Analytical Strategy for the Speciation of Antimony and Chromium with Emphasis on the Preservation of Elemental Species

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With respect to elemental speciation, the extraction of elemental compounds from solid samples without changing the chemical forms, thus to get the information about the original chemical forms of the element of interest, still remains to be a great challenge for analysts. In this paper, we will report the recent research work on the speciation of Sb in airborne particulate matter (APM) and Cr in leaching test solutions of plasma treated slag using HPLC-ICP-MS and ES-MS. Efforts for the development of good separation systems for both Sb and Cr compounds, for the improvement of the sensitivity of HPLC-ICP-MS, and for the preservation of Sb species, especially the prevention of Sb(III) from the oxidation to Sb(V) during the extraction process, will be discussed. In contrast to the oxidation of Sb species, the reduction of Cr(VI) to Cr(III) was observed in the leaching test solutions of plasma treated slag.

Over the years, anthropogenic emission of antimony (Sb) and chromium (Cr) has resulted in an increasing concentration of Sb and Cr in the environment, thus led to pronounced exposure to Sb and Cr of humans. Since the toxicity of Sb and Cr are strongly dependent on their chemical forms and oxidation states, speciation data for Sb and Cr are urgently required in order to have a sound risk assessment and a better understanding of the fate of Sb and Cr in the environment.

With respect to elemental speciation analysis using hyphenated techniques, for instance, the hyphenation of HPLC and ICP-MS, an effective separation system which is capable of the separation of target analytes with good resolution and good matrix tolerance is a precondition to obtain reliable results. On the other hand, the extraction of elemental compounds from solid samples without changing the chemical forms, thus to get the information about the original chemical forms of the element of interest, as a primary task,[1,2] which underpins the reliability of the whole analytical process, still remains to be a great challenge for analysts.

For the speciation analysis of Sb and Cr species, the oxidation of Sb(III) to Sb(V)[3,4] and the reduction of Cr(VI) to Cr(III)[5] during the sample preparation and analysis process are often encountered. In our previous work on Sb speciation analysis,[6,7] a complexation effect of Sb compounds with citric acid was observed and confirmed with electrospray mass spectrometry (ES-MS). The formed Sb(III)-citrate and Sb(V)-citrate complexes were found to be stable in different matrix. This discovery offers a possibility to preserve the oxidation states of Sb species during the extraction process, that is, the Sb(III) and Sb(V) species present in the solid matrix may form the corresponding complexes with citrate when citric acid is used as the extraction solvent, the change of oxidation states, therefore, could be avoided. While for Cr speciation analysis, it has been reported that carbonate buffer was useful for the preservation of Cr oxidation states.[8]

In this paper, we report our recent work on Sb speciation in APM and Cr speciation in leaching test solutions of plasma treated slag. This work was performed based on the following considerations. Firstly, high concentrations of Sb were detected in APM samples during the long-term monitoring of heavy metals in these specimens. Extraction experimental results obtained by using different solvents and sequential extraction techniques revealed that up to 20 % of the total Sb in APM samples was environmentally mobile fraction. Taking into account the different toxicity and environmental fate of Sb, the analytical method for the determination of Sb species in APM was required. Secondly, the application of arc plasma to waste treatment has attracted attention in Japan because of the potential of reducing volume of wastes and rendering hazardous wastes harmless. To evaluate the treatment effect, the information about Cr oxidation states in leaching test solutions using pH controlled water was necessary. For these purposes, HPLC-ICP-MS methods were developed for Sb and Cr speciation analysis.

Experimental

Chemical and reagents

All of the chemical and reagents used in this study were of analytical grade. The water used was Milli-Q purified water (18.3 MΩ cm) (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan). Phthalic acid, HNO_3 (70 %), oxalic acid and EDTA were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Citric acid was purchased from Aldrich (Milwaukee, WI, USA). Stock solutions of Sb(III), Cr(III) and Cr(VI) were made up from a commercially available concentrate, Spex plasma standard (Metuchen, NJ, USA). A stock solution of Sb(V) was prepared from potassium hexahydroxoantimonate (V) (Kanto Chemical Co., Inc., Tokyo, Japan). Working standard solutions of Sb(III), Sb(V), Cr(III) and Cr(VI) were prepared by appropriate dilution from 1000 mg/l stock solutions with Milli-Q water or citric acid. All working standard solutions were prepared daily to prevent any possible species change. The used mobile phases for chromatography were freshly prepared, filtered through a 0.45 μm membrane filter and degassed before use. Rubidium with a concentration of 20 μg/l was added into the mobile phase as an internal standard.

