

Simultaneous separation of tin and bismuth from water and sea water by flotation with thionalide

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Summary. A method is described for the simultaneous flotation of low $\mu\text{g l}^{-1}$ levels of tin and bismuth in water and sea water. Tin(IV) and bismuth(III) in a 1000 ml sample is coprecipitated with thionalide at pH 2–3. The precipitate is floated with the aid of a surfactant and small nitrogen bubbles, then dissolved in acetone and digested with nitric and perchloric acids for hydride generation-atomic absorption spectrophotometry. Recoveries of tin and bismuth at the levels of 20 μg added to water and sea water were more than 88%.

The determination of trace metals has received increasing attention in environmental pollution studies. Particularly, there is an increasing need for a simple and accurate method for determining metals at low parts per billion ($\mu\text{g l}^{-1}$) levels in water. In general, for an accurate determination of trace metals at this concentration, preconcentration is required from water in order to achieve the necessary sensitivity.

Organic reagents are widely used for the collection of trace metals in water. Mizuike and Hiraide reported the usefulness of organic reagents including thionalide as collector precipitates suitable for flotation [1, 2].

In the previous paper [5], a flotation technique [2] in which the precipitate of thionalide is floated with the aid of a surfactant and small nitrogen bubbles was used for the selective preconcentration of arsenic(III) in water and sea water.

The flotation separation with hydrated iron(III) oxide was used for the preconcentration of trace elements such as tin(IV)

[3] and bismuth(III) [4] in water. However, the flotation of low $\mu\text{g l}^{-1}$ levels of tin(IV) and bismuth(III) from water using thionalide has not been reported previously.

This paper describes the application of the simultaneous flotation separation technique using thionalide for the enrichment of microgram amounts of tin(IV) and bismuth(III) in water and sea water. The precipitate of thionalide is readily separated from the mother liquor, then dissolved in acetone and digested with nitric and perchloric acids for atomic absorption spectrophotometry (AAS) by hydride generation.

The recoveries of tin(IV) (20 μg as Sn) and bismuth(III) (20 μg as Bi) were investigated as a function of the amount of thionalide added to 1 l of solution. Recoveries of more than 90% were obtained with > 160 mg of thionalide for both elements. In this work, 200 mg of thionalide were added to 1 l of the solution.

The effect of the pH was examined on the coprecipitation and flotation of tin(IV) and bismuth(III) from 1 l of water and sea water containing 20 μg of each of tin and bismuth and 200 mg of thionalide. The sea water used for these experiments was clear, uncontaminated natural sea water, filtered through 0.45 μm Millipore filters after collection. Hydrochloric acid and sodium hydroxide solution were used to adjust the pH to values within the range of 1–11 (1–9 for sea water).

The effect of pH on the recoveries of tin(IV) is illustrated in Fig. 1. In the case of water, recoveries of tin were > 95% in the pH-range of 1.2–9.5 when the solution was heated. When the solution was not heated, recoveries were > 95% in the pH-range of 1.2–2.5, but decreased with increasing pH values. In the case of sea water, recoveries were 88–90% in the pH-range of 1.1–2.5 and were quantitative in the pH-range of 3.7–7.7.

The results for bismuth(III) are shown in Fig. 2. Satisfactory recoveries of bismuth were obtained over the pH-range 1.2–11 for water when the solution was heated. When the solution was not heated, quantitative recoveries of bismuth were obtained in the pH range of 1.2–3.5, but at pH-values above 4 the efficiency of coprecipitation decreased to about 70%. In the case of sea water, the recovery of bismuth was about 88% at pH 1.1 and recoveries were more than 93% in the pH-range of 1.5–8.5 without heating.

The relation between stirring time and recoveries of tin(IV) and bismuth(III) was also investigated. As a result, the efficiency of coprecipitation was > 90% over the range of 5–40 min. In practice, stirring time was 15 min.

