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Multielement Analysis of Small Plant Tissue Samples Using Inductively Coupled Plasma Mass Spectrometry

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INTRODUCTION

The trace analysis of environmental and biological samples has become one of the most important tasks in analytical chemistry in the past few years. The analysis of plant tissues together with a further decrease in the required sample size is of increasing importance, because detailed knowledge of the chemical composition is usually a prerequisite for the elucidation of biological functions and mechanisms as well as their modification by external factors such as pollution (1-4).

The mechanisms of nutrient uptake and transport in plants are important in plant physiology, plant nutrition, and in the study of environmental effects of pollution on ecosystems. Therefore, essential elements of plant nutrition such as Mg, K, and Ca were added to the nutrient solutions in the study. Barley was used as the plant system because of its widespread importance as a model plant in plant nutrition and related fields. In order to find out if changes in element composition induced by external factors can be monitored with sufficient analytical accuracy, we applied Cs^+ ions and TEA (tetraethylammonium chloride) to the media of hydroponically raised plants. Cs^+ and TEA are known to block K-channels in plant membranes (5), and therefore a reduced uptake of K and smaller changes in the concentration of other elements would be expected. The changes would not be very dramatic due to the short exposure time of six hours as compared to the lifetime of 14 days.

ABSTRACT

Inductively coupled plasma mass spectrometry (ICP-MS) offers excellent possibilities for multielement trace analysis of biological material. In the present study, an analytical method was developed for the determination of essential elements in small plant tissue samples. Sample preparation was performed with closed-vessel microwave digestion. Oriental Tobacco Leaves CTA-OTL-1 (ICHTJ, Poland) were used as the standard reference material (SRM) and rhodium was applied in ICP-MS as an internal standard element in the multielement aqueous solutions and sample solutions. For most analytes, recoveries from the SRM were 95% to 105%. The method developed was successfully applied for the trace element study of 30 barley tissue samples (8-30 mg). The detection limits ranged (except for Ca) from 0.02 µg/g (Cs) to 1.1 µg/g (K) from leaves and roots. The differences in element concentrations between individual plant samples were large compared to the relative standard deviation (RSD) of the results obtained. Small changes in the element composition, induced by modelling external effects on nutrient uptake by blocking the plants K-channels, were observed by ICP-MS measurements.

For element analysis, the organic matrix of the biological samples had to be quantitatively decomposed. Several different digestion methods are available, including open-vessel acid digestion, dry ashing and open- or closed-vessel microwave digestion (6,7). Of these methods, closed-vessel microwave digestion performs excellently for digesting small amounts of biological samples

with minimal sample loss and contamination, and for removing the organic matrix content using an oxidizing digestion mixture, such as a nitric acid–hydrogen peroxide mixture with the addition of hydrogen fluoride to dissolve the silicate content of the samples (6). Inductively coupled plasma mass spectrometry (ICP-MS) provides multielement analytical capabilities, excellent sensitivity (8) and very low detection limits up to sub-fg/mL in aqueous solutions (9). The use of micro-nebulization in ICP-MS reduces the solution uptake rate, thus decreasing the amount of sample required. Microconcentric nebulizers (such as Micromist from Glass Expansion, Australia) can introduce aqueous samples with as low a solution uptake rate as 20 µL/min (10), and DIHEN (direct injection high efficiency nebulizer, Meinhard Co., USA) can reduce the solution uptake rate to 1 µL/min (9).

The limits of the trace analytical methods were determined by the blank values in the chemicals used, instrumental background, memory effects, matrix effects, and possible isobaric interferences by atomic and molecular ions (1). Therefore, the use of standard reference materials (SRMs) during method development and routine analysis is very important in order to monitor the possible contamination and analyte losses during sample pretreatment and analysis, and also to check the accuracy of the analytical method applied. In a recent work (11), a method was developed for the sample preparation and multielement analysis of small amounts of environmental samples. The aim of this work is to apply this multielement analytical method for the determination of selected elements such as

Mg, K, Ca, Fe, Mn, Cu, Zn, Rb, and Cs by ICP-MS in small amounts of 30 barley plant samples.

EXPERIMENTAL

Instrumentation

The multielement analysis was performed with an ELAN® 6000 quadrupole-based ICP-MS (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada). For solution introduction, a microconcentric nebulizer (Micromist AR30-1-FN02, Glass Expansion, Australia) and minicyclonic spray chamber (Glass Expansion, Australia) were used to reduce the solution uptake rate during analysis. The determination of Ca in the samples was carried out by ICP-MS and Thermo Jarrel Ash Iris Duo ICP-OES instruments. The optimized instrumental parameters and measurement conditions are summarized in Table I.

Plant Material

Oriental Tobacco Leaves CTA-OTL-1 (ICHTJ, Poland) were used as the standard reference material. In the case of barley (variety *Alexis*), the seeds were germinated and grown in hydroponic solution for two weeks in a plant growth chamber (day: 16 h, +23°C, 60 % relative humidity, light intensity: 280 μmol photons m^{-2} s^{-1}, night: 8 h, +15°C, 90 % rel. humidity, darkness; slow light/dark changes for dusk and dawn within one hour). We used five plants each as (a) control, (b) with Cs^+ treatment, and (c) with TEA treatment. The composition of the nutrient solution (mmol/L) was as follows:

0.7 K_2SO_4, 0.1 KCl, 0.1 KH_2PO_4, 2.0 $Ca(NO_3)_2 \cdot 4H_2O$, 0.01 H_3BO_3, 0.005 $MnSO_4 \cdot H_2O$, 0.004 ZnCl, 0.002 $CuSO_4$, 0.00001 $(NH_4)_6Mo_7O_{24} \cdot H_2O$, 0.2 Fe-ethyl-ene-diamine-tetraacetate (FeEDTA), 2 MES buffer, pH 5.

In the case of Cs^+ treatment, we used 2 mmol/L CsCl in the nutrient solution and in the case of TEA, a concentration of 5 mmol/L for six hours (a total of 50 mL solution for each plant). After harvesting, two plant fractions were taken: leaves and roots. The samples were stored in 20 mL polypropylene scintillation vials (Packard, No. 6008117).

Tissue Sample Preparation

The plant tissue samples were dried at 70°C for 48 hours prior to further preparation and then stored in a desiccator (mean water content: roots 94.2%; leaves 92.5%). The samples were microwave-digested (Microwave Accelerated Reaction System, MARS-5, CEM Microwave Technology Ltd., USA), using an oxidizing acid mixture of 1 mL nitric acid, 0.5 mL hydrogen peroxide, and 0.2 mL hydrofluoric acid (7). The plant samples were cut into pieces, smaller than 0.5 cm, and weighed into clean PTFE crucibles (6-mL volume, screw cap, Savillex Corp., USA), and the digestion mixture was added. Two crucibles were placed into each vessel of the digestion unit (XP-1500). Outside the crucibles, 10 mL high-purity water was poured into the vessel to provide nearly equal pressure inside and outside the crucibles to prevent opening of the crucibles during digestion. The digestion was carried out with the following heating program: (a) 150 W for 10 minutes; (b) cooling for 2 minutes; (c) 300 W for 10 minutes, (d) cooling for 30 minutes. The digested samples were carefully transferred to disposable plastic sample tubes and made up to 10 mL with high-purity water. Rhodium was added to all samples and calibrating solutions as the internal standard element in a final concentration of 10 μg/L. For quality control of the analytical proce-

TABLE I
Instrumental Parameters and Measurement Conditions

ICP-MS	
RF power	1300 W
Coolant Ar flow rate	17 L/min
Plasma Ar flow rate	1.2 L/min
Nebulizer Ar flow rate	0.87 L/min
Sample uptake rate	0.085 mL/min
Sample size	0.57-2.13 μg
Nebulizer type	Microconcentric "Micromist"
Spray chamber	Minicyclonic "Cinnabar"
Sampler cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.9 mm orifice diameter
Dwell time/ms	200
Replicates	5
Sweeps/replicates	10
ICP-OES	
RF power	1150 W
Nebulizer Ar flow rate	0.7 L/min
Auxiliary Ar flow rate	0.5 L/min
Coolant Ar flow rate	14 L/min
Nebulizer type	Meinhard
Spray chamber	Cyclonic
Sample uptake rate	1.8 mL/min
Detection lines for Ca	184.0 and 317.9 nm

dure, 10 mg Oriental Tobacco Leaves CTA-OTL-1 SRM was digested in every digestion cycle.

Chemicals

Suprapur hydrofluoric acid (40%, Merck, Germany), suprapur hydrogen peroxide (30%, Merck, Germany) and suprapur nitric acid (65%, Merck, Germany) were used for the digestion of the SRM and barley samples. The nitric acid was further purified by subboiling point distillation. Multielement external calibrating solutions (calibration range: 0-100 μg/L) were prepared from single-element standard stock solutions (1000 mg/L, Merck, Germany). High-purity deionized water was used for dilution of the samples and calibrating solutions (prepared by the Milli-Q™ Plus purification system). For tracer experiments, analytical grade CsCl (Merck, Darmstadt, Germany) was used.

RESULTS AND DISCUSSION

Multielement Analysis in Small Amounts of Oriental Tobacco Leaves SRM

The most important problem to be solved during the analytical process is the correct preparation of the sample to avoid sample loss and contamination. Therefore, we studied the recoveries of the measured elements in the Tobacco Leaves reference material in two different ways: (a) independent digestions of the SRM for method development and (b) digestion of the SRM samples together with the barley samples in every digestion cycle for quality control. The measured and the certified concentrations of the selected analytes in the Oriental Tobacco Leaves SRM are shown in Table II for 10-mg samples. In the Oriental Tobacco Leaves SRM, Mg, K, Ca, Fe, and Mn are present in higher concentrations, and Cu, Zn, Rb, and Cs at a trace concentration level. The measured recoveries are in

TABLE II
Concentration of Selected Analytes Measured by ICP-MS in Oriental Tobacco Leaves SRM (concentrations in μg/g, 10-mg sample weight, n=10)

Analytes	Measured value ± SD	Certified value ± SD
Mg	4114±256	4470±210
K	15513±577	15600±500
Ca*	30875±280	31700±1200
Fe	952±76	(989)
Mn	416±3	412±14
Cu	14.7±0.7	14.4±0.5
Zn	53.1±1.5	49.9±2.4
Rb	10.71±0.05	9.79±1.27
Cs	0.214±0.024	0.177±0.022

* ICP-OES results
SD = standard deviation

TABLE III
Detection Limits of ICP-MS Measurements (3σ-criteria)

Analyte	Detection limits in aqueous solution (μg/L)	Detection limits in solid Tobacco Leaves SRM (μg/g)
Mg	0.044	0.88
K	0.057	1.15
Ca*	2.74	54.8
Mn	0.007	0.14
Fe	0.028	0.56
Cu	0.009	0.18
Zn	0.026	0.51
Rb	0.001	0.03
Cs	0.001	0.02

*ICP-OES results

excellent agreement with the certified values for all of the analytes studied. For Fe, only a recommended value was available in the certificate, which agrees well with our measured concentration. Calcium was measured using the ICP-OES method as well. The recoveries of Ca were better with ICP-OES, because of the high sample concentration and molecular interferences of the measured ^{44}Ca isotope ($^{12}C^{16}O_2{}^+$, $^{14}N_2{}^{16}O^+$, $^{28}Si^{16}O^+$) in ICP-MS; hence, only the ICP-OES results are presented.

The ICP-MS detection limits in aqueous solution and for the solid Tobacco Leaves SRM (sample weight 10 mg) are shown in Table III. The limits are estimated using the 3σ-criteria, i.e., the concentration of the analyte, which yields a signal equivalent to three times the standard deviation of the blank signal. The recovery results of the SRMs (CTA-OTL-1 Oriental Tobacco Leaves, NIST SRM 1577 Bovine Liver, NCS DC 73347 Human Hair) and different sample weights (1, 5, 20 and 50 mg) are discussed elsewhere (11).

Element Composition of Barley Root and Leaf Samples

The method developed was applied to determine the concentration of selected elements in two different tissue samples (roots and leaves), both for control, Cs- and TEA-doped barley plants. We found pronounced variations between the two barley tissue types (Table IV). In roots, higher concentrations were found for Fe, Mn, Cu, and partly for Zn. While in the leaves, K, Ca, and Mg were measured with higher concentrations. This effect is attributed to the biological variation commonly detected between individuals. The uptake of Cs in the tracer experiments is demonstrated in general with higher concentrations in the roots. Rubidium was a contaminant in Cs solution for spiking experiments. The total number of individual samples required for a statistically significant analysis will therefore depend on the required precision for a given physiological experiment.

Due to the spiking, small concentration changes were found in both barley leaves and roots. In Figures 1 and 2, a comparison is shown of the concentrations for

TABLE IV
Measured Concentration Ranges of Selected Analytes in Barley Leaves and Roots

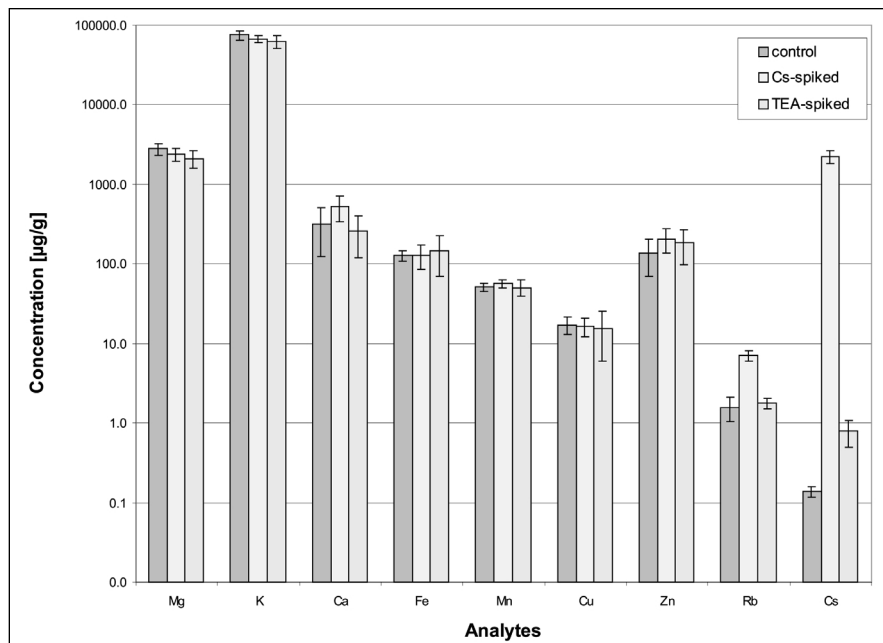| Analytes	Measured range (µg/g)	
	In Roots	In Leaves
Mg	1116-1993	1525-3817
K	26601-60834	45825-95363
Ca	327-3951	806-8125
Fe	8926-22243	88.7-279.1
Mn	70.2-182.8	35.38-77.3
Cu	58.5-523.9	7.48-31.75
Zn	535.7-1261	89.9-1179
Rb	1.15-21.92	1.10-8.42
Cs	0.02-4815*	0.03-2711*

* Spiked Cs in tracer experiments.

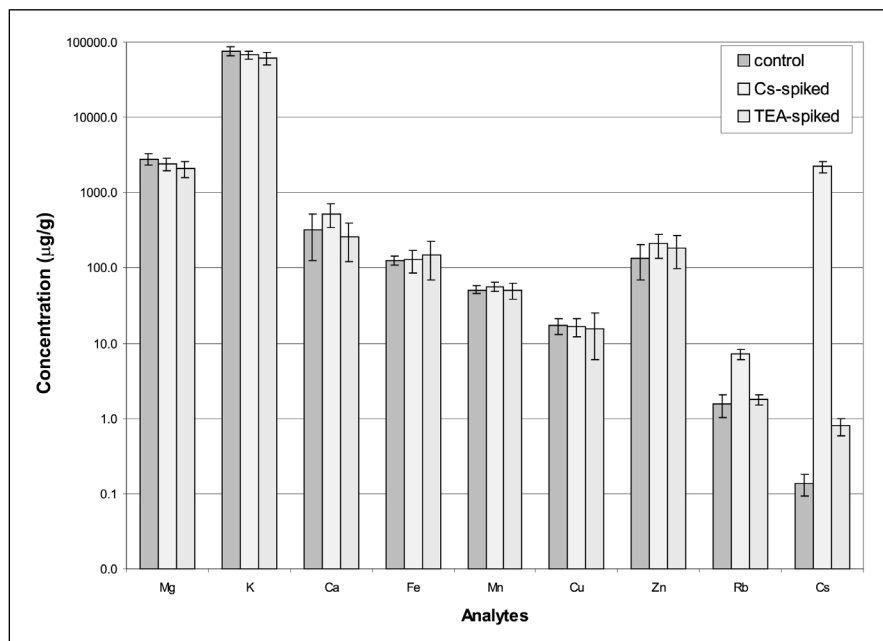Fig. 1. Results of the determination of selected elements in barley leaves measured by ICP-MS.

Fig. 2. Results of the determination of selected elements in barley roots measured by ICP-MS.

selected elements (in µg g^{-1}) in control, Cs-spiked, and TEA-spiked samples in barley leaves and roots measured by ICP-MS. The increased Cs concentration in the Cs-spiked leave samples shows that during the short exposure time, the uptake of the spiked nutrient solution was successful. A small decrease of the Mg, K, and Cu concentrations was found in the Cs-spiked samples. Compared to the concentrations in the control sample, an increased Fe concentration was found in the TEA-spiked samples, and increased Ca and Mn concentrations in the Cs-spiked samples. In the case of Zn, both spiking experiments resulted in an increase in the concentration.

Generally, the observed concentration changes were different in the root samples. As shown in Figure 2, the concentration of Mg, Ca, and Mn was higher in the Cs and TEA-spiked samples than in the control samples, and TEA induced greater changes in concentration than Cs did. In the case of Fe and Zn, slightly higher concentrations were observed in the Cs-spiked samples, and the lowest values were obtained for the TEA-spiked ones not the control samples. The concentration of Cu decreased due to spiking and the lowest value was found in the TEA-spiked samples. Compared to the control sample, the concentration of K decreased in the Cs-spiked roots, indicating the effect of Cs on the K uptake, while it increased slightly in the TEA-spiked roots.

The data presented in Figures 1 and 2 can be used to estimate the potential of the method and to estimate the number of samples required for the study. Genetically identical plants (clones) may give smaller variations, while plants from less controlled environments (e.g., natural stands) will presumably show considerably larger variations. The data given for Rb and Cs may be used as examples of additions to the "normal background" present in laboratory-raised plants, while the differences in K concentrations result from the TEA and Cs treatment, which leads directly to a reduced uptake rate of potassium and, as a secondary effect, may influence the composition of other elements, especially other cations.

CONCLUSION

ICP-MS in combination with micronebulization for solution introduction of microwave-digested biological samples was successfully applied to the routine multielement analysis of a large number of barley samples. The developed analytical method allowed the analysis of small biological samples, down to several mg. For all analytes measured in this study, the determined detection limits were sufficiently low and the recoveries for Tobacco Leaves SRM were in good agreement with the certified values. The standard deviation of the concentrations determined by ICP-MS was significantly lower than the observed biological variation measured in the barley. Small differences in the concentration of some analytes were detectable between control plants and plants treated with the K-channel blockers Cs and TEA. The channel blockers simulate the external effects on element concentration as well as detectability of the elements with the presented methods. However, more experimental data are required to elucidate the effects of modulating a single cation-channel type onto the cation-balance of total plants.

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The Determination of Phosphorus and Other Elements in Plant Leaves by ICP-MS After Low-Volume Microwave Digestion with Nitric Acid

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INTRODUCTION

One of the main water quality issues facing contemporary Australia is excessive growth of nuisance algae in waterways, and associated problems such as low oxygen availability to biota (1). Dissolved phosphorus is an essential nutrient that in many cases exerts primary control over algal growth (2). Most phosphorus entering Australian freshwater systems (57->90%) originates from diffuse sources such as fertiliser use, geological strata and decaying plant litter (1,3,4). Plants immobilise phosphorus, which then enters aquatic systems as litter that is consumed microbiologically and is released into the water column when microbial decay nears completion (4). Because plant litter plays an important primary role in the phosphorus cycle, there is a need to measure the concentration and bio-availability of this and other nutrient elements in plant materials entering waterways.

Many procedures for measuring phosphorus concentrations in plant materials are available (5,6). Our laboratory has developed a digestion technique using low-volume microwave digestion for measuring trace elements in biological tissue (7,8,9). The advantages are its simplicity, speed, and capacity to digest a range of biological materials.

The aim of this study was to examine the application of this procedure for ICP-MS determination of phosphorus in four plant types. This procedure also allows the simultaneous analysis of other elements.

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ABSTRACT

A procedure for measuring phosphorus in plant leaves is described. Dry-leaf homogenates (<0.1g) were placed in 7-mL Teflon vessels with nitric acid (1 mL), microwave digested using the following program: 600 W, 2 min; 0 W, 2 min; 450 W, 45 min, then analyzed by inductively coupled plasma mass spectrometery (ICP-MS). Recoveries were verified by analyzing four plant certified reference materials (CRMs) in parallel with two established procedures for measuring phosphorus: (a) flow injection analysis (FIA) after catalyzed block digestion with sulphuric acid, and (b) FIA after digestion with sulphuric acid and hydrogen peroxide. The ICP-MS procedure allowed relatively simple, rapid analysis of phosphorus that was accurate to within ±15% of certified values, with detection limits (5 µg/g) and precision (relative standard deviation = 4-9%) equivalent to or better than the other procedures. Furthermore, the ICP-MS procedure allowed the accurate determination (±15%) of 12 other elements simultaneously with phosphorus.

EXPERIMENTAL

All chemicals were analytical reagent grade. Glassware was cleaned with phosphate-free detergent, acid-washed, and rinsed with Milli-Q™ deionized water (Millipore).

Instrumentation

Inductively coupled plasma mass spectrometer: PerkinElmer SCIEX ELAN® 6000 (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada).

