

Multielement characterization of soil samples with ICP-MS for environmental studies

J. Arunachalam¹, C. Mohl², P. Ostapczuk², H. Emons²

¹ Centre for Compositional Characterisation, Bhabha Atomic Research Centre, Hyderabad 500 762, India

² Research Center of Jülich, Institute of Applied Physical Chemistry, D-52425 Jülich, Germany

Received: 21 September 1994/Revised: 21 December 1994/Accepted: 28 December 1994

Abstract. The recovery of trace elements of ecotoxic importance has been studied on certified soil and sediment reference samples after pressurized digestions with HNO₃, HNO₃ + HF and HNO₃ + HCl + HF mixtures, respectively. The acid digests have been analyzed by ICP-MS. The results indicate that digestion with nitric acid alone is satisfactory for the recovery of As, Cd, Co, Cu and Zn. Cr and Pb showed lower recoveries with HNO₃ alone but addition of HF improved their extraction. With appropriate corrections, ICP-MS can be used for the routine analysis of soils and sediments. These digestion procedures, evaluated based on reference samples, have been used for the trace element characterization of soil samples from the German Environmental Specimen Bank.

Introduction

The Environmental Specimen Bank (ESB) of the Federal Republic of Germany is an up to date and systematically designed repository for the preservative storage of selected environmental specimens [1] collected, prepared and stored under well-defined conditions described in Standard Operating Procedures (SOP's) [2]. The samples are characterized with respect to various biological and chemical parameters [3].

ICP-MS as a method for inorganic trace analysis shows an excellent sensitivity for a large number of elements of interest and the speed of measurement makes it suitable for routine, multielement determinations at trace and ultratrace levels. However, the sample solution should have a total dissolved solid content of not more than 0.1% to avoid signal depression and drift.

Matrix effects on ICP-MS trace determinations have been extensively discussed in the literature [4–9]. Iso-baric interferences on the analyte masses due to isotopes of other elements can be easily taken into account. Corrections of interferences due to the formation of ions of

oxides, hydroxides and other diatomic species depend on the matrix and on instrumental conditions. Horlick and Shao have listed the major background species of the acids used, the major molecular species of argon, oxide and hydroxide species and the effect of the major matrix elements that affect the quantitative analysis [4]. The analysis of marine sediment samples by ICP-MS has been described by McLaren et al. [5, 6], and the analysis of soil samples for environmental applications by Dolan et al. [7]. Date [8] and Hall [9] have discussed general aspects of the analysis of geochemical samples by ICP-MS.

The aim of this work was to investigate different acid digestion steps for the recovery of trace elements of ecotoxic importance in soil and sediment samples and their quantitation in the extracts using ICP-MS based on the reference materials BCR CRM 141 (calcareous loam soil), BCR CRM 142 (light sandy soil) for the purpose of optimizing the analytical conditions for ICP-MS. A reference sediment sample IAEA SL 1 Lake sediment was also analyzed as this sample provided a larger number and range of concentrations of certified elements. The preparation and trace element characterization of soils samples of the ESB are reported also.

Experimental

Sample collection

Two soil samples from a forest area were collected by the Institute of Biogeography, University of Saarland, Saarbrücken, Germany. Details of the sampling procedure are described elsewhere [10]. A total amount of 2.5 kg of each sample (horizons of 0–5 cm and 5–10 cm, called ESB Soil 1 and ESB Soil 2) were collected and immediately stored at liquid nitrogen temperature.

Sample preparation

The frozen samples were ground in a special vibrating mill using titanium rods under cryogenic conditions [11]. After many cycles of grinding, the samples were partitioned into 250 vials each containing 10 g of sample and

stored under liquid nitrogen. 25 vials randomly selected were lyophilized from each sample set for inorganic analysis.

Chemicals and instrumentation

Subboiled nitric acid, Suprapur hydrofluoric and hydrochloric acids were used for sample digestion.

Deionized water from a Milli-Q-System (18 M Ω) was used for sample dilution of the acidic digests.

The soil digests were analyzed with a PE SCIEX Elan 5000 ICP-MS system using the TotalQuant II program (Perkin-Elmer, Überlingen, Germany). Re and Rh were used as internal standards. The program automatically corrects the intensities for interferences due to isobaric and some molecular ions. Appropriate calibration standards were run periodically interspersing the samples to monitor any loss of efficiency due to instrumental drift, etc.

Potentiometric stripping analysis was performed with a TraceLab system, a Sample Changer SAM 80 and a triburette (all from RADIOMETER, Copenhagen, Denmark).