Table 1 Operating conditions for HPLC and ICP-MS instruments

HPLC	
Column	Hamilton PRP-X100 (250 x 4.6 mm i.d.)
Mobile phases	10 mmol/l EDTA – 1 mmol/l phthalic acid at pH 4.5 for Sb speciation; 20 mmol/l oxalate at pH 3.0 or 7.0 for Cr speciation
Flow rate	1.5 ml/min
Injection volume	100 μl
Column temperature	Ambient
ICP-MS	
Forward rf power	1300 W
Plasma Ar flow	15.0 l/min
Auxiliary Ar flow	1.0 l/min
Nebulizer Ar flow	1.2 l/min
Data acquisition	Time resolved analysis
Integration time	100 ms
Isotopes monitored	^{44}Ca, ^{87}Rb, ^{121}Sb, ^{123}Sb, ^{52}Cr and ^{53}Cr
Total analysis time	600 s for Sb speciation; 800 s for Cr speciation

Instrumentation

The ICP-MS instrument used was HP 4500 (Yokogawa Analytical Systems, Tokyo, Japan). The sample introduction system used included a Scott-type spray chamber fitted with a concentric nebulizer. The chromatographic system consisted of a JASCO PU-1580i (metal-free) intelligent HPLC pump (Japan Spectroscopic Cooperation), a syringe-loading injector (Model 9725i, Rheodyne six-port injection valve) with a 100 μl loop and an inert PRP-X100 anion-exchange column (Hamilton, USA, 250 x 4.6 mm i.d., 10 μm particle size; stable between pH 1 and 13), which was packed with a styrenedivinylbenzene copolymer with trimethylammonium exchange sites. The chromatographic system was interfaced with an ICP-MS instrument using a 200 mm PEEK (polyether ether ketone) capillary tubing (0.25 mm i.d.) to connect the column outlet to the inlet hole of the nebulizer. The chromatographic results were processed using Chromatosoftware (Yokogawa Analytical Systems, Tokyo, Japan). Quantifications

were performed in the peak area mode. The operating conditions for HPLC-ICP-MS are summarized in Table 1.

Results and discussion

Sb speciation in APM

In this study, a Japanese quality control sample for APM (AS-1, 92 μg/g Sb) and APM sample (104 μg/g Sb) collected in Tokyo (June, 2000) were investigated. The details for the APM sampling have been described elsewhere.[3,9] At first, the environmentally mobile fraction of Sb in APM was investigated using different extraction solvents. Experimental details about the extraction were described in previous work.[3,7,9] Figure 1 shows the obtained extraction efficiencies (%) for AS-1. It was found that the extraction efficiency was less than 10 % when water, 0.5 mol/l phosphate (pH 4.2), 10 mmol/l tetramethylammonium hydroxide (TMAH), and 0.1 mol/l NaOH were used as extraction solvents. The higher extraction efficiency could be obtained with 0.05 mol/l EDTA (pH 7.0) and 0.3 mol/l oxalic acid (pH 4.5) because of the dissolution of Fe and Mn compounds resulting in the release of Sb adsorbed on their surfaces.[10] When a three-step sequential extraction procedure (0.25 mmol/l phosphate, 0.05 mol/l EDTA, and de-ionized water) was applied to AS-1 sample, an extraction efficiency of 24 % could be achieved. These results indicated that the environmentally mobile fraction of Sb in APM was around 20 % of the total Sb concentration.
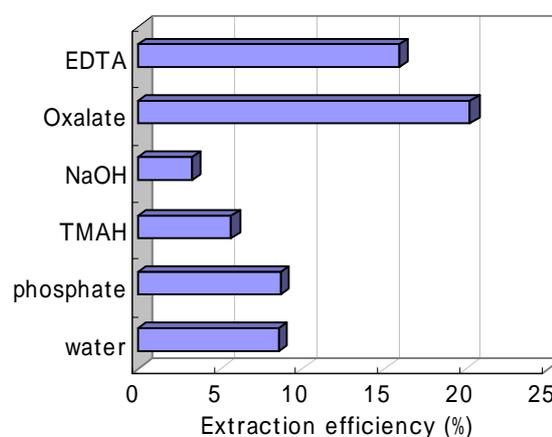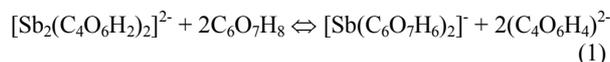

Fig. 1 Antimony extraction efficiency from AS-1 sample using single extraction procedures.

