements necessitated alterations in procedure. Very high iron, manganese, etc., required more than the standard addition of 5 ml. of nitric acid to clear the precipitate formed with sodium acetate.

Time of Boiling. The final boiling had to be carefully controlled. The solution must be brought to a vigorous boil, nitric acid added, and the boiling continued for from 1 to 2 minutes. The extension of the boiling time to 3 minutes caused little change, but any further extension resulted in a definite bleaching of the cobalt color. On the other hand, any decrease in boiling time prevented the full development of the red color. This confirms the work of previous investigators (*1*).

Fading of Color on Exposure to Light. Samples permitted to stand for 24 hours in Erlenmeyer flasks fitted with loose covers were practically unchanged. On standing for a further 24 hours there was an observable lessening of color. The flasks were exposed to diffused sunlight for half of this period. The effect of exposure to light, although slight, is apparently more pronounced than experienced by Haywood and Wood. This is probably due to the more intense sunlight prevailing in Africa.

It would appear that when dealing with quantities of cobalt between 0.01 and 0.50 mg. the control of conditions need not be so critical as described by Kidson and Askew (*2*), who were working with quantities of cobalt as low as 0.0001 mg. While Haywood and Wood (*1*) report good results with very high cobalt-containing steels, the authors have found the greatest range of usefulness of this method to lie in the lower concentrations of cobalt in mining and metallurgical products.

SUMMARY

A modification of the nitroso R salt method for cobalt is described which should have wide adaptability for the determination of small quantities of this element in metallurgical products and similar materials. Results compare very favorably in accuracy and precision with those obtained by the longer standard gravimetric procedures, and the recovery of added cobalt is complete.

A comprehensive review of the effect of other elements and of varied conditions is given. The determination is best carried out on a sample or aliquot containing 0.01 to 0.5 mg. of cobalt. Apart from the elements removed with hydrogen sulfide in the course of the determination, this work to date shows that the final color comparison can be made in the presence of at least 1000 times as much iron, 100 times as much aluminum, zinc, titanium, thorium, uranium, zirconium, tungsten, barium, strontium, calcium, and magnesium, and 25 times as much vanadium. Quantities of manganese in excess of 50 times, nickel beyond 25 times, and chromium in excess of 15-fold the cobalt present, interfere and must be removed.

Although details are presented for the final determination of cobalt in the Spekker absorptiometer, the method is adapted for any other means of photoelectric or visual color comparison.

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Radioactive Studies

Utilization of the Radioactive Isotope Dilution Procedures for Special Types of Chemical Problems. Quantitative Determination of the Three Individual Components of Mixtures of Dibenzyl Sulfide, Sulfoxide, and Sulfone as an Illustrative Example[1]

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ALTHOUGH certain highly specialized instruments, such as spectrometers (infrared, mass, etc.) and polarographs enable the analysis of certain individual components of many multicomponent systems, there are still numerous types of mixtures that cannot be quantitatively analyzed by means of these apparatus.

It has been known for some time that the isotope dilution method is applicable in principle to any analytical problem (*6*). Recently Foster, Rittenberg, and others (*1*, *2*, *7*) have begun to use stable isotopes in the determination of the amino acid content of proteins. In the case of radioactive isotopes, the usual analytical errors of 10 to 15% prevented their usage in the isotope dilution method (*9*). Since recent studies (*3*, *4*) have shown that some of the radioactive tracers most difficult to quantitate—namely, long-lived sulfur, arsenic, carbon, and hydrogen—can be analyzed to within 2%, the accuracies of the isotope dilution method, with either stable or radioactive isotopes, are essentially identical. This communication indicates the full scope of the radioactive isotope dilution method as applied to chemical problems and gives a specific experimental example, using S^{35} of 87-day half-life.

GENERAL CONSIDERATIONS

Let P be a nonradioactive compound. Let P^* be the same compound in which a minute fraction of the molecules contain a tracer element in a stable position, and let the radioactivity per milligram of this compound be denoted by $(act/mg)_{P^*}$. Let $P.P^*$ denote the chemically indistinguishable mixture of P and P^*, and let the radioactivity per milligram of this mixture be denoted by $(act/mg)_{P.P^*}$. Let the ratio of the specific activities, $(act/mg)_{P^*}/(act/mg)_{P.P^*}$, be defined as R.

There are two general procedures in applying the isotope dilution method.

Procedure I. The amount of P in a multicomponent system is unknown. If a known quantity of P^* is added to and dispersed uniformly throughout the mixture, the amount of P can be determined, provided that a weighable aliquot ($\geq$0.05 mg.) of $P.P^*$

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[1] This is the fifth in a series of articles on Radioactive Studies. Previous articles are found in June and July issues.

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The radioactive isotope dilution method is a powerful tool which is applicable to analytical problems that cannot be solved readily by any other means. There are two general variations to this method; one is best suited to the analysis of the individual constituents of multicomponent systems, and the other is useful in the investigation of mechanisms and/or yields of reactions. As an illustrative example utilizing long-lived radioactive sulfur, S^{35}, quantitative data are presented for the analysis of the three individual components of mixtures of dibenzyl sulfide, sulfoxide, and sulfone. These data show that these analyses, if done in triplicate, can be made with an average error of less than 1% and a maximum error of less than 2%.

can be isolated in a pure state. This relationship is given by Equation 1:

$$mg_P = mg_{P^*}\,(R - 1) \qquad (1)$$

PROCEDURE II. The amount of P^* in a multicomponent system containing other radioactive compounds is unknown. The addition of a predetermined amount of P sufficient to isolate subsequently a weighable quantity of $P.P^*$ in a pure state, followed by complete mixing of the active and inactive species, will enable the analysis to be made. Equation 2 gives this relationship:

$$mg_{P^*} = mg_P\,[1/(R - 1)] \qquad (2)$$

For both Procedures I and II, the specific activity of P^* can be predetermined to make $R \gg 1$ and to make each radioactive measurement with a maximum error of 2%; thus the maximum uncertainty of an individual analysis by the radioactive isotope dilution method is 4%.

Procedure I is best suited for any problem involving the analysis for the individual components of a multicomponent system, provided that sufficient P is present to enable the isolation of a weighable amount of PP^*. Thus it cannot be used for the determination of traces of substances.

Procedure II is useful in the investigation of the mechanism and/or yield of reactions. This is most readily shown by considering a specific example—namely, the following hypothetical polymerization:

$$A + P = A_1P + A_2P + A_3P + \ldots = \sum_{1}^{N} A_K P \qquad (3)$$

where A polymerizes in the presence of the catalyst, P, to A_K and the polymerization is terminated by the addition of P to the polymer. It is essential that the polymers, A_KP, can be obtained in pure form—e.g., be reacting large quantities of A and P and subsequent fractional distillation and/or crystallization. Then the synthesis of P^* and the use of this compound instead of P in reaction 3 enables the determination of the exact amount of each A_KP^* formed, since $(act/mg)_{A_KP^*}$ can be computed stoichiometrically from $(act/mg)_{P^*}$, and $(act/mg)_{A_KP \cdot A_KP^*}$ is experimentally determined.

Methods similar to those outlined above are applicable to any reaction. Unlike Procedure I, Procedure II enables the analysis of traces of substances; in fact, since most radioactive isotopes can be obtained in high millicurie strength, it is possible to analyze quantitatively for less than 0.001 microgram of many compounds—e.g., A_KP^*—by the isotope dilution method. It is here that radioactive isotopes come into their own, since the allowable dilution factors are much greater than those of stable isotopes.

Utilizing radioactive sulfur, S^{35}, the authors have used both Procedures I and II; the former is considered in the next section and the latter has been used to investigate the mechanism of mustard gas vesication (*5*). The procedures are interdependent and the accuracy to be expected from either isotope dilution method is essentially identical.

ILLUSTRATIVE EXPERIMENTAL EXAMPLE

In order to evaluate the radioactive isotope dilution method as a quantitative analytical procedure, an illustrative example of Procedure I will be considered in detail—the analysis of the three individual components of mixtures of dibenzyl sulfide, sulfoxide, and sulfone. In essence the procedure consists of the following steps for this particular case:

Dibenzyl sulfide, sulfoxide, and sulfone, each containing radioactive sulfur, are synthesized.

The amount of radioactivity per milligram, $(act/mg)_{P^*}$, is determined for each radioactive compound.

Accurately weighed amounts of each of the radioactive compounds are added to the unknown mixture of dibenzyl sulfide, sulfoxide, and sulfone.

A portion of each substance is isolated in the pure state by fractional crystallizations.

Weighed amounts of the three purified fractions are subjected to radioactive analysis and the $(act/mg)_{P \cdot P^*}$ is computed for each substance. From the reduction in specific activity from $(act/mg)_{P^*}$ to $(act/mg)_{P \cdot P^*}$ together with the known weight of radioactive compound added, the amount of each of the original compounds present in the unknown mixture is calculable by means of Equation 1.

PREPARATION OF THE COMPOUNDS. About 20-gram quantities of nonradioactive dibenzyl sulfide, sulfoxide, and sulfone were prepared by the method described in detail by Shriner *et al.* (*8*).

This procedure is based on the following schematic reactions:

$$C_6H_5CH_2Cl + Na_2S \longrightarrow (C_6H_5CH_2)_2S \qquad (4)$$

$$(C_6H_5CH_2)_2S + H_2O_2 \longrightarrow (C_6H_5CH_2)_2SO \qquad (5)$$

$$(C_6H_5CH_2)_2SO + CrO_3 \longrightarrow (C_6H_5CH_2)_2SO_2 \qquad (6)$$

Since the techniques involved in the preparation of dibenzylsulfide on the milligram scale are rather different, the preparation of this compound containing radioactive sulfur is described in detail. The radioactive sulfur used in this preparation was obtained from the Massachusetts Institute of Technology, Radioactivity Center.

Dry barium sulfate (200 mg.) containing about 30 microcuries of S^{35} (87-day half-life) was placed in a platinum boat which was introduced into a long quartz tube. By heating the tube to 800° C. for 4 hours, while passing through a stream of hydrogen, a 98% reduction to barium sulfide was obtained. The trace of hydrogen sulfide formed by the side reaction

$$BaSO_4 + 4H_2 \longrightarrow BaO + H_2S + 3H_2O \qquad (7)$$

was caught in a zinc chloride trap. The resulting zinc sulfide precipitate was added to the barium sulfide in the platinum boat.

The boat with contents was transferred to a small gas generator containing 1 gram of 20-mesh zinc. Sufficient 6 *M* phosphoric acid to cover the boat was now added through a stopcock and the mixture was heated. The issuing gases were dried with phosphorus pentoxide, and the hydrogen sulfide was condensed in a trap chilled by liquid nitrogen. The purpose of the hydrogen was to sweep out all traces of hydrogen sulfide from the generator with a noncondensable gas. The hydrogen sulfide was then stored in an evacuated bulb attached to a vacuum system.

A tube, containing 1.85 millimoles (235 mg.) of benzyl chloride 1.85 millimoles (75 mg.) of sodium hydroxide, 6 cc. of ethyl alcohol, and 1 cc. of water, was attached to the vacuum system by means of a ground joint and frozen down and evacuated. The hydrogen sulfide (0.85 millimole) was vacuum-distilled into this tube chilled with liquid nitrogen. This tube was then sealed and placed on a steam bath for 3 days. The tube was opened and the contents were extracted four times with petroleum ether (b.p. 40° to 60° C.). The petroleum ether solution was placed in a test tube, and the volatile contents were pumped away; the contents of the apparatus were further pumped for 1.5 hours to remove most of the residual benzyl alcohol and benzyl chloride. The dibenzyl sulfide was recrystallized from ethyl alcohol.

Yield, 168 mg., 92% based on barium sulfate; m.p. 49° C.

To prepare the dibenzyl sulfoxide, 120 mg. of radioactive dibenzyl sulfide were used.

Yield, 107 mg., 83%; m.p. 134° C.

To prepare the sulfone, 60 mg. of the radioactive sulfoxide were used.

Yield, 45 mg., 70%; m.p. 149° C.

For these last two compounds, Shriner's method (*8*) scaled down to these quantities was exactly followed.

Thus, about 45 mg. of each compound containing about 10 microcuries of S^{35} were prepared. This quantity of material would allow the analysis in triplicate of at least 100 unknown mixtures of the three dibenzyl compounds.

Table I. Triplicate Radioactive Sulfur Standardizations of the Three Dibenzyl Compounds

[a]	$(C_6H_5CH_2)_2S^*$	$(C_6H_5CH_2)_2S^*O$	$(C_6H_5CH_2)_2S^*O_2$
ct/mg) P*	169.0 169.6 169.7	156.5 160.0 158.8	148.7 148.1 147.2
Av. (act/mg) P*	169.4	158.4	148.0
Av. (act/micromole) P*	36.2	36.4	36.4

[a] The activity of each sample is computed by the following formula:

$$\text{Activity} = [(d/t)_s - (d/t)_b] \times \frac{10^2}{f} \qquad (8)$$

where d is the number (10) of scale divisions traversed by the electroscope fiber in time t in seconds; s and b denote sample and background, respectively; and f is the beta-ray self-absorption correction factor due to the weight of the benzidine sulfate precipitate (see *3* for further details).

With the electroscope used, one unit of activity represents about 10^{-3} microcurie of S^{35}.

Table II. Analysis of Known Mixtures of Dibenzyl Sulfide, Sulfoxide, and Sulfone by Radioactive (S^{35}) Isotope Dilution Procedure

	Mixture of Nonradioactive Compounds								
	$(C_6H_5CH_2)_2S$			$(C_6H_5CH_2)_2SO$			$(C_6H_5CH_2)_2SO_2$		
Mixture No.	Weight added Mg.	Weight determined by S^{35} analysis Mg. Av.	Individual analysis	Weight added Mg.	Weight determined by S^{35} analysis Mg. Av.	Individual analysis	Weight added Mg.	Weight determined by S^{35} analysis Mg. Av.	Individual analysis
1	400	406	412 395 410	400	399	403 401 392	400	399	409 390 397
2	400	402	396 403 406	400	399	403 395 398	400	397	393 406 393
3	400	396	389 400 399	400	401	392 404 406	400	395	397 401 390
4	200	199	203 197 196	400	400	404 391 404	1400	138_0	1355 1402 1390
5	400	400	399 400 402	1400	139_0	1368 1408 1396	200	203	205 199 206
6	1400	140_0	1382 1415 1404	200	201	206 193 204	400	407	405 406 410

RADIOACTIVE STANDARDIZATIONS. Approximately 1 mg. of each of the three radioactive compounds was carefully weighed out on a microbalance and oxidized to the sulfate ion by the Carius method. Each sample was washed into its respective 100-cc. volumetric flask. Triplicate 3-cc. aliquots were then subjected to S^{35} analyses by the procedure described elsewhere in detail (*3*).

Table I shows the reproducibility of these radioactive standardizations as measured by the modified Lauritzen electroscope.

These data show that with care accurate radioactive sulfur analysis can be made. They also are indicative of the purity of the radioactive compounds.

PREPARATION OF RADIOACTIVE STANDARD SOLUTION. About 15 mg. of the radioactive sulfide, sulfoxide, and sulfone were weighed out, respectively, to within 0.05 mg. This mixture was placed in a volumetric flask and made up to 100 cc. with 95% ethyl alcohol. Thus a known volume of this solution contained a predetermined weight of each of the three radioactive compounds. As an additional check, triplicate radioactive analyses were made on 1-cc. aliquots of this solution. The average of the activities obtained was within 0.4% of that computed from the radioactive standardizations of the individual components.

ISOLATION OF PURE PORTIONS OF EACH COMPOUND (*P.P**) FOR RADIOACTIVE ANALYSIS. To an acetone solution containing the mixture, *P*, of nonradioactive dibenzyl sulfide, sulfoxide, and sulfone to be analyzed, exactly 10 cc. of the radioactive standard solution, *P**, were added. The solution was well stirred and the acetone and alcohol were evaporated off. The solid mixture was now ready for the isolation of the pure portions of the three compounds, *P.P**. The procedure used was based on the relative solubility of these compounds in petroleum ether (b.p. 40° to 60° C.) and 95% ethyl alcohol.

Cold petroleum ether was added; the sulfide was partially separated by filtering, since the sulfoxide and sulfone were somewhat insoluble. The remaining solid was dissolved in alcohol; upon cooling, some of the sulfone precipitated while most of the sulfoxide remained in solution. Thus, there now remained a petroleum ether solution of crude sulfide, alcoholic solution of impure sulfoxide, and solid crude sulfone. The petroleum ether and alcohol were respectively evaporated off and the three impure solids were recrystallized three times, the sulfide from 95% ethyl alcohol, the sulfoxide from petroleum ether (b.p. 40° to 60° C.), and the sulfone from 95% alcohol. The melting point of each compound was taken, and if it were not correct further recrystallizations were made.

Six different mixtures containing various known amounts of the three dibenzyl compounds were subjected to the above procedure. Since 200 mg. was the minimum amount of any of the dibenzyl compounds, *P*, in the original mixture, and 20 mg. more than sufficed for radioactive analysis, it was not difficult to obtain the three substances in a highly purified state. Triplicate radioactive sulfur analyses (*3*) were made on weighed amounts (~6 mg.) of each purified component, *P.P**, and the radioactivities were calculated by means of Equation 8.

The experimental results, as computed by Equation 1, are given in Table II. In order to indicate the magnitude of the experimental error, each individual determination has been included in Table II. The greatest deviation found between the amount of dibenzyl compound added and an individual analysis is 3.2% (1400 mg. of dibenzylsulfone added, 1355 mg. found; mixture 4). The average per cent deviation between an individual analysis and the amount of compound added is 1.4. The maximum and average per cent deviations between the average of the triplicate analyses and the weight of dibenzyl compound added are 1.8 and 0.7, respectively.

Thus the accuracy of these data compares favorably with that obtained by using stable isotopes in isotope dilution Procedure II (*2*). It is believed that with care this error of less than 2% could be duplicated in all analyses, utilizing either radioactive isotope dilution Procedure I or II. Since there are numerous analytical problems that cannot be solved readily in any other manner, the radioactive isotope dilution method will ultimately take its place among the other highly specialized analytical techniques.

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Analytical Chemistry of the Rare Earths

The Active-Oxygen Determination

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A method is described for the measurement of the active oxygen present in a mixture of ignited rare earth oxides. The procedure is superior to the classical Bunsen method in that no difficulty is encountered in the analysis of high ceria mixtures. Data are given for the analysis of pure cerium dioxide, of some cerium dioxide–lanthanum sesquioxide mixtures, and of pure praseodymium oxide.

IN GENERAL, gravimetric methods of analysis are based upon a separation followed by a final weighing of the desired constituent in a pure compound of known composition. However, in the analysis of rare earth materials, separation of the individual earths is impractical and one is faced with the necessity of weighing a mixture which may contain elements of the entire group. Certainly the oxalates of cerium, praseodymium, and terbium yield upon ignition in air oxides containing more oxygen than can be accounted for by sesquioxide formation (*1*), and there is some indication of a higher oxide of neodymium (*6*). The situation is further complicated by the possible influence of certain other rare earths upon the higher oxides formed by the elements mentioned (*2, 3, 5*).

The evaluation of the true rare earth metal content of a mixture of such oxides would be greatly simplified by a method which permitted direct measurement of the so-called "active oxygen", the oxygen present in excess of that in the sesquioxide. Correction of the weight of the oxide mixture would then permit calculation of an accurate metal content.

Such an analytical method would be useful also in obtaining data regarding the composition of rare earth oxides formed under various conditions, both in the pure state and in mixtures. Such studies have been made in this laboratory using the method described below and will form the subject of a later paper.

The method of Bunsen (*4*) has found wide application for the determination of higher-valent cations in compounds similar to the rare earth metal oxides. Hydrochloric acid is added to the compound under investigation and the chlorine liberated by the reaction is absorbed in a potassium iodide solution. The liberated iodine is then titrated with thiosulfate solution in the usual manner.

Such a procedure is not feasible, however, if an appreciable amount of cerium is present in the mixture under investigation. Cerium dioxide, once formed, is extremely inert to all but the strongest reducing agents and even extended contact with concentrated hydrochloric acid results in very little attack.

EXPERIMENTAL

Several modifications of the Bunsen method were attempted, using both arsenious oxide and sodium oxalate as reducing agents. The reaction rate between the oxides proved to be too slow to be useful, while the conditions necessary to complete the reaction with sodium oxalate were so vigorous that appreciable decomposition of the oxalate in the sulfuric acid medium occurred.

A simple procedure using potassium iodide and a modified Bunsen apparatus was finally developed which gave satisfactory results.

The apparatus consisted of a 125-ml. Kjeldahl flask fitted through a ground-glass joint with a water-cooled reflux condenser. To the upper end of the condenser was attached, by a ground-glass joint, a tube bent to a semicircle and terminated with a Bunsen valve. When in use, the valve was immersed in a potassium iodide solution contained in a small beaker.

An accurately weighed sample of the pure oxide or mixture of oxides is placed in the Kjeldahl flask and 20 ml. of a 10% potassium iodide solution are added. Eighty milliliters of a 4% solution of potassium iodide are placed in the beaker to cover the Bunsen valve.

Ten milliliters of 12 *N* hydrochloric acid are added to the flask, the flask is attached immediately to the reflux condenser, and the mixture is heated gently until dissolution of the oxide is complete. The flask is cooled, the vapor trap removed, and any sublimed iodine clinging to the tube of the condenser is washed into the Kjeldahl flask with the vapor-trap solution.

The solution is then transferred to a 500-ml. Erlenmeyer flask, diluted to 350 ml., and titrated to a starch end point with standard 0.1 *N* sodium thiosulfate solution.

A blank is determined under conditions identical to those in the analysis, using similar periods of heating and volumes of solution. The blank in no case should exceed 0.5 ml. The difference between the two volumes is, of course, equivalent to the iodine released by the active oxygen present in the sample.

$$\text{Active oxygen (mg.)} = (N \text{ of } Na_2S_2O_3)\ (\text{ml. of } Na_2S_2O_3)\ (\text{meq. of } O_2) \quad (1)$$

Values obtained by the analysis of samples of pure cerium dioxide with or without admixture of pure lanthanum sesquioxide and using the method described are shown in Table I.

Table I. Active Oxygen in Pure Cerium Dioxide and in Cerium Dioxide–Lanthanum Sesquioxide Mixtures

Weight of Sample *Mg.*	La_2O_3 %	Active Oxygen Taken *Mg.*	Active Oxygen Found *Mg.*
194.7	...	9.0	9.0
285.6	...	13.2	13.3
202.5	4.81	8.9	8.9
237.2	4.81	10.5	10.4
274.0	25.49	9.5	9.5
189.2	25.49	6.6	6.6
197.1	49.37	4.6	4.7
170.8	49.37	4.0	4.0
269.1	72.91	3.4	3.4
271.2	72.91	3.4	3.5
541.8	93.88	1.5	1.6
394.6	93.88	1.1	1.2

COMPOSITION OF PRASEODYMIUM OXIDE

The application of the method is well illustrated by a study of the ignition product of pure praseodymium oxalate.

The material used in this investigation was purchased from Adam Hilger, Ltd., 98 Kings Road, London, England, and bears the laboratory number 6782. It was obtained by Hilger from Professor Rolla at the University of Florence. Independent spectrographic analyses by the Hilger laboratory and by V. W. Prandtl show impurities only of magnesium (0.1%) and dysprosium (0.02%).

The pure oxalate was precipitated from dilute nitric acid in the usual manner and, after oven-drying, was ignited to constant weight at 955° ± 10° C. After cooling, weighed portions of the ignition product were analyzed as described above. Table II illustrates the results obtained.

Table II. Active Oxygen in Pure Praseodymium Oxide

Weight of Sample *Mg.*	Volume of 0.0459 *N* $Na_2S_2O_3$ *Ml.*	Active Oxygen *Mg.*	Active Oxygen %	Active Oxygen Fraction
187.4	16.47	5.98	3.19	0.0319
143.2	12.57	4.61	3.22	0.0322
155.5	13.20	4.94	3.18	0.0318

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Now, representing the general formula of the oxide obtained as Pr_xO_y, the ratio of y/x may be calculated by the relation

$$\frac{x\,(\text{atomic weight of praseodymium}) + y\,(\text{atomic weight of oxygen})}{\frac{x}{2}\,(\text{formula weight of } Pr_2O_3)} =$$

$$\frac{140.92\,x + 16.00\,y}{\frac{x}{2}\,(329.84)} = \frac{1}{1 - \text{fraction of active oxygen}}$$

From the data of Table II, using the average value 0.032 for the fraction of active oxygen, the ratio of y/x is calculated to be 1.84, a value corresponding to the following formulas:

$$Pr_4O_{7.36},\ Pr_5O_{9.20},\ Pr_6O_{11.04},\ Pr_7O_{12.88}$$

From the data presented, it appears that the product of the ignition of pure praseodymium oxalate in air at 955° C. has a composition most closely approximating the formula Pr_6O_{11}. Ignition at temperatures of 670° and 780° C. had little effect upon the fraction of active oxygen in pure praseodymium oxide, the values obtained in these cases being 0.031.

SUMMARY

A procedure for the determination of active oxygen in mixtures resulting from the ignition of mixed rare earth oxalates is particularly applicable to mixtures containing a high percentage of ceria. Additional proof of the composition Pr_6O_{11} for the oxide formed upon the ignition of pure praseodymium oxalate at various temperatures has been obtained.

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Estimation of Ammonium Picrate in Wastes from Bomb- and Shell-Loading Plants

Some Reactions of Ammonium Picrate in Water and Sewage

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A practical spectrophotometric procedure for determining the ammonium picrate content of wastes or the ammonium picrate, alpha-TNT, and colored TNT in wastes containing all three is presented. The procedure, which involves extinction readings at 460 and 505 mμ after three steps of treatment of the sample, is simple and rapid. Ammonium picrate in wastes exhibits no biochemical oxygen demand and in concentrations above 300 p.p.m. inhibits the normal B.O.D. reaction of polluted water. Taste tests on 20 people indicated that concentrations of 1.0 p.p.m. or more of ammonium picrate are objectionable in drinking water.

IN CONNECTION with the study of wastes from U. S. Naval Ammunition Depots, the estimation of ammonium picrate wastes in streams and in waters containing TNT wastes was necessary. It was also desirable to determine the effects of ammonium picrate in such wastes on sewage disposal plants and other disposal methods, as little is known about the fate of such wastes or their effects on natural biological purification.

QUALITATIVE TESTS FOR AMMONIUM PICRATE

Several qualitative and quantitative methods were investigated before the spectrophotometric method was adopted. The following tests were applied to ammonium picrate wastes, with the results noted.

1. The ammonium sulfide reagent (*4*) is insensitive to ammonium picrate solutions under 100 p.p.m.
2. The potassium thiocyanate test (*6*) is sensitive at concentrations of ammonium picrate as low as 5 p.p.m. However, on alkalizing the solution, a brown color due to the presence of alpha-TNT makes this method unsatisfactory for most cases.
3. The methylene blue test (*1*) is very sensitive to ammonium picrate if the precipitate obtained is extracted with chloroform, the shade of color obtained being dependent upon the pH of the water. As 5 p.p.m. of TNT interfere with this test, it is considered less satisfactory than the test with sodium hydrosulfite which is described below.
4. According to Davis (*3*) guanidine picrate is much less soluble than ammonium picrate. However, laboratory experiments showed that a quantitative precipitation was not obtained on concentrations of ammonium picrate below 100 p.p.m. Therefore, this test is too insensitive for normal ammonium picrate wastes.
5. The reaction with sodium hydrosulfite (*2*) and ammonium picrate, forming the red picramate, is sensitive to 0.5 p.p.m. of ammonium picrate. TNT does not appreciably interfere with this reaction. The color produced, however, is of short duration (1 to 2 minutes) and must be read immediately. Following are the details for carrying out this test under optimum conditions:

REAGENTS. Sodium hydrosulfite solution, 1.0%. Dissolve 1.0 gram of sodium hydrosulfite in 100 ml. of approximately 0.2 *N* sodium hydroxide solution.

Buffer solution, pH 7.2. Dissolve 134 grams of potassium dihydrogen phosphate in several hundred milliliters of distilled water. Add a solution of normal sodium hydroxide until a pH of 7.2 is reached and make up to 1 liter.

PROCEDURE. Add 50-ml. portions of the sample to be tested to each of two 100-ml. Erlenmeyer flasks. If the pH of the water is below 7.0, add 1 ml. of the 7.2 pH buffer solution to each flask. Then add 1.0 ml. of the sodium hydrosulfite solution to one flask, swirl the flask, and compare immediately with the untreated control. A white background will facilitate comparison. The appearance of a momentary red intensification indicates that ammonium picrate is present. With low concentrations of ammonium picrate, immediate comparison is important, as the red color of ammonium picramate will fade within 2 minutes.

If a yellow intensification is noted, dilute a part of the sample, treat with sodium hydrosulfite as above, and compare with an untreated diluted portion. A slight yellow to brown more permanent intensification indicates a large amount of alpha-TNT. As the sensitivity of the test is about 0.5 p.p.m., a rough quantitative estimate of the ammonium picrate in p.p.m. in the sample

Table I. Extinction Values of Ammonium Picrate Solutions

Concentrations of Ammonium Picrate, P.P.M.	Extinction at 460 Mμ In distilled water (calculated $K = 0.033$)	In solution of 300 p.p.m. of Na_2CO_3	In distilled water plus 1 gram of Na_2CO_3 per 50 ml.
0.0	0.03	0.03	0.04
2.0	0.10	0.10	..
2.5	0.11	0.11	..
3.3	0.14	0.16	..
4.0	0.16	0.17	..
5.0	0.20	0.19	0.20
8.0	0.29	0.30	..
10.0	0.36	0.36	0.37
20.0	0.69	0.68	..

can be made by multiplying by 2 the highest dilution giving a positive test.

QUANTITATIVE DETERMINATION OF PICRATE WITH VISUAL SPECTROPHOTOMETER

After the investigation of several quantitative and qualitative methods, the spectrophotometric method, was considered most satisfactory for use on ammonium picrate wastes.

In all spectrophotometric determinations, turbidity must be eliminated from the sample. This is usually done by sedimentation, filtration, or centrifugation. If none of these methods removes the extremely fine turbidities sometimes encountered in natural waters, coagulation with alum can be applied. However, this method of clarification should be used only as a last resort, as it will remove as much as 25% of ammonium picrate or TNT in dilute samples containing up to 10 p.p.m. of these materials.

Ammonium picrate in the absence of TNT wastes can easily be determined colorimetrically or with the spectrophotometer. Although the maximum absorption occurs in the ultraviolet range at 335 mμ, the maximum absorption in the visible range can be used for practical purposes. Using dilutions from a stock 300 p.p.m. solution, an absorption curve was first plotted and it was observed that maximum absorption in the visual range occurred at 460 mμ. Extinction values for dilutions of the stock solution in distilled water and in water containing 300 p.p.m. of sodium carbonate were determined. The mean extinction values obtained are shown in Table I.

These data indicate that the concentration of carbonate or bicarbonate present in natural waters would have no effect on the extinction of ammonium picrate. The increment of E per p.p.m. of ammonium picrate is small (0.033); hence, this method of estimating ammonium picrate concentrations is less sensitive and less accurate than the similar determination for TNT (*5*). Nevertheless, concentrations of ammonium picrate between 2 and 40 p.p.m. can be estimated without dilution. Stronger solutions can be diluted before examination. On the basis of data shown in Table I, the concentration of ammonium picrate in clear solutions is obtained as follows:

$$\text{P.p.m.} = \frac{E_s - E_b}{K} \times (d)$$

where E_s = extinction of diluted sample
E_b = extinction of clear water blank
d = dilution factor
K = 0.033 = extinction per p.p.m. of ammonium picrate for the instrument in use

DIFFERENTIATION AND ESTIMATION OF AMMONIUM PICRATE AND TNT WITH VISUAL SPECTROPHOTOMETER

The method used to differentiate and determine the quantity of alpha- and colored TNT present in TNT waste with the spectrophotometer has been described (*5*). This procedure depends upon a measurement of extinction at 460 and 505 mμ on the clear colored liquid, followed by treatment of the solution by sulfite and hydroxide as described and re-examination at 460 and 505 mμ. When dilute solutions of ammonium picrate are put through this procedure for TNT determination, a color intensification is also obtained by the sulfite hydroxide treatment. In this case there is no great change in the shape of the absorption curve after sulfite treatment, for the solution continues to have its highest E values at the lowest visual wave lengths, with a rapid loss in extinction before 505 mμ is reached. However, when the sulfite hydroxide–treated sample of ammonium picrate is acidified with strong hydrochloric acid, the reaction as far as absorption is concerned is so different from that with TNT solutions that differentiation is possible. When the sulfite hydroxide–treated ammonium picrate sample is acidified, the yellow color is reduced in intensity to what it was before the sulfite hydroxide treatment. With alpha-TNT solutions, acidification accomplishes complete decolorization. Colored TNT solutions are also almost entirely decolorized by the strong acid treatment. It would seem reasonable, therefore, for practical purposes to use the color and absorption values remaining after sulfite and hydroxide treatment followed by acidification as a further step in the analysis for ammonium picrate. Acidification of the 50-ml. sample with 5 ml. of c.p. concentrated hydrochloric acid, followed by a third set of extinction readings at 460 and 505 mμ, has therefore been added to the procedure previously described for TNT wastes for analysis of shell- and bomb-loading wastes which may also contain ammonium picrate.

If the sample is turbid, it is settled and filtered through paper and/or centrifuged until clear. If a clear solution cannot be obtained, the extinction determined on the untreated sample cannot be used. If the solution obtained is free from turbidity, the color is due to ammonium picrate, colored TNT, or organic matter, or mixtures of these, and the clarified sample is examined at 460 and 505 mμ. For this examination the sample may be diluted, if necessary, in distilled water, or better in distilled water containing 300 p.p.m. of sodium carbonate. When the extinctions on the clarified sample at 460 mμ are only slightly higher than at 505 mμ, colored TNT (and possibly organic matter) rather than ammonium picrate, are indicated. If the extinction at 460 mμ is considerably higher than at 505 mμ, but finite values are observable at both wave lengths, both ammonium picrate and colored TNT are probably present. Ammonium picrate solutions in concentrations up to about 100 p.p.m. even undiluted show no extinction at 505 mμ, though high E values are given at 460 mμ. Consequently, if there is a finite extinction at 460 mμ but none at 505 mμ, only ammonium picrate is indicated.

Following the examination of the clarified sample, a 50-ml. portion is treated with sulfite and hydroxide as described for the analysis of TNT wastes; and after filtration is diluted if necessary in the special sulfite hydroxide dilution water and examined at 460 and 505 mμ. If there is a new gain in extinction at 505 mμ due to the sulfite hydroxide procedure and if the extinction after this treatment is higher at 505 mμ than at 460 mμ, the indications are that only colored and alpha-TNT are present. Under these circumstances the calculation for colored and alpha-TNT is made as has been described (*5*).

If after the sulfite hydroxide treatment the extinction at 505 mμ is higher than before this treatment, but lower than at 460 mμ after treatment, both ammonium picrate and TNT may be indicated; and the final acidification step is necessary to complete the analysis. However, if the extinctions at both wave lengths are equal or are lower after sulfite hydroxide treatment than before, it indicates that ammonium picrate is absent and either (1) that the higher original extinctions (in perfectly clear samples) were due to colored organic matter and not to TNT, or (2) that colored TNT is present and alpha-TNT absent. The second explanation of the above extinction relationships has been found to be correct on all water samples examined by the authors, and the first explanation was correct only on some sewage effluent samples.

In the case of the examination of relatively highly colored clarified sewage samples, it is best to ignore the original extinction readings and make the analysis on the basis of the qualitative hydrosulfite test for ammonium picrate and the extinction read-

Table II. Extinction Characteristics and Constant and Extinction Symbols for the Three-Step Spectrophotometric Procedure

Step Following	Clarification		Sulfite Hydroxide Treatment		Acidification	
E reading at, mμ	460	505	460	505	460	505
E characteristics						
Ammonium picrate	+	0	++	+	+	0
Colored TNT	+	±	+	±	±	±
Alpha-TNT	0	0	+	++	0	0
Symbol for E						
Observed reading	E_{OL_1}	E_{OH_1}	E_{OL_2}	E_{OH_2}	E_{OL_3}	E_{OH_3}
Component for ammonium picrate	E_{PL_1}	o	E_{PL_2}	E_{PH_2}	E_{PL_3}	o
Colored TNT	E_{CL_1}	E_{CH_1}	E_{CL_2}	E_{CH_2}	E_{CL_3}	E_{CH_3}
Alpha-TNT	o	o	E_{AL_2}	E_{AH_2}	o	o
Symbol for specific constant to be applied						
Ammonium picrate	K_{PL_1}	...	...	K_{PH_2}	K_{PL_3}	...
Colored TNT	K_{CL_1}	K_{CH_1}	...	K_{CH_2}	...	K_{CH_3}
Alpha-TNT	...	...	...	K_{AH_2}	...	...

+ = finite E value.
++ = E value greater than +.
± = E value less than +.
0 = No finite E.

ings after treatment of the sample with sulfite and hydroxide, and again after acidification for alpha- and colored TNT.

If the analysis has proceeded through the sulfite hydroxide treatment and the question of the presence of ammonium picrate remains, a 50-ml. portion after sulfite hydroxide treatment is acidified with 5 ml. of concentrated C.P. hydrochloric acid. After the acid has been allowed to react for about a minute, the sample is examined again at 460 and 505 mμ. Complete decolorization—i.e., extinction readings no longer than the blank for the machine at 460 mμ—indicate that both ammonium picrate and colored TNT are absent. If, however, a decided yellow color remains and there is a considerable fall in extinction from 460 to 505 mμ, ammonium picrate is indicated and colored TNT may also be present. However, all ordinary concentrations of ammonium picrate (up to about 100 p.p.m. undiluted) show no extinction at 505 mμ, so that the E reading at 505 mμ after acidification indicates only colored TNT.

CALCULATION OF EXTINCTION DATA

To help illustrate how extinction data for this procedure can be readily interpreted and calculated to the various constituents, a system of identification of the extinction values for each wave length read and each step in the procedure is introduced.

For this purpose, let us label all observed extinctions as E_O and the calculated or extinction components for ammonium picrate, colored TNT, and alpha-TNT as E_P, E_C, and E_A, respectively. To indicate the wave length at which the readings were made, we will add H for 505 mμ and L for 460 mμ to the above symbols. Finally, to indicate whether the extinctions were read after clarification (step 1), sulfite hydroxide treatment (step 2), or acidification (step 3), let us add the figures 1, 2, and 3, respectively. To illustrate, E_{OL_1} means the observed extinction at 460 mμ after the first step; and E_{AH_2} means the extinction component for the alpha-TNT at 505 mμ after the second step or the sulfite hydroxide treatment. Although the E_P, E_C, and E_A values are not observed directly in a mixed sample, these extinction components must be obtained before the concentrations of these constituents can be estimated. If however, the sample contains only colored TNT, then E_{OL_1} becomes also E_{CL_1}.

In all cases the constant or K value must be known for each constituent at the wave length and step at which the extinction component is to be converted to the concentration of the component. These constants must be determined for each machine on a series of diluted standards for the particular component, step, and wave length needed. For convenience in this discussion, the K values will be lettered and numbered after the same plan as the extinction values. For instance, K_{PL_1} means the constant for a pure ammonium picrate solution when the extinction was read after the first step at 460 mμ, and K_{AH_2} means the constant for alpha-TNT at 505 mμ after sulfite hydroxide treatment.

To indicate how the extinction values will change in this analytical procedure, Table II is presented. In this table + indicates a finite extinction value for the constituent, ++ indicate an increase in extinction, ± indicates a decrease, and 0 indicates that a finite extinction is not observable.

A list of equivalents, conversion factors, and K values that have been determined on pure solutions in this laboratory is given below. Although it is believed that the equivalents and conversion factors will hold for other instruments, the K values will vary with the adjustment of the instrument, and so must be determined for ammonium picrate, colored TNT, and alpha-TNT solutions. Although values for these constants are given here, they cannot be used for data on other instruments if the highest accuracy is desired. It will be noted that there is some difference in the constants given here and those given earlier (*5*). This difference is due to a readjustment of the instrument after a slight accident in the laboratory and illustrates the possible variation in constants with different instruments.