Flow injection analyzer: LaChat QuikChem AE Automated Ion Analyser.

Microwave digester and Teflon® bomb equipment: CEM Matthews Inc., Model MDS-2000.

Aluminum heating block: AI Scientific Model 450.

Reagents and Standard Solutions

The ICP-MS was calibrated with a series of matrix-matched external standards, prepared in blank digests from the following commercial standards: EM Science multi-element standard and PerkinElmer' Pure-Plus multi-element standard. The FIA was calibrated from a stock solution of orthophosphate (240 mg P/L) prepared by dissolving 1.055 g of dried potassium dihydrogen phosphate in 1 L. Phosphate working standards (12-0.6 mg P/L) were prepared by dilution.

Reagents were sulphuric acid (98%, BDH AnalaR), hydrogen peroxide (30%, Ajax Univar), nitric acid (69%, BDH Aristar), potassium sulphate (BDH Analar), copper sulphate pentahydrate (Ajax Univar) and Milli-Q deionized water (Millipore).

Samples

Four CRM standards were used to represent a range of plant leaves for evaluating the procedure. These were NIST 1575 pine needles (National Institute of Standards and Technology), NBS 1572 citrus leaves (National Bureau of Standards), BCR 402 white clover (Commission of the European Communities Community Bureau of Reference), and NIES 7 tea leaves (National Institute of Environmental

Studies). Ten blanks were processed and analyzed at regular intervals in the set of 20 samples.

Digestion Procedures

The three digestion procedures are detailed in the indicated references, and briefly described as follows:

(a) *Low-volume microwave digestion (7,8,9)*

One mL of nitric acid was added to 0.07 g of sample in 7-mL Teflon bombs, which were then loosely capped. After 1 hour at room temperature, caps were tightened to a torque of 2.3 Nm and two 7-mL vials were placed in larger 120-mL Teflon vessels containing a Teflon spacer with pre-drilled holes and 10 mL of deionized water. The deionized water maintains an external pressure on the smaller vessels during digestion, with the spacer keeping the digestion vessels out of the water to facilitate uniform heating. The pressure release valve and cap were placed onto the 120-mL vessel and tightened to a torque of 16.3 Nm. A carousel containing twelve 120-mL digestion vessels was placed into the microwave cavity. The samples were microwaved as follows: 600 W for 2 minutes, 0 W for 2 minutes, 450 W for 45 minutes. When cool, the digests were quantitatively transferred into 10-mL vials with 2x4.5 mL water. One-mL aliquots were diluted tenfold with deionized water for analysis by ICP-MS. Filtration was not required because digestion was complete.

(b) *Peroxide digestion (10)*

Sulphuric acid (4 mL) was added to 0.2 g of sample in 75-mL digestion tubes to wet the tube contents. Complete wetting is necessary to facilitate reaction and to avoid unreactive aggregates of dry sample. Hydrogen peroxide was added with vortex-mixing in the following sequence: 4x0.5 mL in quick succession, then 1 mL. When cool, the solutions were brought to 50 mL and the residues were allowed to settle. An aliquot was diluted tenfold for analysis by FIA.

(c) *Heated block digestion (11)*

Potassium sulphate (1.5 g) and copper sulphate (0.125g) were added to 0.2 g of sample in 75-mL digestion tubes with 1-2 glass beads, and the tube contents were vortex-mixed. Sulphuric acid (3.5 mL) was added to each tube, and tubes capped with condensers. The tubes were placed in a block digester preheated at 160ºC, the temperature was ramped to 390ºC over one hour, and held at 390ºC for a further hour. When cool, the digests were diluted to 50 mL with deionized water, and an aliquot was diluted tenfold for analysis by FIA.

Measurement of Phosphorus and Trace Metals

ICP-MS: Phosphorus and trace metals were measured using the instrumental settings given in Table I.

FIA: Phosphorus was measured as reduced phosphoantimonyl-molydenum blue complex (880nm; 20ºC) (11).

Data Analysis

One-way ANOVA or an equivalent non-parametric test (Kruskal-Wallis), with subsequent post-hoc comparison (Tuckey HSD, Scheffe, Bonferroni), was used to compare phosphorus concentrations measured by the three procedures (12). Differences in the variances of 10 blanks for each procedure were tested for by the Levenes test. This test indicates whether variances of sample sets are constant, and is commonly used in this regard to test for the homogeneity of variance assumption in ANOVA (12). Because the detection limits in this study were calculated as a function of variance (i.e., the 95% confidence interval of these blanks), this test was used to indicate whether detection limits by the three procedures were similar or significantly different.

RESULTS AND DISCUSSION

Recovery of Phosphorus

Phosphorus concentrations in plant materials measured by the low-volume microwave and the heated block procedures were similar, and within ±15% of certified values or close to indicative values (Figure 1). Phosphorus concentra-

TABLE I
ICP-MS instrumental conditions

RF forward power	1100 W
Plasma argon	15 L /min
Nebulizer flow	0.86 L/min
Auxiliary flow	1.2 L/min
Sample uptake	1.0 mL/min
Cross-flow nebulizer	Scotts double-pass spray chamber
Data acquisition	Multichannel analysis (one channel/amu)
Integration time	50 ms dwell time, 16 sweeps per replicate (3replicates), integrating time 800 ms

tions obtained by the peroxide digestion procedure were significantly lower (about 70% of certified values). The peroxide digestion did not completely decompose plant material, as suggested by the presence of residues and brown coloration in some of the digests. Heat for the peroxide digestion is derived only from dilution of the acid when aqueous peroxide is added.

Precision and Detection Limits of Phosphorus Determination

Analytical precision for phosphorus measurements, as given by relative standard deviations, were 4-9% for the microwave procedure, 6-16% for the heated block procedure, and 4-20% for the peroxide digestion procedure.

Instrumental detection limits (defined as the upper 95% confidence limit of the blank) for the measurement of phosphorus by the microwave and heated block procedures were similar (1.4 and 3.6 μg/L P, respectively). The peroxide digestion procedure had a significantly poorer instrumental detection limit (12 μg/L P). After adjusting for dilution and sample mass, the method detection limits were still similar for the microwave and heated block procedures (5.1 and 2.8 μg/g P) and poorer for the peroxide digestion procedure (30 μg/g P).

Recovery of Minor and Trace Elements

The low-volume microwave procedure allowed precise and accurate analyses of several elements in addition to phosphorus (Table II). Other elements (iron, selenium, and chromium) could not be determined accurately because of spectral interferences from plasma-induced polyatomic ions (13, 14), and are not reported.
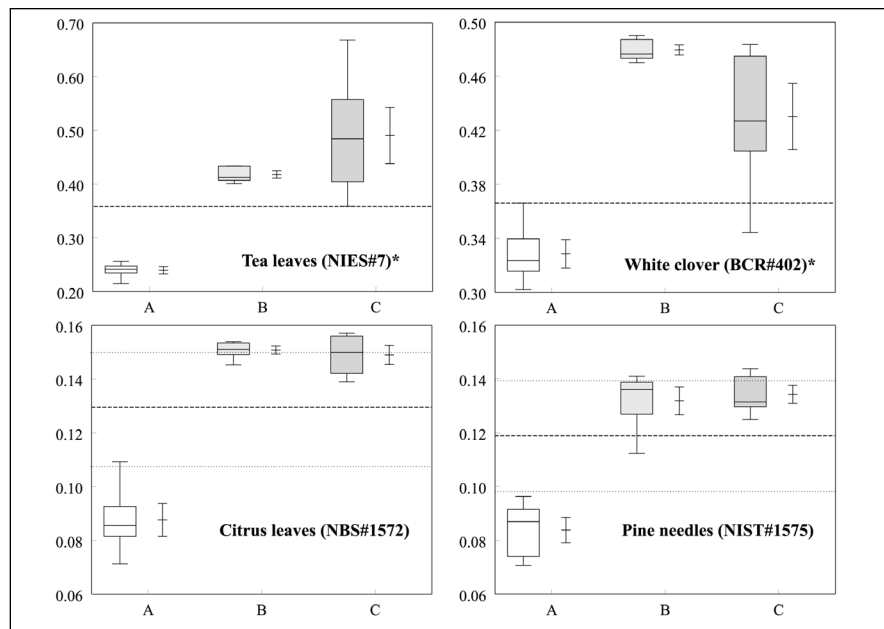
Fig.1. Phosphorus concentrations are represented by medians, inter-quartile ranges (boxes), 5th and 95th percentiles (whiskers). Means and standard errors are also shown. Element concentrations in CRM material are dashed lines, and uncertainties dotted lines. Indicative (non-certified) values are (*).
A: FIA analysis after digestion in sulphuric acid and hydrogen peroxide.
B: ICP-MS analysis after low-volume microwave digestion.
C: FIA analysis after catalyzed digestion in sulphuric acid.

Ease of Use

The time requirements for all procedures were similar (11, 14, and 13 minutes of relative time per sample, for the respective procedures of low-volume microwave digestion, peroxide digestion, and heated block digestion) if the capacities of the microwave digestion unit (24 samples) and the heated block (50 samples) are fully utilized.

For the determination of trace metals in addition to phosphorus, the low-volume microwave procedure allows simultaneous analyses of several elements, taking 150 minutes to determine 30 elements in 30 samples, each of which were represented by one aliquot. In terms of cost, the other procedures are cheaper for determining phosphorus alone. The microwave digestion procedure becomes cost-effective when the determination of more than nine elements is required.

CONCLUSION

Low-volume microwave digestion of plant materials with nitric acid and ICP-MS determination of phosphorus gives accurate measurements of phosphorus in four plant materials. The analytical results were similar and within ±15% of certified values. The detection limits, precision, and time of analysis were similar to the procedure of using a heated block to digest the samples with sulphuric acid followed by FIA. This procedure is widely used to measure phosphorus in environmental samples. The ICP-MS analysis after low-volume microwave digestion procedure is simple and has the added advantage of multi-elemental analysis, because several elements can be analyzed simultaneously from one dilution with good precision and accuracy

TABLE II
Mean Recovery of Elements in CRMs Measured by ICP-MS
After Low Volume Microwave Digestion

Precision represents 95% confidence limits unless indicated[a], in which case precision is that stated by the reference body but not otherwise define..

CRM	CITRUS LEAVES (NBS #1572)			TEA LEAVES (NIES #7)		
	Found	Certified	% recovered	Found	Certified	% recovered
Minor elements	Wt. %	Wt %		Wt. %	Wt %	
Calcium	2.76 ± 0.04	3.15 ± 0.10	88 ± 1%	0.28 ± 0.10	0.320 ± 0.012[a]	86 ± 3%
Magnesium	0.58 ± 0.02	0.58 ± 0.03	101 ± 3%	0.157 ± 0.007	0.153 ± 0.006[a]	103 ± 5%
Phosphorus	0.151 ± 0.004	0.13 ± 0.02	116 ± 3%	0.42 ± 0.02	0.37*	113 ± 5%.
Potassium	1.95 ± 0.04	1.82 ± 0.06	107 ± 2%	2.04 ± 0.98	1.86 ± 0.07[a]	110 ± 5%.
Trace elements	µg/g	µg/g		µg/g	µg/g	
Barium	20.6 ± 0.5	21 ± 3	98 ± 3%	6.5 ± 0.3	5.7*	114 ± 6%
Cadmium	0.033 ± 0.012	0.03 ± 0.01	111 ± 41%	0.023 ± 0.002	0.030 ± 0.003[a]	75 ± 8%
Copper	16.1 ± 1.1	16.5 ± 1.0	98 ± 7%	7.27 ± 1.05	7.0 ± 0.3[a]	104 ± 15%
Lead	14.8 ± 0.1	13.3 ± 2.4	112 ± 1%	0.79 ± 0.1	0.80 ± 0.03[a]	98 ± 13%
Manganese	22.9 ± 0.4	23 ± 2	99 ± 2%	660 ± 39	700 ± 25[a]	94 ± 6%
Rubidium	5.13 ± 0.11	4.84 ± 0.06	106 ± 2%	6.9 ± 0.4	-	n.a.
Sodium	169 ± 53	160 ± 20	106 ± 33%	<34	15.5 ± 1.5[a]	Not detected
Strontium	111 ± 3	100 ± 2	111 ± 3%	4.4 ± 0.2	3.7	119 ± 5%
Zinc	33 ± 4	29 ± 2	114 ± 13%	36 ± 2	33 ± 3[a]	108 ± 6%
CRM	WHITE CLOVER (BCR #402)			PINE NEEDLES (NIES #1575)		
	Found	Certified	% recovered	Found	Certified	% recovered
Minor elements	Wt. %	Wt %		Wt. %	Wt. %	
Calcium	1.50 ± 0.03	1.70 ± 0.03*	89 ± 2%	0.38 ± 0.04	0.41 ± 0.02	93 ± 10
Magnesium	0.229 ± 0.005	0.194 ±0.002*	118 ± 2%	0.12 ± 0.01	-	n.a.
Phosphorus	0.48 ± 0.01	0.373 ±0.006*	128 ± 3%	0.13 ± 0.01	0.12 ± 0.02	110 ± 12
Potassium	≤3.49	2.69 ± 0.04*	≤130%	0.40 ± 0.04	0.37 ± 0.02	109 ± 12
Trace elements	µg/g	µg/g		µg/g	µg/g	
Barium	10.6 ± 0.3	8.9 ± 0.1*	120 ± 4%	6.4 ± 0.6	-	n.a.
Cadmium	0.18 ± 0.02	-	n.a.	0.19 ± 0.02	<0.5*	n.a.
Copper	15 ± 3	12.0 ± 0.8*	126 ± 26%	3.2 ± 0.6	3.0 ± 0.3	107 ± 19
Lead	0.41 ± 0.05	-	n.a.	12.1 ± 1.1	10.8 ± 0.5	112 ± 11
Manganese	29.9 ± 0.6	22.8 ± 0.4*	131 ± 3%	671 ± 69	675 ± 15	99 ± 10
Rubidium	3.20 ± 0.08	-	n.a.	12.2 ± 1.2	11.7 ± 0.1	105 ± 10
Sodium	3002 ± 53	2350 ± 21*	128 ± 2%	9 ± 12	-	n.a.
Strontium	40.1 ± 0.9	29.0 ± 0.3*	138 ± 3%	5.2 ± 0.5	4.8 ± 0.2	109 ± 10
Zinc	28 ± 4	25.2 ± 0.7*	113 ± 15%	66 ± 6	-	n.a.

n.a. certified analyses were not available.
* Shows indicative but not certified reference data.

ACKNOWLEDGEMENTS

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Direct ICP-OES Determination of Low Concentrations of Cu, Fe, Li, Ti, and V in Potassium Lithium Tantalate Niobate Crystals

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INTRODUCTION

In recent years, potassium lithium tantalate niobate (KLTN) crystals have become a material of great scientific and technological interest. They are electro-optic crystals designed to operate at the para-electric phase where the electro-optic effect is quadratic. KLTN possesses unique properties that open several avenues both in basic and applied research. First and foremost, KLTN was developed as the medium for electro-holographic devices (1-3). In addition, it was used to demonstrate the dielectric mechanism of the photo-refractive effect (4,5) and the spontaneous soliton-like behavior at the critical region (6). KLTN was also found to be very attractive for pyro-electric detection since its responsivity supercedes state-of-the-art by over an order of magnitude (~10 $\mu C/cm^2K$).

The growth of KLTN crystals with deliberate addition of trace elements, such as copper, iron, titanium, and vanadium, is therefore of great interest (7). In order to control movement of these trace elements from flux to crystal during growth, it is necessary to quantitatively determine the concentration of the trace as well as the major elements such as lithium, niobium, and tantalum. For this reason, sensitive and accurate analytical methods are required. The determination of tantalum, niobium, and potassium in the crystal can be easily accomplished by electron micro-probe analysis.

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ABSTRACT

A fast method of direct trace element determinations in a potassium-tantalum-niobium matrix has been developed. A new dissolution method was proposed. The PerkinElmer Optima 3300 RL ICP-OES with multicomponent spectral fitting (MSF) of spectral line corrections was used. Because of the complex matrix, less common spectral lines were chosen. The relative standard deviations (RSDs) for trace element (Cu, Fe, Li, Ti, and V) determinations were 0.2 - 0.6%, the limits of detection (LOD) in solutions were 0.005 - 0.015 mg/L, which is equivalent to 5 - 15 ppm in solid samples.

However, the determination of lithium as well as trace photorefractive impurities cannot be performed with this technique due to the low atomic number of the former and the low concentrations of the latter. Flame atomic absorption spectroscopy (AAS) without trace-matrix separation has been shown to lack the sensitivity required for trace element determinations (8).

Inductively coupled plasma optical emission spectrometry (ICP-OES) seems a highly suitable technique for this purpose, but serious spectral interferences due to line-rich spectra of the niobium-tantalum matrix pose problems. Methods have been published for matrix separation prior to ICP-OES analysis (9,10), but they require increased analysis time and may lead to contamination of the sample. Conte et al. (11) determined trace element concentrations in tantalum products without matrix sep-

aration using ICP-OES with a high-resolution spectrometer. However, in a mixed niobium-tantalum matrix, strong interferences are still present. For this reason and for the selection of appropriate spectral lines, ICP-OES analysis with Multi-component Spectral Fitting (MSF) is a suitable technique that allows the direct analysis of these types of samples.

An additional concern in the analysis of niobium-tantalum crystals is the sample digestion procedure. Since this type of matrix has a high total dissolved salts content, the digestion should preferably take place in an acid mixture using PTFE pressure vessels (10,11). Another digestion procedure that has been suggested is fusion with alkali metal salts (12).

EXPERIMENTAL

Instrumentation

A PerkinElmer Optima 3300™ RL ICP-OES spectrometer (PerkinElmer Instruments, Norwalk, CT USA), working in the MSF mode, was employed for the analysis. This instrument is described by Barnard et al. in the literature (13,14). MSF was used for the correction of the interfered elements Cu, Fe, Ti, and V. The operation was fully controlled with a software program using the Microsoft® Windows 95® operating system. The ICP-OES instrumental operating conditions are listed in Table I.

Sample Preparation

The samples were obtained from KLTN crystals, crushed, and then powdered in a porcelain mortar. The samples, weighing 0.1 g, were mixed in quartz crucibles with 3 g

TABLE I
ICP-OES Operating Conditions for the Determination of Trace Elements in KLTN

Spectrometer conditions

Spectral profiling	Yes
Read time	5 sec
No of replicates	3

Plasma parameters

Nebulizer	Cross flow
Plasma gas	15 L/ min
Auxiliary gas	0.8 L/min
Nebulizer gas	0.9 L/min
RF Power	1100 W
View height	15 mm

Peristaltic pump

Sample flow rate	1.3 mL/min

potassium pyrosulfate. The mixture was fused for 30 minutes in a furnace at 700°C. After fusing, the samples were put into glass beakers and were treated with 10 mL distilled water, 20 mL sulfuric acid, 1.5 g oxalic acid, and 1 mL hydrogen peroxide. After dissolution, the solutions were transferred into volumetric flasks and diluted to 100 mL with water. Because of the difference in the amount of TDS in the samples and standards, transport of the solution to the plasma varied significantly. Scandium was added to the blank, standards, and samples as an internal standard to correct for this effect and the physical effects in the plasma. The final concentration was 5 mg/L. It should be noted that the niobium and tantalum solutions are stable in the presence of hydrofluoric acid, but HF also leads to the destruction of the quartz torch. We, therefore, prepared the solutions without hydrofluoric acid and analyzed them on the same day.

Standards

Two calibration standards were prepared, one for the determination of Nb and Ta and one for trace element determination. A mixed Nb and Ta calibration standard (200 mg/L Nb and 400 mg/L Ta) was prepared by dilution of the stock solutions. A Ta stock solution was prepared by dissolution of a Specpure metal rod (Johnson Mathey Corporation, JMC, No. S 51433) in accordance with a procedure described in "Analytical Methods for Atomic Absorbtion Spectrophotometry" (15). SPEX single-element solution standard PLNB9-2X, containing 1000 mg/L Nb was used as the stock solution for niobium. The certified trace element levels for both Ta and Nb in solid material were less than 2 ppm.

For the determination of trace elements, the calibration standards containing 0.5 mg/L of Cu, Li, and V and 5 mg/L of Fe were prepared by dilution of the Merck 10580 ICP Multi-Element Standard VI. Titanium with a final concentration of 0.5 mg/L was added from a stock solution (Merck, Darmstadt, Germany).

Calibration blanks and standards were matrix-matched with respect to the potassium and sulfuric acid concentrations in the samples. A 10000 mg/L potassium solution for the matrix was prepared from Specpure KCl (JMC, No S 54936E).

