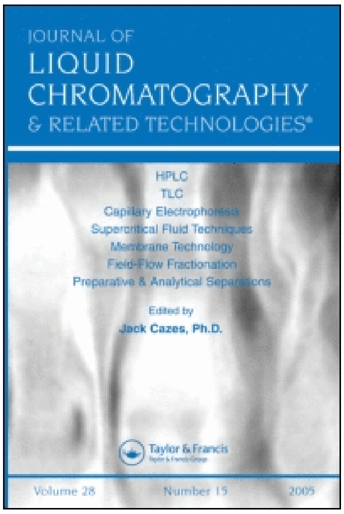

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SPECIATION AND SEQUENTIAL EXTRACTION OF TRACE METALS IN INCINERATOR FLY ASH USING IC AND ICP-MS

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ABSTRACT

This study focuses on the speciation and determination of As, Se, Sb, and Cr in incinerator fly ash, which was sequentially extracted to three kinds of chemical fractions: (1) Exchangeable (2), Carbonates, and (3) Fe/Mn oxides. Using suppressed IC, we could determine the optimum separation condition for the target components. Also, the retention behavior of the metal species was investigated and explained by ion exchange equilibrium. Also, based on the optimum separation condition, the effect of the concentration and pH of the extractants on

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the leachability of chemical species from incinerator fly ash was investigated using IC and ICP-MS. On the whole, as the concentration and pH of the extractants increased, the leached concentration of each chemical species increased.

INTRODUCTION

In recent years, there has been a great interest in speciation study, investigating the determination of the different chemical species in real samples. This is related to the fact that the toxicity, bioavailability, and transfer to organisms are all known to be more affected by the chemical form of an element than its total concentration. For example, it is known that the toxicity of As(III) is about 50 times higher than that of As(V). The LD_{50} for rats is 14 mg/kg for As(III) and 20 mg/kg for As(V).(1) In the same way, Cr(III) and Se(III) are thought to be essential nutrients, while Cr(VI) and Se(VI) are reported to be deleterious to living organisms.

More efficient analytical methods are required to detect the low levels of toxic chemical species. For speciation, chromatographic methods have been mostly used, including GC, HPLC, and CE. Gloyal et al. developed the method of simultaneous determination of arsenite, arsenate, selenite, and selenate in water using suppressed ion chromatography (SIC) with UV detection.(2) Fung et al. optimized the preconcentration of metal oxoanions in environmental water samples by use of nonsuppressed IC.(3) They showed that Chelex-100 resin was effective in removing common inorganic anions and retaining metal oxoanions. Bruzzoniti et al. optimized the simultaneous chromatographic separation and determination of inorganic anions and metal ions precomplexed by EDTA by suppressed ion chromatography.(4) In this process, they optimized the separation condition, investigating the effect of concentration and pH of eluent on capacity factors of the analytes. Casiot et al. used capillary electrophoresis (CE) for the simultaneous speciation of arsenic, selenium, antimony, and tellurium species in water and soil extracts.(5)

In order to improve the sensitivity of the analytes, many kinds of coupled techniques have been adapted to various environmental samples. Recently, chromatographic methods have usually been combined with element specific detectors, such as MS (Mass Spectrometry), DCP (Direct Current Argon Plasma Spectrometry), AAS (Atomic Absorption Spectrometry), and AES (Atomic Emission Spectrometry) to acquire a desirable degree of sensitivity and to avoid possible interferences in matrix.

Several kinds of representative research are as follows: Irgolic et al. have determined arsenic, selenium, and phosphorous compounds using ICP-AES, interfaced with HPLC.(6) Furuta et al. coupled IC and ICP-AES to determine the four kinds of arsenic and selenium species.(7) According to their results, the introduction of a hydride generation (HG) lowered detection limits to 70 ng/mL, 170 ng/mL, and 57 ng/mL for As(III), As(V), and Se(IV), respectively. Kallio et al. made the simultaneous determination of toxic arsenic and chromium species in water samples by IC-ICP-MS.(8) In particular, they established the optimum separation of six kinds of arsenic species: As(III), As(V), MMA, DMA, arsenobetaine (AB), arsenocholine (AC). Jackson et al. coupled IC with ICP-MS to quantify As and Se species in coal fly ash extracts.(9) As, Se, Sb, and Cr are potentially toxic elements that are found in incinerator fly ash, playing the role of an important carrier of hazardous trace metals. The toxicity of fly ash is related to the trace elements present on the surface of it, as well as adsorbed organics; PAH, and their chemical derivatives. Considering the mobility and biological availability of trace metals, the speciation of solid surfaces has significant meaning in the estimation of the fate of trace elements. As far as we know, few studies have been performed about the speciation of multi-elements in incinerator fly ash.

