zinc. This type of reaction represents a novel characteristic of this well-known catalyst. Nickel also catalyzes the cleavage of dibutyl zinc and diphenylmagnesium with the formation of butane and benzene, respectively.

MADISON, WISCONSIN

SOME ANALYTICAL REACTIONS OF ALKYL SULFIDES IN BENZENE AND PURIFIED NAPHTHA SOLUTIONS[1]

JOHN R. SAMPEY,[2] KENNETH H. SLAGLE[2] AND E. EMMET REID[3]

In a study of possible agents for the removal of alkyl sulfides from hydrocarbons either by adsorption or by a chemical reaction an analytical method for the determination of sulfides, either alone or mixed with other sulfur compounds,[4] was required. Reliability and rapidity were of more importance than extreme accuracy. As the most of our work on sulfur compounds has been done, for the sake of reproducibility, in benzene this hydrocarbon was used as the solvent in this investigation. The method devised has been found to be applicable to solutions in a naphtha such as purified "Skellysolve" but, unfortunately, cannot be used when unsaturates are present.

Alkyl sulfides have usually been estimated by precipitation with mercury salts. Mabery and Smith[5] separated sulfides from Ohio petroleum by agitation of the naphtha with aqueous or alcoholic mercuric chloride. Thierry[6] used the same method to identify several sulfides from Persian oil. Faragher, Morrell and Monroe[7] recommend "normal" mercurous nitrate, $HgNO_3 \cdot H_2O$, to precipitate sulfides quantitatively from naphtha solutions.

[4] The limitations of the method in the presence of mercaptans and disulfides will be presented in a later communication on the estimation of mixtures of mercaptans, sulfides and disulfides in benzene solution.

[5] Mabery and Smith, Am. Chem. J., 13, 233 (1891).

[6] Thierry, J. Chem. Soc., 127, 2756 (1925).

[7] Faragher, Morrell and Monroe, Ind. Eng. Chem., 19, 1281 (1927).

More recently Faragher, Morrell and Comay[8] have made a comprehensive investigation of the interaction of alkyl sulfides and salts of mercury.

While the mercury salt method has been applied successfully to petroleum distillates, it is not applicable to the estimation of alkyl sulfides dissolved in benzene, for the complexes formed by the action of various mercury salts on the sulfides are too soluble in this solvent to give quantitative separations.

In a search for a method of analysis which might apply to benzene solutions, the action of bromine on sulfides gave some promise. G. Patein[9] observed that the bromine addition product of methyl sulfide hydrolyzed readily according to the equation $(CH_3)_2SBr_2 + H_2O = (CH_3)_2SO + 2HBr$. He determined that the hydrolysis went to completion by titration of the hydrobromic acid with caustic potash solution. It remained to be shown that the bromine addition product could be formed quantitatively from sulfides dissolved in a hydrocarbon solvent.

Method of Analysis

The procedure adopted for the analysis of alkyl sulfides in low concentration in benzene as the solvent is as follows.

A saturated solution of bromine water is added drop by drop to a mixture of 50 cc. of distilled water and exactly 50 cc. of a benzene solution of the alkyl sulfide in a 250-cc. glass-stoppered Erlenmeyer flask. The flask is shaken during the bromine treatment, and the addition is continued slowly until the color of bromine persists in the solution. Not more than two drops excess of the bromine water should be added, and this should not be permitted to remain longer than one-fourth of a minute before it is removed by the addition of a slight excess of a saturated solution of potassium iodide. The liberated iodine is then reduced with a saturated sodium thiosulfate solution. The aqueous layer is separated from the benzene layer, and the hydrobromic acid in the latter is extracted three times with 20-cc. portions of distilled water; these extracts are added to the original solution, and the hydrobromic acid content is determined by titration with $n/20$ sodium hydroxide solution, using brom cresol purple or a purified litmus solution as indicator.

Attention is invited to two precautions and one correction factor to be applied to the method. The excess bromine must be removed completely by the potassium iodide solution, for otherwise the bromine water will attack the thiosulfate solution and cause the formation of two strong acids according to the equation[10]

$$Na_2S_2O_3 + 4Br_2 + 5H_2O = H_2SO_4 + 8HBr + Na_2SO_4$$
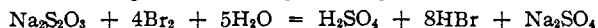
The second precaution is similar. The iodine liberated from the potassium iodide must be removed completely by the thiosulfate solution to prevent it from acting upon the sodium hydroxide. The Erlenmeyer flask must be shaken vigorously, therefore, after the addition of the excess potassium iodide solution, and again after the introduction of the thiosulfate solution.

