Accurate Determination of Total Antimony Using ICP-MS and Optimization Its Extraction Efficiency From Reference and Soil Samples

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Abstract: Two independent digestion techniques (microwave acid digestion with HF and HCl, HNO_3 and Na_2O_2 sintering, respectively) were applied to determine the total Sb concentration in a real soil sample and in reference materials: Icelandic Basalt (BIR-1), Cody Shale (SCo-1) and (Soil-7). ICP-MS was used to determine total antimony concentrations in the digested and the extracted solutions using external calibration and isotope dilution technique. The recoveries of Sb using HF in the acids digestion mixture in closed-vessels microwave digestion system were excellent and the concentrations are in very good agreement with certified or reported concentrations of reference materials. Using closed-vessels combined with microwave heating systems probably prevents the loss of volatile Sb compounds. The use of hydrogen fluoride with other strong acid can help dissociating insoluble antimony silicates. Different extraction reagents were tested for their ability to extract antimony using an ultrasonic bath namely: EDTA disodium salt, potassium hydroxide, citric acid monohydrate, pyridine-2,6-dicarboxylic acid, ammonium acetate, ammonium oxalate, ammonium thiocyanate, ammonium persulphate and di-ammonium hydrogen citrate. A 500 mmol L^{-1} solution of citric acid pH 1.08 proved to be the most efficient extractant. Optimization of the extraction conditions were investigated by studying the effect of pH, concentration, temperature, time of extraction, the ratio of sample mass to the volume of extractant and the number of consecutive extractions. As a result three consecutive extractions for a total time of 45 min at 80 °C was the most efficient condition for Sb extraction. Using these extraction conditions 61%, 3.7% RSD and 42%, 2.2% RSD (n=6) of the total antimony in the real soil and Soil-7 samples, respectively could be extracted.

Introduction

Antimony and its compounds are considered to be priority pollutants by Environmental Protection Agency of the United States (US-EPA) and European Union (EU) (Filella et al. 2002).Sb is on the list of hazardous substances under the Basel convention concerning the restriction of transfer of hazardous wastes across borders (UNEP, 2014).
The maximum contaminate level (MCL) of Sb in drinking water according to USEPA standards is 6 µg L^{-1} (USEPA, 2007). In unpolluted waters the concentrations are below 300 ngL^{-1}. The EU established a maximum admissible concentration of antimony in drinking water of 5 µgL^{-1} (Conical of the EU). The minimal health risk of Sb in soil is about 20 mg kg^{-1} [(NYSDOH, 1993). Organic soils are highly enriched (factor 5–10 compared to mineral soils) in Sb. Soils and stream sediments return comparable median Sb concentrations (Reimann et al. 2010). Sb remained geochemically very stable in wetland (i.e. waterlogged) sediments rich in organic matter (Shrivas et al. 2008). The United States Food and Drug Administration (US-FDA) tolerates a maximum of 2 µg g^{-1} of antimony in food (Iffland, R., 1988) and the accepted daily limits for humans orally exposed to antimony

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compounds (over an extended period of time) range from 24.5-32.5 µg of antimony compound per day (Maeda, 1994). Antimony is usually present at levels less than 1.0 µg g^{-1} in all human tissues, and hair contains the largest amount (Filella et al. 2002). Antimony is a non-essential element in plants, animals and humans but causes toxic effects. Inhalation exposure to Sb compounds can produce a series of diseases, such as fibrosis, bone-marrow damage and carcinomas (Zheng et al. 2000).