In this work, we used the suppressed ion chromatography for determining the optimum separation of one arsenic species (arsenate(As(V))), two selenium species (selenite(Se(IV)), selenate(Se(VI))), two antimony species (antimonite(Sb(III)), antimonate(Sb(V))) and one chromium species (chromate (Cr(VI))). In this process, we investigated and discussed the retention behavior of metal species, related with the concentration and mole fraction of carbonate/bicarbonate buffer. Based on the optimum separation condition, we introduced the extracts of incinerator fly ash into IC, coupled with conductive detector. After collecting the fractions of each chemical species at the outflow of the column, we reintroduced these fractions into ICP-MS to quantify the inorganic species at trace concentration, and to make the multi-element detection possible. Also, in order to investigate the partitioning of trace metals into specific fractions of incinerator fly ash, we applied the modified Tessier's method for sequential extraction procedures.(10) In particular, the distribution of each metal on the chemical fraction is expected to provide basic information for evaluating the environmental toxic effect. In this study, we investigated the effect of the concentration and pH of the extractants on the leaching ability of each metal species, quantifying the concentration of trace metals in three kinds of environmentally mobile chemical fractions, such as exchangeable, bound to carbonates, bound to iron, and manganese oxides.

In the case of incinerator fly ash, during the incineration process, volatilization of metals followed by a partial condensation on the matrix surface occurs. This would make the metals mostly physically adsorbed on the combustion particles and they could not be considered strongly bound to the fly ash matrix. This is the reason why we focused on three kinds of mobile chemical fractions.

EXPERIMENTAL

Instrumentation

A commercial IC system (SLC, Samsung, Korea) and a Model 9725i injector (Cotati, CA, USA) were used. Samples were injected using a 50 µL sample loop. Both IONOPAC guard column (4 mm × 50 mm I. D. 9 µm) and IONOPAC anion exchange column (4 mm × 250 mm I. D. 9 µm) were used for the speciation of several kinds of trace metals. In order to decrease the background conductivity, a Dionex self-regenerating suppresser, ASRS-II (Sunnyvale, CA, USA) in the chemical mode was used. The eluent was prepared from a mixture of $NaHCO_3$ and Na_2CO_3, adjusted to pH 10.2. The flow rate was kept to 1.0 mL/min. Separated metal species were fractionated with conductivity detection. The column temperature was maintained at 25°C. A commercial ICP-MS instrument (Elan 6100, Perkin Elmer, USA) was used for the determination of metal species in each fraction, collected by IC. The detailed operational conditions are listed in Table 1.

Reagents

Multi-element stock solutions were prepared to 1000 ppm in deionized water. The following stock solutions were made: As(III) and As(V) were made from $NaAsO_2$ and Na_2HAsO_4. Se(IV) and Se(VI) were made from Na_2SeO_3 and Na_2SeO_4, Sb(III) and Sb(V) were made from $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$,

Table 1. ICP-MS Instrumental and Operational Conditions

Parameter	Value/Type
RF Generator power	1.0 kW
RF Frequency	40 MHz
Plasma	15 L/min
Auxiliary	1.2 L/min
Nebulizer	0.960 L/min
Nebulizer type	Microconcentric (MCN100, Cetac)
Mass spectrometer	
Mass analyzer	Quadruple
Dwell time per AMU	50 ms
Integration time	2500 ms
Replicates	3

$KSb(OH)_6$, and Cr(VI) was made from $K_2Cr_2O_7$. The standard solutions were prepared to 4 ppm by serial dilution of the stock solutions. All were purchased from Aldrich Chemical Company (Milwaukee, WI, USA).

Sample Digestion Methods

About 0.1 g of fly ash sample was transferred into a Pt crucible (No. 20), followed by the addition of 7 mL of HF and 8 mL of conc. HNO_3. The mixture in the Pt crucible was allowed to react for 14 h at 180°C in a high-pressure, closed poly(tetrafluoroethylene) (PTFE) vessel (model HU-50, Mitsuoshi Corp., Nagoya, Japan). These conditions were shown to be adequate to achieve a complete solubilization of the adsorbed metals on the fly ash sample.