Digestion of the soil samples

The "total dissolution" of the silicate matrices with HNO₃ + HClO₄ + HF treatment [5–7], requires a time consuming evaporation step at elevated temperatures to remove the perchloric acid and HF, prior to quantitation with ICP-MS. Microwave assisted digestion procedures for such silicate matrices have been reported [12–14] but the analyses were carried out using ICP-OES or GFAAS. The approach presented here is based on an earlier study using pressurized digestions with HNO₃ and "inverse aqua regia" for trace element determinations in soil and sediment samples [15]. The ESB soil samples were homogenized in a titanium mill and a complete digestion with HF and HClO₄ would release more titanium and zirconium into the digest which could affect the determination of copper and cadmium by ICP-MS through the formation of oxide ions. Therefore, pressurized digestion steps that would help to extract ecotoxicologically important elements without the release of much of the refractory elements would be desirable. However, the addition of HF

could be necessary to attack any accessory minerals that may contain significant concentrations of certain trace elements.

Pressurized digestions in closed PTFE vessels have been used to study the recovery of trace elements. About 200 mg of the dry soil sample was weighed into the PTFE vessel. 2 mL of subboiled nitric acid has been added and the closed vessel was assembled into a stainless steel digestion set-up with spring loaded encapsulation, which prevents any loss of acid vapours. These assemblies are then electrically heated on a flat platform initially to 180 °C over a period of 2 h and maintained at that temperature for 3 h. Then heating was stopped and the vessels have been allowed to cool to room temperature, usually overnight.

Upon careful opening of the vessels, the acidic digest as well as the undissolved residue were transferred into a 10 mL volumetric flask, using a polyethylene tip. The content was diluted to 10 mL with deionized water and stored until measurement.

Besides HNO₃, similar digestions were carried out using "inverse aqua regia" (1.5 mL HNO₃ + 0.5 mL HCl) and with a little HF (1.5 mL HNO₃ + 0.5 mL HCl + 0.1 mL HF), respectively. Some digestions were carried out with increasing amounts of HF added to a fixed volume of HNO₃ (2.0 mL) and some with varying amounts of HNO₃ and HF but keeping the total volume of the acids to 2.0 mL. The digests with HF were diluted to 10 mL along with 1.0 mL of 40 mg/mL of boric acid and were stored in polyethylene vials.

Results and discussion

Based on preliminary experiments, 1 mL of the clear supernatant of the acidic digest was diluted to 10 mL with deionized water. The acid blanks which were also carried through the digestion steps were analyzed in the same fashion and the final sample concentrations were corrected for the process blanks.

Recoveries in the different digestion procedures

The values obtained for BCR CRM 141 and BCR CRM 142 for elements with certified concentrations after different acid digestion approaches are presented in Table 1. Table 2 gives the values for these and other elements on

Table 1. Recoveries of trace elements in BCR soil CRMs determined by ICP-MS (mg/kg)

Element	HNO ₃		HNO ₃ + HCl + HF		Certified values	
	BCR CRM-141	BCR CRM-142	BCR CRM-141	BCR CRM-142 ^a	BCR CRM-141	BCR CRM-142
Co	10.9	8.7	11.7	8.4 ± 0.2	(9.2)	(7.9)
Cu	32.4	25.2	33.9	24.8 ± 0.5	32.6 ± 1.4	27.5 ± 0.6
Zn	77.9	87.3	82.6	87.4 ± 1.4	81.3 ± 3.7	92.4 ± 4.4
Cd	0.36	0.28	0.37	0.31 ± 0.006	0.36 ± 0.10	0.25 ± 0.09

^a Mean and standard deviation based on 5 digestions

Table 2. Recoveries of trace elements in IAEA Lake Sediment SL-1 (mg/kg)

Element	HNO ₃	HNO ₃ + HCl	HNO ₃ + HCl + HF ^a	Certified values
V	156	158	179 ± 1.4	170 ± 15
Cr	107	107	113 ± 2.4	104 ± 9
Co	18.9	18.5	19.4 ± 1.0	19.8 ± 1.5
Cu	29.2	30.4	31.6 ± 0.3	30 ± 5.4
Zn	191	199	218 ± 16	223 ± 10
As	25.0	25.6	29.2 ± 0.9	27.5 ± 2.8
Cd	0.24	0.26	0.29 ± 0.04	0.26 ± 0.05

^a Mean ± SD based on 5 different digestions

IAEA SL 1 lake sediment sample. These values are based on at least two or more repetitive digestions of the same kind. The recoveries of the elements are discussed below.