The most common methods used for environmental samples are atomic absorption spectrometry (AAS) (either flame or graphite furnace) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Spectrophotometric methods were used for the determination of antimony (Warnken et al. 2017); the best known of these methods is the rhodamine B method (APHA, 1972). Water and waste water samples can be analyzed for antimony by EPA Test Methods 220.1 (atomic absorption, direct aspiration), 220.2 (atomic absorption, furnace technique), or 200.7 (inductively coupled plasma-atomic emission spectroscopy) (USEPA, 1979). . Important Feature of ICP-MS is the capability of the system to perform isotope ratio measurements and consequently isotope dilution analysis due to the mass specificity of the detection system. Isotope dilution analysis is a calibration procedure. The technique is considered the best way of calibration, since the internal calibrant employed will be affected exactly in the same way as the analyte by drift on the instrument with time (Koellensperger, 2003).
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The determination of antimony in solid samples suffers from interference effects due to complex matrices and the loss of analyte during sample preparation (Nash et al. 2000)**.** Therefore, the selection of sample preparation and analysis techniques is critical and must be considered prior to analysis. Sample preparation steps for the determination of total antimony in solids materials involve matrix digestion techniques. This is usually done by decomposition of the sample matrix at high temperatures in acidic media. Mixtures of oxidizing acids like H_2SO_4, HNO_3, $HClO_4$ were used to digest soils with high silicate content leading to low recoveries (10-56%) due to the formation of insoluble Sb(V)-silicate (Nash et al. 2000). Improved sample decomposition is achieved by using HF in conjunction with the above oxidizing acids. HCl is also used for matrix digestion improves the recovery of total antimony in soil and sediments up to 90%.16 Heating systems reported for HCl digestion include furnace, hot block and sand batch technologies. Recent improvements in digestion techniques have resulted largely from advances in microwave technology. These techniques offer the advantages of less reagent and sample usage, reduced cross contamination between samples and reduced analyte loss by volatilization (Neas & Collins, 2003).
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In this work the first task was to determine accurately the total Sb concentration in the tested soil sample, by validating the digestion step and choosing the suitable determination method for total Sb found in the digest solution. ICP-MS is an appropriate choice, since it provides superior sensitivity and selectivity. The next step was to optimize the extraction efficiency of total extractable Sb, by choosing a suitable extractant and optimization all extraction parameters that maximize the extraction yield.

Material and methods

Samples and reference materials
In this work, the samples used for method development was part of the samples collections done by Fritsche, 2003 during his master study (Fritsche, 2003). It was taken from soil surface (0-5 cm) near the edge of a highway (Vienna/A23). The sample is an alkaline soil (pH of water extract (1:5) is 8.6), the conductivity of the filtrate of a water extract was 159 µS cm^{-1} and the organic carbon was 1.71 %(m/m). The collected soil sample was dried at ambient air temperature and then sieved to obtain the 2 mm soil fraction. The sieved sample were grinded using a mixer mill (MM200) obtained from Retsch, Germany. The final fineness of samples particles after grinding was about 0.01 mm. Two reference materials Icelandic Basalt (BIR-1) and Cody Shale (SCo-1) obtained from U.S. Geological Survey and a certified soil reference material (Soil-7) obtained from the International Atomic Energy Agency (IAEA) were used in this work to validate the digestion method of the soil sample.

Chemicals and reagents
For preparation of all solutions RO MilliQ system (18.2 MΩ cm^{-1}) water was used. Sodium peroxide (≥95 %(m/m), Fluka) or acids were used for mineralization of soil samples. The acids were all of analytical grade obtained from Merck company: nitric acid 70 %(m/m) hydrochloric acid 37 %(m/m) and hydrofluoric acid 40 %(m/m). Extraction solutions were prepared from analytical grade reagents: citric acid monohydrate 99.5-100.5

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%(m/m), potassium hydrogen phthalate 99.9-100.1 %(m/m), ammonium persulphate >98 %(m/m), EDTA-disodium Salt 99.0-101.0 %(m/m), potassium hydroxide 88 %(m/m), ammonium acetate ≥97 %(m/m) ammonium thiocyanate >98.5 %(m/m), Ammonium oxalate >99 %(m/m), di-ammonium hydrogen citrate ≥ 98%(m/m). Calibration solutions (0.2 to 50 µg L^{-1}) for Sb were prepared daily by diluting aliquots of ICP-MS standard solution (High-Purity standards, Charleston, SC USA) 10 µg mL^{-1} ± 0.5% in 2% HNO_3 + trace HF. Indium ICP-MS standard (High-Purity standards) was used as internal standard in all measured solutions (40 µg L^{-1} in the final solution). All standard solutions were stored in dark plastic containers in a refrigerator at a temperature 1-4°C.