Line Selection

The Nb and Ta concentration in the solutions was about 200 and 400 mg/L, respectively, which leads to a strong interference of most of

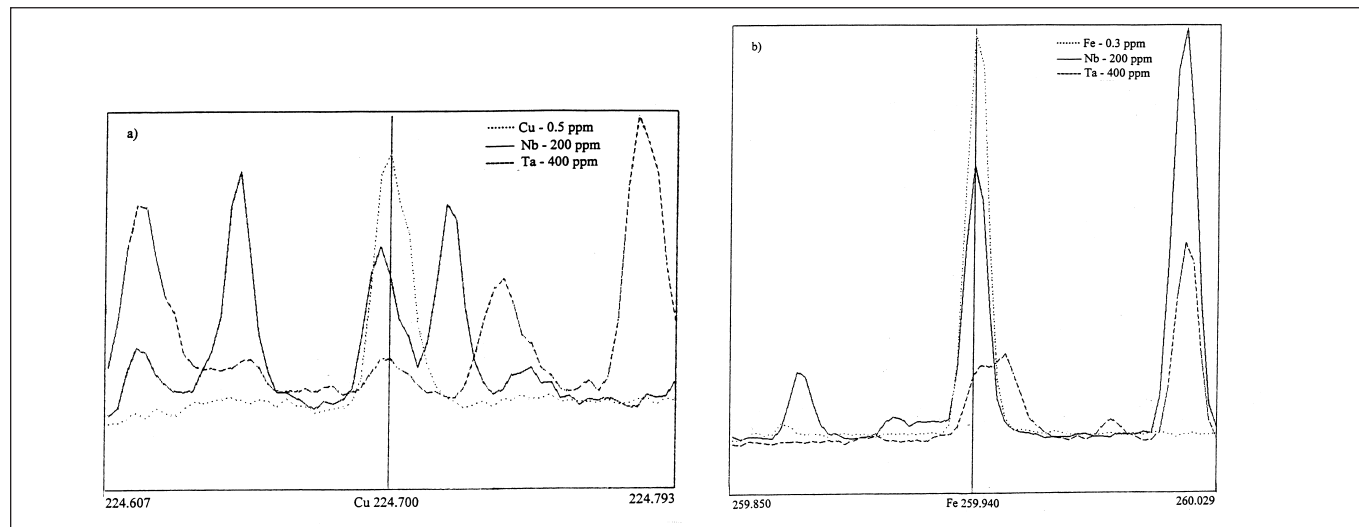Fig. 1. Spectral scan of Cu(II) 224.700 nm interfered by Nb 224.698 nm (a), and of Fe(II) 259.940 nm interfered by Ta 259.940 and Nb 259.952 nm (b). High resolution JY-38 spectrometer; Cu concentration in the sample was 0.5 mg/L and Fe - 0.3 mg/L.
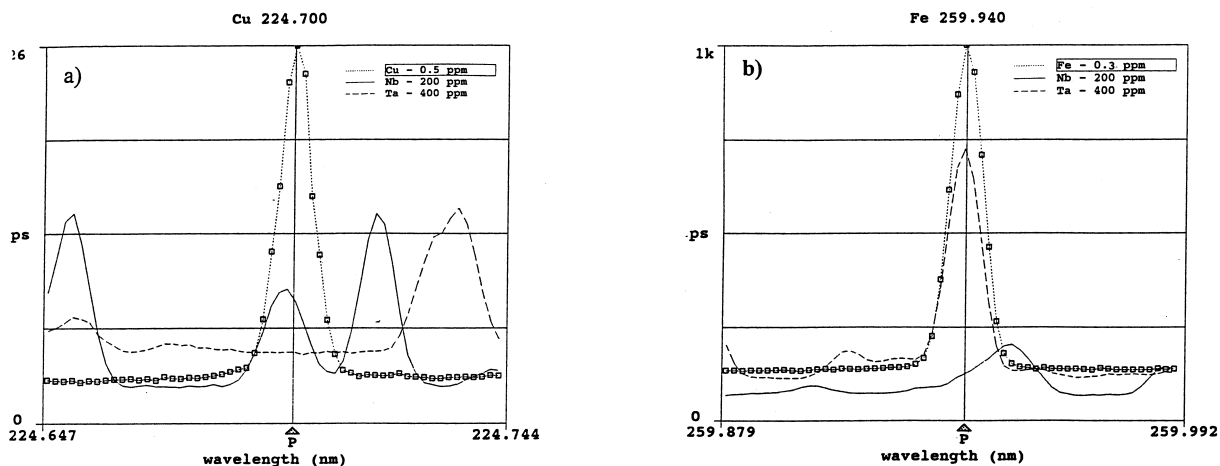
Fig. 2 (a and b). Spectral scan of the same sample as in Figure 1 using the Optima 3300 spectrometer.

the sensitive analyte spectral lines. Therefore, a careful line selection was undertaken. Spectral scans were performed using two spectrometers: the high-resolution Jobine Yvon JY-38 and the PerkinElmer Optima 3300 ICP-OES. Even a high-resolution spectrometer did not resolve the interference problems (see Figures 1a and 1b). For this reason, the Optima 3300 in MSF mode was used.

The most sensitive Cu(I) 324.752-nm line is strongly overlapped by Nb. Therefore, the Cu(II) 224.700-nm line, which is less interfered by Nb, was used instead in spite of its lower sensitivity (see Figure 2a). The Fe(II) 259.940-nm line was used although it is overlapped mainly by Ta and slightly by the Nb tail (see Figure 2b). The most sensitive spectral line of Ti(II) 334.940 nm is strongly influenced by Nb; therefore, Ti(II) 336.121 nm was chosen instead. In addition, the

lines of V(II) 310.230 nm and Ti(II) 336.121 nm occur in the region of OH-bands. Only Li(I) 670.781 nm was free from overlapping. The MSF mode was employed for Cu, Fe, Ti, and V correction, using a matrix solution containing K, Nb, Ta, and H_2SO_4 in concentrations corresponding to the analyzed samples. The spectral lines of Nb and Ta chosen for the analysis are insensitive because of the high concentration of both Nb and Ta in the samples. The spectral lines selected are given in Table II.

RESULTS AND DISCUSSION

The spectra of the pure matrix solution containing 10,000 mg/L potassium, 200 mg/L niobium, and 400 mg/L tantalum (the concentrations are corresponding to those in the samples) before and after MSF correction are shown in Figure 3. As can be seen from Figure 3, MSF correction is very effective, all interferences are suppressed.

Because of the lack of certified reference materials, synthetic samples were used for recovery evaluations. The results of the analysis for the samples with and without MSF correction are given in Table III. As can be seen from the table, the recovery without MSF ranged from 80 to 420% (this high value is due to the very poor sensitivity of the

TABLE II
Line Selection for Elements Determined

Element	Spectral line (nm)
Sc*	361.384
Cu	224.700
Fe	259.940
Li	670.781
Ti	336.121
V	310.230
Nb	269.706
Ta	233.198

* Internal standard.

TABLE III. Results for the Analysis of Spiked Samples Without and With MSF

Concentrations (mg/L)*	Cu		Fe		Li		Ti		V	
	Without	With	Without	With	Without	Without	With	Without	With
0.050	0.209	0.055	0.925	0.518	0.047	0.065	0.055	0.126	0.055
0.100	0.230	0.101	1.37	1.01	0.095	0.121	0.120	0.175	0.111
0.500	0.480	0.492	4.90	4.95	0.506	0.474	0.510	0.440	0.510
1.000	0.804	0.989	9.36	9.80	1.020	0.920	1.010	0.805	1.010

* Fe content in the samples is larger in order of magnitude than the concentrations of the rest of the elements.
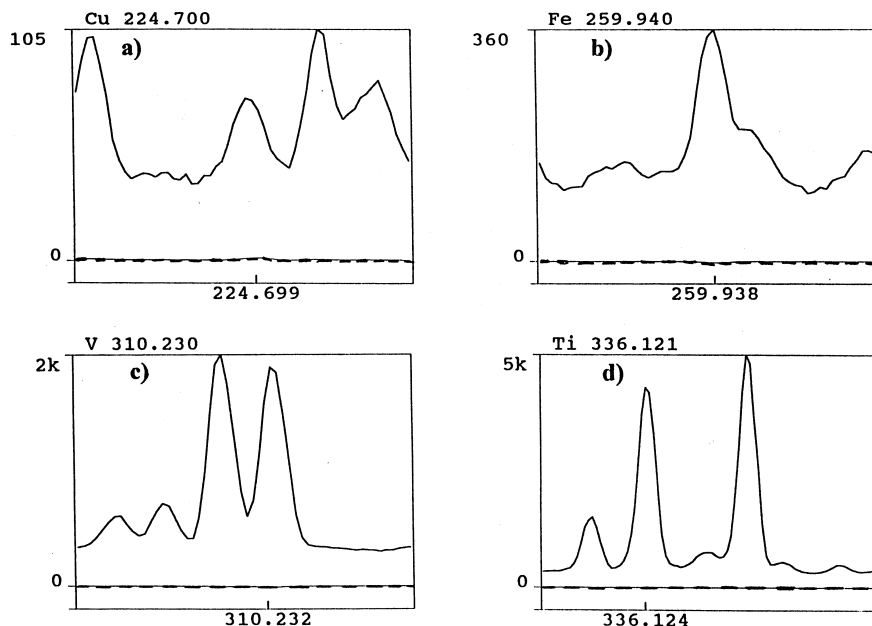
Fig. 3 (a - d). Matrix spectra contained 200 mg/L Nb, 400 mg/L Ta, 10,000 mg/L K and sulfuric acid without MSF correction (solid line) and with MSF correction (dashed line): (a) for Cu (window 0.097 nm), (b) for Fe (window 0.113 nm), (c) for V (window 0.134 nm), and (d) for Ti (window 0.227 nm). X-axis – counts/sec.

elements interfered by the matrix). After MSF correction, the recovery improved to 98 - 110%. The precision (RSD) of the method ranged from 0.2 - 0.6%. The 3σ LODs were determined using a blank solution containing potassium, niobium, tantalum, and sulfuric acid and were subjected to the same treatment as the samples. Table IV shows that the LODs of the determined elements in solutions varied from 0.005 - 0.15 mg/L (5 - 15 ppm in the solid samples).

TABLE IV
LOD for Trace Element Determination in Solutions

Element	LOD (mg/L)
Cu	0.010
Fe	0.015
Li	0.005
Ti	0.01
V	0.01

CONCLUSION

It was demonstrated that the proposed dissolution procedure of samples using an ICP-OES spectrometer in the MSF mode is a rapid and sensitive method for the analysis of KLTN crystals. The MSF mode together with less common spectral lines is effective in correcting for very complicated spectra. It is possible to overcome the problems due to analyte loss and sample contamination, which may occur during the process of matrix separation. The direct method for KLTN crystal analysis was used for the control of trace element movement during the growing cycle of KLTN crystals with certain properties.

Received March 15, 2000.

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Soil and Sediment Analysis by Spectroscopic Techniques Part I: Determination of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn

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INTRODUCTION

For the rapid and accurate determination of trace metals in environmental matrices, an instrumental analytical technique with high sensitivity is required that permits the largest analytical characterization in the shortest possible time. This is particularly true for techniques like ICP-OES and ICP-MS, which can produce large amounts of analytical data in much less time than it takes to prepare the samples. However, for solid samples, before the instrumental determination, it is always necessary to perform long and tedious dissolution treatments, which represents the most restrictive step of the total procedure.

In order to be effective, the digestion treatment of the sample must ensure a complete dissolution of the matrix to allow the release of the analytes in a chemical form compatible with the analytical method. Several years ago, the traditional attack in open beakers or the more classic alkaline fusion procedure was mostly used for the digestions of soils and sediments. For example, in the Dutch standard NEN 6465 (1) and the German standard DIN 38414 Part 7 (2), the metals present in soils and sludges were extracted by refluxing with aqua regia on a hot plate. These methods, however, are prone to environmental contamination and do not guarantee complete recovery for many elements.

To overcome these problems, the acid treatment of the sample was performed in closed vessels or in a Teflon® bomb (3,4), which allowed the dissolution of only a few milligrams of sample and also

ABSTRACT

The determination of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in soils and sediments by ICP-OES, ICP-MS, and GFAAS after acid decomposition of the sample in a microwave oven was investigated. The validation of the method was carried out in two laboratories operating with different instruments. The repeatability and reproducibility were calculated according to ISO 5725.

The use of HNO_3/HCl provided good recoveries for Cd, Cu, Ni, Mn, and Zn (89–114%); but poorer results for Pb (82–89%). Complete solubilization of the materials was achieved with closed-vessel microwave digestion using a mixture of $HF/HNO_3/HCl$. The precision of ICP-OES determination with this second procedure, due to the complexity of the matrix in the final solution, proved to be worse than that achieved with aqua regia. The accuracy of the method was evaluated analyzing five certified reference materials (CRM): Soil BCR CRM 141R, CRM 142, and CRM 143, and Sediment BCR CRM 277 and CRM 320.

employing acid reagents, heating of the sample in a microwave oven using plastic vessels that were able to resist elevated pressures, was published in the technical literature. Since 1975, when the first paper reported the use of acid digestion with a microwave procedure for the dissolution of siliceous materials (5), hundreds of microwave applications have been published (6-8). The advantages of this technique were reduced time required for sample preparation, reduced amounts of acids

employed for the complete dissolution of the matrix, minimal contamination within the laboratory, reduced loss of the more volatile analytes and, consequently, better detection limits and better accuracy of the method. Today, there are many official methods available for the analysis of soils and sediments that employ several acid mixtures and microwave heating: ASTM D5258-92 (9), U.S. EPA Method 3050B (10), U.S. EPA Method 3051 (11), U.S. EPA Method 3052 (12), and two European proposals of method prEN CEN/TC292/WG 3 N310 (13) and prEN CEN/TC292/WG 3 N100 (14).

This paper reports the results obtained during a collaboration between ENEL DP Central Laboratory of Piacenza (Laboratory A) and the Institute of Agricultural and Environmental Chemistry, Catholic University of Piacenza (Laboratory B) for the setup and optimization of a method for the determination of "aqua regia-soluble" and "total" content of trace metals in soils and sediments. The aim of the collaboration was to evaluate, optimize, and validate a procedure for the dissolution of the sample using a microwave oven with subsequent ICP-OES, GFAAS, and ICP-MS analysis.

EXPERIMENTAL

Instrumentation

The microwave digesters used for closed-vessel high-pressure sample digestion were: CEM (Matthews, NC, USA) MDS-2000 model and Milestone (FKV, Sorisole, Bergamo, Italy) MLS 2100 model. The operating conditions are listed in Table I.

A PerkinElmer Optima 3000™ inductively coupled plasma emis-

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TABLE I: Operating Conditions for Microwave Systems

Aqua Regia Procedure[a]

CEM 2000/Milestone 2100

Step	1	2	3
Power (W)	250	400	500
Hold time (min)	2	2	2, 4, 7, 5, 10,15,20,30

HF/HNO$_3$/HCl Procedure[b]

CEM 2000/Milestone 2100

Step	1	2	3	4	5[c]	6
Power (W)	250	400	600	0	300	0
Hold time (min)	8	4	6	2	3	2

[a] *250 mg of soil/sediment treated with 8 mL aqua regia in each of 6 vessels.*
[b] *250 mg of soil/sediment treated with 2 mL HF, 8 mL aqua regia and 2 mL H$_3$BO$_3$ in each of 6 vessels.*
[c] *The acid boric satured solution was added before the step n.5.*

sion spectrometer, equipped with an AS-90 autosampler , a cross-flow nebulizer, and a Scott-type spray chamber in Ryton®, was used by Laboratory A , while a Jobin Yvon 24 spectrometer with a cross-flow nebulizer was used by Laboratory B.

A Zeeman 5100 atomic absorption spectrometer, equipped with an HGA®-600 graphite furnace and an AS-60 autosampler (PerkinElmer Instruments, Norwalk, CT USA), was used by Laboratory A.

The ICP-MS instrument used by Laboratory A was a PerkinElmer SCIEX ELAN® 5000 (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada), equipped with a PerkinElmer Gem-Tip™ cross-flow nebulizer and a corrosion-resistant Scott-type spray chamber.

Reagents and Standard Solutions

Nitric acid (65% m/v), hydrochloric acid (37% m/v), and hydrofluoric acid (40% m/v) were Suprapur reagents (E.Merck, Darmstadt, FRG); boric acid was analytical-reagent grade (BDH).

Multielemental standard solutions were prepared from 10-mg/L multielemental atomic absorption standards, ICP-MS Calibration Standard n.1,2,3,4 (PerkinElmer), by dilution with water containing the same amount of acids as the samples.

High-purity water was produced starting from distilled water using a Milli-Q™ deionizing system (Millipore, Bedford, MA USA).

Standard Reference Material

The accuracy of the method was verified by analyzing five different certified reference material (CRM) samples prepared by the Community Bureau de Reference (BCR):

Soils: CRM 141R Calcareous Loam Soil; CRM 142 Light Sandy Soil; CRM 143 Sewage Sludge Amended Soil

Sediments: CRM 277 Estuarine Sediment; CRM 320 River Sediment

Aqua regia – Microwave Procedure

A 0.25-g dry sample was weighed into each pre-cleaned Teflon® vessel, 8-mL aqua regia was added and heated in a microwave oven using the operating conditions listed in Table I. After cooling, the content of the vessels was filtered through a Millipore 0.45 μm filter and the solution quantitatively transferred into a 50-mL calibrated flask, diluted to volume with deionized, distilled water (DDW).

The samples were diluted 10-fold in DDW prior to analysis by GFAAS and ICP-MS, while no dilution was used for ICP-OES analysis. At least one sample blank, containing the same amount of acids, was processed along each set of samples.

HF / HNO$_3$ / HCl – Microwave Procedure

A 0.25-g dry sample was weighed into each pre-cleaned Teflon vessel, 2 mL HF and 8 mL

aqua regia were added, then heated in the microwave oven using the operating conditions listed in Table I. After cooling of the sample, 2 mL boric acid saturated solution was added , the vessel re-capped, returned to the oven, and heated at 300 watts for 3 minutes. At this stage, the clear solution obtained for soils and sediments was quantitatively transferred into a 50-mL calibrated flask and diluted to volume with DDW. The samples were diluted 10-fold in DDW prior to GFAAS and ICP-MS analysis, while no dilution was used for ICP-OES analysis. At least one sample blank, containing the same amounts of acids, was processed along with each set of samples.

For both procedures and for each material analyzed, each laboratory prepared four replicates on different working days. In order to evaluate the uncertainty associated with the dissolution step and the instrumental measurement, the solutions prepared by Laboratory A were analyzed by Laboratory B, and vice versa.

RESULTS AND DISCUSSION

Aqua Regia Procedure

A series of preliminary tests (trials) were performed to verify the recovery of the analytes with different MW operating conditions. The time of the final step at 500 watts was changed to 2, 4, 7, and 10 minutes for the Milestone oven and to 5, 10, 15, 20, and 30 minutes for the CEM oven. Figure 1 shows the percentage recovery for Cr and Cu as a function of the digestion time in the final step. The release of Cu in solution was more rapid than that of Cr, which reaches a plateau only after 10-15 minutes of heating. Cadmium, Ni, Pb, and Zn exhibit a profile similar to Cu, while the results for Mn were between the Cu and Cr results.
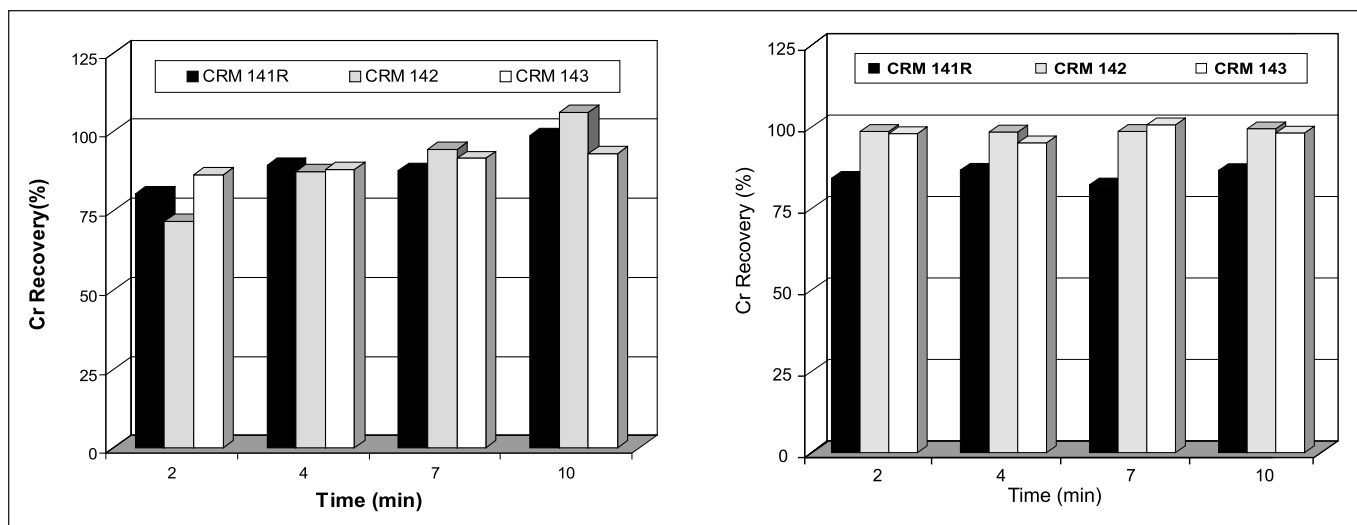
Fig. 1. Percentage recovery of "Aqua regia soluble " Cr and Cu in BCR CRM 141R, CRM 142 and CRM 143 versus heating time at 500 W.

With a 10-minute final step, the recoveries of all elements are quantitative, ranging between 90 and 105% (Table II). The lowest recovery value, obtained for Pb in CRM 141 R (<85%) can essentially be ascribed to the ICP-OES determination and can be improved to 94% with the method of standard additions. The same samples analyzed by ICP-MS gave results closer to certified values, thus indicating a complete dissolution of the material. Finally, the anomalous value found for Zn in CRM 142 (114%) is certainly due to a contamination problem during the dissolution stage.

ICP-OES Determination

The solution derived from the aqua regia procedure was analyzed by the two laboratories with two different instrumental configurations. In order to evaluate the uncertainties associated with the instrumental measurement and the sample preparation step, the solution prepared by Laboratory A was analyzed by Laboratory B, and vice versa.

The possibility of using two different wavelengths for every analyte in order to rapidly verify the presence of spectral "undesired"

TABLE II (A): Wavelengths Used in ICP-OES Analysis and Recovery (%) for the Determination of Metals in aqua regia Dissolution Procedure

Element	Wavelengths (nm)	Recovery (%)		
		CRM 141R	CRM 142	CRM 143
Cd 114[a]	214.438, 228.802*	94	n.d.†	96
Co 59[a]	230.786, 228.616*	103	n.d.†	n.d.†
Cr 52[a]	205.552, 206.149, 267.716*	102	105	89
Cu 63[a]	324.754, 327.396, 234.754*	90	98	93
Mn 55[a]	257.610*, 260.569	89	98	94
Ni 60[a]	231.604*, 221.647	93	100	101
Pb 208[a]	220.353*, 261.418	82	85	89
Zn 66[a]	206.200, 213.856*	92	114	89

[a] Mass of isotopes for elements listed in all tables.
* Wavelength used for the analysis; the other wavelengths were used for interference assessment.
† Not determined.