Vanadium and chromium. Relative to the digestions with nitric acid alone, the addition of HF resulted in an increase in the recoveries of Cr and V (Table 2) in the IAEA SL-1 sediment sample. In digests containing HCl the vanadium values suffer from isobaric interferences due to the formation of ³⁵Cl¹⁶O ions. The equivalent concentration in inverse aqua regia is about 3 mg/kg. Thus a correction for the formation of ³⁵Cl¹⁶O ions needs to be incorporated for the reliable estimation of V by ICP-MS.

Nearly complete recovery of Cr, at levels encountered in IAEA SL-1 sample has been reported by Dolan et al. [7] but in marine sediment samples based on digestions with HF + HClO₄ and HNO₃. However, Stroh and Völlkopf [16] have reported a lower recovery of Cr in a Canadian reference soil sample containing chromite. Lamothe et al. [12] have also made similar observations based on the microwave digestions. Even though the Cr value is not certified in the BCR CRM 142, a value of 74.8 ± 2.2 mg/kg, close to the indicated concentration (74.9 mg/kg) was obtained in our pressurized digestions for CRM 142. Nakashima et al. [13] and Rantala and Loring [14] have also reported complete recoveries of Cr in the marine sediment reference sample MESS-1. Thus satisfactory recoveries of Cr could be obtained in samples where Cr is not present as chromite. But in samples containing chromite it would be necessary to completely dissolve the samples.

Cobalt, copper, zinc, cadmium. Consistent recoveries were obtained for these elements in all digestion procedures, with very good agreement with the certified concentrations for the lake sediment sample (Table 2). In CRM 142 slightly lower values for Cu and Zn were found. However the Zn contents determined after HNO₃ digestion with ICP-AES were in close agreement with the certified values. A similar and somewhat lower content for Zn was estimated by ICP-MS on the NIST 1645 River Sediment. The quantitative estimation of Zn by ICP-MS is being investigated further. Cadmium recoveries were nearly quantitative in HNO₃ as well as in other acid mixtures.

Nickel. The apparent recoveries of nickel in the various acid mixtures were 8–10% higher than the certified values for the CRMs. Interferences caused by the molecular ions of CaO and CaOH on the ICP-MS determination of transition elements, in particular Ni, have been studied by

Vaughan and Templeton [17]. They have proposed a principal component analysis approach to correct for such interferences.

After recalculating the nickel concentrations of our samples based on ⁶⁰Ni with a correction for the ⁴³CaOH species, the values were in very close agreement with the certified values of BCR CRM 142 (Light sandy soil), IAEA SL 1 (Lake sediment) and NIST 1645 (River sediment). But this correction was found to be inadequate for BCR 141, a calcareous loam soil with 12.9% calcium. Table 3 gives the Ni concentrations before and after corrections, together with the Ca concentrations in the acid digests of the CRMs.

Arsenic. Complete recovery of As was obtained in all the different digestion studies for the IAEA sediment SL 1 (Table 2). Even though media containing chloride or HCl are considered unsuitable for the As determination by ICP-MS due to the interference from ⁴⁰Ar³⁵Cl molecular ions [4], the corrections provided by the software were found to be satisfactory in these determinations.

Lead. The recoveries of Pb in the various digestions for the reference samples are shown in Table 4. It is of interest to note that the soil samples showed an increase in the recovery of Pb in the presence of HF. No such increase has been found in the two sediment samples which illustrates the difference in the constituents holding Pb in soils and sediments. It is possible that part of Pb in soil samples may be present in some refractory minerals such as zircon, which are known to incorporate Pb and may not be completely attacked by HNO₃ even under pressurized conditions. While the recovery of Pb in CRM 142 and IAEA SL-1 samples in digestions containing HF are satisfactory, the values were lower in NIST river sediment SRM 1645.