Instrumentation
Soil samples were grinded using a mixer mill (MM200) obtained from Retsch, Germany. a muffle furnace and a microwave sample preparation system (Multiwave, Anton-Paar, Graz) were used for samples digestion. The extraction procedure was carried out using an ultrasonic water bath obtained from Bandelin Sonorex Super, RK 106, Germany. The supernatant was separated using Eppendorf Centrifuge. a programmable pipette and dispense device (EDOS 5222 Eppendorf) was very helpful for the precise dilution of standards and samples. a standard Agilent Technologies HP4500 inductively coupled plasma mass spectrometer (ICP-MS) system with forward rf power of 1300 W, a Babington nebulizer and a cooled quartz glass spray chamber were used for all measurements.

Digestion procedures
The total initial Sb concentrations were determined in the soil sample and in the residues by two independent decompositions methods; sodium peroxide sintering and microwave digestion.

Sodium peroxide sintering: 100 mg of finely powered sample and 0.6 g fine grained Na_2O_2 were sintered at 480 ± 10 ˚C in a muffle furnace for 0.5 hour in glassy carbon crucible. Upon cooling, H_2O was added until reaction ceased. The precipitate was separated using centrifugation (4500 for 5 min) and dissolved in 3mol L^{-1} of HCl after collecting the supernatant in a 100 mL in polypropylene volumetric flask. Two mL of concentrated subboiled HCl were used for rinsing the crucible. The dissolved residue and acidified supernatant were combined and made up to the mark of 100mLcertified volume.

Microwave digestion: 100 mg of soil sample were placed in high pressure PTM vessels together with 5 mL HNO_3 plus 1 mL of HF and digested using microwave for half an hour. The important parameters of the digestion method were a maximal power setting of 1000 W, a maximum temperature of 220 ˚C and maximum pressure of 75 bars. After cooling 2 mL HCl were added and the digestion process continued for another half an hour with the same conditions. The digestion was done on two stages to overcome any possible coprecipitation of, especially trivalent, trace elements as fluorides. The digested mixture was subsequently transferred to 100 mL volumetric polyethylene flasks and diluted to the mark with highly purified water. Two reference materials (BIR-1 and SCo-1, USGS) and a certified reference material (Soil-7, IAEA) were used in order to validate the completeness of digestion.

Extraction procedure
Choosing a suitable extractant: 10 mL of 10 mmol L^{-1} concentration of one of tested extractants (citric acid monohydrate, potassium hydrogen phthalate, ammonium persulfate, EDTA-disodium Salt, potassium hydroxide, ammonium acetate, ammonium thiocyanate, Ammonium oxalate and di-ammonium hydrogen citrate) were added to 0.5 g of test soil in a 10 mL screws-cap polystyrene tube. Subsequently, the tube was sonicated for 60 min in an ultrasonic bath at room temperature. The solution was then centrifuged at a speed of 4000 rpm for 5 min and filtered using a 0.45 µm syringe filter.

Optimizing extraction conditions for total extractable Sb: The extraction efficiency using citric acid as an extractant for total Sb in soil was optimized by studying the effect of important extraction conditions like concentration, pH, temperature, time of extraction, the ratio of sample mass to volume of extractant and the number of consecutive extractions. Extraction of antimony was done by weighing 0.1-0.5 g of soil into a screw-capped polystyrene tube (10 mL), and then 3.3-10 mL of 0-500 mmol L^{-1} citric acid of pH 1.08-6.0 were added. The pH was adjusting using different combinations of citric acid and 500 mmol L^{-1} of ammonium hydroxide and nitric acid. The extraction was preformed in an ultrasonic water bath at a temperature of 22-80 ˚C, and sonicated