Although the different single extraction procedure and the sequential extraction procedure are capable of providing the proportion of environmentally mobile fraction of Sb, the information about the chemical forms of Sb in APM sample is not available. Some extraction procedures applied are too harsh to preserve the oxidation state. Indeed, even for the soft extraction with water, the change of oxidation state may occur. In our previous work on the speciation of Sb in aqueous extracts of APM,[3,9] Sb(V) was found to be the major species, no Sb(III), the most toxic form could be detected. In order to get the original information about the Sb species exist in APM sample, a special extraction procedure which is capable of preservation of original Sb species has to be developed.

Recently, we observed a complexation effect of Sb compounds with citric acid using electrospray time-of-flight mass spectrometry (ES-TOF-MS).[7] Based on the obtained ES mass spectrum data, the complexation effect may be described with equation 1 and 2 for Sb(III)-citrate and Sb(V)-citrate, respectively. Then, a HPLC-ICP-MS method was developed to separate and detect the Sb(III)- and Sb(V)-citrate complexes with sufficiently low detection limits of 0.05 μg/l and 0.07 μg/l.

$$[Sb_2(C_4O_6H_2)_2]^{2-} + 2C_6O_7H_8 \Leftrightarrow [Sb(C_6O_7H_6)_2]^- + 2(C_4O_6H_4)^{2-} \quad (1)$$

$$Sb(OH)_6^- + C_6O_7H_8 \Leftrightarrow [Sb(OH)_3(C_6O_7H_5)]^- + 3H_2O \quad (2)$$

Also, it was found that Sb(V) in the aqueous extracts of APM sample could be changed to Sb(V)-citrate, when the aqueous extract was mixed with 0.05 mmol/l citric acid. This finding gives us an impetus to investigate the possibility of using citric acid for the extraction of Sb, thus to obtain the original species information in APM sample. The strategy is the *in-situ* formation of Sb(III)- and Sb(V)-citrate complexes during the extraction process, then they are separated and detected with the developed HPLC-ICP-MS method.[7]

Figure 2 shows the HPLC-ICP-MS chromatogram obtained from an APM sample collected in Tokyo using 0.026 mol/l citric acid as an extraction solvent with microwave-assisted extraction (100 W, 10 min). With a microwave power of 100 W, the extraction efficiency could be improved by increasing the extraction time; the obtained extraction efficiency with 5, 10 and 20 min extraction was 18 %, 25 % and 35 %, respectively. Besides the major Sb(V) species, the obtained results clearly indicated the existence of toxic Sb (III) species in APM sample. It was for the first time that such an existence of the most toxic Sb(III) species in APM sample was confirmed. This finding, in turn, demonstrated the effectiveness of the proposed analytical strategy for Sb speciation analysis. It is our conviction that this analytical strategy is not only effective for APM samples, but also effective for other environmental samples, such as soils and sediments, and especially for the speciation analysis of Sb in water samples.

Cr speciation in leaching test solutions of plasma treated slag

Considering the potential of reducing volume of wastes and rendering hazardous wastes harmless, the application of arc plasma to waste treatment has attracted attention in Japan.[11-14] To evaluate the treatment effect, leaching test of the plasma treated slag was performed using pH controlled water (pH 1, 4, 7, 9, 13) according to the regulations issued by the Japanese Environmental Agency. A high concentration of Cr up to 380 ng/ml was detected in the resulted solutions with pH 1 water. For a better risk assessment of the plasma treated slag, the information on the chemical forms of Cr in the test solutions is required. Because Cr(III) and Cr(VI) have contrasting physiological effect; Cr(III) is considered as an essential trace element for the proper functioning of human beings, while Cr(VI) can be toxic to human body tissue owing to its oxidizing potential and easy permeation of biological membranes.

