

Determination of Trace Amounts of Sb, Pb, Tl in Water Samples by Inductively Coupled Plasma Atomic Emission Spectrometry after a Diantipyrylmethane-Iodide Third Phase Preconcentration

Xiaojia Li¹, Peter Schramel^{2,*}, Zao Wang¹, Peter Grill², Ayfer Yediler², and Antonius Kettrup²

¹ Central Iron and Steel Research Institute, Chemistry Department, No. 76 Xueyuan Nanlu, Haidian District, Beijing 100081, Peoples Republic of China

² GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, Institut für Ökologische Chemie, Neuherberg, D-85758 Oberschleißheim, Federal Republic of Germany

Abstract. A preconcentration method based on third phase extraction has been developed and combined with inductively coupled plasma atomic emission spectrometry (ICP-AES) for determination of Sb, Pb, Tl at trace levels in water samples. The reagents diantipyrylmethane and potassium iodide were applied for complexing Sb, Pb, Tl and producing a third phase extraction system. This third phase system produces relatively large enrichment factors and complete isolation of trace elements from high salt-containing matrices which influence strongly the plasma condition. Experimental parameters of the extraction, such as concentrations of complexing reagents, pH and extraction time have been optimized. Under the selected conditions, this third phase ICP-AES combination procedure gave multielemental detection limits for Sb, Pb, Tl which are superior by an order of magnitude or more to those obtained by ICP-AES alone without preconcentration. Precision of the technique is better than 10% at the 10 µg/l level. The accuracy of this approach is demonstrated by its application to tapwater, artificial seawater and reference seawater samples.

Key words: Preconcentration, third phase, trace elements, ICP-AES

The elements Sb, Pb, Tl are of high environmental interest, due to their toxicity. Normally their concentrations in the atmosphere, dust, foods and water are limited to very low levels. Various analytical techniques, based on neutron activation [1], graphite furnace atomic absorption spectrometry, GFAAS [2, 3], flame atomic

* To whom correspondence should be addressed

absorption spectrometry, FAAS [4], inductively coupled plasma mass spectrometry, ICP-MS [5] and capacitively coupled microwave plasma atomic emission spectrometry [6], have been used for their determination. ICP-AES is one of the most important and commonly preferred methods for measuring trace elements because of its detecting power. It features multielemental detection with low detection limits for most elements in the periodic table. For the elements Sb, Pb, Tl, however its superiority remains limited. The detection limits of conventional pneumatic nebulization ICP-AES for Sb, Pb, Tl are in the range of 10–20 $\mu\text{g/l}$ respectively. Therefore a pretreatment step is desirable. Schramel et al. [7] applied continuous flow hydride generation ICP-AES for measuring Sb in biological and environmental samples. A detection limit of 0.8 $\mu\text{g/l}$ was achieved. Hartenstein and his colleagues improved the detection limit of Pb to 2 $\mu\text{g/l}$ by using a miniature ion-exchange column of Chelex 100 preconcentration system coupled to ICP-AES [8]. Liquid-liquid extraction is a widely used preconcentration and separation technique. For Sb, Pb, Tl, there are many well developed extraction systems described in the literature [9], for example, DDDC- CHCl_3 (diethylammonium diethyldithiocarbamate) DDTC- CCl_4 (diethyldithiocarbamate) and DAM- CHCl_3 systems. For the DAM (diantipyrylmethane) extraction system, chloroform is used as solvent. Provided that DAM is present together with hydrochloric acid and some other anions, e.g. SCN^- or I^- , the use of a mixture of chloroform with an inert diluent such as kerosene or an aromatic hydrocarbon as solvent results in the formation of a liquid three-phase system (third phase extraction system) [10]. That is apart from the normal aqueous and organic phases, another organic phase is produced, which is called the third phase or the microphase owing to its small volume (about 1 ml). This third phase was found to have strong extraction capability for some trace elements existing in the aqueous phase.

