The data suggest the possibility of a method of structural analysis for the determination of the position of a substituting group in a complex molecule, and a reverse of this in the prediction of the absorption spectra of compounds of known formula and structure. Additional data on the effects of substituting groups, including those of nitro,[13] chlorine and bromine substitutions, are now being collected with this object in view.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A METHOD FOR THE QUANTITATIVE ANALYSIS OF TIN IN ORGANIC COMPOUNDS

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Introduction

In connection with studies on organotin compounds a need was felt for a convenient method for the quantitative estimation of total tin. The successful method described recently by Gilman and Robinson[1] for the estimation of total lead in organolead compounds suggested a similar technique for the analysis of tin. That method, applied to non-volatile organolead compounds, involved decomposition with concentrated sulfuric and nitric acids in the open. It was soon found to be without value when applied to a variety of alkyl tin compounds because of loss due to spattering and volatilization. We have shown that the method is applicable to the analysis of essentially non-volatile organotin compounds, and prior to our analytical studies Krause and Becker[2] used fuming sulfuric and fuming nitric acids for the analysis of some *aryl* tin compounds.

The obvious convenience of carrying out the analysis in open dishes directed efforts to find reagents that would decompose *all* organotin compounds without risk of losing any of the sample as a consequence of spattering or volatility due to vigorous decomposition incidental to the formation of stannic oxide. Several reagents were tried.[3] A satisfactory

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[13] Brode, *Ber.*, **61**, 1722 (1928).

[1] Gilman and Robinson, THIS JOURNAL, **50**, 1714 (1928).

[2] Krause and Becker, *Ber.*, **53**, 178 (1920). In an article which has just appeared, Fichter and Herzbein, *Helv. Chim. Acta*, **11**, 562 (1928), analyzed tin dichlorodiacetate by hydrolyzing the aqueous solution of the compound with ammonia and ammonium nitrate.

[3] One of these involved a *preliminary* decomposition by concd. hydrochloric acid, followed by the nitric–sulfuric acid oxidation to stannic oxide. In this method the compound is first dissolved in carbon tetrachloride, which is an excellent solvent for organotin compounds. The preliminary decomposition by hydrochloric acid is slower than the preliminary decomposition by bromine. However, satisfactory results were obtained by this method with the few compounds tried. We prefer the bromine method that is more fully described in this paper.

reagent for non-volatile tin compounds, such as tetraphenyltin, was found in a mixture of one part by volume of concd. nitric and six parts of concd. sulfuric acids. This mixture with volatile compounds gave results that were barely acceptable, and the consistently low values indicated a loss of material.

The lesser volatility of organotin halides, their smooth oxidation to stannic oxide, and their ready formation by the addition of bromine to organotin compounds suggested a method based on a preliminary decomposition by bromine in carbon tetrachloride followed by a nitric–sulfuric acid oxidation to stannic oxide. This method has been successfully applied to a wide variety of organotin compounds and has been checked by several workers in this Laboratory. The total time required for an analysis is about six hours, but for a great part of this time (during evaporation and ignition) the analysis requires little or no attention.

Method of Analysis

About 0.5 g. sample of compound is placed in a previously weighed 60-cc. porcelain crucible.[4] The crucible is then partially immersed in an evaporating dish containing cold water.[5] A solution of bromine in carbon tetrachloride (of about 4% concentration) is added slowly with shaking.[6] Two cc. of a concd. nitric (one part) and concd. sulfuric (six parts) acid mixture is then added dropwise[7] with shaking or agitation. A reaction generally sets in with the first few drops of the acid mixture and a white precipitate forms and rises to the surface. After the first few drops of acid mixture have been added it is well to wait for a few minutes until a reaction begins. Thereafter the dropwise addition of acid is regulated by the subsidence of reaction.

In like manner there is then added 3–4 cc. of a 1:1 mixture of concd. nitric and concd. sulfuric acids. With the more volatile and reactive alkyl tin compounds it may be advisable at or prior to this point to replace the warm water in the evaporating dish by cold water. There is then added 2 cc. of concd. nitric acid and 4–5 cc. of fuming nitric acid.

The crucible is then covered by a small watch glass in a manner to permit the ready escape of fumes, and allowed to stand on a steam-plate or its equivalent for about half an hour. The contents are then heated[8] to expel the residual oxides of nitrogen and the carbon tetrachloride until a clear solution is obtained.

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[4] Thorough shaking is difficult in a smaller-sized crucible.

[5] Such cooling is helpful in the decomposition of the more volatile compounds. Also it reduces the time required for the preliminary decomposition of all organotin compounds.

[6] The bromine should be added to a slight excess. The appearance of a brown color is not always evidence of an excess of bromine. The characteristic reddish color of bromine will appear when an excess has been added. The addition of bromine may be omitted with organotin halides of high molecular weight.

[7] The reagents are best added by keeping the tip of the pipet near the side of the crucible and above the edge of the material. During the addition, the contents of the crucible are agitated by a circular motion.

[8] This may be effected by heating in an air-bath, a convenient form of which is provided by placing a clay triangle on an evaporating dish and then heating the dish directly. Or, if time permits, the crucible may be allowed to remain on the steam-plate for a longer period than one-half hour.

The watch glass is now removed and the heat regulated until there is a slow evolution of sulfuric acid fumes. This heating is continued until all of the acid has been expelled. A grayish residue generally results. The crucible is then heated slowly by means of a small direct flame until the evolution of white fumes has practically ceased. A more intense heat is then applied, finally ending with ignition by a Méker burner. The crucible and contents are ignited to constant weight and the tin is estimated as stannic oxide.

The results of some representative analyses follow.

Table I

Results of Analyses

	Sn, %		
Compound	Calcd.	Found	
Tetraethyl tin	50.53	50.66, 50.30	50.54, 50.13
Tetra-*n*-butyl tin	34.21	34.06	34.02
Tri-*n*-butyl tin bromide	32.14	32.39	32.26
Di-*n*-butyl tin dibromide	30.22	29.81	29.99
Triethyl-*p*-bromophenyl tin	32.81	32.33	32.12
Tetraphenyl tin	27.80	27.85	27.95
Triphenyl tin iodide	24.89	24.60	24.82
Triphenyl-*p*-chlorophenyl tin	25.72	25.81	25.74

The authors wish to acknowledge some check analyses carried out by C. C. Vernon and W. L. Wall.

Summary

A method has been described for the quantitative estimation of total tin in a variety of organotin compounds. The method consists of a preliminary decomposition by bromine in carbon tetrachloride followed by a nitric–sulfuric acid oxidation to stannic oxide.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

NATURAL AND SYNTHETIC RUBBER. I. PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF NATURAL RUBBER

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The destructive distillation of rubber has been studied by many investigators. Isoprene and dipentene have been isolated many times, identified and shown to be the predominating products. The existence of other products has often been detected and empirical names have been given to them. Ipatiew and Wittorf[1] have positively identified trimethylethylene; Harries[2] identified myrcene and also a terpene with a boiling point of 168–169°. Heveen (b. p. 252°) was found by Bouchardat[3]

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[1] Ipatiew and Wittorf, *J. prakt. Chem.*, **55**, 2 (1897).

[2] Harries, *Ber.*, **35**, 3662 (1902).

[3] Bouchardat, *Bull. soc. chim.*, **24**, 108 (1875).