EQUATIONS AND FACTORS FOR CALCULATIONS

$$E_{OH_1} = E_{CH_1} \text{ (as both picrate and alpha-TNT have 0.0 } E \text{ values at 505 m}\mu) \tag{1}$$

$$E_{OL_1} = E_{PL_1} + E_{CL_1} \tag{2}$$

$$E_{OH_2} = E_{PH_2} + E_{CH_2} + E_{AH_2} \tag{3}$$

$$E_{CL_1} = E_{CH_1} \times 1.63 \tag{4}$$

$$E_{CH_1} = E_{CH_2} \tag{5}$$

$$E_{PH_2} = E_{PL_1} \times f \text{ or } E_{PL_3} \times f \tag{6}$$

where f is a factor depending upon the ammonium picrate concentration and dilution of ammonium picrate:

Under 20 p.p.m., no dilution, $f = 1.92$
20 to 300 p.p.m., $^1/_7$ dilution or higher, $f = 0.3$

$$\text{P.p.m. of colored TNT} = \frac{E_{CL_1} - 0.03}{0.170} \times d \tag{7}$$

$$\text{P.p.m. of ammonium picrate} = \frac{E_{PL_1} - 0.03}{0.033} \times d \tag{8}$$

$$\text{P.p.m. of alpha-TNT} = \frac{E_{AH_2} - 0.03}{0.39} \times d \tag{9}$$

where d in Equations 7, 8, and 9 = the dilution factor.

The simplest way to complete the calculations when all three components are present is on the basis of Equations:

1 and 7 for colored TNT
2, 4, and 8 for ammonium picrate
3, 5, 6, and 9 for alpha-TNT

Although at first glance this spectrophotometric system of analysis may seem slightly formidable, it is really very simple. It is, of course, subject to a number of observational errors, but it presents a sound and practical procedure which enables the estimation of all these constituents when they are present together and indicates the absence of any one that is not present.

BIOCHEMICAL OXIDATION OF AMMONIUM PICRATE WASTE

Concentrations of ammonium picrate in wash waters and evaporation ponds vary between 100 and 300 p.p.m. A series of ammonium picrate dilutions was made up in 1% sewage diluted with mineralized phosphate dilution water and containing concentrations of 0 to 1000 p.p.m. of ammonium picrate. This series was put up in standard B.O.D. bottles and incubated at 20° C. B.O.D. determinations in duplicate were run at the end of 2, 3, and 5 days' incubation, and residual ammonium picrate concentrations were determined by the spectrophotometer for each sample after each incubation period. The results are shown in Table III.

These data indicate: (1) that there is no attack on the above concentrations of ammonium picrate by the microflora of 1% sewage during the 5-day incubation period. (2) As the maximum deviation from the mean B.O.D. for the first five samples at each incubation period was no greater than 10% (which is considered a satisfactory check in B.O.D. work), it is concluded that concentrations of ammonium picrate up to 100 p.p.m. have no effect on the 5-day B.O.D. of the medium. (3) With higher concentrations of ammonium picrate, an inhibiting effect increasing with the concentration of ammonium picrate is indicated.

To determine the effect of prolonged incubation on the biochemical oxidation of ammonium picrate solutions, 300 p.p.m. of ammonium picrate in 1% sewage were incubated for 50 days and B.O.D. determinations were run at regular intervals during the incubation period. With the concentration of ammonium picrate used, a lower B.O.D. was found at the 5- and 10-day intervals than that of the control, but at the end of the 20-day period there was very little difference. The B.O.D. of the ammonium picrate solutions showed very slight variation from the 15th to the 50th day. The concentration of ammonium picrate as measured by the spectrophotometer was practically unchanged to the 15th day.

EFFECT OF AMMONIUM PICRATE ON ACTIVATED SLUDGE

Fresh filtered sewage containing 300 p.p.m. of ammonium picrate was fed to activated sludge and the usual determinations were made after intervals of aeration. The results of this experiment (Table IV) show: (1) an immediate loss of 100 p.p.m. of the ammonium picrate dosed, with no further loss during the period of aeration. (2) Removal of B.O.D. by activated sludge was retarded after 2 hours' aeration. (3) No significant change in suspended solids was noted.

REDUCTION OF AMMONIUM PICRATE BY SEWAGE

Upon adding ammonium picrate solutions to strong sewages, a reduction of the picrate was observed similar to the reduction of sodium hydrosulfite. This reduction is dependent upon the concentrations of ammonium picrate and sewage and the pH of the medium, the reaction proceeding more rapidly at higher pH values. The color change is from orange to reddish brown, and, upon long standing, a large reduction in color is noted.

Removal of Ammonium Picrate by Coagulation, Activated Carbon, Soil Percolation, and Sunlight. Tests were carried out using the above methods for removing ammonium picrate from the waste previously described. None of the methods proved economically feasible. Coagulation resulted only in partial removal. Large amounts of activated carbon are required for effective removal. Only one type of soil tested removed an appreciable amount of picrate on the first portion passed through and none removed a finite amount of subsequent portions. Sunlight had no effect on ammonium picrate.

Table III. B.O.D. and Ammonium Picrate Concentrations in a 1% Sewage Dilution Containing Increasing Increments of Ammonium Picrate

	Ammonium Picrate Concentration, P.P.M.					B.O.D., P.P.M.		
		Residual Determined after						
Sample No.	Dose	Initial	2 days	3 days	5 days	2 days	3 days	5 days
Control	0	0	....	....	...	174	224	278
1	10	8.1	7.5	9.4	9.6	172	223	275
2	20	17.9	16.5	18.9	18.9	182	250	269
3	40	38.8	37.6	40.8	39.6	158	217	278
4	60	58.3	56.8	60.8	58.3	173	223	265
5	100	97.0	94.0	97.9	102.1	182	228	267
		Mean				173	227	272
		Maximum deviation from mean				−15	+23	−7
Control	0	0	....	....	...	128	171	192
6	300	316.0	316.0	300.8	300.8	111	149	162
7	600	635.5	645.5	615.0	625.0	122	129	146
8	800	833.0	865.0	833.0	822.5	118	131	153
9	1000	1083.0	1000.0	1166.0	979.1	108	110	124

Table IV. Effect of Ammonium Picrate on Activated Sludge

	5-Day B.O.D.		Removal		Picrate Remaining	Suspended Solids	
	A	B	A	B	B	A	B
	P.p.m.	*P.p.m.*	%	%	*P.p.m.*	*P.p.m.*	*P.p.m.*
Feed	126.0	152.0	..	..	325.0	..	..
Initial	99.0	101.3	..	..	220.8	..	..
After 2-hr. aeration	16.7	12.0	83.1	88.1	225.0	..	..
After 4-hr. aeration	26.9	21.1	72.8	79.1	220.8	..	..
After 6-hr. aeration	7.0	15.5	92.9	84.7	237.4	2155	2065
After 24-hr. aeration	2.6	17.9	97.3	82.3	229.2	1930	1865

A = sludge fed with sewage only.
B = sludge fed with sewage plus 300 p.p.m. of ammonium picrate.

Table V. Effect of Time on Reduction of Ammonium Picrate by Domestic Sewage

Days	Total P.P.M. of Reduced and Unreduced Ammonium Picrate
0	22.0
1	10.0
2	13.2
3	10.5
5	10.3
7	10.3
10	9.7
15	9.1
17	7.4
Loss	14.6

Potability of Drinking Water Containing Ammonium Picrate. Amounts of ammonium picrate as low as 0.5 p.p.m. can be detected in drinking water by taste, 1.0 p.p.m. becomes objectionable, and amounts up to 3.0 p.p.m. render the water unfit for human consumption. These results were arrived at by submitting various concentrations of ammonium picrate in drinking water to twenty persons who were unaware of the contents for appraisal..

SUMMARY

A simple colorimetric or spectrophotometric procedure was found satisfactory for estimating ammonium picrate concentrations in clear wash waters from lines loading ammonium picrate. If the samples are turbid, the samples should be clarified by filtering, settling, and/or centrifuging until free from any turbidity. Chemical flocculation should not be used for clarification unless absolutely necessary, for this may remove some of the picrate.

The qualitative tests for ammonium picrate are reviewed and a technique for a sodium hydrosulfite test which will detect 0.5 p.p.m. of ammonium picrate in the presence of colored and alpha-TNT is presented.

A quantitative three-step spectrophotometric procedure for estimating ammonium picrate, colored TNT, and alpha-TNT in mixed waste waters containing all three is presented. This procedure depends upon extinction readings made at 460 and 505 mμ on the sample after 3 steps: (1) clarification, (2) sulfite hydroxide treatment procedure for TNT wastes, and (3) acidification of the sulfite hydroxide–treated portion. The procedure is simple and direct. After the necessary constants have been determined and the sample is clarified, it enables estimation of all three possible constituents within about 30 minutes. Details of the procedure are given.

A study was made of some of the chemical and biochemical properties of ammonium picrate waste. It was found that the ammonium picrate in the waste has no B.O.D. and that it inhibits the normal B.O.D. reaction of sewage dilutions when present in concentrations over 300 p.p.m. With activated sludge a partial removal of about 30% of the ammonium picrate takes place with the remainder inhibiting the removal of B.O.D. after 2 hours' aeration. Other methods of treatment attempted were of little practical value. Taste tests with a group of people indicated that 1 p.p.m. may be considered the upper permissible limit of ammonium picrate in water for human consumption.

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Determination of Hiding and Contrast-Obliterating Power of Paints

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Determination of the hiding power of paints is commonly based on the application of increasing quantities of paint, until complete (or the same degree of incomplete) concealment of a given design is obtained. Values obtained by different procedures do not agree and in some cases are contradictory: when the quantities applied are increased, the contrast does not increase in the same ratio for different paints. For this reason, every method based exclusively on application of increasing quantities of paint should be rejected.

To determine hiding power, the paint should be applied in normal thickness, establishing the degree of contrast between design and background which may be completely obliterated under these conditions. This may be done by painting on sheets which have a scale of gray shades of increasing darkness, on both a black and a white background, and ascertaining the hiding power by two constants which represent (1) the contrast between the black background and the lightest gray spot which may be concealed completely, and (2) the contrast between the white background and the deepest gray which may be concealed completely, after the paint is applied in normal thickness. To avoid confusion with values obtained by other methods, this type of hiding power may be called contrast-obliterating power.

HIDING power, according to A.S.T.M. D344, is the ability of a paint to reduce the contrast of a black and a white surface to which it is applied (*2*). According to A.S.T.M. D16, it is the power of a paint to render a surface invisible or to cover it up, so that it cannot be seen (*3*). This condition is complied with when designs on the surface are completely concealed.

These two definitions refer to the two more usual methods of determining hiding power. In the first case, paint is applied on sheets which have black geometrical figures sharply outlined on a white background, and the hiding power is indicated by the quantity of paint that just allows the design to be seen against its background (method 1). In the second case, the same test charts may be used. Here hiding power is defined as the least quantity of paint necessary to conceal the designs completely (method 2).

In practice the contrast to be concealed by a paint is generally much weaker, and according to the test, one product may be found inferior to another, yet still good enough to conceal the existing contrasts, so that in practice no difference would be observed. For this reason, the quantity of paint necessary to render a design invisible is often determined on test charts with designs of reduced contrast—for instance, dark gray figures on a light gray background (method 3).

The results obtained with method 2 are often designated as "complete hiding power", and those with methods 1 and 3 as "incomplete hiding power" (*4*, *5*, *6*, *11*, *13*).

The quantities of paint required for complete hiding will be greater than those for incomplete hiding, and in the case of incomplete hiding this quantity will be a function of the degree of contrast that has been covered. But if the values thus obtained are to be employed as a standard for hiding power, for two different paints the ratio of the quantities of paint necessary to give same hiding effect should be constant, independent of the method of comparison.

COMPARATIVE TESTS

For comparative tests, methods 1 and 2 were used, in the expectation that No. 3 would yield results similar to 1.

Paints of different types, colors, and gloss were applied by brush on carton sheets with 8 × 5 white and black squares each measuring 25 sq. cm., distributed alternately on a rectangular area of 0.1 sq. meter. Several brushouts with increasing quantities of each paint gave a series of sheets from which the cartons could be selected in which the contrast of the designs had been reduced to the same degree. These observations were made with the naked eye after the paint had dried.

In Table I are reproduced the results obtained with three white enamels of high gloss and three red enamels. The tests which correspond to the same final contrast are arranged in the same horizontal lines; lines 1 to 5 and 7 to 10 refer to incomplete, and lines 6 and 11 to complete hiding. In the last two vertical columns are inserted the ratios of quantities necessary for the same degree of concealing, which should be constant for each pair of paints. But this condition is never fulfilled. For instance, 3.8 times more of paint *C* is needed than paint *B* for the same degree of incomplete hiding (line 1); whereas the relation is 1.9 for nearly complete hiding (line 5) and 1.5 for complete hiding (line 6). Comparison of paints *F* and *E* yields a contradictory result: *F* is superior to *E* if the contrast of the surface designs is incompletely concealed (line 10), and inferior for complete hiding (line 11).

In order to evaluate the significance of these discrepancies, the variation in paint quantities which may be determined for the same hiding effect should be known.

In the case of incomplete hiding power and observation by the naked eye we can estimate this variation by A.S.T.M. method D344 (1939) (*2*). This prescribes that the quantities to be applied on the test charts shall increase by the factor 1.15 and that 10 intermediate values may be estimated; that means that the uncertainty amounts to $\sqrt[10]{15\%} = 1.3\%$. This precision,

Table I. Quantities of Paint for the Same Hiding Degree

Line No.	Quantities of Paint			Hiding	Ratio of Quantities	
	A	*B*	*C*		*C* and *A*	*C* and *B*
	Grams/sq. meter					
				White Paints		
1	...	12.1	46	Incomplete, medium contrast	..	3.8
2	...	15.6	55	Incomplete, medium contrast, somewhat less than 1	..	3.5
3	20.7	...	66	Incomplete, medium contrast, somewhat less than 2	3.2	..
4	115	...	166	Incomplete, very small contrast	1.5	..
5	...	95	179	Incomplete, very small contrast, somewhat less than 4	..	1.9
6	180	157	235	Complete	1.3	1.5
				Red Paints		
	D	*E*	*F*		*F* and *D*	*F* and *E*
7	32	...	45	Incomplete, medium contrast	1.4	..
8	37	...	47	Incomplete, medium contrast, somewhat less than 7	1.3	..
9	40	...	50	Incomplete, medium contrast, somewhat less than 8	1.25	..
10	53	68	57	Incomplete, medium contrast, somewhat less than 9	1.1	0.84
11	230	265	280	Complete	1.21	1.15

Table II. Quantities of Paint for the Same Degree of Hiding (6)

Line No.	Quantities of Paint[a]				Hiding	Ratio of Quantities		
	G	*H*	*J*	*K*		*G* and *H*	*G* and *J*	*G* and *K*
	Grams/sq. meter							
1	108	26	15	14	Medium, contrast 0.40	4.2	7.1	7.6
2	348	63	60	84	Good, contrast 0.10	5.5	5.8	4.1
3	507	83	129	210	Complete, contrast 0.022	6.1	3.9	2.4

[a] Paints *G*, *H*, *J*, and *K* correspond to products 4, 2, 3, and 1, respectively, of Gordon and Gildon.

however, can be expected only for paints of exactly the same color and gloss. The least difference in these factors makes much more difficult the comparison of the test charts. According to tests carried out with a great number of persons of different sexes, ages, and occupations, the uncertainty for red enamels of high gloss with very few differences in the red hue, is estimated as at least 10%.

The difficulty is still greater if we have to determine the quantities necessary for completely concealing the designs. For well-known physiological reasons, the least contrast which may be perceived with the naked eye corresponds to a smaller reflectance ratio for shades of medium reflectance than for shades of very low or very high reflectance. On the other hand, differences in color and gloss do not interfere in such a pronounced manner, so that paints of very different color and gloss may be compared. The author estimates the variation in the determination of the complete hiding power as at least 15%.

This indicates that the discrepancies deduced from Table I cannot be explained by test errors.

These results are confirmed by a paper published by Gordon and Gildon (6), found after the author's experiments had been completed. [The author's tests were made in the second quarter of 1944 during the preparation of an Argentine specification for a method of determining the hiding power of paints (*Norma Iram*, 1072, in preparation). See *Informaciones Iram*, 9, 159 (1945).] Although these authors do not directly treat the problem of the present publication, useful values have been extracted from their tables and curves.

Gordon and Gildon also made brushouts on sheets which had black and white squares. Using a photometer, they determined the ratio of light reflectance between dark and light squares after applying increasing quantities of paints of different colors and finishes. (They use the term "contrast ratio" instead of "reflectance ratio", which the author prefers.) In Table II are given the quantities found in their curves.

For medium concealment, leaving a medium contrast ($C = 0.40$; $\Delta D = 0.40$)
For good concealment, leaving a little contrast ($C = 0.80$; $\Delta D = 0.10$)
For almost complete concealment, leaving an almost imperceptible contrast ($C = 0.95$; $\Delta D = 0.022$)

C indicates the reflectance ratio between the dark and the light squares of the painted sheet, and ΔD the corresponding (logarithmic) contrast.

Comparing the quantities of two paints necessary for the same hiding effect—that is, the values in the same horizontal line of Table II—the ratios are not constant, nor do they vary always in the same sense, which is in accordance with results deduced from Table I.

For example, on applying paint *G* in a film 7.6 times heavier than *K*, Gordon and Gildon obtained in both cases the same contrast of $\Delta D = 0.40$ between the dark and the light squares (line 1, Table II); on the other hand, they needed only 2.4 times as much of paint *G* as of *K* to render the squares invisible (line 3). The comparison of paint *H* with *J* and *K* yields contradictory results: *H* is superior for covering the designs completely (line 3) and inferior for concealing them only partially (line 1). The producer of paint *H*, consequently, is interested in determining the "complete" hiding power, whereas the manufacturer of *J* and *K* will prefer the "incomplete" hiding power.

The study of hiding power published by the Baltimore Club (4) refers only to white paints, so that its results cannot claim such general application as those treated in Tables I and II. Nevertheless Table III gives the values deduced from their curves.

The investigations were carried out by brushouts on test charts provided with black designs on a white background. These show that the relative hiding power of a paint depends on the contrast which is agreed upon for the comparison. The "H. O. lithopone 60% paint" is better than the "lithopone paint" for contrast $\Delta D = 0.10$, but inferior for $\Delta D = 0.022$. In Figures 4 and 6 of (4), the discrepancies pointed out occur even with paints which contain the same pigment and the same vehicle, the only variation being the ratio between these components. According to Figure 6 the "H. H. lithopone paint" with 50% pigment concentration covers better than that with 40% if a reflectance ratio of less than 0.96 is to be obtained (ΔD greater than 0.018, "incomplete hiding"), whereas for a ratio greater than 0.96 ("nearly complete hiding") the 40% paint is superior.

Another confirmation of the author's results may be found in Haslam's paper (7). He indicates that the same quantities of two different white paints, I and II, are necessary to cover up a black background completely; but to conceal it incompletely, leaving the same light reflectance, with both paints, he had to apply a greater quantity of II than of I, the ratio depending on the degree of obliteration. For this reason, Haslam rejects the determination of incomplete hiding power.

According to all the above experiments, it is not permissible to stipulate a simple proportion for transforming incomplete hiding power into complete hiding power, as is assumed by the formula (5, p. 25).

$$\frac{\text{Incomplete H. P. of sample}}{\text{incomplete H. P. of standard}} = \frac{\text{complete H. P. of sample}}{\text{complete H. P. of standard}}$$

All the arguments adduced prove that the hiding power values for paints depend on the degree to which the original contrast of the designs on the test chart has been reduced. There is no general value for the hiding power, neither absolute nor relative, if this magnitude is defined and determined by the methods to which reference has been made and which are the most commonly used.

Table III. Quantities of Paint for the Same Degree of Hiding (4)

Paint	Quantities of Paint		Figure of (4)
	$C = 0.80$, $\Delta D = 0.10$	$C = 0.95$, $\Delta D = 0.022$	
	Grams/sq. meter		
Titanium-lithopone, 50%	3.2	8.9	2
Titanium-barium, 50%	3.9	11.2	4
H. O. lithopone, 60%	4.1	12.3	3
Lithopone	4.4	10.4	1
L. O. lithopone, 60%	5.6	13.2	5
H. H. lithopone, 40%	5.7	12.8	6

CAUSES OF DISCREPANCIES

The causes of the discrepancies pointed out above are the same as those mentioned to explain the effect of pigment concentration on hiding power (4). The concealing effect of a pigment depends not only on its quantity per unit area, but also on its dispersion and distribution within the layer; and the concealing behavior of a paint coat is determined by its light absorption as well as by light scattering. If we apply a greater quantity of paint, we may expect the areal pigment concentration and its light absorption to increase in the same ratio, but the scattering will change for each paint in a different manner, thereby causing the discrepancies mentioned above.

The author is indebted to Deane B. Judd, National Bureau of Standards, for the suggestion that Kubelka and Munk's study (*10*) of the relationship between light reflection and thickness of homogeneous layers might aid in this investigation. The latter expounded an equation expressing this relationship by two constants: reflectivity—the reflectance of an infinitely thick specimen of the material—and coefficient of scatter. Judd, Hickson, and Eickhoff (*9*) showed that this equation applies sufficiently well to white and near-white cold-water paints. If it could be proved that the theory of Kubelka and Munk is also valid for oil paints, both glossy and flat, it would be possible to base the specification of hiding power of paint simply on the scattering coefficient, and the discrepancies pointed out above would not exist. This decision would have to be checked by brushing out known quantities of paint over black and white backings, and measuring the reflectances.

Judd (*9*) gives a curve chart calculated by means of the Kubelka-Munk equation, which permits in a very simple manner deduction of the reflectivity and the product of thickness and scattering coefficient, from the ratio of the reflectances on black and white backgrounds and from the reflectance on a black background; knowing the thickness we may calculate the scattering coefficient. Once these two constants—reflectivity and scattering coefficient—are determined we may find with the aid of the same curve or the corresponding equations, the values of light reflectance on any background (black, white, or gray) and for every desired thickness of film. These two numbers would, consequently, characterize the hiding behavior of the paint in a general manner.

In practice, however, this method would have two disadvantages. Apart from the necessity for using a reflectometer, results obtained by measuring the reflectances with daylight would be satisfactory only in the case of white or near-white paints; materials having highly chromatic colors will require values of reflectivity and coefficient of scatter as functions of wave length (*9*).

SUGGESTED NEW METHOD

General Principles. The determination of hiding power is usually carried out by applying increasing quantities of paint, until complete—or the same degree of incomplete—concealment of a design is obtained. In order to secure the desired covering, the paint must sometimes be applied in a thickness which is far from normal; values determined under such extreme conditions are not of practical interest, as they give no indication of the hiding behavior of the paints under normal conditions of painting.

In view of this fact, it seems best to face the problem from the inverse aspect. We should not raise the usual question "what thickness of paint is to be applied for concealing a given contrast (partially or completely)?", but should ask "which contrast may be concealed when the paint is applied in normal thickness?".

The A.S.T.M. method (*2*) is based on this second point of view. But this test has to be carried out in a rather inconvenient manner and for this reason has not received wider acceptance (*6*). According to this method, paint should be applied in a normal thickness on a white sheet with black designs, and the concealing degree determined by visual comparison with a scale of contrasts obtained by brushouts of increasing quantities of a standard paint on other sheets which have the same designs. This method is not an absolute one and requires a standard paint; satisfactory results can be obtained only with products of very similar hue and finish.

In order to avoid all these inconveniences, a new method for the determination of hiding power is proposed here. The paint is to be applied in normal thickness, establishing the degree of contrast between background and design which may be completely obliterated under these conditions. In order to comply with this stipulation, paint is applied on test charts which have, on both a black and a white background, a scale of gray shades of increasing darkness and the hiding power is ascertained by two constants which are numerically equal to the value of (1) the contrast between the black background and the lightest gray spot which may be concealed completely, and (2) the contrast between the white background and the darkest gray spot which may be concealed completely, when the paint is applied in a normal degree of thickness. As a consequence of these definitions, we obtain positive values for the standards if the test is carried out on a black background, and negative ones for tests on a white background.

This contrast is found as the difference of the densities of background and gray spot, the density being the negative logarithm of the light reflectance ratio of these two areas. In consequence, the "contrast" may also be defined as the negative logarithm of the ratio of the light reflections of background and gray spot. Many papers indicate directly the numerical value of this reflectance ratio (sometimes called contrast ratio, although the term "contrast" itself involves a ratio) in order to describe a contrast between two areas, but according to the law of Weber and Fechner the impression on the human eye corresponds to the densities and their difference, and not to the reflectances and their ratio.

Although the term "contrast" should be reserved for the density difference, the term "logarithmic contrast" is sometimes found, since this difference is equal to the logarithm of the reflectance ratio and in order to differentiate from the "numerical contrast", which is the numerical value of the reflection ratio.

The magnitudes mentioned are defined and connected to one another by the following relations:

If I is the intensity of the incident light, and I', I'', etc., are intensities of the reflected light, we have:

Light reflectance: $$R' = \frac{I'}{I}$$

Density: $$D' = \log \frac{I}{I'} = -\log R'$$

Reflectance ratio (contrast ratio, numerical contrast): $$C = \frac{I'}{I''}$$

Contrast (logarithmic contrast): $$\Delta D = D' - D'' = \log \frac{I''}{I'} = -\log C$$

In scientific photography the magnitudes "density" and (logarithmic) "contrast" are used exclusively, never the "reflectance" and their ratio (the numerical contrast).

Whenever we wish to differentiate the reflectances, densities, reflectance ratios, and contrasts which exist in the surface to be painted, from those which exist in the applied paint coat, we use

R, R', D, D', C, ΔD, etc., for magnitudes which refer to the background

and

$R_{R'}$, $D_{D'}$, $C_{R'}$, $D_{D'}$, etc., for magnitudes which refer to the paint film

indicating, for example, $D_{D'}$ (or $D_{0.50}$), the density of a paint film which has been applied on a surface, the density of which is D' (or 0.50).

To avoid confusion this type of hiding power might be called "contrast-obliterating power" since usually "hiding power" is understood to be the quantity of paint necessary for a definite hiding effect, whereas according to the present method a contrast value is used for measuring the concealing behavior.

If it is more convenient, the gray scale may also be on a uniform gray background. In this case, the hiding behavior of the paint would be characterized by two constants which are numerically equal to the contrasts existing between the gray background and the lightest and darkest gray spots which have been rendered invisible, the first value being a positive number and the second a negative one. For reasons explained later, this paper is restricted to measurements with black and white backgrounds.

The new method gives absolute, not relative values (as, for example, the A.S.T.M. method and many others); no standard paint is necessary. It is independent of the color and the finish of the paint. It may be carried out in a simple manner, with a single application of paint, whereas for the other proceedings it is generally necessary to paint a greater number of test charts in order to obtain one with the required reduction of the original contrast. The observation is carried out by the naked eye, without any optical instrument, on both fresh and dried films.

Thus the values of contrast-obliterating power are not only more closely related to the practical performance of the paint than the conventional hiding power, but the determination may be carried out more easily.

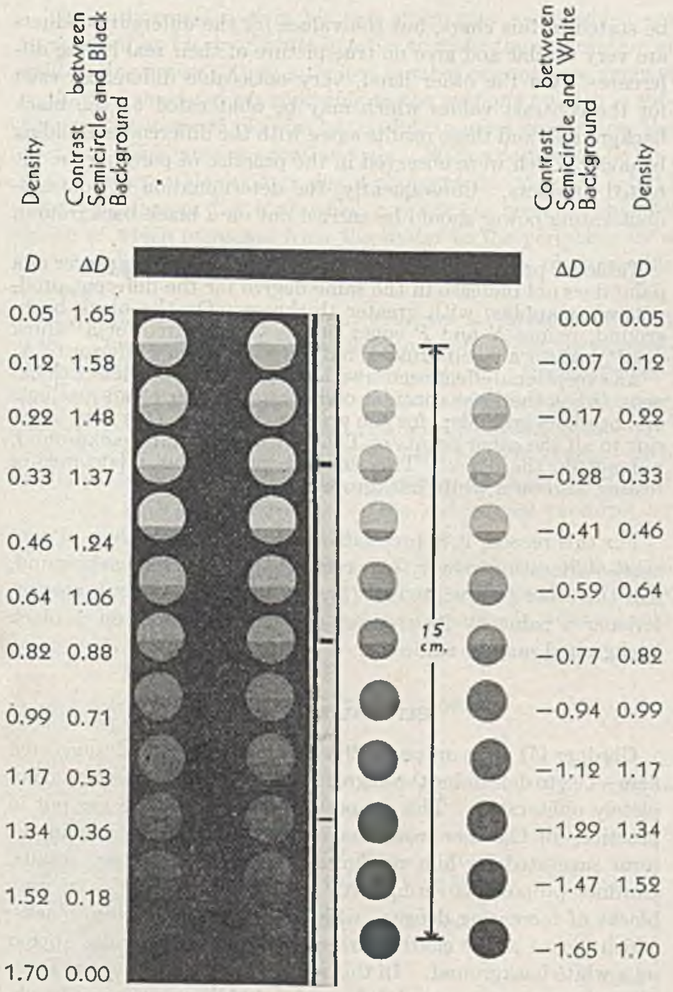

Figure 1. Test Chart for Determining Contrast-Obliterating Power

THE METHOD. Figure 1 shows a gray scale prepared by photography, in which the gray shades have the form of semicircles in order to make observation easier. The first semicircle is white, whereas the remaining part of the circle is a very light gray. The same gray is repeated in the upper semicircle of the next sphere, the adjoining semicircle following with a little deeper gray.

In a darkroom, a fine-grained film of soft graduation was covered with a carton perforated in a manner which corresponds to the circles of Figure 1. A weak light was mounted at such a distance that with a 4-second exposure and after normal development, very little blackening was brought about. With this illumination, the rows of circles were exposed, the exposure time being augmented so that each row was blackened very little more than the preceding (time factor for film was $\sqrt{2}$). A contact copy was prepared from the negative, utilizing a paper of very hard graduation and a special developer in order to obtain blacks of a high density. Adapting the exposures and developments to the special characteristics of the photographic material, columns of gray spots were obtained, varying from a very light to a very dark gray. In order to have the circles on a white background and to obtain a white semicircle, the corresponding part of the negative was covered with the special photographic opaque color commonly used for this purpose.

If many test charts are to be prepared it is convenient to have them made by lithography. Each copy of the set has the same densities of the white, gray, and black spots, and of the backgrounds, so that the density measurements of one test chart are good for all.

In this manner, the gray of the semicircles gradually increases in darkness, the last one being black. The gray of the lower semicircle is always repeated in the upper part of the next circle in order to facilitate control of the reading. This arrangement has been repeated in four columns, two on a white background, and two on a black. The four semicircles in the same horizontal line have the same gray, but by a contrast effect those on the white backing seem darker. The vertical black lines and the two horizontal black blocks have been included so as to make possible controlling the uniformity of the paint film.

On the two frames are indicated the densities, *D*, of the different grays, determined by the Goldberg densitometer. The contrasts, Δ*D*, which exist between the black (left) and the white (right) background and each gray spot, are also given.

In order to obtain satisfactory results with this method, it is necessary to apply the paint in a layer of exactly uniform thickness. Such films have been produced by the use of the Bird film applicator, otherwise known as the Bradley blade. [In a general description of methods of applying uniform films (*12*), this doctor blade is dealt with; a sketch of this applicator may be seen in Figure 591 of Gardner's publication (*5*). A special method was described by Howard (*8*). See also (*1*).]

This device is an accurately machined steel bar with a bevel edge and a specific clearance between the edge and the ends. For these tests three different applicators were used, one with a clearance of 0.0075 ± 0.001 mm. and a width of 5 cm., another with a clearance of 0.150 ± 0.002 mm. and a width of 5 cm., and a third with a clearance of 0.150 ± 0.002 mm. and a width of 15 cm.

The thickness of the films obtained with these blades depends to a certain extent on the characteristics of the paint—for example, viscosity, flowing—and the manner of operating. But the differences of film thickness are not so pronounced as in the case of brush application.

Painting enamels *A* and *D* normally with a brush, fresh films 0.07 and 0.04 mm. thick, respectively, were obtained. With brushouts well spread out, paint *A* also gave a thickness of 0.04 mm. On the other hand, the applicator rendered the same thickness with both paints, 0.042 mm. with the clearance of 0.075 mm. and 0.074 mm. with the clearance of 0.150 mm. It may therefore be assumed that the films obtained with the two clearances of 0.075 and 0.150 mm. correspond for these paints to a well brushed out layer and to a heavy coat, respectively; which means in both cases the thickness of one coat in the normal paint job.

In order to have the photographic papers well flattened—necessary for uniform application with the Bradley blade—it was fixed on a glass plate with a nondrying adhesive which could be easily washed off once the test had been finished. Howard (*8*) recommends holding the test charts flat by suction on a plane plate-glass cover drilled with holes.

PREPARATION. Heat 34 parts of glycerol to the boiling point, add 51 parts of white dextrin, mixing well, and, after cooling, 14 parts of water and 1 part of turkey red oil or the corresponding quantity of another wetting agent.

Practical Results. Figure 2 shows the test chart after a paint has been applied in the manner described, and in Table IV are reproduced some results of tests. A higher absolute value indicates that the product has a superior hiding power, the positive values corresponding to the obliteration of spots lighter than the background, and the negative ones to spots darker than the background.

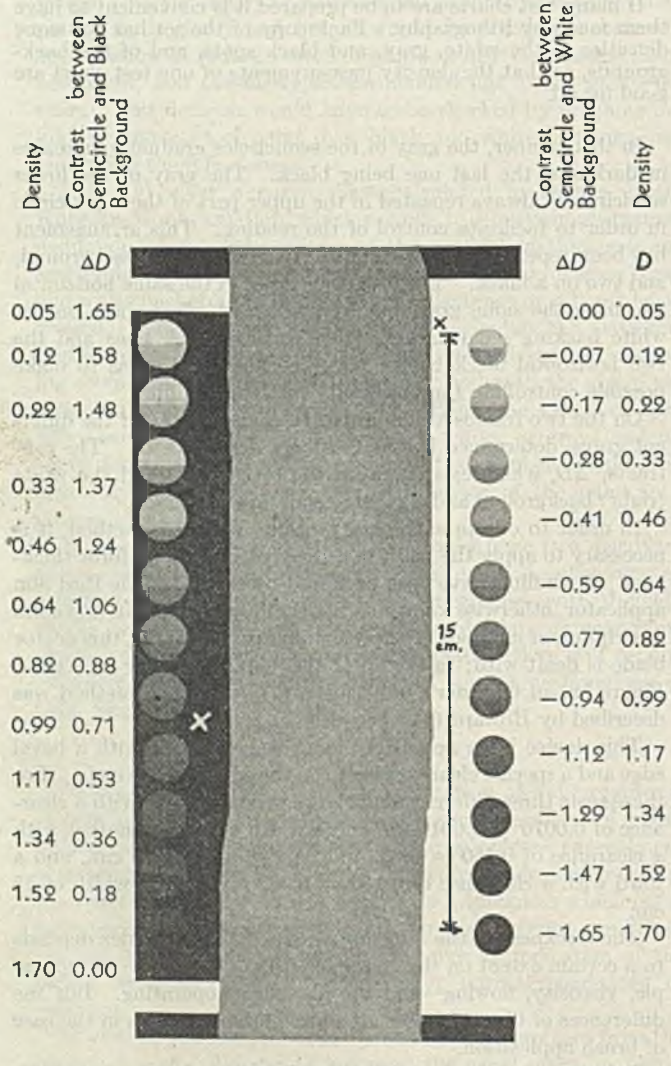

Figure 2. Test Chart after Applying Paint

Semicircles with the greatest contrast which have been completely obliterated are marked with a cross; they correspond to a contrast $\Delta D = 1.26$ on the black background, and greater than −0.07 but less than 0 on the white background. If the paint is applied with a blade of 0.075-mm. clearance, the tested product is characterized by

$$\begin{aligned} COP_{c-0.075} \text{ on black} &= 1.26 \\ COP_{c-0.075} \text{ on white} &> -0.07 \\ &< \ \ 0.00 \end{aligned}$$

As the paints tested showed in practice considerable differences in hiding behavior, it may cause surprise that according to Table IV no differences were found when the products were well sprayed out on a gray scale appearing on a white background. In this case, the obliterated contrast is still smaller than that of the lightest gray spot. If any differences exist, they must be within the very small contrast range of $\Delta D = 0$ and $\Delta D = -0.05$, and therefore not determinable by the test chart. Applying the same paint in a thick coat, the obliterated contrast is great enough to be stated in this chart, but the values for the different products are very similar and give no true picture of their real hiding differences. On the other hand, very noticeable differences exist for the contrast values which may be obliterated on the black background, and these results agree with the differences of hiding behavior which were observed in the practice of painting for the tested products. Consequently, the determination of contrast-obliterating power should be carried out on a black background.

Table IV. Contrast-Obliterating Power of Different Paints

(Greatest contrast obliterated by a paint film of normal thickness)

		Greatest Contrast Obliterated			
		Well Brushed Out[a]		Thick Coat[b]	
Paint	Color	White background	Black background	White background	Black background
D	Red	−0.05	0.78	−0.07	1.05
E	Red	....	..	−0.05	0.58
F	Red	−0.05	0.39	−0.05	0.84
L	White	−0.05	0.72	....	..
M	White	....	..	−0.05	1.01
N	White	−0.05	1.01	−0.09	1.15
P	Yellow	−0.05	0.72	−0.07	1.15
Q	Bordeaux-maroon	−0.05	0.30	−0.59	0.88

[a] Applicator clearance, 0.075 mm.
[b] Applicator clearance, 0.150 mm.

Table IV presents another proof that the concealing power of a paint does not increase in the same degree for the different products when applied with greater thickness. On the black background, paints *N* and *P* cover in the same degree for a "thick coat", but for a "well brushed out" layer *P* is very inferior to *N*. An exceptional effect occurs with paint *Q*. For the lesser thickness, *Q* has the least contrast-obliterating power of all products on both backgrounds; for the greater thickness, *Q* is very superior to all the other paints of Table IV on the white background, but not on the black. This example proves the importance of testing also on a white background.

For this reason, it is preferable to indicate two values of contrast-obliterating power, one referring to a black background, and the other to a white one (Figure 2), but in general, characterizing a paint by its contrast-obliterating power on a black background may be sufficient.

GENERAL REMARKS

Gardner (*5*) gives on page 19 a hint on the method suggested here—i.e., to determine the degree of contrast which may be completely obliterated. This proposal was apparently never put in practice, for Gardner would have observed that the test in the form suggested by him produces rather unsatisfactory results. Gardner proposes covering with the test paint a series of gray blocks of increasing density, which alternate with white blocks; which means a test chart in which different gray shades appear on a white background. In this way, as may be seen from Table IV, only very pronounced differences of hiding power can be observed. It is imperative to observe the concealment of contrasts between the single gray degrees and a black background.

Others may prefer a gray background, several gray backgrounds of different shades, or black and white and grays, arguing that one or the other of these proposals more nearly approaches practical conditions. In this case, however, the gray shades would have to be well defined, and the advantage would possibly be annulled by difficulty of obtaining the shade agreed upon wherever the test should be carried out.

Considering the fact that the author's method is designed for practical purposes, we must limit to the minimum the number of constants used to characterize the hiding behavior and choose among the different possibilities those which may be put in practice in the easiest manner, because a somewhat less exact characterization is satisfactory if we may obtain a sufficiently good one with fewer samples and less work. Finally, it is shown below that for theoretical reasons also the use of gray backgrounds is inadmissible.

In the test chart the author has utilized ten gray shades as well as black and white. It is not necessary to use the same graduation as in this test chart. A finer graduation is possible, but should not be necessary for practical purposes. If required, intermediate values may be obtained by interpolation.