The major advantage of the third phase extraction for preconcentration of trace elements is the high enrichment factor. In conventional two-phase systems, the enrichment factors are in the range of 1–10 due to the limitation of the phase-volume ratio (organic solvent:aqueous phase). The concentration factor obtained in three-phase extraction is only dependent on the ratio between the aqueous phase and the third phase, rather than the initial volume ratio between the aqueous solution and organic solvent. Petrov et al. used third phase for the concentration of Pd(II) [11], Pt(IV) [12] and Re(VII) [13]. These elements can be concentrated from 1L of aqueous solution into 1 ml of the third phase. The concentration factor is 1000 which is 1–2 orders of magnitude greater than those of two-phase systems.

In spite of their strong extraction ability and wide application, few two-phase or three-phase extractions have been used for ICP-AES. This is attributed to the poor tolerance of the ICP to organic solvents which can produce cooling effects on the ICP, or even extinguish the plasma. This paper describes a preconcentration system based on third phase extraction coupled to ICP-AES by stripping of the third phase. In an acidic medium a third phase in which the main components are ion pairs $(\text{DAM} \times \text{H}) \times (\text{MI}_m)$ and $(\text{DAM} \times \text{H}) \times (\text{I}_n)$, is formed when H^+ , I^- and Pb, Sb, Tl ions coexist in aqueous solution and diantipyrylmethane (DAM) dissolved in a mixture of chloroform and benzene is used as extractant. The volume of the third phase is about 1 ml under the selected conditions and was found to be efficient for preconcentration of Sb, Pb, Tl simultaneously. On the other hand, these ion pairs

can be easily decomposed in a basic medium. Thus by a basic solution stripping, the metal ions will be released back to the aqueous stripping solution which is suitable for determination by ICP. In these experiments, decomposition was carried out by using tetramethylammonium hydroxide (TMAH) as stripping reagent. The factors which influence the enrichment of metal ions, including the acidity of the solution and concentrations of complexants were optimized. Limits of determination in the range of 0.3–0.8 $\mu\text{g/l}$ were obtained. Third phase extraction was for the first time successfully combined with ICP-AES for multielement analysis in environmental samples.

The interferences from saline matrices were also studied here. The excitation characteristics of ICP can be affected severely by salt ions, such as Na^+ , Mg^{2+} , Ca^{2+} . This limits the applications of ICP-AES to some samples, for example seawater. The elimination of these interferences of salt ions on ICP-AES by third phase extraction were investigated. The results show that the influence of Na^+ , Mg^{2+} , Ca^{2+} could be eliminated completely. The system has been successfully applied to the determination of Sb, Pb, Tl in reference seawater sample NASS-3.

Experimental

Instrumentation

The ICP-AES system used in this work was a Jobin-Yvon Model 70P ICP-spectrometer. A cross-flow nebulizer and a Gilson autosampler were used. Sb, Pb, Tl were measured on sequential mode. Table 1 summarizes important instrumental features, operating conditions and analyte emission lines which were used.

Reagents and Standards

Ultrapure water was prepared by a Milli-Q plus system (Millipore, Germany). Stock solutions of 1000 mg/l Sb, Pb, Tl were obtained from commercial sources (SPEX). The multielement solutions with each of the analytes present at a concentration of 10 mg/l or 200 $\mu\text{g/l}$ were prepared by successive dilution of 1000 mg/l stock solutions. Potassium iodide (2 mol/l) was made by dissolving 33.2 g analytical grade potassium iodide salt in 100 ml ultrapure water. 0.2 mol/l diantipyrylmethane (DAM) solution was prepared by dissolving 7.7 g DAM in a 100 ml mixture of chloroform and benzene

Table 1. Operating conditions of ICP-AES

RF output		1.2 kW
Frequency		40.86 MHz
Argon flow rate,	coolant	15 l/min
	carrier	0.8 l/min
	sheath	0.1 l/min
Integration time	Sb	1 s
	Pb	0.5 s
	Tl	1 s
Wavelength	Sb	206.833 nm
	Pb	220.353 nm
	Tl	190.864 nm
Observation height		appr. 10 mm

(chloroform:benzene = 1:1, v/v). 5% TMAH (tetramethylammonium hydroxide) was prepared from dilution of 25% TMAH stock solution (TAMA Chemicals Japan). Hydrochloric acid, sodium chloride, magnesium nitrate and calcium chloride were analytical grade reagents. Open ocean seawater reference material for trace metals NAAS-3 were purchased from National Research Council Canada.

