

Figure 2. Effect of Sample Size

Calculation.

$$\frac{\text{Ml. of CTAB} \times N \text{ CTAB} \times 1701}{\text{Mg. of sample}} = \% \text{ OH}$$

PRECISION

Ten determinations on a sample of Eastman Kodak 1-dodecanol gave 8.86, 8.92, 8.95, 8.71, 8.77, 8.77, 8.86, 8.89, 8.89, and 8.92% OH (calculated 9.14); estimated standard deviation is 0.079. These values imply a bias toward low results if the sample is pure. By the acetic anhydride-pyridine method this sample contains 9.16 and 9.10% OH. Since another sample of 1-

dodecanol gave 9.00, 9.05, and 8.96% OH by the semimicro method, there is no known explanation for the low values obtained above. The results in Table I do not indicate a bias toward low results.

APPLICATION OF THE METHOD

The results of the application of the method to a variety of materials which react with chlorosulfonic acid are tabulated in Table I. Normal, primary alcohols from 1-decanol to 1-dodecanol and slightly branched primary alcohols within this range are analyzed accurately. Accuracy (95% with 1-octanol) and precision decrease as the homologous series is descended; 1-butanol is inert. Only three secondary alcohols were analyzed, but the results are consistent with the range established by the primary alcohols. The tertiary alcohol, 2-methyl-2-hendecanol, gave low results, which, very likely, is a general property of tertiary alcohols. As would be expected, the amide group in $\text{RC}(\text{O})\text{NHC}_2\text{H}_5\text{OH}$ does not interfere in the accurate determination of the hydroxyl group.

Ethylene glycol, glycerol, and mono- and distearin are inert. In the light of the inertness of 1-butanol, that of ethylene glycol and glycerine is not surprising. On the other hand, mono- and distearin are sufficiently long chained to be analyzed by this method. The explanation lies in the fact that the ester links hydrolyze during the first step in the determination. 1,2-Hexadecanediol, which bears a structural resemblance to a mono-glyceride but lacks its ester link, analyzes for from 70 to 80% of its hydroxyl content.

Mercaptans, olefins, and cholesterol also react, but incompletely, so that they would be expected to interfere in the determination of fatty alcohols. It is entirely possible that an accurate analysis of these interfering compounds could be developed by a slight alteration of the existing method. For example, it is known that the polyisobutylenes are sulfonated in 90% yield by chlorosulfonic acid in ether when a 3-hour reaction time is used (4).

Glycerol does not interfere in the analysis of 1-hendecanol, and neither ethyl alcohol (up to 25%) nor trilaurin interferes with the analysis of 1-dodecanol.

Where comparisons were made, the accuracy by this method for the most part was equivalent to or better than that obtained by the acetic anhydride-pyridine method.

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RECEIVED for review September 30, 1953. Accepted January 4, 1954. Presented before the Division of Analytical Chemistry at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, Chicago, Ill.

Determination of Organic Halogen with Sodium Biphenyl Reagent

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THE determination of organic halogen is one of the common analyses encountered in analytical work and a voluminous literature exists covering many useful methods. All of the methods for the determination of halogens in organic compounds involve first, decomposition of the sample to reduce the halogen to ionizable form, and second, determination of the halide ion by conventional means. For sample decomposition the Parr peroxide bomb, Winter combustion (8), oxygen bomb (1), sodium fusion (3, 4) and sodium in liquid ammonia (7) have all been used in this laboratory for sample decomposition. However, in spite of these and other excellent methods, problems are occasionally encountered for which none of the existing methods is ideally suitable or directly applicable. For a rapid routine control test all of the methods cited are too time consuming. Likewise for samples of low halogen content, in the 0.01 to 1.0% range,

the accuracy of the more common methods leaves something to be desired because of the limitation on sample size.

The use of sodium naphthalene and sodium biphenyl for the determination of organic halogen has been suggested by Benton and Hamill (2) and Pecherer *et al.* (5), respectively. The method described is an extension of the use of reagents of this type in a very simple and rapid analytical procedure. A convenient method for the preparation of the alkali metal biphenyl reagent is described. The limited stability of this type of reagent, which may have been an objection to its use in many laboratories, has been overcome by the manner of storage recommended. The reagent used for decomposition of the organic halide consists of a solution of sodium or lithium biphenyl in ethylene glycol dimethyl ether. Following extraction with water, the halide ion may be determined by conventional volumetric or gravimetric means.

The Volhard chloride titration was used for most of the work described.