TABLE II (B): Instrumental Parameters for ICP-MS Analysis

RF power	1085 W	Dwell time	50 ms
Plasma argon	14.6 L/min	Sweeps / replicates	3
Nebulizer flow	1.1 L/min	Number of replicates	5
Auxiliary flow	0.83 L(min	Sample time	1 min 6 sec
Sample flow rate	1 mL/min	Sample read delay	50 s
Nebulizer	Cross-flow	Autosampler wash delay	60 s
Data	Peak hop transient	Calibration mode	External calibration
Resolution	Normal	Calibration standard	10, 20, 30,50, 100 µg/L
Reading time	150 ms	Curve fit	Linear through zero

interferences was evaluated using the PerkinElmer Optima 3000 ICP-OES. The difference in analyte concentration measured at the two wavelengths is not larger than 5–7%, which confirms that the spectrometric measurement does not present a real problem at these operating conditions. Using the wavelengths assigned an asterisk (*) in Table II, the typical precision for 1 mg/L of different elements (RSD% for 5 replicates) was always less than 1.5%.

Tables III–V report the experimental values found in the present work and those certified by BCR. The anomalous results, labelled as OUT (outliers), were discarded and not considered in the definition of a general mean. The repeatability and reproducibility of the method was calculated according to the ISO 5725 standard (15). No significant differences were detected for the three materials solubilized by aqua regia.

There was good agreement between the experimental and the certified values; the largest difference obtained for Zn in CRM 142 is certainly due to contamination in Laboratory A as demonstrated by the analysis of the same samples done in the Laboratory B.

In the CRM sample, the Cd results fell below the method dectection limit.

TABLE III: Determination of Metals (µg/g) in CRM BCR 141 Calcareous Loam Soil by ICP-OES and ICP-MS After aqua regia Microwave-Oven Procedure by ICP-OES, ICP-MS and GFAAS

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	14.0 ± 0.4	13.5 ± 0.2	12.9 ± 0.2	13.5 ± 0.3	12.8 ± 0.2	13.2 ± 0.4	3.03	14.9 ± 0.3	14.4 ± 0.9	13.6 ± 0.3	13.6 ± 0.4
Co	9.2 ± 0.5	11.0 ± 0.1	10.5 ± 0.4	10.7 ± 0.2	9.9 ± 0.1	10.5 ± 0.5	4.76	10.3 ± 0.3	9.9 ± 0.4	10.1 ± 0.5	10.2 ± 0.7
Cr	138 ± 5	140 ± 1	152 ± 1	130 ± 4	140 ± 2	141 ± 9	6.38	151 ± 15	135 ± 9	140 ± 5	138 ± 6
Cu	46.9 ± 1.8	39.5 ± 0.5	43.7 ± 0.3	40.6 ± 0.7	44.1 ± 0.4	42.0 ± 2.3	5.48	46.5 ± 0.9	48.1 ± 0.7	44.6 ± 1.5	49.2 ± 1.1
Mn	653 ± 16	564 ± 3	591 ± 9	574 ± 10	591 ± 6	580 ± 15	2.58	652 ± 13	658 ± 20	n.a.	n.a.
Ni	94 ± 5	88 ± 1	86 ± 1	89 ± 4	86 ± 3	87 ± 3	3.45	91.9 ± 4.7	96.5 ± 2.9	90 ± 5	89 ± 3
Pb	51.3 ± 2	43.2 ± 2.2	36 OUT(*)	43.2 ± 1.2	43.1 ± 1.0	43.2 ± 1.3	3.01	52.0 ± 3.3	53.5 ± 1.8	50.5 ± 2.7	54.1 ± 2.2
Zn	270 ± 8	239 ± 2	257 ± 9	241 ± 10	255 ± 2	248 ± 11	4.44	255 ± 21	256 ± 10	n.a.	n.a.

OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
N.A. : not analyzed

TABLE IV: Determination of Metals (µg/g) in CRM BCR 142 Light Sandy Soil by ICP-OES and ICP-MS After aqua regia Microwave-Oven Procedure by ICP-OES, ICP-MS and GFAAS

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	0.22 ± 0.10	< MDL	< MDL	< MDL	< MDL	-		0.25 ± 0.09	0.65 ± 0.23	0.27 ± 0.11	0.85 ± 0.28
Co	-	9.9 ± 0.1	9.6 ± 0.1	10.4 ± 0.3	9.4 ± 0.3	9.8 ± 0.5	5.10	9.5 ± 0.4	8.1 ± 1.2	9.6 ± 0.6	9.0 ± 1.1
Cr	44.4 ± 5.4	47.7 ± 2.6	53.5 ± 3.2	42.7 ± 2.9	51.4 ± 2.1	48.8 ± 5.3	10.86	47.0 ± 4.2	45.6 ± 6.8	43.6 ± 3.2	44.2 ± 4.7
Cu	25.3 ± 2.0	22.7 ± 0.2	25.1 ± 0.3	24.5 ± 0.5	27.1 ± 0.3	24.9 ± 1.8	7.23	29.7 ± 1.0	29.6 ± 0.7	27.8 ± 1.5	28.3 ± 0.9
Mn	527 ± 35	499 ± 3	511 ± 9	515 ± 6	534 ± 10	515 ± 15	2.91	588 ± 9	579 ± 8	n.a.	n.a.
Ni	28.9 ± 8.0	29.0 ± 0.5	26 OUT(*)	30.5 ± 1.6	29.4 ± 1.4	29.7 ± 1.4	4.71	32.6 ± 2.4	32.4 ± 1.1	30.6 ± 1.2	31.4 ± 0.8
Pb	30.9 ± 6.7	25.4 ± 1.2	19 OUT(*)	26.8 ± 1.0	26.4 ± 1.4	26.2 ± 1.3	4.94	29.0 ± 0.9	30.8 ± 1.6	28.6 ± 1.4	29.7 ± 1.1
Zn	79.6 ± 11.7	95.4 ± 3.1	98.7 ± 13.1	81.8 ± 3.4	87.8 ± 3.1	90.9 ± 9.8	10.78	75.6 ± 5.7	84.2 ± 7.8	n.a.	n.a.

< MDL : less than Method Detection Limit.
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
N.A. : not analyzed
OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B

TABLE V: Determination of Metals (µg/g) in CRM BCR 143 Sewage Sludge Amended Soil by ICP-OES and ICP-MS After aqua regia Microwave-Oven Procedure by ICP-OES, ICP-MS and GFAAS

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	31.5 ± 1.9	29.5 ± 0.2	31.5 ± 0.1	29.5 ± 0.2	30.6 ± 0.6	30.2 ± 1.0	3.31	33.5 ± 0.4	33.2 ± 0.3	32.4 ± 0.7	33.1 ± 0.4
Co	-	12.5 ± 0.3	13.1 ± 0.5	13.1 ± 0.4	11.6 ± 0.5	12.6 ± 0.8	6.35	13.1 ± 0.3	13.1 ± 0.5	13.0 ± 0.6	13.1 ± 0.2
Cr	208 ± 20	182 ± 3	199 ± 5	183 ± 3	223 OUT(*)	188 ± 10	5.32	209 ± 13	205 ± 30	206 ± 11	203 ± 14
Cu	236 ± 13	212 ± 3	224 ± 8	220 ± 3	223 ± 2	220 ± 7	3.18	235 ± 3	246 ± 6	232 ± 7	237 ± 6
Mn	935 ± 100	846 ± 8	908 ± 19	878 ± 18	886 ± 26	880 ± 30	3.41	1018 ± 22	1080 ± 19	n.a.	n.a.
Ni	92.7 ± 4.7	92.6 ± 0.4	93.3 ± 1.4	99 OUT(*)	94.2 ± 4.4	93.4 ± 2.5	2.68	92.3 ± 10.4	92.4 ± 12.9	91.5 ± 5.5	89.8 ± 7.6
Pb	1317 ± 55	1144 ± 9	1218 ± 37	1176 ± 16	1153 ± 29	1173 ± 40	3.41	1326 ± 11	1367 ± 26	n.a.	n.a.
Zn	1301 ± 60	1119 ± 23	1332 OUT(*)	1169 ± 18	1179 ± 32	1155 ± 39	3.38	1183 ± 22	1147 ± 11	n.a.	n.a.

OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
N.A. : not analyzed

TABLE VI: Inter- and Intra-Laboratory Precision for ICP-OES Analysis of BCR CRMs After aqua regia Microwave-Oven Procedure

Element	CRM 141R r %	CRM 141R R %	CRM 142 r %	CRM 142 R %	CRM 143 r %	CRM 143 R %
Cd	5	9	-	-	3	9
Co	10	15	7	15	10	10
Cr	4	18	16	30	4	6
Cu	3	15	4	20	6	9
Mn	4	7	4	8	6	10
Ni	8	9	11	19	8	9
Pb	10	12	11	13	7	10
Zn	8	12	22	30	6	9

r = repeatability; R = reproducibility

The intralaboratory precision was better than 5-6% (RSD%), for reasons as discussed above, with the exception of the anomalous results for Zn and Cu in the CRM 142 sample reported by Laboratory B, which were due to instrumental problems. The same samples analyzed by ICP-MS gave results that were in agreement with the certified values.

The interlaboratory precision, expressed as repeatability (r), was generally less than 10% and the reproducibility (R) was always better than 20%, except for Cr and Zn for the CRM 142 sample.

The r and R values reported in Table VI have to be evaluated based on the type and the concentration of the element; for example, an r value of 22% for Zn in CRM 142 is for 79.6 µg/g, while 6% for Zn in CRM 143 is for 1301 µg/g.

On the contrary the repeatability for Cd, Cu, Co, Mn, and Pb does not vary significantly with the concentration of the element and the matrix of the investigated samples.

ICP-MS Determination

The 1/10 or 1/100 diluted solutions resulting from the aqua regia dissolution of the samples in the microwave oven were analyzed by ICP-MS and the results are reported in Tables III-V. In general, the data obtained by this technique are slightly higher than those given by ICP-OES and thus are closer to the certified values. In addition, we adopted the external calibration technique and found that working with more diluted solutions, the influence of the sample matrix was therefore reduced.

On the other hand, too high a dilution of the sample can induce an appreciable deviation of the results, as probably detected for Mn in CRM 142 and CRM 143.

HF/HNO$_3$/HCl Procedure

Five standard reference materials, three soils and two sediments, were solubilized according to the procedure described in the Experimental section and subsequently analyzed by different spectroscopic techniques: ICP-OES, ICP-MS, and GFAAS.

Table VII shows the percentage recoveries obtained for the analytes of main interest calculated by comparing the experimental data obtained by ICP-OES with the certified values. The good values obtained for all the elements in all the matrices indicates a complete dissolution of the samples and the absence of problems during the instrumental measurement.

ICP-OES Determination

Tables VIII-XII list the results obtained by the two laboratories as well as the analytical data for the ICP-MS and GFAAS analyses. The accuracy of the determinations is quite good and comparable with that of the aqua regia dissolution, while the precision obtained by the inter- and intra-laboratory studies is worse (see Table XIII). The repeatability and reproducibility values are

significantly higher than those found for the aqua regia procedure, in particular for Cd, Co, and Pb.

These figures suggest some difficulties in analyzing this more complex matrix derived from the complete dissolution of the samples. The results for Pb, which is a "difficult" element for ICP-OES determinations, shows R values of 50% for CRM 142 (30.9 µg/g) and of 70% for CRM 277 (42.3 µg/g).

TABLE VII: Recovery (%) for ICP-OES Determination of Metals in HF/HNO₃/HCl Dissolution

Element	Recovery (%)				
	CRM 141R	CRM 142	CRM 143	CRM 277	CRM 320
Cd	90	n.d.†	102	104	n.d.†
Co	105	103	95	104	106
Cr	83	92	94	90	90
Cu	89	93	100	96	93
Mn	92	97	88	93	89
Ni	86	95	100	98	96
Pb	101	99	85	98	96
Zn	96	99	96	101	98

† Not determined.

TABLE VIII: Determination of Metals (µg/g) in CRM BCR 141R Calcareous Loam by ICP-OES, ICP-MS, and GFAAS After HF/HNO₃/HCl Microwave-Oven Procedure

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	14.6 ± 0.5	11.9 ± 0.6	14.9 ± 0.9	12.7 ± 0.7	23.0 OUT(*)	13.2 ± 1.7	12.90	14.5 ± 0.2	15.4 ± 1.3	15.5 ± 0.6	16.6 ± 1.3
Co	10.5 ± 0.4	11.2 ± 0.9	10.7 ± 0.7	11.9 ± 0.5	11.3 ± 0.5	11.3 ± 0.5	4.42	10.4 ± 1.1	10.9 ± 0.9	11.1 ± 0.2	10.8 ± 0.3
Cr	195 ± 7	173 ± 4	160 ± 13	162 ± 11	163 ± 10	164 ± 10	6.10	195 ± 3	190 ± 4	167 ± 1.7	163 ± 9.2
Cu	46.4 ± 1.8	41.8 ± 1.4	41.2 ± 2.6	41.0 ± 3.4	45.6 ± 1.2	42.4 ± 2.9	6.84	47.4 ± 2.6	49.4 ± 3.6	52.0 ± 2.1	48.2 ± 3.2
Mn	683 ± 16	634 ± 26	646 ± 34	609 ± 18	630 ± 17	630 ± 27	4.29	650 ± 27	525 ± 25	n.a.	n.a.
Ni	103 ± 3	90 ± 3	87 ± 3	86 ± 5	89 ± 2	88 ± 3	3.41	103 ± 2	105 ± 7	102 ± 5	98 ± 6
Pb	57.2 ± 1.2	60.2 ± 3.6	52.6 ± 3.6	57.8 ± 8.4	52.4 ± 5.3	55.8 ± 5.9	10.57	58.3 ± 1.6	53.6 ± 1.7	57.9 ± 3.0	53.5 ± 1.3
Zn	283 ± 5	285 ± 16	281 ± 20	262 ± 11	265 ± 5	273 ± 17	6.23	319 ± 17	312 ± 10	n.a.	n.a.

OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
n.a. : not analyzed

TABLE IX: Determination of Metals (µg/g) in CRM BCR 142 Light Sandy Soil by ICP-OES, ICP-MS, and GFAAS After HF/HNO₃/HCl Microwave-Oven Procedure

Elemnt	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	0.25 ± 0.09	< MDL	< MDL	< MDL	< MDL	-		0.3 ± 0.05	0.4 ± 0.13	0.20 ± 0.01	0.35 ± 0.13
Co	(7.9 ± 1.1)§	9.3 ± 0.3	9.5 ± 0.5	10.7 ± 0.6	10.9 ± 0.4	10.1 ± 0.8	7.92	8.9 ± 0.4	9.0 ± 0.4	8.1 ± 0.5	8.4 ± 0.4
Cr	(74.9 ± 9.4)	75.4 ± 2.4	70.3 ± 6.7	62.7 ± 6.8	67.8 ± 4	69.1 ± 7.0	10.13	77 ± 4	74 ± 5	75.7 ± 3.6	74.9 ± 3.2
Cu	27.5 ± 0.06	25.3 ± 0.9	26.2 ± 1.1	23.1 ± 1.9	27.4 ± 1.3	25.5 ± 2.2	8.63	29.3 ± 1.5	28.8 ± 1.2	30.7 ± 3.0	30.3 ± 1.5
Mn	(569 ± 26)	572 ± 15	544 ± 17	552 ± 23	530 ± 9	550 ± 23	4.18	632 ± 21	620 ± 12	n.a	n.a
Ni	29.2 ± 2.5	27.9 ± 1.2	25.4 ± 0.9	27.3 ± 0.8	28.1 ± 0.9	27.1 ± 1.5	5.54	28.0 ± 0.8	30 ± 0.4	27 ± 2	28 ± 3
Pb	37.8 ± 1.9	41.6 ± 4.2	33.3 ± 2.8	46.3 ± 2.3	32.1 ± 0.7	38.0 ± 6.8	17.89	38.1 ± 2.3	39.3 ± 4.4	40.6 ± 3.1	41.2 ± 4.5
Zn	92.4 ± 4.4	98.3 ± 4.3	86.2 ± 9.8	92.1 ± 2.9	88.2 ± 4.4	91.2 ± 7.5	8.22	100 ± 4.8	99.1 4.4	n.a	n.a

§ Values in brackets are reported by BCR and are indicative only
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
n.a. : not analyzed
< MDL : less than Method Detection Limit.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B

The higher R values for Cd and Co are probably correlated with an elemental concentration close to the detection limits of the technique.

ICP-MS Determination

In Tables VIII-XII list the ICP-MS results obtained by Laboratory A, which analyzed the samples dissolved by the Laboratory B. The data obtained for microwave dissolution carried out by the two laboratories are in good agreement for all matrices investigated. The interlaboratory precision (RSD%), for four replicates, and for concentration higher than 1 µg/g, are always better than 5-10%.

Comparison With Other Techniques

The solutions derived from the dissolution with aqua regia and HF/HNO$_3$/HCl of the samples were analyzed, for some analytes, by GFAAS in Laboratory A to check the suitability of the proposed method for analysis by GFAAS. The comparisons for Cd in CRM 141R are shown in Figures 2 and 3, while the comparison data for Pb in CRM 142 are shown in Figures 4 and 5.

The ICP-OES results are those produced by laboratory A and B, while the ICP-MS and GFAAS results were obtained by Laboratory A only. The ICP-OES analysis of metals soluble in aqua regia gives concentration values slightly lower than those obtained by ICP-MS and GFAAS, but are still close to the certified values. The variability between the two laboratories is very little, because the matrix of the solution is very simple.

TABLE X: Determination of Metals (µg/g) in CRM BCR 143 Sewage Sludge Amended Soil by ICP-OES, ICP-MS, and GFAAS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	31.1 ± 1.2	29.02 ± 0.45	33.97 ± 0.9	32.55 ± 0.14	45.2 OUT(*)	31.8 ± 2.7	8.49	35.5 ± 0.7	33.3 ± 1.2	33.6 ± 1.9	30.8 ± 4.1
Co	(11.8 ± 1.2)§	11.2 ± 0.6	11.6 ± 0.3	12.0 ± 0.6	11.2 ± 0.9	11.2 ± 0.9	8.04	12.0 ± 0.7	12.0 ± 1.2	10.4 ± 0.4	11.0 ± 0.5
Cr	(228 ± 19)	214 ± 2	213 ± 3	221 ± 6	210 ± 8	215 ± 6	2.79	202 ± 20	199 ± 31	241± 14	221 ± 9
Cu	236 ± 8.2	236 ± 5	234 ± 5	238 ± 8	236 ± 12	236 ± 8	3.39	234 ± 5	221 ± 7	231 ± 5	227 ± 11
Mn	(999 ± 62)	872 ± 12	886 ± 36	732 OUT(*)	892 ± 86	883 ± 48	5.44	1002 ± 34	1059 ± 60	n.a.	n.a.
Ni	99.5 ± 5.5	97.1 ± 2.0	101.2 ± 5.3	99.2 ± 2.1	99.5 ± 3.6	99.2 ± 3.5	3.53	104.3 ± 3.4	101.2 ± 4.3	103 ± 3	100 ± 5
Pb	1333 ± 39	1146 ± 21	1135 ± 19	1194 ± 6	1131 ± 25	1151 ± 33	2.87	1294 ± 11	1283 ± 68	1333 ± 13	1324 ± 22
Zn	1272 ± 30	1215 ± 8	1296 ± 39	1231 ± 15	1219 ± 35	1240 ± 45	3.63	1225 ± 34	1294 ± 43	n.a.	n.a.

§ Values in brackets are reported by BCR and are indicative only.
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
n.a. : not analyzed

OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B

TABLE XI: Determination of Metals (µg/g) in CRM BCR 277 Estuarine Sediment by ICP-OES, ICP-MS, and GFAAS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	11.9 ± 0.4	10.3 ± 0.2	13.2 ± 0.4	13.5 ± 1.5	23.8 OUT(*)	12.3 ± 2.0	16.26	11.6 ± 0.7	11.2 ± 0.1	13.4 ± 0.4	14.8 ± 0.6
Co	(15-19.8)§	17.2 ± 0.1	18.1 ± 0.4	17.0 ± 0.3	18.8 ± 0.8	17.7 ± 0.8	4.52	18.4 ± 1.1	19.0 ± 0.4	17.9 ± 0.7	18.2 ± 0.6
Cr	192 ± 7	213 ± 2	213 ± 3	221 ± 6	210 ± 8	215 ± 6	2.79	188 ± 10	184 ± 4	169 ± 7	165 ± 5
Cu	101.7 ± 1.6	97.0 ± 2.6	97.1 ± 4.5	92.8 ± 4.4	98.8 ± 3.7	96.4 ± 4.2	4.36	103.2 ± 5.1	100.6 ± 1.2	91.7 ± 1.6	92.8 ± 1.1
Mn	(1502 - 1620)	1523 ± 27	1486 ± 50	1439 ± 71	1437 ± 55	1471 ± 62	4.21	1576 ± 64	1604 ± 58	n.a.	n.a.
Ni	43.4 ± 1.6	44.5 ± 1.1	40.6 ± 0.6	43.3 ± 0.9	42.0 ± 1.1	42.6 ± 1.9	4.46	46.6 ± 3.1	48.8 ± 2.4	44 ± 2	41 ± 2
Pb	146 ± 3	152 ± 3	137 ± 6	152 ± 3	132 ± 7	143 ± 11	7.69	152 ± 7	163 ± 5	153 ± 5	163 ± 3
Zn	547 ± 12	567 ± 10	575 ± 21	533 ± 27	530 ± 14	551 ± 28	5.08	541 ± 13	496 ± 7	n.a.	n.a.

