Indirect AAS Determination of Iodide at the 10^{-7} mol l⁻¹ Level by Distillation of Iodine Followed by Its Reaction with Arsenic(III)

Il Yong KIM, Hiroki NAKAMURA, Kazuhisa YAMAYA and Minoru YOSHIDA

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan

A new indirect method for the determination of iodide at the 10^{-7} mol l⁻¹ level based on the reaction of distilled I₂ with As(III) followed by the determination of the excess As(III) with hydride generation AAS is proposed. Iodide is oxidized to iodine by Ce(IV), distilled with a nitrogen carrier gas and absorbed in a KI solution. Absorbed iodine reacts quantitatively with excess As(III) in a slightly alkaline solution at 80–90°C. After the reaction iodine in the solution is removed as an AgI precipitate. The amount of distilled iodine can be determined indirectly by measuring the atomic absorbance of As by a hydride-generation technique. The calibration curve is linear over the range from 2.5×10^{-8} mol l⁻¹ to 2×10^{-7} mol l⁻¹, and the relative standard deviation is 2.9% ($n=7$) for 1×10^{-7} mol l⁻¹ iodide.

Keywords Iodide determination, indirect method, hydride-generation atomic absorption spectrometry, I₂-As(III) reaction, distillation

Recently reported methods for the determination of trace amounts of iodide in various matrices include colorimetry by means of its catalytic action, ion chromatography and HPLC. Deguchi *et al.* determined 1–50 ppb of iodide with FIA¹ by using its catalytic action on the reduction of cerium(IV) by arsenious acid.² The catalytic effect of iodide on the 4,4'-bis(dimethyl-amino)diphenylmethane–Chloramine T reaction³ was applied to a flow-injection spectrophotometric determination of 0.1–10 ppb of iodide by Yonehara *et al.*⁴ This reaction was also applied to ion chromatography for the determination of iodide in biological materials by Buchberger.⁵ Hurst *et al.* determined the iodide in serum by using HPLC in combination with electrochemical detection at a silver electrode.⁶ Although these methods are sufficiently sensitive to determine nanogram iodide in solution samples, they can not be directly applied for complex materials, such as silicate rock samples. It is therefore necessary to separate iodide from coexisting materials before the determination. The extraction of iodine with organic solvents after the oxidation of iodide to iodine in aqueous solutions is widely used for the separation of iodide. For example, Yonehara *et al.*⁷ have reported that iodine can be separated by extraction with carbon tetrachloride, and have determined iodine in silicate rocks by a method based on the catalytic effect of iodine on the color-fading of ferric thiocyanate.⁸ However, it was difficult to separate trace amounts of iodide quantitatively from sample solutions by solvent extraction.

Since the vapor pressure of elementary iodine is high,

it is possible to separate iodine by means of distillation. Although Joerin determined iodine at the 10^{-5} mol l⁻¹ level in bovine milk with a colorimetric method after distillation⁹, the recovery was rather low (approx. 85%).

In the present work the conditions under which trace amounts of iodide can be quantitatively distilled as I₂ were examined first.

A hydride-generation technique using sodium tetrahydroborate, with subsequent atomic absorption spectrophotometry, is now a well-known method for the determination of As(III). As(III) is reduced to AsH₃ by sodium tetrahydroborate, and can be determined with high sensitivity by hydride generation AAS, though As(V) is not reduced. On the other hand, As(III) is oxidized quantitatively to the As(V) state by iodine in slightly alkaline solutions. Therefore, traces of iodide may be determined indirectly by reacting distilled elementary iodine with excess As(III) followed by a determination of the residual As(III) with hydride generation AAS. Based on this principle, a new indirect AAS method for the separation and determination of iodide at the 10^{-7} mol l⁻¹ level based on the reaction of distilled I₂ with As(III) was established.

Experimental

Reagents

Pure water was prepared by purifying distilled water using the NANO Pure II system of Barnstead Co. Reagent-grade chemicals were used throughout.

An iodide standard solution (0.1 mol l^{-1}) was prepared by dissolving 16.6 g of potassium iodide in 1000 ml of water, which was standardized by using Volhard's method. Working solutions ($10^{-3} \text{ mol l}^{-1}$ and $10^{-7} \text{ mol l}^{-1}$) were prepared by suitable dilution with water and used within 7 d.

An iodine (I_2) standard solution (0.005 mol l^{-1}) was prepared by dissolving 1.2692 g of iodine together with 1 ml of hydrochloric acid (6 mol l^{-1}) in 100 ml of 36% potassium iodide solution, and diluting to 1000 ml with water. This solution was standardized with a 0.01 mol l^{-1} thiosulfate standard solution.