EXPERIMENTAL

Apparatus. Standard laboratory apparatus required include 125- or 250-ml. iodine titration flasks, 250-ml. separatory funnels, and burets. A modified separatory funnel as shown in Figure 1 was found convenient for this work. These funnels were made on special order by Corning Glass Co.

Reagents. Biphenyl, minimum melting point 68° C.; halogen-free.

Ethylene glycol dimethyl ether, halogen-free and must contain <0.3% of water.

Toluene, reagent grade.

Sodium metal, c.p.

Nitric acid, c.p., approximately 3*N*.

Silver nitrate approximately 0.1*N*, standardized.

Ammonium thiocyanate, approximately 0.1*N*, standardized.

Indicator, saturated solution of c.p. ferric alum, 1*N* in nitric acid.

Nitrobenzene, reagent grade.

Reagent Preparation. In a dry 2-liter, 3-necked flask equipped with a sealed stirrer of adjustable speed, an inlet for nitrogen gas, and a reflux condenser, place 300 ml. of dry toluene and 58 grams of metallic sodium. With the stirrer off, and with a slow stream of nitrogen passing through the flask, warm until the toluene starts to reflux and the sodium is entirely melted. Start the stirrer and agitate vigorously until sodium is finely dispersed, then cool to 10° C. or below. Remove the reflux condenser and add 1250 ml. of anhydrous ethylene glycol dimethyl ether (Arapahoe Chemical Co.). With the stirrer operating at moderate speed and with a slow stream of nitrogen passing through the flask, add 390 grams of biphenyl. The reaction should commence within a few minutes, as evidenced by a blue or green color which gradually darkens to black. The temperature should be maintained below 30° C. by means of an oil bath or other cooling medium which would not involve hazard should the reaction flask containing metallic sodium break. The reaction should be complete in 1 hour. The reagent must be protected from air and moisture.

Stability of Reagent. The reagent prepared in the manner described, if protected from moisture and air, will have a useful life of 1 to 2 months when stored at 25° C. It has been found convenient in this laboratory to store the main lot of reagent in a number of 250-ml. bottles with foil-lined caps in a refrigerator at 5° C. Stored in this manner the reagent is usable after more than 1 year.

Analytical Procedure. Place 10 to 15 ml. of dry halogen-free toluene (benzene, ether, or other dry, inert, water-immiscible solvent also may be used) in a clean dry separatory funnel. Add the weighed sample to the funnel stopper, and shake to dissolve. Add 20 ml. of biphenyl reagent, stopper, and shake for 30 seconds (invert and carefully vent the funnel after first few seconds). The funnel contents may become warm. A dark green color should remain. If it clears or turns brown, add more reagent. After 5 minutes, extract with 20 ml. of distilled water, agitating cautiously until the excess reagent is destroyed as evidenced by disappearance of the dark green color. Draw off the lower aqueous layer and then extract twice with 50 ml. of dilute (3*N*) nitric acid. To complete the determination, combine the extracted fractions, add 5 ml. of ferric alum indicator, 1 drop of standard thiocyanate, then silver nitrate in excess (about 5 ml.) as indicated by disappearance of the red color. Add 2 ml. of nitrobenzene and shake vigorously to agglomerate the silver halide. Remove stopper, wash the solution from it back into the flask. Backtitrate with thiocyanate to a permanent reddish-brown color. Record buret readings, including the first drop of thiocyanate.

Determine a blank for each lot of reagent by extracting 20 ml. of the sodium biphenyl with water and dilute nitric acid in the manner described, completing the titration in the usual manner.

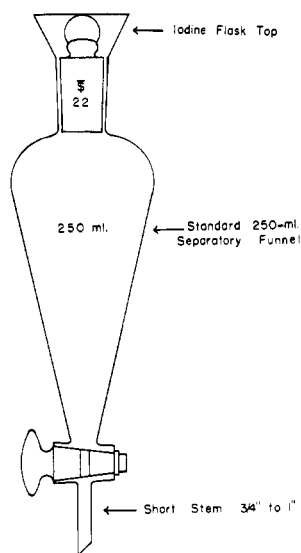


Figure 1. Modified Extraction Funnel

Inside diameter of funnel tip, $\frac{3}{16}$ inch

Notes. The sample size should be selected to contain 0.02 to 0.15 gram of chlorine or its equivalent.

In handling very volatile samples the sample should be sealed in a thin glass ampoule.

It is essential for quantitative halogen recovery, regardless of the nature of the sample, that complete solution be effected. A wide variety of solvents are available such as benzene, various ethers, dioxane, or petroleum solvents such as heptane.