Table 3. Correction for nickel concentrations based on calcium content (mg/kg)

CRM	Ca content (%)	Conc. of Nickel		Cert. values
		Observed	Corrected	
BCR 141	12.89	38.0	34.4	(30.9)
BCR 142	3.53	34.0	30.1	29.3 ± 2.5
IAEA-SL1	0.25	48.3	45.0	44.9 ± 7.6
NIST-1645	(2.9)	49.3	45.6	45.8 ± 2.9

Table 4. Recoveries of Pb in different digestions (mg/kg)

Digestion	CRM 142	NIST 1645	SL-1	ESB Soil 1
2 ml HNO ₃	29.4	665	36.2	119
2 ml HNO ₃ + 0.1 ml HF	34.4	–	36.7	145
2 ml HNO ₃ + 0.5 ml HF	36.3	–	–	143
1.5 ml HNO ₃ + 0.5 ml HCl	34.1	672	36.9	126
1.5 ml HNO ₃ + 0.5 ml HCl + 0.1 ml HF	–	666	37.7	135
Certified values	37.8 ± 1.9	714 ± 28	37.7 ± 7.1	–

Effects of HF in the digests

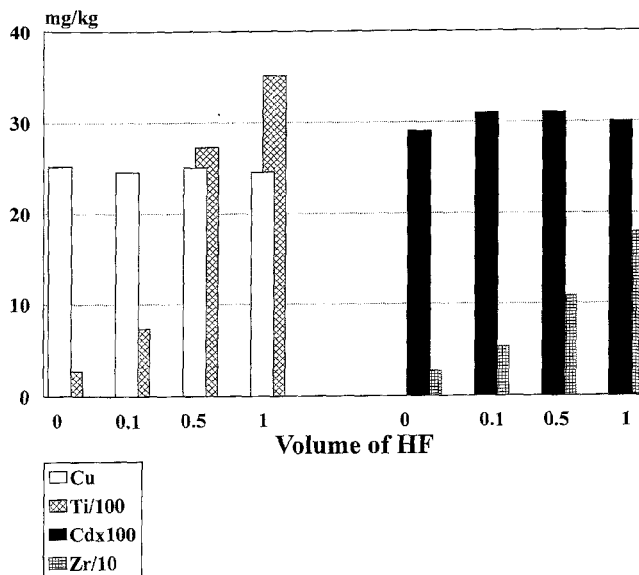
In digestions with HNO₃ + HF mixtures, increasing the amount of HF in excess of 0.5 mL, while keeping the volume of acids to 2 mL, was found to lower the recovery of Mg, Sr, Ba and Th. While a small quantity of HF (typically 100 µL) was found to release more of these elements, further increase in the amount of HF resulted in a decrease, possibly due to the precipitation of fluorides. Similar results were obtained when increasing amounts of HF were added to a constant volume of HNO₃ (2 mL). This precipitation, however, was not found to influence the recovery of the elements discussed above.

The recovery of Sn and Sb in digestions with nitric acid were found to be low and inconsistent. Addition of HCl/HF showed increased and stable recoveries. The BCR soil CRMs were not certified for Sn or Sb. On the IAEA SL-1 sediment sample, a value of 3.5 ± 0.2 mg/kg for Sn was obtained in digestions with HNO₃ + HCl + HF (indicated value 4 mg/kg) but the value for Sb was lower (0.74 ± 0.05 mg/kg) than the certified value of 1.31 ± 0.21 mg/kg.

Increasing the amounts of HF released increasing amounts of Ti and other refractory elements like Zr. The formation of TiO molecular ions (⁴⁷Ti¹⁶O and ⁴⁹Ti¹⁶O, two minor isotopes of Ti) could in principle affect the estimation of Cu but the formation of TiO species is reported to be dependent of the nebulizer gas flow rate [5]. In our digests with increasing amounts of HF (0.1, 0.5 and 1.0 mL) added to 2 mL HNO₃, the increased amounts of Ti released were not found to influence the estimated Cu concentrations in the digests, indicating the formation of TiO species was insignificant under the operating conditions of our instrument (nebulizer flow rate of 0.8 L/min). Further, the two potential interfering isotopes of Ti being of minor abundance, their influence on the Cu estimation could be well under the variability of Cu concentration itself. Similarly, the estimation of Cd was also not found to be influenced by the increased amounts of Zr released into the digest with increasing amounts of HF. These aspects are illustrated in Fig. 1.

Analysis of ESB soil samples

Homogeneity studies. Elemental recovery studies based on the CRMs indicated that the digestion with nitric acid can be used for evaluation of the homogeneity of the ESB soil samples with respect to many of these elements. Therefore, it was decided to examine the sample homogeneity by analyzing an aliquot from each of the 25 vials per sample, based on digestion with HNO₃.