To develop a HPLC-ICP-MS method for Cr speciation analysis, an ion-exchange chromatography with oxalate as a mobile phase was used for the separation of Cr(III) and Cr(VI) prior to their on-line detection by ICP-MS. In order to get good separation for Cr(III) and Cr(VI), the concentration of the oxalate buffer and the pH of the mobile phase were optimized.[15] It was found that good separation could be obtained on a PRP-X 100 anion-exchange column using 20 mmol/l oxalate as a mobile phase at pH 3.0 or 7.0 with an eluent flow rate of 1.5 ml/min under ambient temperature. When the optimized HPLC separation system was coupled to ICP-MS, polyatomic-ion interferences resulted from $^{40}Ar^{12}C^+$ for ^{52}Cr and $^{16}O^{37}Cl^+$ for ^{53}Cr have to be considered. Since the carbon-containing oxalate was employed as the mobile phase, a high background at *m/z* 52 was observed due to the contribution of $^{40}Ar^{12}C^+$. This effect hampered the obtaining of low detection limit by using ^{52}Cr signal although ^{52}Cr is the isotope with the highest abundance (83.76%). With respect to ^{53}Cr signal, the possible interference from $^{16}O^{37}Cl^+$ was checked by the injection of 1000 μg/ml chloride (NaCl) into the HPLC system, and it was found that the chloride could be separated chromatographically from both Cr(III) and Cr(VI) species. The developed HPLC-ICP-MS analytical method is therefore free from chloride-induced interference. Under the optimized conditions, low detection limits were obtained: 0.08 ng/ml for Cr(III) and 0.2 ng/ml for Cr(VI), respectively.
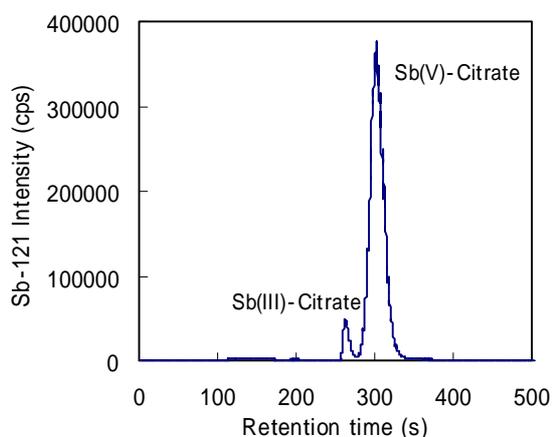

Fig. 2 Chromatogram obtained from an APM sample collected in Tokyo using citric acid as extraction solvent with microwave-assisted extraction. Experimental details were described in Ref. 7.
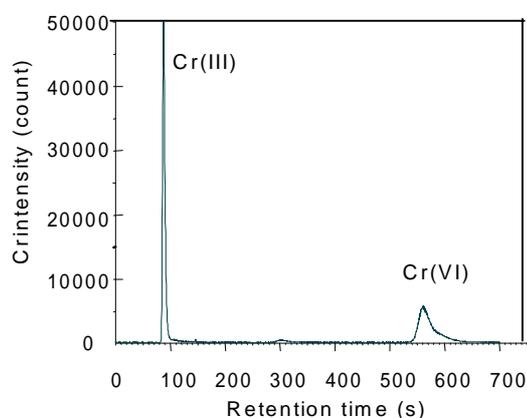

Fig. 3 Chromatogram obtained from a Cr standard solution (100 ng/ml). Chromatographic conditions: PRP-X100 column, 20 mmol/l oxalate (pH 3.0) mobile phase with a flow rate of 1.5 ml/min.

The developed method was applied to the Cr speciation analysis in the leaching test solutions of plasma treated slag. The experimental details for leaching test were described elsewhere.[16] Two types of slag were investigated. One is the resulted slag when ash was treated directly with plasma (Slag). The other is the resulted slag when ash mixed with sulfur powder (ash:sulfur, 5:3, weight:weight) was treated with plasma (Slag+S). The pH values of resulted leaching test solutions were also measured using a pH meter. With a water of pH 1, 4 and 7, the pH values in the resulted leaching test solutions were 3.4, 8.4 and 8.9, respectively. These results indicated the basic properties of the plasma treated slag. Concerning the high concentration of Ca in the leaching test solutions, ^{44}Ca signal was also monitored to check the possible interference from $^{40}Ca^{13}C$.
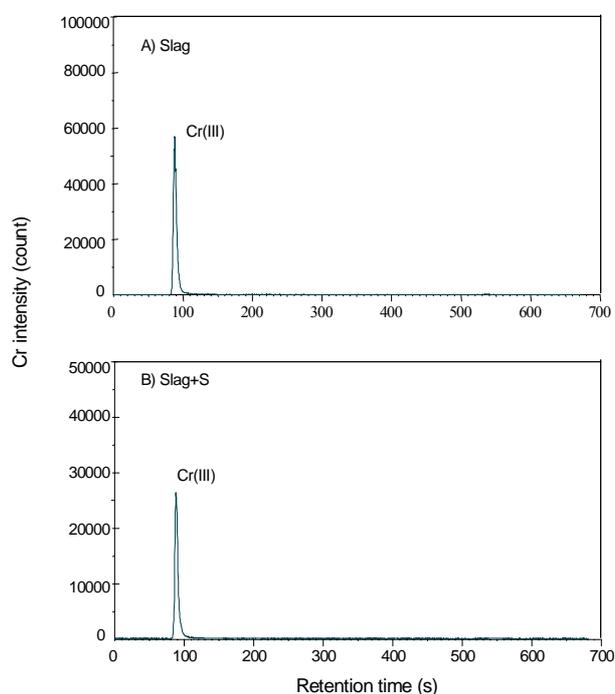

