

Technical Notes

Room-Temperature Isopiestic Distillation of in Situ Generated Arsenious Chloride and Its Application for the Determination of Trace Level Impurities in Arsenious Oxide

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The room-temperature vapor pressures of HCl and AsCl₃ in the presence of hydrochloric acid have been utilized in situ for the removal of arsenious oxide matrix as AsCl₃ by isopiestic distillation. Reagent purification, sample dissolution, and matrix separation have been carried out in one step with a clean environment for both analyte and analyst. Quantitative recoveries have been achieved for most of the elements including volatile elements. Blank levels were found to be in nanograms per gram of As₂O₃ despite use of common reagents and simple reaction vessel. The utility of the present method for the analysis of As₂O₃ samples has been demonstrated.

The presence of impurities at trace levels in semiconductor materials such as Ga and As affect their properties. Arsenious oxide is used as a precursor for the manufacture of high-purity arsenic. Hence, analysis of As₂O₃ for a large number of impurities at extremely low levels is required, for which matrix separation with minimum contamination is desirable. Among the separation methods, matrix volatilization is commonly used due to retention of large number of impurities with lower blanks. Volatilization of As as As₂O₃ or AsCl₃ from acid solution or acid vapors is reported at elevated temperatures.^{1–3} Major disadvantages of these procedures are the use of a complicated volatilization setup, loss of volatile elements, and higher blanks due to the use of large quantities of acids or its vapors generated externally. Reduction in blank levels can be achieved using vapor-phase digestion. A dual-vessel vapor-phase digestion of silicon-rich matrix on a water bath at atmospheric pressure is reported in which drastic reduction of blank levels has been achieved.⁴ However, the same cannot

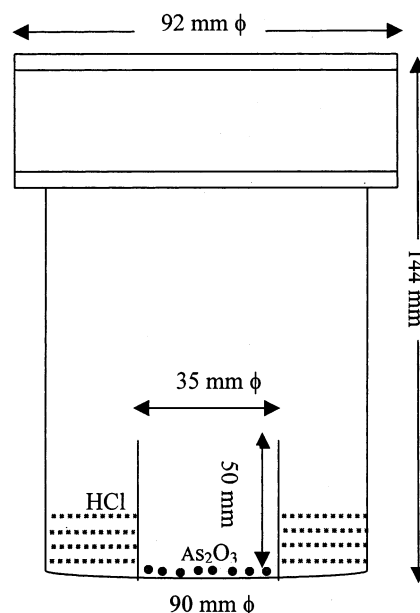


Figure 1. Isopiestic distillation setup.

be applied if the matrix also needs to be removed along with retention of volatile elements. Therefore, there is a need for a low-temperature matrix dissolution and volatilization procedure. Isopiestic distillation is being used for the preparation of high-purity reagents,^{5,6} and its capability for matrix removal is yet to be demonstrated. In the present procedure, dissolution and separation of As₂O₃ matrix through isopiestic distillation is reported.

EXPERIMENTAL SECTION

Analytical Procedure. Arsenious oxide sample (2–5 g) was taken in a polypropylene (PP) sample container, which is placed in an outer container (PP) having 50 mL of concentrated HCl, and the outer container was closed (Figure 1). After 24 h, the