§ Values in brackets are reported by BCR and are indicative only.
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
n.a. : not analyzed

OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B

TABLE XII: Determination of Metals (µg/g) in CRM BCR 320 River Sediment by ICP-OES, ICP-MS, and GFAAS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified value µg/g	ICP-OES				Mean µg/g	IntraLab RSD %	ICP-MS		GFAAS	
		LAB A-A	LAB B-A	LAB A-B	LAB B-B			LAB A-A	LAB A-B	LAB A-A	LAB A-B
Cd	0.533 ± 0.026	< MDL	< MDL	< MDL	< MDL	-		0.62 ± 0.06	0.68 ± 0.09	0.72 ± 0.08	0.69 ± 0.12
Co	(17.3 - 22.1)§	19.5 ± 0.2	21.0 ± 0.5	20.2 ± 0.6	21.1 ± 0.6	20.5 ± 0.8	3.90	19.4 ± 0.3	20.6 ± 0.7	18.6 ± 0.7	19.5 ± 0.4
Cr	138 ± 7	124 ± 2	114 ± 5	126 ± 2	123 ± 5	122 ± 6	4.92	127 ± 4	130 ± 4	130 ± 2	136 ± 9
Cu	44.1 ± 1.0	40.9 ± 0.7	37.5 OUT(*)	42.2 ± 2.6	43.0 ± 2.3	42.0 ± 2.1	5.00	43.1 ± 1.4	43.9 ± 1.6	43.1 ± 1.5	44.0 ± 2.2
Mn	(619 - 786)	686 ± 7	666 ± 22	732 ± 49	702 ± 56	697 ± 44	6.31	770 ± 10	788 ± 15	n.a.	n.a.
Ni	75.2 ± 1.4	73.8 ± 1	69.8 ± 1.2	74.3 ± 0.9	71.6 ± 2.6	72.4 ± 2.5	3.45	72.3 ± 1.0	75.4 ± 3.7	73 ± 2	72 ± 4
Pb	42.3 ± 1.6	47.5 ± 2.8	31.7 ± 2.3	50.5 ± 4.9	32.6 ± 2.9	40.6 ± 10.3	25.37	43.0 ± 0.7	45,4 ± 4.2	44.4 ± 1.5	45.2 ± 8.9
Zn	142 ± 3	146 ± 2	142 ± 2	133 ± 2	132 ± 3	138 ± 7	5.07	151 ± 7	136 ± 5	n.a.	n.a.

§ Values in brackets are reported by BCR and are indicative only.
OUT(*) : outlier not considered in the mean calculation.
LAB B-A : Sample prepared by B, Analyzed by A
LAB B-B : Sample prepared by B, Analyzed by B
< MDL : less than Method Detection Limit.
LAB A-A : Sample prepared by A, Analyzed by A
LAB A-B : Sample prepared by A, Analyzed by B
n.a. : not analyzed

TABLE XIII: Inter- and Intra-Laboratory Precision for the ICP-OES Analysis of BCR CRMs After HF/HNO$_3$/HCl Microwave-Oven Procedure[a]

Element	CRM 141R		CRM 142		CRM 143		CRM 320		CRM 277	
	r %	R %	r %	R %	r %	R %	r %	R %	r %	R %
Cd	16	36	-	-	8	23	21	45	-	-
Co	15	30	11	47	8	41	7	26	7	38
Cr	15	17	21	28	7	8	9	12	7	9
Cu	13	15	15	24	8	9	8	9	13	20
Mn	11	12	8	11	13	15	10	12	16	18
Ni	11	12	9	10	9	10	6	12	6	10
Pb	26	30	26	49	7	8	10	22	23	70
Zn	15	17	18	23	5	7	10	14	5	15

[a] r = repeatability ; R = reproducibility

The determination of elemental concentrations in more complex matrices, as those derived from a complete dissolution of soil samples, confirms the good accuracy of the analytical techniques such as GFAAS and ICP-MS, but suggests a larger variability for ICP-OES, mainly due to the results obtained by Laboratory B.

CONCLUSION

The extraction of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn from soils and sediments by means of the aqua regia procedure assisted by microwave digestion seems to be a valid alternative to the conventional reflux extraction procedure. The time for sample preparation is notably shorter and the level of contamination is greatly reduced. The results obtained for the certified standard materials CRM 141R, CRM 142 and CRM 143 are in good agreement with the certified values. The analytical techniques generally used in check laboratories assure the accurate determination of several elements present in the solutions derived from the MW dissolution of the samples. The use of HF/HNO$_3$/HCl allows the determination of the total analyte concentration in soils and sediments without problems with respect to aqua regia dissolution. In this latter case, the ICP-OES precision data for elements present at lower concentrations (e.g., Pb, Cd) are slightly poorer than those obtained for aqua regia solutions. This can reflect the variability associated with the analysis of more complex solutions derived from the complete dissolution of the sample. GFAAS and ICP-MS analysis provides more accurate results than ICP-OES at low concentrations because of better instrumental detection limits.

Fig. 2. Comparison of the results obtained by ICP-OES, ICP-MS and GFAAS in the analysis of "aqua regia soluble" Cd in BCR CRM 141R. Note: (LAB A-A : sample prepared by A, analyzed by A; LAB B-A : sample prepared by B, analyzed by A; LAB A-B sample prepared by A, analyzed by B; LAB B-B : sample prepared by B, analyzed by B).
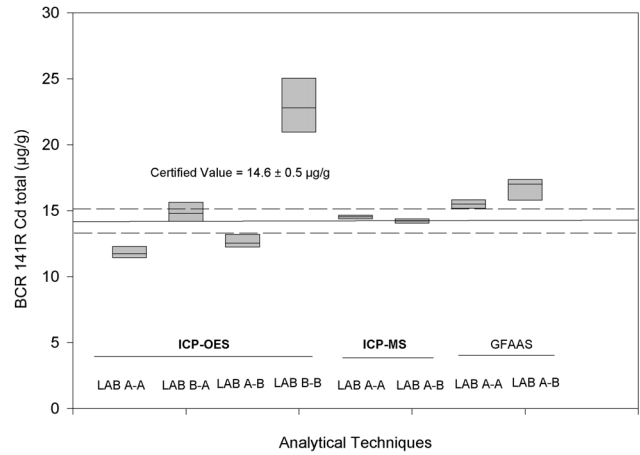
Fig. 3. Comparison of the results obtained by ICP-OES, ICP-MS and GFAAS in the analysis of "total" Cd in BCR CRM141R. Note: (LAB A-A : sample prepared by A, analyzed by A; LAB B-A : sample prepared by B, analyzed by A; LAB A-B sample prepared by A, analyzed by B; LAB B-B : sample prepared by B, analyzed by B).
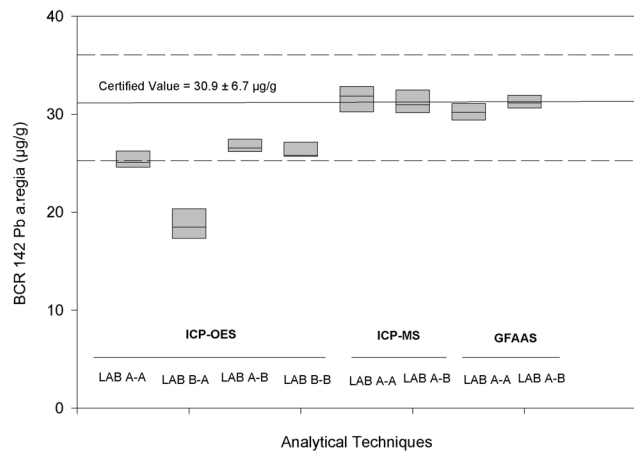
Fig. 4. Comparison of the results obtained by ICP-OES, ICP-MS and GFAAS in the analysis of "aqua regia soluble" Pb in BCR CRM 142. Note: (LAB A-A : sample prepared by A, analyzed by A; LAB B-A : sample prepared by B, analyzed by A; LAB A-B sample prepared by A, analyzed by B; LAB B-B : sample prepared by B, analyzed by B).

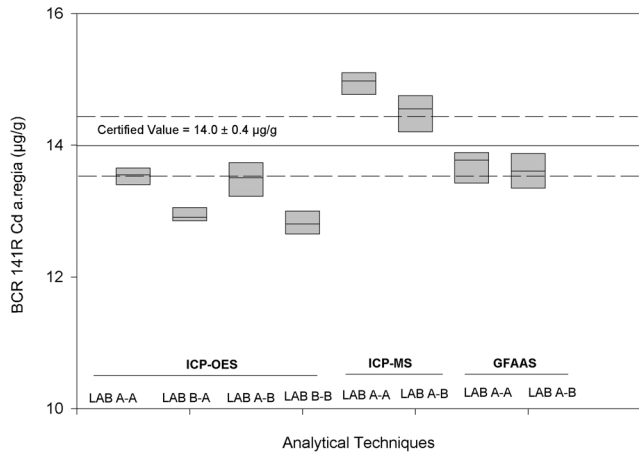*Fig. 5. Comparison of the results obtained by ICP-OES, ICP-MS and GFAAS in the analysis of "total" Pb in BCR CRM 142. Note: (LAB A-A : sample prepared by A, analyzed by A; LAB B-A : sample prepared by B, analyzed by A; LAB A-B sample prepared by A, analyzed by B; LAB B-B : sample prepared by B, analyzed by B).*
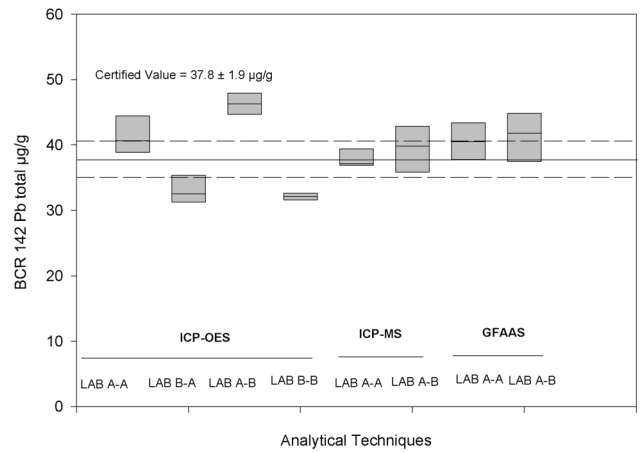
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Soils and Sediments Analysis by Spectroscopic Techniques
Part II: Determination of Trace Elements by ICP-MS

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INTRODUCTION

The elemental analysis of soils and sediments has become important in the environmental sciences, particularly for the identification of the contaminants present in the matrix and the relative threshold levels of toxicity. A major issue in the determination of soil elemental constituents is represented by the refractory nature of these materials (1).

Traditional methods for the analysis of soils, based on instrumental techniques, require the complete dissolution of samples, typically through alkaline fusion or acid digestion on hot plates at atmospheric pressure. After that, the spectrometric measurement is carried out on the digests using different spectrometric techniques, such as flame atomic absorption spectroscopy (FAAS), graphite furnace AAS (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or ICP mass spectrometry (ICP-MS).

Although the procedures of solubilization are effective, they are time-consuming and can often result in the loss of the most volatile species (2). In 1975, Abu-Samra et al. (3) described the use of microwave energy as a means for obtaining rapid and complete acid-assisted wet digestions. Since then, microwave heating for sample decomposition has become a well-established technique. Open-vessel (4,5), closed-vessel (6,7), and focused techniques (8) have been extensively used, as reported in the specific literature. Today, there are various official methods for the analysis of soils and sediments,

ABSTRACT

The determination of trace elements in soils and sediments by ICP-MS was investigated, following the acid decomposition of samples in a microwave oven. The validation of the method was carried out in two laboratories equipped with two different microwave systems. The use of a HNO_3/HCl mixture gave good recoveries for 20–25 analytes; the complete solubilization of materials was achieved by microwave digestion in closed vessels using a mixture of HF/HNO_3/HCl. The accuracy of the aqua regia procedure was evaluated by analyzing three certified soils as reference materials: CRM 141 R, CRM 142 and CRM 143. The HF/HNO_3/HCl procedure was tested on the above-mentioned materials and on two certified sediments: CRM 277 and CRM 320.

which employ different acid mixtures and microwave heating techniques: ASTM D5258-92 (9), U.S. EPA Method 3050B (10), U.S. EPA Method 3051 (11), U.S. EPA Method 3052 (12), and two European proposals of methods prEN CEN/TC292/WG 3 N310 (13) and prEN CEN/TC292/WG 3 N100 (14).

In the most common types of natural soils, the main component is SiO_2, which typically ranges from 40% wt to 70% wt. Other components are Al_2O_3, (from 5% to 20% wt), Fe_2O_3 and CaO (from 2 to 10% wt), and MgO Na_2O and K_2O (from 0.5 to 5 % wt).

After the complete digestion of the samples, these elements maintain their original concentrations in the solution. Therefore, the sample solutions require dilutions of 1:1000 or 1:10000 before carrying out the measurements. With these

dilution factors, the contents of the above matrix elements are less than 50 mg/L, while the analyte concentrations are expected to range between 10 and 1000 ng/L. The analytical techniques that could be used should present both high tolerance for the solids dissolved in the sample (typically between 0.05% and 0.1%), and high sensitivity to detect and quantify these low levels of analytes. In a previous paper (15), we reported the results obtained from the analysis of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn in five certified materials by ICP-OES, GFAAS, and ICP-MS. In the current paper, we describe the use of ICP-MS techniques for the analysis of 20–25 elements in solutions after microwave (MW) dissolution of certified soils and sediments.

EXPERIMENTAL

Instrumentation

Two different microwave ovens (digesters) were used in two different laboratories: MLS 1200 Milestone (FKV, Sorisole, Bergamo, Italy) in Laboratory A and MDS-2000 CEM (Matthews, NC, USA) in Laboratory B. The operating conditions are reported in a recent paper (15).

The ICP-MS instrument, used in Laboratory A only, was the model PerkinElmer SCIEX ELAN® 5000 (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada), equipped with a PerkinElmer Gem-Tip™ cross-flow nebulizer and a corrosion-resistant Scott-type spray chamber (Table I).

Reagents

Nitric acid (65% m/v), hydrochloric acid (37% m/v), and hydrofluoric acid (40% m/v) were Suprapure reagents (E.Merck,

Darmstadt, FRG); boric acid was analytical-reagent grade (Analar; BDH, Chemical Poole England).

Standard solutions were prepared from 10 mg/L multielemental atomic absorption standards, ICP-MS Calibration Standard n.1,2,3,4 (PerkinElmer), by dilution with water, containing the same amount of acids as the samples.

High-purity water was produced by a Milli-Q™ deionizing system (Millipore, Bedford, MA USA) using distilled water.

Standard Reference Materials

The accuracy of the method was verified by analyzing five different samples prepared by the Community Bureau de Reference (BCR): CRM 141 R Calcareous Loam Soil; CRM 142 Light Sandy Soil; CRM 143 Sewage Sludge Amended Soil; CRM 277 Estuarine Sediment; CRM 320 River Sediment.

Microwave Procedures

Sample dissolution procedures were described in a previous paper (15). The ICP-MS analysis was carried out with final solutions diluted by 1/10 or 1/100.

For both procedures and for each analyzed material, four replicates were prepared by the two laboratories on different working days. The instrumental measurement was performed in one laboratory only (Laboratory A).

RESULTS AND DISCUSSION

The accuracy and precision of the digestion procedures was assessed through a comparison between ICP-MS data and CRM certified values or between the ICP-MS results obtained from the samples digested at Laboratory A and Laboratory B.

This comparison was carried out by Linear Regression (LR) and Maximum Likelihood Fitting of Functional Relationship (MLFR) analyses. It is worth highlighting the basic assumptions of these two statistical methods. The LR model considers variable Y as dependent from variable X and assumes that the relative error of the X variable is irrelevant with respect to the relative error of the Y variable. The MLFR model considers variable Y as a functional relationship to variable X and both relative errors are assumed to be unrelated with each other. In addition, this method establishes a more realistic relation between relative errors and concentration levels. In the case of a comparison between two laboratories or analytical methods, each having its own degree of uncertainty, the MLFR analysis appears to be the more reliable and realistically statistical method as suggested by Ripley and Thompson (16).

Aqua regia Procedure

Tables II-IV show the ICP-MS results obtained from the analysis of three certified soils following the procedure described in a recent paper (15). Good agreement was found between the experimental and certified values of Cd, Cr, Cu, Mn, Ni, Pb, and Zn in all reference samples. A similar agreement exists for Co, P, Sb, Sn, and Sr in sample CRM 141 R. Other elements (As, Ba, Bi, Ce, Co, Dy, Er, Eu, Ga, Gd, La, Mo, Nb, Nd, P, Rb, Sb, Sc, Sn, Sr, Th, Tl, V, W, Y, and Yb) could only be compared with informative values of the "total concentration" reported for the samples. For noncertified elements, only the values given by the two labs could be compared and this provided the information on the reproducibility of microwave oven solubilization.

The precision obtained at both laboratories was comparable and on average, it was less than 5-10% (RSD %), with some values equal to 20–30% for low-concentration elements (Cd in CRM 142 and Sb in CRM 141 R) or for elements that might have some problems with solubilization (Mo, W, Th, and Ce).

The accuracy was good, as proved by the MLFR statistical parameters illustrated in Figure 1, which refers to the comparison between "found" and "certified" values (n=22; a=0.1149 ± 0.1309; b=1.0194 ± 0.0146). The same figure also shows the diagram of the function obtained with the LR method. The statistical parameters of this second function (a=5.3829 ± 9.0807; b=0.9869 ± 0.0186; r=0.9964) basically confirm the results obtained with the MLFR method. A similar comparison between the results obtained, in both labs, was carried out for non certified analytes with a concentration range of 0–100 µg/g (see Figure 2). This showed a basic agreement between experimental values, proving the fact that the solubilization procedure is fully reliable. MLFR parameters (n=117; a=0.01163 ± 0.0144; b=1.0172 ± 0.0052) indicated the intercept "a" and the slope "b" as statistically not different from the corresponding theoretical values (a=0 and b=1). The use of LR analysis instead highlighted a negative bias in Laboratory A as the intercept "a" was negative and statistically different from its theoretical value (a=–5.3336 ± 2.3512; b=1.0801± 0.0057; r=0.9983). This proves that significantly different evaluations can be made from the same experimental data, depending on the statistical criteria adopted. Anyway, the positive comparison found with the MLFR method, particularly for various non-certified elements, must be considered with care, from a chemical viewpoint, as it might conceal a systematic bias that could be due, for example, to the incomplete solubilization of the matrix concerned.

In this respect, the results concerning the determination of Ba were as follows: The average values obtained at the two laboratories

TABLE I
Instrumental Parameters for ICP-MS Analysis

RF power	1085 W
Plasma argon	14.6 L/min
Nebulizer flow	1.1 L/min
Auxiliary flow	0.83 L(min
Sample flow rate	1 mL/min
Nebulizer	Cross-flow
Data	Peak hop transient
Resolution	normal
Reading time	150 ms
Dwell time	50 ms
Sweeps / replicates	3
Number of replicates	5
Sample time	1 min 6 sec
Sample read delay	50 s
Autosampler wash delay	60 s
Calibration mode	External calibration
Calibration standard	10, 20, 30, 50, 100 µg/L
Curve fit	Linear through zero

Isotopes	mass
As	75
Ba	138
Be	9
Bi	209
Cd	114
Ce	140
Co	59
Cr	52
Cu	63
Cs	133
Ga	71
La	139
Li	7
Mn	55
Nd	142
Ni	60
Pb	204, 206, 207, 208
Rb	85
Sb	121
Sn	120
Sr	88
Th	232
Tl	205
U	238
V	51
W	184
Y	89
Yb	174
Zn	66

Interelement Corrections:

$^{75}As = {}^{75}As - 3.087\ {}^{77}Se + 2.619\ {}^{82}Se$

$^{51}V = {}^{51}V - 3.09\ {}^{53}Cr + 0.353\ {}^{52}Cr$

TABLE II
Determination of Metals (µg/g) in CRM BCR 141R Calcareous Loam Soil by ICP-MS After aqua regia Microwave-Oven Procedure

Ele-ment	Certified Value (µg/g)	LAB A-A Mean (µg/g)	RSD%	LAB A-B Mean (µg/g)	RSD%
As	(8.84 ± 0.43)[a]	8.53 ± 0.26	3.1	9.7 ± 1.3	13.0
Ba	(143 ± 3)[a] (348 ; 437)[c]	237 ± 15	6.3	245 ± 41	16.9
Be	-	1.97 ± 0.18	8.9	2.52 ± 0.36	14.4
Bi	-	1.52 ± 0.15	9.8	1.83 ± 0.06	3.1
Cd	14.0 ± 0.4	14.9 ± 0.3	2.0	14.4 ± 0.9	6.25
Ce	-	59.9 ± 2.1	3.4	50.4 ± 2.7	5.30
Co	9.2 ± 0.5	10.3 ± 0.3	2.9	9.9 ± 0.4	4.04
Cr	138 ± 5	151 ± 15	9.9	135 ± 9	6.67
Cu	46.9 ± 1.8	46.5 ± 0.9	1.9	48.1 ± 0.7	1.46
Cs	-	5.95 ± 0.38	7.0	6.43 ± 0.40	6.2
Dy	-	2.86 ± 0.10	3.4	2.91 ± 0.26	8.9
Er	-	1.44 ± 0.15	10.3	1.42 ± 0.18	12.7
Eu	-	1.03 ± 0.06	6.1	1.03 ± 0.07	6.8
Ga	-	13.3 ± 0.4	3.3	10.7 ± 1.2	11.2
Gd	-	4.06 ± 0.72	17.7	5.05 ± 0.15	2.9
La	(31.8 ± 1.09)[b]	29.9 ± 1.2	4.1	25.5 ± 1.6	6.45
Li	-	32.3 ± 1.6	4.9	36.1 ± 4.7	12.9
Mn	653 ± 16	652 ± 13	2.0	658 ± 20	3.0
Mo	-	3.24 ± 0.34	10.5	1.43 ± 0.56	39.2
Nb	-	1.85 ± 0.11	6.1	3.85 ± 0.34	8.8
Nd	-	22.4 ± 0.7	3.2	21.4 ± 0.8	3.7
Ni	94 ± 5	91.9 ± 4.7	5.1	96.5 ± 2.9	3.0
P	(1010 ± 65)[a] (955 ± 50)[b]	933 ± 32	3.4	905 ± 15	1.7
Pb	51.3 ± 2	52.0 ± 3.3	6.3	53.8 ± 1.8	3.3
Pr	-	6.10 ± 0.20	3.3	6.65 ± 0.11	1.6
Rb	-	84.9 ± 2.6	3.1	70.6 ± 3.22	4.6
Sb	(0.699 ± 0.025)[a] (1.2 ; 1.38)[c]	1.05 ± 0.14	13.4	1.03 ± 0.19	18.4
Sc	-	7.42 ± 0.67	9.0	8.13 ± 0.81	10.0
Sm	-	4.49 ± 0.11	2.5	4.87 ± 0.16	3.3
Sn	(7.45 ± 0.2)[a] (8.3 ± 0.3)[b]	7.4 ± 0.4	5.4	7.59 ± 0.3	3.9
Sr	(461 ± 9)[a] (524 ± 10)[b]	544 ± 16	2.9	513 ± 18.4	3.6
Th	(9.88 ± 0.45)[b]	9.37 ± 0.31	3.3	9.36 ± 0.39	4.2
Tl	(0.246 ±0.028)[a] (0.638 ±0.034)[b]	0.453 ± 0.022	4.7	0.502 ± 0.015	3.0
U	(2.39 ± 0.12)[b]	1.16 ± 0.07	5.7	1.81 ± 0.13	7.2
V	(77.2 ± 2.8)[b]	76.8 ± 4.5	5.9	71.2 ± 3.4	4.7
W	(3.44 ± 0.14)[b]	3. 29 ± 0.21	6.4	3.37 ± 0.30	8.9
Y	-	15.3 ± 0.8	5.4	15.6 ± 0.7	4.5
Yb	-	1.19 ± 0.09	7.6	1.16 ± 0.08	7.6
Zn	270 ± 8	255 ± 21	8.2	256 ± 10	3.9

[a] Indicative value, one single result for the aqua regia-soluble part.

