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THE ANALYSIS OF LITHIUM ARSENIDE

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ABSTRACT

A method is described for the quantitative determination of lithium and arsenic in lithium arsenide. The sample is treated with distilled water in a special apparatus, the arsine formed is absorbed in bromine water, and the lithium in the residual aqueous solution is determined by titration with standard acid. The entire sample is then combined, the excess bromine is boiled off, and hydrazine hydrochloride and potassium bromide are added. The arsenic is distilled as arsenic trichloride after the solution has been made approximately 6 N in hydrochloric acid, and the arsenic is determined by potentiometric titration with standard potassium bromate solution. An average recovery of 100.1 percent, with a standard deviation 0.1 percent, was obtained for 32 determinations of 17.86 milligrams of lithium in the presence of 11 to 100 milligrams of arsenious oxide. An average recovery of 100.0 percent, with a standard deviation of 0.6 percent, was obtained for 21 determinations of 17 to 155 milligrams of arsenic; the method is less reliable for smaller quantities of arsenic.

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INTRODUCTION

The problem initiating this work was the necessity for analyzing materials consisting essentially of a hetereogeneous mixture of elementary lithium, elementary arsenic, monolithium arsenide and trilithium arsenide. The inhomogeneity of the materials made advisable reducing them to a powder before weighing samples for analysis and using macro-size samples and macro amounts of each element. It was also indicated that a quantitative separation of the elements would be desirable, if not actually necessary, before each was measured. A survey of the literature indicated that existing procedures for both lithium and arsenic(1,3) would probably be satisfactory once a separation of the two elements was made. The main problem, then, appeared to be one of quantitatively separating the two elements, after first dissolving the materials under conditions that would prevent the loss of arsenic as arsine.

Although the arsenides of lithium both react with water to form lithium hydroxide and arsine, the reactions are not quantitative. In addition, the possible presence of elemental arsenic precluded the possibility of separating the two elements in this manner. In view of this condition, it was thought that quantitative distillation of the arsenic as the trichloride might be made applicable to macro amounts of the element. Conditions were found under which this could be done.

The determination of lithium appeared possible by a simple acid-base titration providing the arsenite ion, which always seemed to be present after dissolving the sample in water, did not interfere. This was tried and found to be the case. The only effect of the arsenite ion on the titration seemed to be a slight broadening of the end point due to a buffering action.

APPARATUS AND REAGENTS

Apparatus

Solution Apparatus. The apparatus, as shown in Figure 1, was composed of a round-bottomed, three-necked reaction flask, attached to a series of four scrubbers, an air inlet tube reaching near the bottom of the flask, and a dropping funnel. Scrubbers A, B, and C were half-filled with bromine water to collect the arsine evolved in the solution process. The fourth scrubber, D, contained a concentrated solution of sodium hydroxide to trap bromine vapors and prevent them from being carried into the house vacuum system. Carbon dioxide-free air was aspirated through the assembly to sweep the arsine into the scrubbers. (In order to determine if the scrubbers would trap all of the arsine, a solution of mercuric chloride was placed in the fourth scrubber and a lithium arsenide sample was dissolved in water in the reaction flask. After several hours of sweeping, the absence of the red-brown precipitate which mercuric chloride forms with arsine indicated that the first three scrubbers efficiently trapped the arsine.)

Distillation Apparatus. This apparatus, as shown in Figure 2, consisted of a 500-ml., round-bottomed, four-necked flask, a condenser, a dropping funnel, and a helium-entry tube. The flask was connected to the condenser by a tube having a standard taper joint that would accommodate a thermometer. The dropping funnel, which was used for adding hydrochloric acid during the distillation, and the helium-entry tube both reached nearly to the bottom of the flask. The fourth neck of the flask was used for the introduction of the sample. The adapter tube of the condenser dipped into the distilled water in the receiving beaker which was chilled in an ice bath. Standard taper joints were used throughout.