The resulting solution in the Pt crucible was heated to evaporate the gaseous silicon fluoride and unreacted hydrogen fluoride for 3 hours at 50°C after 1 mL of saturated H_3BO_3 was added into the solution.

Sequential Extraction Procedure

Three kinds of fractions were selected to establish the partitioning of metals: exchangeable, carbonate, and Fe/Mn oxides. These fractions are known to be the most probable carriers of toxic components. In this study, the sequential extraction procedure was systematically investigated to acquire information on the partitioning of metals into three kinds of chemical fractions. First, various concentrations (0.1–5 M) and pH (3.8–7.8) of 8 mL NH_4Oac were added to 0.2 g incinerator fly ash samples and shaken for 7 hours, so as to extract the exchangeable fraction. This extraction is assumed to give the most easily available fraction. Next, this solution was centrifuged for 10 minutes at the speed of 1000 rpm. The solid residue was then separated from the extract and the supernatant liquid was decanted to a 25 mL volumetric flask, followed by dilution, filtering, and introduction to IC and ICP-MS. The above-mentioned solid residue was reextracted with the second extractant, acetic acid, of which the concentration was varied from 0.1 M to 5 M. Acetic acid is known to dissolve, selectively, the carbonate fraction (not removed by the first extractant, NH_4Oac), releasing the bound metals on that.

The same procedures were also applied to the second extract, including centrifugation, dilution, filtering, decantation of supernatant liquid, and introduction to IC and ICP-MS. The third fraction, Fe/Mn oxide, was extracted with hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), varying its concentration (0.1–5 M) and pH (2.0–4.0), followed by the above-mentioned procedures.

The most successful methods for leaching iron and manganese oxides involve the combined action of reagent, reducing these metals to their ferrous and manganous forms, and of an agent capable of keeping the solution in the relatively large amounts of metals liberated. Mostly two coupled reagents, hydroxylamine hydrochloride-acetic acid and sodium dithionite-citrate are used. However, according to Anderson and Jenne, in case of the latter, substantial precipitation of trace metals has been reported.(11) Besides, lower leaching ability of trace metals was observed using dithionite-citrate by Gupta and Chen.(12) Therefore, in this study, hydroxylamine hydrochloride-acetic acid was selected for leaching iron and manganese oxides.

RESULTS AND DISCUSSION

Retention Behavior of Each Metal Species

Generally, the elution strength in IC is affected by the concentration and the pH of eluent. As its concentration increases, the retention of solutes decreases. This trend is as shown in Figure 1(a). The peak for As(III) was not detected. This would be explained by the weaker interaction between the solutes and the stationary phase, due to having their singly negatively charged form, $H_2AsO_3^-$ in the basic pH condition of the eluent. However, baseline separation was not achieved under the investigated conditions, ranging from 13 mM to 21 mM of the mixture of one-to-one molar ratio of Na_2CO_3 and $NaHCO_3$. As shown in Figure 1(b), the mole fraction of Na_2CO_3 was changed from 0.4 to 1.0, in order to increase the resolution among the analytes at the fixed condition of 19 mM $Na_2CO_3/NaHCO_3$. As the mole ratio of $Na_2CO_3/NaHCO_3$ decreased, retention of all analytes increased, due to the reduced ion exchange capacity of eluents. It is reasonable that the retention time is shorter for singly charged species, $Sb(OH)_6$, which is expected to be easily displaced by eluent ions. At the condition of 0.6 mole fraction of Na_2CO_3, peak resolution was pronounced for As(V)/Se(IV) or As(V)/Sb(III). Among the investigated mole fraction of Na_2CO_3, 0.6 mole fraction of Na_2CO_3 was determined to be the optimum separation condition. The chromatogram for a standard solution is shown in Figure 2.