[b] Indicative value, one single result for the total concentration.

[c] Indicative value, range of results for the total concentration.

were comparable for all the three certified samples (237± 15 and 245 ± 41 µg/g for CRM 141 R; 213 ±18 and 245 ± 21 µg/g for CRM 142; 970 ± 12 and 979 ± 13 µg/g for CRM 143), but only the experimental values for sample CRM 143 were close to the "total concentration" established by the BCR. The value found for material CRM 141 R was between the indicative values for "soluble in aqua regia" and "total concentration" reported by only one laboratory. The value found for CRM 142 corresponded to half the value stated in the certificate.

These experimental results prove that the MW solubilization treatment with use of aqua regia, even if partial, is capable of producing the release of analytes in the solution. The release is proportional to the operating conditions (power/heating time) and closely connected to the sample matrix. On the other hand, the concentrations of Dy, Er, Ga, Nb, Rb, Th, U, Y, and Yb appear to be significantly lower than the reference values in BCR, where available, with La, Sc, and Sm concentrations close to the bottom of the BCR indicative range. It should be remembered that, in most cases, the certificate only indicates two values for these analytes and both refer to the "total content" of the element. From this point of view, it is all too plausible that slightly lower values are found when "soluble in aqua regia" applies.

HF/HNO$_3$/HCl Procedure

Tables V-IX show the results of the ICP-MS analysis for three certified soils and two sediments analyzed with the procedure discussed in a recent paper (15). The values obtained are in good agreement with the certified values for As (Lab A only), Cd, Co, Cr, Cu, Ga, Ge, Mn, Nb, Ni, Pb, Sb, Sn, Tl, V, and Zn, while greater values were found for Ti, especially in materials CRM 141 R, 142, and 143. The accuracy was

TABLE III
Determination of Metals (µg/g) in CRM BCR 142 Light Sandy Soil by ICP-MS After aqua regia Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A Mean (µg/g)	RSD%	LAB A-B Mean (µg/g)	RSD%
As	(15.7 - 18.0)[c]	14.8 ± 2.3	15.8	14.0 ± 1.9	13.8
Ba	(435 – 472)[c]	213 ± 18	8.3	245 ± 21	8.4
Be	-	1.35 ± 0.3	23.0	1.50 ± 0.14	9.4
Bi	-	0.25 ± 0.02	7.1	0.24 ± 0.01	2.1
Cd	0.22 ± 0.10	0.25 ± 0.09	36.0	0.65 ± 0.23	35.4
Ce	(69.5 – 97)[c]	54.4 ± 9.5	17.4	63.3 ± 4.7	7.4
Cs	-	5.25 ± 0.11	2.1	5.33 ± 0.10	1.9
Co	-	9.5 ± 0.4	4.2	8.1 ± 1.2	14.8
Cr	44.4 ± 5.4	47.0 ± 4.2	8.9	45.6 ± 6.8	14.9
Cu	25.3 ± 2.0	29.7 ± 1.0	3.4	29.6 ± 0.7	2.4
Dy	(5.15)[b]	3.4 ± 0.2	7.5	3.5 ± 0.2	7.2
Er	(2.84)[b]	1.63 ± 0.10	6.3	1.68 ± 0.09	5.7
Eu	(0.87 - 1.15)[c]	1.10 ± 0.07	6.4	1.10 ± 0.08	7.4
Ga	(11.0)[b]	7.6 ± 1.1	14.5	7.8 ± 0.9	11.6
Gd	(5.7)[b]	5.7 ± 0.5	8.8	5.8 ± 0.5	8.6
La	(29.5 - 33.3)[c]	25.9 ± 1.9	7.3	30.5 ± 2.6	8.5
Li	-	26.5 ± 2.3	8.7	26.7 ± 2.0	7.6
Mn	527 ± 35	588 ± 9	1.4	579 ± 8	1.4
Mo	-	0.40 ± 0.08	20.1	0.46 ± 0.06	13.1
Nb	(14.0)[b]	5.10 ± 0.08	1.6	5.5 ± 0.4	7.0
Nd	(28.1)[b]	27.9 ± 2.1	7.6	28.2 ± 2.3	8.2
Ni	28.9 ± 8.0	32.6 ± 2.4	7.4	32.4 ± 1.1	3.4
P	-	854 ± 20	2.3	926 ± 15	1.6
Pb	30.9 ± 6.7	29.0 ± 0.9	3.1	30.8 ± 1.6	5.2
Pr	-	6.9 ± 0.7	10.1	6.5 ± 0.5	7.2
Rb	(75 - 100)[c]	52.5 ± 5.5	10.5	53.7 ± 4.8	9.0
Sb	(1.7 - 3.2)[c]	1.78 ± 0.15	8.2	1.73 ± 0.08	4.6
Sc	(7.0 - 9.5)[c]	5.1 ± 0.8	16.4	6.6 ± 0.7	10.7
Sm	(6.2 - 7.4)[c]	5.0 ± 0.6	11.3	5.8 ± 0.6	9.9
Sn	(3.0 - 4.0)[c]	3.0 ± 0.3	10.6	3.2 ± 0.5	14.2
Sr	(164 - 165)[c]	118 ± 9	7.2	124 ± 7	5.3
Th	11.9	7.6 ± 1.3	16.7	8.8 ± 0.6	7.2
Tl	-	0.415 ± 0.029	7.0	0.400 ± 0.038	9.6
U	-	1.95 ± 0.13	6.6	2.13 ± 0.10	4.5
V	-	47.7 ± 0.5	1.1	48.1 ± 2.5	5.2
W	(1.2)[b]	3.2 ± 1.0	32.1	3.0 ± 0.3	10.5
Y	(30 - 30.7)[c]	14.4 ± 1.4	9.8	16.1 ± 0.9	5.4
Yb	(2.7 - 2.84)[c]	1.18 ± 0.17	14.5	1.30 ± 0.08	6.3
Zn	79.6 ± 11.7	75.6 ± 5.7	7.5	84.2 ± 7.8	9.3

[a] Indicative value, one single result for the aqua regia soluble part.
[b] Indicative value, one single result for the total concentration.
[c] Indicative value, range of results for the total concentration.

good and comparable with the one achieved with the aqua regia dissolution as to the analytes of major interest. The MLFR statistical parameters of the regression reported in Figure 3 (n=37, a=0.0788 ± 0.0539; b=1.0463 ± 0.0088) prove the general consistency between the values found at Laboratory A and the BCR values. The linear regression (LR) also leads to similar conclusions, statistical parameters being the following: n = 37, a = -1.7307± 5.4029; b = 1.0256 ± 0.0139; r = 0.9967. Ba, Ce, Cs, Eu, La and Rb concentrations were lower than the certified values, as clearly reported in previous papers (17), while the anomalous Sc value confirms the presence of a silicon-related interference (18) which was not found during the solubilization with aqua regia. Laboratory B found anomalous values of As in all five materials; of Ba particularly in samples CRM 141 R and 142; and of Ce in samples CRM 277 and 320.

Such anomalies, unquestionably related to contamination at Laboratory B, are probably due to the greater complexity of the procedure, involving the use of hydrofluoric acid and a consequent complexation with boric acid.

The precision of the results obtained at both labs was comparable and, for most analytes, it was less than 10% (RSD %) on average, with some values over 30%, especially as far as Laboratory B was concerned, where some contamination has occurred. In contrast with the ICP-OES analytical results reported in a recent paper (15), the use of the ICP-MS provided accuracy values much closer to those obtained with the aqua regia procedure. As a matter of fact, diluting the initial solution by 1/10 or 1/100 reduces the effects due to the greater complexity of the matrix.

The results provided by both labs for non-certified elements were compared with each other as it was

TABLE IV
Determination of Metals (µg/g) in CRM BCR 143 Sewage Sludge Amended Soil by ICP-MS After aqua regia Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A		LAB A-B	
		Mean (µg/g)	RSD%	Mean (µg/g)	RSD%
As	(15 - 19.5)[c]	16.7 ± 1.9	11.8	15.5 ± 3.9	25.5
Ba	(920 - 940)[c]	970 ± 12	1.2	979 ± 13	1.3
Be	-	1.73 ± 0.47	27.3	1.88 ± 1.15	8.0
Bi	(10.0)[b]	8.8 ± 0.3	3.3	8.3 ± 0.7	9.2
Cd	31.5 ± 1.9	33.5 ± 0.4	1.2	33.2 ± 0.3	0.9
Ce	(65 - 94)[c]	52.3 ± 12.2	23.4	58.1 ± 2.8	4.8
Co	-	13.1 ± 0.3	2.3	13.1 ± 0.5	3.8
Cs	-	5.25 ± 0.11	2.1	5.33 ± 0.10	1.9
Cr	208 ± 20	209 ± 13	6.2	205 ± 30	14.6
Cu	236 ± 13	235 ± 3	1.3	246 ± 6	2.4
Dy	(4.3)[b]	3.3 ± 0.3	9.6	3.3 ± 0.1	1.5
Er	(2.47)[b]	1.53 ± 0.10	6.3	1.65 ± 0.13	7.6
Eu	(0.6 - 1.01)[c]	1.29 ± 0.08	6.3	1.40 ± 0.05	3.2
Ga	(12.0)[b]	10.4 ± 0.6	5.8	11.4 ± 0.2	1.6
Gd	(5.0)[b]	4.7 ± 0.5	11.2	5.1 ± 0.2	4.9
La	(26.1 - 29.99)[c]	25.7 ± 2.0	7.8	28.4 ± 0.9	3.3
Li	-	35.2 ± 3.1	8.8	36.5 ± 0.8	2.1
Mn	935 ± 100	1018 ± 22	2.2	1080 ± 19	1.8
Mo	(5.5 - 8)[c]	8.4 ± 0.3	4.2	8.1 ± 0.4	5.4
Nb	(10.0)[b]	2.50 ± 0.4	17.3	3.4 ± 0.2	4.8
Nd	(25.17)[b]	24.7 ± 3.1	12.5	25.7 ± 0.7	2.5
Ni	92.7 ± 4.7	92.3 ± 10.4	11.3	92.4 ± 12.9	13.9
P	-	3352 ± 37	1.1	3760 ± 56	1.5
Pb	1317 ± 55	1326 ± 11	0.8	1367 ± 26	1.9
Pr	-	6.25 ± 0.20	3.2	6.30 ± 0.21	3.3
Rb	(75 - 100)[c]	69.4 ± 12.8	18.4	76.5 ± 1.8	2.3
Sb	(13.6 - 16.7)[c]	14.7 ± 0.3	1.9	14.2 ± 0.7	4.8
Sc	(8.2 - 9.5)[c]	7.4 ± 1.2	16.0	8.7 ± 0.7	7.6
Sm	(5.23 - 7.0)[c]	5.1 ± 0.6	11.9	5.6 ± 0.05	0.9
Sn	(35 - 58)[c]	52.7 ± 1.4	2.6	52.5 ± 1.2	2.3
Sr	(135.7 – 140)[c]	117.7 ± 9.1	7.7	119.2 ± 5.4	4.6
Th	(9.4)[b]	6.0 ± 1.4	23.2	5.2 ± 3.3	63.6
Tl	-	1.00 ± 0.04	3.6	0.98 ± 0.05	5.5
U	-	2.75 ± 0.26	9.6	2.95 ± 0.06	2.0
V	-	85.2 ± 0.9	1.1	84.7 ± 1.2	1.4
W	(5.1)[b]	11.7 ± 1.9	16.7	11.35 ± 1.2	10.5
Y	(26.7 - 27)[c]	16.9 ± 1.1	6.8	17.3 ± 0.2	0.9
Yb	-	1.50 ± 0.05	3.3	1.31 ± 0.07	5.3
Zn	1301 ± 60	1183 ± 22	1.9	1147 ± 11	1.0

[a] Indicative value, one single result for the aqua regia-soluble part.
[b] Indicative value, one single result for the total concentration.
[c] Indicative value, range of results for the total concentration.

done with the aqua regia treatment. Figures 4 and 5 show the relationship between the experimental data from Laboratory A and Laboratory B with a concentration range of 0–5000 µg/g and 0–300 µg/g, respectively. MLFR parameters (n=147, a=0.1038 ± 0.0200; b=1.0003 ± 0.0065) indicate the general agreement between the values given by both laboratories. Only a significant deviation from the ideal value can be found in some pairs of data, notably the ones about the Ti element, which was present in all matrixes at higher concentrations. This set of data was analyzed with the LR method and a significant difference was noticed between the results obtained at the two laboratories. Actually, statistical parameters gave "a" and "b" values other than the theoretical ones (n=147; a=13.1479 ± 9.0058; b=1.0278 ± 0.0197; r=0.9907). However, for both solubilization procedures, the MLFR and LR methods gave similar results as to the comparison between the certified values and those supplied by Laboratory A, while different conclusions have to be drawn from the comparison between the non-certified values given by both laboratories.

The method detection limits (MDL), calculated as three times the standard deviation of five blank tests, were assessed through the analysis of a set of five blanks obtained with the HF/HNO$_3$/HCl procedure in five non-consecutive days. Refer to Figures 5 and 6 for data from both laboratories. Figure 5 indicates that, in both laboratories, the MDL values for Be, Cd, Bi, Ce, Co, Cs, Ga, La, Li, Nb, Rb, Sb, Sn, Sr, Ti, and Tl, are similar, ranging from 0.1–0.2 µg/g.

Figure 6 shows the MDL values found for the most common elements in Laboratory B (As, Ba, Cr, Cu, Mn, Ni, Pb, V, and Zn). These are definitely worse, partly

because of the greater variability of the various analyte concentrations in the blank samples. Since the instrumental measurement was only carried out in one laboratory, such variability can be ascribed to the sample preparation and consequently to the contamination caused by the "lab system".

TABLE V
Determination of Metals (µg/g) in CRM BCR 141R Calcareous Loam Soil by ICP-MS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A		LAB A-B	
		Mean (µg/g)	RSD%	Mean (µg/g)	RSD%
As	(8.84)[a]	7.62 ± 0.40	5.2	-	
Ba	(348 ; 437)[a]	233 ± 18	7.5	-	
Be	-	2.8 ± 0.6	21.5	2.5 ± 0.3	12.7
Bi	-	1.8 ± 0.9	47.2	1.9 ± 1.0	52.4
Cd	14.6 ± 0.5	14.5 ± 0.2	1.2	15.4 ± 1.3	8.3
Ce	-	14.3 ± 1.2	8.3	16.7 ± 2.4	14.2
Co	10.5 ± 0.4	13.4 ± 1.1	7.8	13.9 ± 0.7	5.3
Cr	195 ± 7	195 ± 3	1.3	185 ± 12	6.5
Cu	46.4 ± 1.8	47.4 ± 2.6	5.4	49.4 ± 3.6	7.3
Cs	-	5.1 ± 0.3	6.6	4.5 ± 0.4	8.0
Eu	-	0.12 ± 0.02	16.7	0.19 ± 0.02	10.5
Ga	-	13.9 ± 1.2	8.6	13.8 ± 1.1	8.2
Ge	-	1.39 ± 0.06	4.6	1.52 ± 0.08	5.0
La	(31.8)[a]	7.6 ± 1.7	22.5	8.8 ± 1.6	17.8
Li	-	28.6 ± 1.4	5.0	29.5 ± 2.0	6.7
Mn	683 ± 16	650 ± 57	8.8	625 ± 25	3.9
Mo	-	4.2 ± 0.8	19.4	3.7 ± 0.5	14.0
Nb	-	14.9 ± 0.8	5.5	14.0 ± 0.6	4.4
Ni	103 ± 3	103 ± 2	2.1	105 ± 7	6.9
Pb	57.2 ± 1.2	58.3 ± 1.6	2.7	53.6 ± 1.7	3.1
Rb	-	84.4 ± 3.1	3.7	81.9 ± 6.4	7.8
Sb	(1.2; 1.38)[b]	1.43 ± 0.29	20.0	1.35 ± 0.31	23.0
Sc	-	223 ± 42	18.6	247 ± 32	12.9
Sn	(8.3)[a]	7.7 ± 0.2	3.2	7.9 ± 0.4	5.3
Sr	(524)[a]	557 ± 9	1.7	628 ± 33	5.3
Ti	(3094)[a]	3290 ± 57	1.7	3607 ± 248	6.9
Tl	(0.638)[a]	0.500 ± 0.008	1.6	0.550 ± 0.047	8.5
U	(2.39)[a]	1.66 ± 0.10	6.3	1.62 ± 0.12	7.5
V	(77.2)[a]	76.1 ± 3.2	4.2	80.4 ± 5.9	7.3
Zn	283 ± 5	320 ± 47	14.7	313 ± 10	3.2

[a] Indicative value, one single result for the total concentration.
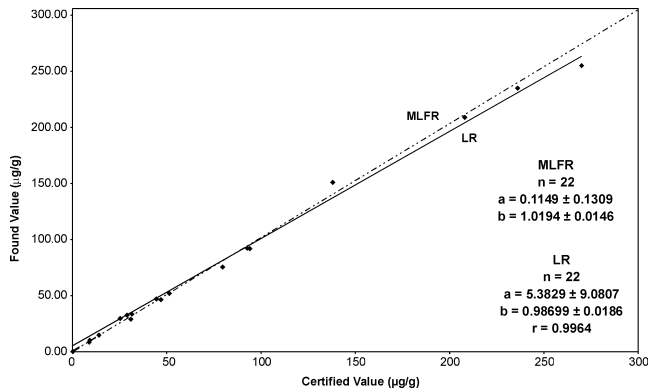[b] Indicative value, range of results for the total concentration.