Procedures

1. *Extraction of metal ions into the third phase (formation of the third phase).* According to the requirements of the experiments, a certain amount of sample (metal ions Sb, Pb, Tl), 40 ml of the 2 mol/l solution of potassium iodide and 16 ml hydrochloric acid (30%) were placed into a 250 ml separating funnel. Ultrapure water was added resulting in a total volume of aqueous phase of 200 ml. 5 ml of 0.2 mol/l DAM solution was added and extracted for 5 mins. After standing for 5 mins, the third phase was separated carefully into another 25 ml separating funnel which contained 2 ml chloroform.

2. *Setting free metal ions from the third phase (decomposition of the third phase).* 4 ml of 5% TMAH solution was placed into a 25 ml separation funnel containing the third phase from the above procedure and extracted for 1 min. The aqueous phase was then separated and analysed by ICP-AES under the operating conditions summarized in Table 1.

The calibration solutions and blanks were treated in the same way as the samples.

Results and Discussion

As soon as the acidity and the concentration of I^- in the system reach a certain level, the third phase is produced and remains at the bottom of the separating funnel as the most heavy one.

1. Effect of the Hydrochloric Acid Concentration on the Extraction

The effect of the hydrochloric acid concentration in the aqueous phase on the relative intensities of ICP-AES, which is corresponding to the extractabilities of Sb, Pb, Tl is shown in Fig. 1. The dependence of the emission intensities on the acidity was very similar for all three elements. The intensities were strongly dependent on the acid concentrations in the range of 0.04 mol/l, where the intensities increased with increasing the acidity. At higher acidity, emission intensities were constant and maximum extractability was obtained respectively. It was also found that no third phase appeared when the concentration of HCl was lower than 0.02 mol/l. Therefore, 0.8 mol/l of hydrochloric acid concentration was selected for further work.

2. Effect of the Concentration of Potassium Iodide on the Extraction

The results indicate that at least 0.16 mol/l potassium iodide in aqueous solution is required to obtain constant and maximum extraction (Fig. 2). For concentrations of potassium iodide lower than 0.04 mol/l no third phase was produced. All the subsequent studies were carried out at 0.4 mol/l.

3. Effect of the Extraction Time

No significant differences in the extraction capacity was observed between 1 and 15 min extraction time. Five min were chosen for all the experiments.

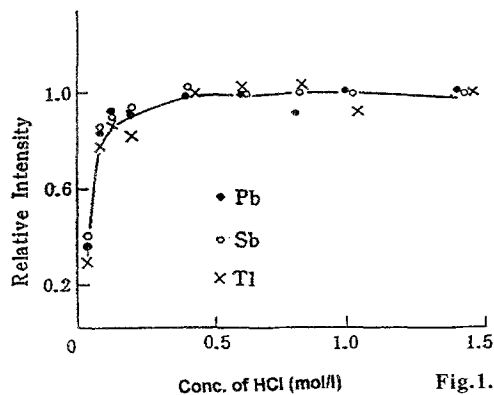


Fig. 1.