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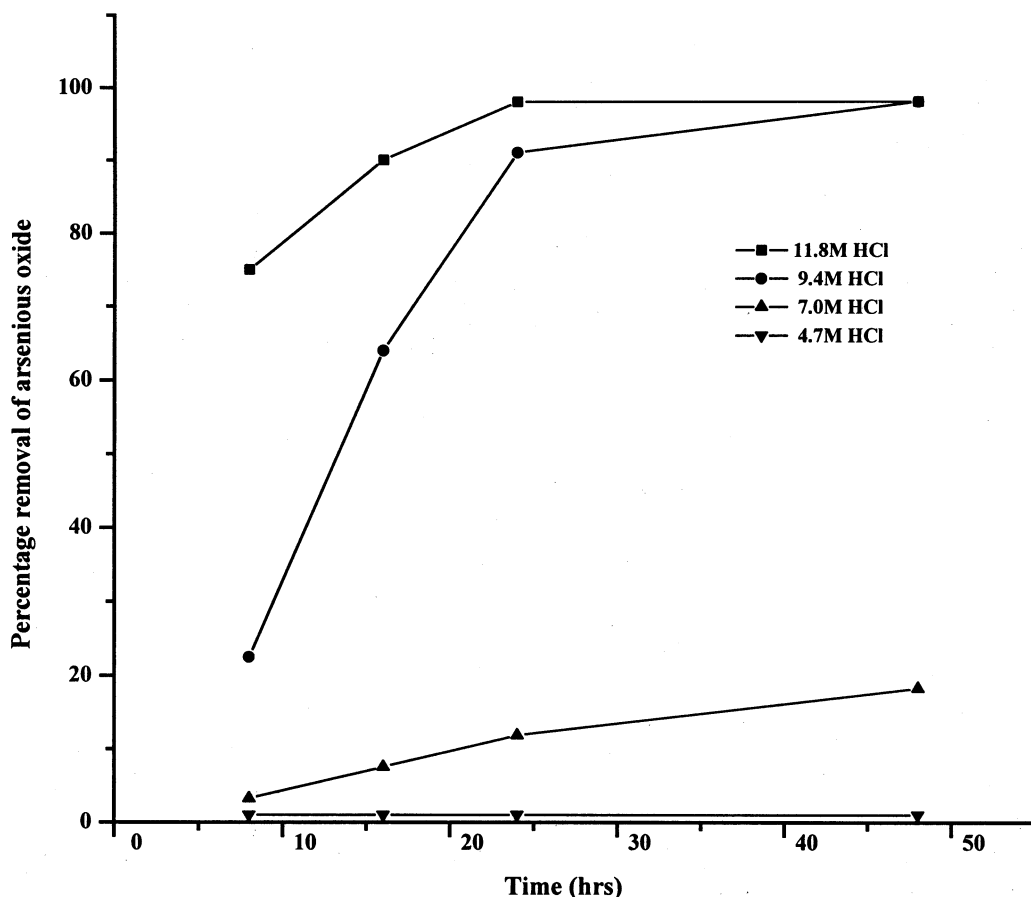


Figure 2. Percentage removal of arsenious oxide with time at various concentrations of HCl (ambient temperature 30 °C)

outer container was opened in a fume hood, the inner container was taken out with Teflon tongs, and the residual liquid was diluted to the required volume with Milli-Q water and analyzed by inductively coupled plasma- atomic emission spectrometer (ICP-AES model JY-2000, Jobin Yvon) using aqueous standards. Blank solution was also prepared in the same way. Equilibration was repeated with fresh acid, depending upon the sample weight. For recovery studies, the above procedure was repeated by adding 0.5 mL of mixed standard solution containing elements of interest in chloride form. To study the rate of matrix removal, the experiment was conducted with 0.5 g of sample for various concentrations of HCl (4.7–11.8 M) from which 1-mL aliquots were taken after 8-, 16-, 24-, and 48-h intervals and analyzed for As concentration.

For the analysis of high-purity arsenious oxide sample 0.5 g of sample was equilibrated twice with 50 mL of concentrated HCl and made up to 5 mL with Milli-Q water. Blank solution was also prepared as mentioned above, and both the solutions were analyzed by ICP-QMS (VG-Plasma Quad 3, VG Elemental).

Safety Note. Arsenious oxide and arsenious chloride are highly toxic and carcinogenic. Precautions during handling of these substances are absolutely necessary. They must, therefore, be handled in a well-equipped fume hood to avoid inhalation and gloves as well as other protecting clothes must be worn.

