Notes

Microgram Determination of Bismuth by Sequential High-Fold Chemical-Amplification Reactions

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Iodometric chemical-amplification procedures with their simplicity and sensitivity are still of special attraction.¹⁻⁶ The extraction of BiI_3 with benzene from an H_2SO_4 -KI solution, followed by the reoxidation of BiI_3 with bromine, forms the basis of a very sensitive indirect starch-iodine amplification method for bismuth(III) determination.⁶ In this paper, two simple titrimetric and spectrometric methods are described for the determination of bismuth(III) and (V) in aqueous media. The methods are based on the use of sodium periodate to oxidize the bismuth(III) ions to the pentavalent state and a subsequent titrimetric or spectrophotometric determination of the released iodine after the addition of KI.

Experimental

Apparatus

A Pye-Unicam double-beam UV-visible spectrophotometer (Model Sp-8-400) with 10-mm quartz cells and a Philips digital pH meter (Model 9418) were used for absorbance and pH measurements, respectively.

Reagents and materials

Analytical reagent-grade chemicals were used without further purification. A bismuth(III) solution (100 $\mu\text{g}/\text{ml}$) was prepared by accurately dissolving a weighed amount of $\text{Bi}(\text{NO}_3)_3$ in 10% HNO_3 and standardized with Na_2EDTA .⁷ A bismuth(V) solution (100 $\mu\text{g}/\text{ml}$) was prepared by dissolving 0.1234 g of bismuthic acid in 100 ml of 0.5 mol dm^{-3} KOH , and diluted with distilled water whenever required. A 2.5% (m/v) sodium diethyldithiocarbamate (NaDDC) was freshly prepared in water before use. Sodium thiosulfate solutions (0.005–0.01 mol dm^{-3}) and sodium molybdate solution (5% m/v) were prepared in distilled water. Buffer solutions of pH 2.3–4.7 were prepared by mixing 200 ml of glacial acetic acid with 100 ml of water, and adjusting the pH with a saturated solution of sodium acetate. Sodium periodate (0.35 m/v) sodium and sulfite (1% m/v) solutions were freshly prepared in distilled water.

Artificial seawater⁹ with a salinity of about 36 g/kg was prepared from demineralized water and salts in the following molar concentrations: NaCl , 0.4; MgCl_2 , 0.029; MgSO_4 , 0.028 and KCl , 0.009 mol dm^{-3} .

Recommended procedures

I. Determination of bismuth(III). Transfer aliquot portions of a bismuth(III) solution containing 10–200 μg of the element into a 100-ml conical flask. Add 10 ml of an acetate buffer (pH 2.3–3.5) and 5-ml of sodium periodate solution. Heat the solution mixture on a boiling-water bath for 15 min. Let the reaction mixture cool, and then add 5-ml of sodium molybdate to mask the unreacted sodium periodate, followed by adding a few crystals of KI at pH 3. Extract the liberated iodine with two 10-ml portions of CCl_4 . Collect the extracts in a separating funnel and shake with 10-ml of water containing 1-ml of sodium sulfite to reduce the iodine to iodide. Transfer the aqueous (upper) layer to a 100-ml Erlenmeyer flask, and determine the iodide by one of the following methods:

[48-fold amplification] To the iodide solution add 5-ml of bromine and stir for 3 min. Destroy any excess bromine by dropwise addition of formic acid, add 5-ml of 1 mol dm^{-3} sulfuric acid and 3–4 crystals of KI and determine the released iodine as triiodide by measuring the absorbance of the solution at 350 nm (ref. 10) against a blank or by titration with 2.5×10^{-3} mol dm^{-3} thiosulfate using starch as an indicator. Run a blank to correct any reagent error.

[192-fold amplification] To the iodide solution, add 5-ml of NaIO_4 , stopper and allow the reaction mixture to stand for 10 min at room temperature, then place the flask in a boiling-water bath for 20 min. Cool the solution, add 5 ml of sodium molybdate, 10 ml of acetate buffer (pH $\approx$ 3) and 2–3 crystals of KI and determine the released iodine as triiodide in the usual manner.