Preparing test charts in different places, it is certain that other gray shades will be obtained than those which appear in the author's chart. But these changes are without importance because the contrast-obliterating power values refer to the contrast values which have been determined for the gray spots, and not to the number of spots obliterated. These contrasts are defined as differences of densities; the measurement need be carried out only once for every set of test charts and may be done in any physical or scientific-photographic laboratory.

The author preferred in his test chart gray spots which are surrounded by black or white in order to make the observation of obliterating easier. Only a limited number of contrasts appears in the test chart (which according to the author's opinion is sufficient), but it would likewise be possible to use a gray stripe, the depth of which increases continuously. Such a design can be prepared, for example, by exposing a photographic material behind a rotating opaque disk from which a sector has been cut out, the width of which increased from the center to the periphery by a factor which depends on the characteristics of the photographic material.

The method is to be carried out with normal thickness of paint film. This normal thickness is the most convenient for application, but not necessarily equal for all products. It might therefore be better to use a series of applicators with corresponding clearances (or one with variable clearance), but the author prefers to test paints of similar type with the same thickness—such as is obtained by the use of an applicator—because the painter generally levels the differences of the commercial products by dilution and his manner of working.

To avoid misunderstandings respecting thickness, it is advisable to indicate the clearance of the applicator used, and if the paint has been diluted for application to describe in what manner this has been done.

For example, according to Table IV, paint *D* should be characterized by

$$\text{COP}_{c\,=\,0.075}\text{ on black} = 0.78$$

which means that by paint *D*, applied with a blade of the clearance of 0.075 mm., a gray spot may be obliterated the contrast of which is $\Delta D = 0.78$.

With the knowledge that the paint film in this case has a thickness of 0.042 mm., the same paint may be described by

$$\text{COP}_{t\,=\,0.042}\text{ on black} = 0.78$$

Values obtained by the usual methods may lead to conclusions concerning the quantities of paint which give the same concealing result, whereas the suggested method permits no correlation with paint quantities. But the experiments described at the beginning of this paper show that such an advantage does not exist, at least for paints of greater hiding differences (and in the case of products of little hiding differences, the method may yield the same correlation). Results obtained with a certain film thickness hold only for that particular thickness, and therefore varying results may be obtained from tests where the film thickness is very different. Quantitative statements are of interest for practical purposes only if they refer to entire coats of a normal thickness, because the painter does not apply the paint in a thickness which is a fraction of one coat, although he may to a certain degree change the paint quantity by dilution and manner of working. The hiding behavior of films of the thickness of a normal coat is the problem to be solved by the suggested method.

If paints applied in normal thickness conceal the greatest contrast which exists in the author's test chart, they must be considered as best, and it will be of no practical interest if differences arise in hiding behavior when these products are applied in a thinner coating.

The tests are not necessarily to be carried out with the same thickness for every kind of paint, but the thickness should correspond to normal conditions of painting. This thickness, however, may change within certain limits. For this reason, in the case of paints of similar hiding power, increasing quantities of paint may be used, in order to obtain values which allow conclusions concerning the quantities which give the same concealing result, but only the relatively small variation of thickness is permitted which corresponds to those occurring in the practical paint job for one coat, as a consequence of different manners of diluting and working.

The same result will not always be obtained from two coats of thickness *t* as from one coat of thickness 2 × *t*. Nor is the relation of hiding behavior of two paints the same for one coat as for two coats. For this reason, it will sometimes be necessary to determine the contrast-obliterating power for one and for two coats. In this case the first coat is applied with the applicator 15 cm. wide, and the second one, after the first one is dry, with the 5-cm. applicator.

For example,

$$\text{COP}_{c\,=\,2\,\times\,0.150}\text{ on black} = 1.59$$

means that the tested paint, applied with a doctor blade of 0.150-mm. clearance and in two coats, will obliterate a gray shade on a black background which has a contrast of 1.59.

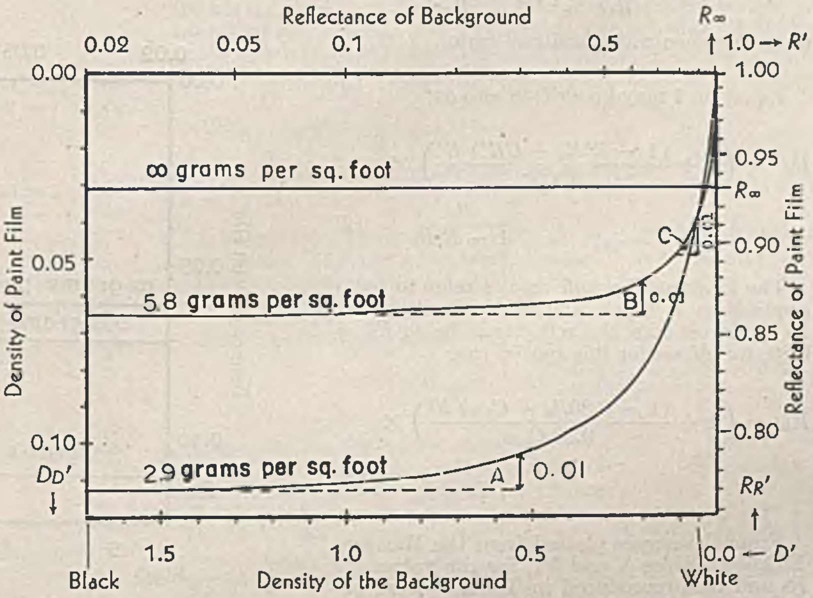

Figure 3. Density $D_{D'}$ (Reflectance $R_{R'}$) of Paint a_1 Applied in a Coat of Constant Thickness on Background of Density D' (Reflectance R')

Calculated according to Kubelka-Munk theory with constants found by Hickson and Eickhoff. Gray areas correspond to threshold zones (*A*, light gray; *B*, gray; *C*, dark gray).

Table V. Light Reflectance of White Cold-Water Paints

(According to Hickson and Eickhoff)

Paint	Thickness	Light Reflectance of Paint on Black Background	Ratio of Reflectances on Black and White Backgrounds	Reflectance of Infinitely Thick Paint Film	Average Value
	G./sq.ft.	R_0	$C_{0.80}$	R_∞	R_∞
a_1	2.9[a]	0.770	0.880	0.940	0.931
a_1	5.8[b]	0.860	0.960	0.922	
c	2.9[a]	0.780	0.920	0.865	0.870
c	5.8[b]	0.850	0.980	0.875	

[a] 31 grams per sq. meter.
[b] 62 grams per sq. meter.

INTERPRETATION OF CONTRAST-OBLITERATING POWER BY THE KUBELKA-MUNK THEORY

Judd, Hickson, and Eickhoff (*9*) have proved that the hiding behavior of white or near-white cold-water paints may be described by the Kubelka-Munk equation (*10*). It should therefore be possible to expound by this theory the significance of the standard proposed for that characteristic of paints, at least for the paint type mentioned. For this study the author took advantage of Judd's equations and the measurements by Hickson and Eickhoff (*9*).

According to Judd's Equations 2a and 2b, the reflectance ratio, $C_{R'}$, may be expressed by the following equation:

$$C_{R'} = \frac{R_0}{R_{R'}} = \frac{1 - R'R_0}{(1 - R') + \dfrac{R'(1 - R''R_0 - C_{R''} + R''C_{R''})}{R''C_{R''}}} \tag{1}$$

when

R' and R'' are light reflectance of the background
$R_{R'}$ and $R_{R''}$ are light reflectance of a paint film applied on a background, reflectance of which is R' and R'', respectively
R_0 is light reflectance of a paint film applied on a background, the reflectance of which is 0 (black background)

$$C_{R'} = \frac{R_0}{R_{R'}} \text{ and } C_{R''} = \frac{R_0}{R_{R''}}$$

are reflectance ratio (contrast ratio)

Equation 1 may be written also as:

$$R_{R'} = \left(1 + \frac{(1 - R''R_0 - CR'')\,R'}{R''C_{R''}}\right) \times \frac{R_0}{1 - R'R_0} \tag{2}$$

The Hickson-Eickhoff results refer to paint applied on a black and white background. In the latter case, the reflectance being $R'' = 0.80$, we obtain for this special case

$$R_{R'} = \left(1 + \frac{(1 - 0.80R_0 - C_{0.80})\,R'}{0.80\;C_{0.80}}\right) \times \frac{R_0}{1 - R'R_0} \tag{3}$$

From the curves plotted from the Hickson-Eickhoff Tables V and VI, for the values for R_0 and $C_{0.80}$ reproduced in Table V were obtained. Indicated there is also the "light reflectivity" R_∞—that is, the light reflectance of an infinitely thick paint film—this magnitude has been determined from Figure 2 of Judd's paper.

Substituting in Equation 3 the magnitudes R_0 and $C_{0.80}$ from the figures of Table V, we obtain the following formulas:
For paint a_1 and thickness 2.9 grams per square foot

$$R_{R'} = \frac{(1 - 0.704R') \times 0.770}{1 - 0.770R'}$$

For paint a_1 and thickness 5.8 grams per square foot

$$R_{R'} = \frac{(1 - 0.843R') \times 0.860}{1 - 0.860R'}$$

For paint c and thickness 2.9 grams per square foot

$$R_{R'} = \frac{(1 - 0.712R') \times 0.780}{1 - 0.780R'}$$

For paint c and thickness 5.8 grams per square foot

$$R_{R'} = \frac{(1 - 0.842R') \times 0.850}{1 - 0.850R'}$$

These four expressions enable us to calculate the light reflectance, $R_{R'}$ of a paint film of thickness 2.9 and 5.8 grams per square foot, respectively, which has been applied on a background the reflectance of which is R'. The results have been used to plot the curves of Figures 3 and 4. Since these curves are intended to expound an optical-physiological phenomenon, they are plotted to a logarithmic scale, according to the law of Weber and Fechner. The transformation of the (numerical) reflectances, R' of the background and $R_{R'}$ of the paint films, to the (logarithmic) densities, D', of the background and $D_{D'}$ of the paint film has to be made according to the relation:

$$\text{Density} = -\log \text{reflectance}$$

The curves of Figures 3 and 4 represent the density, $D_{D'}$ (reflectance $R_{R'}$) of a paint film of constant thickness which has been applied on a background of density D' (reflectance R').

Figure 3 shows that paint a_1, applied in a constant thickness of 2.9 grams per square foot, gives a density of 0.113 on a black background. On backgrounds of less depth, gray backgrounds, this density decreases more and more as the background turns lighter, being $D_{D'=0} = 0.004$ on an ideal white background. The difference of light reflection, however, cannot be noticed until the density has become modified to a certain degree, which

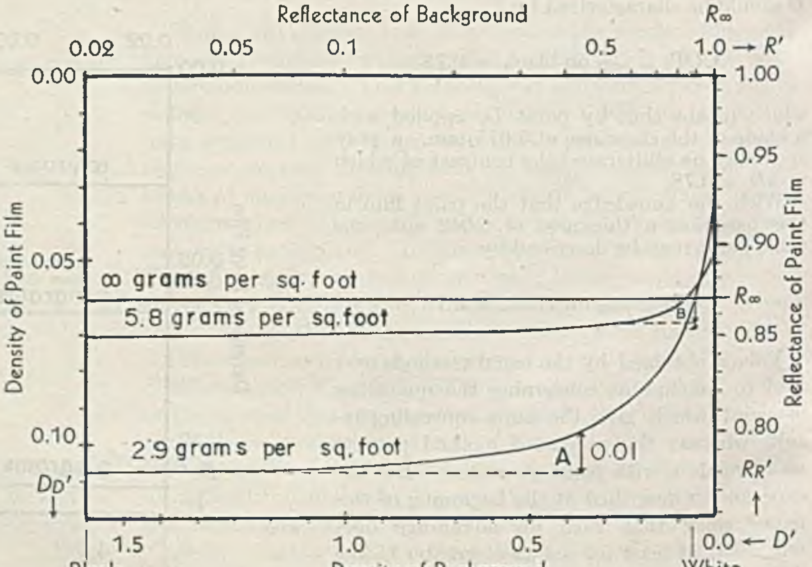

Figure 4. Density $D_{D'}$ (Reflectance $R_{R'}$) of Paint c Applied in a Coat of Constant Thickness on a Background of Density D' (Reflectance R')

Calculated according to Kubelka-Munk theory with constants found by Hickson and Eickhoff. Shaded areas (*A*, light gray; *B*, dark gray) correspond to threshold zones.

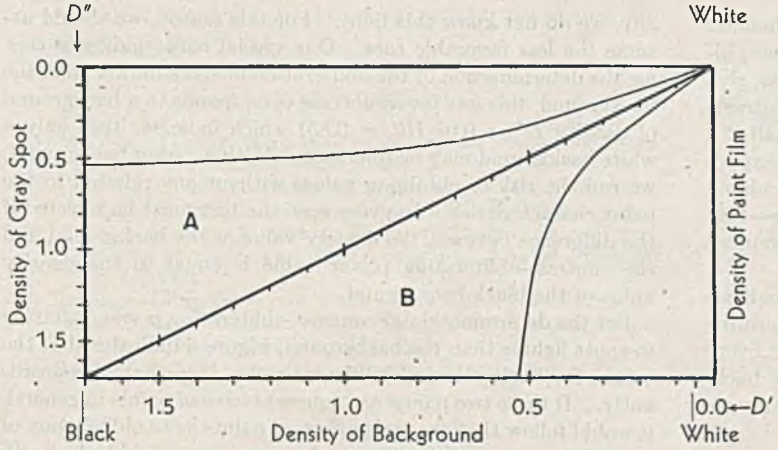

Figure 5. Densities D″ of Gray Spots Obliterated by Paint a′ Applied in a Coat of 2.9 Grams per Square Foot on a Background of Density D′

Calculated from Figure 3. Gray areas correspond to obliteration of gray spots lighter (*A*, light gray area) and darker (*B*, dark gray area) than background.

is commonly called "threshold value". The author estimates the threshold contrast for this case at approximately $\Delta D_{D'} = 0.01$. Since the paint film density on the black background is $D_{1.70} = 0.113$, we observe, the first reflectance difference with a film density of $D_{D'} = 0.113 - 0.01 = 0.103$. Figure 3 shows that such a reflectance occurs if the paint has been applied on a background that has a density $D' = 0.53$. Therefore, the deepest gray spot that may just be obliterated on a black background of density $D' = 1.70$, has density $D' = 0.53$, which means

$$\text{COP}_{t = 2.9 \text{ grams per sq. foot on black}_{D' = 1.70}} = 1.70 - 0.53 = 1.17$$

In order to facilitate these readings, in Figures 3 and 4 the threshold zones, which correspond to the black background ($D' = 1.70$; $R' = 0.02$) and to the white background ($D' = 0.05$; $R' = 0.89$), are indicated.

In the manner described, the following contrast-obliterating power values were obtained:

For paint a_1 (Figure 3)
$\text{COP}_{t = 2.9}$ grams per square foot
On black$_{D' = 1.70}$ 1.70 − 0.53 = 1.17
On white$_{D' = 0.05}$ 0.05 − 0.07 = −0.02

$\text{COP}_{t = 5.8}$ grams per square foot
On black$_{D' = 1.70}$ 1.70 − 0.20 = 1.50
On white$_{D' = 0.05}$ 0.05 − 0.11 = −0.06

For paint c (Figure 4)
$\text{COP}_{t = 2.9}$ grams per square foot
On black$_{D' = 1.70}$ 1.70 − 0.36 = 1.34
On white$_{D' = 0.05}$ 0.05 − 0.08 = −0.03

$\text{COP}_{t = 5.8}$ grams per square foot
On black$_{D' = 1.70}$ 1.70 − 0.07 = 1.63
On white$_{D' = 0.05}$ 0.05 − 0.25 = −0.20

According to these results, paint c hides better than a_1, the difference being not very pronounced. This agrees with the result computed by Hickson and Eickhoff on the basis of amount required for incomplete hiding (method 1). However, such agreement will not always occur.

In order to complete Figures 3 and 4, the curves for an infinitely thick layer of paint which has reflectance R_∞ (Table V) were also plotted; the reflectance of the paint film in this case being independent of that of the background, straight lines parallel to the abscissa are obtained.

If the paint is applied on a background, the reflectance, R', of which is just equal to R_∞, the resulting reflectance, $R_{R'}$, of the coat cannot be other than the original one of the background, independent of the film thickness; this means that all the curves plotted for different thicknesses must pass through a point, the coordinates of which are $R' = R_\infty$, $R_{R'} = R_\infty$, a condition which is sufficiently well complied with in Figures 3 and 4.

With the aid of these curves, we may also calculate contrast-obliterating power values for every gray background, as is shown by the following example:

We observe in Figure 3 that a paint film of the constant thickness 2.9 grams per square foot gives a density $D_{D'} = 0.097$, if applied on a gray background, the density of which is $D' = 0.40$. The threshold value being $\Delta D_{D'} = 0.01$ we may, in consequence, expect to distinguish from this paint film only coats which have densities, $D_{D'}$ greater than $0.097 + 0.01 = 0.107$ and less than $0.097 - 0.01 = 0.087$. The curves indicate that paint films of densities $D = 0.107$ and 0.087 are obtained on gray backgrounds of densities $D' = 0.70$ and $D' = 0.26$, respectively. That means: if we apply paint a_1 in a thickness of 2.9 grams per square foot on a gray background that has a density of $D' = 0.40$, we may obliterate all spots darker than the background, which have densities between $D' = 0.40$ and $D' = 0.70$, the corresponding densities for spots lighter than the background being between $D' = 0.40$ and $D' = 0.26$. Therefore, we obtain the following values for the contrast-obliterating power:

$$\text{COP}_{t = 2.9} \text{ grams per square foot on gray}_{D' = 0.40} \begin{cases} 0.40 - 0.26 = 0.14 \\ 0.40 - 0.70 = -0.30 \end{cases}$$

Of these two values, as usual, the positive refers to the obliteration of spots lighter than the background, and the negative to spots darker than the background.

In the same manner, the densities, D'', of the lightest and the darkest gray spots which may be obliterated on backgrounds of different gray shades were calculated. Figure 5 shows the results for the Hickson-Eickhoff paint, a_1, applied in a thickness of 2.9 grams per square foot. The areas which correspond to obliteration are shaded. On a gray background of $D' = 0.50$ all spots which have densities between $D'' = 0.32$ and $D'' = 1.24$ are obliterated, resulting in:

$$\text{COP}_{t = 2.9} \text{ grams per square foot on gray}_{D' = 0.05} \begin{cases} 0.50 - 0.32 = 0.18 \\ 0.50 - 1.24 = -0.74 \end{cases}$$

On a gray background of density $D' = 0.525$, the obliterated gray spots may have a density between $D'' = 0.325$ and $D'' = 1.70$—i.e., black—which means

$$\text{COP}_{t = 2.9} \text{ grams per square foot on gray}_{D' = 0.525} \begin{cases} 0.525 - 0.325 = 0.20 \\ 0.525 - 1.70 = -1.175 \end{cases}$$

With this background of density $D' = 0.525$, we have for our special case reached the limit for the obliteration of spots darker than the background. For all backgrounds with a deeper gray density, we have always the same density value of $D'' = 1.70$ (black) for the darkest obliterated spot. Carrying out the test in the areas beyond this limit-density, we would consequently find for all paints—independent of their special characteristics and the film thickness—contrast-obliterating power value which is equal to the difference of the density value of the background and 1.70; for the background with the density $D' = 0.80$, for example, we would obtain in all cases COP = 0.80 − 1.70 = −0.90.

The contrast-obliterating power values obtained in the manner described are shown graphically in Figure 6. These curves, although describing the special case of white cold-water paints, give a true and very general picture of the significance of the contrast-obliterating power. The values are in all cases very small if a white background is used: the same result obtained with experiments described above. On the other hand, the calculated curves show—also in agreement with the practical tests—that the contrast-obliterating power values vary in a pronounced manner if the contrasts refer to a black background.

The dot-dash curve of Figure 6 refers to the limit case, indicating that the tests always give the same contrast-obliterating power values for spots darker than the background, for every paint and film thickness, once the limit depth of the gray background has been passed. In the special case, these limits are according to Figure 6:

For paint a_1 and thickness 2.9 grams per square foot

$$D' = 0.53\ (R' = 0.30)$$

For paint a_1 and thickness 5.8 grams per square foot

$$D' = 0.20\ (R' = 0.64)$$

For paint c and thickness 2.9 grams per square foot

$$D' = 0.36\ (R' = 0.44)$$

For paint c and thickness 5.8 grams per square foot

$$D' = 0.07\ (R' = 0.85)$$

It is obvious that values obtained on backgrounds which are darker than the indicated limits are of no interest at all. Generally, we do not know this limit. For this reason, we should assume the less favorable case. Our special curve indicates that for the determination of the obliteration of spots darker than the background, this less favorable case corresponds to a background of density $D' = 0.07$ ($R' = 0.85$) which indicates that only a white background may be tolerated. With a darker background, we run the risk of obtaining values without any relation to the paint characteristics. In every case the test must be rejected if the difference between the density value of the background and the contrast-obliterating power value is equal to the density value of the black background.

For the determination of contrast-obliterating power, referring to spots lighter than the background, Figure 6 indicates that the values for backgrounds of different reflectance change concordantly. If these two paints are representative of paints in general, it would follow that the comparison of paints as to obliteration of spots lighter than the background, on any gray (or black) background, is generally valid for every background. Since Figure 6 shows that the differences of obliteration are more pronounced on a black background than on a gray one, it is recommended that the tests be carried out on a black and not on a gray background.

All these conclusions, derived from the Kubelka-Munk theory, agree with the results of practical investigation:

> The contrast-obliterating power test should primarily be carried out on a black background, thereby obtaining the most interesting values (which refer to the obliteration of spots lighter than the background).
>
> In special cases, the results on a white background (which refer to the obliteration of spots darker than the background) may also be of interest.
>
> The test on a gray background brings no advantage; for spots lighter than the background we obtain results which agree with those on a black background but are less exact, and for spots darker than the background, we run the risk of obtaining values which are without any relation to the paint characteristics.

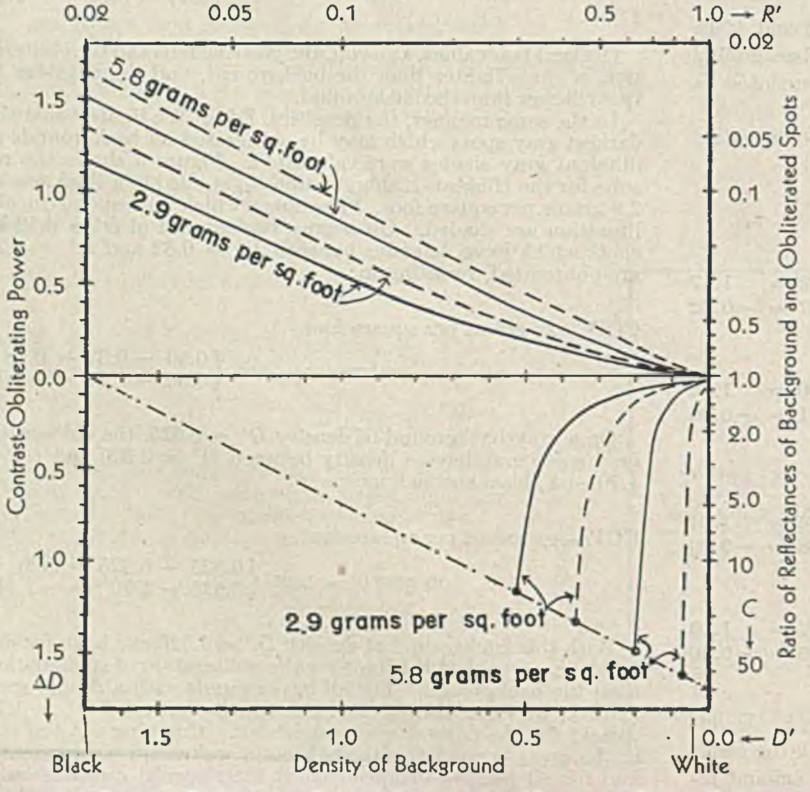

Figure 6. Contrast-Obliterating Power, Expressed as Contrast ΔD (or Reflectance Ratio C) between Background and Obliterated Gray Spot

Upper part of figure refers to spots lighter than the background ($\Delta D > 0$, $C < 1$) and lower part to spots darker than the background ($\Delta D < 0$, $C > 1$). Abscissas of intersection points of dot-dash line with curves indicate limit densities of background for obliteration of spots darker than background.

SUMMARY

The usual methods for determining hiding power of paints are not entirely satisfactory and a new method is proposed which is more closely related to practical performance of the paint.

The paint is applied in normal thickness—for example, with a Bird film applicator—on a test chart provided with a gray scale on both black and white backgrounds, and the contrast of the lightest gray shade, which under these conditions is obliterated on the black background, is considered as a standard of hiding behavior, as well as the contrast of the darkest gray shade obliterated on the white background. This method is easy to carry out and independent of color and finish. No standard paint is necessary. The observations may be made on fresh or dried paint, with the naked eye and without instrumental aid. The results are obtained as absolute values, indicating the (logarithmic) contrast of the obliterated spot, which is found as the difference between the densities of the background and this spot on the unpainted chart.

It is suggested that the characteristics of the paint determined in this manner be specified as contrast-obliterating power.

The practical results obtained in the determination of the contrast-obliterating

power are confirmed by a theoretical study based on the Kubelka-Munk theory.

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Nomographic Procedure for a Two-Component Colored System

Copper in a Nickel Plating Bath

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A graphical procedure is described for the calibration of a filter-type electrophotometer for a mixed-color system by measuring the relative absorption at two wave lengths. A simplified method is described for the construction of a nomograph in terms of electrophotometer scale readings. The procedure is applied to the mixed-color dithizone method for copper in a nickel plating bath.

MANY reactions giving colored products suitable for colorimetric analysis involve the treatment of two-component colored systems. The mixed color in some cases may consist of the excess colored reagent and the colored product. In other cases a foreign substance may be present which gives a colored product with the reagent. In the calibration of an electrophotometer with such a mixed-color system two general procedures have been followed; the transmittancy may be measured at one wave length in the vicinity of the maximum absorption of one of the colored components, or at two different wave lengths with the development of some relationship in the form of simultaneous equations or nomograph for the calculation. The object of this paper is to study the nomographic calculation procedure and attempt to simplify the calibration of a filter-type electrophotometer for the two-color system.

The adaptation of a monocolor method to a two-component color system offers a number of practical difficulties. Because of the broad absorption bands characteristic of most colored products, the two components invariably overlap, which makes it necessary to carry out difficult separations or to select less sensitive regions of the spectrum for the photometric measurements. If the absorption of the colored reagent occurs at the wave length selected, any variation in the concentration of the reagent will cause serious errors in the results. Unstable organic reagents which are subject to fading or oxidation are especially troublesome. Standardization of each lot of reagent is the usual procedure with this type of calibration.

The mixed-color dithizone method for copper (*8*) illustrates some of the difficulties encountered with this calibration method. Copper reacts with dithizone in dilute mineral acid solutions (0.1 *N*) to form the red-violet keto complex. The transmittancy of the mixed color may be measured at 500 to 550 mμ, the region of the maximum absorption of the copper dithizonate, or at 600 to 650 mμ, the region of maximum absorption of the dithizone (*8*). The dilute dithizone solutions customarily used (0.001 to 0.0012% by weight volume) are not very stable and tend to change on standing through evaporation or oxidation unless special precautions are taken. Since dithizone absorbs in the vicinity of 650 mμ and to a lesser extent at 525 mμ, variations in the concentration of the reagent are important. This makes it necessary to standardize each lot of reagent and make frequent checks against standards if the reagent is kept for an appreciable time. The monocolor method in which the excess dithizone is removed with ammonium by hydroxide (*1, 3*) or pyrophosphate (*7*) has been used with this system. The difficulties encountered in the removal of the excess dithizone with ammonia are shown by Mehurin (*7*) and Sandell (*8*). The development of a calibration relationship in which the final results are independent of the initial dithizone concentration would simplify and increase the accuracy of the method.

A more permanent calibration relationship may be made by measuring the relative absorption of light in different spectral regions. This technique was applied by Kozelka and Kluchesky (*6*) to the determination of lead by the dithizone mixed-color method.

If Beer's law is obeyed, light of a given wave length from color filter A passing through a solution containing two colored components should be expressed by the relationship

$$L^A = K_1^A C_1 + K_2^A C_2 \tag{1}$$

where L^A represents the log transmittancy with filter A, and C_1 and C_2 represent the concentration of the two colored components such as, for example, dithizone and metal dithizonate. The constants K_1^A and K_2^A depend on the characteristics of color filter A, the cell thickness, and the color of components C_1 and C_2. Similarly for filter B

$$L^B = K_1^B C_1 + K_2^B C_2 \tag{2}$$

In practice only one of the concentrations of the two colored components is desired. The other colored component, usually the reagent, may vary somewhat owing to the difficulties in preparing exact concentrations of intensely colored materials but, in general, may be held within reasonable concentration limits governed by the method. If we let C_2 represent the concentration of the colored component to be measured, it follows by combining Equations 1 and 2 that $\frac{\partial L^A}{\partial C_1}$ and $\frac{\partial L^B}{\partial C_1}$ are constants. This may be shown graphically by plotting log transmittancy L^A obtained with filter A against L^B obtained with filter B on linear graph paper as shown in Figure 1. A straight line is formed for a series of standards containing the same concentration of C_2 and variable amounts of C_1. Such a straight line will establish a relationship representing all the possible log transmittancy values of L^A and L^B for any given concentration of C_2 and variable concentrations of C_1. The C_1 concentration limits may be conveniently varied to give a suitable range for the photometric measurements.

A nomograph may be prepared from the $L^A - L^B - C_2$ relationship as shown in Figure 1. By selecting a fixed value for L^A, the L^B values may be obtained from the graph for each known concentration of C_2. A series of lines may be drawn in this manner, giving a nomograph similar to the one given in Figure 2. Interpolation may be used for the values of L^A within 1 or 2 scale division steps used in preparing the chart.

Kozelka and Kluchesky (*6*) obtained this relationship by adding measured volumes of dithizone solution to the standard lead dithizonate. Constants K are calculated from the electrophotometric values of L^A. Owing to the change in concentration of the metal complex brought about by the change in volume of the organic solvent, Taylor's expansion must be employed to correct the values for the change in C_2. This procedure is somewhat complicated and assumes no change in the log transmittancy of the metal dithizonate at 660 mμ, which may not always be true. A simple procedure which eliminates this difficulty would be to hold the volume of the organic solvent layer constant and obtain variations in the dithizone concentration by dilution with carbon tetrachloride. A stronger dithizone solution may be used and the sum of the volume of dithizone solution plus the solvent used for dilution may be held at a fixed value, such as, for example, 10 ml. Four or five separate standards prepared in this manner should suffice to establish a well-defined straight line for the $L^A - L^B$ relationship for each increment of copper. A series of lines is shown in Figure 1. Such a series of lines represents all the possible combinations of L^A and L^B in the most useful range of dithizone–copper dithizonate concentrations. From this relationship obtained with the two color filters a nomograph may be prepared for any particular value of L^B, as in Figure 2.

Another possible simplification is the establishment of the relationship given in Equations 1 and 2 in terms of electrophotometer scale rather than log transmittancy values. This simplifies the calculation and the use of the nomograph given in Figure 2. The log scale on the Fisher electrophotometer has been described (*2*).

Copper is one of the impurities frequently encountered in a nickel plating bath. Copper is especially objectionable in bright nickel plating, since darkening of the deposit may occur at low current density areas. Accordingly, some rapid method for the estimation of small amounts of copper would be useful in the control of the plating operations. The mixed-color dithizone method with the extraction of the copper as copper dithizonate from 0.1 *N* hydrochloric acid solution has been used by Knapp (*5*) for this purpose. Nickel does not form a colored complex at a pH of 1.3 to 2.3 and small amounts of copper from 0.001 to 0.05 gram per liter may be separated from the nickel without interference. This separation eliminates the well-known sulfide separation which has been shown to offer a number of difficulties (*4*).

MATERIALS AND REAGENTS

Electrophotometer. The AC Model Fisher electrophotometer equipped with 5-mm. test-tube type cells, 525 and 650 mμ color filters, was used.

Hydrochloric Acid, approximately 0.1 *N*. Dilute 8.9 ml. of reagent grade acid, specific gravity 1.18, to 1000 ml. with redistilled water.

Carbon Tetrachloride. Best grade analytical reagent quality free from impurities that inhibit the reaction between the dithizone and copper should be used. Check each lot for extractability by noting the shaking time required to develop the maximum color. Mallinckrodt's analytical reagent grade was found satisfactory without distillation.

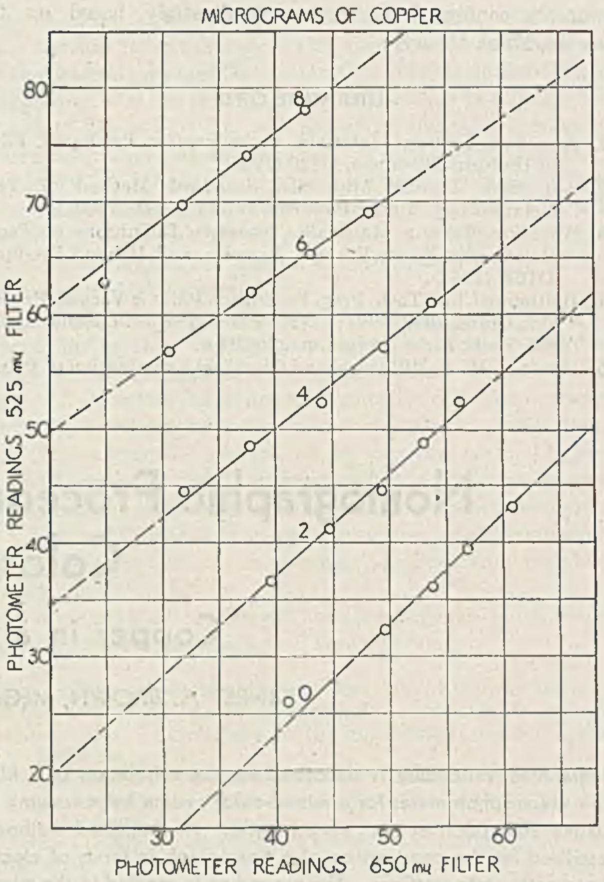

Figure 1. Photometric Relationship at 525 and 650 mμ

Dithizone Solution. For the calibration dissolve 12 mg. of diphenylthiocarbazone in 1 liter of carbon tetrachloride. For the method dissolve 1 to 1.2 mg. in each 100 ml. of carbon tetrachloride. Store at 5° C. and prepare fresh each week. Dithizone may be obtained commercially in a high state of purity or recrystallized if necessary.

Copper Standard. Dissolve 0.1000 gram of electrolytic copper foil in dilute nitric acid and dilute to 1000 ml. Pipet 10 ml. into a 1000-ml. volumetric flask, add 8.9 ml. of hydrochloric acid, and dilute to 1000 ml.

PROCEDURE AND APPLICATION

Calibration. Prepare a series of four or five standards containing the same copper concentration by taking a measured volume of copper standard in 125-ml. separatory funnels and sufficient 0.1 *N* hydrochloric acid to make the volume 25 ml. Add 10 ml. of dithizone solution to one separatory funnel, 9 ml. of dithizone plus 1 ml. of carbon tetrachloride to the second, 8 ml. of dithizone plus 2 ml. of carbon tetrachloride to the third, and so forth. Shake vigorously for 3 minutes. If a purple color is developed shake for 2 additional minutes. Filter the chloroform layer into the absorption cells through a small pledget of cotton to remove droplets of the aqueous layer. Measure the A scale or log scale, reading the electrophotometer with the 525 and 650 mμ color filters, using an absorption cell filled with carbon tetrachloride at 0 scale as a reference standard.

Repeat this procedure for each increment of copper. Five different copper concentrations should suffice for the construction of the nomograph. Plot the 525 mμ electrophotometer readings as ordinate against the 650 mμ readings as abscissa on linear graph paper. A series of straight lines should be formed, as in Figure 1.

Prepare a nomograph by obtaining from Figure 1 the electrophotometer values for the 525 mμ photometer reading for a given 650 mμ value. Plot the values for 0, 2, 4, 6, and 8 micrograms of copper for each 2 divisions on the 650 mμ values.

To use the nomograph select the particular line corresponding to the 650 mμ photometer value and determine the intersection of this line with the 525 mμ value. Read the copper concentration from the abscissa axis. For example, a photometer reading of 36 at 650 mμ and 60 at 525 mμ would indicate a copper concentration of 6 micrograms.

Method. Pipet a 10-ml. sample of a nickel plating solution into a 100-ml. volumetric flask, and dilute to the mark with 0.1 *N* hydrochloric acid. Pipet a suitable aliquot from 1 to 10 ml. into a 125-ml. pear-shaped separatory funnel. Adjust the volume to 25 ml. with 0.1 *N* hydrochloric acid. Add exactly 10 ml. of dithizone solution and shake vigorously for 3 to 5 minutes. Allow the layers to separate and filter the colored carbon tetrachloride layer through a small pledget of cotton into a photometer cell. Measure the transmittancy against the carbon tetrachloride as a reference with the 525 and 650 mμ color filters, respectively. Refer to the nomograph for the copper concentration.

Results. Known amounts of copper were added to a sample of a Watts type nickel plating solution containing 240 grams per liter of nickel sulfate hexahydrate, 60 grams per liter of nickel chloride hexahydrate, and 45 grams per liter of boric acid with a pH of 3.0. Traces of copper found in the salts were removed by extraction at pH 2 with 0.01% (weight volume) dithizone solution in carbon tetrachloride followed by washing with pure carbontetrachloride. The copper was then determined on a suitable aliquot by the mixed color procedure given in the method. The results obtained are given in Table I.

DISCUSSION

The advantages in the establishment of a relationship given in the nomograph for a relatively wide range of dithizone concentration are readily apparent. The dithizone carbon tetrachloride solution may be prepared in small quantities as needed, with the approximate concentrations governed by the calibration. In this manner the difficulties due to the oxidation of the reagent or evaporation of the solvent in storage are avoided. Checking the calibration curve at frequent intervals is made unnecessary. The errors due to the oxidation of the dithizone to a colorless keto form are minimized by using freshly prepared solutions. Little change due to oxidation of the reagent was observed over a 1-week period.

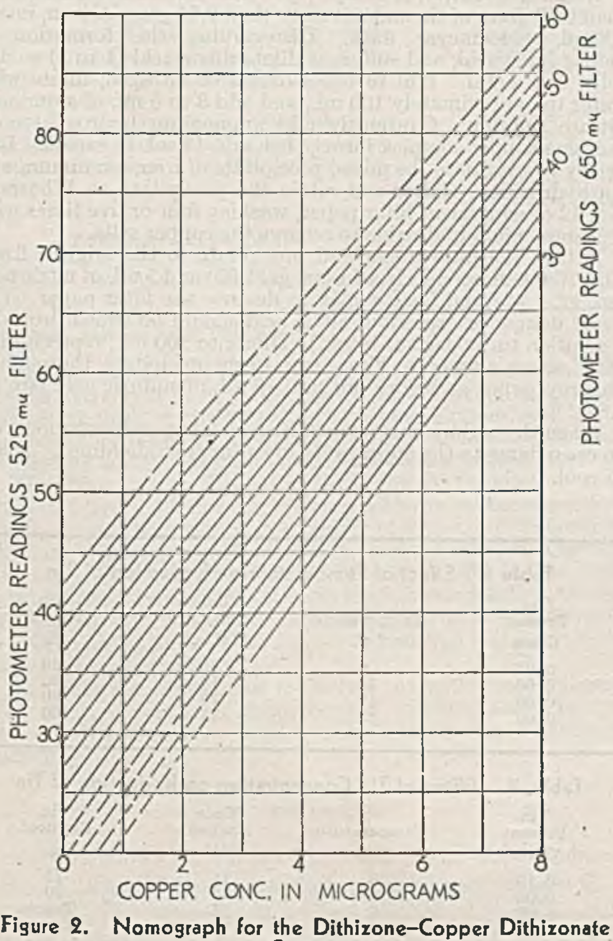

Figure 2. Nomograph for the Dithizone–Copper Dithizonate System

Table I. Recovery of Copper Added to a Nickel Plating Solution

Sample Size	Copper Added		Copper Found	Difference
Ml.	γ	*G./l.*	*G./l.*	*G./l.*
1	0.0	0.0000	0.0001	+0.0001
	0.0	0.0000	0.0002	+0.0002
	0.8	0.0008	0.0010	+0.0002
	1.8	0.0018	0.0019	+0.0001
	2.4	0.0024	0.0026	+0.0002
	6.4	0.0064	0.0064	±0.0000
	7.4	0.0074	0.0076	+0.0002
	8.0	0.0080	0.0079	−0.0001
0.1	0.4	0.004	0.005	+0.001
	1.6	0.016	0.016	±0.000
	2.4	0.024	0.022	−0.002
	3.2	0.032	0.033	+0.001
	4.4	0.044	0.043	−0.001
	5.6	0.056	0.054	−0.002

Care should be exercised in keeping the $L^A - L^B$ values within the limits of the experimental values given in Figure 1, because of possible deviations from Beer's law with greater differences in concentrations. This may be conveniently done by the use of dotted lines in the nomograph to cover values outside the limits of the experimental data. A rough check made by measuring the transmittancy of the original dithizone solution with the two filters, and referring to the nomograph will aid in governing the proper concentrations.