A thiosulfate standard solution (0.1 mol l^{-1}) was prepared by dissolving about 26 g of sodium thiosulfate and 0.2 g of sodium carbonate in 1000 ml oxygen-free water. This solution was standardized with potassium iodate. Working solutions (0.01 mol l^{-1} and 0.001 mol l^{-1}) were prepared by suitable dilution before use.

An arsenic standard solution (0.01 mol l^{-1}) was prepared by dissolving 1.9784 g of arsenic(III) oxide in 25 ml sodium hydroxide solution (4 mol l^{-1}), then acidifying with 24.7 ml of perchloric acid (4 mol l^{-1}), and finally diluting to 1000 ml with water. Working solutions (0.001 mol l^{-1} and $10^{-6} \text{ mol l}^{-1}$) were prepared by suitable dilution, and used within 7 d.

A cerium(IV) solution ($2.5 \times 10^{-2} \text{ mol l}^{-1}$) was prepared by dissolving 1.581 g of ammonium cerium(IV) sulfate dihydrate in 33.3 ml sulfuric acid (3 mol l^{-1}) and diluting to 100 ml with water.

A phosphate buffer solution (pH 8.0) was prepared by mixing a potassium dihydrogenphosphate solution (0.2 mol l^{-1}) with a sodium hydroxide solution (0.2 mol l^{-1}).

A sodium tetrahydroborate solution (1%) was prepared by dissolving sodium tetrahydroborate in a 2% sodium hydroxide solution. This solution was stored in a refrigerator.

Apparatus

Distillation apparatus. The distillation apparatus used in this study is shown in Fig. 1. The flow rate of the carrier gas (N_2) was regulated by using a Kojima Seisakujo (Model RK 1300V) gas-flow meter. The cylindrical reaction vessel (B) (28 mm o.d., 220 mm long, 90 ml capacity) has a Teflon stopcock at the bottom and a side mouth with a glass stopper. The absorption tube (25 ml capacity, T15/25) is a test tube with a ground stopper. All parts are connected by ground-glass joints. Sintered-glass balls of 10–20 μm pore size are fitted at the ends of the gas-inlet tubes of both the reaction and absorption tubes.

Hydride-generation apparatus. The apparatus used for the hydride-generation procedure is shown in Fig. 2. A hydride generating vessel and a silica atomizing cell (a quartz tube heated with an air-hydrogen flame) was connected via a water trap and a glass column (4 m long, 3 mm i.d.). The water trap was inserted into a Dewar bottle which contained dry-ice and acetone.

A Shimadzu atomic absorption/flame emission spectrophotometer (Model AA-640-12) with a Shimadzu

Fig. 1 Distillation apparatus: A, gas flow meter; B, reaction vessel; C, absorption tube; a, three way plastic connector; b, gas-inlet tube; c, sintered-glass filter ball; d, glass stopper; e, ball joint.

Fig. 2 Schematic diagram of apparatus for hydride-generation: A, gas flow meter; B, sodium tetrahydroborate solution; C, peristaltic pump; D, hydride generating vessel; E, water trap with dry-acetone cooling; F, buffer volume; AAS, atomic absorption spectrophotometer; a, needle valve; b₁ & b₂, three-way plastic connector; c, gas-inlet tube; d, glass stopper; e, ball joint; f, adaptor; g, Teflon coupling joint; h, Teflon tube.

chart recorder (Model R-111M) was used for measuring the atomic absorption.

Procedure

Distillation of iodide at the $10^{-3} \text{ mol l}^{-1}$ level

Place 10 ml of 10% KI solution in the absorption tube and 10.0 ml of a sample solution in the reaction vessel.

Add 1.5 ml of 70% HClO_4 and 0.5 ml of $2.5 \times 10^{-2} \text{ mol l}^{-1}$ Ce(IV) solution to the reaction vessel *via* the side mouth (d); then introduce nitrogen gas at a rate of 750 ml min^{-1} for 10 min. After distillation, transfer the absorption solution to a 100 ml beaker. Wash the absorption tube and the gas-inlet tube 6 times each with 1 ml water and combine all of the washings in the beaker. Titrate the absorbed iodine with the thiosulfate standard solution (0.001 mol l^{-1}) by using a starch solution as an indicator.