Determination of Total Concentration of Trace Metals in Coal (NIST SRM) and Incinerator Fly Ash

Prior to the application of metal speciation for incinerator fly ash, we investigated the total amount of As, Se, Sb, and Cr in incinerator fly ash using

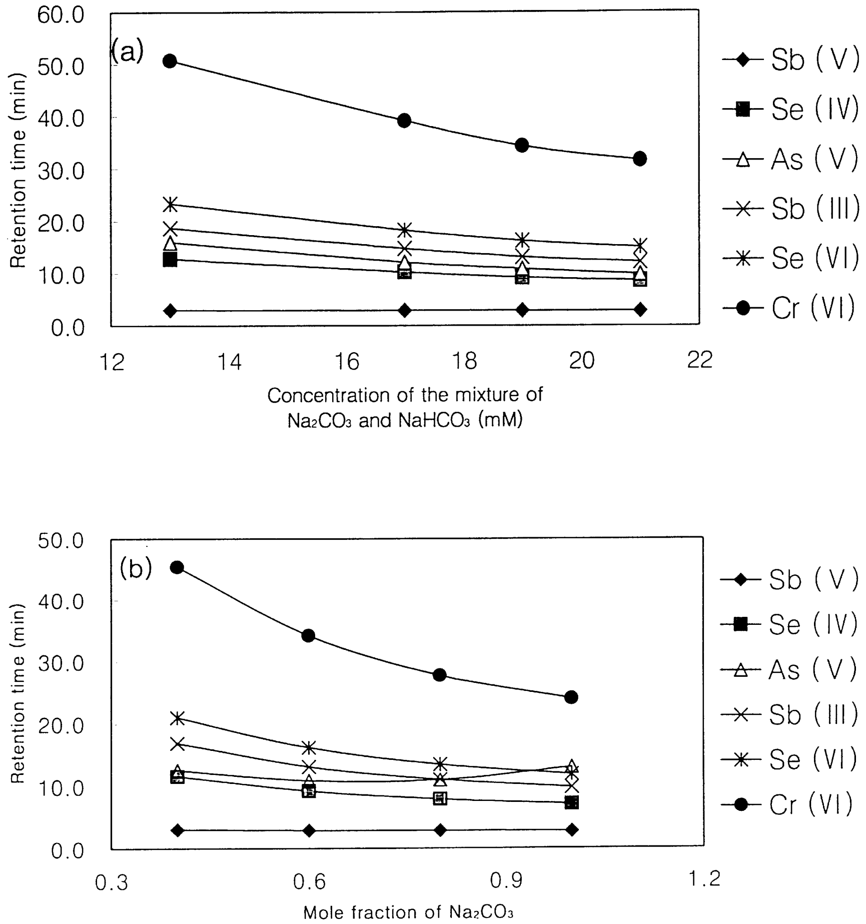


Figure 1. Retention behavior of investigated metal species as a function of (a) the concentration of the mixture of Na_2CO_3 and $NaHCO_3$; under the condition of 1 : 1 molar ratio of $Na_2CO_3/NaHCO_3$ (b) mole fraction of Na_2CO_3 at the fixed condition of 19 mM of the mixture of Na_2CO_3 and $NaHCO_3$.

adequate acid digestion procedures. Table 2 shows the accuracy of the acid digestion procedure, applied to coal fly ash (NIST SRM (1633a)) and Table 3 shows the concentration of trace metals investigated in incinerator fly ash using the same acid digestion method as that of coal fly ash. On the whole, in case of coal fly ash, the average recovery of Cr, As, and Sb was shown to be satisfactory, being over 85%, but not for Se. This can be explained considering

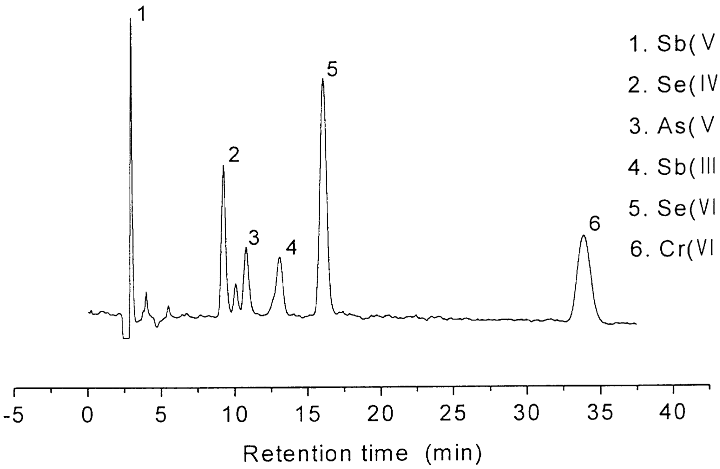


Figure 2. The chromatogram of 4/l Sb(V), Se(IV), As(V), Sb(III), Se(VI), Cr(VI), obtained at the optimum separation condition of 0.6 : 0.4 mole fraction of $Na_2CO_3/NaHCO_3$ at the fixed condition of 19 mM of the mixture of Na_2CO_3 and $NaHCO_3$ with conductivity detection.

the very low level of Se in coal fly ash itself. Applying the same digestion procedure to incinerator fly ash, we could determine the concentration of the target metals. It was shown that the concentration of Cr and Sb was much higher than that of As and Se. Also, the repeatability was acceptable, taking into consideration the relative standard deviations being less than 10% for all analytes.

Table 2. Evaluation of Accuracy of Digested Method on a Coal Fly Ash Certified Reference Material; NIST SRM (1633a) (n = 3)

	Certified Value		Experimental Value		
Elements	Mean	RSD (%)	Mean	RSD (%)	Accuracy (%)
Cr	198.2 ± 4.70	2.3	204.93 ± 0.52	0.25	103.4
As	136.2 ± 2.60	1.9	120.26 ± 0.19	0.16	88.3
Se	10.26 ± 0.17	1.7	7.77 ± 0.17	2.2	75.7
Sb	6.00 ± N.D.	N.D.	5.14 ± 0.29	5.6	85.7

N.D.: Not determined.

Table 3. Determination of the Total Concentration of Trace Elements in Incinerator Fly Ash Using the Same Digestion Method as that of NIST SRM (1633a) (n = 3)

	Sample		Blank	
Elements	Mean	RSD (%)	Mean	RSD (%)
Cr	158.03 ± 4.70	3.0	<0.10	N.D.
As	4.55 ± 0.40	8.8	<0.10	N.D.
Se	1.83 ± 0.17	9.3	<0.10	N.D.
Sb	141.26 ± 1.98	1.4	<0.10	N.D.

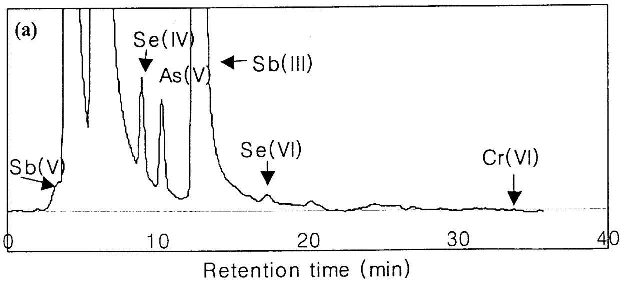
N.D.: Not determined.

Determination of Each Metal Species in Different Chemical Fractions of Incinerator Fly Ash

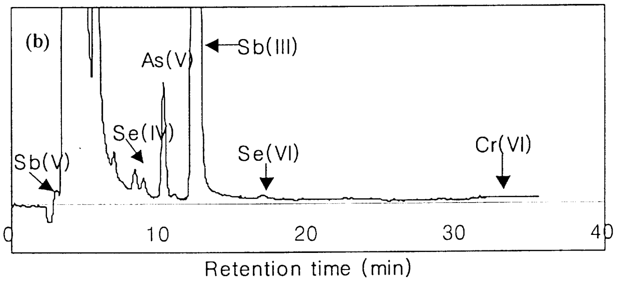
Based on the optimum separation condition for six kinds of metal species, we introduced the sequentially extracted incinerator fly ash into IC with conductivity detection. Figure 3 shows the chromatograms of different metal species in three kinds of chemical fractions, such as exchangeable, carbonate, and Fe/Mn oxide fraction, extracted in incinerator fly ash. These data indicate to us that there are few problems with separation and fractionation of metal species in sequentially extracted incinerator fly ash. Enormous peaks eluting ahead, seem to be due to the extractant used itself. Coelution of non-analyte anions is not a problem, for ICP-MS is element-specific detection. Collecting each metal species for the period of peak elution, we reintroduced these fractionated solutions into ICP-MS to determine the concentration of each metal species.

In order to characterize the partitioning of metal species among chemical fractions, we investigated the effect of the condition of extractant on the released amount of each metal species from incinerator fly ash. Figure 4 shows the effect of pH and concentration of the first extractant, NH_4Oac, on the extraction efficiency of metal species. As shown in Figure 4(a), as the concentration of NH_4Oac increased, the extracted concentration of the metal species also increased. This trend can be explained by the higher ion exchange capacity of the extractant, causing more metal ions to be released from the matrix surface. Among the metal species, Cr(VI) and Sb(V) were released more than the other species. Figure 4(b) gives a plot between pH of NH_4Oac and leached concentration of trace metals. As the pH of NH_4Oac increases, the extracted concentration of metal species increases. This is thought to be related to the formation of anionic species in more

1 st fraction



2 nd fraction



3 rd fraction

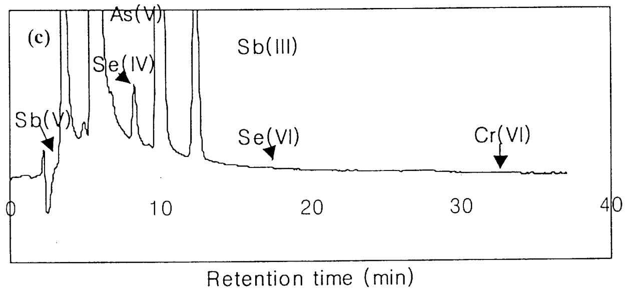


Figure 3. The chromatograms of ciprofloxacin and its metabolites in spiked urine at different pH, back washed by 0.01 M NaH_2PO_4, adjusted to pH 3.0. (a) pH 3.0; (b) pH 5.0; (c) pH 7.0.

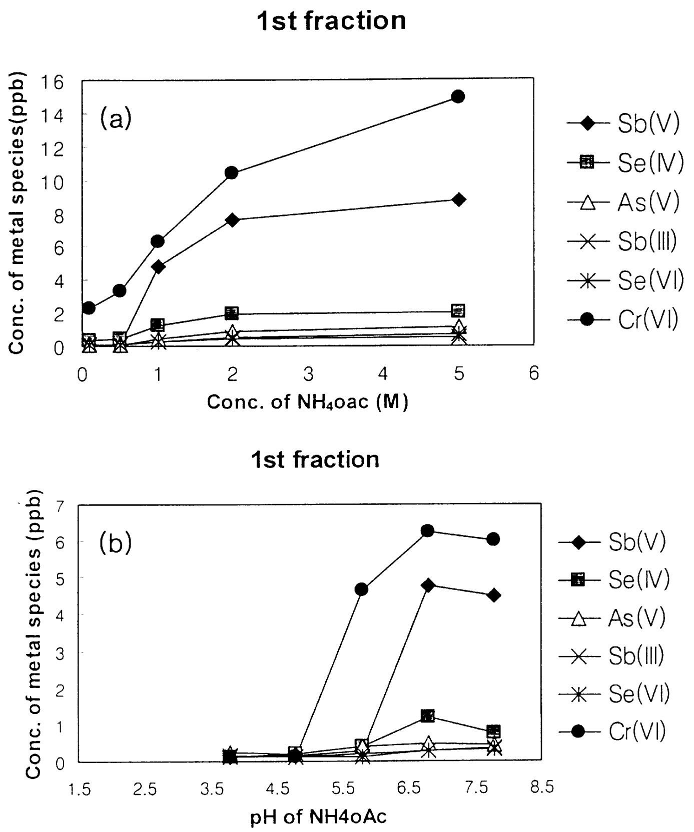


Figure 4. The quantification of metal species, extracted from the first chemical fraction when varying: (a) the concentration of NH_2Oac as an extractant; (b) pH of NH_2Oac as an extractant.

basic conditions, in which they would be expected to be more easily leached from the matrix. For the second fraction (Figure 5), the extracted concentration of Sb(V) decreased as the concentration of acetic acid increased.

This trend would be related to the increased solubility of $CaCO_3$ at the acidic pH condition, leading to more release of Sb(V). But in the case of other metal species, various concentrations of acetic acid were little affected by the leaching concentration of each metal species. The reason for this is not clear, but it is assumed that the amount of each metal species adsorbed on $CaCO_3$ is relatively lower than that of Sb(V), or reversible desorption from the matrix occurs. Finally, for the third fraction (Figure 6(a)), as the concentration of

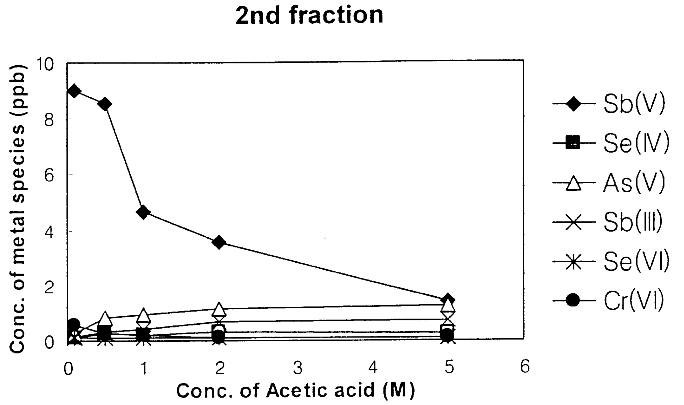


Figure 5. The quantification of metal species, extracted from the second chemical fraction when varying the concentration of acetic acid as an extractant.

NH_2OH HCl increased, the released concentration of metals slightly increased, except for Sb(V). In the case of Sb(V), the increased trend was more pronounced.

It leads us to believe that higher amounts of Sb(V) are associated with Fe/Mn oxides. This trend is also considered to be the result of the increased ion exchange capacity, causing Fe/Mn oxides in their more reduced form to release more metal species by leaching. Figure 6(b) shows that the pH trend of NH_2OH HCl was almost similar to that of NH_4Oac and can be explained in the same way as that of NH_4Oac.

CONCLUSION

Using suppressed IC, we could determine the optimum separation condition for the target components. Also, the retention behavior of the metal species was investigated and explained by ion exchange equilibrium. Applying the acid digestion procedure to incinerator fly ash, we could determine the total concentration of each metal species. Among the target metals, the concentration of Cr and Sb was found to be over 140 ppb in incinerator fly ash. In order to quantify the target metal species in various chemical fractions, modified sequential extraction procedures were applied to the incinerator fly ash, followed by IC separation and ICP-MS detection. On the whole, the extraction efficiency increased as the concentration and pH of the extractant increased, but only for the second chemical fraction. This trend was explained by the higher ion exchange capacity of the extractants and formation of anionic metal species, leading to

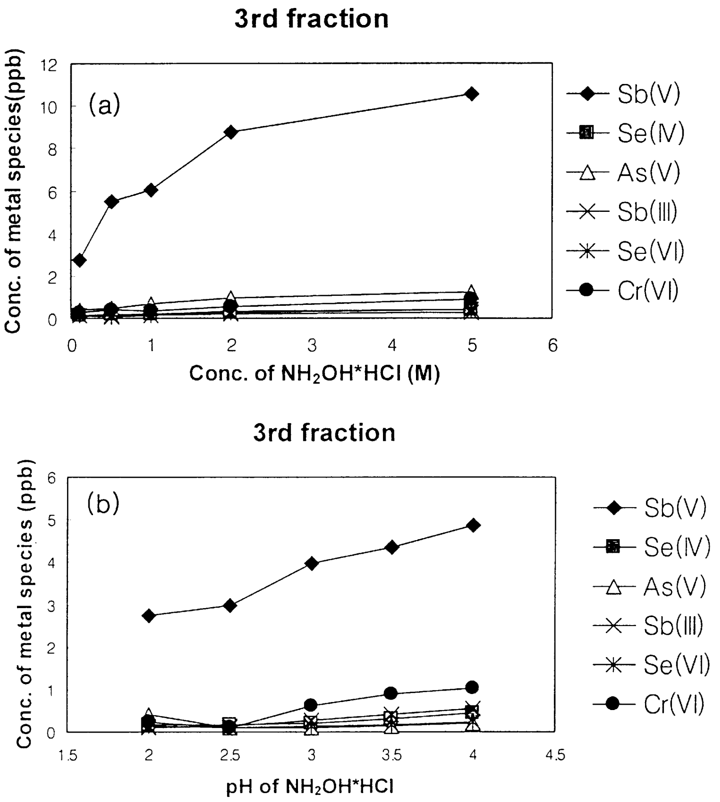


Figure 6. The quantification of metal species, extracted from the third chemical fraction when varying: (a) the concentration of $NH_2OH \cdot HCl$ as an extractant; (b) pH of $NH_2OH \cdot HCl$ as an extractant.

more metal species leaching out of each chemical fraction. Compared to the leached concentration of other metal species, that of Sb(V) was more sensitive to the change of pH and concentration of the extractant used. This might be due to the higher concentration of Sb(V), adsorbed on three kinds of chemical fractions: exchangeable, carbonate, and Fe/Mn oxides.

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