Bendix and Grabenstetter (*1*) found a shaking period of 10 minutes necessary in order to obtain an equilibrium between the copper in the acid aqueous solution and the copper dithizonate in the carbon tetrachloride solution. An examination of several lots of reagent grade carbon tetrachloride showed some variation in the extractability of the copper dithizonate. Four out of five lots examined gave a maximum color development with 3 to 5 minutes' shaking. One lot required 7 minutes to establish an equilibrium. Sandell (*8*) suggests the presence of traces of impurities, probably sulfur compounds, which tend to inhibit the reaction between copper and dithizone in acid solution. Since serious errors may be caused through failure to develop the equilibrium condition with an insufficient shaking period, each lot of carbon tetrachloride must be examined for extractability by noting the time required to develop a maximum color. No difficulty was experienced in obtaining carbon tetrachloride which developed a maximum color within 3 to 5 minutes' shaking. The addition of a small amount of a wetting agent such as 2 drops of a 1% aqueous solution of aerosol OT (a product of the American Cyanamid Company) tends to improve the extractability without disturbing the equilibrium value.

Nickel in concentrations up to 78 mg. does not seriously interfere with the estimation of copper without a preliminary separation. The results in Table I show the interference to be less than 0.2 microgram. Interfering metals that form colored dithizonates from dilute acid solutions, such as mercury, palladium, gold, and silver, are not likely to be present in a nickel plating bath; however, interference may be expected if they are present.

The calibration procedure described could be adapted to other mixed-color procedures. The well-known dithizone methods for the heavy metals are merely examples of the general nomographic calibration method. The procedure is by necessity limited to a two-component colored system.

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Differential Reduction of Iron and Tin

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A method is described for the titrimetric determination of iron and tin on the same weighed sample of material. The method is suitable for bronze and other copper alloys containing less than 1% antimony. After separation from copper, the iron is reduced in an inert atmosphere with metallic nickel in cold dilute hydrochloric acid and titrated with potassium dichromate solution. Following this, the tin is reduced with metallic nickel in the hot, concentrated acid, cooled under an inert atmosphere, and titrated with iodine solution. The method requires 1.5 hours for a determination and is suitable for routine analysis.

THE method described herein was developed to overcome the usual difficulties encountered in the determination of iron in bronze and similar alloys containing tin. In the nitric acid separation of tin as metastannic acid, considerable iron is brought down in the precipitate. For this reason, the often described procedure of separating iron as the hydroxide, after prior removal of tin, lead, and copper in nitric acid solution, will lead to low results in the determination of iron. This error is often neglected in routine analysis, on the assumption that it is small. It has been found in this laboratory that as much as one half of the total iron present may be held in the tin precipitate—i.e., in a sample containing 0.0056 gram of iron and approximately 0.075 gram of tin, 0.0023 gram of iron was found in the metastannic acid precipitate, after careful washing.

Of the available methods for recovery of this iron from the tin precipitate, the use of hot ammonium sulfide is perhaps the most satisfactory. A procedure involving ignition of the metastannic acid, volatilization of the tin by the use of ammonium iodide as in the method of Caley and Burford (*1*), and recovery of iron from the residue has also been used with success. Both methods are time-consuming and unpleasant to use. In the presence of precipitated tin, efforts to determine the iron by titration with potassium dichromate, using a modified Knop's (*2*) procedure, were only partially successful.

It is customary, in this laboratory, to determine tin by the method of McDow, Furbee, and Clardy (*3*). The tin is collected by precipitation as hydroxide in ammoniacal solution, using aluminum hydroxide as a collector to ensure complete precipitation of the tin. Iron is also completely precipitated at this point and it was desirable to use this sample for the determination of both iron and tin.

Since tin was subsequently to be determined, the reduction of which necessitated a fairly concentrated solution, it was desirable that the iron be reduced by a method that would cause no loss of tin and would not increase the volume materially, and where the reagent used would be without effect on the titration of iron and tin or be easily removable.

It was found that nickel in cold dilute hydrochloric acid solution would effectively reduce iron without causing appreciable reduction of tin. Since this same reagent in hot concentrated acid is effective for the reduction of tin and it meets the requirements outlined above, it appeared that nickel could be made the basis for a method for the determination of both tin and iron. This assumption has been verified by subsequent investigation.

REAGENTS REQUIRED

ALUMINUM NITRATE. Dissolve 10 grams of aluminum nitrate, C.P. reagent, in 100 ml. of water.

POTASSIUM DICHROMATE. Stock Solution. Dissolve 87.81 grams of C.P. potassium dichromate, $K_2Cr_2O_7$, in water and dilute to 1000 ml.

Standard Solution. Dilute 10 ml. of the stock solution of potassium dichromate to 1000 ml. with water. Standardize against C.P. iron. One milliliter of the potassium dichromate solution is approximately equivalent to 0.001 gram of iron.

MERCURIC CHLORIDE. A saturated solution of mercuric chloride in water.

SODIUM DIPHENYLAMINE SULFONATE. This indicator is prepared by the method of Willard and Young (*4*). Dissolve 3.2 grams of C.P. barium diphenylamine sulfonate in 1000 ml. of water, add an excess of sodium sulfate, and filter.

NICKEL, C.P. nickel shot, less than 6 mm. in diameter.

STANDARD IODINE SOLUTION. Dissolve approximately 11 grams of iodine and 20 grams of potassium iodide in 100 ml. of water and dilute to 1000 ml. Standardize against pure tin, using the method of reduction described in the text.

STARCH SOLUTION. Prepare a thin paste consisting of 5 grams of soluble starch, 10 grams of sodium bicarbonate, and water. Pour the paste into 300 ml. of boiling water, and boil for a minute or two, with stirring. Cool the solution and dilute to 1000 ml.

PHOSPHORIC-SULFURIC ACID REAGENT. Mix carefully 800 ml. of water, 100 ml. of sulfuric (sp. gr. 1.84), and 100 ml. of phosphoric (sp. gr. 1.69) acids.

METHOD

Weigh a quantity of sample, preferably containing not more than 0.10 gram of tin and not more than 0.05 gram of iron, into a 300-ml. Erlenmeyer flask. Disregarding the formation of metastannic acid, add sufficient dilute nitric acid (1 to 1) to dissolve the metal. Boil to expel oxides of nitrogen, dilute with water to approximately 100 ml., and add 3 to 5 ml. of aluminum nitrate solution. Cautiously add ammonium hydroxide until the blue copper complex forms, then add 10 ml. in excess. Boil gently to coagulate the mixed precipitate of iron, aluminum, and tin hydroxides. Filter and retain the precipitate on Whatman No. 42 or equivalent filter paper, washing four or five times with 2% ammonium hydroxide to remove the copper salts.

Return the filter paper and precipitate to the original flask. Add 10 ml. of perchloric acid (sp. gr. 1.67) and 5 ml. of nitric acid (sp. gr. 1.42) and heat gently to destroy the filter paper. (To avoid danger of explosion, nitric acid should be added dropwise if solution turns dark or black.) Dilute to 100 ml., reprecipitate with excess ammonia, filter, and wash precipitate thoroughly. Destroy paper as before but add 10 ml. of sulfuric acid (sp. gr. 1.84).

When the organic matter is destroyed, evaporate solution over an open flame to the appearance of sulfur trioxide fumes. Allow to cool.

Table I. Effect of Temperature on Reduction of Tin

Tin Present	Temperature	Time Shaken	Tin Reduced
Gram	*° C.*	*Min.*	*%*
0.06	6	15	20
0.06	12	15	25
0.06	17	15	30
0.06	23	15	60

Table II. Effect of Tin Concentration on Reduction of Tin

Tin Present	Temperature	Time Shaken	Tin Reduced
Gram	*° C.*	*Min.*	*%*
0.10	6	15	75
0.06	6	15	20
0.02	6	15	Trace
0.01	6	15	Trace

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Table III. Analyses of Alloys of High Percentage Tin

(Determination of blank)

Bureau of Standards Sample No.	No. of Analyses	% Iron Present	% Iron Found	% Iron Difference
124a (4.82% tin)	6	0.004	0.027	0.023
52b (8.00% tin)	6	0.032	0.057	0.025
52 (7.89% tin)	3	0.12	0.14	0.02
63 (9.91% tin)	3	0.28	0.30	0.02
63a (9.76% tin)	3	0.52	0.55	0.03
Synthetic Standards				
A (124a + 0.05% iron)	1	0.054	0.073	0.019
B (124a + 0.10% iron)	1	0.104	0.127	0.023
C (52b + 0.05% iron)	3	0.082	0.105	0.023
D (52b + 0.10% iron)	3	0.132	0.157	0.025
E (5.00% tin)	2	0.10	0.12	0.02
F (5.00% tin)	2	0.50	0.51	0.01
G (5.00% tin)	3	1.00	1.01	0.01

Average difference (36 samples), 0.02%.

DETERMINATION OF IRON

Cautiously dilute contents of flask with water to a volume of 150 ml., add 15 ml. of concentrated hydrochloric acid, and boil until solution is clear. Remove to water bath. Add solid carbon dioxide. Cool below 20° C. in ice bath, add approximately 30 grams of small nickel shot, close flask with rubber stopper as last lumps of carbon dioxide disappear, and shake vigorously on a mechanical shaker for 15 minutes. Chill again in ice bath and decant the solution into a 500-ml. vial-mouth extraction flask. Wash the nickel shot twice by decantation with small portions of cold water. Reserve the nickel shot for the tin determination.

To the reduced iron solution add 10 ml. of mercuric chloride solution, 3 drops of sodium diphenylamine sulfonate as indicator, and 20 ml. of the sulfuric-phosphoric acid reagent. Titrate the solution with standardized potassium dichromate to the appearance of a purple end point which persists. In high tin alloys a blank correction of 0.02% must be subtracted.

Return the reserved nickel shot to the solution, add 60 ml. of hydrochloric acid, and proceed with the tin determination.

DETERMINATION OF TIN

The method used for the determination of tin was substantially as described by McDow, Furbee, and Clardy (*3*).

The apparatus was modified to make use of a 500-ml. vial-mouth extraction flask and consisted of a heating element, the extraction flask, a one-hole No. 10 rubber stopper, and a glass tube suitably bent so that it extended from the flask to a beaker containing water or the sodium bicarbonate solution.

The 500-ml. extraction flask, containing the tin solution, nickel shot, and hydrochloric acid, is closed with the rubber stopper and the exhaust tube is placed in a beaker of water. The solution in the flask is brought rapidly to boiling and the reaction allowed to proceed for 0.5 hour at low heat. The glass tube is then placed in a beaker containing 10% sodium bicarbonate solution, the flask is removed from the heater, and the contents are cooled below 20° C. in an ice bath. The stopper is removed and a small piece of dry ice rapidly added.

The solution of stannous tin is titrated with standardized iodine solution, under an atmosphere of carbon dioxide, to a permanent dark blue color change, using 5 ml. of starch solution as indicator.

DISCUSSION

Table I shows the effect of temperature on the reduction of tin. With increasing temperature, increasing amounts of tin are reduced. The reduction of a small amount of tin is desirable, as it is evidence that all the iron is in the ferrous state. In alloys containing a large amount of tin this reduction should be minimized by cooling, so that the amount of mercuric chloride will be ample to affect its purpose.

Table II shows the per cent of tin reduced in an inert atmosphere by shaking with nickel shot. As the concentration of tin increases, the percentage reduction becomes greater.

Table III establishes a correction factor when high-percentage tin alloys are encountered. This blank of 0.02% is presumably due to the increased amount of mercurous chloride because of the reaction of the larger amount of stannous salts with mercuric chloride.

Table IV establishes the accuracy of the method in simple bronzes and brasses, manganese bronze, phosphor bronze, and samples containing up to 1% antimony. (Pure samples of antimony, 0.01, 0.05, and 0.10 gram, which were treated according to the prescribed procedure, required 0.1, 0.4, and 1.3 ml. of the titrating solution, respectively.) Out of fifty-five analyses the maximum deviation was less than ±0.02% on samples containing as much as 1% iron.

Table IV. Determination of Iron and Tin

Bureau of Standards Sample	No. of Detns.	% Iron Max. deviation	% Iron Present	% Iron Found	No. of Detns.	% Tin Max. deviation	% Tin Present	% Tin Found
Sheet brass No. 37	3	0.00	0.29	0.29	4	0.02	1.01	1.00
Sheet brass No. 37b	4	0.01	0.21	0.21	3	0.01	0.99	1.00
Manganese bronze No. 62	3	0.01	1.13	1.13	4	0.01	0.82	0.81
Manganese bronze No. 62a	3	0.01	1.04	1.04	4	0.01	0.84	0.83
Manganese bronze No. 62b	4	0.02	0.82	0.82	4	0.00	0.97	0.97
Effect of Antimony								
Cast bronze No. 52 (0.16% Sb)[a]	3	0.00	0.12	0.12	2	0.03	7.90	7.89
Phosphor bronze No. 63 (0.55% Sb)[a]	3	0.01	0.27	0.28	3	0.02	9.91	9.91
Phosphor bronze No. 63a (0.49% Sb)[a]	3	0.01	0.52	0.53	2	0.04	9.76	9.74
Synthetic Samples								
Sample A (0.20% Sb)	2	0.02	0.50	0.49	.	..	..	..
Sample B (0.50% Sb)	2	0.01	0.50	0.50	.	..	..	..
Sample C (1.00% Sb)	2	0.01	0.50	0.50	.	..	..	..
Effect of Tin								
Sample D (0.00% Sn)	2	0.01	0.10	0.11	.	..	..	...
Sample E (0.00% Sn)	2	0.02	0.50	0.49	.	..	..	..
Sample F (0.00% Sn)	4	0.02	1.00	0.99	.	..	..	..
Sample G (1.00% Sn)	2	0.01	0.10	0.11	.	..	..	..
Sample H (1.00% Sn)	2	0.01	0.50	0.51	.	..	..	..
Sample I (1.00% Sn)	4	0.01	1.00	1.00	.	..	..	..
Sample J (5.00% Sn)[a]	2	0.02	0.10	0.10	.	..	..	..
Sample K (5.00% Sn)[a]	2	0.01	0.50	0.49	.	..	..	..
Sample L (5.00% Sn)[a]	3	0.02	1.00	0.99	.	..	..	..

[a] See Table III.

PRECAUTIONS

The final fuming of the salts to sulfuric acid fumes is essential. Discordant results are obtained if this is not accomplished.

An inert atmosphere is necessary for complete reduction, but caution is advised in stoppering the flask before all the lump carbon dioxide is evolved.

The nickel shot should be cleaned by boiling for a few minutes in hydrochloric acid. It will brighten on repeated use, probably because of amalgamation with the mercury in the mercuric chloride.

The complete reduction of the iron depends upon vigorous mechanical shaking because of the small surface presented by the nickel shot. With samples containing a high percentage of tin, the time required for shaking can be reduced if desired.

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Detection of Elemental Sulfur in Gasoline by the Sommer Test

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The sensitivity of various tests for the detection of elemental sulfur in gasoline has been determined; and a modification of the Sommer test is described which is about five times as sensitive as the customary inverted doctor test using butyl mercaptan.

SOMMER (*1*) describes a color test for free sulfur in pyridine solution, in which the addition of a small amount of an alkaline solution precipitates the sulfur as a blue colloidal solution. A positive reaction was obtained with as little as 2 parts per million of free sulfur; but hydrocarbons were observed to decrease the sensitivity of the test. In the presence of pyridine, doctor solution gave a visible reaction with 10 micrograms of free sulfur per cubic centimeter (10 p.p.m. on w/v basis).

Sommer's test was applied to the detection of free sulfur in gasoline by mixing the sample with pyridine and adding caustic soda solution. In the test, three phases were formed: an upper gasoline phase, a middle pyridine phase, and a lower aqueous phase. The color appeared in the middle pyridine phase, occasionally in the lower aqueous phase, but never in the upper gasoline phase. A preliminary survey showed that this test was at least as sensitive as the inverse doctor test, using butyl mercaptan solution. This is customarily used in plant testing but has, at times, appeared to be insufficiently sensitive.

The alternative mercury test is generally considered too sensitive for plant control.

The conditions for the maximum sensitivity of the Sommer test were determined, and the sensitivity of the various tests was compared.

EXPERIMENTAL

REAGENTS USED. Gasoline. For the purposes of this investigation, except as noted below, commercial iso-octane of specific gravity 0.691, freed of possible traces of sulfur and filtered before use, was used as gasoline and is referred to as such. The commercial iso-octane, as received, was shaken with mercury to remove possible traces of free sulfur and filtered before use. Only a negligible amount of mercuric sulfide was formed.

Standard Sulfur Solution, prepared by dissolving flowers of sulfur in 1 cc. of hot pyridine and allowing the solvent to evaporate almost to dryness before adding sufficient gasoline to give a solution containing 0.01% of sulfur by weight. Other concentrations were obtained by diluting the original standard with gasoline.

Pyridine. A water-white, commercial grade of pyridine containing approximately 5% of alpha-picoline was used untreated as it was not discolored on shaking with mercury.

Butyl Mercaptan Solution, 1 cc. of *n*-butyl mercaptan dissolved in 1400 cc. of gasoline, thoroughly shaken with mercury, and filtered before use. This treatment satisfactorily removed any free sulfur present, and did not affect the mercaptan content of the solution.

Doctor Solution, 10% caustic soda solution shaken with excess litharge for a quarter of an hour, allowed to settle, and the clear supernatant liquor decanted for use.

Caustic Soda Solution, 2 *N*.

Sodium Bicarbonate Solution, cold saturated.

SOMMER TEST. The necessary conditions for the test to give maximum sensitivity were obtained as follows:

Alkaline Solution. Sommer used 2 *N* caustic soda and saturated sodium bicarbonate solutions and obtained greater sensitivity with the latter. However, in the presence of gasoline, the caustic soda solution was found to give several times the sensitivity of the sodium bicarbonate solution, which also required boiling to develop the color. The caustic soda solution was therefore used.

Order of Mixing. The addition of the caustic soda solution to the pyridine-gasoline mixture gave a color several times as intense as that produced by the addition of the pyridine to the gasoline–caustic soda mixture.

Pyridine-Gasoline Ratio. Various volumes of a 0.001% (w/w) solution of free sulfur in gasoline were added to 5 cc. of pyridine and 1 cc. of 2 *N* caustic soda solution was added and shaken. The results were:

Test positive	2 to 20 cc. of gasoline
Test strongly positive	3 to 15 cc. of gasoline
Test maximum color	7 to 9 cc. of gasoline

Pyridine–Caustic Soda Ratio. Different volumes of 2 *N* caustic soda solution were added to a mixture of 3 cc. of pyridine and 5 cc. of 0.001% (w/w) solution of sulfur in gasoline. The test was definitely positive with up to 1.6 cc. and questionable with 2.0 cc. of caustic soda solution. The maximum color was obtained with 0.3 cc., though there was very little difference between the colors produced with 0.3 to 0.6 cc. The maximum was obtained with the same pyridine–caustic soda ratio (10 to 1) as used by Sommer.

Nature of Gasoline. The conditions of the test (5 cc. of gasoline, 3 cc. of pyridine, and 0.5 cc. of 2 *N* caustic soda solution) and the sensitivity were unchanged with 100% cracked gasoline (from the thermal cracking of shale oil).

No highly aromatic gasoline was available, so mixtures of motor benzene and commercial iso-octane were examined. It was found that the proportion of the middle pyridine phase decreased as the benzene content of the blend increased but the sensitivity of the test appeared to be unchanged. Sixty per cent of benzene in the blend was the maximum that could be tested without changing the conditions of the test. Increasing the amounts of pyridine and caustic soda and decreasing the caustic soda concentration enabled the test to work satisfactorily with higher benzene blends:

Benzene in Blend %	Volume of Blend *Cc.*	Volume of Pyridine *Cc.*	Caustic Soda Solution *Cc.*
60	5	4	1.5 2 *N*
70	5	5	2 2 *N*
80	5	5	2 *N*

Blends containing much more than 80% benzene did not give three phases in the test, though a blue color was developed in the pyridine-gasoline phase. The sensitivity of the test was, however, much reduced.

With the benzene blends, the blue color was less stable to air and was destroyed by shaking for a minute or so.

TESTS COMPARED FOR SENSITIVITY. In order to compare the relative sensitivity of the different tests available, the following tests were carried out:

Inverse Doctor Test. Five cubic centimeters of the sulfur-containing gasoline were shaken with 5 cc. of butyl mercaptan solution and 5 cc. of doctor solution. In the absence of free sulfur, the lead butyl mercaptide formed colored the gasoline phase yellow and some yellow mercaptide collected at the interface. In the presence of free sulfur, the color deepened through orange to dark brown or even black, depending on the concentration. Owing to the color of the mercaptide, it was necessary to use a blank test for comparison with borderline tests.

Modified Inverse Doctor Test. Five cubic centimeters of the sulfur-containing gasoline were mixed with 5 cc. of pyridine and 5 cc. of butyl mercaptan solution before addition of 5 cc. of doctor solution. The addition of the pyridine prevented the color formation due to the lead mercaptide. Three liquid phases were formed and, in the presence of sufficient free sulfur, the lead sulfide formed collected mainly at the liquid phase interfaces, making this test easier to observe than the unmodified test.

Sommer Test. Five cubic centimeters of the sulfur-containing gasoline were mixed with 3 cc. of pyridine and then shaken with 0.5 cc. of 2 *N* caustic soda solution. In the presence of free sulfur, a sky-blue coloration was formed in the middle phase. On long shaking in the presence of air, the color disappeared, this being due to the oxidation of the colloidal sulfur to thiosulfate.

Mercury Test. Five cubic centimeters of the sulfur-containing gasoline were shaken with a little mercury. In the presence of free sulfur, black mercury sulfide was formed and the suspension colored the gasoline gray.

Other Application of Tests. Attempts to use purified pyridine homologs (boiling range 120° to 250° C.), isolated from the cracked pressure distillate, in place of pyridine in the Sommer test failed. This was due to the higher miscibility of these bases with the gasoline, and the failure of the mixture to separate into three phases on the addition of water. This is probably the desensitizing action of hydrocarbons on the test that was observed by Sommer. An attempt was made to apply these different tests to detect free sulfur in crude shale oil, but alkali-soluble coloring matter in the oil masked any color reactions.

RESULTS

The results are expressed in sulfur concentration in parts per million by weight required to give a definite, questionable, or negative test. With the standard solutions used, 1 p.p.m. (w/w) is equal to 0.7 microgram per cubic centimeter.

Test	Definite *P.p.m.*	Questionable *P.p.m.*	Negative *P.p.m.*
Inverse doctor test	20	15	10
Inverse, modified by presence of pyridine	15	10	8
Sommer test	4	3	2
Mercury test	Positive even below 0.1 p.p.m.		

The mercury test is by far the most sensitive, but it is too sensitive for plant control. The inverted doctor test is positive to 15 p.p.m. of free sulfur, but the color of the lead mercaptide tends to make detection difficult near the limiting concentration; in the presence of pyridine, the modified test is easier to observe and a shade more sensitive. The Sommer test is sensitive to 3 p.p.m. of free sulfur in the gasoline, being therefore about five times as sensitive as the inverted doctor test, and yet not too sensitive for plant control.

With experience, a plant operator is able to obtain an approximate estimate of the free sulfur content of the gasoline from any of the first three tests, but much more readily from the Sommer test. The Sommer test has been found both quicker to operate and easier to observe than the inverse doctor test previously used.

If the gasoline being tested is highly aromatic, it would be advisable to determine the optimum proportions of the reagents for the test before putting it into routine operation.

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Qualitative Test for Carbohydrate Material

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A solution of anthrone in concentrated sulfuric acid gives a permanent green coloration with carbohydrate material. The reaction is of value as a qualitative test and for the preliminary classification of synthetic resins into a cellulose or noncellulose group.

ALTHOUGH there are a large number of specific tests for certain types of saccharides (*1*, *2*), there are very few general tests for carbohydrate materials. The Molisch test, using α-naphthol, is well known and generally applicable to soluble carbohydrates.

Anthrone, which is used for the determination of glycerol (*4*), was found to give a green color with cellulose. Further experiments indicated that a positive test was obtained with all of a group of eighteen carbohydrate materials examined, including several cellulose derivatives. Furfural is the only noncarbohydrate material, thus far encountered, which gives a green color with anthrone. The test as given by furfural is, however, different from that given by carbohydrate materials. The green color given by a furfural test is rapidly obscured by a brown precipitate, and when the sample is diluted with 50% sulfuric acid or glacial acetic acid, a heavy brown precipitate forms. Carbohydrate samples, on the other hand, may be diluted to any extent with these reagents, and the green color persists even at extreme dilutions.

Positive Test with Anthrone

Cellulose
Starch
Dextrin
Dextrose
l-Arabinose
Gum arabic
Gum tragacanth
Agar
Pectin
Algin
Ethylcellulose (ether)
Methylcellulose (ether)
Cellulose acetate
Cellulose acetate phthalate
Cellulose acetate butyrate
Cellulose acetate stearate
Cellulose propionate
Cellulose nitrate
Furfural (noncarbohydrate)

A negative test was obtained by all of a large group of noncarbohydrate materials examined, which included a variety of noncellulose synthetic resins, organic acids, aldehydes, phenols, fats, terpenes, alkaloids, and proteins.

PROCEDURE

One milliliter of water is placed in a small test tube containing approximately 1 mg. of the material to be tested, and 2 ml. of a 0.2% solution of anthrone in concentrated sulfuric acid are then added. The final sulfuric acid concentration in the test solution should always be greater than 50%; otherwise the anthrone will come out of solution and produce a milky suspension. The heat produced by the dilution of the sulfuric acid is a necessary part of the test. In the presence of carbohydrate material a clear green color will appear and rapidly increase in intensity until a dark blue-green solution results. The test solution can be diluted for comparison with glacial acetic or 50% sulfuric acid. In the absence of carbohydrate material, but in the presence of other organic compounds, a brown color is often produced by the action of the concentrated sulfuric acid.

The anthrone, which is not a readily available chemical, can be prepared according to the directions of Schutz (*4*), or following the procedure given in Organic Syntheses (*3*). Care should be taken during the preparation to avoid contamination of the anthrone by carbohydrate material, especially filter paper pulp, which would cause a green color to develop in a blank test with the reagent.

DISCUSSION AND APPLICATIONS

No study was made of the mechanism of the reaction, but the appearance and deepening of the color seemed to be as rapid with a polysaccharide as with an equal weight of a monosaccharide. This would suggest that hydrolysis may not be a necessary step in the test.

A useful application of this reaction is the identification of synthetic resins. Even the most insoluble cellulose resins will give a positive test with anthrone, thus affording a preliminary classification into a cellulose or noncellulose group. However, many plastic molding compositions contain wood flour and would give a positive test for that reason.

An attempt is now being made to apply this reaction to the quantitative colorimetric determination of small quantities of cellulose in solution, particularly to the analysis of β- and γ-cellulose.

The anthrone test is extremely sensitive. In tests with starch it proved to be 10 to 40 times as sensitive as iodine for the detection of this carbohydrate. Approximately 1 part of starch in 900,000 parts of water can be detected.

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Determination of Ethers and Esters of Ethylene Glycol

A Modified Alkoxyl Analysis

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A modified alkoxyl method and apparatus have been devised by which the ethylene glycol content in esters and ethers may be determined quantitatively on a semimicro scale. Hot, constant-boiling hydriodic acid decomposes the ethylene glycol residue quantitatively into ethyl iodide and ethylene, which are collected and determined volumetrically in standard solutions of silver nitrate and bromine, respectively. The method has been applied to solvents, polyethylene ethers, plasticizers, and hydroxyethylcellulose, as well as to compounds containing halogen or sulfur substituents in place of oxygen upon the ethylene glycol residue.

SINCE, during recent years, derivatives of ethylene glycol have attained considerable technical importance as solvents, plasticizers, sizes, etc., there is frequently a need for an analytical method by which these compounds may be determined and identified.

To the author's knowledge, the only previously described method for the analysis of glycol ethers is that of Elkins (*6*) and Werner and Mitchell (*21*) which depends upon the chromic acid oxidation of the ether and titration of the excess dichromate. This method distinguishes readily between such compounds as monomethyl and ethyl ethers of ethylene glycol but is difficult to apply where the glycol ether is only a small part of a complex structure as in hydroxyethylcellulose or many glycol ether and ester plasticizers.

Methods for the analysis of methyl and ethyl ethers have been known since the work of Zeisel (*24*) who used constant-boiling hydriodic acid to split the ethers into the corresponding alkyl iodides.

$$\text{ROR}' + 2\,\text{HI} \longrightarrow \text{RI} + \text{R}'\text{I} + \text{H}_2\text{O}$$

The alkyl iodide then was distilled out and reacted with alcoholic silver nitrate to form silver iodide which was determined gravimetrically.

Pregl (*15*) adapted the Zeisel method to a micro scale and Vieböck and others (*19*) developed an iodometric method for determining the alkyl iodide. Further modifications in the apparatus were made by Clark (*2*), Elek (*5*), Vieböck (*19*), Samsel and McHard (*16*), and others (*12*).

None of these investigators reported any attempt to adapt the method to the analysis of 1,2-glycol ethers. Meisenheimer (*11*) found that ethylene glycol and hydriodic acid produced low and variable quantities of ethyl iodide. Grün and Bockisch (*8*) abandoned the idea of using the Zeisel method on glycols, after finding that ethylene and propylene glycols with constant-boiling hydriodic acid yielded about 50% of the alkyl iodides and gases identified as ethane and propane, respectively. The identification of these gases has now been shown to have been incorrect. Davis (*4*) applied the Zeisel analysis to phenoxyethanol and obtained low and variable results. Lawrie and others (*10*) obtained ethyl iodide by a Zeisel analysis of hydroxyethylcellulose, but did not report data to indicate what reproducibility was obtained. Small amounts of ethyl iodide have been reported from the decomposition of dioxane with hydriodic acid in a sealed tube at 100° (*13*).

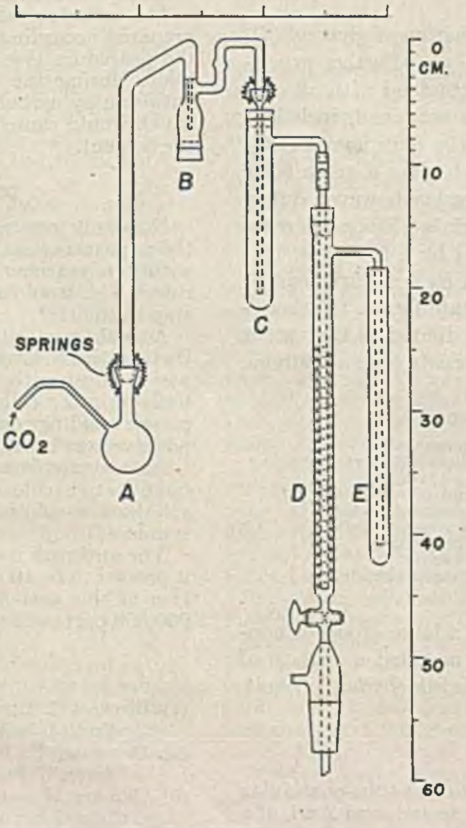

Figure 1. Apparatus

Still other reports show that gaseous hydrogen iodide converts ethylene glycol to ethylene iodide (*17*) and concentrated hydriodic acid at 100° likewise decomposes diethylene glycol to ethylene iodide (*23*). Alkylene iodides have long been known to be unstable to heat and light (*1, 14, 18*) and this instability has been used for the preparation of pure olefins. Such decompositions into olefin and iodine are favored by the presence of iodide ions (*18*).

From the foregoing review, it appears probable that ethyl iodide and ethylene would be two of the products of the reaction of ethylene glycol derivatives and hot, concentrated hydriodic acid.

A preliminary macrodecomposition of polyethylene oxide with constant-boiling hydriodic acid and analysis of the gaseous products showed that the ethyl iodide and ethylene produced accounted quantitatively for the starting material. This finding shows why the various alkoxyl analyses fail to give quantitative and reproducible results with such compounds. If silver nitrate is used as the absorption medium for ethyl iodide, the ethylene escapes. If a bromine–acetic acid solution (*2, 5, 19*) is used, ethylene may react with the excess bromine, but it is not detected and does not interfere with the subsequent titration of the iodate ions from the oxidation of ethyl iodide. On the other hand, when the usual alkoxyl analysis is applied to determine methoxyl or ethoxyl groups in a compound containing ethylene glycol residues, the results are always too high for the alkoxyl content because of the ethyl iodide from the glycol residues.

The method presented here provides a means by which ethylene glycol residues or methoxyl and ethoxyl groups combined with ethylene glycol residues may be determined quantitatively.

APPARATUS

An arrangement of apparatus for the analysis is shown in the scale diagram (Figure 1). It consists in part of the reaction flask, condenser, and first absorption tube of a Clark (*2*) alkoxyl apparatus. These are followed by an absorption tube, *D*, made from a section of a spiral from a Widmer distillation column and a standard-taper (24/40) gas inlet adapter.

Dimensions of the apparatus not readily determined from the diagram are as follows: carbon dioxide inlet capillary, 1-mm. inside diameter; flask *A*, 28-mm. diameter, 12/18 standard-taper joint; condenser, 9-mm. inside diameter; inlet to trap *B*, 2-

mm. inside diameter; inlet to trap *C*, 7/15 standard-taper joint, 2-mm. inside diameter tube; trap *C*, 14-mm. inside diameter; trap *D*, inner tube, 8-mm. outside diameter, 2-mm. opening at bottom of spiral; spiral, 1.75-mm. rod, 23 turns, 8.5-mm. rise per turn; outer tube, approximately 12.5-mm. inside diameter; side arm 7 cm. from top of inserted spiral, 3.5-mm. inside diameter, 2-mm. opening at bottom.

The stopcock is lubricated with Silicone grease. The absorption tubes may be conveniently suspended by a series of properly spaced sheet metal clips attached to a stick clamped at an angle of about 60°.

For the analysis of lowly substituted cellulose ethers a reaction flask of double the illustrated capacity is used. Although a minimum number of connections is desirable and an apparatus may be built with all ground-glass connections, no particular difficulty has been experienced with the rubber connections for tubes *C* and *D*, and they produce a desirable degree of flexibility.

REAGENTS

HYDRIODIC ACID. Constant-boiling hydriodic acid (specific gravity 1.70; boiling point 126–7° C.) is prepared by distilling reagent grade acid over red phosphorus in an atmosphere of carbon dioxide. Adequate precautions should be taken to avoid possible violent explosions of mixtures of air and phosphorus hydrides in the receiver. The acid should be distilled within a few days of the period of use or else stored after distillation in an atmosphere of carbon dioxide or nitrogen in dark-colored, sealed bottles. It should be free from sulfur compounds and from phosphine and hypophosphorous acid. Hypophosphorous acid, which is sometimes used as a stabilizer for hydriodic acid, may be destroyed by the addition of a few iodine crystals followed by distillation over red phosphorus. Phosphine in the distilled acid is indicated by unusual stability to atmospheric oxygen and by the blackening of silver nitrate paper held above the acid. This contamination is frequently present in acid distilled from phosphorus, but is readily removed by refluxing the hydriodic acid until the vapors no longer color silver nitrate paper gray or black. Hydriodic acid vapors stain paper brown or brownish black.

SILVER NITRATE SOLUTION. Silver nitrate (15 grams) is dissolved in 50 ml. of water and then added to 400 ml. of absolute ethanol. Several drops of concentrated nitric acid are added. This solution is standardized against 0.05 *N* ammonium thiocyanate by the Volhard method (*20*). It is very stable and shows very little change with use.

BROMINE SOLUTION. Bromine (1 ml.) is added to 300 ml. of C.P. glacial acetic acid saturated with dry potassium bromide (5 grams). Fifteen milliliters of this solution require about 40 ml. of 0.05 *N* sodium thiosulfate. This solution is stored in a dark bottle and kept in the dark. It is standardized at least once a day during use.

Alternatively, a methanolic solution of bromine and potassium bromide may be used (*9*). Absolute methanol (500 ml.) is saturated with dry potassium bromide (10 grams) and 1.8 ml. of bromine are added. Fifteen milliliters of this solution require between 40 and 50 ml. of 0.05 *N* sodium thiosulfate. This solution is stored as directed above. It is standardized against sodium thiosulfate with each analysis.

OTHER REAGENTS. The following required solutions need no special description:

Potassium iodide, 10% aqueous solution.
Sulfuric acid, 10% aqueous solution.
Sodium thiosulfate, 0.05 *N* standard solution.
Ammonium thiocyanate, 0.05 *N* standard solution.
Starch indicator, 1% aqueous solution.
Ferric ammonium sulfate indicator, saturated aqueous solution (filtered).

SAMPLE SIZE

The choice of sample size is important for accuracy and complete decomposition. Samples of very high ether content should weigh from 50 to 100 mg. and may require 1, 2, or more hours for complete decomposition. For samples containing less than 10% of glycol residue, 200 to 300 mg. of material and a reaction flask of twice the illustrated capacity are used. The amount of hydriodic acid is correspondingly increased.

PROCEDURE OF ANALYSIS

The apparatus is cleaned and dried. Trap *B* is filled with a suspension of a small amount of red phosphorus in enough water to cover the inlet tube. If the sample to be analyzed contains sulfur, the phosphorus is suspended in 5% aqueous cadmium sulfate solution instead of water. Ten milliliters of silver nitrate solution are pipetted into the first absorption tube, *C*, 15 ml. of bromine solution are pipetted into the spiral absorption tube, *D*, and 10 ml. of 10% potassium iodide solution are placed in the final tube, *E*. A weighed sample of glycol ether (0.05 to 0.12 gram) is placed in reaction flask *A*, together with a Hengar boiling granule and 10 ml. of hydriodic acid. When the sample has poor solubility in the acid or tends to sublime, a mixture of 1 ml. of phenol and 2 ml. of propionic anhydride is added to the reaction flask, as recommended by Elek (*5*) (*cf. 16*). The flask is connected to the apparatus, a slow stream of carbon dioxide (1 bubble per second) is passed through, and the flask is heated slowly with an oil bath to 140° to 145° C.

The flask is kept at this temperature a minimum of 40 minutes and frequently 1 to 2 hours are required for compounds with very high ether contents. Two indications of the completion of the decomposition are the absence of any cloudy reflux in the condenser above the reaction flask and the nearly complete clarification of the supernatant liquid in the silver nitrate trap. Five minutes before the completion of the reaction the silver nitrate trap is heated to 50° to 60° C. with a hot-water bath to drive out any dissolved olefin.

At the completion of the decomposition, tubes *D* and *C* are disconnected cautiously in that order. The carbon dioxide source then is disconnected and the heat removed from flask *A*. The spiral absorption tube, *D*, is then connected by its lower adapter to a 500-ml. iodine-titration flask containing 10 ml. of 10% potassium iodide solution and 150 ml. of water. The potassium iodide tube, *E*, is removed and the side arm rinsed into it. The bromine solution is allowed to run into the titration flask through the stopcock and the tube and spiral are rinsed with water. The contents of the potassium iodide tube are added to the titration flask, which is then stoppered and allowed to stand 5 minutes. Five milliliters of 10% sulfuric acid are added and the solution is titrated at once with 0.05 *N* sodium thiosulfate, using 2 ml. of starch indicator solution for the end point.