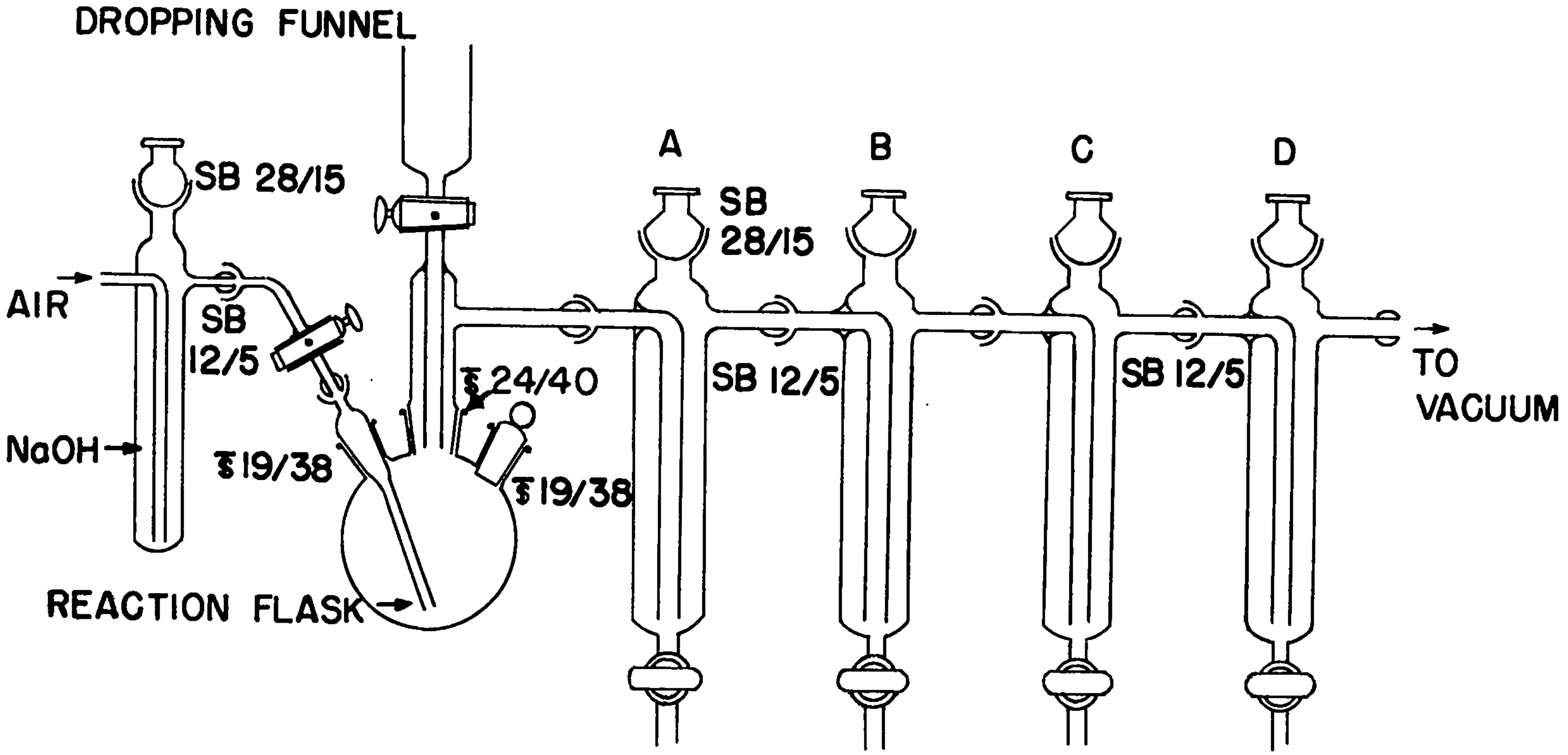

Figure 1. Solution Apparatus

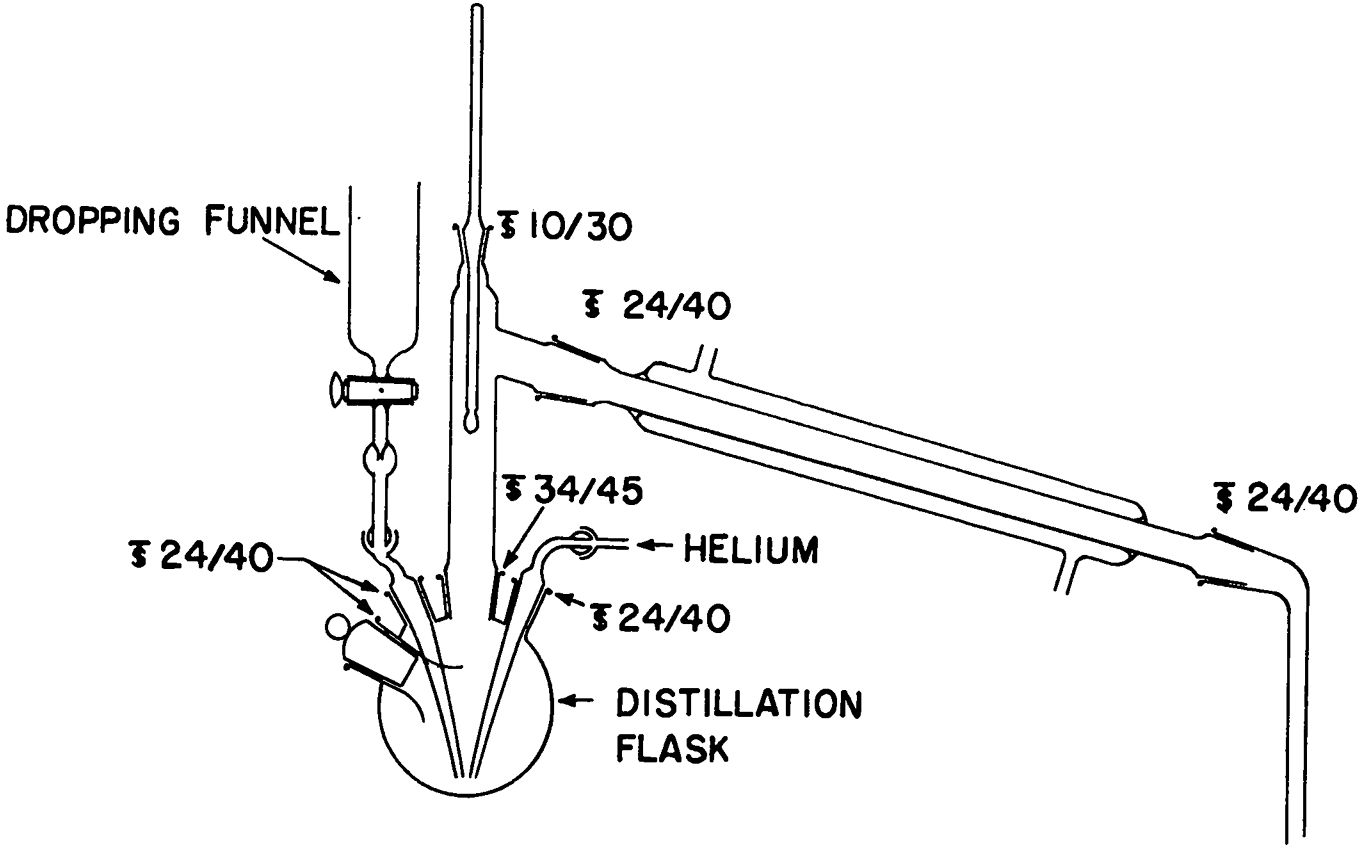

Figure 2. Distillation Apparatus

Titration Apparatus. The titration apparatus consisted of a Beckman Model G pH meter, equipped with platinum-calomel electrodes, and the usual laboratory volumetric glassware.

Reagents

Arsenious Oxide, oxidimetric standard, National Bureau of Standards.

Arsenic Oxide, analytical grade, Baker Chemical Company.

Bromine Water, saturated.

Hydrazine Hydrochloride, Eastman White Label.

Hydrochloric Acid Solution, 6 N, analytical reagent grade.

Hydrochloric Acid Solution, 0.1 N, standardized against sodium carbonate.

Indicator, Mixed. Dissolve 0.1 gram methyl red and 0.1 gram bromocresol green in 100 ml. of 95 percent ethanol. This indicator is green in base, pink in acid, and gray at the end point.