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for 15-120 min. The supernatant was separated after centrifuging (4000 rpm) for 5 minutes. This successive extraction was repeated 1-4 times. An extraction procedure for total was evaluated after optimization of all extraction conditions to yield the maximum extractable Sb under the experimental conditions. Fig. 1 represents this extraction procedure in a schematic way.
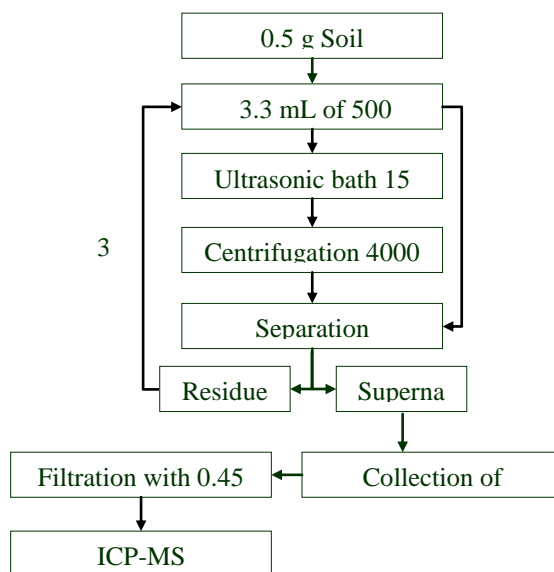
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  3   │   │ Ultrasonic bath 15│
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Figure 1. The optimized extraction procedure

Concentrations measurements

External Calibration: ICP-MS was used to determine total antimony in the digested and extracted solutions using external calibration after filtering the solutions through 0.45 μm membrane syringe tip filters (Lactan, Austria). Further dilutions in the range of (104-5200) were done depending on the expected concentration range. Indium ICP-MS reference solution was used as internal reference in all measured solutions (40 µg L^{-1} in the final solution).

Isotope Dilution: This was done by blending appropriate amounts (1.0, 2.0, 3.0 and 4.0 g) of (nominal 10 µg g^{-1}) isotope enriched spike with proper amounts (4.0, 3.0, 2.0 and 1.0 g) of 10 µg g^{-1} natural soil digested or extracted solutions. The isotope ratios of ^{121}Sb/^{123}Sb or ^{123}Sb/^{121}Sb were measured in the isotope ratio mode following a special measurement protocol (Fig. 2) in order to correct for the blank contribution.

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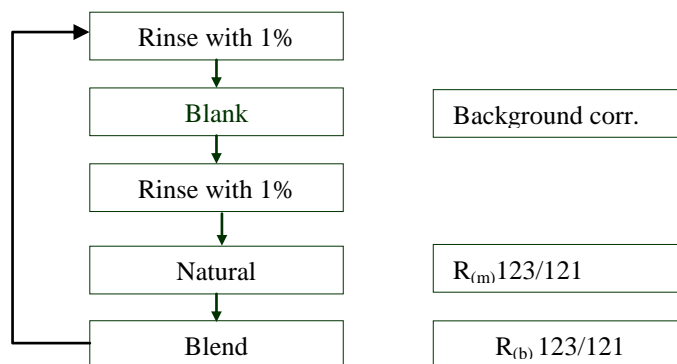
Figure 2. Measurement protocol for reverse isotope dilution

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The basic principle of IDMS is that an amount of sample (N_x) is blended with an amount of an enriched spike (N_y), R_y and R_x are the isotope ratio of the spike and the sample respectively.

$$\frac{N_x}{N_y} = \frac{R_y - R_b}{R_b - R_x} \times \frac{h_{iy}}{h_{ix}}$$

(1)

h_i represents the isotopic abundance of the reference isotope in the spike (y) and in the sample (x), respectively.