The contents of the silver nitrate trap are rinsed into a flask, diluted to 150 ml. with water, heated to boiling, cooled to room temperature, and titrated with 0.05 *N* ammonium thiocyanate, using 3 ml. of ferric ammonium sulfate solution as an indicator (*20*).

CALCULATIONS

After the titrations of the bromine and silver nitrate traps are subtracted from the corresponding blank titrations, the following calculations hold for ethylene glycol ethers:

$$\frac{\text{Difference in ml. of } Na_2S_2O_3 \times N \times 2.203}{\text{wt. of sample}} = \%\ C_2H_4O \text{ as } C_2H_4$$

$$\frac{\text{Difference in ml. of } NH_4SCN \times N \times 4.405}{\text{wt. of sample}} = \%\ C_2H_4O \text{ as } C_2H_5I$$

The C_2H_4O unit has been chosen as convenient for calculating the results of the analysis of compounds having greatly differing structures. Other groups, such as —C_2H_4—, —OCH_2CH_2O—, or $HOCH_2CH_2O$—, may be used by simply changing the factors in the equations and their use may appear more logical when dealing with particular types of derivatives.

CORRECTION FOR REAGENTS

Repeated blank determinations on the reagents in the apparatus showed that there was no change in the silver nitrate solution and there was an average loss in the bromine solution equivalent to 0.30 ml. of 0.05 *N* sodium thiosulfate. This correction was applied to all the determinations made using methanolic bromine–potassium bromide and bromine–acetic acid for the absorption of ethylene.

ANALYTICAL DATA

Tables I to IV contain the results of the analysis of various typical substances containing ethylene glycol residues.

THEORY OF PROCEDURE

When an ethylene glycol ether or ester is decomposed by constant-boiling hydriodic acid, the points of attachment of the ether and ester linkages are replaced by iodo and hydroxyl groups. Eventually all aliphatic hydroxyl groups are replaced by iodine or hydrogen, while phenolic hydroxyls and carboxyl groups are unchanged. Reports in the literature (*17*, *23*) indicate that ethylene iodide can be isolated as an intermediate in the reaction of ethylene glycol or diethylene glycol with hydriodic acid and the formation of the final products, ethyl iodide and ethylene, is best explained by assuming the intermediate production of ethylene iodide.

$$ROCH_2CH_2OH + 3\,HI \longrightarrow RI + ICH_2CH_2I + 2\,H_2O \quad (1)$$

The exact course which the reaction takes preceding the formation of ethylene iodide probably varies with the number and type of substituents upon the glycol residue. One may reasonably assume that in many cases ethylene iodohydrin precedes ethylene iodide. In the case of polyethylene ethers, ethylene glycol, ethylene iodohydrin, and ethylene iodide may all be simple primary decomposition products.

As soon as ethylene iodide has been formed, several courses of further reaction are possible: the diiodide may decompose into iodine and an olefin, which escapes; part of the alkylene iodide may be reduced by hydriodic acid to alkyl iodide; part of the olefin formed by the first reaction may react with hydriodic acid to produce alkyl iodide.

Table I. Analysis of Ethylene Glycol Derivatives

Substance	Formula	Ethylene Trap	Per Cent —C_2H_4O— Found: As RI	Found: As C_2H_4	Found: Total	Calculated
Ethylene glycol di-O-(pentaacetyl-*d*-gluconate)[a]	$C_2H_4O_2[C_6H_6O_6(COCH_3)_5]_2$	MeOH–Br_2–KBr	4.45	0.91	5.36	5.25
		MeOH–Br_2–KBr	3.72	1.52	5.24	
		MeOH–Br_2–KBr	3.45	2.01	5.46	
2-Phenoxyethanol	$C_6H_5OCH_2CH_2OH$	MeOH–Br_2–KBr	21.83	10.16	31.99	31.88
		MeOH–Br_2–KBr	27.29	4.65	31.94	
		MeOH–Br_2–KBr	22.84	9.01	31.85	
		Br_2–CCl_4	23.13	8.79	31.92	
		Br_2–CCl_4	21.99	11.09	33.08	
		Br_2–CCl_4	20.12	12.61	32.73	
		Br_2–CH_3COOH	24.97	6.35	31.32	
		Br_2–CH_3COOH	28.42	3.39	31.81	
		Br_2–CH_3COOH	17.82	14.17	31.99	
Diethylene glycol dicresyl ether	$C_7H_7OC_2H_4OC_2H_4OC_7H_7$	MeOH–Br_2–KBr	19.68	11.28	30.96	30.76
		MeOH–Br_2–KBr	13.89	16.99	30.88	
		MeOH–Br_2–KBr	20.87	9.73	30.60	
		Br_2–CH_3COOH	14.80	16.11	30.91	
Ethylene glycol	$HOCH_2CH_2OH$	MeOH–Br_2–KBr	57.36	14.37	71.73	70.97
		MeOH–Br_2–KBr	42.07	29.56	71.63	
Diethylene glycol	$HOC_2H_4OC_2H_4OH$	MeOH–Br_2–KBr	69.68	13.22	82.90	83.05
		MeOH–Br_2–KBr	59.69	22.58	82.27	
Polyethylene oxide[b]	$HO(C_2H_4O)_{91}H$	MeOH–Br_2–KBr	82.48	15.57	98.05	99.59
		MeOH–Br_2–KBr	85.15	12.45	97.60	
		MeOH–Br_2–KBr	81.88	15.39	97.27	
		Br_2–CCl_4	60.11	42.18	102.3	
Dioxane	$(C_2H_4O)_2$	MeOH–Br_2–KBr	90.40	9.34	99.74	100.00
		MeOH–Br_2–KBr	86.90	11.54	98.44	
2-Methoxyethanol[c]	$CH_3OCH_2CH_2OH$	MeOH–Br_2–KBr	105.8	9.47	115.3	115.8
		MeOH–Br_2–KBr	102.6	11.21	113.8	

[a] For preparation see (*22*). [b] Carbowax-4000 of Carbide and Carbon Chemicals Corp.
[c] Methoxyl content calculated as —C_2H_4O—.

Table II. Analysis of Commercial Plasticizers

Substance	Formula	Ethylene Trap	Per Cent —C_2H_4O— Found: As RI	Found: As C_2H_4	Found: Total	Calculated[a]
Methoxyethyl oleate[b]	$CH_3OC_2H_4OOC_{18}H_{33}$	MeOH–Br_2–KBr	21.64	2.07	23.71	25.88
		MeOH–Br_2–KBr	20.32	3.03	23.35	
		MeOH–Br_2–KBr	21.96	1.89	23.85	
Triethylene glycol di-2-ethylhexoate[c]	$C_6H_{12}O_2(C_7H_{15}COO)_2$	MeOH–Br_2–KBr	23.48	7.79	31.27	32.82
		MeOH–Br_2–KBr	24.94	6.36	31.30	
		MeOH–Br_2–KBr	19.23	11.75	30.98	
		MeOH–Br_2–KBr	22.25	9.37	31.62	
		Br_2–CCl_4	19.74	11.71	31.45	
β-Ethoxyethyl-*o*-benzoyl benzoate	$C_6H_5COC_6H_4COOC_2H_4OC_2H_5$	MeOH–Br_2–KBr	24.55	3.75	28.30	29.54
		MeOH–Br_2–KBr	23.38	4.66	28.04	
Butoxyethylphthalate	$C_6H_4(COOC_2H_4OC_4H_9)_2$	MeOH–Br_2–KBr	18.13	6.94	25.07	24.05
		MeOH–Br_2–KBr	18.20	5.38	23.58	

[a] Methoxyl and ethoxyl groups calculated as —C_2H_4O—.
[b] Kapsol as received from Ohio Apex, Inc.
[c] Flexol 3GO of Carbide and Carbon Chemicals Corp.

$$ICH_2CH_2I \longrightarrow CH_2{=}CH_2 + I_2 \quad (2)$$

$$ICH_2CH_2I + HI \longrightarrow CH_3CH_2I + I_2 \quad (3)$$

$$CH_2{=}CH_2 + HI \longrightarrow CH_3CH_2I \quad (4)$$

In any case, the two final products are ethyl iodide and ethylene and the sum of these products is equivalent to the glycol ether groups in the substance. There may be present, of course, volatile alkyl halides from other sources. No paraffin hydrocarbons are produced.

The following equation is a summation of Equations 1 to 4, in which x is a variable number less than 1:

$$ROCH_2CH_2OH + (3 + x)\,HI \longrightarrow RI + (x)\,CH_3CH_2I + (1 - x)\,CH_2{=}CH_2 + I_2 + 2\,H_2O \quad (5)$$

The ratio of ethyl iodide and ethylene obtained varies with several reaction conditions, as is pointed out in the discussion on application of the procedure. No exception to the above course of reaction has been found among the wide variety of structures represented in the tables. Other 1,2-glycols and their derivatives are decomposed by hydriodic acid in a similar way, forming alkyl iodides and olefins.

DEVELOPMENT AND APPLICATION OF METHOD

In developing an absorption system a single silver nitrate trap was found to be sufficient to absorb all alkyl iodide vapors. Simple traps of bromine solution would not absorb all of the ethylene, even when several were used in series. Therefore, the spiral tube was devised to provide a longer contact of the gases with the bromine solution. The standard-taper adapter was added to this tube to permit the transfer of the bromine solution to a titration flask without loss. It was found advisable to place the side arm well above the upper end of the spiral or to enlarge the upper part of the tube into a bulb in order to provide room for the contents of the tube if the flow of gas through the system became too rapid. Rushes of gas frequently occurred just as the reaction was brought to boiling. Caution must therefore be taken in bringing the mixture to a boil, even though good boiling stones are provided.

A final simple trap containing potassium iodide solution was added to the system to collect any bromine swept out by the flow of carbon dioxide. Practically no bromine was found to escape from methanolic bromine–potassium bromide solution, while bromine equivalent to 0.75 ml. of 0.05 *N* sodium thiosulfate was often obtained in 40 minutes from bromine–acetic acid solution. The volatility of the bromine was reduced by saturating the solution with potassium bromide.

A solution of bromine in carbon tetrachloride was unsatisfactory for the absorption of ethylene because of the volatility of the solution. The resulting losses produced values for the percentage of glycol residues which were too high (Table I). Bromine in methanol saturated with potassium bromide was used in the majority of determinations reported. This solution was very easily handled without bromine losses, but the titer dropped rapidly during storage and use and it therefore required frequent standardization. Occasionally solutions were obtained which were very unstable and gave high blank determinations. These blanks may be reduced to small and reproducible values by storing new solutions for at least 10 days before use (*2A*). An acetic acid solution of bromine had the best stability to storage and use and was readily handled without losses.

Because a single absorption system would greatly simplify the determination of ethylene glycol derivatives, several attempts were made to achieve this end. In one experiment the vapors from the reaction flask, *A*, were passed through a second heated flask of hydriodic acid. No marked increase in the yield of ethyl iodide was obtained.

Another approach to a simplified absorption system is the use of a single standard bromine solution, which reacts with both the alkyl iodide and olefin from glycol derivatives but not in an equivalent manner.

$$RI + Br_2 \longrightarrow RBr + IBr$$

$$IBr + 3\ H_2O + 2\ Br_2 \longrightarrow HIO_3 + 5\ HBr$$

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

The reactions represented by the first two equations are the basis of the Vieböck absorption system for alkyl iodides (*2*, *19*). If a standardized selective reducing agent could be found which would react with the excess bromine and not with the iodate ions, this single solution system could be used for the determination of glycol ethers. The alkyl iodide would be determined by titration of the iodate ions and the olefin by the difference between the total bromine at the beginning and the sum of the excess bromine and that used to react with alkyl iodide. Standard formic acid reacts selectively but not stoichiometrically with the excess bromine and attempts to use it for this purpose were therefore unsuccessful.

Except for various adjustments in the adopted procedure to accommodate samples of varying ether content and solubility, as noted earlier, most derivatives of ethylene glycol were analyzed without difficulty.

Several factors were found to affect the ratio of alkyl iodide and olefin obtained. Factors which promoted the formation of high percentages of alkyl iodide were (1) freshly distilled hydriodic acid, (2) small sample size, and (3) low temperatures during the first part of the reaction. The values obtained in the analysis of ethylene glycol di-O-(pentaacetyl-*d*-gluconate) (Table I) illustrate the effect of aging hydriodic acid, which for succeeding samples was 1, 2, and 6 days old, respectively. The ratio of ethyl iodide to ethylene in general had no bearing on the total result, except that, if the amount of ethylene became too great and was evolved too rapidly, the absorption tube failed to take it up completely. No combination of conditions was found which yielded 100% alkyl iodide in a period of time suitable for an analytical method.

Chlorine-containing compounds required no changes in the procedure, but sulfur-containing compounds required the use of cadmium sulfate in the phosphorus scrubbing trap in order to collect the hydrogen sulfide which was evolved.

Table III. Analysis of Miscellaneous Substances

Substance	Formula	Per Cent —C_2H_4O— Found As RI	As olefin	Total	Calculated[a]
β,β′-Dichloroethyl ether	$(ClCH_2CH_2)_2O$	47.73	12.87	60.60	61.61
		50.89	10.30	61.19	
4,7-Dithiasebacic acid	$CH_2S—C_2H_4COOH$ | $CH_2S—C_2H_4COOH$	13.36	5.02	18.38	18.48
		12.54	6.15	18.69	
Thiodiglycol	$(HOCH_2CH_2)_2S$	26.29	9.41	35.70	72.10
		13.06	24.09	37.15	
		31.49	7.88	39.37	
Dipropylene glycol	$(CH_3CHOHCH_2)_2O$	45.34	12.65	57.99	58.67
		44.33	13.14	57.47	

[a] Alkylene groups in samples calculated to theoretical yield of —C_2H_4O—.

Table IV. Typical Analyses of Hydroxyethylcellulose

Sample	Moles of Ethylene Oxide Used per Glucose Unit	Per Cent —C_2H_4O— Found As C_2H_5I	As C_2H_4	Total	Hydroxyethyl Groups per Glucose Unit From modified alkoxyl method	From saponification of triacetate	Solubility
A	0.25	3.06	0.54	3.60	0.17	..	Soluble in 7% NaOH
		3.14	0.66	3.80	0.17	..	Soluble in 7% NaOH
B	0.50	4.52	2.06	6.58	0.26	..	Soluble in 7% NaOH
		5.18	1.16	6.34	0.25	..	Soluble in 7% NaOH
C	0.75	8.45	2.08	10.53	0.43	..	Swollen by cold H_2O
		7.04	3.18	10.22	0.42	..	
D	1.50	14.77	2.08	16.85	0.75	..	Swollen by many solvents; not swollen by acetone
		13.89	2.20	16.09	0.71	..	
E[a]	4.05	28.25	5.60	33.85	1.88	..	Soluble in H_2O, AcOH, and C_5H_5N
		19.02	13.72	32.74	1.79	..	
F[a]	10.0	30.96	21.66	52.62	4.09	..	Soluble in H_2O and aq. EtOH; insoluble in acetone
		35.64	17.16	52.80	4.12	..	
Ceglin D[b]	...	3.34	1.32	4.66	0.18	..	Soluble in 7% NaOH
		3.49	1.23	4.72	0.18	..	
Ceglin H[b]	...	3.12	3.07	6.19	0.24	..	Soluble in 7% NaOH
		3.44	2.12	5.56	0.22	..	
Cellosize WS-100[a,c]	...	20.32	7.82	28.14	1.44	1.45	Soluble in H_2O and nearly soluble in AcOH or C_5H_5N
		22.65	5.61	28.26	1.45	1.49	
		23.15	4.89	28.04	1.44	..	

[a] Analytical values corrected for ash content.

[b] Product of Sylvania Industrial Corp.

[c] Product of Carbide and Carbon Chemical Corp.

Thiodiglycol (Table III) produced only a 50% yield of ethylene and ethyl iodide and a crystalline sublimate. The sublimate was identified as 1,4-dithiane (melting point 110°) rather than β,β′-diiodoethylsulfide, which is reported to form very readily with thiodiglycol and hydriodic acid (*7*). 4,7-Dithiasebacic acid was successfully analyzed by using a solvent mixture of phenol and propionic anhydride in the flask and heating the reaction mixture at 110° for 2 hours before going higher.

In the analysis of butoxyethyl phthalate (Table II) much too high results were obtained unless the carbon dioxide flow was slowed down and the oil bath kept below a maximum of 140°. For the satisfactory separation of ethyl and methyl iodides from propyl and butyl iodides, a water-cooled condenser as used by Elek (*5*) and others would be required.

1,2-Propylene glycol ethers were found to follow the same course of reaction as ethylene glycol ethers, forming propylene and isopropyl iodide. The latter was distilled from the reaction flask with considerable difficulty and it was necessary to heat the condenser and the phosphorus trap and keep a very high reflux in order to drive it over.

DISCUSSION

The data show that the precision and accuracy of the method are satisfactory for the analysis of a wide variety of glycol derivatives. The columns in the tables showing the percentages of alkyl iodide found are the values which would have been obtained if the substances had been analyzed by the Zeisel or Vieböck methods. In general, these values are low and variable. The yields of alkyl iodide in duplicate analyses are often of a similar magnitude because consecutive analyses were performed under similar conditions. When the percentage of glycol units determined as ethylene is added to the percentage as alkyl iodide, the total checks well with the calculated values. The duplicate values found for a number of unpurified plasticizer samples (Table II) agree well among themselves but are all lower than the calculated values. The probable presence of impurities accounts for these results.

Substances or structures which would interfere with the analysis are any volatile alkyl iodide from an ether, ester, sulfide, etc., or structures which might produce 1,2-diiodides and eventually gaseous olefins but from which relatively nonvolatile monoiodides would result. Methyl, ethyl, and possibly isopropyl iodide, if they are known to be potentially present, may be easily taken into account by calculating the over-all results as glycol residue, as was done in the case of methoxy- and ethoxyethanol derivatives in this work (Tables I and II). Acetone is an interfering substance because it reacts readily with bromine. If it is used for drying purposes, the apparatus must be carefully freed of it before the analysis is performed.

Methoxyl and methyl ester groups may be determined in the presence of glycol residues by a separate analysis according to the recent modification of the Willstätter method by Cooke and Hibbert (*3*). Of course, methyl and ethyl ester groups, as well as other ester groups, may also be determined separately by saponification.

The correct degree of substitution of various hydroxyethylcellulose derivatives is presented here for the first time (Table IV). Most previous estimations have been based upon the amount of etherifying agent used or upon the gain in weight of the product. Obviously the method of analysis described here does not determine whether the hydroxyethyl ether groups are present as individual units or are built up in polyethylene oxide units of varying sizes. It seems more than probable that the latter is increasingly the case as the substitution is increased and it must be so in the case of sample F (Table IV) in which 4.1 glycol residues are distributed over 3 cellulose hydroxyls.

An independent check on the hydroxyethyl content in cellulose derivatives was obtained in the case of Cellosize WS-100 by preparing the triacetate with pyridine and acetic anhydride and calculating the number of glycol residues necessary to produce the observed difference in acetyl value between this sample and cellulose triacetate. Such a method is applicable to the more highly substituted hydroxyethylcellulose derivatives.

Since a direct analysis of hydroxyethylcellulose has not previously been realized, a few comments on the relation of substitution to the method of preparation and solubility of these derivatives are in order. The data in Table IV show that the efficiency of the reaction between ethylene oxide and alkali cellulose (18% sodium hydroxide; 33% cellulose) varied from as high as 68% down to 40% as the portions of ethylene oxide were increased from 0.25 to 1.0 mole. Larger amounts of ethylene oxide were added in successive 1-mole portions. Considerably higher efficiencies were obtained by adding the ethylene oxide in smaller portions.

Certain generalities concerning the solubility of these derivatives in relation to substitution are not clear from the number of analyses presented. Above 0.35 mole hydroxyethyl groups per glucose unit (g. u.), the derivatives become increasingly sensitive to cold water and eventually dissolve at substitutions between 1.0 and 1.2 moles per g. u. Up to 0.5 mole per g. u. they may be handled in hot water. Above 0.75 mole per g. u. they are considerably swollen by alcohols and acetic acid but not by acetone. Solubility in powerful organic solvents is attained at about 1.3 moles per g. u. and eventually solubility in common solvents is obtained. These solubility rules are based on derivatives having degrees of polymerization between 500 and 800 anhydroglucose units. In contrast with other cellulose ethers, hydroxyethylcellulose ethers show increasing solubility in all media with increasing substitution. In other words, once solubility in a given solvent is reached, it is not lost by increasing the hydroxyethyl substitution.

In conclusion, in addition to the analysis of simple ethylene glycol derivatives as described, the method may be used for the determination of glycol derivatives in mixtures, such as aqueous solutions or plasticized polymeric materials. It is believed that the method may be applied by proper adaptation to many other types of compounds containing chains of two methylene groups linked to noncarbon functional groups and should prove useful for the identification and proof of structure of such compounds.

ACKNOWLEDGMENT

The author expresses his appreciation to W. W. Watkins and E. F. Izard for advice and counsel, to C. E. Bryan, who prepared some of the hydroxyethylcellulose samples, and in particular to Miss D. J. McKenica, who assisted in developing the method and performed many of the analyses.

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Precision Semimicromethod for Gas Analysis

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An apparatus is described which is capable of complete analysis of small samples of carbon dioxide, carbon monoxide, methane, hydrogen, nitrogen, and/or oxygen. The operations of analysis are simple and reliable, and the danger of loss of a valuable sample is reduced to a minimum. With a sample of volume approximating 1 cc. at N.T.P. an accuracy of a few tenths of a per cent of the total gas sample may be anticipated; but an accuracy of about 1% is maintained with samples as small as 0.1 cc. N.T.P. The conditions for a satisfactory fractional combustion on a platinum catalyst of hydrogen and carbon monoxide in the presence of methane and excess oxygen are defined.

IN THE course of an investigation of the gases in meteorites a sensitive method for the analysis of low-pressure gases has been developed, which provides data of high accuracy with very small gas samples, and in which the danger of accidental loss of the sample is reduced to a minimum.

Figure 1 illustrates the apparatus, in which all the measurements are made at diminished pressures.

Only solid adsorbents are employed, and Apiezon stopcock grease is used throughout. The 1000-cc. reservoir, *A*, containing purified mercury, is linked with the 500-cc. chamber of the Töpler pump, *B*. The rise and fall of the mercury in *B* is controlled through stopcock 1, whose two leads give access to an aspirator line and to the atmosphere, respectively. The buret, *C*, is made from 12-mm. Pyrex tubing, and is graduated from 1 to 10 cc. in steps of 1 cc. The buret bulb has an additional capacity of 10 cc., permitting the accommodation of particularly large gas samples. The barometer, *D*, is made from the same piece of tubing as *C*, and is provided with the overflow attachment, *E* (*2*). The difference of the height of the mercury columns in *C* and *D*, which represents the gas pressure in *C*, may be read accurately from a graduated mirror scale set behind the tubes. A calibrated thermometer set close to *C* indicates the gas temperature.

The drying tube, *F*, contains a small amount of Anhydrone, trap *G* permits convenient separation of any condensable material in the gas sample, and tube *H* contains Ascarite, for the absorption of carbon dioxide and other acid gases. The combustion catalyst tube, *J*, consists of a short section of quartz capillary tubing, connected to the rest of the line through ground quartz to Pyrex joints. The capillary contains a 5-cm. length of No. 22 platinum wire, and is heated by a small closely fitting furnace with Alundum core, Nichrome winding, and asbestos lagging. The presence in each branch of the adsorption train of a small spiral spring made of 4-mm. (outside diameter) Pyrex tubing (not shown in the diagram) prevents any strains from developing in the line.

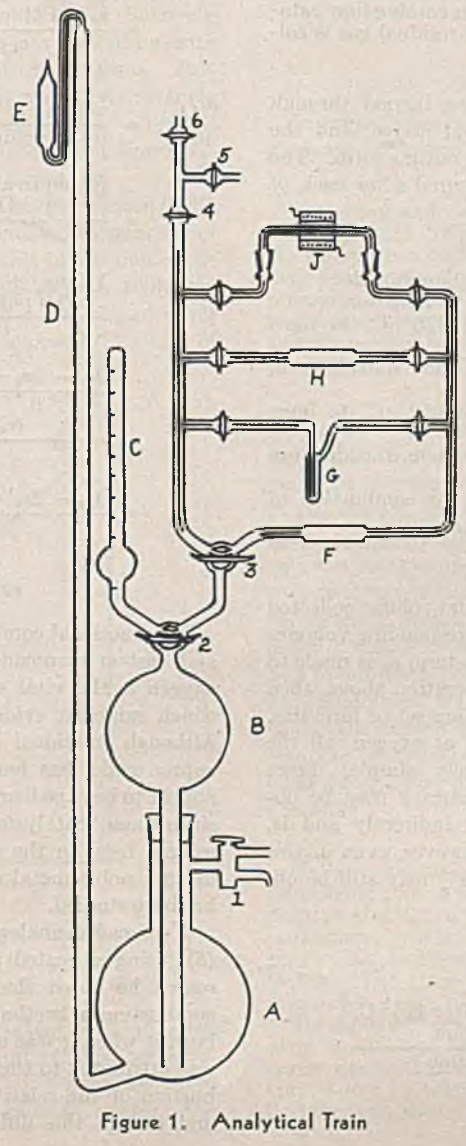

Figure 1. Analytical Train

Stopcock 5 gives access to a series of bulbs containing various pure gases and determinate gas mixtures, while stopcock 6 leads to the line from which the gas sample is to be collected, and thence to the evacuating pumps. For cases where a small gas sample is to be collected from a very large volume it has proved advantageous to precede stopcock 6 with a small volume and a mercury diffusion pump in that order. The diffusion pump rapidly concentrates the gas sample in the small volume, from which it may be readily conveyed to the buret by the Töpler pump.

In determining the graduations of the buret, the 10-cc. mark was determined directly, by weighing the mercury delivered through a stopcock temporarily attached to the bottom of the buret before the latter was sealed in place. The other points are then most simply determined after the buret has been permanently mounted—e.g., by compressing a sample of gas to the 10-cc. mark, reading the pressure, and then slowly compressing it until the new pressure, corrected for any small fluctuations in temperature, is just 10/9 the former value. The new position of the mercury meniscus in the buret now corresponds to 9 cc., and may be marked as such. The other buret graduations are located in similar fashion. Nitrogen is used as the calibration gas and, by occasionally discarding part of the gas sample, the pressures are kept below 200 mm., so that no errors due to gas imperfection can be introduced.

Calibration by this method is advantageous because the buret is calibrated after it has been permanently set in place; and is calibrated in the same way, and with the same precision, as in later use. Furthermore, it is somewhat simpler to secure markings corresponding exactly to unit numbers of cubic centimeters by this method than by any other method.

OPERATIONS OF ANALYSIS

The dry gas sample is collected in the buret by repeated strokes of the Töpler pump, and the mercury is run up into the buret until the gas is compressed to that mark which most nearly corresponds to a sample pressure of 150 mm. The pressure is then determined with an accuracy of 0.1 mm., the temperature is read to the nearest 0.1° C., and, since the probable accuracy of the volume calibration is 0.001 cc., it becomes possible to compute the gas volume under standard conditions with a probable accuracy of 0.1%.

This calculation is predicated upon the behavior of the sample as a perfect gas, a valid assumption in this instance, since it has been shown (*1*) that under pressures of 150 mm. even a gas as imperfect as carbon dioxide behaves relatively ideally. Furthermore, any volume change produced by mixing is of negligible magnitude. Measurement at diminished pressure, as practiced in this mode of analysis, therefore not only serves to increase the effective gas volume to a readily determinable magnitude, but also obviates any aberrations due to imperfection of the gases involved.

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Consider now the operations involved in the analysis of a sample containing carbon dioxide, carbon monoxide, methane, hydrogen, oxygen, and nitrogen. After measurement of the total original volume, the sample must be circulated over the Ascarite to absorb the carbon dioxide. To perform this operation the analytical train is first thoroughly evacuated, and then shut off from the evacuating pumps. The gas is withdrawn from the buret with the Töpler pump (ordinarily two or three strokes are required to empty the buret completely), and passed into the absorption train through the left branch of the three-way stopcock, 3, the mercury rising as far as the base of stopcock 3. To complete the circulatory cycle, the bulk of the gas is collected through the right branch of stopcock 3, by turning the stopcock to the appropriate position and then lowering the mercury in the pump. To ensure perfectly complete absorption this cycle may be repeated two or three times. By circulating the gas over the absorbent in this fashion it is possible to avoid any danger of the dead gas diffusion blocking occasionally encountered in the Orsat apparatus. Finally, the residual gas sample is completely collected through the right branch of stopcock 3 with three or four strokes of the Töpler pump, and conveyed back into the buret where its temperature, pressure, and volume are again measured. Recovery of the residual sample is more than 99.9% complete after four strokes of the Töpler pump. By invariably collecting the residual gas through the right branch of cock 3 any water liberated by the Ascarite (or, later, in the combustion of hydrogenous material) is absorbed by the Anhydrone, and the gas reaching the buret is always in a state of uniform dryness.

To provide a small excess of oxygen for the impending combustion analysis, a suitable quantity of this gas is drawn from its storage bulb with the Töpler pump, and added to the sample in the buret, whereupon the new volume is measured. The difference between this volume and that of the previous measurement represents the volume of oxygen added. The diluted gas sample is then repeatedly circulated over the combustion catalyst, which is maintained at 475° C., and the residual gas is collected and remeasured.

The further operations of the analysis are carried through by the same general procedures as indicated above, and the complete analytical scheme is shown below in outline form. The volume, pressure, and temperature are measured after each of the following operations:

1. Complete collection of original sample
2. Circulation over Ascarite to remove carbon dioxide
3. Addition of oxygen in small excess, for combustion
4. Circulation over platinum catalyst at 450° C. to burn hydrogen and carbon monoxide
5. Circulation over Ascarite to remove carbon dioxide from carbon monoxide combustion
6. Circulation over platinum catalyst at 950° C. to burn methane
7. Circulation over Ascarite to remove carbon dioxide from methane combustion
8. Addition of hydrogen in small excess, for combustion of excess oxygen
9. Circulation over hot platinum catalyst to burn excess oxygen

All the readings of temperature, pressure, and volume collected in the above scheme are converted to the corresponding volumes at normal temperature and pressure. If the term v_x is made to refer to the N.T.P. volume after the x'th operation above, then the analytical results are given in the following set of formulas. It will be observed that, with the exception of oxygen, all the components are determined from relatively simple, direct formulas, and a relatively high order of accuracy may be obtained. The oxygen content is calculated indirectly and is, therefore, subject to cumulative errors. However, even in this unfavorable case, a probable accuracy of 0.5% may still be obtained.

$$\frac{\%CO_2}{100} = \frac{\text{volume of } CO_2}{\text{total volume}} = \frac{v_1 - v_2}{v_1}$$

$$\frac{\%CO}{100} = \frac{\text{volume of CO}}{\text{total volume}} = \frac{\text{volume of } CO_2 \text{ after 475° C. combustion}}{\text{total volume}}$$

$$= \frac{v_4 - v_5}{v_1}$$

$$\frac{\%H_2}{100} = \frac{\text{volume of } H_2}{\text{total volume}} = \frac{2/3\ (\text{volume of contraction due to } H_2 \text{ combustion})}{\text{total volume}}$$

$$= \frac{2/3\ (\text{total 475° C. volume of contraction} - \text{contraction due to CO})}{\text{total volume}}$$

$$= \frac{2/3\,[(v_3 - v_4) - 1/2\,(v_4 - v_5)]}{v_1} = \frac{2v_3 - 3v_4 + v_5}{3v_1} =$$

$$\frac{\%CH_4}{100} = \frac{\text{volume of } CH_4}{\text{total volume}}$$

$$= \frac{CO_2 \text{ volume after 850° C. combustion}}{\text{total volume}} = \frac{v_6 - v_7}{v_1}$$

$$= \frac{1/2\ (\text{volume of contraction due to 850° C. combustion})}{\text{total volume}} = \frac{v_5 - v_6}{2v_1}$$

$$\frac{\%N_2}{100} = \frac{\text{volume of } N_2}{\text{total volume}} = \frac{(\text{total } N_2 \text{ and } O_2 \text{ residue after 3rd Ascarite passage} - \text{residual oxygen})}{\text{total volume}}$$

$$= \frac{v_7 - 1/3\,(v_8 - v_9)}{v_1} = \frac{3v_7 - v_8 + v_9}{3v_1}$$

$$\frac{\%O_2}{100} = \frac{\text{volume of } O_2}{\text{total volume}} = \frac{(O_2 \text{ theoretically used} - O_2 \text{ apparently used})}{\text{total volume}}$$

$$= \frac{(O_2 \text{ equivalent of } H_2\text{, CO, and } CH_4 - O_2 \text{ apparently used})}{\text{total volume}}$$

$$= \frac{1/2\ v_{H_2} + 1/2\ v_{CO} + 2\ v_{CH_4} - (O_2 \text{ put in} - O_2 \text{ residue})}{\text{total volume}}$$

$$= \frac{\frac{2v_3 - 3v_4 + v_5}{6} + \frac{v_4 - v_5}{2} + 2\,(v_6 - v_7) - (v_3 - v_2) + 1/3\,(v_8 - v_9)}{v_1}$$

$$= \frac{3v_2 - 2v_3 - v_5 + 6v_6 - 6v_7 + v_8 - v_9}{3v_1}$$

FRACTIONAL COMBUSTION

The fractional combustion on a platinum catalyst of hydrogen and carbon monoxide in the presence of methane and excess oxygen is the vital step in this procedure, for the validity of which sufficient evidence is not to be found in the literature. Although fractional combustion on oxide catalysts, especially cupric oxide, has long been known and practiced, it does not appear to be expedient if a determination of oxygen is in prospect, since these "catalysts" may themselves furnish a portion of the oxygen used in the combustion. Therefore, the possibility of using a noble metal catalyst in fractional combustion processes has been studied.

A somewhat analogous case has been investigated by Richardt (*5*), using a heated palladium tube. In the course of his research he noted that if hydrogen were mixed with methane, combustion of methane occurred at temperatures far too low to burn it when it was unmixed with hydrogen. This phenomenon was attributed to the strong heating of the catalyst by the combustion of the relatively large quantities of hydrogen present, and though this difficulty has been rather generally noted in fractional combustion work, it is not to be anticipated in the present instant in view of the low pressures of the gases involved.

Because of the cost, fragility, and tendency of a palladium tube catalyst to develop leaks, preliminary tests were made to discover whether an entirely enclosed platinum catalyst could be used for the fractional combustion.

In the first trial 1 gram of platinized asbestos, previously heated to redness in air, was packed into the quartz tube. It was then found that when measured small quantities of oxygen were circulated over the catalyst, while the latter was heated to bright redness, 1 to 2% of the sample was lost. A second passage of the same gas sample over the catalyst resulted in a further loss of 1 to 2%, so that the loss cannot be attributed to a combustible impurity in the oxygen, which, moreover, had already been treated with hot platinized asbestos during its purification. Consequently, the asbestos was discarded in favor of a small roll of platinum foil. The oxygen loss was then reduced to 0.5%.

The combustion catalyst tube was then remodeled along lines originally suggested by Hempel (*4*), and the combustion catalyst consisted of a 5-cm. length of No. 22 platinum wire inserted in the 2-mm. bore of the quartz combustion capillary tube. With this catalyst renewed tests with small measured oxygen samples revealed a loss of only 0.1% when the sample was circulated over the catalyst at 475° C., and a loss of 0.2% when the circulation was performed at 850° C. These losses were accurately reproducible, and since they were close to the limiting experimental error, no further attempt to reduce them has been made.

The explanation of these oxygen losses, while it may lie in a trace of copper in the platinum, probably resides in physical adsorption or solution of oxygen by the platinum. Such absorption has been reported by Sieverts (*6*) as increasing with rising temperature, in line with the present observations. Furthermore, the recovery of such dissolved gas would be extremely slow (*7*), in line with the author's experience that, after the passage of oxygen over the catalyst, prolonged evacuation is required before the combustion tube can be pumped flat.

A very small, though unmistakable, loss of oxygen (circa 0.05%) when a measured sample of this gas was circulated through other parts of the line is almost certainly attributable to reaction of the oxygen with the stopcock grease, especially since a 100% recovery was always secured when measured quantities of other gases were circulated through the line. The error in the case of oxygen is negligible in any event.

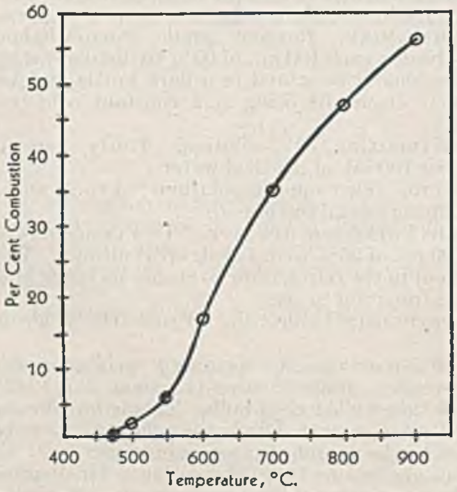

Figure 2. Combustion of Methane on a Platinum Catalyst

With the final form of catalyst tube the extent of combustion of methane-oxygen mixtures, as a function of catalyst temperature, was studied. The results shown in Figure 2 represent the per cent combustion during a single slow passage through the catalyst tube of a uniform methane-oxygen mixture containing excess oxygen. It is apparent that at 475° C. only about 0.1% of the methane is burned on passage over the catalyst, yet at this temperature hydrogen-oxygen and carbon monoxide-oxygen mixtures were found to burn rapidly and completely on the catalyst. Consequently, the preliminary data collected with these binary mixtures strongly indicate the possibility of a successful low-pressure fractional combustion on a platinum catalyst. That such fractionation does occur satisfactorily even for mixtures of all the combustible components is proved by the outcome of control analyses.

Table I. Tests of Synthetic Mixtures

Analysis No.	Total Volume of Sample *Cc. N.T.P*		H_2 %	CO %	CH_4 %
1	1.104	Given	55.7	28.15	16.15
		Found	55.7	28.3	16.0
2	1.031	Given	58.3	31.1	10.6
		Found	58.0	31.4	10.6
3	0.926	Given	64.45	30.1	5.5
		Found	64.3	30.3	5.4
4	1.237	Given	79.3	17.3	3.5
		Found	79.1	17.5	3.45
5	1.258	Given	52.9	43.3	3.8
		Found	52.9	43.3	3.9

CONTROL ANALYSES

In preparation for the control trials, several samples of pure gases were prepared.

Hydrogen and oxygen were generated in an all-glass cell, by electrolysis of 10% sulfuric acid between platinized platinum electrodes, and purified in identical trains by successive passage over fused potassium hydroxide, hot platinized asbestos, fused potassium hydroxide, and phosphorus pentoxide. The hydrogen so prepared assayed 100% pure when burned with excess oxygen; and the oxygen, when freshly prepared, assayed 100% pure when burned with excess hydrogen.

Despite the original high purity of the oxygen, it was found to contain small but appreciable quantities of volatile, partially oxygenated organic compounds after standing for some months in the storage bulb. The source of this material probably lies in the vaseline-rubber (Ramsay) grease originally used to lubricate the bulbs' stopcocks. Although it has been known for some time that oxygen attacks such grease (*3*), the formation of volatile reaction products does not appear to have been previously noted. Considerably better though not perfect preservation was found when the Ramsay grease was replaced with Apiezon M. Analytical aberrations due to the progressive contamination of the oxygen may be avoided by always drawing the oxygen into the analytical train through a liquid air trap packed with glass wool; or by preparing a fresh supply of oxygen about once a month.

Carbon monoxide was generated by the action of hot 85% phosphoric acid on 85% formic acid (*8*). The gas was purified by passage through a sodium hydroxide scrubber and over fused potassium hydroxide and phosphorus pentoxide. The final purity, as assayed by combustion with excess oxygen, was 99.9%. The trace of impurity may have been due to slightly incomplete removal of dissolved air in the formic acid.