II. Determination of bismuth(V). Transfer aliquot portions of bismuth(V) containing 10–100 μg of the element into 100 ml Erlenmeyer flasks, add 2 ml of a sodium sulfite solution to each flask followed by adding

5 ml of HNO_3 (1:1). Allow the reaction to stand for 3 min and evaporate the solution gently on a hot plate until any excess SO_2 is completely removed. Add 5 ml of water, and determine the released bismuth(III) using procedure I.

III. Determination of bismuth in seawater. A seawater sample (400 μl) acidified to 0.1 mol dm^{-3} in hydrochloric acid is filtered through a $0.45 \mu\text{m}$ Millipore filter followed by adding 10 ml of 1 mol dm^{-3} tartaric acid, 10 ml of $1 \times 10^{-3} \text{ mol dm}^{-3}$ of disodium salt of EDTA and 10 ml of $1 \times 10^{-3} \text{ mol dm}^{-3}$ NaF. Allow the reaction mixture to stand for 10 min, and add 1 ml of sodium sulfite solution, and 2 ml of conc. HCl. Then boil the solution, and finally leave it to cool. The pH of the solution is adjusted to between 9–10 by the addition of ammonia, and then transferred into a separating funnel containing 10 ml of 2% (m/v) NaDDC. The produced Bi-DDC complex is extracted into 10-ml of xylene by shaking for 2 min, as previously reported.¹¹ The back extraction of bismuth is then carried out with 5 ml of conc. HNO_3 , and the contents shaken for 5 min. The aqueous phase is then collected in a 10 ml measuring flask after washing the organic phase with another 5 ml (2×2.5) of conc. HNO_3 . Finally, determine the total bismuth content following procedure II.

IV. Analysis of bismuth in real samples. Transfer different aliquot volumes (1–5 ml) of a laboratory-synthesized aluminum-bismuth alloy (prepared as described earlier)¹⁰ to 100-ml conical flask. Add 2 ml of saturated Na_2SO_3 , 10 ml of nitric acid (1:1) and follow the recommended procedure II.

Results and Discussion

The proposed method for bismuth(III) determination is based principally on its oxidation to the pentavalent state in acid media with sodium periodate according to the following equation:

The released iodate and bismuth(V) can oxidize potassium iodide according to

and

Reaction (2) takes place rapidly and proceeds quantitatively in an acidic medium at $\text{pH} \leq 3.5$. Moreover, reaction (3) is a function of the solution pH, as can be predicted from the redox potential concerned.⁹ Preliminary experiments showed that bismuth(V)-KI reacts and proceeds forward quantitatively at $\text{pH} < 4$ i.e. bismuth(V) ions release iodine upon a reaction with KI; the released iodine can be determined iodometry or

Table 1 Determination of various amounts of bismuth(III), iodometry (a) and spectrophotometry (b) using 8-fold amplification procedure

Bismuth(III) taken/ μg	Bismuth(III) found/ μg		Error, %	
	a	b	a	b
10	10.2 ± 0.2	10.1 ± 0.1	1	2
20	20.3 ± 0.3	20.2 ± 0.2	1.5	1
50	51.2 ± 0.3	50.6 ± 0.28	2.4	1.2
100	101.2 ± 0.35	101 ± 0.1	1.2	1
150	153 ± 0.3	151 ± 0.20	2	0.7
200	202 ± 0.20	201 ± 0.25	1	0.5

Average $\pm$ standard deviation ($n=5$).

Error = (average bismuth found/bismuth added) $\times$ 100.

spectrophotometrically as triiodide at 350 nm against reagent blank.