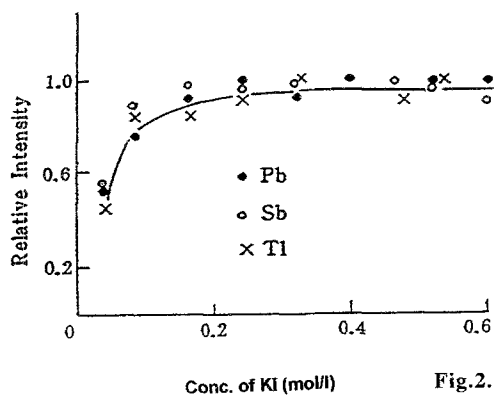


Fig. 2.

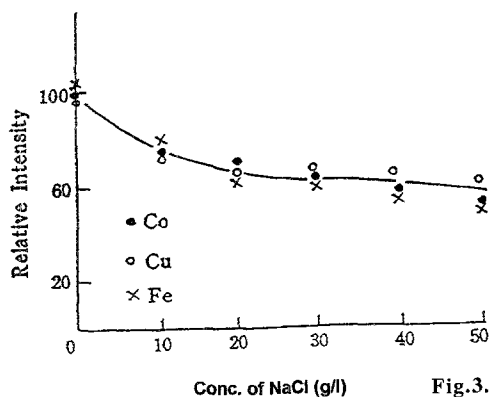


Fig. 3.

Fig. 1. Effect of HCl on the relative intensities of Sb, Pb, Tl (200 $\mu\text{g/l}$)

Fig. 2. Effect of KI on the relative intensities of Sb, Pb, Tl (200 $\mu\text{g/l}$)

Fig. 3. Suppression by Na^+ on ICP-AES signal responses of Sb, Pb, Tl (200 $\mu\text{g/l}$)

4. Stripping of the Third Phase

The third phase can be decomposed by a basic medium and the metal ions in the third phase would be released back to aqueous phase. Sodium acetate and TMAH were tested for their stripping capability. In spite of sodium acetate showing a better enrichment factor compared to TMAH in case of Sb, the latter was used for all the experiments because of the decreased influence to the ICP. The concentration used was 5% (v/v).

5. Detection Limits and Precision of the System

The detection limits reported here are related to $2s$ of the background values. The data are shown in Table 2 also compared with the detection limits obtained by conventional ICP-AES without preconcentration. Obviously the detection limits derived by the combination of ICP-AES and third phase preconcentration are improved by at least ten-fold. They were obtained by treating 200 ml sample or blank solutions.

The precision of the present method was estimated by determining 10 $\mu\text{g/l}$ multi-element solution. The relative standard deviations for Sb, Pb, Tl are shown in Table 3.

Table 2. Detection limits of the method (n = 10)

Element	Detection limit with the third phase extraction ($\mu\text{g/l}$)	Detection limit without the third phase extraction ($\mu\text{g/l}$)
Pb	0.3	10
Sb	0.7	7.4
Tl	0.8	12

Table 3. Precision of the method^a (n = 10)

Element	Precision
Sb	4.5%
Pb	3.5%
Tl	7.2%

^aThe concentration used for estimating precision was 10 $\mu\text{g/l}$.

6. Effect of Matrices

It is well known that the excitation characteristic of ICP can be strongly interfered by some matrix elements, especially Na^+ , Mg^{2+} , Ca^{2+} . In this work, it was found that the ICP-AES signal intensities of Sb, Pb, Tl were inhibited by about 40%–50% by 50 g/l NaCl present in solutions (Fig. 3). Similar effects can be observed for Mg and Ca. The elimination of interferences of the elements Na^+ , Mg^{2+} , Ca^{2+} by the third phase extraction was examined by determining the recoveries of 200 $\mu\text{g/l}$ of Sb, Pb, Tl in the presence of different concentrations of Na^+ , Mg^{2+} or Ca^{2+} . The results reveal that the signal suppression from Na^+ , Mg^{2+} and Ca^{2+} could be completely eliminated by using the third phase extraction. The recoveries are all within 90 to 110%. So third phase extraction can be used as a preconcentration and separation approach for high salt-containing samples.