Results and discussion

Digestion

The results of antimony recovery using the two methods (sodium peroxide sintering and microwave digestion) for the tested samples (Table 1) show no statistically significant difference. The concentrations of Sb in the majority of digested samples by HF microwave digestion method are more precise and accurate. The recovery of antimony using HF microwave digestion is slightly higher than that obtained using sodium peroxide sintering. High temperature (480°C) used in sodium peroxide sintering method may cause loss of volatile antimony compounds including $SbCl_3$ and $SbCl_5$ which seems to be found in very low amounts (Koellensperger, 2003). Using closed-vessels with microwave heating systems to prevent volatilization at high temperature helps to overcome the problem of analyte loss. When using sodium peroxide sintering, the resulting solutions contain high dissolved solids which in some cases are troublesome to the ICP-MS measurements especially at low concentrations of the analyte. Hydrogen fluoride with other strong acids is generally required to release antimony from soil particularly if present as insoluble antimony silicate (Koellensperger, 2003). Precautions must be taken into account to avoid coprecipitation of insoluble fluorides with some trace elements during acid digestion. This was done by minimizing the amount of HF used at a level where only complete digestion can be achieved and also by carrying out the digestion in two stages. The second stage will help in dissolving the possible precipitates. The results obtained for reference materials are in agreement to the extent shown in table 1 with the certified results. Hence, the recovery of Sb concentration in the tested soil sample after HF microwave digestion was higher and Sb concentration more precise than Sb concentration in the digested soil solution done by sodium peroxide sintering. Total antimony concentration (4.25 µg g^{-1}) which was determined after HF-microwave digestion method represents total Sb used for calculations of the fraction of extractable Sb.

Table 1. Comparison of two digestion methods for determination of total antimony concentration.

Sample name	Kind of the method	Mean of Sb concentration (µgg^{-1}), n=3	SD (µgg^{-1})	Mean value reported or certified (µgg^{-1})
Soil-7 (CRM)	Na$_2$O$_2$ Sintering	1.56	0.13	1.7±0.2
	Microwave	1.85	0.07	1.7±0.2
BIR-1 (RM)	Na$_2$O$_2$ Sintering	0.68	0.09	0.58±0.16
	Microwave	0.55	0.06	0.58±0.16
SCo-1 (RM)	Na$_2$O$_2$ Sintering	2.37	0.14	2.5±0.13
	Microwave	2.5	0.02	2.5±0.13
Examined soil	Na$_2$O$_2$ Sintering	4.17	0.3	
	Microwave	4.25	0.18	

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Optimization of Extraction efficiency

The extraction efficiencies of a series of extractants with concentrations of 10 mmol L^{-1} are shown in Fig. 3. The majority of the selected extractants contain sulfur or oxygen groups where complexation with antimony may occur. Citric acid was the most efficient extractant among the tested reagents. The results of the effect of the citric acid concentration in the range of 0-500 mmol L^{-1} on the extraction efficiency are represented in Fig. 4. The height of each column in this figure and the following figures represents the mean of three replicates and the uncertainty bars represent the standard deviation. It was found that as the concentration of citric acid increases the amount of extractable antimony rises. The optimum extraction efficiency was achieved using the highest tested concentration (500 mmol L^{-1}).
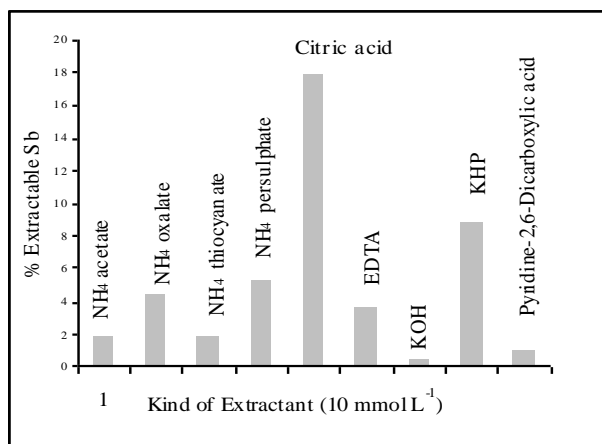

Figure 3. Effect of extractant kind. Extraction conditions: extraction temp. room temp., no. of repeated extractions 1, conc. of extractant 10 mmol L^{-1}, soil m/v extr. 0.5/10 g ml^{-1}, extraction time 60. min.
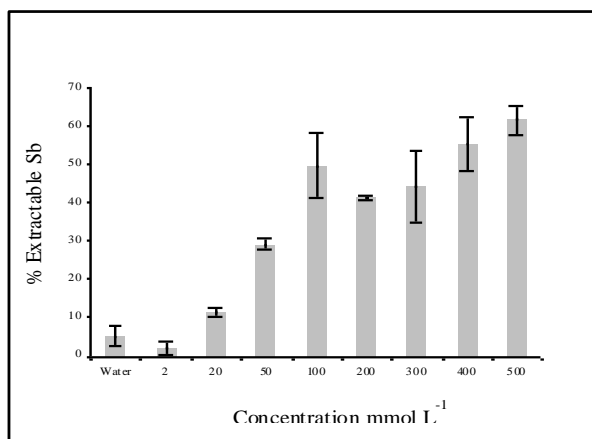