Moreover, the oxidation of bismuth(III) with sodium periodate is pH, temperature and reaction time dependent. Therefore, the effects of these factors were studied on a fixed concentration (80 μg) of bismuth(III) in the pH range 2.2–5.4. These solutions were then allowed to react with 5 ml of NaIO_4 for different time intervals (5–60 min) and different temperatures (ambient or 100°C) on a boiling-water bath. After cooling, the solutions were adjusted to pH 3 by adding 10 ml of acetate buffer; the excess sodium periodate was masked with molybdate ions at the same pH. The released iodate and bismuth(V) (reaction (1)) were then allowed to react with KI ($\approx 40 \text{ mg}$), and the liberated iodine was determined by both iodometry and spectrophotometry. The results indicated that, the optimum pH range for complete oxidation of bismuth(III) with periodate was obtained in the pH range 2.3–4.0 after boiling the solution on a water bath for 15 min. At $\text{pH} \geq 4$ reactions (1)–(3) proceeded slowly. A $\text{pH} < 2.2$ it proceeded rapidly, but the molybdate did not mask the unreacted periodate ions quantitatively, since the molybdate-periodate complex was partially decomposed. Thus, the blank values are erroneously high due to the reaction of the released periodate with iodide.¹² Fortunately, the pH values suitable for the quantitative oxidation of bismuth(III) with periodate ions (pH 2.3–3.5) are quite appropriate for masking any excess unreacted periodate. Thus, an acetate buffer solution (pH 3) was added at the beginning of the experiments. Each original bismuth(III) ion release eight equivalents of iodine; i.e. the proposed method affords 8-fold amplification for each one bismuth(III) ion. The developed method was employed for the determination of various amounts of bismuth (10–200 μg) iodometrically as well as spectrophotometrically at 350 nm. The results are summarized in Table 1. Satisfactory results were obtained employing iodometric and spectrophotometric procedures with standard deviations in the 0.2–0.35 and 0.15–0.28, ranges respectively.

Bismuth(V) can be determined either iodometrically or

spectrophotometrically employing Eq. (3). The sensitivity and the detection limit of this method can be improved by a prior reduction of bismuth(V) to bismuth(III), followed by the determination of the produced bismuth(III) element by the 8-fold amplification procedure described earlier. A series of reducing agents was used to reduce Bi(V)→Bi(III) quantitatively without interfering with the proposed procedure. Sodium sulfite (1%) in acid media was found to be the most convenient reducing agent, where the unreacted sulfite ion can be removed by boiling off sulfur dioxide formed. The determination of various levels (10–100 µg) of bismuth(V) in aqueous media was carried out and satisfactory results were obtained with a standard deviation in the 0.2–0.5 range.

An analysis of a binary mixture of bismuth(III) and (V) in an aqueous media was carried out using the proposed procedure. An aliquot mixture was allowed first to react with sodium periodate employing the procedure described for bismuth(III) determination. Another aliquot mixture was allowed to react with KI at pH<3, followed by a determination of the released iodine. On the basis of these procedures, the volume (V_1 ml) of sodium thiosulfate or the absorbance (A_1) of the released iodine for the first aliquot was equivalent to the sum of bismuth(III)+(V). The volume (V_2 ml) of sodium thiosulfate or the absorbance of the released iodine (A_2) for the second aliquot was equivalent to bismuth(V). Thus the volume ($V_1 - V_2$ ml) or the absorbance ($A_1 - A_2$) was equivalent to bismuth(III). Satisfactory results were obtained with an absolute error in the 0.5–2.4 range.

Moreover, the sensity of the proposed 8-fold amplification procedure of bismuth(III) determination could be increased employing the oxidation with bromine water and sodium periodate. The released iodine from Eqs. (2) and (3) is extracted quantitatively upon shaking with two 10-ml portions of CCl_4 and shaken with sodium sulfite solution to reduce the iodine to iodide according to the equation¹³

The released iodide in the aqueous (upper) layer is allowed to react with bromine or sodium periodate to produce iodate according to the following equations:¹³

The released iodate produced from Eq. (5) or (6) is quantitatively determined iodometrically and also spectrophotometry after the addition of KI (50–70 mg). Thus, according to Eq. (5), the overall amplification employing the oxidation of iodide by bromine is 48-fold while Eq. (6) produces an overall 192-fold amplification of the iodine equivalent to each bismuth(III) element originally present. The proposed two amplification procedures have been successfully for an analysis of

Table 2 Determination of various amounts of bismuth(III) by iodometry (a) and spectrophotometry (b) using 48-fold and 192-fold amplification procedures

Bismuth(III) taken/µg	Bismuth(III) found/µg			
	48-fold		192-fold	
	a	b	a	b
5	5.1±0.2	5.0±0.1	5.0±0.1	5.0±0.1
10	10.1±0.2	10.1±0.1	10.1±0.1	10.1±0.2
20	20.1±0.2	20.2±0.1	20.1±0.1	20.1±0.3
50	50.2±0.3	50.2±0.1	50.1±0.2	50.6±0.2
100	100.6±0.4	100.4±0.2	100.5±0.3	100.4±0.3

Average±standard deviation ($n=3$).