The correction factor which must be applied arises from the acid present in the bromine water. The exact amount of bromine water used during the oxidation must be

[8] Faragher, Morrell and Comay, THIS JOURNAL, **51**, 2774 (1929).

[9] Patein, *Bull. soc. chim.*, [2] **50**, 203 (1888).

[10] Mellor, "Inorganic Chemistry," Vol. II.

noted, and its acid content determined by shaking a like amount, dissolved in 50 cc. of water and 50 cc. of benzene, with excess potassium iodide and thiosulfate solutions, and titrating the acid.   The figure thus obtained must be subtracted from the total number of cubic centimeters of alkali used in the estimation of the sulfide.

Results of Analyses

The results of the analyses with several different alkyl sulfides, and with varying concentrations of n-butyl sulfide, are given in Tables I and II. The solutions in Table I were prepared by weighing out in a stoppered weighing bottle the calculated amount of sulfide to give a liter of solution of 0.0500% sulfur by weight; 50-cc. portions of these solutions were pipetted for the bromine water treatment into 250-cc. glass-stoppered flasks.   The samples of alkyl sulfides were supplied by Dr. L. M. Ellis, Jr.

TABLE I
ACTION OF BROMINE WATER ON ALKYL SULFIDES

Sulfide	S present, %	S found, %	Error, %
Ethyl	0.0500	0.0498	−0.4
	.0500	.0499	−0.2
Isopropyl	.0500	.0504	+0.8
	.0500	.0503	+0.6
n-Propyl	.0500	.0495	−1.0
	.0500	.0495	−1.0
Isobutyl	.0500	.0496	−0.8
	.0500	.0496	−0.8
n-Butyl	.0500	.0497	−0.6
	.0500	.0496	−0.8

The first three solutions in Table II were prepared by making up weighed quantities of the sulfide to one liter.   The fourth solution (0.0045% S) was made by pipetting 5 cc. of the 0.0500% S solution into 50 cc. of benzene.

TABLE II
CHANGE IN CONCENTRATION OF n-BUTYL SULFIDE

S present, %	S found, %	Error, %	S present, %	S found, %	Error, %
0.2000	0.2002	+0.1	0.0500	0.0497	−0.6
.2000	.2004	+0.2	.0500	.0496	−0.8
.1000	.1002	+0.2	.0045	.0045	0.0
.1000	.1000	0.0	.0045	.0046	+2.2

Application to a Naphtha Solution Free from Unsaturated Hydrocarbons.

—As was to be expected, alkyl sulfides cannot be estimated by the bromine water method when unsaturated hydrocarbons are present.   An attempt was made to analyze a benzene solution of n-butyl sulfide in the presence of amylene.   Twenty-five cc. of benzene containing about one per cent. of β-n-amylene (Eastman) was added to 25 cc. of a benzene solution of n-butyl sulfide (0.0500% S).   This solution decolorized several times as much bromine water as that required for the oxidation of the sulfide.

The bromine water method was found applicable to a naphtha solution of n-butyl sulfide which was free from unsaturated hydrocarbons. "Skellysolve C," essentially normal heptane, boiling range 90 to 100°, of water white color, and sulfur free (Doctor Test), purchased from the Skelly Oil Company, was freed from a small amount of unsaturated hydrocarbons by prolonged agitation with concentrated sulfuric acid; the acid was washed out, and the naphtha steam distilled and dried. Twenty-five cc. of this purified naphtha was added to 25 cc. of a benzene solution of n-butyl sulfide containing 0.1000% sulfur. Duplicate analyses by the bromine water method gave results which were 0.2 and 0.4% higher than those obtained in the benzene solution alone.

Summary

1. A method has been devised for the estimation of alkyl sulfides dissolved in benzene.

2. The method is applicable to a naphtha solution free from unsaturated hydrocarbons.

BALTIMORE, MARYLAND

SOME ANALYTICAL REACTIONS OF ALKYL MERCAPTANS IN BENZENE SOLUTION[1]

BY JOHN R. SAMPEY[2] AND E. EMMET REID[3]

It has been customary to estimate mercaptans by an iodimetric method.[4] In an examination of this method as applied to dilute solutions in benzene, it has been found that the time allowed for the oxidation is an important factor. The present paper describes also a study of two additional methods for the estimation of mercaptans in dilute concentrations in hydrocarbon solvents. One of these methods involves the titration of the hydriodic