RESULTS AND DISCUSSION

Direct analysis of As_2O_3 dissolved in HCl has been carried out at 10, 5, and 2.5, mg/mL As_2O_3 . In 10 mg/mL solution suppression

of signals is observed whereas in 2.5 mg/mL solution concentrations of impurities present in the solution are not sufficient to get a quantifiable signal. In 5 mg/mL solution though, concentrations of most of the elements are very low; some of the elements, namely, Ba (0.8), Ca (16.0), Fe (58.5), Mg (1.2), Sb (4300) and Zn (1.4), only could be determined as their levels are at the micrograms per gram level in the sample. Hence, to analyze for more elements, matrix separation and preconcentration of impurities is desirable.

AsCl_3 is known to volatilize at room temperature.^{7,8} Due to the appreciable vapor pressure of concentrated HCl (25 kPa at 25 °C) and AsCl_3 (1.29 kPa at 23 °C), isopiestic distillation was performed for dissolution and volatilization of the As_2O_3 matrix. During the process, small droplets are observed on the surface of As_2O_3 within 4 h, which is converted to liquid completely within 24 h. For a 0.5-g sample, residual volume in the inner container is ~0.5 mL, which increases with increase in sample size. About 98% of the matrix is found to be removed within 24 h, for a single equilibration. Another equilibration is required to achieve 99.8% matrix removal. For 2 and 5 g of sample, two and three equilibrations are needed, respectively, to achieve 99.6% matrix removal. The rate of matrix removal decreases with decrease in HCl concentration in the outer container (Figure 2).

The whole phenomenon is explained in the following manner: Once the outer container is closed, the container is filled

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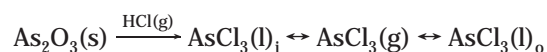
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Table 1. Comparison of Concentrations of Impurities in As₂O₃ Sample Using the Present Method and the Solvent Extraction Method (SE) along with Corresponding Process Blank and Detection Limit (DL)^a

element	blank levels ×10 ⁻³		recoveries (n = 3, μg)		DL ×10 ⁻³ (μg/g)	concentration of impurities (n = 3)		
	present method (n = 6)	SE method (n = 3)	added	recovered		A	B	SE method (B)
Al	<20	33 ± 12	2.0	2.10 ± 0.2	20	1.56 ± 0.10	1.43 ± 0.06	1.53 ± 0.10
B	70 ± 10	70 ± 15	2.0	1.80 ± 0.1	30	<0.10	<0.10	<0.10
Ba	5 ± 1	20 ± 4	1.0	1.10 ± 0.4	3	1.20 ± 0.2	0.80 ± 0.1	0.90 ± 0.1
Bi	<200	<200	10.0	9.6 ± 0.5	200	7.03 ± 0.06	7.30 ± 0.03	6.3 ± 0.05
Ca	52 ± 12	500 ± 80	15.0	15.82 ± 0.2	36	15.70 ± 0.08	15.87 ± 0.08	16.36 ± 0.10
Cd	<30	58 ± 14	1.0	0.98 ± 0.06	30	0.15 ± 0.05	0.15 ± 0.01	0.16 ± 0.02
Co	<20	40 ± 10	1.0	0.99 ± 0.05	20	0.17 ± 0.05	0.18 ± 0.01	0.25 ± 0.05
Cr	<30	163 ± 26	1.0	0.98 ± 0.1	30	0.08 ± 0.02	0.07 ± 0.01	0.08 ± 0.04
Cu	<30	<30	1.0	1.1 ± 0.10	30	<0.1	<0.1	<0.1
Fe	22 ± 5	41 ± 8	50.0	51.45 ± 0.5	15	61.75 ± 0.65	62.94 ± 0.59	59.00 ± 0.60
Hg	<90	<90	5.0	4.5 ± 0.1	90	1.40 ± 0.10	1.40 ± 0.05	0.370 ± 0.10
K	<90	<90	1.0	1.0 ± 0.05	90	2.24 ± 0.10	1.88 ± 0.08	1.90 ± 0.1
Mg	21 ± 6	58 ± 4	1.0	1.12 ± 0.15	18	1.56 ± 0.15	1.31 ± 0.11	1.08 ± 0.12
Mn	<18	50 ± 5	1.0	1.05 ± 0.15	18	0.13 ± 0.01	0.12 ± 0.01	0.09 ± 0.03
Na	<90	1110 ± 500	1.0	1.07 ± 0.13	90	0.31 ± 0.20	0.29 ± 0.20	4.7 ± 1.5
Ni	<30	95 ± 20	1.0	1.01 ± 0.1	30	0.12 ± 0.02	0.09 ± 0.01	0.12 ± 0.01
Sb	<60	<60	10 ^b	9.8 ± 0.2 ^b	60	0.42 ± 0.01 ^c	0.42 ± 0.01 ^c	0.42 ± 0.01 ^c
Se	<300	<300	10	9.5 ± 0.5	300	<1.0	1.1 ± 0.1	<1.0
Sn	<350	<300	10	9.7 ± 0.1	350	21.70 ± 0.50	22.60 ± 0.1	14.50 ± 0.5
Te	<250	<250	10	9.6 ± 0.1	250	0.60 ± 0.10	0.85 ± 0.08	0.60 ± 0.2
Ti	<24	<24	2.0	1.95 ± 0.05	24	0.08 ± 0.04	0.10 ± 0.01	0.08 ± 0.04
Zn	12 ± 4	35 ± 10	1.0	1.10 ± 0.10	12	1.90 ± 0.15	1.85 ± 0.12	1.60 ± 0.15