Indicator, Two End Point. Dissolve 0.1 gram methyl red, 0.1 gram bromocresol green and 1 gram of phenolphthalein in 100 ml. of 95 percent ethanol. This indicator changes from deep red to green at approximately pH 7.8 and green to gray at approximately pH 5.1.

Lithium Hydroxide Standard Solution. Dissolve approximately 0.7 gram of lithium metal in distilled water and dilute to 1 liter. Standardize the solution by titrating aliquots with a standard hydrochloric acid solution. The solution used in this work contained 17.86 mg. of lithium per 25-ml. aliquot (0.7144 mg./ml.).

Potassium Bromate Solution, 0.1 N. Dissolve 2.7835 grams of the dried salt in 1 liter of water. This solution may be standardized against arsenious oxide(2) although the dried salt may be considered as a primary standard.

EXPERIMENTAL WORK

The Effect of the Arsenite Ion on the Determination of Lithium

A study was made to determine the effect of the arsenite ion on the titration of lithium hydroxide with standard hydrochloric acid. Weighed amounts of arsenious oxide from 11 to 100 milligrams were dissolved in 25-milliliter aliquots of a standard lithium hydroxide solution, and the aliquots were titrated with standard hydrochloric acid using the mixed indicator described under Reagents. The average value for the lithium found in 32 determinations was 17.87 milligrams, with a standard deviation of 0.01 milligram; the lithium taken was 17.86 milligrams. These data are given in Table II under EXPERIMENTAL RESULTS. Because of the buffering action of the arsenite ion, a slight broadening of the end point was observed; no other effect was noticed.

The Effect of Condenser Deposit on the Recovery of Arsenic

During some distillations of relatively large amounts of arsenic, a brown deposit collected in the upper part of the condenser tube. Spectrographic analysis of this deposit showed that it contained arsenic. It was found that the distillation of a few milliliters of bromine water through the apparatus would dissolve this condenser deposit and that the arsenic could be recovered by reducing and redistilling the resulting solution. The deposit did not form in significant amounts when less than 100 milligrams of arsenic were being distilled. To determine the efficiency of the recovery of the arsenic in the condenser, a series of determinations was performed using samples which contained from 78 to 160 milligrams of arsenic. Whenever a condenser deposit formed, it was dissolved with bromine vapor, reduced with hydrazine hydrochloride and redistilled. As shown in Table I, as much as 1.9 milligrams of arsenic were recovered by this redistillation step for samples containing 150 to 160 milligrams of arsenic. When the arsenic content of the condenser deposit was included in the amount of arsenic found, an average recovery of 99.8 percent with a standard deviation of 0.4 percent was obtained for 25 determinations. The results indicate also that essentially all of the arsenic is distilled in the first 300 milliliters of distillate except for the arsenic trapped in the condenser deposit.

Table I

THE EFFECT OF THE CONDENSER DEPOSIT ON THE RECOVERY OF ARSENIC

Arsenic taken, mg.	Arsenic found, mg.			Arsenic found, %
	1st 300 ml. of distillate	2nd 100 ml. of distillate	Condenser deposit	
78.0	77.78	0.00		99.7
79.0	78.84	0.08		99.9
79.2	78.9	0.07		99.7
79.8	79.14	0.08		99.3
80.2	79.37	0.38		99.4
152.8	152.53	0.08	None	99.9
153.1	151.24	0.43	None	99.2
153.3	152.30	0.23	0.53	99.9
154.4	153.2	0.31	None	99.4
154.4	154.27	0.00	None	99.9
154.7	152.61	0.60	1.14	99.8
154.9	154.58	0.07	0.08	99.9
155.0	154.27	0.23	None	99.7
155.0	154.5	0.08	0.37	100.0
155.1	154.95	0.16	None	100.0
155.2	153.21	0.08	0.91	99.4
155.6	155.03	0.08	Lost	99.7
156.0	154.95	0.13	0.30	99.7
156.1	156.32	0.00	None	100.2
156.4	155.64	0.00	0.68	100.0
157.9	157.38	0.30	0.61	100.2
158.7	156.85	0.30	1.89	100.2
159.2	159.88	0.15	None	100.5
159.6	158.29	0.07	Lost	99.2
160.7	160.56	0.23	0.30	100.2