Recommended procedure for the determination of iodide at the $10^{-7} \text{ mol l}^{-1}$ level

Place 10 ml of a 0.3 mol l^{-1} KI solution in the absorption tube and 10.0 ml of a sample solution (from $2 \times 10^{-8} \text{ mol l}^{-1}$ to $10^{-7} \text{ mol l}^{-1}$ I^-) in the reaction vessel. Add 1.5 ml of 70% HClO_4 and 0.5 ml of $2.5 \times 10^{-2} \text{ mol l}^{-1}$ Ce(IV) solution to the reaction vessel; then introduce nitrogen gas at a rate of 750 ml min^{-1} for 25 min. After distillation, transfer the absorption solution to a 50 ml centrifuge tube. Wash the absorption tube and the gas-inlet tube 6 times each with 1 ml water and combine all of the washings in the centrifuge tube. Add 3 ml of a phosphate buffer solution (pH 8.0) and 2 ml of a $1 \times 10^{-6} \text{ mol l}^{-1}$ As(III) standard solution to the centrifuge tube and mix thoroughly. Place the centrifuge tube in a water bath at $80-90^\circ\text{C}$ for 25 min. Add 10.2 ml of a 0.3 mol l^{-1} AgNO_3 solution and centrifuge at about 3000 rpm for 3 min; then transfer the supernatant to a 50 ml calibrated flask. Wash the precipitate by shaking well with 6 ml of a 0.25 mol l^{-1} NaH_2PO_4 solution and centrifuge again. Combine the supernatant in the calibrated flask; then dilute to the mark with water.

Pipette 10 ml of the solution prepared above together with 6.3 ml HCl (12 mol l^{-1}) into the hydride-generating vessel. Set the three-way stopcocks (b_1 , b_2) so as to introduce nitrogen carrier gas into the hydride-generating vessel at a rate of 3000 ml min^{-1} , and displace all of the air from the system. Then, turn the stopcocks as the carrier gas to pass directly in the silica atomizing cell *via* the Teflon tube (h). Inject the 1% NaBH_4 solution into the hydride generating vessel for 60 s at a flow rate of 3 ml min^{-1} with a peristaltic pump, stirring the solution with a magnetic stirrer. Introduce the carrier gas again to the hydride-generating vessel for sweeping the generated arsine into an atomizing cell, and record the atomic absorbance of As. The operating conditions of AAS and analytical parameters for determining arsenic(III) by the hydride-generation technique are described in Table 1.

Table 1 Optimum operating conditions of AAS and the optimum analytical parameters for determining arsenic(III) by the hydride-generation technique

Wavelength	(nm)	193.7
Slit width	(nm)	9.5
Lamp current	(mA)	6.0
Flow rate of nitrogen	(ml min^{-1})	3000.0
Flow rate of 1% NaBH_4 soln.	(ml min^{-1})	3.0
Injection time of 1% NaBH_4 soln.	(s)	60
HCl	(ml)	6.3
Sample volume	(ml)	10.0
Acidity	(mol l^{-1})	4.5

Results and Discussion

Distillation of iodide at the $10^{-3} \text{ mol l}^{-1}$ level

1. Effect of the reaction variables for the oxidation of iodide.

First, the oxidizing condition of iodide was examined at an iodide concentration on the $10^{-3} \text{ mol l}^{-1}$ level. The $10^{-3} \text{ mol l}^{-1}$ level iodine solution can be titrated with a $10^{-3} \text{ mol l}^{-1}$ $\text{Na}_2\text{S}_2\text{O}_3$ solution with a precision of $\pm 2.2\%$. Ce(IV) and $\text{Cr}_2\text{O}_7^{2-}$ were examined as oxidizing agents for iodide; Ce(IV) was chosen because of its higher recovery (Table 2).

The effect of acidity was investigated over the range from 0.05 to 2.5 mol l^{-1} HClO_4 . Iodide was completely oxidized to iodine by Ce(IV) at an acidity of 0.5 mol l^{-1} to 1.5 mol l^{-1} ; accordingly, the reaction solution was acidified to be 1.5 mol l^{-1} HClO_4 . The effect of the amount of Ce(IV) added on the oxidation of iodide was investigated (Fig. 3). Iodide of $10^{-3} \text{ mol l}^{-1}$ was quantitatively oxidized to iodine at Ce(IV) concentration from $10^{-3} \text{ mol l}^{-1}$ to $7.5 \times 10^{-3} \text{ mol l}^{-1}$.

2. Effect of distillation variables for I_2 .

A 10% KI solution was used as the absorption solution. The effect of the flow rate of the carrier gas is shown in Fig. 4. When the flow rate was between 700 and 970 ml min^{-1} , 10^{-5} mol iodine in a 10 ml solution was distilled and absorbed quantitatively. More than 5 min was needed for complete distillation at a flow rate of 750 ml min^{-1} . The distillation was therefore carried out for 10 min at a flow rate of 750 ml min^{-1} . The distillation efficiency of iodide was affected by the sample volume; the effect is shown in Fig. 5. The recovery of 10^{-5} mol iodide in the 10 ml sample volume was 99.4%, but decreased as the sample volume increased.