^aBlank values are computed for 5 g of sample diluted to 10 mL and normalized to 1 g. Uncertainties expressed as 1σ variation in the respective repeated measurements; Sample weight: A, 2 g; B, 5 g. ^bRecovery studies of Sb have been carried out on the standard solution without sample as the level of Sb in the sample is high (0.42%). ^cIn percent; concentrations of Au, Gd, La, Li, Nd, Pd, Pr, Pt, Rh, and Zr are <0.1 μg/g.

with HCl vapors that react with solid arsenious oxide forming AsCl₃, which is liquid at room temperature (mp -13 °C; bp 130 °C). Due to its appreciable vapor pressure, it gets converted to AsCl₃ vapors and distributed in the pool of HCl kept in the outer container as it is soluble in HCl. This can be explained schematically in the following reaction.



where i is the inner container and o is the outer container.

Major advantages of this procedure are quantitative recoveries (Table 1) of impurities including volatile elements (except Ge) along with very low blank levels. The loss of Ge as GeCl₄ can be attributed to its low boiling point (86 °C) and high vapor pressure (10 kPa, 21 °C). The four major contributions to the blanks are the environment, reagent, leaching of impurities from digestion vessel, and the skill of the analyst carrying out the procedure.⁹ In the present procedure, the closed container provides a clean environment and the pool of HCl acts as a source for the generation of pure acid for sample dissolution and sink for trapping AsCl₃. As the whole experiment is performed at room temperature, PP or poly(4-methyl-1-pentene) (TPX) vessels, which are less expensive than and superior to the Teflon and Vycor vessels, can be used with minimum leaching of impurities.¹⁰ The skill of analyst, which is the most difficult component to evaluate, has also been taken care of to a large extent because the analyst performs lesser and simpler operations for the sample preparation. As a result, the impurities in the blank are found to be same as

Table 2. Concentrations of Impurities in High-Purity As₂O₃ Sample along with Process Blank and Detection Limits (DL) Analyzed by ICP-QMS^a