Average arsenic found 99.8%
Standard deviation 0.4%

RECOMMENDED PROCEDURE

Operation

Because of the reactivity of lithium arsenide, all sample preparation prior to the actual analysis must be performed in a dry, inert atmosphere. A dry box filled with inert gas which is continually dried over magnesium perchlorate or some other equally efficient drying agent should be used. The samples, as received, may be inhomogeneous and must be ground and mixed before analyses are performed. A large mortar and pestle is satisfactory for the grinding operation, and any efficient mechanical blender may be used for sample mixing. After the sample has been mixed for several hours, it is pressed into pellets weighing 100 to 200 milligrams in a pellet press and stored in weighing bottles in the dry box until the time of analysis.

Analysis of Sample

1. Remove the weighing bottle containing the sample pellets from the dry box, wipe the surface of the bottle with moist cotton gloves, and place in the balance case.

2. After 5 minutes, weigh the bottle and contents to the nearest 0.1 mg.

3. Replace the bottle in the dry box and transfer a pellet to a small stoppered bottle.

4. Remove the weighing bottle and the small stoppered bottle containing the sample from the dry box, and reweigh the weighing bottle as described in Steps 1 and 2. (The difference between the two weights is the sample weight.)

5. Half fill the first three scrubbers of the solution apparatus with bromine water.

6. Transfer the sample to the clean dry reaction flask of the solution apparatus and quickly stopper the flask.

7. Adjust the flow of air in the apparatus so that the air bubbles slowly through the scrubbers.

8. Add distilled water dropwise through the dropping funnel until the reaction stops. (A clear solution results if the water is added dropwise; the solution is brown if the water is added too rapidly.)

9. Sweep the apparatus with the slow stream of air for 2 hours after the reaction stops.

10. Filter off the black residue in the reaction flask on a fine glass filter, wash with water, and titrate the filtrate with standard hydrochloric acid to the steel gray end point of the mixed indicator.*

11. Calculate the percentage of lithium as follows:

$$\frac{\text{ml. of HCl} \times N \times 0.00694 \times 100}{\text{sample weight in grams}} = \text{percent lithium}$$

12. Dissolve the black residue from Step 10 in bromine and bromine water, and combine it with the solutions from the first three scrubbers and the lithium solution.

13. Boil the solution until it is free of bromine and allow it to cool.

14. Add approximately 1 gram of hydrazine hydrochloride and a few crystals of potassium bromide.

15. Add to the solution an equal volume of concentrated hydrochloric acid and transfer it to the distillation flask.

16. Adjust the helium to give a very slow flow of gas through the apparatus.

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*If a determination of the carbonate content of the sample is desired, use the two end point indicator described under <u>Reagents</u>. The carbonate may be calculated from the milliliters of acid used between the two end points, D, and the normality of the acid, N, as follows:

$$\frac{2D \times N \times 60.01 \times 100}{\text{sample weight in grams}} = \text{percent carbonate}$$

17. Carry out the distillation, collecting 300 ml. of distillate in 100 ml. of water in a 600-ml. beaker cooled in an ice bath. (At this altitude, 7300 feet, the arsenic trichloride distills over at 101°C.)

18. During the distillation add 6 N hydrochloric acid through the dropping funnel as needed to maintain the volume essentially constant.

19. When 300 ml. of distillate have been collected, change receiving beakers and collect another 100 ml. of distillate.

20. If a brown deposit forms in the condenser, add some bromine water to the distilling flask, distill over the bromine, and flush out the system with helium; then transfer this distillate to the distilling flask, add more hydrazine hydrochloride, and distill another 100 ml.

21. Titrate the combined distillates with standard bromate solution using a Beckman Model G pH meter with platinum-calomel electrodes to detect the equivalence point.