Fig. 1. Correlation MLFR (maximum- likelihood fitting of a functional relationship) and LR (linear regression) between certified and found values (µg/g) for aqua regia procedure and ICP-MS analysis.
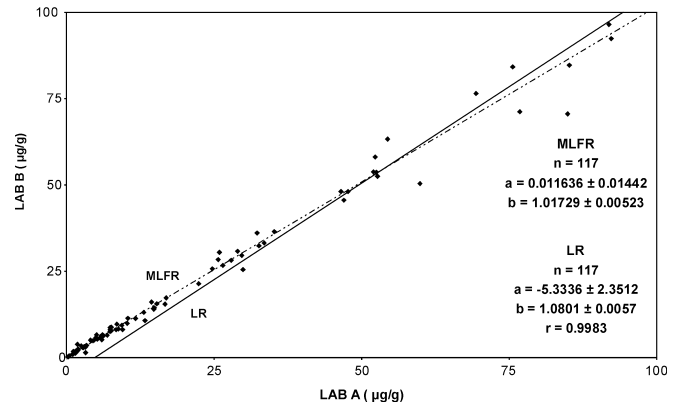

Fig. 2. Correlation MLFR (maximum- likelihood fitting of a functional relationship) and LR (linear regression) between experimental values (µg/g) found by LAB A and LAB B for aqua regia procedure and ICP-MS analysis relative to non-certified elements.
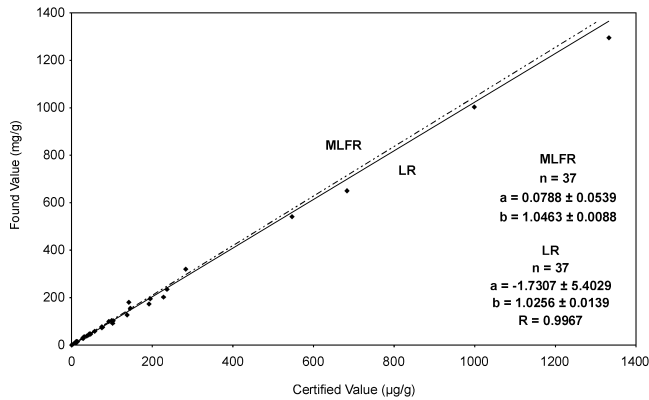

Fig. 3. Correlation MLFR (maximum- likelihood fitting of a functional relationship) and LR (linear regression) between certified and found values (µg/g) for HF/HNO₃/HCl procedure and ICP-MS analysis.
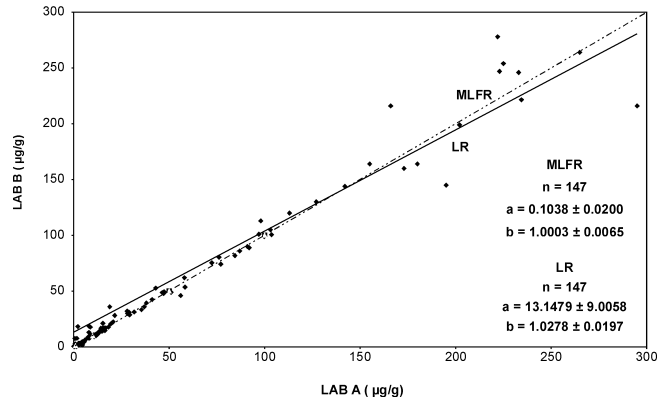

Fig. 4. Correlation MLFR (maximum- likelihood fitting of a functional relationship) and LR (linear regression) between experimental values (µg/g) found by LAB A and LAB B for HF/HNO₃/HCl procedure and ICP-MS analysis relative to non-certified elements.
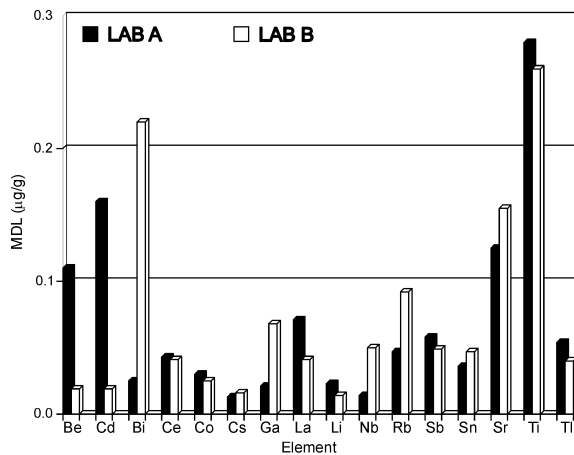

Fig 5. Method Detection Limits (MDL) for the two laboratories relative to less common elements determined by HF/HNO₃/HCl and ICP-MS.
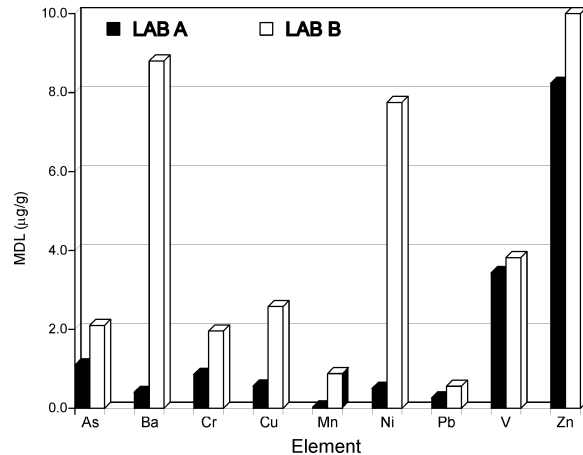

Fig 6. Method Detection Limits (MDL) for the two laboratories relative to less common elements determined by HF/HNO₃/HCl and ICP-MS.

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CONCLUSION

The extraction of numerous elements from soils and sediments through microwave-assisted aqua regia solubilization seems to be a viable alternative to the traditional reflux procedures. The sample treatment time is definitely shorter and the contamination level reduced. The results obtained with samples CRM 141 R, 142, and 143 are in good agreement with certified values. The use of a multielemental technique, such as ICP-MS, gives a significantly wider set of chemical information, providing analysts with a better knowledge of the contents of about 20-25 analytes at concentration levels of some µg/g.

The precision is on average lower than 5-10% (RSD %).

The use of HF/HNO$_3$/HCl mixtures allows the determination of the total contents of several analytes present in soils and sediments, without particular problems as far as aqua-regia dissolution is concerned. The results obtained from about 20-25 elements are in good agreement with certified values. The precision, also in such a complex matrix, does not appear biased as with the aqua regia partial dissolution, since the high sensitivity of ICP-MS allows the use of dilution factors of 1/10 or 1/100 with the initial solution. The method detection limits are less than 0.2 µg/g for Be, Cd, Bi, Ce, Co, Cs, Ga, La, Li, Nb, Rb, Sb, Sn, Sr Tl, and Ti and 2-5 µg/g for As, Ba, Cr, Cu, Mn, Ni, V, and Zn. These values are therefore fully compatible with the analytical requirements deriving from the characterization of trace metals in soil and sediment matrixes.

TABLE VI
Determination of Metals (µg/g) in CRM BCR 142 Light Sandy Soil by ICP-MS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A Mean (µg/g)	LAB A-A RSD%	LAB A-B Mean (µg/g)	LAB A-B RSD%
As	(15.7 ; 18)[b]	15.3 ± 1.27	8,3	270 ± 89	32.9
Ba	(435 ; 472)[b]	376 ± 36.3	9,7	537 ± 61	11.4
Be	-	2,80 ± 0.43	15,3	2.32 ± 0.24	10.3
Bi	-	1.5 ± 0.85	57.1	0.3 ± 0.16	53.3
Cd	0.25 ± 0.09	0.35 ± 0.05	13.2	0.37 ± 0.13	35.1
Ce	(69.5 ; 97)[b]	5.5 ± 1.1	20.7	4.7 ± 1.3	28.7
Co	7.9 ± 1.1	9.7 ± 0.4	4.3	10.3 ± 0.4	3.5
Cr	74.9 ± 9.4	77.0 ± 4.4	5.7	74.2 ± 4.8	6.4
Cu	27.5 ± 0.6	29.3 ± 1.5	5.3	28.8 ± 1.2	4.3
Cs	-	4.6 ± 0.12	2.6	1.8 ± 0.9	51.5
Eu	(0.87 ; 1.15)[b]	0.24± 0.04	17.5	0.43 ± 0.08	17.9
Ga	(11 ± 1)[a]	11.0 ± 0.7	6.3	10.2 ± 0.2	1.9
Ge	-	1.4 ± 0.07	4.7	1.5 ± 0.08	5.3
La	(29.5 - 33.3)[b]	1.7 ± 0.5	27.2	7.7 ± 2.5	32.6
Li	-	31.7 ± 1.7	5.2	31.3 ± 1.7	5.3
Mn	569 ± 26	633 ± 21	3.3	670 ± 12	1.8
Mo	-	0.5 ± 0.1	19.1	0.4 ± 0.14	33.5
Nb	(14 ± 1)[a]	16.4 ± 0.3	1.7	14.7 ± 0.33	2.3
Ni	29.2 ± 2.5	28.2 ± 0.8	3.0	30.1 ± 0.4	1.4
Pb	37.8 ± 1.9	38.1 ± 2.3	6.1	39.3 ± 8.4	21.4
Rb	(105 ± 25)[a]	56 ± 2	4.2	46 ± 9	20.3
Sb	1.7; 3.2)[b]	2.6 ± 0.3	10.3	3.3 ± 0.9	27.2
Sc	(7 ; 9.5)[b]	225 ± 22	10.0	254 ± 20	7.8
Sn	(3 ; 4)[b]	4.2 ± 0.4	9.1	4.2 ± 0.7	16.6
Sr	(164 ; 165)[b]	142 ± 4	3.0	144 ± 5	3.3
Ti	(2530 ± 60)[a]	3565 ± 147	4.1	3778 ± 71	1.9
Tl	-	0.6 ± 0.04	6.4	0.55 ± 0.05	9.7
U	-	2.9 ± 0.1	2.7	2.6± 0.1	3.1
V	-	58 ± 3	4.9	62 ± 2	3.0
Zn	92.4 ± 4.4	99.8 ± 4.8	4.8	98.8 ± 3.4	3.4

[a] Indicative value, one single result for the total concentration.
[b] Indicative value, range of results for the total concentration.

TABLE VII
Determination of Metals (μg/g) in CRM BCR 143 Sewage Sludge Amended Soil by ICP-MS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified Value (μg/g)	LAB A-A		LAB A-B	
		Mean (μg/g)	RSD%	Mean (μg/g)	RSD%
As	(15 - 19.6)[b]	16.0 ± 2.1	13.4	375 ± 88	23.5
Ba	(920 ; 940)[b]	881 ± 15	1.7	859 ± 15	1.8
Be	-	3.26 ± 0.34	10.5	2.86 ± 0.32	11.1
Bi	(10 ± 0.1)[a]	8.7 ± 0.6	6.9	9.1 ± 1.1	11.9
Cd	31.1 ± 1.2	35.5 ± 0.7	2.1	33.3 ± 1.2	3.8
Ce	(65 ; 94)[b]	21.5 ± 2.2	10.4	28.2 ± 2.0	6.9
Co	11.8 ± 1.2	15.4 ± 0.7	4.4	14.8 ± 1.2	8.5
Cr	228 ± 19	202 ± 20	10.0	199 ± 31	15.7
Cu	236.5 ± 8.2	234.4 ± 4.6	2.0	221.5 ± 6.6	3.0
Cs	-	0.14 ± 0.03	18.2	0.30 ± 0.14	49.1
Eu	(0.6 ; 1.01)[b]	0.5 ± 0.06	10.8	0.6 ± 0.05	7.9
Ga	(12 ± 1)[a]	11.9 ± 0.3	2.4	11.4 ± 0.5	4.0
Ge	-	1.6 ± 0.2	10.7	1.9 ± 0.1	5.3
La	(26.1 - 29.99)[b]	8 ± 1	12.6	13 ± 1	8.5
Li	-	28 ± 2	7.0	32 ± 3	7.9
Mn	999± 62	1003 ± 33	3.3	1059 ± 161	15.2
Mo	(5.5 ; 8)[b]	8.3 ± 0.2	3.0	8.0 ± 0.4	4.7
Nb	(10 ± 1)[a]	11.7 ± 0.5	4.4	10.0 ± 0.4	4.3
Ni	99.5 ± 5.5	103.6 ± 3.4	3.3	100.6 ± 4.3	4.3
Pb	1333 ± 39	1295 ± 11	0.9	1283 ± 68	5.3
Rb	(75 ; 100)[b]	8.7 ± 1.6	18.6	17.8 ± 4.8	26.9
Sb	(13.6 ; 16.7)[b]	16.8 ± 0.5	3.2	17.0 ± 0.9	5.2
Sc	(8.2 ; 9.5)[b]	166 ± 11	6.8	216 ± 31	14.3
Sn	(35 ; 58)[b]	51 ± 1	3.0	49 ± 3	5.1
Sr	(135.7 - 140)[b]	97 ± 1	1.6	101 ± 6	6.0
Ti	(3580 ± 90)[a]	4299 ± 123	2.9	4114 ± 274	6.7
Tl	-	0.9 ± 0.04	3.7	0.91 ± 0.04	4.8
U	-	3 ± 0.1	4.1	3 ± 0.1	4.2
V	-	91 ± 3	3.0	90 ± 5	5.5
Zn	1272 ± 30	1426 ± 34	2.4	1294 ± 43	3.3

[a] Indicative value, one single result for the total concentration.
[b] Indicative value, range of results for the total concentration.

TABLE VIII
Determination of metals (µg/g) in CRM BCR 277 Estuarine Sediment by ICP-MS After HF/HNO$_3$/HCl Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A Mean (µg/g)	RSD%	LAB A-B Mean (µg/g)	RSD%
As	47.3 ± 1.6	46.4 ± 2.4	5.2	-	-
Ba	(306 – 350)[b]	222 ± 14	6.2	278 ± 33	12.0
Be	(1.60 ; 1.66)[b]	3.47 ± 0.32	9.1	2.59 ± 0.09	3.3
Cd	11.9 ± 0.4	11.6 ± 0.7	6.1	11.2 ± 0.1	0.8
Ce	(76.4 ; 86)[b]	18.9 ± 2.1	10.9	36.0 ± 1.5	4.3
Co	(15 - 19.8)[b]	15.6 ± 1.0	6.5	15.5 ± 0.4	2.6
Cr	192 ± 7	173 ± 16	9.0	160 ± 4	2.4
Cu	101.7 ± 1.6	91.9 ± 6.1	6.6	88.9 ± 3.3	3.7
Cs	(5.7 ; 6.92)[b]	0.96 ± 0.14	14.4	1.35 ± 0.15	10.8
Eu	(1.44 ; 1.7)[b]	0.2 ± 0.03	19.2	0.67 ± 0.04	6.5
Ga	(5.2 ; 11.6)[b]	12.5 ± 0.6	4.6	11.2 ± 0.1	1.2
Ge	(1.6 ± 0.3)[b]	2.3 ± 0.1	2.6	1.9 ± 0.1	8.0
La	(43.2 - 53.7)[b]	8.1 ± 1.0	12.9	18.5 ± 0.8	4.4
Li	-	37 ± 1.4	3.7	36 ± 3.3	9.1
Mn	(1520 - 1620)[b]	1602 ± 102	6.4	1576 ± 64	4.1
Mo	(1.43 - 1.47)[b]	4.78 ± 0.61	12.9	3.62 ± 0.33	9.0
Nb	(10± 1.2)[a]	10.7 ± 1.0	9.5	9.1 ± 0.2	1.7
Ni	43.4 ± 1.6	46.4 ± 6.0	12.9	48.7 ± 3.7	7.6
Pb	146 ± 3	155 ± 3	2.1	164 ± 2	0.9
Rb	(84.3 ; 105)[b]	41.1 ± 2.6	6.3	42.4 ± 3.0	7.1
Sb	(3.5 - 4.3)[b]	4.5 ± 0.7	16.0	4.4 ± 0.5	10.4
Sc	9.00 ± 0.12	295 ± 37	12.5	216 ± 5	2.3
Sn	(8 ; 12.2)[b]	10.6 ± 0.6	5.6	11.0 ± 0.3	2.3
Sr	(301 - 437)[b]	265 ± 11	4.2	264 ± 7	2.8
Ti	(2600 - 4400)[b]	3658 ± 174	4.7	4073 ± 870	21.4
Tl	-	1.1 ± 0.1	11.9	1.1 ± 0.1	9.1
U	(2.94 - 3.4)[b]	3.3 ± 0.1	2.0	3.3 ± 0.1	2.0
V	(102 ; 102.6)[b]	87 ± 4	5.0	86 ± 2	1.9
Zn	547 ± 12	541 ± 33	6.1	496 ± 7	1.4

[a] Indicative value, one single result for the total concentration.

[b] Indicative value, range of results for the total concentration.

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TABLE IX
Determination of Metals (µg/g) in CRM BCR 320 River Sediment by ICP-MS After HF/HNO₃/HCl Microwave-Oven Procedure

Element	Certified Value (µg/g)	LAB A-A		LAB A-B	
		Mean (µg/g)	RSD%	Mean (µg/g)	RSD%
As	76.7 ± 3.4	75.2 ± 4.9	6.5	-	-
Ba	(517 – 600)[b]	273 ± 8	2.9	377 ± 53	14.0
Be	(2.5 - 2.6)[b]	5.2 ± 0.6	10.7	3.9 ± 0.2	4.5
Cd	0.533 ± 0.026	0.638 ± 0.056	8.7	0.661 ± 0.138	20.9
Ce	(93.8 - 95)[b]	2.2 ± 0.8	37.2	18.3 ± 1.2	6.6
Co	(17.3 - 21)[b]	19.4 ± 0.3	1.7	20.6 ± 0.7	3.5
Cr	138 ± 7	127 ± 4	2.9	130 ± 4	3.3
Cu	44.1 ± 1	47.1 ± 1.4	3.0	47.9 ± 1.6	3.4
Cs	(4.5 - 5)b	0.35 ± 0.1	20.7	0.47 ± 0.34	72.5
Eu	(1.42 - 1.7)[b]	0.22 ± 0.03	11.7	0.59 ± 0.09	14.3
Ga	(19.2 - 20.8)[b]	20.7 ± 0.4	2.0	22.5 ± 1.2	5.4
Ge	(1.9 ± 1)	1.5 ± 0.4	26.3	1.8 ± 0.4	19.8
La	(43 - 47.9)[b]	0.7 ± 0.3	46.0	7.6 ± 0.8	10.5
Li	-	29 ± 2	5.2	31 ± 7	22.8
Mn	(619 - 782)[b]	770 ± 10	1.3	888 ± 55	6.2
Mo	(0.63 - 0.65)[b]	0.73 ± 0.30	41.0	0.67 ± 0.31	46.6
Nb	(14.8 ± 1.2)[a]	18.2 ± 0.9	4.8	17.8 ± 0.3	1.5
Ni	75.2 ± 1.4	72.3 ± 1.0	1.4	75.4 ± 3.7	4.9
Pb	42.3 ± 1.6	43.0 ± 0.7	1.6	52.7 ± 4.0	7.6
Rb	(134.8 - 169.4)[b]	15.3 ± 1.1	7.1	21.2 ± 8.0	37.9
Sb	(0.5 - 0.8)[b]	0.8 ± 0.2	24.3	2.7 ± 0.9	34.7
Sc	15.25 ± 0.36	221 ± 7	3.1	311 ± 25	8.0
Sn	(5.5 - 5.8)[b]	6.0 ± 0.3	5.6	6.3 ± 0.2	3.6
Sr	(193 - 277)[b]	98 ± 4	3.6	113 ± 5	4.6
Ti	(4110 - 5900)[b]	4642 ± 178	3.8	4673 ± 227	4.9
Tl	(0.5 - 0.53)[b]	0.73 ± 0.08	10.7	0.68 ± 0.05	7.4
U	(5.5 - 6.0)[b]	4.6 ± 0.3	6.5	4.7 ± 0.2	4.4
V	(104 - 105)[b]	113 ± 1	1.0	120 ± 3	2.8
Zn	142 ± 3	180 ± 2	1.0	164 ± 8	4.8

[b][a] Indicative value, one single result for the total concentration.
[b] Indicative value, range of results for the total concentration.

TABLE X
Method Detection Limit MDL (µg/g) for HF/HNO3/HCl MW Procedure and ICP-MS Analysis

Element	MDL (µg/g)	
	LAB A-A	LAB A-B
As	1.10	2.10
Ba	0.41	8.80
Be	0.11	0.02
Cd	0.16	0.02
Bi	0.03	0.22
Ce	0.04	0.04
Co	0.03	0.03
Cr	0.86	1.96
Cu	0.57	2.58
Cs	0.01	0.02
Ga	0.02	0.07
La	0.07	0.04
Li	0.02	0.01
Mn	0.04	0.88
Nb	0.01	0.05
Ni	0.51	7.75
Pb	0.27	0.56
Rb	0.05	0.09
Sb	0.06	0.05
Sn	0.04	0.05
Sr	0.13	0.16
Ti	0.28	0.26
Tl	0.05	0.04
V	3.44	3.82
Zn	8.24	14.20

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In situ Matrix Volatilization Studies and Characterization of Some Trace Elements in High-Purity Arsenic by Graphite Furnace AAS

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INTRODUCTION

Graphite furnace atomic absorption spectroscopy (GFAAS) provides a sensitive method for the determination of trace impurities in a variety of matrices. The relatively long residence time in the observation volume of the furnace as well as the lack of sample transport losses are such that the absolute limits of detection can surpass even those of ICP-MS (1). However, the potential of GFAAS is often not fully realized, because of the matrix effects on the analytical signals, especially when they result in the degradation of sensitivities. Hence, the development of any GFAAS procedure starts with an investigation of matrix effects and ways of eliminating any undesirable ones (2). The matrix effects in GFAAS result in a contribution to the analyte atomic absorption signal from concomitants in the sample. This is mainly due to absorbance/scattering by undissociated molecular species and/or particulate matter /smoke from the sample falling within the path of the beam of the hollow cathode lamp. Temperature programming in the graphite furnace is one method of minimizing such matrix interferences. In this process, ashing temperatures are set so as to eliminate interferences due to the concomitants by evaporating them prior to the atomization step. However, in many cases, the temperature program alone does not suffice and it often becomes necessary to remove major elements in a preliminary

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ABSTRACT

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) is a sensitive method for the estimation of trace and ultra-trace impurities. In this paper, a method for the estimation of trace impurities, Ag, Bi, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Sb in high-purity arsenic, has been described. The method involves the in situ removal of arsenic matrix in the furnace using an appropriate volatilization step prior to the atomization stage. This permits the use of concentrated arsenic solutions up to 20 mg/mL without resorting to a prior matrix removal step, thereby enhancing the detectability of trace amounts of impurities. Trace elements ranging from 0.04 ppm (Cd) to 1.3 ppm (Sb) can be determined by this procedure.

chemical separation. GFAAS has been used both directly and after matrix separation for the estimation of high-purity arsenic (3-5). Trace elements in arsenic have been estimated after separation of the arsenic matrix by volatilization as chloride or bromide in an open system (6,7). When low concentrations of trace impurities have to be measured, the detection limits are largely determined by the magnitude of the blank. Such chemical processing of the sample contributes to an increase in the blank and any method that eliminates the need for such chemical processing should be considered desirable. In this study, the feasibility of measuring trace amounts of impurities in high-purity arsenic without resorting to a matrix separation and chemical pretreatment were exam-

ined. Arsenic, a volatile matrix, can be distilled off at the ashing stage without affecting the analyte atomic absorption signal. This was achieved by carefully monitoring the atomic and background absorbances, while optimizing the ashing temperatures. This work is especially relevant due to the well-known technological importance of semiconductor groups III-V, especially for applications in the fields of optical communication and ultra-high-speed integrated circuits. High-purity elemental arsenic is a primary starting material for the synthesis of gallium arsenide and indium arsenide which, because of it's intrinsic properties, gives superior performance in applications such as laser diodes, photovoltaic devices, semi-insulating detectors, etc. These applications require high-quality substrate material. One of the important aspects of semiconductor substrate material is the purity of the basic substances. These semiconductor devices must be prepared from substances of at least 99.999 (5–6 N) purity. Hence, the accurate characterization with respect to trace elemental concentrations of high-purity arsenic is of critical importance.

EXPERIMENTAL

Instrumentation

Hitachi 180-80 polarized Zeeman AAS unit, using the electrothermal mode of atomization, was used in the present investigation. Cup-type cuvettes and tube-type pyro-cuvettes were used in the estimations.