Table 2 Recovery of iodide by using Ce(IV) and $\text{Cr}_2\text{O}_7^{2-}$ as oxidizing agent

Oxidizing agent	Acidity/ mol l^{-1}	I^- taken/ mol l^{-1}	Found/ mol l^{-1}	Recovery, %
$\text{Ce(NH}_4)_4(\text{SO}_4)_4$ ($2.5 \times 10^{-2} \text{ mol l}^{-1}$)	0.5 – 1.5 HClO_4	0.978×10^{-3}	$(0.973 \pm 0.020) \times 10^{-3}$	99.4 ± 2.2 ($n=10$)
$\text{K}_2\text{Cr}_2\text{O}_7$ ($2.5 \times 10^{-2} \text{ mol l}^{-1}$)	0.3 – 0.5 H_2SO_4	1.005×10^{-3}	$(0.967 \pm 0.009) \times 10^{-3}$	96.2 ± 0.9 ($n=4$)

Fig. 3 Effect of Ce(IV) concentration on the oxidation of 10^{-3} mol l^{-1} iodide.

Fig. 4 Effect of flow rate of carrier gas on the distillation of iodide. Iodide concentration, 10^{-3} mol l^{-1} 10 ml; cerium(IV) concentration, 2.5×10^{-2} mol l^{-1} 0.5 ml; gas delivery time, 10 min; acidity, 1.5 mol l^{-1} $HClO_4$.

Based on the condition established above, iodide can be quantitatively distilled from 10^{-3} mol l^{-1} level solutions and determined with the recovery of $99.6 \pm 2.2\%$ (95% confidence interval, $n=14$).

Indirect determination of iodide by determining arsenic by means of the AAS with hydride generation method

1. Reaction of iodine with As(III) and pretreatment for the AAS determination.

The optimum analytical parameters for determining arsenic(III) by AAS with hydride generation were examined for our apparatus and are compiled in Table 1.

Arsenic(III) was oxidized quantitatively to the As(V) state by iodine in slightly alkaline solutions. We then attempted to absorb the evolved iodine in an As(III) solution. At a pH of 8, the reaction between iodine and

Fig. 5 Effect of sample volume on the distillation of iodide. 10^{-5} mol iodide; cerium(IV) concentration, 2.5×10^{-2} mol l^{-1} 0.5 ml; gas flow rate, 750 ml min^{-1} ; gas delivery time, 10 min; acidity, 1.5 mol l^{-1} $HClO_4$.

As(III) is represented by

The pH of the absorption solution was controlled by adding a phosphate buffer solution. Considering the principle of the method, the As(III) concentration must be on the same order as the I^- concentration. The iodine distilled from the 10^{-3} mol l^{-1} I^- solution was absorbed into an As(III) solution (10^{-3} mol l^{-1}) with a recovery of 100.5%. However, 10^{-5} mol l^{-1} iodine was incompletely absorbed, because the rate of the reaction is slow at such a low concentration level. We therefore examined the distilled iodine to be absorbed in the KI solution of a large excess concentration, and then reacted it with As(III).

Reaction (1) is reversible, depending on the oxonium ion concentration in the solution. If the solution for hydride generation contains iodide, As(V) which is formed by the oxidation of As(III) is reduced again to As(III). Therefore, iodide in the absorption solution must be removed before the hydride-generation procedure. It can be removed as an AgI precipitate with the addition of a 2% excess silver nitrate solution an equivalent amount of iodide. However, the presence of silver ion in the solution resulted in a low recovery of As(III). Hence, any excess silver ion must also be removed. Fortunately, by reacting with the phosphate ion which was used in the previous procedure as the buffer solution, excess silver ion precipitated as Ag_3PO_4 .

Since, As(III) was adsorbed to the precipitate, washing the precipitate was necessary in order to obtain a sufficient recovery. Washings with water gave unsatisfactory results. Although washing twice each with 3 ml of a 0.25 mol l^{-1} NaH_2PO_4 solution gave the highest recovery, washing once with 6 ml of the NaH_2PO_4

Table 3 Atomic absorbance of As(III) by various washing solutions of the precipitate

Washing solution	Absorbance
Water 6 ml	0.189
Water 3 ml×twice	0.236
0.25 mol l ⁻¹ NaH ₂ PO ₄ 6 ml	0.276
0.25 mol l ⁻¹ NaH ₂ PO ₄ 3 ml×twice	0.285

Iodide concentration, 2×10^{-7} mol l⁻¹ 3 ml; As(III) concentration, 1×10^{-6} mol l⁻¹ 2 ml.

solution gave almost the same results. To simplify the operation, the precipitate was washed once with 6 ml of the NaH₂PO₄ solution (Table 3).