5–100 µg bismuth(III). The obtained results are summarized in Table 2 with good accuracy. The spectrophotometric procedure employing 192-fold amplification can be extended to a lower concentration (≤ 0.1 µg) of bismuth by the extraction of the released iodine in CHCl_3 containing alcoholic KI, and measuring the absorbance of the triiodide at 360 nm, as previously reported.¹⁴

The absorbance–concentration relationship was found to be linear for 0.3–20 µg ml⁻¹ of bismuth(III) or (V) employing 48-fold amplification. A linear calibration graph was also obtained over a concentration range of 0.1–12 µg ml⁻¹ at 192-fold amplification for Bi(III) determination. The optimum concentration range for the effective spectrophotometric determination evaluated by the Ringbom's method¹⁵ is 5–16 ppm for 48-fold amplification and 1.2–10 ppm for 192 amplification. The relative standard deviation ($n=5$) was in the range 1.3–1.7%. The detection limit ($3\times\text{noise}$) and correlation coefficient were found to be 0.1 ppm and 0.987 for 1–20 ppm, respectively.

Application of the proposed method

The applicability of the proposed procedures for the analysis of bismuth(III) or (V) in tap, polluted potable or seawater and artificial seawater (0.1–1 l) has been examined employing the recommended procedure (IV) using the standard addition method. Negative results were obtained, indicating the absence of bismuth. In separate experiments water samples spiked with various amounts (5–50 µg) of bismuth were analyzed employing procedure (III). Satisfactory results with a relative standard deviation in the range 1.3–1.7% ($n=3$) and a correlation coefficient of 0.96 were obtained. The analysis of a very low concentration of bismuth (as low as <0.1 µg/ml) in seawater is also possible by the proposed procedure after preconcentration and recovery of bismuth from large sample volume on polyurethane foam column¹⁶ and a determination of the produced bismuth according to the described procedure II.

A spectrophotometric analysis ($n=3$) of two weighed samples of bismuth in laboratory synthesized Al-Bi alloy by the proposed 192-fold amplification procedure

($\text{Bi}_2\text{O}_3\%$ =5.7) was in good agreement with the values obtained by the standard method ($\text{Bi}_2\text{O}_3\%$ =5.82).¹⁷ A relative standard deviation in the 1.7–2.2% range was obtained.

Effect of foreign ions

The interference of various ions (Zn^{2+} , Pt^{2+} , Sn^{4+} , K^+ , Ni^{2+} , Al^{3+} , Na^+ , Li^+ , Co^{2+} , Fe^{3+} , Pd^{2+} , Mo^{6+} , Cd^{2+} , Ca^{2+} , Mg^{2+} , Ba^{2+} and La^{3+}) which are commonly in association with bismuth, was investigated at a concentration (50 μg) approximately exceeding those normally found in seawater employing the recommended procedure (III). The selectivity of the proposed 8-fold procedure was tested by a determination of a fixed concentration (10 μg) of bismuth(III). Satisfactory results were obtained with a percentage recovery of 99.2 ± 1.2 . Mn(II) , Au(I) , Ti(I) and Ru(III) seriously interfered. The determination of a fixed concentration (40 μg) of bismuth(III) in the presence of a relatively high excess (0.5 mg) of various ions: (WO_4^{2-} , HCO_3^- , Br^- , Cl^- , PO_4^{3-} , SO_4^{2-} , AsO_3^{3-} , SbO_3^- and CO_3^{2-}) was examined. The percentage recovery of bismuth(III) was $100 \pm 3\%$.

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