Fig. 4 Chromatograms obtained from the leaching test solutions of the plasma treated slag using pH 1 water. A). Slag, B). Slag+S. Chromatographic conditions: PRP-X100 column, 20 mmol/l oxalate (pH 3.0) mobile phase with a flow rate of 1.5 ml/min.

Typical HPLC-ICP-MS chromatograms obtained from the leaching test solutions of plasma treated slag using pH 1 water were shown in Fig. 4. It was clearly indicated that only Cr(III) exist in the leaching test solutions obtained with pH 1 water. Toxic Cr(VI) was not detected within the detection limit of the developed method. To evaluate the stability of Cr compounds in the leaching test solutions, the test solutions of Slag and Slag+S obtained with the water of pH 1 were stored in a refrigerator at 4 ^0C for one month. The obtained results showed that no oxidation of Cr(III) to Cr(VI) occurred during one month storage. The question whether Cr(VI) exists in the plasma treated slag still remains unknown because the reduction of Cr(VI) to Cr(III) may take place during the rather harsh leaching process. In fact, we observed the reduction of spiked Cr(VI) in the leaching test solutions. This result indicates that the leaching test procedure currently used may provide the information on the possible release of heavy metals from slag in the environment, it is, however, not capable of providing the information on the original Cr species in the plasma treated slag. Again, similar to that described for Sb speciation analysis, the preservation of oxidation states of elemental species becomes the most important factor to be considered. In order to obtain the original information on the oxidation states of Cr in the plasma treated slag, further studies to develop efficient extraction methods without the modification of Cr oxidation state are highly required.

References

1. R. Cornelis, H. Crews, O. Donard, L. Ebdon, L. Pitts, and P. Quevauviller, *J. Environ. Monit.*, **2001**, *3*, 97.
2. M. Krachler, H. Emons, and J. Zheng, *Trends Anal. Chem.*, **2001**, *20*, 79.
3. J. Zheng, M. Ohata, and N. Furuta, *Anal. Sci.*, **2000**, *16*, 75.
4. M. Krachler and H. Emons, *Anal. Chim. Acta*, **2001**, *429*, 125.
5. H. M. Kingston, D. Huo, Y. Lu, and S. Chalk, *Spectrochim. Acta B*, **1998**, *53*, 299.
6. J. Zheng, A. Takeda, and N. Furuta, *J. Anal. At. Spectrom.*, **2001**, *16*, 62.
7. J. Zheng, A. Iijima, and N. Furuta, *J. Anal. At. Spectrom.*, **2001**, in press.
8. K. Vercoutere, R. Cornelis, L. Mees, and P. Quevauviller, *Analyst*, **1998**, *123*, 965.
9. J. Zheng, M. Ohata, and N. Furuta, *Analyst*, **2000**, *125*, 1025.
10. N. Belzile, Y. Chen, and Z. Wang, *Chem. Geol.*, **2001**, *174*, 379.
11. T. Inaba, Y. Watanabe, M. Nagano, T. Ishida, and M. Endo, *Trans. Thin Soild Films*, **1998**, *316*, 111.
12. T. Inaba, M. Nagano and M. Endo, Electr. Eng., **1999**, 126, 73.
13. T. Iwao, H. Miyazaki, T. Hayashi, T. Hirano, and T. Inaba, *Vacuum*, **2000**, *59*, 88.
14. Y. Kubo, T. Hosoi, Y. Kaneko, M. Ohata, T. Iwao, N. Furuta, and T. Inaba, *Trans. IEE of Japan*, **2001**, *121-D(4)*, 493.
15. J. Zheng, Y. Kaneko, K. Hirose, M. Ohata, and N. Furuta, *Proceedings of 4th Symposium on the Characteristics of Ultra-High Temperature Plasma and its Applications to Environmental Process.* Chuo University, Tokyo, Japan, March 19, **2001**, 68-73.
16. N. Furuta, T. Hosoi, M. Ohata, and T. Inaba, *"Sustainable Construction: Use of incinerator ash"*, ed. R. K. Dhir, T. D. Dyer, and K. A. Paine, **2000**, Thomas Telford, 67.