22. Calculate the percentage of arsenic as follows:

$$\frac{\text{ml. of } KBrO_3 \times N \times 0.03746 \times 100}{\text{sample weight in grams}} = \text{percent arsenic}$$

EXPERIMENTAL RESULTS AND RELIABILITY OF METHOD

Because no standard samples of lithium arsenide were available, two sets of known samples were prepared and analyzed to determine the reliability of the described procedure. In the first set, samples of lithium with known amounts of arsenious oxide were prepared. Solutions containing 17.86 milligrams of lithium and from 11 to 100 milligrams of arsenious oxide were titrated with standard hydrochloric acid. The results, as given in Table II, show an average value of 17.87 milligrams for the lithium content of the samples with a standard deviation of 0.01 milligram.

Table II

DETERMINATION OF LITHIUM IN PRESENCE OF ARSENITE ION
(Lithium taken in each case, 17.86 milligrams)

Determination No.	Li found, mg.	As_2O_3 added, mg.	Determination No.	Li found, mg.	As_2O_3 added, mg.
1	17.86	11.4	17	17.85	34.8
2	17.87	11.8	18	17.88	36.3
3	17.87	11.9	19	17.85	38.3
4	17.89	12.2	20	17.88	40.4
5	17.86	13.4	21	17.87	41.7
6	17.85	13.5	22	17.88	43.2
7	17.88	19.3	23	17.90	46.6
8	17.88	20.3	24	17.87	49.5
9	17.88	20.5	25	17.88	51.2
10	17.85	21.3	26	17.89	52.7
11	17.86	21.8	27	17.88	54.1
12	17.86	23.4	28	17.89	56.4
13	17.88	24.5	29	17.87	58.5
14	17.86	30.6	30	17.88	59.5
15	17.89	32.0	31	17.89	75.2
16	17.86	33.0	32	17.87	100.0

Average lithium found 17.87 mg.
Standard deviation 0.01 mg.

The second set of known samples consisted of basic solutions in which weighed amounts of arsenic pentoxide or arsenious oxide were dissolved. Each known sample was analyzed according to the RECOMMENDED PROCEDURE, Steps 14 through 22. The results of these analyses, as given in Table III, show no significant difference in the recovery of arsenic from comparable amounts of arsenious oxide or arsenic pentoxide. High recoveries were obtained for small amounts of arsenic. When determinations 1 and 2 were omitted, an average recovery of 100.0 percent with a standard deviation of 0.6 percent was obtained for the remaining 21 determinations of 17 to 155 milligrams of arsenic.

Table III

RECOVERY OF ARSENIC FROM KNOWN SAMPLES

Determination No.	Compound used	Arsenic taken, mg.	Arsenic found, mg.	Arsenic found, %
1	As_2O_3	3.48	3.63	104.3
2		3.48	3.70	106.3
3		17.4	17.40	100.0
4		17.4	17.50	100.6
5		17.4	17.55	100.9
6		17.4	17.50	100.6
		Average		102.1
		Standard deviation		2.6
7	As_2O_3	38.8	39.0	100.6
8		39.2	39.4	100.5
9		40.5	40.7	100.5
10		42.2	41.9	99.3
11		76.5	76.4	99.9
12		77.0	76.9	99.9
13		77.3	77.3	100.0
14		153.3	153.3	100.0
15		153.5	153.7	100.1
16		153.8	153.6	99.9
17		154.4	154.3	100.0
		Average		100.1
		Standard deviation		0.4
18	As_2O_5	35.4	35.8	101.1
19		66.2	65.7	99.1
20		67.7	67.2	99.1
21		67.9	67.2	99.8
22		69.2	68.6	99.1
23		79.7	79.1	99.2
		Average		99.6
		Standard deviation		0.8

SUMMARY

Using the analytical procedures described for the determination of lithium and arsenic, an average recovery of 100.1 percent, with a standard deviation of 0.1 percent, was obtained for 32 determinations of 17.86 milligrams of lithium in the presence of 11 to 100 milligrams of arsenious oxide. The recovery of 17 to 155 milligrams of arsenic from 21 known samples averaged 100.0 percent, with a standard deviation of 0.6 percent; high results were obtained for smaller quantities of arsenic. The lithium determination was not significantly affected when the amount of arsenious oxide was varied from 11 to 100 milligrams, and lithium had no effect on the determination of arsenic. The possible effects of other elements on the determination of lithium and arsenic were not investigated.

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