Figure 4. Effect of conc. of citric acid. Extraction conditions: extraction temp. 80 ˚C, no. of repeated extractions 3, soil m/ v extr. 0.5/10 g ml^{-1}, extraction time 45 min.

Changing the pH of 500 mmol L^{-1} citric acid highly affects the extraction efficiency as shown in Fig. 5. The extraction yield increases as pH decreases; this can be explained by the mobilization effect of the acidic pH. The latter effect increases the surface area where complexation might occur between antimony species that are adsorbed to mineral surfaces and citric acid. The mobilization of antimony that is bound to the mineral surface as Sb(III) will also increase at acidic pH. This observation is supported by the work of Pilarski et al. 1995(Pilarski et al. 1995) who report that adsorption of Sb(OH)$_3$ was reduced by about 15% as the pH was increased from 3.1 to 5.4. Heavy metals, among them antimony, form less soluble phosphates, carbonates, hydroxides and sulfides, here metal sulfides remain insoluble within a pH range of about 5 to 9. Sorption and many metal precipitation processes are highly pH dependent with increased sorption with higher pH(Basta, 2000). Further, complexation between citric acid and antimony has been observed at very acidic pHs. Thus more complexation of Sb results in a higher mobility in soil (Hammel et al. 2000), and the extraction efficiency increases as the pH decreases. The pH of the highest extraction efficiency was 1.08 pH of 500 mmol L^{-1}citric acid.

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Careful consideration of the temperature effect on extraction yield is required. The temperature dependence of antimony leaching in the range 40-80 ˚C is plotted in Fig. 6. Both extractant and the ultrasonic bath temperatures were adjusted before starting sonicating. The graph in Fig. 6 is indicating an increase of the extraction yield as the temperature increases. Temperature exerts a positive influence in soil matrix dissociation and on diffusion process involving antimony and citric acid species, an effect of major importance. The maximum extraction yield was obtained at the highest temperature (80˚C) of extractant in ultrasonic bath.
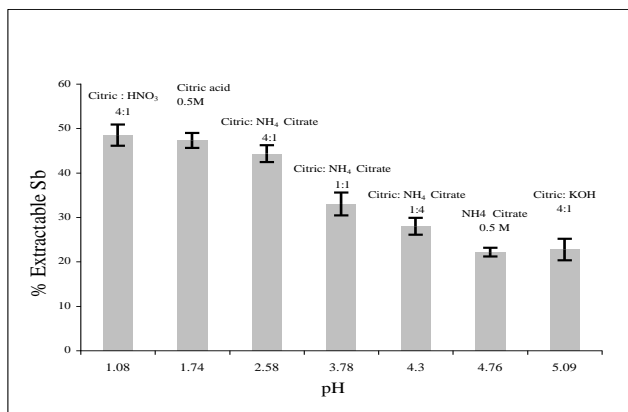

Figure 5. Effect of pH of extraction solution. Extraction conditions: extraction temp. 40 ˚C, no. of repeated extractions 1, soil m/v extr. 0.5/10 gmL^{-1}, extraction time 45 min.
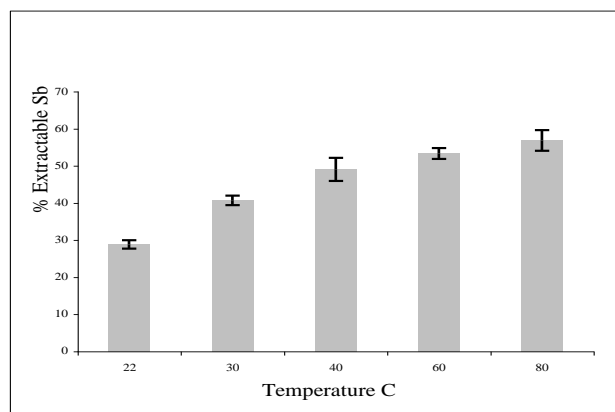
Figure 6. Effect of temperature. Extraction conditions: conc. of citric acid 500 mmolL^{-1}, pH 1.08 no. of repeated extractions 3, soil m/v extr. 0.5/10 gmL^{-1}, extraction time 45 min.