2. Effects of the concentration of the absorption solution and delivery time.

When the KI concentration of the absorption solution was between 0.1 and 0.5 mol l⁻¹ the distilled iodine was completely absorbed. We then used a 0.3 mol l⁻¹ KI solution as the absorption solution. Although 10 min is sufficient for complete distillation at a concentration level of 10^{-3} mol l⁻¹ I⁻, 25 min was necessary for a quantitative recovery of the 10^{-7} mol l⁻¹ I⁻ level at a flow rate of 750 ml min⁻¹ of the carrier gas.

3. Effect of reaction variables on the oxidation of As(III) with I₂.

At room temperature since the reaction between trace amounts of iodine and As(III) is very slow, the reaction must be accelerated by being heated at 80–90°C. The heating time for completing the reaction between iodine and As(III) at the 10^{-7} mol l⁻¹ level was investigated. The atomic absorbance of As became constant upon heating for longer than 20 min; 25 min was chosen as the recommended procedure. Various amounts, ranging from 1 ml to 2 ml of 10^{-6} mol l⁻¹ As(III) solution, were added. When 1.5–2.0 ml of 10^{-6} mol l⁻¹ As(III) was used, the iodine and As(III) reacted quantitatively. Therefore, the addition of 2 ml of 10^{-6} mol l⁻¹ As(III) was chosen as the optimum amount.

4. Calibration graph and reproducibility.

The calibration graph of iodide obtained by the proposed method is shown in Fig. 6. It is linear over the range from 2.5×10^{-8} mol l⁻¹ to 2×10^{-7} mol l⁻¹. Seven replicate analyses of a 10 ml aliquot of 1×10^{-7} mol l⁻¹ iodide solution (12.76 ng) gave a mean value of 12.50 ng and a relative standard deviation of 2.9%.

5. Effect of foreign ions.

The effect of foreign ions on the determination of iodide was investigated. The results are given in Table 4. Up to 3000 ppm of chloride ion and 125 ppm of bromide ion no interference appeared. Furthermore, 0.5 ml of a rock-simulated solution did not interfere with the distillation of iodide. One milliliter of this solution contains major ions which will be supplied by dissolving 50 mg of average Japanese igneous rock.

In conclusion, an indirect determination of iodide at the 10^{-7} mol l⁻¹ level has been achieved by means of AAS

Fig. 6 Calibration graph for iodide obtained by the recommended procedure.

Table 4 Effect of foreign ions on the determination of 0.978×10^{-6} mmol iodide by the recommended procedure

Ion/mg	Weight ratio	I ⁻ found / mmol	Recovery, %
None		0.978×10^{-6}	100
Cl ⁻ 30.0	236400	0.958×10^{-6}	98
Br ⁻ 1.25	9850	0.978×10^{-6}	100
Br ⁻ 2.50	19700	1.036×10^{-6}	106
Ti ⁴⁺ 0.16	1260	0.978×10^{-6}	100
Al ³⁺ 2.0	15760		
Fe ³⁺ 1.0	7880		
Ca ²⁺ 0.9	7000		
Mn ²⁺ 0.065	510		
Mg ²⁺ 0.87	7000		
Na ⁺ 1.81	14260		
K ⁺ 1.12	8800		
PO ₄ ³⁻ 0.15	1200		
Ti ⁴⁺ 0.32	2520	1.056×10^{-6}	108
Al ³⁺ 4.0	31520		
Fe ³⁺ 2.0	15760		
Ca ²⁺ 1.8	14000		
Mn ²⁺ 0.130	1000		
Mg ²⁺ 1.74	14000		
Na ⁺ 3.62	28520		
K ⁺ 2.25	17600		
PO ₄ ³⁻ 0.30	2400		

A half milliliter^a or 1.0 ml^b of a rock-simulated solution was added. One milliliter of a rock-simulated solution contains the major components corresponding to 50 mg of averaged igneous rock.

with hydride generation. In the proposed method since iodide is first separated by distillation as I₂ the effect of any foreign ions is very limited. A linear calibration graph was obtained over a concentration range from 2.5×10^{-8} mol l⁻¹ to 2×10^{-7} mol l⁻¹ iodide, and the relative standard deviation was 2.9% at the 1×10^{-7} mol l⁻¹ iodide

level. This method will be applicable to most natural and environmental samples.

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