Methane was prepared by the cautious pyrolysis of an equivalent mixture of sodium acetate and sodium hydroxide. This crude gas was purified by successive passage through a dust trap, a dry ice trap (for the removal of water vapor), a packed dry ice trap containing a good grade of coconut charcoal previously outgassed at 500° C. (for the removal of the bulk of the ethane and any other materials of low volatility), and thence into a liquid air trap. There followed ten bulb-to-bulb fractional distillations in which large fore and after fractions were discarded. The best fraction finally collected assayed 100% pure on the basis of the volume contraction consequent upon combustion with excess oxygen, and also on the basis of the carbon dioxide produced in such combustion.

Several synthetic test mixtures were made up from the pure gas samples and used to test the satisfactory operation of the apparatus as a whole, and the validity of the fractional combustion in particular. The results obtained, as shown in Table I, were gratifying in both respects.

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It is a pleasure to acknowledge the continued advice and assistance of Gregory P. Baxter in the conduct of this research.

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Determination of Nicotine in the Air

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A method for detemining nicotine in the air, existing either in the form of tobacco dust or as free vapor, has been outlined. The method consists of collecting the dust or vapor by means of an impinger, freeing the nicotine (in the case of dust) by alkalizing, developing a characteristic color with β-naphthylamine and cyanogen bromide in the presence of acetate, and suitably measuring the intensity of the color so produced. Optimum conditions of pH, temperature, time of development, concentration, and volume of reagents were determined. Data are also given on the extent of potential interfering compounds. A minimum concentration of 0.25 microgram of nicotine per milliliter of solution can be determined by the method outlined with a cell depth of 2 cm.

A SEARCH of the literature reveals the absence of any satisfactory method for the determination of nicotine in the air. In order properly to evaluate either existing or potential health hazards in industrial establishments, where workers are exposed to either nicotine vapors or tobacco dust, this determination is necessary. Moskalev (*13*) has published a method which involves a differential titration using a mixture of indicators, preceded by lengthy removal of interfering substances and steam-distillation. When dealing with small quantities of either nicotine or dust and with numerous samples—conditions usually encountered in industrial hygiene investigations—the need for a more satisfactory method of determination is obvious.

Nicotine produces a colorimetric reaction with cyanogen bromide in the presence of an aromatic amine. König (*7*) first observed the reaction, which has since been utilized by Barta and Marschek (*3*) and by Markwood (*11*) for the determination of nicotine in tobacco leaf. It was felt that the method as developed by Markwood (*9, 10*) held promise for industrial hygiene work, and with some modifications could be made to yield satisfactory results.

Nicotine may exist in the air in the form of the vapor itself, or as the chief alkaloid of tobacco dust. In either case, it can be satisfactorily collected by the impinger. This device has been described by Bloomfield and DallaValle (*4*), Jacobs (*6*), and others. In its use by the authors for nicotine, distilled water was used as the collecting liquid.

REAGENTS AND APPARATUS

Impinger. Standard Pyrex all-glass graduated model as described by DallaValle (*5*) and sold commercially by laboratory supply houses. A source of suction, with a suitable flow-measuring device, to operate the impinger at a rate of flow of 1 cubic foot per minute is needed.

Centrifuge. Any commercial model on which 15-ml. tubes can be used and which can be operated at 3000 r.p.m. is satisfactory.

Spectrophotometer (or photoelectric colorimeter). Any commercial model on which the measurement can be satisfactorily made at 490 mμ with necessary cells (or tubes) and other accessories. In this investigation an Evelyn photoelectric colorimeter (Rubicon Co., Philadelphia, Pa.) was used for all readings except the S-T data, which were obtained on a Coleman spectrophotometer, Model 11.

Centrifuge Tubes, 15-ml. Pyrex, graduated in 0.1 ml.

Chemical Glassware. Graduated pipets, 1-, 5-, 10-ml. sizes, all graduated in 0.1 ml.; volumetric flasks and reagent bottles.

Microburet.

Cyanogen Bromide. Six grams of reagent grade cyanogen bromide (Eastman No. 919) dissolved in each 100 ml. of 95% (redistilled) ethyl alcohol.

Caution. The vapors of cyanogen bromide are extremely irritating and toxic and should not be inhaled. The solid reagent readily vaporizes at room temperature. It should therefore be thoroughly cooled in the refrigerator before being dissolved, and the weighing and dissolving should be done under an exhaust hood. The solution keeps well in a dark bottle at room temperature, but for use it is desirable that it be cold. It is therefore recommended that it be kept in the refrigerator. When so stored, it keeps almost indefinitely.

β-Naphthylamine. Reagent grade β-naphthylamine (0.6 gram) dissolved in each 100 ml. of 95% (redistilled) ethyl alcohol. The solution should be stored in a dark bottle and kept in the refrigerator to ensure its being at a constant cold temperature prior to use.

Sodium Hydroxide, 30% solution. Thirty grams of sodium hydroxide per 100 ml. of distilled water.

Acetic Acid. Two aqueous solutions: 1 to 20 and 1 to 2000, made by diluting glacial acetic acid.

Alcoholic Potassium Acetate. Two grams of the salt dissolved in 100 ml. of 95% (redistilled) ethyl alcohol. This solution should be kept in the refrigerator to ensure its being at a constant cold temperature prior to use.

Phenolphthalein Indicator. Usual 0.04% alcoholic solution.

Standard Nicotine. An accurately weighed portion (20 to 25 mg.) of reagent grade nicotine (Eastman No. 1242) is sealed into a small thin-walled glass bulb. This is broken under water into a 50-ml. glass-stoppered flask, the volume of water being equal in milliliters to the weight of nicotine in milligrams. Thus, 1 ml. of this solution contains 1 mg. of nicotine. The required volume of water is accurately added from a graduated pipet or buret, with the last few drops rinsing the stirring rod used for breaking the bulb. Ten milliliters of this solution are made up to 500 ml. with distilled water in a 500-ml. glass-stoppered volumetric flask. This final solution contains 20 micrograms of nicotine per milliliter and is used for preparing the standards. Both solutions will keep for some time (at least 2 months) in the dark without any noticeable depreciation in strength.

Distilled Water (adjusted pH). For making up to volume the standards used in preparing the calibration curve, distilled

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water should be neutralized (with potassium hydroxide and acetic acid) just to the disappearance of the phenolphthalein end point, thus ensuring pH of the standard solutions within the proper range.

PROCEDURE

The contaminated air is drawn through the impinger in the usual manner at a rate of 1 cubic foot per minute. The volume of air sampled should be such that the total quantity of nicotine collected is at least 50 micrograms. If protected from light, the field samples can be kept for several days without any noticeable deterioration in nicotine content.

Sufficient distilled water is added to the impinger to bring the total volume to the 100-ml. mark. After thorough shaking, a 10 to 11-ml. aliquot is removed to a graduated (15-ml.) centrifuge tube. The exact volume of the aliquot is noted, 0.1 ml. of 30% sodium hydroxide is added, and the tube is stoppered and occasionally shaken during a 10- to 15-minute period. The alkali releases free nicotine from the tobacco dust. (If free nicotine vapor is being determined, this step can be eliminated. The solution should, however, be carefully neutralized and centrifuged as described below.) At the end of that time, 2 drops of phenolphthalein indicator are added and the solution is carefully neutralized with acetic acid to the disappearance of any pink color. The neutralization is accomplished with the 1 to 20 solution until the end point is approached and then carefully completed with the 1 to 2000 solution, using a small-bore pipet. An excess of acid must be avoided. The volume is read accurately to the nearest 0.1 ml. The tube is then centrifuged for at least 20 minutes at approximately 3000 r.p.m. At the end of this time all the suspended dust should be deposited in the bottom of the tube. If not, additional centrifuging is necessary.

Exactly 10 ml. are carefully pipetted from the centrifuge tube and transferred to the colorimeter tube. The volume in the centrifuge tube should be at least 11 ml. for ease of removal of the aliquot. Two milliliters of the alcoholic potassium acetate solution and 4 ml. of the β-naphthylamine reagent are added. The tube is shaken to ensure thorough mixing, the transmission measured (to correct for any color resulting from the tobacco as described below), and 1 ml. of the cyanogen bromide solution added. The tube is again thoroughly shaken and then placed in the dark for development of the color for 30 minutes at 22° to 28° C. In order to minimize temperature variations and to obtain uniform results, the potassium acetate, β-naphthylamine, and cyanogen bromide reagents should be cooled to some constant temperature, say 5° C., and used at this temperature. The cooling is also desirable to reduce the heat of dilution which results upon mixing. The light transmission is then measured on a photoelectric colorimeter or spectrophotometer at 490 mμ and the nicotine determined by referring the reading obtained to a previously prepared calibration curve of micrograms of nicotine *vs.* galvanometer readings. A blank tube, containing 10 ml. of distilled water and the same volume of all the reagents as used in the unknown, is used to obtain the 100% transmission reading.

The total quantity of nicotine in the impinger is calculated from the formula:

$$\gamma_T = \frac{10\gamma V_2}{V_1}$$

where γ_T = micrograms of nicotine in impinger
γ = micrograms of nicotine in 10-ml. aliquot as read from curve
V_1 = volume (ml.) of aliquot removed from impinger for analysis
V_2 = volume (ml.) after final neutralization

If the colorimeter or spectrophotometer employed utilizes a transmission cell inadequate in size to accommodate mixing the above volumes of sample and reagents, the solutions can be mixed and developed in suitable volumetric flasks and then transferred to the instrument cell for transmission measurement.

Preparation of Calibration Curve. The curve against which the samples are referred for determination of nicotine content is prepared in the customary manner by adding to four colorimeter tubes 0.25, 0.5, 1.0, and 2.0 ml., respectively, of the standard nicotine solution. This corresponds to nicotine contents of 5, 10, 20, and 40 micrograms. A microburet should be used for the measurement. A sufficient quantity of the distilled water, whose pH has been adjusted as described above, is added to make up each to a total of 10 ml. The reagents and the development of color are identical to those already described for the samples. The transmission readings are plotted on the logarithmic axis *vs.* the nicotine content, in micrograms, on the arithmetic axis of semilogarithmic graph paper. A straight line should result.

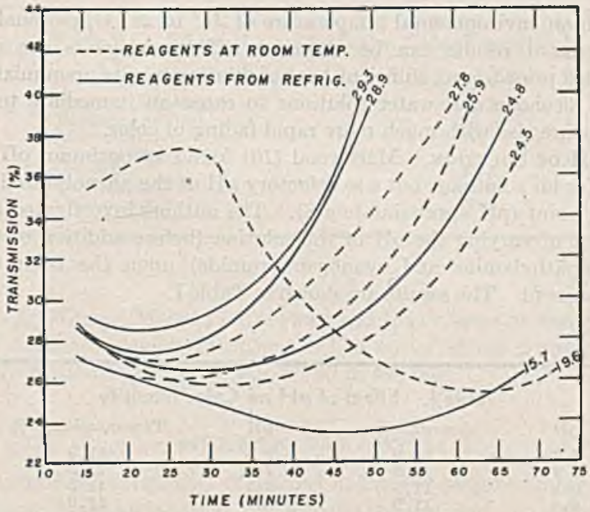

Figure 1. Time and Temperature Effects on Color Intensity

VARIABLES DETERMINING COLOR DEVELOPMENT

Markwood (*10*) has investigated thoroughly the quantitative characteristics of this color reaction, and his investigations have formed the basis of the authors' work. In several cases, however, they have been able to obtain increased sensitivity and more consistent results by changing both the concentration and the order of the addition of some or all of the reagents. The results of their investigations into the several variables and the determination of the optimum conditions entering into the chromogen formation, are described below.

Temperature and Development Time. The effect of temperature and time of development was investigated by using a series of eight solutions, all containing 40 micrograms of nicotine in 10 ml. of distilled water, and all developed as outlined in the Procedure. The environmental temperature at which development occurred was varied by using either small water baths or heated cabinets. The actual temperature of the solution itself is determined not only by the environmental temperature but by the temperature of the reagents. Accordingly, four of the solutions were developed with reagents taken directly from a refrigerator kept at a temperature of 5° C., while the remaining four were developed with reagents at room temperature (28° C.). The temperature of each solution was checked at 15-minute intervals as the color development proceeded and the mean of these values is given on each curve in Figure 1. The transmission was also read at 15-minute intervals, and the results are shown graphically in the figure, with time of development plotted against transmission readings (%).

The curve corresponding to the temperature of 15.7° C. was obtained by development in the refrigerator (5° C.). The solution became turbid, owing to salt crystallization at this temperature. With the exception of this curve, the remaining data indicate that the time required for maximum intensity of color increases markedly as the temperature becomes lower and vice versa, and that the intensity is more greatly affected by temperature changes as the time of development proceeds. This is especially true after 30 minutes. For this reason, because the point of maximum intensity approximates 25 to 30 minutes, depending upon the temperature, and finally because the interference from nornicotine is relatively small at the end of this time, 30 minutes was selected as the proper time of development. By keeping the reagents at a constant temperature in the refrigerator, less variation results in the intensity readings, and with an environmental temperature of 22° to 28° C. reasonably consistent results can be obtained. If the reagents are not cooled prior to use, sufficient heat of dilution results upon mixing the alcoholic and water solutions to cause an immediate temperature rise with much more rapid fading of color.

pH OF SOLUTION. Markwood (*10*) found an optimum pH of 10 for his solutions, but a satisfactory pH at the phenolphthalein end point (pH approximately 8). The authors investigated the effect of varying the pH of the solution (before addition of the β-naphthylamine and cyanogen bromide) upon the color development. The results are shown in Table I.

Table I. Effect of pH on Color Intensity

pH	Transmission	pH	Transmission, %
5.7	14.0	7.4	11.3
5.7	14.3	7.4	11.3
6.8	11.3	9.1	11.3
6.8	11.0	9.1	11.0

These data were procured prior to the establishment of the final procedure, and differ from it only in that 5 ml. of β-naphthylamine instead of the finally adopted 4 ml. were used. All the samples contained 80 micrograms of nicotine in 10 ml. of distilled water. Following the addition of the acetate solution, the pH was varied by using a few drops of very dilute potassium hydroxide and acetic acid and measuring the pH with a glass electrode potentiometer. The color was developed with β-naphthylamine and cyanogen bromide and read in the usual manner. The results indicate no measurable difference in color intensity over the range 6.8 to 9.1 and satisfactory neutralization to the phenolphthalein end point. An excess of acid, however, decreases the intensity of color.

ACETATE CONCENTRATION. Markwood (*10*) reported that the presence of acetate markedly intensified the color, while the presence of either chloride or sulfate decreased it. These same facts were confirmed by the authors. In some preliminary experiments they observed that tartrate ion will also intensify the color, but to a lesser extent than acetate. They observed no measurable difference in results when using either sodium or potassium acetate, but adopted the potassium salt because of its greater solubility in alcohol. The need for the alcoholic solution is discussed below.

The effect of varying the acetate concentration on color intensity is shown in Table II. All samples contained 40 micrograms of nicotine in 10 ml. of distilled water, and 2 ml. of alcoholic potassium acetate of the indicated concentration. They were developed as outlined in the Procedure.

Table II. Effect of Acetate Concentration on Color Intensity

Sample No.	Concentration of $KC_2H_3O_2$ Used	$KC_2H_3O_2$ Concentration in Final Volume	Transmission
	%	G./100 ml.	%
1	0	0	45.0
2	0.5	0.06	39.0
3	1.0	0.12	31.0
4	2.0	0.24	27.0
5	4.0	0.47	31.0

The maximum intensity occurring at or near a concentration of 0.24 gram per 100 ml. agrees with Markwood's value (*10*) (sodium acetate) of 0.2 gram per 100 ml. Additional determinations in the 0.25 region might shift the value somewhat either way, but the small difference in intensity observed between the 0.12 and 0.47 values did not warrant these. Hence 2 ml. of 2% solution were adopted as the final acetate concentration to be used.

SEQUENCE OF ADDITION OF REAGENTS. In the initial phase of this investigation, the cyanogen bromide solution was added prior to the β-naphthylamine, but it was impossible to obtain consistent results. The reason for this inconsistency could not be determined until quite by chance the order of adding these reagents was reversed; reproducible results could then be obtained readily. The time elapsing between the addition of the cyanogen bromide and β-naphthylamine solutions, when this was the order of addition, was an inverse function of the color intensity obtained, the greatest intensity being obtained with the least elapsed time between the additions. No quantitative study was made of this, inasmuch as it was found that the difficulty could be overcome by merely reversing the order in which the two reagents were added to the solution. Sometime after observing this, the authors' attention was called to the work of Lamb (*8*) with nicotinic acid in which he found, when using cyanogen bromide and aniline as reagents, that consistent results were obtained only if the aniline was added prior to the cyanogen bromide. His results differ from the authors', however, in that he found the color intensity increasing as the elapsed time increased, when adding the cyanogen bromide before the aniline.

It is important, therefore, that in all cases the β-naphthylamine solution be added prior to the cyanogen bromide.

Table III. Effect of β-Naphthylamine and Cyanogen Bromide Concentrations on Color Intensity

	Transmission, Per Cent					
	0.3% β-naphthylamine		0.6% β-naphthylamine		0.9% β-naphthylamine	
CNBr, Ml.	4 ml.	5 ml.	4 ml.	5 ml.	4 ml.	5 ml.
1 (1%)	50.0	50.0	53.5	60.0	Turbid	64.0
1 (4%)	30.8	33.3	28.8	31.0	Turbid	36.3
1 (6%)	31.3	31.3	25.0	28.3	Turbid	30.8
1 (8%)	36.5	34.5	30.0	32.3	Turbid	32.0

CONCENTRATIONS AND VOLUMES OF CYANOGEN BROMIDE AND β-NAPHTHYLAMINE. The concentrations of both cyanogen bromide and β-naphthylamine were believed to influence the intensity of color. Likewise, the final volume of solution determines inversely the concentration of chromogen. The use of a 10-ml. aliquot of sample appeared to be most logical from the standpoint of representative sampling, sensitivity, and suitability for centrifuge tubes. A minimum volume of aliquot was desired, inasmuch as additional determinations were frequently required on the same impinger sample. Accordingly the effects of varying the concentrations of both cyanogen bromide and β-naphthylamine, and the volume of the latter, were studied, with the results shown in Table III.

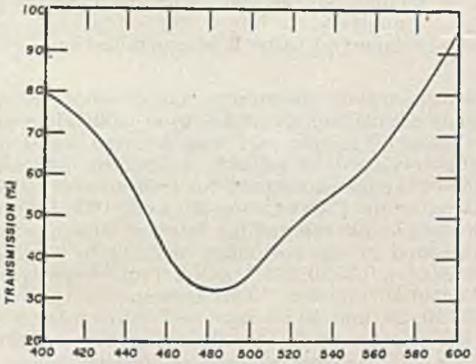

Figure 2. Spectral Transmission Curve for Nicotine

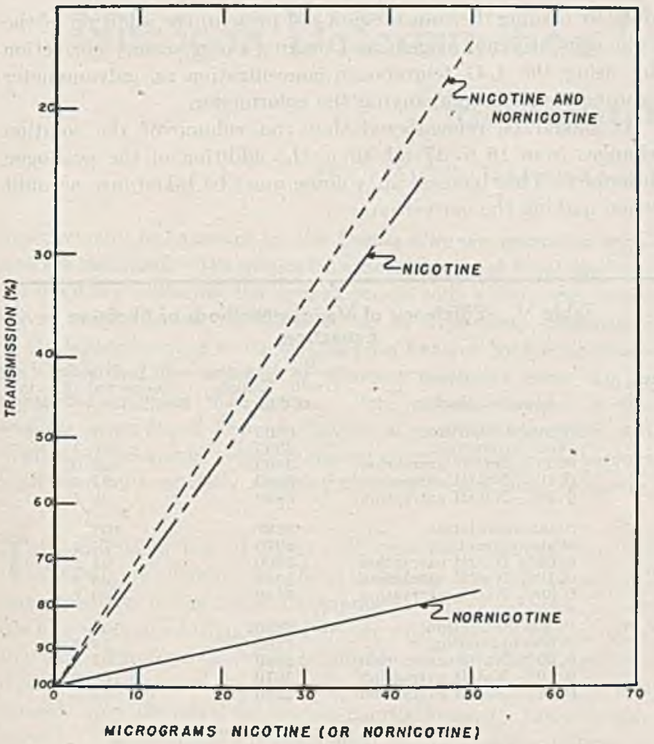

Figure 3. Interference of Nornicotine

All the previously mentioned solutions contained 40 micrograms of nicotine in 10 ml. of distilled water (the pH of which had been adjusted as described under Procedure to the phenolphthalein end point), 1 ml. of alcoholic potassium acetate reagent, and the indicated volumes of β-naphthylamine and cyanogen bromide. In all cases the percentage concentration refers to the weight of the amine in grams, equal to the indicated percentage, dissolved in 100 ml. of 95% ethyl alcohol. The colors were developed in the usual manner as outlined in the Procedure.

An inspection of Table III reveals that the maximum intensity of color results from the use of 1 ml. of 6% cyanogen bromide and 4 ml. of 0.6% β-naphthylamine with the volume of aliquot used (10 ml.). Markwood (*9, 10*) used a cyanogen bromide solution approximating 0.8% and a β-naphthylamine solution of 0.2%. The data in Table III show the concentrations recommended by the authors to be considerably better for obtaining increased intensity. Minimum nicotine concentrations of 0.25 microgram per ml. can be estimated with a light transmission path of 2 cm. ($^7/_8$ inch test tube). This is believed to be the most sensitive means yet developed for determining nicotine. Markwood's (*9*) minimum value, although numerically the same as the authors', was attained with a much greater thickness (10 cm.) of liquid layer.

In the initial phases of this investigation, it was observed that turbidity of the samples depended not only upon the reagent concentrations but upon the final alcoholic concentration and final volume of the solution, with increasing alcoholic concentrations and total volumes decreasing the turbidity. Accordingly, in order to keep the final volume to a minimum and to prevent turbidity, alcoholic rather than aqueous reagents were used. Even with the volumes of reagents finally standardized upon, turbidity will result upon several hours' standing. The 4-ml. β-naphthylamine and the 2-ml. potassium acetate volumes are the minimum which can be used to prevent turbidity.

SPECTRAL TRANSMISSION DATA FOR NICOTINE

The usual type of S-T (spectral wave length *vs.* per cent transmission) curve was determined, with the results shown in Figure 2. A Coleman Model 11 Universal spectrophotometer was used for making the determinations. The curve shows a minimal transmission at a wave length of 480 to 490 mμ.

Table IV. Effect of Insecticides on Color Intensity

Insecticide	% Transmission
None (nicotine only)	28.3
Bordeaux mixture	28.5
Lime-sulfur	27.5
Lead arsenate	28.0
Cryolite	27.5
Paris green	28.5
Calcium arsenate	27.8

INTERFERING SUBSTANCES

Interfering substances of interest in this investigation were the various insecticides used on tobacco plants and nornicotine. The latter compound is an alkaloid—similar in many respects to nicotine—found in varying degrees in tobacco. Markwood (*11, 12*) has reported it to be the predominating alkaloid in certain types of tobacco. Accordingly, the extent to which it and the various insecticides interfered in the method of analysis was determined.

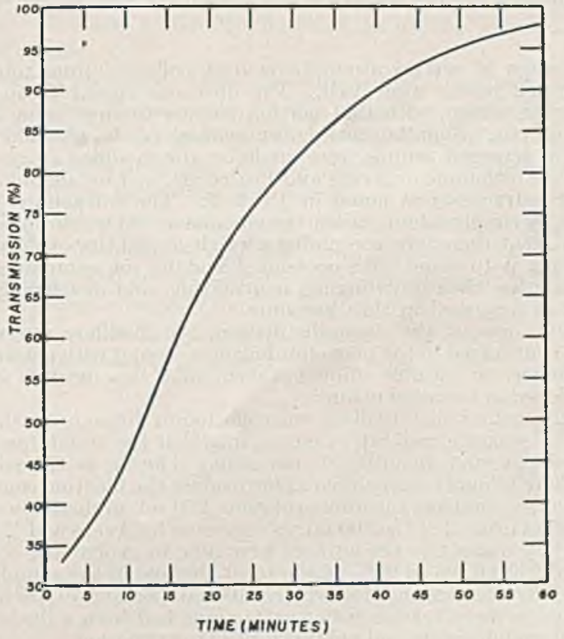

Figure 4. Effect of Developmental Time on Nornicotine Color

The insecticides used were lead arsenate, calcium arsenate, cryolite (synthetic), lime-sulfur, Paris green, and Bordeaux mixture. All were of the commercial grade normally sold for insecticidal uses. The nornicotine was from a sample of the pure alkaloid obtained from the Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, and was predominantly the *l*-stereoisomer. Except for the varying times as noted, all results were obtained by developing the solutions as outlined in the Procedure. In the case of nornicotine, transmission curves of per cent transmission *vs.* concentration (micrograms) were determined for solutions containing only nornicotine, in amounts from 5 to 50 micrograms, and for solutions containing both nicotine and nornicotine, each in amounts from 5 to 50 micrograms. The results are shown in Figure 3 in comparison with a similar curve for solutions containing only nicotine. All these results were obtained by reading the transmissions at the end of 30 minutes' development time.

The nornicotine color fades very rapidly. This is shown in the curve of Figure 4 where the transmission *vs.* time of development of a solution containing 40 micrograms of nornicotine is plotted.

This curve shows clearly that by choosing a proper time of development, the interference produced by nornicotine can be almost completely eliminated. By reading the transmission at the end of 30 minutes' development (the optimum time for nicotine), the results will be approximately 10 to 12% high when the two alkaloids are present in equal amounts (see Figure 3).

The results of Table IV are the average of duplicate samples, all developed for 30 minutes in the usual manner. All samples contained 40 micrograms of the indicated insecticide and 40 micrograms of nicotine.

The results show no significant difference in any of the solutions. They are similar to those obtained by Markwood in his insecticide method, except that he found a significant interference resulting from lime-sulfur.

DISCUSSION AND NOTES

Extraction of Nicotine. The standard A.O.A.C. method (*1*) of determining nicotine in tobacco leaf involves a steam-distillation of the nicotine from alkaline solution, followed by gravimetric determination with silicotungstic acid. In order to dispense with the steam-distillation procedure, the possibility of extracting the nicotine from tobacco dust by merely alkalizing the aqueous suspensions was investigated.

Samples of settled atmospheric dust collected from tobacco stemming plants were used. The dust was sieved through a 150-mesh screen, with that portion passing through being used for analysis. Simultaneous determinations of the nicotine content of screened sample were made by the modified steam-distillation technique of Avens and Pearce (*2*), and by alkaline and water extractions as noted in Table V. The extractions were made by simply adding either the alkaline or water solutions to a 15-ml. centrifuge tube containing a weighed quantity of the dust, allowing it to stand with occasional shaking for approximately 10 minutes, then centrifuging, neutralizing, and developing the color as described in the Procedure.

In the case of the steam-distillation, the distillate was carefully neutralized to the phenolphthalein end point with potassium hydroxide, a suitable aliquot taken, and the nicotine color developed in the usual manner.

Inasmuch as the distillate was collected in dilute hydrochloric acid, a separate calibration curve, in which the standards contained the same quantity of potassium chloride as the steam-distillate aliquots, was prepared for reading the nicotine content. To ensure complete nicotine evolution, 250 ml. of distillate were collected instead of the 100 ml. as suggested by Avens and Pearce (*2*). By doing this the authors were able to evolve and collect in the 250 ml. 98 to 99% of the total nicotine in the sample, as shown by the analysis of successive 100-ml. portions of distillate. The water used for the water extractions had been adjusted to the phenolphthalein end point prior to the extraction.

These results indicate that the alkaline extraction method is approximately 95% as efficient as the steam-distillation procedure on atmospheric tobacco dust. This is certainly satisfactory for field determination.

Volatilization of Nicotine by Aeration. To determine whether any appreciable loss of nicotine occurs by volatilization by continuous bubbling of air through the solution, such as occurs in the impinger, four impingers were made up with an aqueous nicotine solution (1 mg. of nicotine in 100 ml. of water in each), and room air was drawn through each for 30 minutes at a rate of 1 cubic foot per minute. The average loss of nicotine of all four was 1.5%.

Correction for Color from Tobacco. If the tobacco dust concentration is appreciable, a yellow to light brown coloration will result with the alkaline extraction. A correction for this must be made before developing the nicotine color. This can be done by reading the transmission just prior to the addition of the cyanogen bromide reagent and making the necessary correction by using the L-G (chromogen concentration *vs.* galvanometer reading) table accompanying the colorimeter.

It should be remembered that the volume of the solution changes from 16 to 17 ml. upon the addition of the cyanogen bromide. This increase in volume must be taken into account when making the correction.

Table V. Efficiency of Various Methods of Nicotine Extraction

Sample No.	Method	γ Nicotine per Gram Sample of Dust	% Nicotine Recovered (Steam Distillation = 100%)
1	Steam distillation	3695	100
	Water extraction	3005	81.3
	0.05% NaOH extraction	3400	92.0
	0.10% NaOH extraction	3380	91.5
	0.30% NaOH extraction	3540	95.7
2	Steam distillation	3787	100
	Water extraction	2970	78.4
	0.05% NaOH extraction	3600	95.2
	0.10% NaOH extraction	3420	90.2
	0.30% NaOH extraction	3420	90.2
3	Steam distillation	2890	100
	Water extraction	2200	76.3
	0.05% NaOH extraction	2820	97.5
	0.10% NaOH extraction	3010	104.0
	0.30% NaOH extraction	2880	99.6

Average % nicotine recovery

Water extraction	78.7
0.05% NaOH	94.9
0.10% NaOH	95.2
0.30% NaOH	95.2

ACKNOWLEDGMENTS

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Nitrogen Determination by the Micro-Dumas Method

Improvements in Apparatus

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Improvements in apparatus for the Dumas nitrogen microdetermination are described. The original microazotometer of Pregl has been modified by replacing the top stopcock with a ball and socket valve, which requires no lubricant for its operation. Elimination of the tapered surface of contact prevents freezing by the potassium hydroxide and the absence of lubricant precludes errors due to contamination from that source. Pure carbon dioxide for the analysis is produced from dry ice in a modified Hershberg and Wellwood generator. Precise control over combustion of sample is effected by a specially designed chimney for the movable burner.

THE extensive use of Pregl's (*5*) micro-Dumas method for determining nitrogen in this laboratory has led to several improvements in the original equipment. These changes include use of a specially designed azotometer with ball and socket valve to replace the stopcock-type azotometer, a carbon dioxide generator utilizing solid carbon dioxide as the source of gas, and a special lamp chimney for use in connection with the movable burner. For heating the permanent filling of the combustion tube, a standard electric microfurnace has been found desirable. A photograph of the assembled equipment is shown in Figure 1.

MICROAZOTOMETER

The standard Pregl-type azotometer (*6*) with stopcock at the top of the graduated column introduces errors in the analysis for the following reasons:

> Lubricant from the stopcock gets down into the graduated column and sticks to the walls, causing incorrect volume readings. This is due not only to the bulk of the lubricant itself but also to the lubricant's preventing free drainage of the potassium hydroxide from the walls of the column.
>
> The potassium hydroxide attacks the walls of the stopcock, causing it to stick and eventually to leak.

With the exception of methods by which the quantity of nitrogen is determined indirectly by weighing displaced mercury (*1*) or water (*2*), few major changes have been made in the original azotometer introduced by Pregl (*5*). Milner and Sherman (*4*) describe an azotometer designed without a stopcock at the top of the graduated column. It consists of a cup arrangement attached to the top of the graduated column with a glass rod ground into the azotometer tube. Ceresin is applied to the ground surface to prevent sticking. This apparatus, although superior to the original design of Pregl, still has the disadvantages inherent in those requiring wax or grease on the ground joint to prevent freezing.

By replacing the top stopcock of the Pregl azotometer with a vertical ball and socket valve, a nitrometer has been devised which eliminates all the disadvantages of the stopcock-type closure and operates without the use of wax or lubricant other than the potassium hydroxide itself.

The spherical surface of contact favors separation, and freezing by the alkali does not take place, owing to the absence of the wedging action inherent in tapered type closures. The ball and socket valve, which is completely immersed in the alkali, allows the entire surface of contact to be wet evenly with the alkali and channeling is prevented. This is not the case with the stopcock-type arrangement, since the plug of the latter is wet by the alkali only along that portion of its surface which traverses the openings to the graduated column below and the funnel above. The corrosion thus localized in that section causes leakage after the azotometer has been in use for an extended period of time.

The error in volume caused by corrosion of a ball and socket closure would, theoretically, be less than that of the vertical tapered stopper arrangement of Milner and Sherman; in the case of the spherical joint, the rest position of the ball would change only to the extent of the depth of corrosion, since the effective surface of contact is practically horizontal, whereas with the tapered stopper arrangement the surface of contact is almost vertical and a small amount of corrosion would cause a relatively large change in the rest position of the stopper.

The closed bulb arrangement above the opening at the top of the graduated column instead of the open funnel (*6*) or cup

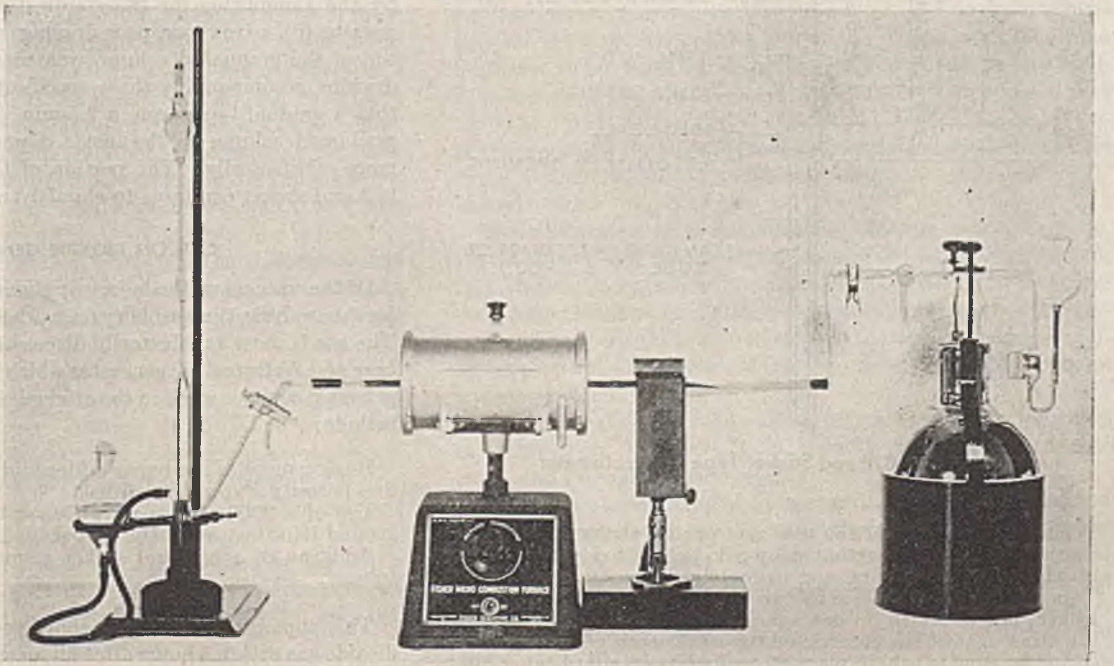

Figure 1. Assembled Equipment

Table I. Reliability of Azotometer after Extended Service, as Shown by Analysis of Pure Acetanilide

Period of Service of Azotometer at Time of Test	Nitrogen Content, % Found		Calculated
Initial	10.38	10.43	10.36
Ten months later	10.41	10.37	10.36

(*4*) eliminates spilling or dust contamination of the potassium hydroxide.

Pyrex has been used in fabricating the azotometer, since it has shown much greater resistance to the action of alkali than soda glass.

Table I gives results of the analysis of a sample of pure acetanilide carried out when the azotometer was initially put into service and after approximately 10 months of continuous use which the instrument had had at the time this paper was submitted for publication. The close agreement of these values shows that the instrument does not lose its reliability after extensive service. The azotometer also showed no measurable leakage when tested after the 10-month period of service. The author's experience with the conventional azotometer indicates the latter to have a much smaller average leakproof period of operation.

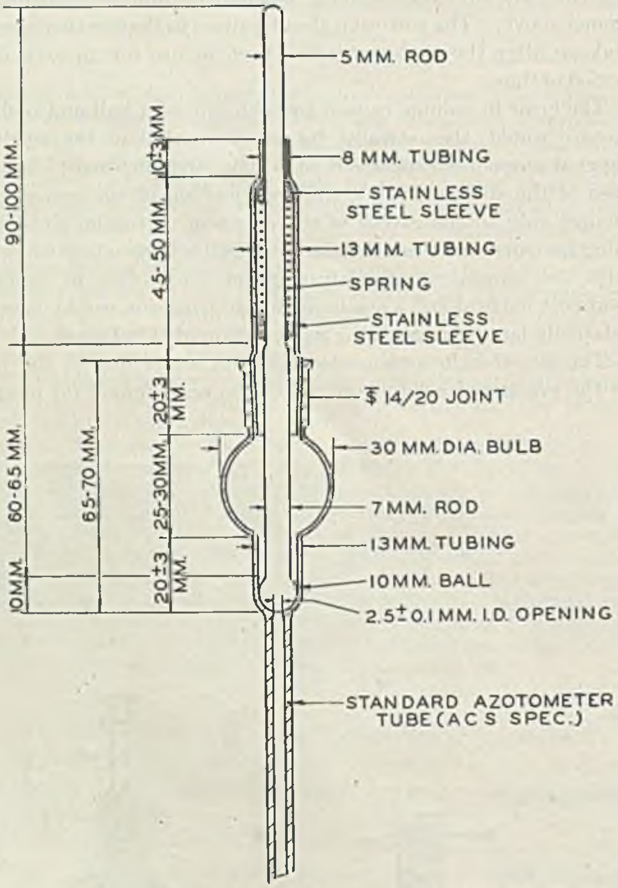

Figure 2. Ball and Socket Type of Azotometer

The upper section of the new azotometer, shown in Figure 2, consists of a plunger actuated by a loosely fitted spring of No. 21-gage music steel wire, approximately fifteen turns in length. This spring is held in place by two stainless steel sleeves of 5-mm. length, one of which presses against a shoulder on the plunger, the other against the constricted top of the spring housing. The spring housing is held in place by sealing its standard-taper joint into that of the azotometer proper with Krönig's cement. When necessary, the apparatus can easily be disassembled for cleaning, by simply reheating the cemented joint. The opening in the top of the graduated column is 2.4 to 2.6 mm. in diameter and tapers gradually to the inside diameter (3.3 to 3.6 mm.) of the graduated column.

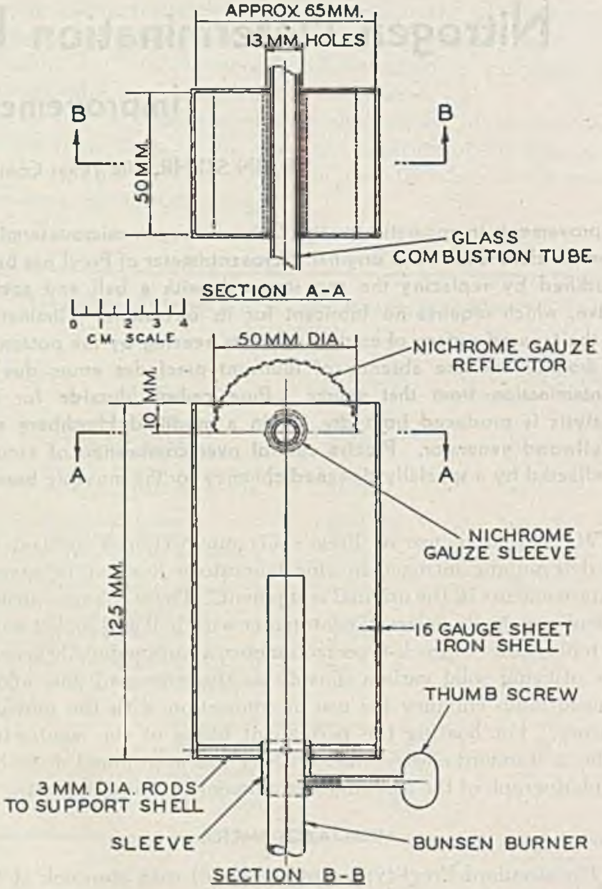

Figure 3. Movable Burner Chimney

When designing this apparatus, it was considered desirable to follow where possible the recommended specifications set forth by the Committee for Standardization of Microchemical Apparatus (*6*). However, poor drainage was experienced when the top of the graduated column was constructed as shown in the drawing accompanying these specifications. The author found that a gradual taper from a 2.5-mm. opening at the top of the graduated column to the inside diameter of this tube worked more satisfactorily. The portion of the azotometer below the ball and socket conforms to standard specifications (*6*).