7. Application of the Method

The recoveries of 2 μg of Sb, Pb and Tl in tapwater and artificial seawater were also determined. Satisfactory results within 97% and 103% were obtained. The artificial seawater contained 3.5 g NaCl, 0.5 g $\text{Mg}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$ and 0.1 g $\text{CaCl}_2 \times 2\text{H}_2\text{O}$ in 100 ml water. Tap-water was taken from the pipe in the laboratory.

To check the applicability of the proposed method, the determination of antimony, lead and thallium in reference seawater NASS-3 was carried out. The concentration of lead in the NASS-3 is 0.039 $\mu\text{g/l}$ that is lower than the detection

Table 4. Analytical results of the reference seawater NASS-3

Element	Added (μg)	Measured (μg)	Recovery %
Sb	5	4.9	99
	10	9.6	96
	15	14.6	97
	20	20.1	100
Pb	5	4.9	98
	10	10.6	106
	15	16.6	111
	20	21.6	108
Tl	5	4.9	98
	10	9.0	90
	15	16.2	108
	20	21.1	105

limit of our method. Antimony and thallium are not certified. Because of no other available suitable reference samples, known amounts of Sb, Pb and Tl were added to NASS-3 (200 ml). The spiked samples were analysed by the proposed procedure. The results are summarized in Table 4. All recoveries obtained were satisfactory.

Conclusion

This work shows that the third phase extraction is an efficient and feasible preconcentration and pre-separation technique for ICP-AES. The procedure described here can be applied to preconcentrate Sb, Pb, Tl from water samples and separating them from highly saline matrices. 0.3–0.8 $\mu\text{g}/\text{l}$ detection limits were obtained. Precision, recovery of the method are satisfactory. Suppression of Na^+ , Mg^{2+} and Ca^{2+} to ICP-AES signals can be eliminated completely. This makes analysis of trace amount of Sb, Pb, Tl especially in seawater by ICP-AES possible. For these applications higher enrichment factors are necessary, that means the ratio between the aqueous and the third phase has to be increased, which is easily possible as mentioned in the beginning. The purpose of this paper was to describe the procedure in combination with ICP-AES as the elemental detector.

References

- [1] A. D. Matthews, J. P. Riley, *Anal. Chim. Acta* **1969**, *48*, 25.
- [2] L. Fangruo, X. D. Hou, *Atomic Spectroscopy*, **1994**, *15*, 216.
- [3] H. W. Sun, X. O. Shan, I. M. Ni, *Talanta* **1982**, *29*, 589.
- [4] Y. P. Pena, M. Gallego, M. Valcarcel, *Talanta* **1995**, *42*, 211.
- [5] D. Beauchemin, J. W. McLaren, A. P. Mykytiuk, S. S. Berman, *Anal. Chem.* **1987**, *59*, 778.
- [6] M. W. Wensing, B. W. Smith, J. D. Winefordner, *Anal. Chem.* **1994**, *66*, 531.
- [7] P. Schramel, L. Q. Xu, *Fresenius Anal. Chem.* **1991**, *340*, 41.

- [8] S. D. Hartensten, J. Ruzicka, G. D. Christian, *Anal. Chem.* **1985**, 57, 21.
- [9] Zhongnan Mineral and Metallurgical College, *Handbook of Analytical Chemistry*, Science Press, Beijing, China, 1982.
- [10] B. I. Petrov, V. P. Zhivopistev, *Talanta* **1987**, 34, 175.
- [11] B. I. Petrov, V. N. Vilsov, I. N. Ponosov, V. P. Zhvopistsev, *USSR Patent 446797*, 15 October, 1974.
- [12] B. I. Pertov, V. P. Zhivopistsev, I. N. Ponosov, V. N. Vilisov, *USSR Patent 446801*, 15 October, 1974.
- [13] B. I. Petrov, V. P. Zhivopistsev, M. I. Degter, Y. A. Makhnev, *USSR Patent 446803*, 15 October, 1974.

Received July 31, 1995. Revision November 30, 1995.