

Microdetermination of Arsenic in Organic Compounds by Iodometry

SIR: A method for the micro-Carius determination of arsenic is described by Steyermark (6) in which the sample is digested with fuming nitric acid to form quinquevalent arsenic (AsO_4^{-3}). The arsenic content is then found by an iodometric titration.

This paper presents the modifications that were found necessary to achieve precise and accurate results.

EXPERIMENTAL

Procedure for Standardization of Sodium Thiosulfate. Dissolve 2 to 3 mg. of solid potassium biiodate in 4 ml. of distilled water in a 125-ml. glass-stoppered Erlenmeyer flask. Add 1.5 ml. of 1:14 hydrochloric acid, then add 2 ml. of 10% potassium iodide, and stopper the flask. After 2 minutes, titrate the liberated iodine with 0.01N thiosulfate solution using starch indicator.

Arsenic Analysis. Place 5 to 10 mg. of sample in a clean, dry, micro-Carius combustion tube. Introduce approximately 25 mg. of potassium chloride and 0.5 to 0.7 ml. of fuming nitric acid and seal. Then heat the tube in a micro-Carius oven for 10 hours at 300° C. After cooling, transfer the contents quantitatively to a 30-ml. beaker, using a rubber policeman if necessary, and evaporate to dryness on a steam bath. Now transfer the arsenic acid residue to a 125-ml. glass-stoppered Erlenmeyer flask with 10 ml. of 5N hydrochloric acid. Flush the space above this solution with a rapid stream of nitrogen for 1 minute, and immediately add 2 ml. of 10% potassium iodide, and stopper. Let the mixture stand 10 minutes, then add 12 ml. of distilled water and titrate the free iodine with standard thiosulfate solution using starch indicator. No blank correction is required when nitrogen flushing is employed. However, a blank correction of 0.04 to 0.08 ml. is necessary when the determination is made in the presence of air.

RESULTS AND DISCUSSION

To evaluate the procedure several arseno-organic compounds of varying composition were chosen for analysis after their purity had been ascertained by a carbon and hydrogen analysis. None of these compounds yielded correct values for arsenic using the Steyermark procedure (Table I, column I). Because incomplete destruction of the arseno-organic compound was suspected, the digestion temperature and time were increased to 300° C. for 10 hours. Following this relatively more severe treatment, all solutions remained clear upon the addition of potassium iodide and the end points became sharp. Nevertheless, low results were obtained

Table I. Comparison of Percentage Arsenic Found by Micro-Carius Method at Different Temperatures, with and without Presence of Alkali-Metal

Sample	Theory	I	II	III	IV ^a
		250° C., 8 hr., KCl absent	300° C., 10 hr., KCl absent	300° C., 10 hr., KCl present	300° C., 10 hr., KCl present
As_2O_3	75.73	71.99	71.32		76.04
		72.01	72.17		75.66
					75.59
					75.66
$\text{C}_6\text{H}_5\text{CH}_2\text{AsO}_3\text{H}_2$	34.67	31.12	24.06	34.97	34.50
		31.63	27.03	35.10	34.49
$\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$	37.08	36.62	26.08		36.91
		34.06	25.44		36.88
		35.26			36.97
		35.21			
$\text{HO}(\text{C}_6\text{H}_4)_2\text{AsO}(\text{OH})_2$	34.36	30.76	25.88	34.94	34.46
		31.70	25.14	34.94	34.42
$(\text{C}_6\text{H}_5)_3\text{As}$	24.46	turbid	19.74	25.28	24.40
				25.05	24.46
				25.25	24.51
				24.93	24.49
$[(\text{C}_6\text{H}_5)_3\text{AsCH}_3]\text{I}$	16.72	turbid		17.03	16.83
				17.16	16.72

^a With scaled-down Kolthoff procedure for determination of normality of thiosulfate.

(Table I, column II) and the presence of an easily noticeable, insoluble residue was observed on the inside wall of the micro-Carius tubes.

In an earlier paper, DiPietro, Kramer, and Sassaman (2) reported that the formation of phosphorus and arsenic deposits on the inside wall of micro-Carius tubes was prevented by the addition of an alkali metal salt to the reaction mixture. In the present study no sign of an arsenic residue was found on the wall of the Carius tube when the sample was digested at a temperature of 300° C. for 10 hours with approximately 25 mg. of potassium chloride and the usual amount of fuming nitric acid. Although samples analyzed after these modifications provided clear solutions and sharp end points, the arsenic values were still unacceptable, now ranging from 0.3 to 0.7% higher than theory (Table I, column III).

The error could not be accounted for by a blank on the reagents for this was constant and well within established limits. Cause for the error was sought, therefore, either in the iodometric procedure used for the analysis of arsenic following the digestion, or in the standardization of thiosulfate.

In the Steyermark procedure for arsenic, the free iodine is developed in an approximately 7.5N hydrochloric acid solution. However, Smith (5), in a theoretical treatment of the arsenate-iodide reaction, suggests a 4N hydrochloric acid solution for the oxidation of iodide and diluting to 2N before titrating with thiosulfate. These are

Table II. Comparison of Normalities

Numerical sequence	Procedure	
	I ^a	II ^b
1	0.01008	
2	0.01006	
3	0.01008	
4		0.01016
5		0.01024
6		0.01016
7	0.01008	
8		0.01021
9	0.01009	
10		0.01021
Av.	0.01008	0.01020
Std. dev.	0.00001	0.000033

^a Scaled-down Kolthoff procedure.

^b Steyermark procedure.

the optimal conditions, according to Smith (5), because acidities higher than 4N tend to promote an increase in the so-called oxygen error and to accelerate the rate of thiosulfate decomposition, both of which lead to high arsenic values.

Accordingly, the digested arsenic sample was dissolved in 10 ml. of 5N hydrochloric acid and 2 ml. of 10% potassium iodide solution were added. After 10 minutes 12 ml. of water were added and titration with standard thiosulfate was completed. Although these results were again 0.3 to 0.7% high, the procedure was retained because the modifications eliminated the necessity of preboiling hydrochloric acid and facilitated the transfer of sample.

With evidence of consistently high results, in spite of variations within

controlled limits of both the potassium iodide and hydrochloric acid concentrations, attention was focused on a possible error in obtaining the normality of the thiosulfate solution. Normalities of the thiosulfate solution determined by a scaled-down macro procedure of Koltzoff (3) and Clark (1) were compared with those determined by Steyermark's procedure (6). The values shown in Table II were obtained the same day and in the order shown. Data for the Steyermark procedure show a higher value of the normality and also a greater deviation in the results.

Although this deviation may explain some erratic results obtained earlier, even more significant is the large difference in normality of the thiosulfate solution found by the two methods. The normalities recorded in Table II reveal an average difference of 12 parts per thousand, which is equivalent to

0.9% arsenic in the case of arsenious oxide. No serious attempt was made to determine the cause of this discrepancy in the normality values, but the moderately high hydrochloric acid concentration employed by Steyermark is favorable to the formation of one of the mixed halogens (4). Any iodine thus removed would tend to increase the normality of the thiosulfate.

With the normality found by the scaled-down procedure all determinations were repeated and the results are shown in Table I, column IV. These results are well within the acceptable limits ($\pm 0.2-0.3\%$) and the values for an N.B.S. arsenious oxide sample agreed with theory.

ACKNOWLEDGMENT

The authors are indebted to Charles Merritt, Jr., for helpful suggestions in the preparation of this manuscript.

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