Studying the influence of the total contact time between the extraction solution and the soil sample under sonicating showed a positive correlation. The maximum extraction yield could be obtained after 45 min. This time reflects the total time of extraction which was repeated three times, 15 minutes for each replicated extraction using 3.3 mL for each one. A prolonged extraction interval did not lead to any significant increase (Fig. 7). In order to take into account all parameters that could affect the extraction procedure the mass of soil sample to the volume of extractant (500 mmol L^{-1} citric acid) ratio and the effect of number of replicated extractions also were investigated. Results are represented in Fig. 8 and 9, where an increase in mass to extractant volume (0.01 to 0.1) did not lead any significant change in the extraction yield. The inconsistency of results in figures 7 and 8 may it is due to an adsorption effect at higher soil masses. Also, there was also no significant difference between three or four replicate extractions.

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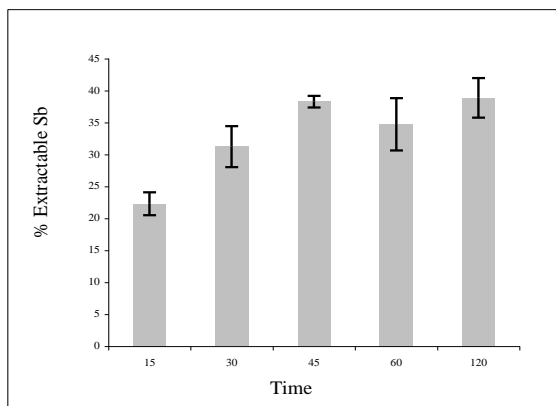

Figure 7. Effect of extraction time. Extraction conditions: conc. of citric acid 500 mmol L^{-1}, pH 1.08, extraction temp. 30°C, no. of repeated extractions 3, soil m/v extr. 0.5/10 g mL^{-1}
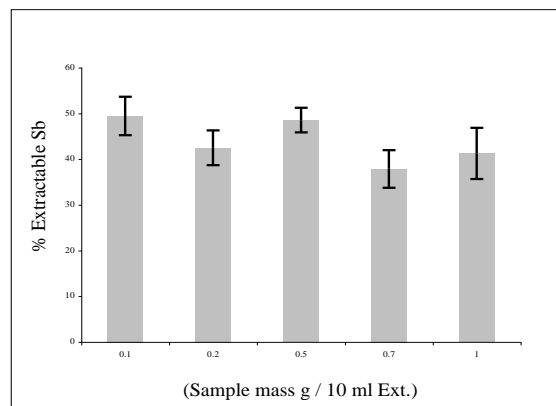

Figure 8. Effect of sample mass to extractant volume. Extraction conditions: conc. of citric acid 500 mmol L^{-1}, pH 1.08, no. of repeated extractions 3, extraction temp. 40 °C, time of extraction 45 min.
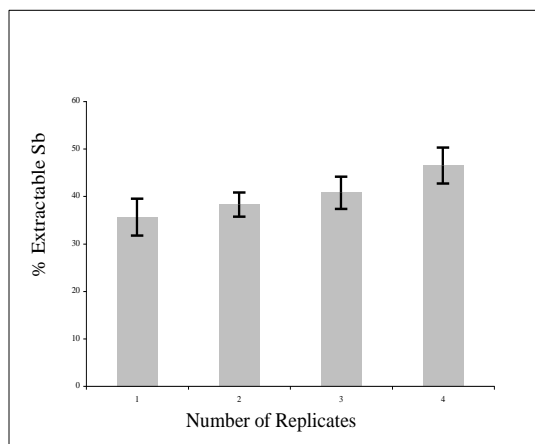