Hollow cathode lamps, manufactured by ECIL, India, and Cathodeon, were used.

A two-pen Rikadenki X-Y recorder was used for taking the background and analyte atomic absorption scans.

A CEM MDS-2100 Microwave Sample Preparation System was used for sample dissolutions. The dissolutions were carried out in a CEM Advanced Composite Vessel capable of withstanding pressures up to 200 psi.

All containers and glassware were cleaned by soaking in 10% AR HNO_3 for one week and rinsing thoroughly with high-purity water before use.

Reagents

Arsenic (>5N purity) from Fluka Chemicals was used in the present study. Suprapure nitric acid (65%) from E.Merck, Darmstadt, Germany, was used for all sample dissolutions. ICP multielement standard from E.Merck, Germany, was used for preparation of the standards of required strengths by sequential dilutions every day.

High-purity water of 18 MΩ resistivity was used for all dilutions and rinsings. The containers used were of quartz or PTFE.

PROCEDURE

a. Sample Dissolution

The vessels were initially cleaned by thoroughly rinsing with ultrapure water. Five mL of suprapure nitric acid was then added to the vessels. The vessels were then placed inside the microwave system and subjected to microwave energy at the following settings.

Microwave Power	30%
Time	5 Minutes
Maximum Pressure	100 psi

The vessels were cooled and the contents discarded. This step ensured the removal of any trace elements adsorbed on the walls of the containers. The vessels were rinsed thoroughly with ultrapure water. One g of accurately weighed 5N arsenic (Fluka Chemicals) was transferred to one of the vessels. Seven mL of suprapure nitric acid was then added to both vessels, the second vessel providing the sample blank. The sample was subjected to microwave energy as follows:

	Stage I	Stage II
Microwave Power	30%	35%
Time	10 min	10 min
Maximum Pressure	100 psi	150 psi

The vessels were cooled and the contents transferred to a 25-mL volumetric flask and made up to volume. This gave a sample solution of 40 mg/mL and the corresponding sample blank. These two solutions were used in all subsequent experiments.

b. Estimation of Trace Impurities by GFAAS

Spectral scans of the backgrounds and analyte atomic absorption signals were taken for Ag, Bi,Cd, Cr, Cu, Co, Mn, Ni, and Sb, using standard 5N arsenic solution spiked with these elements. The scans were carried out by employing a two-pen recorder using the standard temperature programs recommended by the manufacturer (Table I) for both aqueous standards as well as the arsenic sample at the 20-mg/mL level. In the case of Ag, Cu, Cr and Mn, the presence of the matrix did not pose any problem as atomic absorption and background signals were well separated (Figure 1). In the case of Cd, Bi and Sb, the ashing temperatures recommended were lower (300-400°C). In these cases, arsenic remained incompletely volatilized and a very strong background signal was obtained during the atomization stage. This signal was seen to be overlapping with the analyte atomic absorption signal and swamping it completely (see Figures 2 – 4). Under these conditions, it was not possible to obtain a background-corrected signal for the analyte atomic absorption in the normal fashion as the instrument was unable to resolve the analyte atomic absorption signal from the background signal. For these elements, scans were carried out for the analyte atomic absorption, and background signals at increasing ashing temperatures and modified temperature programs were developed based on the information obtained. It was found that by increasing the ashing temperature to 600°C for these elements, it was possible to volatilize arsenic at the ashing stage itself and a clean peak was obtained for the analyte atomic absorption with no background sig-

TABLE I
Temperature Programs and Wavelengths Used for GFAAS Analysis

Element	Ashing temperature (°C)	Atomization temperature (°C)	Wavelength used for absorbance measurement (nm)
Ag	500	2600	328.1
Cu	700	3000	324.8
Cr	800	3000	359.3
Mn	600	2800	279.5
Pb	400	2000	283.3
Co	600	2700	240.7
Ni	800	2900	232.0
Bi	300	2000	223.3
Cd	300	1500	228.8
Sb	400	2500	217.6

nal overlap. No significant drop in the analyte atomic absorption signals was observed, thus enabling us to carry out the analysis at the same concentration levels (Figure 5).

The effect of the matrix was also studied by comparing the absorbances of the aqueous standards with those of matrix-matched standards (Table II). The

estimations were validated using spike recovery studies for all the elements. The arsenic matrix was spiked with known amounts of standards and the recoveries were estimated against calibration using aqueous standards (Table III).

The detection limits for individual elements were estimated by preparing a series of blanks over

several days. The mean and standard deviation were computed and 3s values plus the mean were taken as a measure of the detection limits of the individual elements as per the IUPAC definition. The detection limit values were then calculated on a per sample basis, assuming a sample size of 1 g dissolved in 25 mL (Table IV).
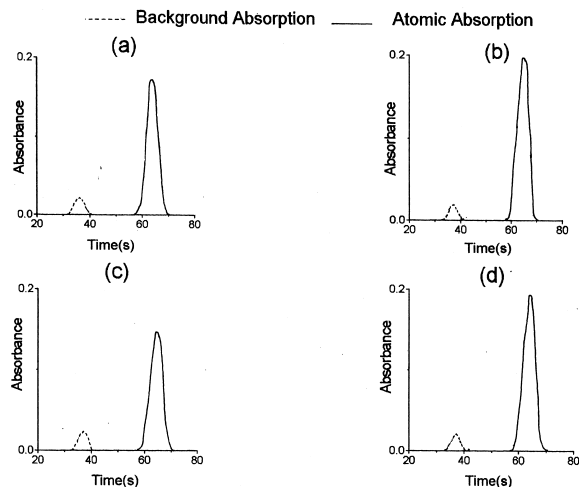
Fig. 1. Atomic absorption and background results for Ag, Cu, Mn, and Cr under standard conditions in arsenic matrix using 10 µL As (20 mg/mL) solution spiked with (a)10 µL of Ag (20 ng/mL), (b) Cr(20 ng/mL), (c) Cu (100 ng/mL) and (d) Mn (20 ng/mL) standards.
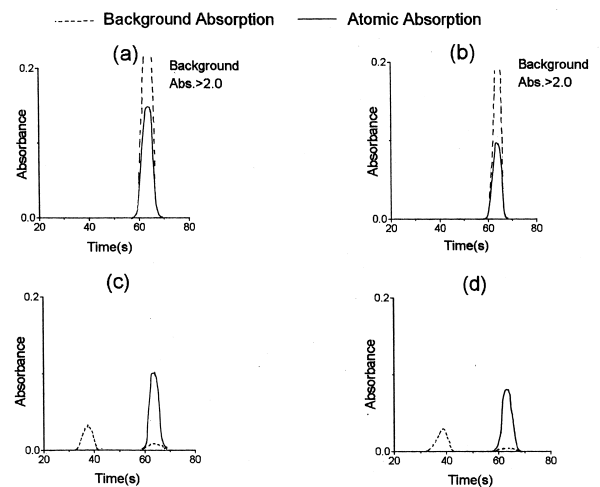

Fig. 2. Atomic absorption and background results for Bi in arsenic matrix using 10 µL As (20 mg/mL) solution spiked with 10 µL Bi standard (100 ng/mL), using ashing temperatures of (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.
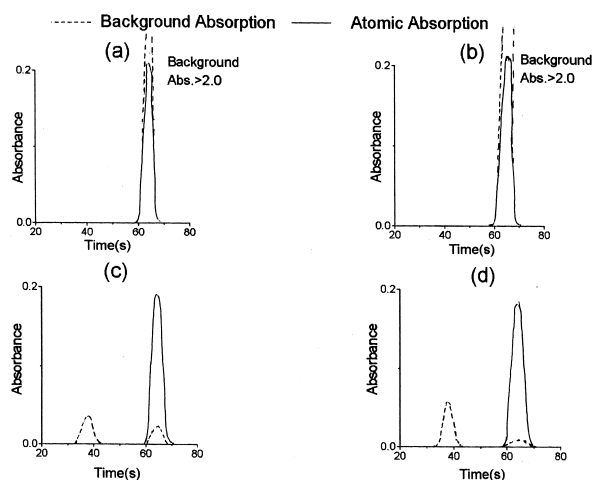

Fig. 3. Atomic absorption and background results for Cd in arsenic matrix using 10 µL As (20 mg/mL) solution spiked with 10 µL of Cd standard (5 ng/mL). Ashing temperatures were (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.
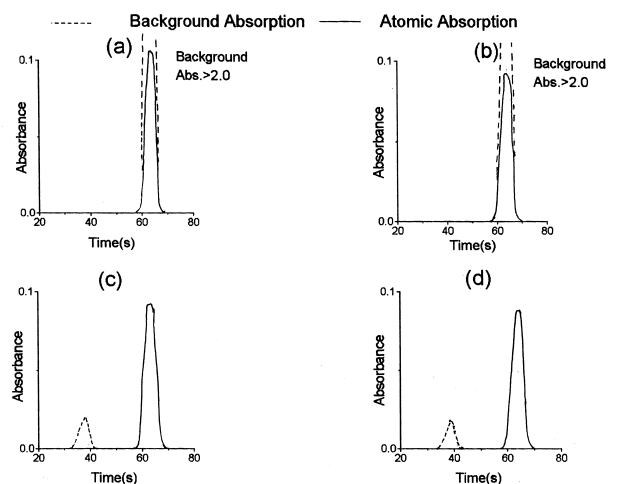

Fig. 4. Atomic absorption and background results for Sb in arsenic matrix using 10 µL of As (20 mg/mL) solution spiked with 10 µL of Sb standard (100 ng/mL). Ashing temperatures were (a) 300°C, (b) 400°C, (c) 500°C, and (d) 600°C.
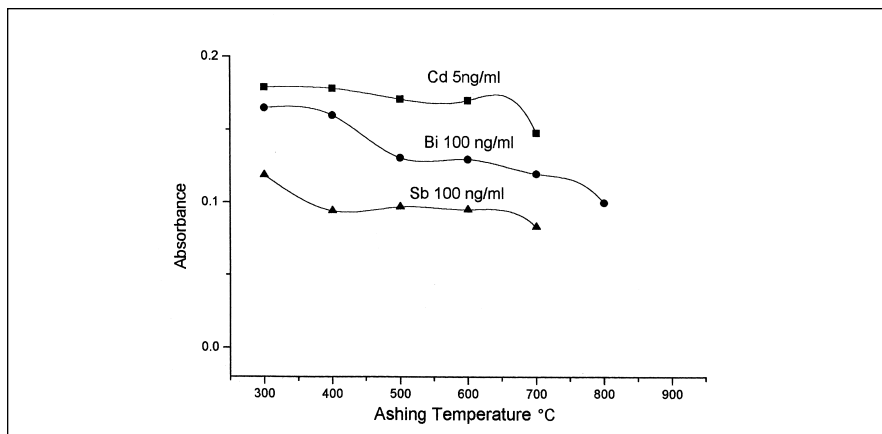
Fig. 5. Plots of ashing temperature vs. absorbance for 10 µL of Bi, Cd, and Sb standard solutions.

RESULTS AND DISCUSSION

Optimization of GF Temperature Programs

The results for background and analyte atomic absorption for Ag, Bi, Cd, Cr, Co, Cu, Ni, Mn, Pb, and Sb were obtained using the conditions recommended by the manufacturer (8) (Table I).

In the case of Ag, Cu, Mn, and Cr, clean analyte atomic absorption signals were obtained with negligible background signals at the recommended ashing and atomization temperatures (Figure 1). This is attributed to the high ashing temperatures used for these elements, which ensures a complete removal of the matrix by evaporation. The resonance wavelengths of these elements are greater than 280 nm and background absorbance due to scatter and molecular absorption is also very low at these wavelengths.

It was observed that in the case of Bi, Cd, and Sb, strong background absorption peaks were observed at the atomization stage under the recommended conditions (Figures 2–4). These elements have low boiling points and therefore the ashing temperatures recommended were 300 - 400°C. The ashing temperatures for these elements were increased in steps of 100°C, and the background and analyte atomic absorption signals were recorded. It was observed that as the temperature was increased, the background peak at the atomization stage reduced in size and intensity and at 600°C, it was almost negligible. Though the higher ashing temperatures used resulted in a minor reduction in analyte atomic absorption signal (Figure 5), this reduction in the analyte atomic absorption signal is more than compensated for by the total absence of background signal at the atomization stage and would therefore not lead to a reduction in the detection limits. This minimal decrease in the analyte atomic absorption signal can be attributed

TABLE II
Comparison of Absorbances of Aqueous and Matrix-matched Standards

Element	Aqueous Standards calibration (Abs/25 ng)	Calibration using Arsenic 20 mg/mL solution (Abs/25 ng)
Ag	0.058	0.064
Bi	0.088	0.072
Cd	0.425	0.450
Co	0.086	0.089
Cr	0.072	0.075
Cu	0.111	0.115
Ni	0.032	0.030
Pb	0.055	0.043
Sb	0.044/100ng	0.036/100ng

TABLE III
Standard Addition and Recovery Studies

Element	Amount Added (ng)	Amount Recovered (ng)	(%) Recovery
Ag	250	275	110
Bi	1000	818	82
Cd	50	53	106
Cu	400	384	96
Co	100	103	103
Cr	250	264	105
Mn	50	60	120
Ni	100	104	104
Pb	500	432	86

TABLE IV
Estimation of Detection Limits (DL)

Element	Mean (x) (n=8) (ng/mL)	Std. Dev. (s)	Solution DL x + 3s (ng/mL)	Sample DL (1-g sample in 25 mL) (ppm)
Ag	1.8	0.4	3.0	0.08
Bi	15	1.0	18	0..45
Cd	0.93	0.22	1.6	0.04
Co	15.0	1.2	18.6	0.47
Cr	10	1.3	13.9	0.35
Cu	23.0	2.1	29.0	0.73
Mn	3.3	0.6	5.1	0.13
Ni	27	2.7	35	0.88
Pb	27	2.3	34	0.85
Sb	35	6.1	53	1.33

to the fact that in the presence of an oxidizing acid like nitric acid, the analyte element produces a thermally stable oxide at the ashing stage, which permits setting higher ashing temperature. Standard recovery studies were carried out at the elevated ashing temperatures, which gave sharp analyte atomic absorption peaks proportional to the amounts of analyte added (Figure 6).

In the Pb scan (Figure 7), it was observed that even though the ashing temperature was 400°C, no background peak was observed at the atomization temperature. This could be attributed to the fact that particulate scattering and molecular absorption are more severe at lower wavelengths and relatively insignificant at higher wavelengths (283.3 nm) used for the measurements.

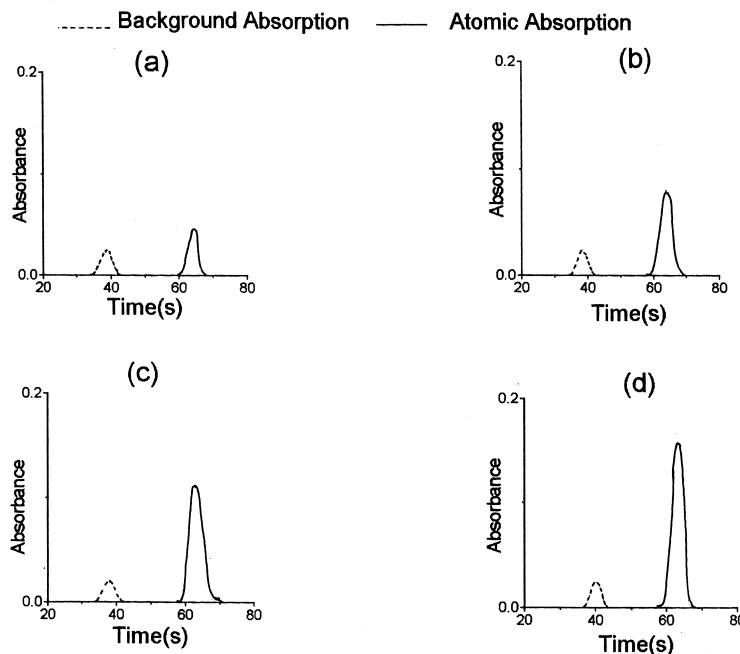In the Co and Ni graphs (Figure 8), it was observed that a background absorption peak did

Fig. 6. Standard addition recovery for Sb in arsenic matrix. Using 10 μL arsenic (20 mg/mL) solution spiked with 10 μL of varying concentrations of Sb standard solutions at ashing temperature of 600°C. The atomic absorption signals obtained with (a) blank spike, (b) 100 ng/mL, (c) 200 ng/mL, and (d) 300 ng/mL, spikes respectively.
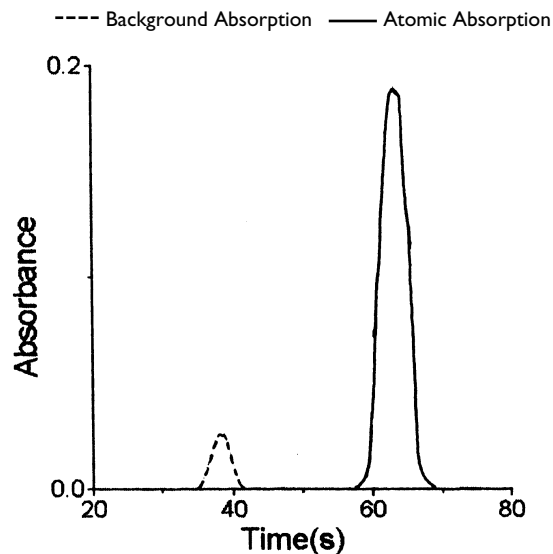

Fig. 7. Atomic absorption and background results for Pb in arsenic matrix using 10 μL As (20 mg/mL) solution spiked with 10 μL of Pb standard (40 ng/mL) at ashing temperature of 400°C.
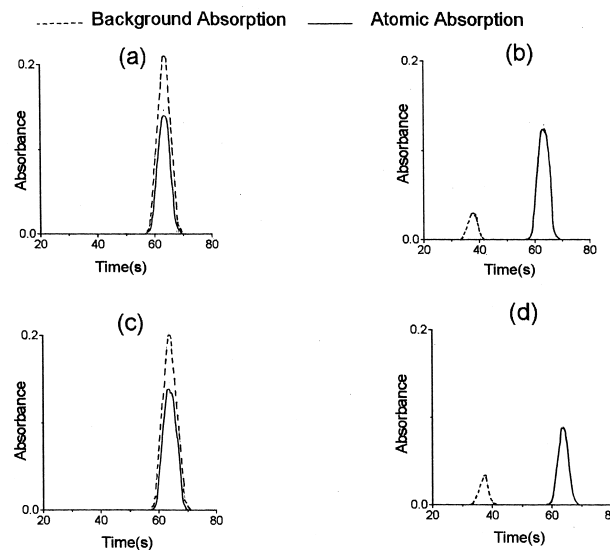

Fig. 8. Atomic absorption and background results for Co and Ni in arsenic matrix with 10 μL of arsenic (20 mg/mL) solution spiked with 10 μL of Co (50 ng/mL) and Ni (100 ng/mL) standards. (a) and (b) Co determinations at ashing temperatures of 600°C and 800°C, respectively. (c) and (d) Ni determinations at ashing temperatures of 600°C, and 800°C, respectively.

appear at the atomization stage in spite of the high ashing temperature of 600°C. This peak disappears when the ashing temperature to 800°C with no significant loss of analyte atomic absorption signal The presence of background peak is attributed to scattering and molecular absorption at resonance wavelengths for these elements, which are below the threshold value of 280 nm.

Comparison of Absorbances and Recovery Studies

A comparison of the absorbances using aqueous and matrix-matched standards is given in Table II. These absorbances have been obtained using the modified temperature programs developed for Sb, Cd, and Bi and standard temperature programs for the other elements. There is no significant difference in the absorbances between aqueous standards and calibrations carried out with standards matched with the matrix at the 20-mg/mL level of arsenic, except in the case of Bi, Sb, and Pb. Even for these elements, the depression in the signal is in the 10-20% range, which does not restrict the applicability of this procedure for these elements.

The recoveries obtained for the elements are given in Table III. The somewhat lower recoveries for Bi and Pb may perhaps be attributed to their volatility, though such a trend is not evident for Cd and Sb, which are also volatile elements. The recoveries ranged between 82–120%, which is satisfactory considering the low levels of concentrations measured and the technique used for the measurement. The procedure developed is routinely applied for the determination of trace impurities in purified arsenic metal samples. Some typical results obtained are shown in Table V. Sample concentrations corresponding to 20 mg/mL of arsenic were prepared to carry out the analysis.

TABLE V
Results of Analysis of Arsenic Samples (values in ppm)

Sample/ Element	Sample 1	Sample 2	Fluka 5N
Ag	N.D.	<0.1	0.1
Bi	0.5	N.D.	N.D.
Cd	<0.1	<0.1	<0.1
Co	0.2	0.2	0.2
Cr	N.D.	N.D.	N.D.
Cu	N.D.	N.D.	N.D.
Mn	<0.1	<0.1	<0.1
Ni	0.7	0.4	0.4
Pb	0.1	N.D.	0.1
Sb	4.0	N.D.	N.D.

Sample 1 and Sample 2 are purified arsenic metal samples (arsenic concentration >99.9%)

N.D.: Not Detected. Indicates that the values are less than or equal to the blank values.

In cases where the signal obtained is not above the mean ples 3s level, the concentration is reported as < computed detection limit.

CONCLUSION

The results obtained show that the background absorption signal is dependent on both the ashing temperature and the wavelength of measurement of the analyte atomic absorption signal. By carefully controlling the ashing temperature, the effects of background can be minimized and in some cases completely eliminated. This method of in situ matrix volatilization is a fast, reliable, and accurate method for the determination of trace impurities in high-purity arsenic up to 5N purity. Needless to say, safety procedures should be strictly adhered to in view of the known toxicity of the arsenic matrix. However, for samples >5N purity, it would be necessary to adopt a preconcentration method for the estimation of trace impurities as the detection limits offered by GFAAS would not be adequate to quantify the trace impurities.

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