With samples which are difficultly soluble in cold solvents, it may be advisable to dissolve the sample in a separate flask by gentle refluxing with the best available solvent. In some instances it has been satisfactory to reflux the sample with biphenyl reagent and the solvent for a few minutes. The rate of decomposition of the biphenyl reagent is accelerated at elevated temperatures and under such conditions additional reagent may be necessary.

It was found in the course of running a large number of determinations that the usual 250-ml. separatory funnel was not entirely satisfactory, for two reasons: It was difficult to rinse off the glass stopper after successive extractions without losing some wash solution and the funnel stems did not drain. Both of these difficulties made quantitative extraction uncertain. A separatory funnel of the design shown in Figure 1 having an iodine flask-type top and a short stem which is less prone to remain filled with a column of water, was found more satisfactory.

Analysis of Various Compounds. A number of pure chlorine- and bromine-containing organic compounds were analyzed by the described procedure to check the accuracy and range of applicability of this method. The compounds shown in Table I were selected to include both aliphatic and aromatic halogens of varying structure and stability. In Table II are shown the results obtained on a variety of research samples which in general contained the halogen compound as a minor constituent. Results by a recognized alternative method are also shown.

Effect of Reaction Time. Pecherer, Gambrill, and Wilcox (5) have studied reaction times from 10 minutes to 24 hours for the reaction between sodium biphenyl and ethylene bromide and ethylene chloride in gasolines. Their work indicated the halogen recovery to be quantitative at the shortest time studied. Benton and Hamill (2) state "the formation of sodium halide is

Table I. Analysis of Chloro and Bromo Compounds

Compound	Halogen, Wt. %			Sample Source
	Calcd.	Found	Difference, %	
1,4-Dichlorobutane	55.82	55.8 56.0	0.0 +0.2	Wyandotte Chemicals Corp. research lab. sample n_D^{20} 1.457
1,2-Dichloroethane	71.74	71.6 71.8	-0.1 +0.1	Eastman Kodak Co. White Label as received
1-Chloro-3-ethyl-3-methylpentane	23.82	23.8 24.4	0.0 +0.6	Universal Oil Products research sample as received
3-(Chloromethyl) heptane	23.82	24.5 24.5	+0.7 +0.7	Universal Oil Products research sample as received
Ethyl chloroacetate	28.94	29.2 29.3	+0.3 +0.4	Eastman Kodak Co. White Label as received
Hexabromobenzene	86.94	86.4 86.2	-0.5 -0.6	Sample obtained from Dow Research Laboratories
4-Chloroaniline	27.80	27.3 27.6	-0.5 -0.2	Eastman Kodak Co. recrystallized
1-Bromo-4-fluorobenzene	45.67 ^a	45.7 45.9	0.0 +0.2	Eastman Kodak Co. White Label as received
4-Chloro- α,α,α -trifluoro-3-nitrotoluene	15.7 ^b	15.0 14.7	-0.7 -1.0	Hooker Electrochemical Co.
Hexachlorobenzene	74.75	74.7 74.7	0.0 0.0	Hooker technical grade
Hexachlorocyclohexane	73.2	72.2	-1.0	Commercial Solvents, technical grade
1-Bromonaphthalene	38.61	38.5 38.7	-0.1 +0.1	Eastman Kodak Co. as received

^a Bromine only determined.

^b Chlorine only determined.

Table II. Comparison of Sodium Biphenyl Reagent with Other Methods for Analysis of Complex Mixtures

Sample Description	Halogen, %	
	Sodium biphenyl method	Check method
Alkyl chloride in a benzene alkylate	1.09	1.13, oxygen bomb
	1.10	
Alkyl chloride in kerosine	2.31	2.20, oxygen bomb
	2.30	
Alkylbenzyl chloride in an alcohol	11.5	11.3, Parr peroxide bomb
Alkylbenzyl chloride in an ester	1.68	1.63, Parr peroxide bomb 1.56
Sodium chloroethane sulfonate	20.4	21.3, Parr peroxide bomb
Alkylbenzyl quaternary ammonium salt	11.49	11.4, Parr peroxide bomb
	11.35	
Alkylbenzyl chloride	10.7	10.3, Parr peroxide bomb 10.4, gravimetric chloride
	10.8	
Dichloroamine B	31.5	Specification 31% minimum, Wyandotte Chemicals Corp.
	30.9	
1,2-Dichloroethane in approximately 70-20 ethyl alcohol-water solution	6.8	See next sample for verification of result
	6.8	
Synthetic sample similar to above	3.24 meq. Cl found	3.24 meq. Cl present

probably instantaneous." On the basis of the author's experimental work it would appear that the reaction is very rapid. Even a 10-second reaction time was sufficient where the sample was readily soluble and no insoluble reaction products were formed. For quantitative recovery of the halogen the sample should be entirely in solution before the reagent is added. In instances where an insoluble reaction product may be formed, as is the case with 4-chloroaniline, a longer reaction period might prove advisable. For most materials the over-all procedure is very rapid, requiring only the time necessary to carry out the various mechanical manipulations.