element	blank (n = 6, ng/g)	DL (ng/g)	recoveries (n = 3, ng)		conc'n (n = 3, ng/g)
			added	recovered	
Al	3.03 ± 0.95	2.85	50	52.0 ± 4.0	104 ± 8
Ba	2.42 ± 0.31	0.93	25	24.5 ± 1.5	14 ± 3
Bi	0.45 ± 0.05	0.15	25	23.4 ± 1.2	<0.5
Cd	1.80 ± 0.15	0.45	25	24.5 ± 1.0	<1.5
Co	0.19 ± 0.01	0.03	25	25.0 ± 1.5	<0.1
Cr	19.6 ± 2.0	6.00	25	24.2 ± 4.2	31 ± 5
Cu	6.6 ± 1.2	3.60	25	25.8 ± 2.0	16.0 ± 1.5
Gd	0.50 ± 0.05	0.15	25	25.0 ± 0.5	0.48 ± 0.05
Hg	1.41 ± 0.18	0.54	50	44.6 ± 4.2	120 ± 8
La	0.30 ± 0.04	0.12	25	25.0 ± 1.0	<0.4
Mn	2.60 ± 0.40	1.20	25	26.4 ± 2.0	19 ± 2
Nd	0.12 ± 0.02	0.06	25	25.0 ± 0.5	<0.2
Ni	1.24 ± 0.60	1.80	25	25.5 ± 2.0	8.8 ± 1.0
Pr	0.10 ± 0.01	0.03	25	25.0 ± 0.8	0.13 ± 0.03
Sb	0.23 ± 0.06	0.18	150	148.0 ± 5.0	304 ± 8
Se	7.8 ± 1.1	3.30	25	23.4 ± 2.2	<11
Sn	0.34 ± 0.10	0.30	25	23.5 ± 2.5	31 ± 2
Te	0.40 ± 0.01	0.03	25	24.1 ± 1.0	4.3 ± 1.0
Ti	6.1 ± 1.0	3.00	100	98.0 ± 4.0	215 ± 5
Zn	10.0 ± 3.0	9.0	25	26.2 ± 2.0	<30
Zr	0.77 ± 0.11	0.33	25	25.0 ± 1.0	<1.0

^aUncertainties expressed as 1σ variation in the respective repeated measurements, DL expressed as 3σ variation in blank measurements; for the analysis and recovery studies, 0.5 g of sample is diluted to 5 mL after matrix separation.

that of water used for dilution. For only few elements such as Fe, Na, Mg, and Ca some counts above water level have been obtained which may be due to the short exposure of sample in the normal

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laboratory environment (Table 1). The blank values for most of the elements are less than the detection limits of ICP-AES. However, measurements by ICPMS represent the actual blank levels (Table 2). Detection limits (DLs) are computed based on 3σ variation in the measurements of blank ($n = 6$). The method has been applied for the determination of impurities in an As_2O_3 sample. The values obtained using the present procedure are compared with the solvent extraction procedure (Table 1). In the solvent extraction procedure, sample taken in concentrated HCl is extracted with benzene and the aqueous phase is evaporated on a water bath to remove excess of HCl and made up to the required volume. A discrepancy, in the case of Na, arises possibly due to contamination and Hg, Se, and Sn due to loss during evaporation. As an application of this method for the analysis of high-purity arsenious oxide, a high-purity sample is analyzed using ICP-QMS. The concentrations of impurities along with blank levels and DLs are given in Table 2.

Two main disadvantages of the present procedure are long sample preparation time and generation of a large quantity of acid waste. In a laboratory with very high sample load, the average sample preparation time can be significantly reduced by processing large numbers of samples simultaneously in different vessels.

From the acid waste, pure arsenic can be recovered by extracting it with CCl_4 followed by back extraction into Milli-Q water, and finally, both acid and CCl_4 can be reused after matrix removal.

CONCLUSION

Combination of vapor pressures of reactant and reaction product and their solubilities in HCl leads to the development of a new method for matrix separation in which the major disadvantages of normal volatilization methods (lack of simplicity and loss of volatile elements) have been eliminated in a very simple way. Extremely low blank level and quantitative recovery of most of the elements makes it a promising method for the analysis of high-purity As_2O_3 .

ACKNOWLEDGMENT

The authors thank Dr. J. Arunachalam, Head, CCCM, for his encouragement and Mr. D. Karuna Sagar for ICP-QMS measurements.

Received for review March 4, 2002. Accepted September 3, 2002.

AC020136A