CARBON DIOXIDE GENERATOR

Of the various methods for supplying pure carbon dioxide gas for the analysis, the use of dry ice has been found most convenient. The gas is most satisfactorily dispensed from a modified Hershberg and Wellwood (*3*) generator which is shown in Figure 1. The principal changes made in the original equipment of these authors include:

Replacement of the paper diffusion disk by a 30-mm. diameter fine porosity Pyrex fritted disk.

Use of a 2000-ml. capacity Dewar flask with standard-taper ground joint instead of the pint-size vacuum bottle.

Addition of a ball and socket connection to the combustion tube.

This apparatus furnishes a continuous stream of pure carbon dioxide gas within 5 hours after filling and lasts for approximately 10 days when a flask evacuated to 6 × 10^{-7} mm. of mercury is used.

CHIMNEY FOR MOVABLE BURNER

The conventional circular-type movable burner chimney does not give precise control of the combustion of sample in microanalysis because of fluctuations in the flame during heating. A simple unit for this purpose, which also acts as a support for the short Nichrome gauze sleeve and reflector, has been devised and found very effective for all types of microcombustions. The flame is entirely enclosed within the walls of a metal shell and only the portion of the combustion tube within those limits is subjected to the heating.

The construction of the apparatus is shown in Figure 3. It consists of a rectangular sheet-iron shell open at the top and bottom and attached to a Bunsen burner by means of a sleeve and set screw. The sleeve is fastened to the shell by four 3-mm. diameter rods welded to the lower center portion of each face of the shell and to the sleeve. Two holes are drilled on opposite sides of the shell near the top through which the combustion tube is inserted; the Nichrome gauze sleeve is placed around the combustion tube and between the two sides of the chimney. The heat reflector (a semicircular piece of Nichrome gauze, 55 mm. long and 50 mm. in diameter) is notched at the four corners for a distance of approximately 10 mm. in length and 2.5 mm. from the edges to fit into the top of the shell and above the combustion tube.

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Identification of Organic Bases by Means of the Optical Properties of Dilituates (Nitrobarbiturates)

Primary Aromatic Amines

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The dilituates of forty-three primary aromatic amines have been prepared and their optical and crystallographic properties recorded. The components of mixtures of isomeric amines may be recognized by a determination of the optical and crystallographic properties of the crystals of the dilituates prepared from the mixtures.

THE use of the crystallographic and optical properties of the dilituates has been suggested as a means of identification of organic bases by the authors in a previous paper (*1*), in which they reported the optical constants for the dilituates of some primary aliphatic amines. The present communication reports similar constants for the dilituates of primary aromatic amines.

The methods employed are similar to those used in the earlier work. In preparing the dilituate of a solid amine, the amine was dissolved in hydrochloric or acetic acid and an equivalent quantity of a hot aqueous solution of dilituric acid was added. The amine dilituate precipitated either immediately or on cooling. Equivalent quantities of dilituric acid and the amine are not important unless dilituric acid itself crystallizes out. If less than an equivalent quantity is added, the dilituate crystallizes out and the acetate or hydrochloride, being more soluble, remains in solution. Generally speaking, the primary amine dilituates are less soluble than dilituric acid and so the acid does not complicate the identification, even if added in excess.

The dilituates were recrystallized from water one or more times. The identity and purity of the salts were established by determination of the nitrogen content by the Kjeldahl method modified to include nitro compounds. The deviation of the percentages found from those calculated did not exceed 0.2 except for the following salts: *p*-bromoaniline, *p*-chloroaniline, and *m*-phenylenediamine, each 0.25; and *o*-nitroaniline, 0.31. Benzidine forms only the monodilituate, as indicated by the determination of the nitrogen content. The remaining diamino compounds all produce didilituates, even though the dilituric acid is added in less than equivalent quantities.

The optical data for the dilituates of forty-three primary aromatic amines are included in Table I. The usual orientation of the dilituates of *p*-aminophenol, benzidine, *m*-bromoaniline, 2,4-diaminophenol (both forms), 2,4-diaminotoluene, 2,6-dibromo-4-aminophenol, 2,5-dichloroaniline, α-naphthylamine (triclinic), *m*-nitroaniline (from water), *p*-nitroaniline, 3-nitro-4-chloroaniline, *o*-phenylenediamine, *m*-phenylenediamine, and *m*-toluidine does not present a true value for any principal index, but the values can be determined from crushed crystals. The usual orientation of the dilituates of *p*-aminodiethylaniline, *p*-aminodimethylaniline, 2-amino-5-hydroxytoluene, 2-amino-4-nitrophenol, *o*-aminophenol, *m*-aminophenol (both forms), 3-bromo-4-aminotoluene, *o*-bromoaniline, *p*-bromoaniline (rectangles), *o*-chloroaniline, *p*-iodoaniline, *o*-nitroaniline, and *o*-toluidine permits the determination of one index—β. The crystals of aniline dilituate (monoclinic) are so oriented that α can be observed. The crystals of the other dilituates examined are so oriented that the true values for two of the principal indices can be determined—α and β for all except *m*-chloroaniline and *m*-nitroaniline (from alcoholic solution) which show β and γ; and *o*-aminodiphenyl which shows α and γ.

The dilituates of *m*-aminophenol, aniline, *p*-bromoaniline, 2,4-diaminophenol, and α-naphthylamine exhibit polymorphism. In different preparations the relative proportions of the polymorphs varied, but both forms were always present. When *m*-nitroaniline is crystallized from ethanol the product possesses different properties than those of the compound crystallized from an aqueous solution.

The systems to which the various crystals belong are indicated in column 2 by the letters O, M, and T—orthorhombic, monoclinic, and triclinic, respectively.

The dilituates of many of the aromatic amines are so flattened that when suspended in a liquid nearly all crystals assume the same or nearly the same orientation. In Table II some optical and crystallographic values are recorded which were observed on the most frequently occurring orientations. The optical orientation designated as acute, obtuse, or optic normal indicates that a centered figure is observed in the usual position of the crystal. The term "inclined" indicates that the interference figure is not centered. Some crystals show slight variations in orientation, so that the values for the extinction angle and the refractive indices are slightly different on different crystals. Such values are recorded as variable. Many of the crystals present, in their usual orientations, refractive indices which cannot be satisfactorily determined within narrow limits. These indices are also reported as variable.

In Figures 1 to 4 are diagrams of the crystals showing front views as the crystals appear in their most frequently occurring orientations, side views, and in some cases top views. Side and top views were obtained by rolling the crystals in Canada balsam. Extinction angles were all measured between the long direction of the crystal in its particular orientation and the position of nearest extinction. Dotted lines indicate vibration directions and apparent refractive indices are recorded for those crystals which show constant values. An asterisk is used to indicate the higher refractive index in an orientation unless a value is given for it. Observed crystal angles (determined microscopically) which occur consistently are indicated at the corners of the diagrams. Diliturates of 2-amino-1,3-dimethylbenzene, 2-amino-1,4-dimethylbenzene, and β-naphthylamine exhibit two habits; hence two sets of drawings are presented for each of these compounds. Each of those diliturates showing polymorphism (mentioned above) also has two sets of drawings. The various properties recorded in the drawings identify the forms—e.g., one form of *m*-aminophenol has a 135° crystal angle, whereas the other form possesses a 112° angle.

Some of the amine diliturates, when crystallized from water, do not always form large enough or sufficiently well-defined crys-

Table I. Optical Properties of Some Primary Aromatic Amine Diliturates

Amine	System	Extinction Angle	Optic Sign	Refractive Indices Alpha	Beta	Gamma	Elongation	Dispersion
2-Aminocymene	O	Parallel	−	1.507	1.648	1.679	−	$v > \rho$
p-Aminodiethylaniline	M	22	−	1.455	1.659	1.744	±	$v > \rho$
p-Aminodimethylaniline	M	42	−	1.462	1.668	>1.785	+	$v > \rho$
2-Amino-1,3-dimethylbenzene	M	20	+	1.583	1.670	>1.785	−	$\rho > v$
2-Amino-1,4-dimethylbenzene	M	28	+	1.572	1.657	1.752	−	$\rho > v$
4-Amino-1,3-dimethylbenzene	O	Parallel	−	1.522	1.671	>1.785	−	$v > \rho$
5-Amino-1,3-dimethylbenzene	M	39	−	1.543	1.642	1.723	±	$\rho > v$
o-Aminodiphenyl	O	Parallel	−	1.461	1.768	>1.785	−	$\rho > v$
p-Aminodiphenyl	M	12	+	1.603	1.653	>1.785	−	$\rho > v$
2-Amino-5-hydroxytoluene	M	7	−	1.520	1.651	1.763	−	$v > \rho$
2-Amino-4-nitrophenol	M	16	+	1.672	1.722	>1.785	±	...
o-Aminophenol	M	29	+	1.618	1.673	>1.785	±	$\rho > v$
m-Aminophenol (135° angle)	T	26	−	1.501	1.689	>1.785	±	$v > \rho$
(112° angle)	M	33	−	1.480	1.750	>1.785	±	$v > \rho$
p-Aminophenol	T	22	−	1.508	1.715	>1.785	−	$v > \rho$
Aniline	M	16	−	1.535	1.659	1.772	−	$v > \rho$
	O	Parallel	−	1.447	1.738	>1.785	−	$v > \rho$
Benzidine	T	37	+	1.571	1.684	>1.785	−	$\rho > v$
3-Bromo-4-aminotoluene	M	19	+	1.578	1.679	>1.785	−	$\rho > v$
o-Bromoaniline	M	35	+	1.580	1.647	1.788	−	$\rho > v$
m-Bromoaniline	M	16	−	1.525	1.708	1.735	±	$v > \rho$
p-Bromoaniline								
Rectangular	M	18	+	1.456	1.749	>1.785	−	$\rho > v$
Diamond-shaped	M	21	+	1.597	1.688	>1.785	±	$\rho > v$
o-Chloroaniline	M	34	+	1.532	1.657	1.789	−	$\rho > v$
m-Chloroaniline	O	Parallel	−	1.554	1.777	>1.785	+	$\rho > v$
p-Chloroaniline	M	22	+	1.575	1.670	>1.785	±	$\rho > v$
2,4-Diaminophenol								
Tabular	T	43	−	1.498	1.695	>1.785	−	$v > \rho$
Acicular	M	17	−	1.508	1.701	>1.785	±	$v > \rho$
2,4-Diaminotoluene	T	35	−	1.470	1.751	>1.785	±	$v > \rho$
2,5-Diaminotoluene	M	17	−	1.513	1.749	>1.785	±	$v > \rho$
2,6-Dibromo-4-aminophenol	T	44	+	1.590	1.653	>1.785	±	$v > \rho$
2,4-Dichloroaniline	M	24	+	1.572	1.660	>1.785	±	$v > \rho$
2,5-Dichloroaniline	T	28	+	1.532	1.700	>1.785	±	$v > \rho$
p-Iodoaniline	M	9	+	1.500	1.751	>1.785	−	$v > \rho$
α-Naphthylamine	M	14	+	1.635	1.684	>1.785	−	$v > \rho$
	T	44	−	1.650	1.783	>1.785	−	$v > \rho$
β-Naphthylamine	O	Parallel	−	1.483	1.758	>1.785	−	$v > \rho$
o-Nitroaniline	M	33	−	1.540	1.714	>1.785	−	$v > \rho$
m-Nitroaniline, from water	T	28	+	1.522	1.650	1.786	+	$v > \rho$
From ethanol	O	Parallel	−	1.562	1.750	>1.785	+	$\rho > v$
p-Nitroaniline	T	36	+	1.615	1.698	>1.785	−	$v > \rho$
3-Nitro-4-chloroaniline	T	25	+	1.605	1.680	>1.785	−	$v > \rho$
o-Phenylenediamine	T	18	−	1.438	1.737	1.772	−	$v > \rho$
m-Phenylenediamine	T	30	−	1.493	1.683	>1.785	±	$v > \rho$
p-Phenylenediamine	M	25	−	1.501	1.716	>1.785	−	$v > \rho$
Tolidine	M	25	+	1.590	1.705	>1.785	±	$v > \rho$
o-Toluidine	M	38	+	1.552	1.632	1.766	−	$\rho > v$
m-Toluidine	T	42	+	1.567	1.675	>1.785	±	$\rho > v$
p-Toluidine	M	24	+	1.670	1.680	1.734	±	$\rho > v$

Table II. Apparent Properties of Some Primary Aromatic Amine Diliturates from Most Frequently Observed Orientation

Diliturate	Habit	Optical Orientation	Extinction Angle	Refractive Indices	
2-Aminocymene	Foliated	Obtuse	Parallel	1.507	1.648
p-Aminodiethylaniline	Tabular	Inclined obtuse	Parallel	Variable	1.659
p-Aminodimethylaniline	Tabular	Inclined optic axis	Variable	Variable	1.668
2-Amino-1,3-dimethylbenzene	Lath-shaped	Acute	20	1.583	1.670
2-Amino-1,4-dimethylbenzene	Foliated	Acute	28	1.572	1.657
4-Amino-1,3-dimethylbenzene	Tabular	Obtuse	Parallel	1.522	1.671
5-Amino-1,3-dimethylbenzene	Lamellar	Obtuse	39	1.543	1.642
o-Aminodiphenyl	Lath-shaped	Optic normal	Parallel	1.461	>1.785
p-Aminodiphenyl	Lamellar	Acute	12	1.603	1.653
2-Amino-5-hydroxytoluene	Tabular	Inclined obtuse	Parallel	1.527	1.651
2-Amino-4-nitrophenol	Acicular	Inclined optic axis	Parallel	Variable	1.722
o-Aminophenol	Lamellar	Inclined optic axis	Variable	Variable	1.673
m-Aminophenol (135° angle)	Tabular	Inclined optic axis	Variable	Variable	1.689
(112° angle)	Tabular	Inclined obtuse	Parallel	Variable	1.750
p-Aminophenol	Tabular	Inclined obtuse	Variable	Variable	Variable
Aniline, monoclinic	Tabular	Inclined obtuse	Parallel	1.535	1.671
Orthorhombic	Tabular	Obtuse	Parallel	1.447	1.738
Benzidine	Lath-shaped	Inclined optic axis	30	Variable	1.690
3-Bromo-4-aminotoluene	Tabular	Inclined acute	Parallel	Variable	1.679
o-Bromoaniline	Tabular	Optic axis	Variable	Variable	1.647
m-Bromoaniline	Tabular	Inclined obtuse	Variable	Variable	Variable
p-Bromoaniline, rectangular	Tabular	Inclined acute	Parallel	Variable	1.749
Diamond-shaped	Tabular	Acute	21	1.597	1.688
o-Chloroaniline	Tabular	Inclined optic axis	Parallel	Variable	1.657
m-Chloroaniline	Tabular	Acute	Parallel	1.777	>1.785
p-Chloroaniline	Tabular	Acute	22	1.575	1.670
2,4-Diaminophenol	Tabular	Inclined obtuse	Variable	1.502	Variable
	Acicular	Variable	Variable	Variable	Variable
2,4-Diaminotoluene	Columnar	Variable	Variable	Variable	Variable
2,5-Diaminotoluene	Lamellar	Obtuse	17	1.513	1.749

Table II *Contd.*

Diliturate	Habit	Optical Orientation	Extinction Angle	Refractive Indices	
2,6-Dibromo-4-aminophenol	Tabular	Inclined optic normal	44	Variable	Variable
2,4-Dichloroaniline	Lamellar	Acute	24	1.572	1.660
2,5-Dichloroaniline	Tabular	Inclined optic axis	28	Variable	Variable
p-Iodoaniline	Tabular	Inclined acute	Parallel	Variable	1.751
α-Naphthylamine, monoclinic	Lamellar	Acute	14	1.635	1.684
Triclinic	Tabular	Inclined obtuse	Variable	Variable	>1.785
β-Naphthylamine	Tabular	Obtuse	Parallel	1.483	1.758
o-Nitroaniline	Tabular	Inclined optic axis	Parallel	Variable	1.714
m-Nitroaniline, from water	Tabular	Inclined optic normal	3	Variable	Variable
From ethanol	Lath-shaped	Acute	Parallel	1.750	>1.785
p-Nitroaniline	Tabular	Inclined optic normal	17	1.626	>1.785
3-Nitro-4-chloroaniline	Equant	Inclined optic normal	16	Variable	Variable
o-Phenylenediamine	Lath-shaped	Inclined obtuse	6	1.470	1.756
m-Phenylenediamine	Lamellar	Inclined obtuse	7	Variable	1.694
p-Phenylenediamine	Tabular	Obtuse	25	1.501	1.716
Tolidine	Lamellar	Acute	25	1.590	1.705
o-Toluidine	Tabular	Inclined optic axis	Variable	Variable	1.632
m-Toluidine	Tabular	Inclined optic axis	Variable	Variable	Variable
p-Toluidine	Tabular	Acute	24	1.670	1.680

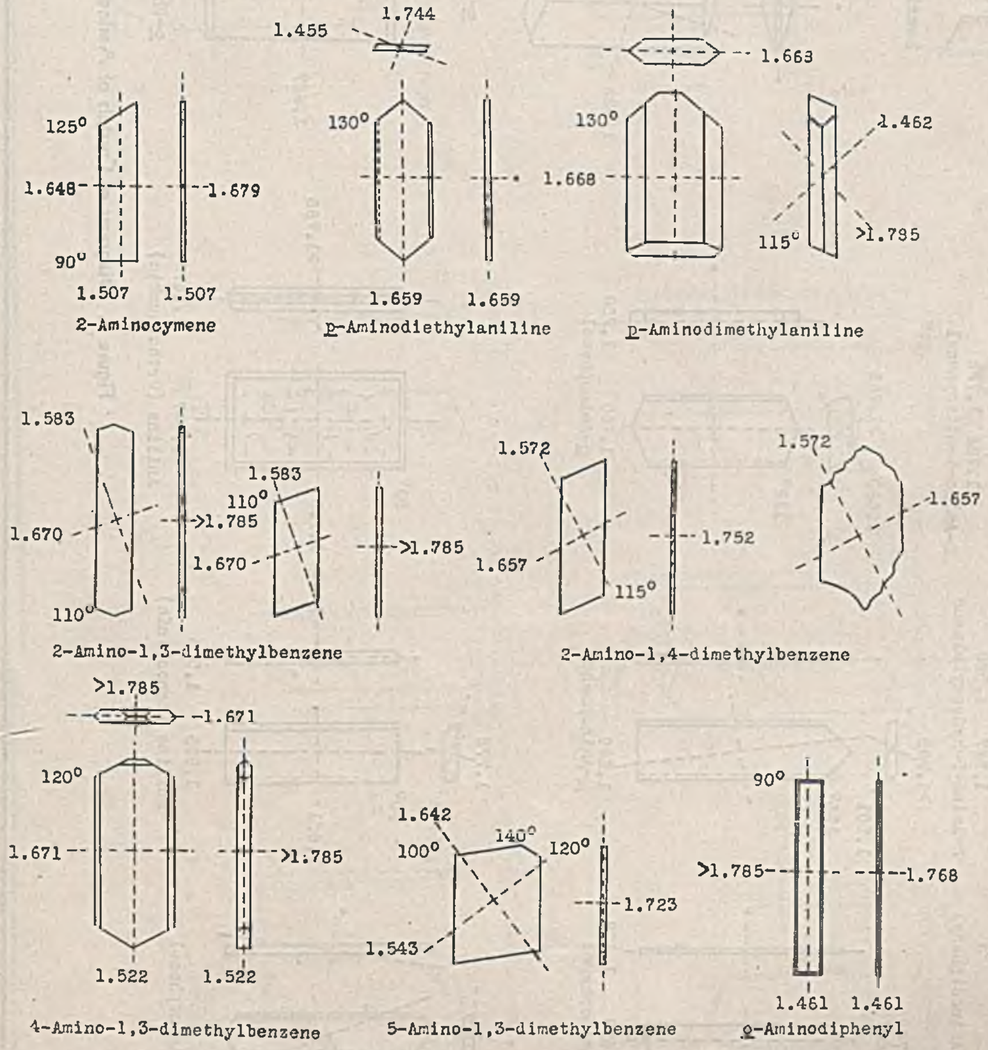


Figure 1. Diagrams of Crystals of Amine Diliturates

tals to make the crystal shape of individual crystals valuable for identification. Attempts at recrystallization from ethanol, ethyl acetate, ether, petroleum ether, and acetic acid failed to produce more regularly formed crystals. Some characteristics of such crystals are the following:

2-Aminocymene forms dendrites, spherulites, and pink masses of crystals. Crystal angles are occasionally 125°, but more frequently 90°. Ends of the crystals are often broken or irregular. 2-Amino-1,4-dimethylbenzene forms some spherulites and masses of crystals, fragments of which show gray polarization colors. Many of the crystals are very thin. 5-Amino-1,3-dimethylbenzene also forms masses of crystals, but fragments show vivid polarization colors. *p*-Aminodiphenyl produces many fragments with dull polarization colors. 2,5-Dichloroaniline crystallizes in masses which show dull polarization colors. α-Naphthylamine forms dendrites along with well-formed crystals. It exhibits polymorphism with the lamellar crystals in greater proportion than the tabular form. *p*-Phenylenediamine often forms masses of very small crystals; larger crystals have 110° crystal angles, but also frequently show broken ends. Tolidine produces masses of crystals which show vivid polarization colors.

Additional descriptions of some of the diliturates will facilitate identification of them. The properties of *p*-aminodiethylaniline diliturate should be taken from freshly prepared crystals or from those which have been properly protected to prevent loss of water of crystallization. Crystals of the dried product retain their shapes nicely, have the appearance of being composed of bundles of needles or fibers, and possess higher refractive indices.

Diliturates of *p*-aminodimethylaniline, *o*-bromoaniline, and *o*-toluidine exhibit no extinction in the usual orientation, but the interference figures (optic axis or slightly inclined optic axis) indicate β to show perpendic-

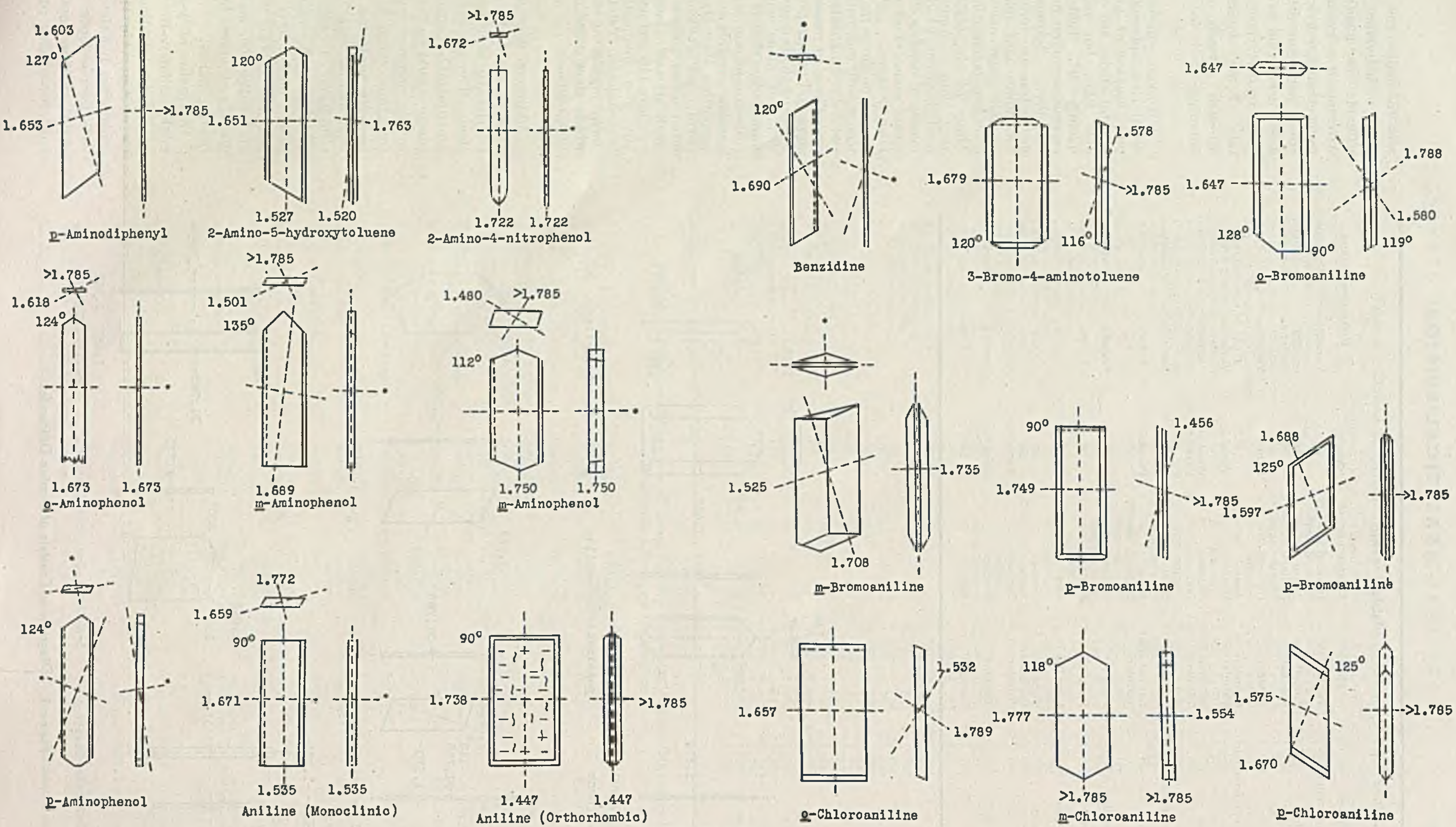
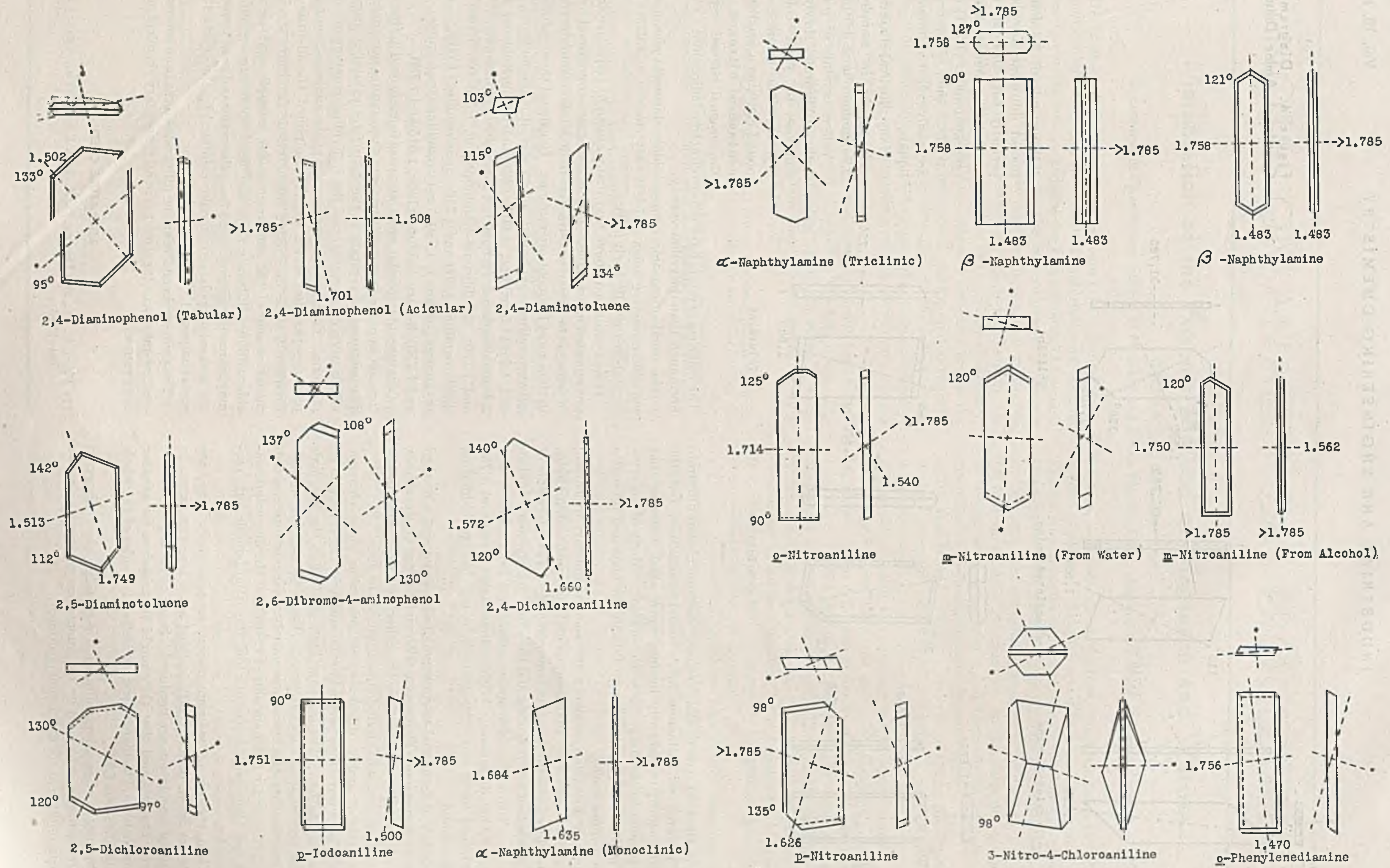


Figure 2. Diagrams of Crystals of Amine Diliturates

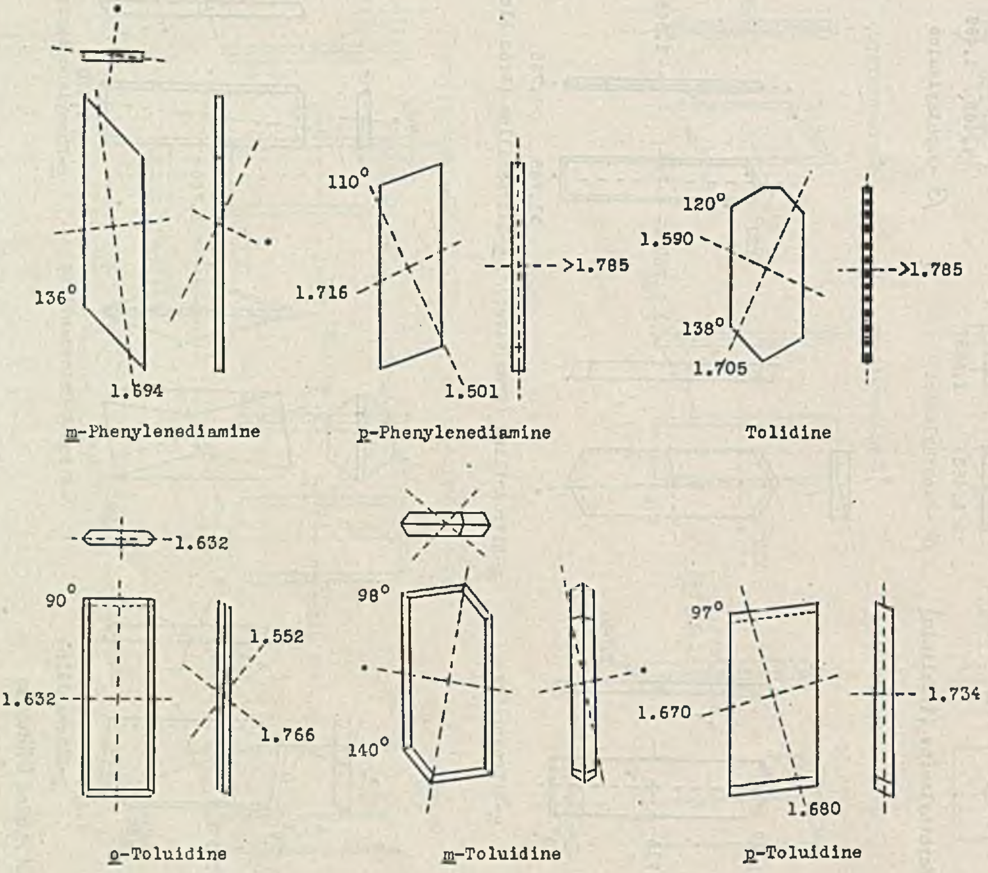


2,4-Diaminophenol (Tabular) 2,4-Diaminophenol (Acicular) 2,4-Diaminotoluene α-Naphthylamine (Triclinic) β-Naphthylamine β-Naphthylamine

2,5-Diaminotoluene 2,6-Dibromo-4-aminophenol 2,4-Dichloroaniline o-Nitroaniline m-Nitroaniline (From Water) m-Nitroaniline (From Alcohol)

2,5-Dichloroaniline p-Iodoaniline α-Naphthylamine (Monoclinic) p-Nitroaniline 3-Nitro-4-Chloroaniline o-Phenylenediamine

Figure 3. Diagrams of Crystals of Amine Diliturates



m-Phenylenediamine p-Phenylenediamine Tolidine

o-Toluidine m-Toluidine p-Toluidine

Figure 4. Diagrams of Crystals of Amine Diliturates

ular to the long axis of the crystals. *o*-Aminophenol diliturate also presents no extinction in its usual orientation, but the interference figure (slightly inclined optic axis) indicates that β is parallel to the long axis of the crystal. Many of the crystals of this compound are very thin at the ends and present a broken appearance.

Marked dispersion is shown by *o*-aminodiphenyl diliturate; hence it was necessary to determine β (1.768) with sodium light. With white light the value is approximately 1.774. Crystals of this compound are very long and therefore present many broken ends. *m*-Nitroaniline diliturate, crystallized from ethanol, also presents high dispersion. With sodium light a value of 1.750 is obtained for β and with white light a value approximating 1.762 is found.

Crystals of 2-amino-4-nitrophenol diliturate present a marked inclined dispersion. The isogyre with violet fringe on the convex side seems to be thicker than the other isogyre. Many of the crystals are somewhat rounded and thin at the ends.

Crystals of aniline diliturate, orthorhombic, show cleavage lines in both directions parallel to the outline of the crystal in its usual orientation. The cleavage lines parallel to the long axis of the crystal are somewhat wavy. The orthorhombic crystals are broader than the monoclinic variety. Some samples of aniline diliturate are made up almost entirely of the monoclinic variety, but there are samples in which the orthorhombic form predominates.

When crystals of *m*-bromoaniline, usually fairly large, are lightly crushed, platelets with inclined acute bisectrix figures in the usual orientation are produced. Some of these platelets are so well proportioned that they might be mistaken for another crystal habit. The higher apparent refractive index of the whole crystals lies near 1.708.

Diliturates of *m*-chloroaniline and *p*-toluidine show dispersed birefringence as evidenced by the anomalous polarization colors (purple or blue) at the extinction position.

If crystals of 2,4-diaminophenol diliturate acicular lie perfectly flat, then an acute bisectrix interference figure is presented and β (1.701) and v (>1.785) show. The crystals are easily rolled in immersion liquids.

Many thin oval-shaped crystals appear in samples of 2,5-diaminotoluene diliturate.

Yellow crystals of *p*-nitroaniline diliturate slowly decompose to yield colorless crystals. The colorless compound contains a smaller percentage of nitrogen than the original colored crystals. The colorless crystals have lower refractive indices and a smaller optic angle than the yellow variety.

The usual orientation of *m*-toluidine diliturate shows a low variable refractive index which is very close to β (1.675). The crystals are usually fairly large.

It was explained above that many apparent refractive indices are reported as variable. The following are approximate values of some of the apparent refractive indices taken from the crystals in their most frequent orientations. In general these values vary between rather wide limits: diliturates of *p*-aminophenol, 1.521 and 1.715; benzidine, 1.607; 3-bromo-4-aminotoluene, 1.602; 2,4-diaminophenol (tabular), 1.705; 2,4-diaminotoluene, 1.496 and 1.770; 2,6-dibromo-4-aminophenol, 1.595 and 1.760; 2,5-dichloroaniline, 1.560 and 1.710; *p*-iodoaniline, 1.508; α-naphthylamine (triclinic), 1.780; *m*-nitroaniline (from water), 1.532 and 1.756; 3-nitro-4-chloroaniline, 1.615 and 1.780.

Mixtures of the ortho, meta, and para isomers used in this investigation were made and diliturates of the mixtures were prepared. The mixtures of crystals of the diliturates exhibited properties which were characteristic of the individual components of the mixtures. Fractional crystallization of the mixtures resulted in a partial separation which usually simplified the identification. Frequently some distinctive characteristic facilitates the recognition of one of the components—for example, crystals of *m*-chloroaniline diliturate show dispersed birefringence, and they may be readily distinguished from the ortho and para isomers by the anomalous polarization color exhibited by the crystals of the meta compound.

The primary aromatic amine diliturates have been successfully used as unknowns for students in an elementary chemical microscopy course.

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NOTES ON ANALYTICAL PROCEDURES

Modification of the Arsenic Method of Magnuson and Watson

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THE method of Magnuson and Watson (*1*) for the microdetermination of arsenic in biological materials was selected for use in a program concerned with the pharmacology of arsenical drugs and their application to the chemotherapy of certain tropical diseases. Preliminary tests indicated that recoveries were within 5 to 10% of theoretical in the 1- to 10-microgram range, and the method was therefore of the required accuracy. The choice of this method over others which also utilize the molybdenum blue reaction was based chiefly on the rapidity with which samples can be run through. As the authors state, 20 to 30 determinations can be done each day with no difficulty. A simple microstill, commercially available, is the only special apparatus required.

In this laboratory positive blanks and aberrant high values were occasionally encountered in handling this technique. The present paper describes an investigation of the cause of these false readings, and indicates how they can be eliminated by a modification of one of the reagents.

The following steps are carried out in the determination of arsenic in blood, excreta, and organs. Details are described in the original paper (*1*).

The organic material is destroyed in a wet digestion using nitric and sulfuric acid. Perchloric acid may also be used at the end of the process.

Following digestion the arsenic is in pentavalent form in sulfuric acid. This is transferred to the microstill, potassium bromide is added, and arsenic, probably in the form of the pentabromide, is distilled together with a small but significant amount of hydrobromic acid.

The distillate is treated with ammonium molybdate, to form a heteropoly compound with arsenic as the central atom in the complex (*2*).

The heteropole is reduced with hydrazine sulfate to form molybdenum blue, which gives a color with a sharp absorption maximum at 840 mμ. In the final solution, 1 part of arsenic in 25,000,000 may be readily detected and measured, using a Beckman spectrophotometer and a light path of 50 mm.

Woods and Mellon (*2*) found that in the analogous case of phosphorus the hydrochloric acid–molybdate ratio was important. If this ratio was too low, the reaction corresponding to the fourth step would involve reduction of ammonium molybdate itself, to form molybdenum blue even in the absence of the heteropole. Thus, in any method of this type it is necessary to have the acid sufficiently high so that only the heteropole, which contains the element sought, is reduced. Magnuson and Watson (*1*) depended on the hydrobromic acid distilled in the prescribed 4-minute period for this purpose. They state (*a*) that 2.5 to 4.0 milliequivalents of hydrobromic acid are distilled in this time and (*b*) that as low as 1.0 milliequivalent is permissible. In their experiments, as well as the author's, hydrobromic and hydrochloric acid were used interchangeably in the color development steps.

Table I. False Positive Arsenic Readings Due to Low Halogen Acid Concentration in Magnuson-Watson Procedure

(All reagents tested and free of As, Si, and P. Readings from standard As curve, using Coleman Spectrophotometer at 790 mμ.)