Figure 9. Effect of no. of repeated extractions. Extraction conditions: conc. of citric acid 500 mmol L^{-1}, pH 1.08, extraction temp. 30 °C, soil m/v extr. 0.5/10 g mL^{-1}

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The optimized extraction conditions for total Sb
The extraction efficiency using citric acid as an extractant for total Sb in soil was optimized as was previously discussed in detail by studying the effect of the most important extraction parameters like concentration, pH, temperature, time of extraction, the ratio of sample mass to the volume of extractant and the number of consecutive extractions. The results are presented in Table 6. It was observed that the parameters that had the largest effect on the extraction efficiency were citric acid concentration; the pH and temperature (see Table 2). Using the best extraction conditions 61% (3.7% RSD n=3) of total Sb could be extracted. Applying these condition to Soil-7 (CRM) yielded only 42% (2.2% RSD, n=3) (Table 3). This indicates that a reliable extraction procedure for a certain material may not be applied to another material because the adsorption/binding forces of the analyte of interest to the solid are strongly matrix dependent. The difference in the amount of extractable antimony between the CRM and the soil sample may be due to the considerable higher amount of Sb in the traffic contaminated soil.

Table 2. Optimization of extraction efficiency for total Sb using citric acid

Parameter	Tested Range	Results (Yield%)	Best Condition
Extraction Time	15 - 120 min	22.3 - 40.4	45 min
No. of Replicates	1 - 4	35.5 - 46.5	3
Temperature	22 - 80 ºC	28.9 - 56.9	80 ºC
Citric acid Concentration	0 - 500 mmol L^{-1}	5.1 - 61.6	500 mmol L^{-1}
pH	1.08 - 5.9	22.7 - 58.5	1.08

The extraction efficiency was gross-checked by carrying out a mass balance experiment. This involved the quantification of Sb remaining in the extracted sample residue plus that found in the sample extract. The extraction yield (%) was then calculated in two ways (A and B):

$$\% \, Extraction \, yield = \frac{Sb \, in \, extractant \times 100}{Total \, Sb \, in \, the \, digested \, soil \, solution} \cdots\cdots\cdots (A)$$

$$\% \, Extraction \, yield = \frac{Sb \, in \, extractant \times 100}{Sb \, in \, extractant + Sb \, in \, digested \, residue} \cdots\cdots\cdots (B)$$

The results (table 3) were obtained using the optimized extraction procedure (Fig. 1). By applying the above formulas A and B for calculating the extraction yield for our soil sample and for CRM (Soil-7) were calculated. Since both approaches lead to the same results no significant loss of antimony during the extraction procedure occurred.

Table 3. Comparison between the final optimized extraction efficiency calculated by two ways.

Sample	Extraction yield A, (RSD, n=3)	Extraction yield B, (RSD, n=3)
Soil-7 (CRM)	42%, 2.2%	39, 2.5%
Examined Soil	61%, 3.7%	60, 4.0%

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Conclusion

The recoveries of Sb using HF in the acids digestion mixture in closed-vessels microwave digestion system were excellent and the concentrations are in very good agreement with certified or reported concentrations of reference materials. Using closed-vessels combined with microwave heating systems probably prevents the loss of volatile Sb compounds. The use of hydrogen fluoride with other strong acid can help dissociating insoluble antimony silicates. ICP-MS was used to determine total antimony concentrations in the digested and the extracted solutions using isotope dilution technique, since this technique is considered the best way of calibration, since the internal calibrant employed will be affected exactly in the same way as the analyte by drift on the instrument with time. A 500 mmol L^{-1} solution of citric acid pH 1.08 proved to be the most efficient extractant. As a result three consecutive extractions for a total time of 45 min at 80 ˚C was the most efficient condition for Sb extraction. . Using these extraction conditions 61%, 3.7% RSD and 42%, 2.2% RSD (n=6) of the total antimony in the real soil and Soil-7 samples, respectively could be extracted.

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