DISCUSSION

Reagent Preparation. The method of reagent preparation described offers some advantages over previously described procedures (5, 6). By reducing the metallic sodium to a very finely divided form in toluene the reaction with biphenyl in ethylene glycol dimethyl ether is greatly facilitated. The presence of unreacted sodium in the final reagent is highly undesirable because of the potential danger involved during the water-extraction step of the analytical procedure. The presence of a small amount of toluene in the reagent facilitates separation of the water layer when the analytical procedure is carried out. The use of a sodium dispersion of particle size 20 to 50 microns (obtained from National Distillers Chemicals Corp.) in the preparation of the reagent was investigated. Sodium in this form was found extremely convenient and the reaction with biphenyl was rapid, requiring only 15 minutes in comparison to 60 to 90 minutes for the procedure as outlined. Difficulty was encountered in the use of this reagent because of the formation of an emulsion in carrying out the water extraction step. This was attributed to the presence of traces of oleic acid and pyridine used as a stabilizer in the sample of sodium dispersion. Where substantial quantities of biphenyl reagent are used, however, freshly prepared sodium dispersions which require no stabilizers might be employed to advantage.

The literature (2, 5, 6) mentions several possible solvents for the reagent and the list includes ethylene glycol dimethyl and diethyl ethers, methyl isopropyl ether, dioxane, and tetraethylene glycol dimethyl ether. This study confirmed the results of Pecherer *et al.* (5) that ethylene glycol dimethyl ether is the most satisfactory solvent of those mentioned. The stability of either the biphenyl or naphthalene reagent in the corresponding diethyl ether is very poor. The solubility of sodium biphenyl in dioxane is too low for practical purposes.

Lithium Biphenyl. In connection with the studies on reagent stability, lithium biphenyl was prepared in a manner similar to that described for the sodium compound. This reagent gave quantitative recovery of halogen from monochlorobenzene and hexabromobenzene. Results of stability and storage tests indicate the lithium reagent to be more stable than the sodium reagent. In view of the very good stability of the sodium reagent when stored in a refrigerator at 5° C., there is little to recommend the use of the lithium biphenyl reagent.

Analytical Results. The results shown indicate quantitative recovery of chlorine and bromine within the limit of the method for a wide variety of organic compounds including mono and polyhalogen substituted aliphatics, aromatics, and aromatic halides containing other negative substituents which may render the halide particularly refractory. Benton and Hamill (2) have indicated that the method appears to have broad applications but indicate several compounds which did not give satisfactory results with sodium naphthalene. Compounds for which the method did not appear applicable included 4-chloroaniline, some nitro-substituted aliphatic and aromatic compounds, and hexabromobenzene. In this investigation quantitative recovery of halogen was obtained with all of these compounds using the biphenyl reagent. No chloro or bromo compounds have been found to date for which the reagent is ineffective. Application to fluorine compounds was not investigated. The method is particularly adapted to samples containing small amounts of halogen as there is no limit on sample size, although it is equally satisfactory with small samples having a higher halogen content. The method is less suitable for samples containing large amounts of substances with reactive hydrogen such as water, alcohol, etc. The procedure is particularly suitable for routine work because it is simple, rapid, and readily adaptable to multiple determinations. A single determination can be made in 20 minutes once a stock of reagent has been prepared. For routine work eight samples per hour can be run. The method has been used in the author's research and control laboratories for the past 5 years.

Accuracy and Precision. In making this study the organic compounds analyzed were in general used as received without special purification; accordingly, an exact assessment of the accuracy of the method has not been made. From the results shown, however, the accuracy is probably 2 parts per 100 or better. A precision study of the method in which 12 replicate analyses were made on *p*-dichlorobenzene gave a maximum deviation of 1.5 parts per 100. The Volhard titration method was used throughout this study for the final determination of ionic halogen. With some samples which tend to give colored extracts potentiometric titration can be employed to advantage.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of W. A. Cannon and J. W. Compton in conducting several of the analyses reported herein. Samples supplied by Universal Oil Products Co. and Dow Chemical Co. are also gratefully acknowledged.

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RECEIVED for review August 21, 1953. Accepted December 28, 1953.