**Fig. 1.** Influence of HF in the digest to the determination of Cu and Cd**Table 5.** Test for homogeneity by ICP-MS measurements. Mean and standard deviation ($n = 25$ digestions, HNO₃), mg/kg

Element	ESB Soil 1	ESB Soil 2
Co	7.2 ± 0.3	5.3 ± 0.2
Ni	31.3 ± 1.2	26.6 ± 1.6
Cu	21.6 ± 0.8	14.4 ± 0.8
Zn	100 ± 4	62 ± 3.4
Cd	0.41 ± 0.02	0.21 ± 0.02
Ti	0.49 ± 0.02	0.53 ± 0.04
Pb	124 ± 3	89.7 ± 6.3

The mean values along with the standard deviations for the two ESB soils are given in Table 5. The RSDs for the determinations in ESB soil 1 are better than 4% for many elements, except for Cd (5.6%). The RSDs for the determinations on ESB soil 2 range from 4 to 7% with again Cd with 10%, indicating that it is slightly less homogeneous than ESB soil 1.

The concentrations of Pb in the soil digests were also determined using potentiometric stripping analysis (PSA). Mean values of 129 mg/kg (RSD = 7%) and 89 mg/kg (RSD = 9%) were obtained for the two ESB samples which are in very good agreement with those obtained by ICP-MS, using digestions with HNO₃ (Table 5).

A comparison of the values obtained based on total digestion with HNO₃ + HClO₄ + HF and pressurized

Table 6. Comparison of acid digestions for ESB Soil 1 (mg/kg)

Element	HNO ₃ + HCl + HF	Total digestion
Cr	61.5	63.1
Co	7.5	7.8
Ni	29.4	30.7
Cu	22.6	24.9
Zn	111	112
Cd	0.41	0.44
Sn	3.4	3.8
Sb	1.7	1.6
Tl	0.62	0.63
Pb	135	130

digestion with HNO₃ + HCl + HF (1.5 mL + 0.5 mL + 0.1 mL) on the ESB soil 1 is given in Table 6. The values are based on duplicate digestions. The close agreement of the values for many elements indicate that pressurized digestion with a small aliquot of HF (usually 100–200 µL) along with nitric acid and HCl in inverse aqua-regia proportions is quite suitable for the extraction and quantitation with ICP-MS for many elements of environmental interest in the soil samples.

Conclusions

The homogeneity studies have shown that the sample preparation steps adopted in the ESB are capable of providing soil samples of acceptable homogeneity for trace element analysis. The elemental recovery studies on the CRMs indicate that pressurized digestion with nitric acid is suitable for the analysis of As, Cd, Co, Cu and Zn. For the complete recovery of Cr and Pb, an addition of a little aliquot of HF is essential. Digestions with nitric acid alone is not suitable for the recovery of Sn and Sb. In calcareous soils, the determination of Ni with ICP-MS would require elaborate corrections. With appropriate software corrections ICP-MS is capable of providing rapid, reliable and quantitative estimates for many trace elements of environmental interest.

The nearly complete recovery of many trace elements under acidic digestion conditions which are known to incompletely dissolve the silicate or refractory minerals under open digestion conditions suggests that pressurized digestion conditions are capable of releasing the fraction of trace elements bound to these fractions also. The release of additional Pb with HF clearly indicates their presence in refractory mineral phases in the soil samples.

While the total contents of trace elements in soil samples is merely a pointer to potentially contaminated sites, the release of toxic elements under milder chemical conditions would be of greater interest from the point of view of environmental concern. Further work in this direction is in progress.

Acknowledgements. The strong and generous support from the International Bureau of the Research Center of Jülich for J.A. is greatly appreciated. Soil collection by colleagues of the Institute of Biogeography, University of Saarland, and sample homogenisation by J.D. Schlodot and F. Backhaus (Research Center of Jülich) are gratefully acknowledged. Part of this work was supported by the German ESB program of the Federal Ministry of the Environment, Nature Conservancy and Reactor Safety via the German Federal Environmental Agency.

References

1. Stoeppler M, Dürbeck HW, Nürnberg HW (1982) *Talanta* 29:963–972
2. Rossbach M, Schlodot JD, Ostapczuk P (eds) (1992) *Specimen banking environmental monitoring and modern analytical approaches*. Springer, Berlin Heidelberg New York
3. Schlodot JD, Stoeppler M, Kloster G, Schwuger MJ (1992) *Analisis* 20:45–49
4. Horlick G, Shao Y (1992) In: Montaser A, Golightly DW (eds) *Inductively coupled plasmas in analytical atomic spectrometry*, 2nd ed. VCH Publications, New York
5. McLaren JW, