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Measurement of total antimony and antimony species in mine contaminated soils by ICPMS and HPLC-ICPMS

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This paper describes the measurement of total antimony and antimony species in ''real world'' mine contaminated sediments using ICPMS and HPLC-ICPMS. Low and high temperature microwave extraction procedures (90 °C and 150 °C, respectively) using a range of nitric–hydrochloric acid combinations were examined as to their efficacy to extract antimony from six mine contaminated soils and a certified reference material. The use of the higher temperature with nitric–hydrochloric acid (1 : 2 (v/v)) was suitable to release antimony from sediments and the certified reference material, NIST 2710 Montana soil. Antimony concentrations obtained using this acid mixture were similar to those obtained using a more aggressive extraction with nitric, hydrochloric, perchloric and hydrofluoric acid mixture. A 25 mM citric acid solution at 90 °C for 15 min extracted 47–78% of antimony from soils. A Hamilton PRP X-100 anion exchange column with 20 mM EDTA mobile phase, pH 4.5, flow rate 1.5 mL min^{-1} and column temperature of 50 °C was used to separate antimony species. Column recoveries ranged from 78–104%. The predominant form of antimony was Sb^{5+}. Little conversion of Sb^{5+} occurred (< 5%) during extraction, however, significant conversion of Sb^{3+} occurred (~ 36%). The extraction of antimony species with citric acid should be useful in the determination of inorganic antimony available to plants, as plants commonly excrete carboxylic acids, including citric acid, into their rhizospheres to mobilise trace elements for nutritional purposes.

Introduction

Antimony is present in the earth's crust at low concentrations (0.2–0.3 μg g^{-1}) but is enriched in coals and some shales.[1,2] Antimony primarily exists in two oxidation states (III and V) in soils and sediments but bacteria and fungi are known to produce di- and tri-methyl antimony species.[3–5] Antimony concentrations in the environment are increasing with unambiguous evidence, for example, the enrichment of antimony in arctic air has increased 50% during the last three decades.[6] As antimony is considered to be non-essential for plants and animals, [7] there is concern about its potential toxicity and other biological effects.[8]

The Hillgrove mine near Armidale, NSW, has yielded an estimated 20 412 kg of gold as well as 50 000 metric tonnes of antimony over the last 140 years.[9] Large volumes of waste from mining activities and mill tailings have been produced. Erosion of this material has grossly contaminated the Macleay River system[10] which supports grazing, agriculture and recreational activities.

An understanding of antimony's biogeochemical cycle requires accurate measurements of total antimony for mass balances and antimony species to elucidate the movement and fate of antimony and assessment of biological effects. Previous studies have reported procedures measuring antimony concentrations and species in soils,[11] atmospheric dusts,[12,13] coal fly ash[14] and certified sediment reference materials[15] but not soils contaminated by effluent (solubilised antimony) from mine operations. Low recoveries of antimony from geological samples when H_2SO_4, $HClO_4$ or HNO_3 and H_2O_2 were used alone or in combination have been attributed to the formation of insoluble antimony–silicate complexes.[16–18] The use of hydrofluoric acid is often advocated to release antimony from silicates[19–21] but there are significant analytical and health issues associated with the use of this acid. Aqua regia has been reported to be effective in extracting antimony from soils.[22–24] As well, the use of elevated temperatures and pressures[25,26] will enhance extraction efficiencies.

In this paper, we describe procedures for measuring total antimony and antimony species in ''real world'' mine runoff contaminated soils using inductively coupled plasma mass spectrometry (ICPMS) and high pressure liquid chromatography (HPLC-ICPMS). A range of HCl–HNO_3 acid concentrations (2 : 1, 1 : 5, 1 : 2, 5 : 1 (v/v)) and two temperatures (90 °C and 150 °C) to extract antimony from soils were evaluated. Citric acid was chosen to extract antimony species from soils as it is known to complex Sb^{+3} and Sb^{+5} and prevent changes in oxidation state.[12,15,27]

Methods

Reagents and standards

Nitric, hydrochloric and citric acids (BDH, Australia) were used in extraction solutions. Ethylenediamine tetra acetic acid

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(EDTA) and ammonia solution (>99.9%, Aldrich, Australia) were used for the preparation and adjustment of the HPLC mobile phase. Stock standard solutions (1000 mg L^{-1}) of antimonite (Sb^{+3}) and antimonate (Sb^{+5}), were prepared by dissolving potassium antimonyl (III) tartrate (AJAX Laboratory Chemicals, Australia), antimony (III) chloride (Merck, Germany) and potassium hexahydroxoantimonate (V) (AJAX Laboratory Chemicals Australia), respectively, in 0.02 M HCl (Trace Pur, Merck, Australia)–deionised water (Sartorius, Germany). Working standards were prepared in either 1% (v/v) nitric acid or 25 mM citric acid. All standards were deoxygenated with nitrogen before storage.

The certified reference materials analysed was NIST CRM 2710 Montana soil. Six surface soils, known to be contaminated with antimony were collected from near the Hillgrove mine.

Total antimony analysis

Preparation of samples. Soil samples were placed into nitric acid-washed 300 mL plastic containers and oven dried at 40 °C for 72 h, passed through a 250 μm nylon mesh twice and ground to less than 100 μm using a Ringmill zircon crusher (Rocklabs, USA).

Low temperature extraction. Approximately 0.2 g of dried sample was weighed into 50 mL polyethylene centrifuge tubes (Sarstedt, Australia), 3 mL acid extraction solution added and heated in a MDS-81D microwave oven (CEM, USA) at 90 °C for 45 min. After digestion, vessels were allowed to cool at room temperature (~25 °C) and extracts transferred to 50 mL polyethylene vials and diluted to 30 mL with deionised water (Sartorius, Germany).

High temperature extraction. Approximately 0.2 g of dried sample was weighed into 55 mL polytetrafluroacetate (PTFE) digestion vessels (CEM, USA), 3 mL acid extraction solution added and heated in a MARS microwave oven (CEM, USA) using a four step time and temperature program: (1) ramp to 120 °C over 10 min, (2) hold for 5 min at 120 °C, (3) ramp to 150 °C over 3 min, (4) hold for 15 min at 150 °C. After digestion, vessels were allowed to cool at room temperature (~25 °C) and extracts were transferred to 50 mL polyethylene vials and diluted to 30 mL with deionised water (Sartorius, Germany).

ICPMS. Total antimony concentrations were determined with a Perkin-Elmer Elan-6000 inductively coupled plasma-mass spectrometer (ICPMS) by measuring the signal intensity at m/z 121 and 123. Samples were diluted to 1% (v/v) acid concentration prior to being analysed on the ICPMS. Internal standards were added on-line to compensate for any acid effects and instrument drift.[28]

Four acid extraction procedure. Soil samples were also extracted with a combination of HNO_3, HCl, perchloric and hydrofluoric acids, considered to release all antimony, by ALS Chemex laboratories, Brisbane, Australia. Antimony concentrations were subsequently measured in these extracts by ALS using inductively coupled plasma-atomic emission spectrometry.

Inorganic antimony species analysis

Preparation of samples. Soil samples were not dried and were stored at −10 °C prior to analysis.

Citric acid extraction. Approximately 0.5 g of homogenised wet soil were weighed into 55 mL polytetrafluroacetate vessels (Savillex, USA) and 10 mL of 25 mM citric acid added. The citric acid solution was purged using nitrogen gas for 20 min to remove oxygen, sealed, and samples heated in a MARS microwave oven (CEM, USA) at 90 °C for 20 min to assist in antimony extraction. Samples were cooled to room temperature and decanted into 50 mL polyethylene vials, homogenised using a vortex mixer for 0.5 min and centrifuged at 5000 rpm for 20 min using an Eppendorf 5804 centrifuge. Total antimony concentrations extracted in citric acid extracts were determined by acidifying 5 mL of the supernatant to 1% (v/v) HNO_3 (Aristar, BDH, Australia) prior to ICPMS analysis.

HPLC-ICPMS. Prior to chromatography, 0.5–1 mL of extracts were filtered through 0.45 μm Iso-Disc N-4-4 Nylon filters (Supelco, USA). Aliquots of 40 μL were injected onto an HPLC system consisting of a Perkin Elmer Series 200 mobile phase delivery and auto sampler system (Perkin Elmer, Australia). A PEEK Hamilton PRP-X100 anion-exchange column (250 mm × 4.6 mm, 10 μm, Phenomenex, USA) and an aqueous 20 mM EDTA (pH 4.5) mobile phase, flow rate 1.5 mL min^{-1}, temperature: 50 °C was used for the identification and quantification of inorganic antimony species.[29]

The eluant from the HPLC column was directed by PEEK (polyether-ether-ketone) (i.d. 0.02 mm) (Supelco, Australia) capillary tubing into the cross flow nebuliser of a Perkin Elmer Elan-6000 ICPMS, which was used as an antimony specific detector by monitoring the signal intensity at m/z 121 and 123. The chromatography package Total Chrom (Perkin Elmer, Australia) was used to quantify antimony peak areas.

Results and discussion

Total antimony analysis

Effect of acid composition. Mean antimony concentrations measured in each of the six contaminated soils and the CRM Montana soil using the low and high temperature extraction techniques are shown in Table 1. A significant difference ($P < 0.0001$) was found in the antimony concentrations extracted using the acid combinations (Table 1). The efficiency of extraction was concentrated HCl = 2 : 1 (v/v) = 1 : 5 (v/v) = 1 : 2 (v/v) > 5 : 1 (v/v) > concentrated HNO_3.

In this study, HCl was clearly required to extract antimony from the soil samples. Iron oxyhydroxides, silicates and sulfide phases are thought to play a significant role in the binding of antimony.[25,30–31] HCl is capable of dissolving silicate, iron and sulfide minerals, especially at elevated temperatures and pressures.[25,26] Although antimony recoveries from soils were low when using concentrated HNO_3 alone, the use of this acid is vital in the digestion of soil samples to release antimony from any organic inclusions. An acid mixture containing 1 : 2 (v/v) HNO_3 : HCl was selected for further study.

Table 1 Mean total antimony concentrations measured in the six antimony contaminated soil samples and NIST Montana soil digested at 90 °C and 150 °C

Digestion temperature	Acid ratio (v/v)	Soil 1 Sb/μg g^{-1} dry mass[a]	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Montana soil[b]
90 °C	HNO_3	227 ± 4	286 ± 58	698 ± 55	215 ± 11	525 ± 22	360 ± 66	2 ± 0.5
	5 : 1	501 ± 39	495 ± 67	1455 ± 508	322 ± 145	874 ± 33	463 ± 82	3 ± 1.0
	2 : 1	897 ± 25	1812 ± 39	2365 ± 100	1452 ± 9	1672 ± 19	1962 ± 53	22 ± 4
	1 : 2	966 ± 17	1886 ± 23	2202 ± 38	1543 ± 17	1699 ± 62	2033 ± 16	22 ± 3
	1 : 5	1072 ± 44	1842 ± 42	2108 ± 25	1614 ± 189	1660 ± 8	2146 ± 205	22 ± 7
	HCl	1126 ± 25	2107 ± 41	2258 ± 32	1670 ± 22	1715 ± 12	2261 ± 46	18 ± 2
150 °C	HNO_3	148 ± 29	283 ± 11	286 ± 62	176 ± 31	210 ± 36	273 ± 56	<1
	5 : 1	483 ± 42	1049 ± 295	1119 ± 13	729 ± 39	804 ± 84	958 ± 96	9 ± 3
	2 : 1	939 ± 40	2026 ± 71	2096 ± 55	1506 ± 72	1522 ± 31	2049 ± 62	27 ± 4
	1 : 2	978 ± 4	2081 ± 45	2274 ± 77	1599 ± 31	1704 ± 43	2166 ± 77	34 ± 7
	1 : 5	1097 ± 52	2284 ± 44	2320 ± 22	1643 ± 11	1679 ± 32	2205 ± 107	34 ± 6
	HCl	1127 ± 77	2126 ± 73	2387 ± 31	1992 ± 498	1757 ± 24	2242 ± 48	30 ± 5

[a] Mean ± standard deviation, $n = 5$ replicate extractions. [b] Certified reference value = 38.4 ± 3 μg g^{-1}.

Effect of temperature and time. The recoveries of antimony from the contaminated soils using the 1 : 2 (v/v) HNO_3 : HCl acid mixture were similar for both temperatures examined (Table 1). However, significantly greater antimony concentrations (df = 1, 7; $F = 11.57$; $p = 0.0114$) were extracted from the Montana soil when the higher temperature was used (Table 1). Generally, extraction time had no influence in the range 10–30 min. As mentioned above, elevated temperatures and pressures enhance the dissolution of antimony containing phases.[25] At 150 °C, HCl has been shown to dissolve the iron minerals, magnetite, haematite, siderite and goethite; calcium containing apatite; the silicates, montomorillionite and biotite and the sulfite minerals galena, sphalerite, chalcopyrite and pyrrhotite. However, silicate (pyroxene, kalonite, hornblende, muscovite, albite and orthoclase) and sulfide (pyrite and marcasite) minerals were unaffected.[25]

Comparison with four acid extraction procedure. Antimony extracted from contaminated soils by the 1 : 2 (v/v) HNO_3 : HCl acid mixture at 150 °C were similar to that extracted by the four acid mixture (92–97%, Table 2). Mean percent recovery of antimony from NIST 2710 (Montana soil, reference value: 38.4 ± 3 μg g^{-1}) using the high temperature digestion, and the four acid extraction procedure were 90 ± 7% and 120 ± 15%, respectively (Table 2). Although significantly higher recoveries of antimony from the Montana soil were produced using the four acid digestion procedure, the high temperature 1 : 2 (v/v) HNO_3 : HCl acid extraction best estimated the certified value for Montana soil (Fig. 1), although it is still outside the uncertainty values of the certified reference material. Recoveries using this acid mixture are also similar to those previously reported when aqua regia was used to extract antimony from Montana soil.[22] In a comprehensive study comparing a four acid mixture and aqua regia[20] for the digestion of 18 Chinese geological certified rock reference materials, aqua regia, on average, extracted 88 ± 15% of antimony present. The mean was biased by four samples from which only 55–75% of the antimony could be extracted. Thus, it is expected that the use of 1 : 2 (v/v) HNO_3 : HCl acid extraction will give good recoveries for most soil samples.

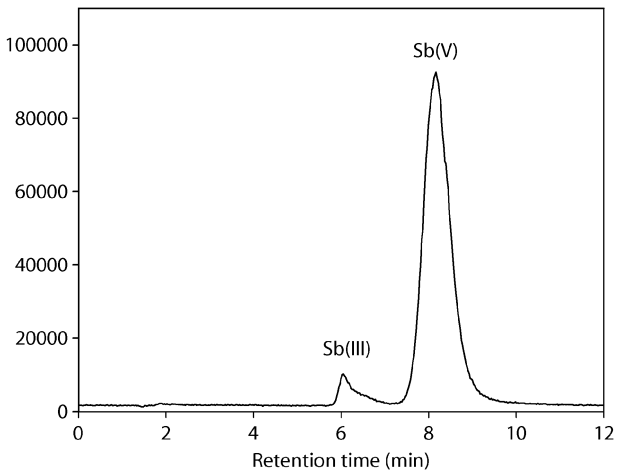

Fig. 1 Antimonite and antimonate extracted from Soil 1 with 25 mM citric acid, separated using a Hamilton PRP-X100 anion exchange column at 50 °C with a 20 mM EDTA, pH 4.5, temperature 50 °C.

Figures of merit. The precision in the analysis of soil samples was 2–5% and a detection limit of 0.08 μg g^{-1} based on five replicates of extracted samples and blanks.

ICPMS interferences and limitations. We have investigated the influence of poly atomic interferences on the measurement

Table 2 Antimony concentrations measured in six contaminated soil samples and Montana soil extracted using 1 : 2 (v/v) HNO_3 : HCL at 150 °C, and the Four acid (HNO_3, HF, $HClO_4$, HCl) procedure

Acid Type	Soil 1 Sb/μg g^{-1} dry mass[a]	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Montana soil
1 : 2 (v/v) HNO_3 : HCL	978 ± 4	2081 ± 45	2274 ± 77	1599 ± 31	1704 ± 43	2166 ± 77	35 ± 3
Four acid	1068 ± 63	2147 ± 158	2347 ± 97	1693 ± 6	1783 ± 26	2317 ± 55	46 ± 6

[a] Mean ±1 standard deviation of the mean, $n = 5$ replicate extractions.

Table 3 Antimony concentrations and species extracted using 25 mmol L^{-1} citric acid from six contaminated soil samples collected from the Hillgrove mine, Armidale, NSW

Soil sample	Mean Sb/μg g^{-1} wet mass[a]	Extracted (%)	Sb(III)/μg g^{-1} wet mass[a]	Sb(V)/μg g^{-1} wet mass[a]	Column recovery (%)
1	470 ± 172	47 ± 2	14 ± 1	211 ± 6	104 ± 4
2	592 ± 201	64 ± 7	13 ± 4	277 ± 92	78 ± 17
3	849 ± 74	49 ± 3	12 ± 0	351 ± 21	89 ± 1
4	625 ± 23	78 ± 29	22 ± 11	346 ± 105	78 ± 6
5	655 ± 136	58 ± 5	21 ± 3	347 ± 18	99 ± 11
6	703 ± 116	64 ± 7	27 ± 9	384 ± 60	93 ± 16

[a] Mean ± standard deviation, $n = 5$ replicate extractions.

of antimony and other elements in a range of biological and sediment samples and found no significant interferences.[28,32] Unlike other elements, no severe interferences (except tellurium) for antimony have been reported in the literature.[33]

Inorganic antimony species analysis

Extraction efficiencies. Extraction efficiencies for the citric acid method ranged from 47% to 78% (Table 3) and are greater than results reported for other published studies of soils using different extraction reagents *i.e.* sodium phosphate (9%),[34] water (0.5%).[11] Extraction time had no influence in the range 10–30 min. Comparisons with other studies that have used citric acid as an extraction reagent are difficult, as the sample matrices analysed were coal fly ash,[14] air particulate matter[12] and dried certified sediment reference materials PAC1 and PAC2,[15] that are very different to soils, with recoveries of antimony, respectively, of 16–222%, 11–15% and 55–56%. As previously mentioned, iron oxyhydroxides and sulfides are thought to bind antimony. The combination of citrate and the low pH is likely to solubilise antimony from these phases. Citrate is commonly used in extraction reagents used to solubilise trace metals adsorbed to iron oxides.[35] The high recoveries of antimony from the six contaminated soil samples are probably due to the mode of adsorption of antimony to soils. Runoff waters have elevated antimony concentrations and antimony will be adsorbed to the surface of the soils. It is unlikely citric acid is capable of releasing antimony from the crystalline structure of soils and sediments. HPLC column recoveries for all six soils ranged from 78% to 104% (Table 3). Sb^{+5} was the predominant form of antimony in all soils (Fig. 1). The ratio of the mean Sb^{+3} to Sb^{+5} concentrations measured across all six soils is approximately 1 : 5 (m/m).

Sb^{+3} is unstable in aqueous solutions, readily oxidising to Sb^{+5}. Chelation of Sb^{+3} and Sb^{+5}, for example using citric acid, is advocated as being necessary to preserve the antimony species present.[14] Recoveries of Sb^{+3} and Sb^{+5} added to soils (20 μg g^{-1}) before extraction with citric acid in this study showed Sb^{+5} to be stable (95 ± 4%) while oxidation of Sb^{+5} occurred (36 ± 5%). Point-Gautier *et al.*[15] investigated a series of different extractants and reported that losses of Sb^{+3} extracted from marine sediments using a 100 mM citric acid extraction solution were less then 5% within the first hour, compared to 50% loss of Sb^{+3} when sediments were extracted with either 100 mM EDTA pH 4.5 or 100 mM oxalic acid in 1% (m/v) ascorbic acid pH 2.0. Zheng *et al.*[12] used 26 mM citric acid to extract antimony species from airborne particulate matter with sonication and recovered 74% of an Sb^{+3} spike and 90% of an Sb^{+5} spike. When extracts were deoxygenated *via* purging with nitrogen gas, recoveries increased to 84% and 97%, respectively. They considered losses to be due to adsorption, not oxidation of Sb^{+3}. Using a microwave extraction procedure without purging instead of sonication, they recovered 100% of a Sb^{+5} spike but only 40% of the Sb^{+3} spike. It would appear that to prevent oxidation of Sb^{+3} and to gain good recoveries, deoxygenation of extraction mixtures (as used in this study) is essential, however, oxidation of Sb^{3+} to Sb^{5+} still occurs.

The extraction of antimony species using citric acid should be a useful tool in the determination of antimony species available to plants. Plants commonly excrete carboxylic acids, including citric acid, into their rhizospheres.[36–39] Extraction with citric acid should give a good estimate of plant available antimony present in soils.

Figures of merit. The precision of extraction of species from soil samples was 1–37%. The precision of analyzing Sb^{+3} and Sb^{+5} were 1% and 2%, respectively, for 2 μg L^{-1} solutions. Detection limits were 0.01 μg g^{-1} and 0.02 μg g^{-1} for Sb^{+3} and Sb^{+5}, respectively.

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