Undistilled		Distilled	
Milliequivalents of HCl used	Reading as As, γ	Milliequivalents of HBr found	Reading as As, γ
0	14.5	1.8	1.6
1.0	1.5, 1.7, 2.7	2.0, 2.0	1.0, 2.0
1.5	1.4, 0.6	2.1	1.3
2.0	0, 0, 1.0, 0.6	3.1, 3.1	0
2.5	0, 0, 0	3.5	0
3.0	0, 0, 0	4.0 (5-minute distillation)	0
3.5	0, 0, 0		
4.0			
5.0	0, 0, 0		

Ten successive distillations were run following the Magnuson-Watson procedure exactly. The distillates were titrated with 0.1 *N* sodium hydroxide using bromothymol blue as indicator. Hydrobromic acid in the distillates was between 1.3 and 3.6 m.e. This range is lower than that given by Magnuson and Watson (*a*, above). The difference is significant, since the experiments recorded in Table I show that a positive blank occurs regularly if less than 2 m.e. of acid is present. Thus, the permissible lower limit of acidity in the original paper (*b*, above) was also subject to revision in the author's hands. Table I indicates that over 2.1 m.e. of halogen acid must be present to avoid formation of molybdenum blue in the absence of arsenic.

In view of these findings it has been possible to eliminate the occasional high values and false positives by the addition of 1 m.e. of hydrochloric acid to the distillate. Since the lowest titer ever found for a distillate was 1.3 m.e., this increment should always be sufficient to bring the total amount of halogen acid to the range where reduction of the simple molybdate and the resulting high values and false positives are completely eliminated. Approximately 500 determinations have been carried out with this modification, and no aberrant results of the type originally found have been observed. The over-all procedure has been found satisfactory with regard to accuracy, speed, and simplicity.

MODIFIED PROCEDURE

In order to avoid the handling of an extra solution, the extra milliequivalent of hydrochloric acid is added along with the ammonium molybdate solution. To two volumes of molybdate color reagent, made up according to the directions of Magnuson and Watson, add one volume of *N* hydrochloric acid. In the color development procedure, add 3 ml. of this combined solution instead of 2 ml. of molybdate solution as called for in the earlier paper. All other solutions and directions are unchanged.

SUMMARY

A study has been made of the Magnuson and Watson molybdenum blue method for arsenic in biological materials, which offers certain advantages over others described in the literature. It was found that in their distillation process, insufficient acid was carried over, and the result was occasional high values in the presence of arsenic and positive readings in the absence of arsenic and the other possible interfering elements, silicon and phosphorus. This was ascribed to reduction of simple molybdate ion in insufficiently acid solution, and has been eliminated by addition of hydrochloric acid to the distillate.

ACKNOWLEDGMENT

The author wishes to thank Mildred Salchunas for her assistance in this work.

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Determination of Free Carbon in Butyl Reclaim by Modified A.S.T.M. Method

J. E. McCREADY AND H. H. THOMPSON, Reclaim Laboratory, Goodyear Tire & Rubber Co., Akron, Ohio

THE production and use of regenerated GR-I (Butyl) elastomer, which has scrap inner tubes as a main raw material, made it desirable to develop methods for analysis of the constituent materials. In applying the A.S.T.M. procedure (*1*), it was difficult to obtain satisfactory filtering and washing of the dissolved sample in determination of the free-carbon content, because of the inherent resistance of GR-I to nitric acid oxidation. In view of this factor, a satisfactory way to disintegrate GR-I reclaim was sought that would result in acceptable filtering and washing.

In fairly extended trial disintegrations with possible solvents or reagents (acetone, petroleum ether, chlorosulfonic acid, mineral-seal oil, and others), mineral-seal oil gave the best filtering and washing and was tested for accuracy of results. It was found satisfactory and selected for regular use.

APPARATUS AND REAGENTS

Reagents needed are described in A.S.T.M. D-297-43T. The apparatus consisted of pieces normally found in a general analytical laboratory.

OUTLINE OF METHOD

Essentially, the proposed method follows the A.S.T.M. method for free carbon content of rubber (*1*, Section 23), except that the *a* extraction with chloroform-acetone is omitted and a hot digestion in mineral-seal oil precedes the treatment with nitric acid.

The general steps in the analysis are, in order:

Preparation and weighing of sample
Digestion in hot mineral-seal oil for breakdown and partial separation of the elastomer fraction
Filtering
Alternate washing with solvents and hydrochloric acid to remove oils, waxes, and carbonates
Washing with nitric acid for further removal of mineral fillers, other than carbon, that would change upon ignition
Final washes with acetone–hydrochloric acid mix to remove last traces of oils or fillers
Drying, weighing, igniting, and final weighing to determine loss of carbon

PROCEDURE

Weigh a 0.5000-gram sample of the GR-I reclaim, previously sheeted thinly (approximately 0.5 mm. thick), and place in a 250-ml. Erlenmeyer flask. Add 50 ml. of mineral-seal oil, cover flask with a watch glass, and heat overnight (or 12 hours minimum) in an oven set at 150° C.

Remove from the oven and allow to cool to room temperature. Dilute the contents of the Erlenmeyer with about 200 ml. of petroleum ether and 50 ml. of benzene. Shake carefully, to mix solvents, then filter with moderate suction through a Gooch crucible fitted with a moderately heavy asbestos mat. In this first transferral to the Gooch, take care that the crucible is not filled over $^3/_4$ full, to prevent creepage of the carbon over top edge. Wash and police flask free of adhering particles, using hot acetone for the cleansing. Wash the solids, now all on the Gooch mat, using alternate applications of warm 10% hydrochloric acid and boiling acetone. Continue these alternate washings several times, until the filtrate comes through clear, washing last with 10% hydrochloric acid to avoid any violent reaction between acetone and the nitric acid added in next step. Empty the filter flask at this time to eliminate the same possible effect.

Table I. Carbon in Butyl Reclaims

Sample	Per Cent Free Carbon Test 1	 Test 2	 Test 3	 Av.	Maximum Deviation from Average
A	30.86	31.07	31.00	30.98	0.12
B	31.16	31.39	31.27	31.27	0.12
C	30.09	30.22	29.81	30.04	0.19
Av.	30.70	30.89	30.69	...	...
Maximum deviation from average	0.61	0.67	0.88		
Theoretical				31.00	

Table II. Per Cent of Free Carbon in Vulcanized Butyl Stock

Sample	Test 1	Test 2	Av.
D	31.50	32.19	31.85
E	31.81	31.60	31.71

Calculated value – 30.30

Resume treatment of the material in the Gooch, still using moderate suction, by washing once with cold nitric acid, five times with progressively warmer nitric acid, and three or four times with boiling nitric acid. After the nitric acid wash, empty the filter flask and resume washing, making the first filling of the Gooch with a mixture of equal parts (by volume) of acetone-chloroform–glacial acetic acid, followed by several washes with the same mixture, moderately heated. Next, wash with a hot 1 to 1 mix of acetone-chloroform and repeat until the filtrate runs clear, plus several additional washings. Finally, wash alternately with warm 10% hydrochloric acid and with boiling acetone until the filtrate is again clear. Remove the Gooch from the holder, clean the outside with a cloth moistened in acetone, and dry in oven for 2.5 to 3 hours at 105° C. Cool in desiccator, weigh (*a*), and then burn off carbon in an electric muffle at 800° C. Cool in desiccator and weigh again (*b*). The difference in weight ($a - b$) represents approximately 105% of the carbon originally present in the form of lampblack or gas black.

CALCULATION.

$$\% \text{ free carbon} = \frac{a - b}{1.05 \times \text{weight of sample}} \times 100$$

a = weight of crucible with carbon
b = weight of crucible after ignition
1.05 = factor covering effect of nitric acid on carbon black

DATA

In making determinations on Butyl (GR-I) reclaims, three samples of different production lots were run, with three parallel tests on each sample. Results are shown in Table I.

Such values indicate satisfactorily close agreement between check or parallel tests on a given sample, with a maximum deviation from the average of 0.19% in a given series. When comparing results from different samples, a somewhat greater deviation is noted, but this is undoubtedly due to existing differences in composition found from one batch to another, resulting from the fact that varying amounts of reclaiming oils are lost in processing.

While not of direct connection to this work, this modified procedure was used in determining the free carbon content of a cured, unreclaimed Butyl (GR-I) tube stock. Such trial indicated that the method is usable and fairly accurate, but further checking is desirable before applying it to the vulcanized stock. Data on vulcanized Butyl stock are given in Table II.

SUMMARY

Because of difficulty in filtering and washing when the regular A.S.T.M. method for free carbon was applied to Butyl reclaim, a modified procedure was developed. The essential change is the addition of a hot digestion in mineral-seal oil, rather than use of nitric acid alone for disintegration of the elastomer, with some variation in the solvent and acid washes used to eliminate fillers and oils. Improved speed and ease of manipulation were obtained, with results checking well, when compared with each other and with calculated values. While intended for use on reclaimed stock, preliminary trial on cured Butyl stock was satisfactory, from both technique and accuracy phases.

ACKNOWLEDGMENT

The authors wish to thank Harry E. Rutledge, Goodyear Tire and Rubber Co. analytical laboratories, for valued consultation and scanning of the completed paper.

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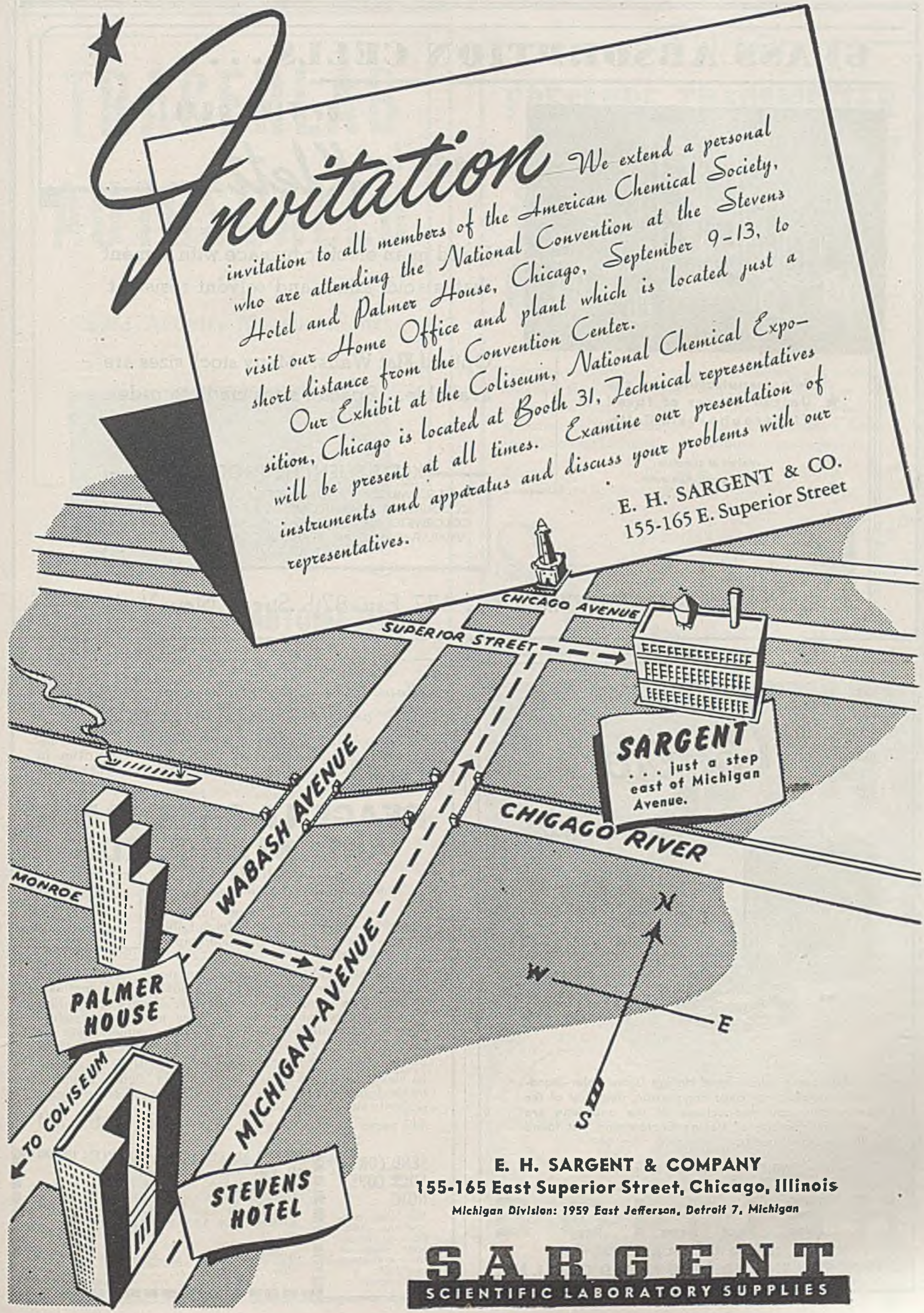
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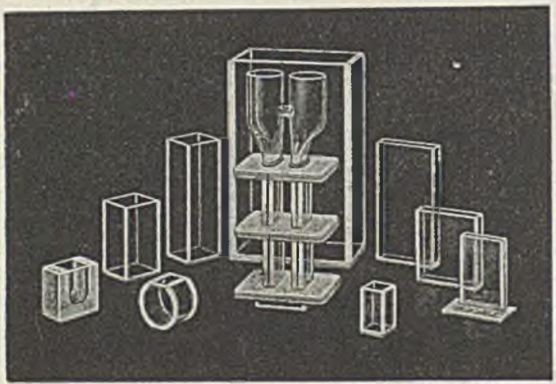

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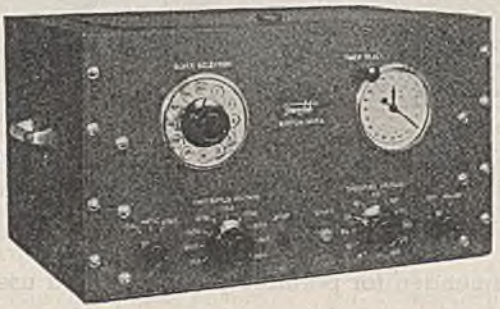

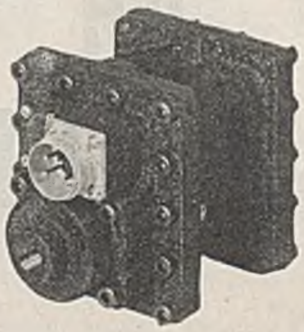


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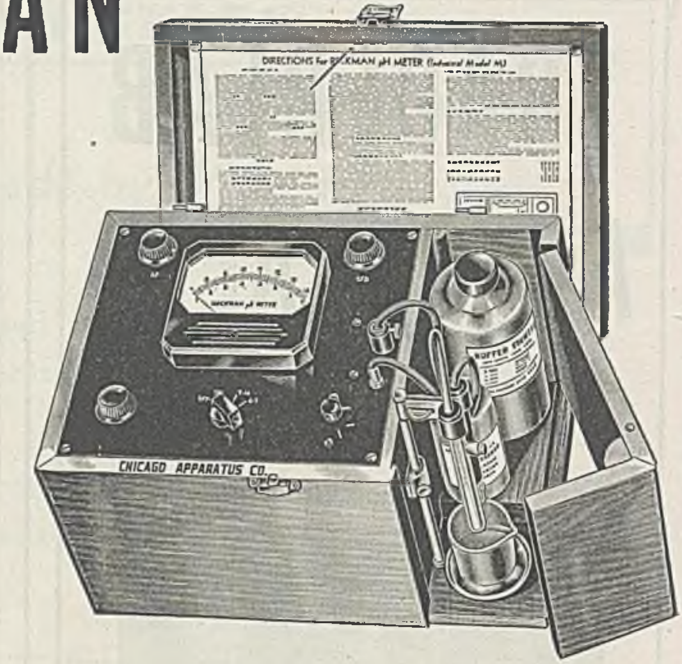
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Current Developments in

INSTRUMENTATION IN ANALYSIS

Discussed by Ralph H. Müller

TO DETERMINE eleven elements in 45 seconds is a new record, we believe, but it seems to be indicative of what may be expected in the future for the routine spectrographic examination of metals and alloys. An instrument for the automatic spectrographic analysis at such prodigious speeds is the Quantometer, now available from the Applied Research Laboratories of Glendale, Calif.

The Quantometer

The Quantometer is a special instrument designed specifically for its function of direct reading. The accuracy is superior to ordinary spectrographic methods which employ the photographic process, although the Quantometer's lower limit of measurement needs about three times the concentration of an element required by the best spectrographic methods.

The spectrometer unit of the Quantometer is provided with a source stand and bench, primary slit, and a choice of diffraction gratings. High resolution original gratings of 1 × 2 inch surface can be supplied in two types each having a radius of curvature of 150 cm. One ruling of 24,000 lines per inch covers the range of 2000 to 6000 Å. with a dispersion of 6.9 Å. per mm. Another grating with 36,000 lines per inch provides a range of 2100 to 4700 Å. with a 50% increase in dispersion and resolution. Beyond this stage, the Quantometer differs from conventional spectrographs in that it is designed with a long focal curve along which slit-covered receivers are placed in order to intercept any desired spectral lines. As many as twelve receivers can be moved into position without serious interference between them, such that several lines close together in the spectrum can be measured simultaneously. The radiation entering each receiver falls on an electron multiplier phototube. The output of this tube, which is proportional to the light intensity, is integrated and converted into a series of electrical impulses. These impulses, after suitable amplification, are passed on to the recording console. The results appear as percentages of each element, exhibited on a printed tape.

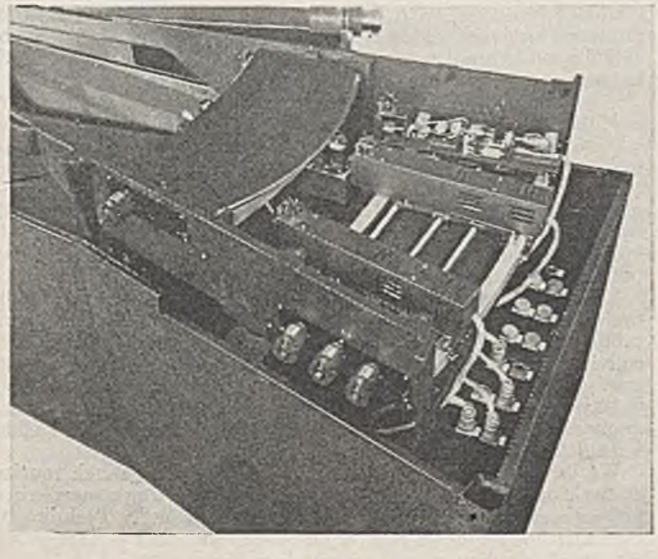


Figure 1. Receiver Assembly of Quantometer

The receiver assembly of the Quantometer is shown in Figure 1. Each receiver consists of a mechanical and electrical assembly which moves along the ways and supports the mirror and slit components. The electrical unit is readily removable for inspection or repair and contains the multiplier phototube, its voltage divider, and the integrating and amplifying circuits.

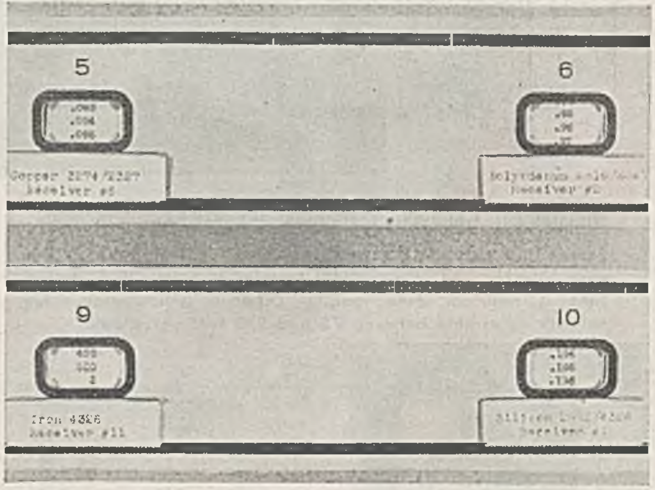


Figure 2. Front of Console. Direct Recording of Per Cent Composition

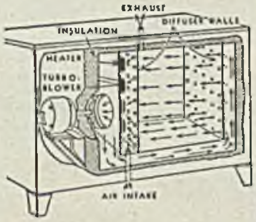
The positioning of each unit is accomplished by precision screws turned from a control panel at the side of the spectrometer. A dial and indicator permit the correct setting on a desired spectral line with a few Ångströms by means of a wave length *vs.* dial-setting graph. Final adjustment is made in less than a minute with the aid of a line profiling meter.

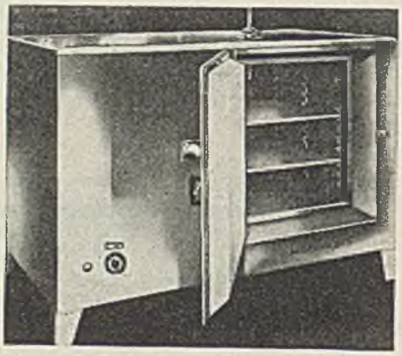
The maximum complement of receivers consists of three receivers mounted on each of four bridges, or a total of twelve. Since one of these is scanning an internal reference line, the remaining eleven can simultaneously measure eleven other elements.

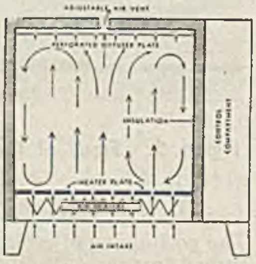
The final analytical results are furnished by the integrating recorders. These consist of motor-driven electromagnetic counters which drive 50-inch tapes on which percentages of the various constituents are printed. These values appear in little windows or apertures in the front of the console (Figure 2). After a reading has been noted by the operator, the tape can be restored to its original or zero position by pushing a button.

Analytical Procedure

The analytical procedure is simple. One receiver is placed so that it scans a line of the internal standard element. The sensitivity of this monitoring receiver is so adjusted that it completes a cycle of 500 counts during the sparking period, say 25 seconds. Other receivers, which are scanning appropriate lines of the elements that are to be determined, are accumulating counts during this interval in proportion to the amount of those elements present. The sensitivity of each recorder is adjusted until the correct percentage of each element is indicated when a standard sample is being sparked. The sensitivity adjustment







Instrumentation

can be made with ease and precision by means of a coarse and fine tapped-switch control. A hundredfold variation in receiver sensitivity can be made in steps of 0.3%. When the calibration procedure is finished, the operator can assure himself at any time that everything is in order, merely by sparking the standard sample. At the conclusion of the sparking period, the percentage of each element appears at the appropriate window.

Advantages

Several advantages over the conventional photographic method are apparent, of which speed is one. A second is the wide range of relative line intensities which can be accommodated. A third advantage is the fact that variations in contrast as a function of wave length do not arise, because the photomultiplier cells have a linear response with intensity at all wave lengths.

Additional refinements include a switching system which permits the operator to terminate the recordings on certain lines, while others are in progress. This is especially convenient for elements which have short "spark-out" times. Also, several receivers may be used separately or simultaneously as internal standard receivers, each controlling the termination of its own group of receivers. This is useful when the instrument may be called upon to analyze two or three different alloys at a moment's notice.

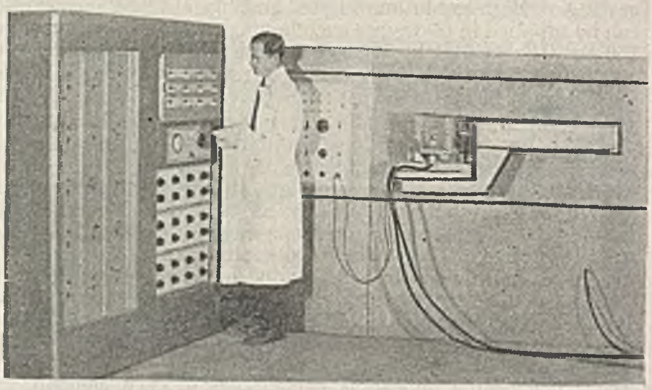
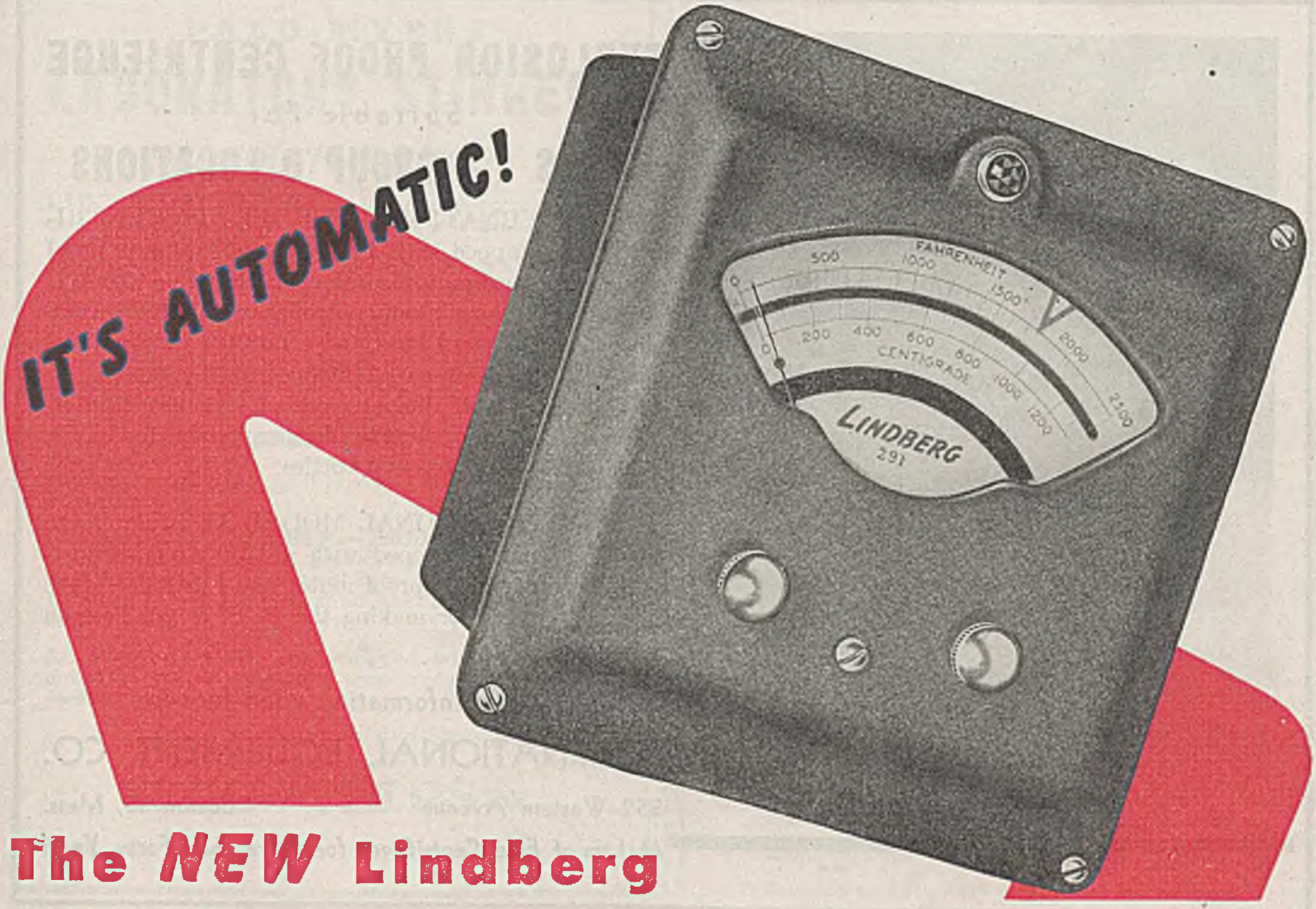


Figure 3. General View of Quantometer Installation

A general view of a Quantometer installation is shown in Figure 3, with excitation unit and spectrometer on the right and the recording console on the left. The best practices of electronic engineering are to be found in the console, with multiple channel units, readily accessible and removable for inspection. Convenient gang cables with multipronged aircraft connectors are freely employed. All critical power supplies are controlled with Sola voltage regulators and, in addition, critical high voltages for amplifiers and multiplier tubes are electronically regulated.

The manufacturer has had 3 years' experience with the Quantometer, during which extensive data have been accumulated to establish the precision and reliability of this instrument. Rather convincing evidence is at hand to indicate that where a large amount of repetitive work is to be done, the instrument is likely to pay for the cost of installation in a very short time, and that many metallurgical processes are likely to be radically changed as a result of its widespread use.

We have often been rebuked for implying that much routine analysis of the future would be a matter of "putting a sample in a hopper and having the answer printed on a ticket". Technically, that attitude seems to require no further defense; it is merely a matter of expediency, and, on occasion, a necessity.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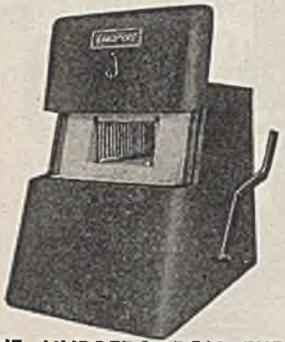

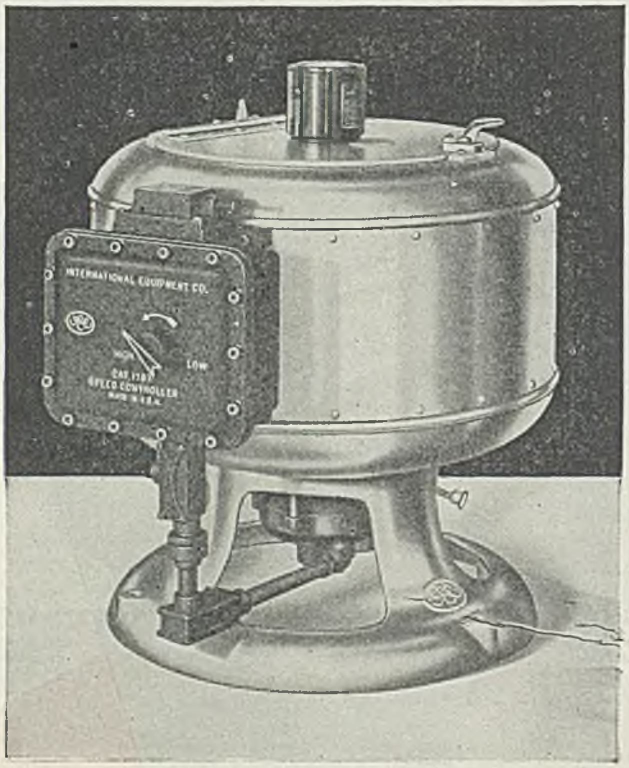
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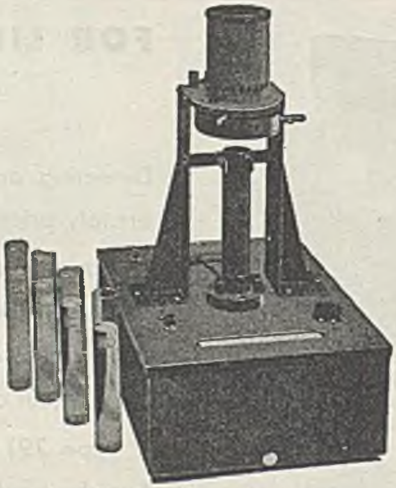

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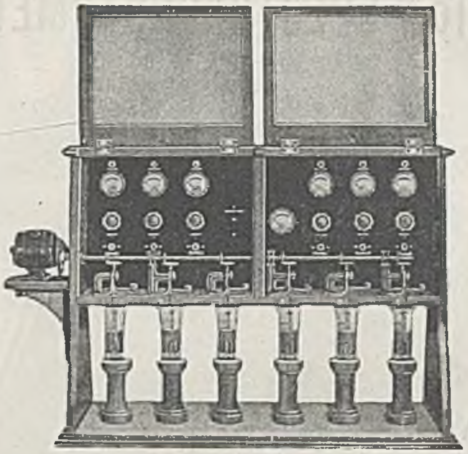

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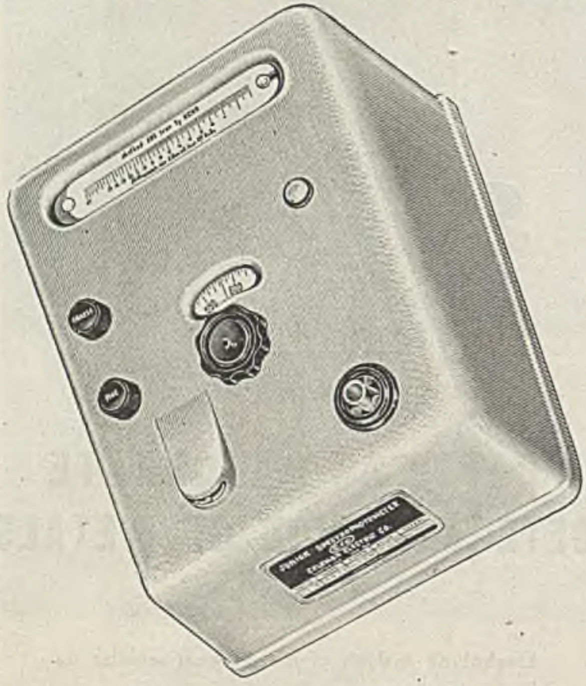

Originally designed for the United States Army, the Coleman model 6A Junior Spectrophotometer brings to your laboratory the inherent precision and speed of spectrochemical analysis in an economically priced instrument. Qualified by precision and reliability for real research tasks, this new instrument is equally adaptable for rapid clinical routines where it will be found almost unbreakable and so simple that its operation can be mastered by the regular technician in a matter of minutes.

The Junior is a true Spectrophotometer, not an abridged colorimeter. It utilizes the same Wood's diffraction grating and substantially the same optical system and direct reading galvanometer scale as the more expensive Coleman Universal Spectrophotometer. It differs from this latter by a wavelength range limited to the visible spectrum (400–700 mμ) and by cuvette mountings specifically designed to accept the several test tubes most popular to clinical laboratories.

The persistent demand of microchemistry is answered by a 3/8 inch diameter cuvette, allowing exact spectrophotometric measurements with as little as 1.0 ml. of sample. Other adapters allow tests with the 12 mm. Kahn tube, also with both long and short 3/4 inch test tubes, the former being particularly convenient for bacteriological studies. Without adapters, the cuvette will accept 1 x 4 1/8 inch test tubes.

The photo circuit of this instrument is so sensitive that the 8 1/2 volt exciter lamp is actually operated at only 6 volts. This results in lamp life expectancy of better than 3000 hours and allows operating either from any 6 volt, 80 AH storage battery or from a 6 volt constant voltage transformer.

Readings appear directly on illuminated subpanel scales, and both scale windows and control shaft bearings are of water-tight construction to minimize spillage hazards.

The instrument is housed in a tan vitreous enamelled cast-iron case. It is 9 inches wide by 11 1/2 inches deep by 6 1/2 inches high. It uses 5 amperes at 6 volts AC or DC supplied from either storage battery or constant voltage transformer (not integral).

A-5636 Coleman Junior Spectrophotometer, model 6A, complete with plastic light shield, mounting pads, removable transmittance density scale panel, and operating directions. **Each $310.00**

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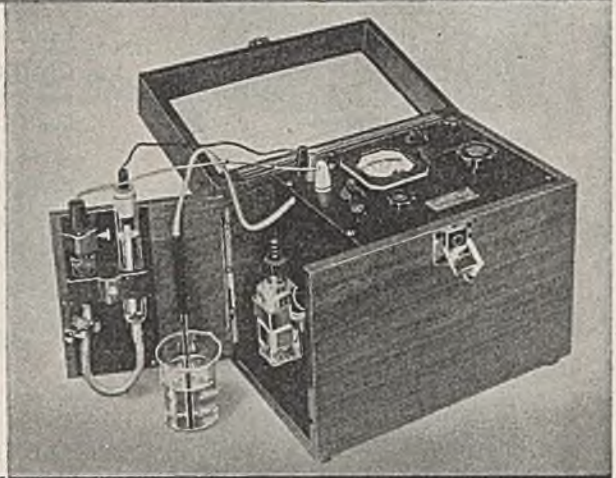

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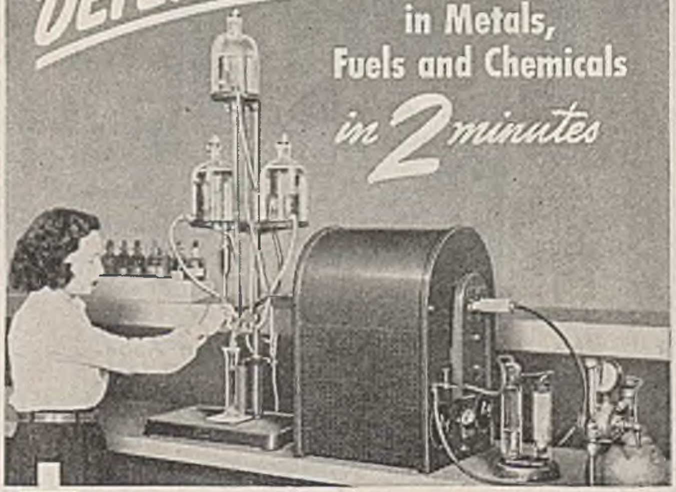

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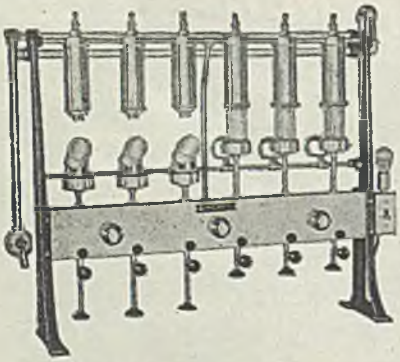

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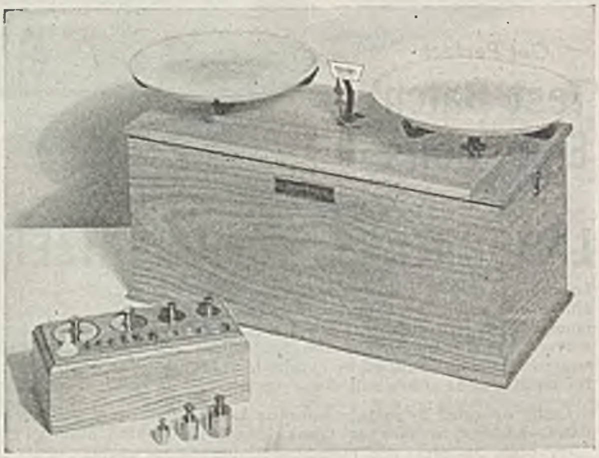

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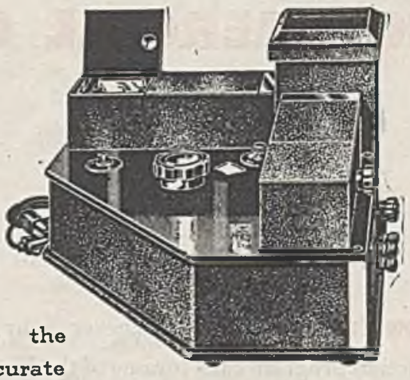

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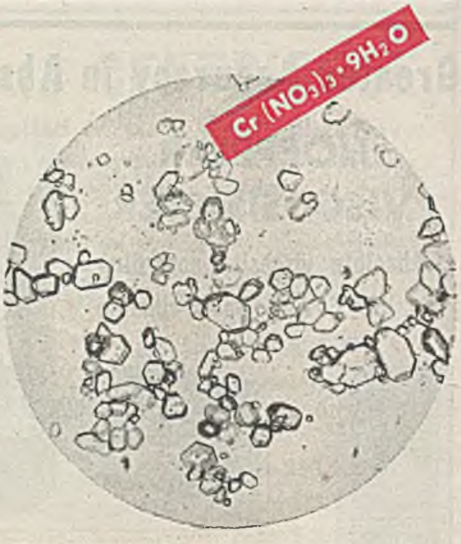
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