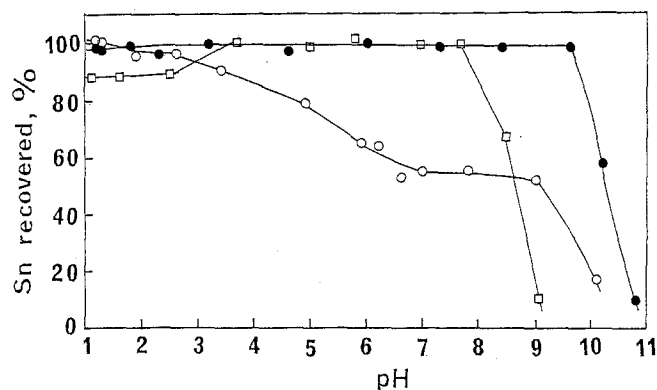


Fig. 1. Coprecipitation of tin with thionalide as a function of pH. Solution containing 20 μg of Sn(IV) and 200 mg of thionalide; sample volume 1 l. ● Water, heated; ○ water, not heated; □ sea water, not heated

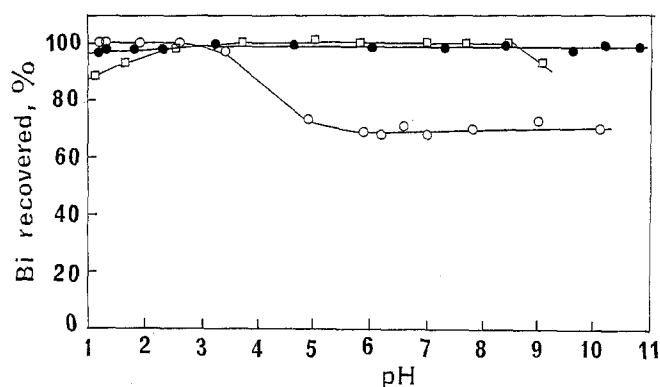


Fig. 2. Coprecipitation of bismuth with thionalide as a function of pH. Solution containing 20 μg of Bi(III) and 200 mg of thionalide; sample volume 1 l. ● Water, heated; ○ water, not heated; □ sea water, not heated

Compared with the flotation separation using hydrated iron(III) oxide as a collector, the flotation with thionalide can be performed in the lower pH range. Therefore, careful attention for the pH adjustment of the sample solution is not necessary.

The flotation of tin and bismuth coprecipitated with thionalide at pH 2–3 is thus useful for the enrichment of low $\mu\text{g l}^{-1}$ levels of tin(IV) and bismuth(III) from water and sea water. The subsequent AAS measurement of hydrides of tin and bismuth is rapid and sensitive.

Experimental

Apparatus and reagents were almost the same as those described previously [3, 4]. Thionalide was purchased from Tokyo Kasei and Merck.

Procedure. Place 1 l of acidified water or sea water sample (pH 2–3) in a 1 l beaker, add 10 ml (200 mg as thionalide) of thionalide-acetone solution (2% w/v) and stir for 15 min. (When heating the solution, do this in a boiling water bath for about 30 min and allow to stand overnight). Add 1 ml of mixed surfactant solution into the beaker and transfer into a flotation cell. The procedure for the flotation separation and for the digestion with nitric and perchloric acids were almost the same as previously reported [5]. For the determination of bismuth, transfer adequate aliquots of the resultant solution (20 ml) into a 20 ml calibrated flask, add 4 ml of hydrochloric acid and 1 ml of potassium iodide solution (20% w/v) into the flask and dilute to 20 ml with water. For the determination of tin, transfer adequate aliquots of the resultant solution into a 20 ml calibrated flask, add 2 ml of 6 mol/l hydrochloric acid and dilute to 20 ml with water. Run a blank through the whole procedure using 1 l solution containing 200 mg of thionalide. The whole procedural blanks were < 20 ng of tin and bismuth for the use of 200 mg of thionalide purchased from Tokyo Kasei and from Merck, respectively.

The procedure for the AAS determination of tin and bismuth after the separation were almost the same as previously reported [3, 4].

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Research in environmental pollution

VII. Identification of non-*o,o'*-Cl and mono-*o,o'*-Cl substituted PCB congeners in Hessian human milk

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Summary. Five non-*o,o'*-Cl and 15 mono-*o,o'*-Cl substituted PCB congeners were identified in Hessian human milk by GC-MS. For risk and hazard assessment the concentrations

of these analysed PCB congeners were transformed into the corresponding TCDD-equivalents (TE). It was found that the concentrations of the analysed coplanar PCB congeners in human milk expressed in TE are by a factor of about 4 higher than that of the polychlorinated dibenzo-*p*-dioxins (PCDD's) and dibenzofurans (PCDF's).

1 Introduction

In part IV [1], V [2] and VI [3] of this series the identification and concentrations of non-*o,o'*-Cl (non-ortho) and mono-*o,o'*-Cl (mono-ortho) substituted PCB congeners in Main river fish, in Rhine river fish and in Hessian cow milk were reported. For risk and hazard assessment the concentrations of individual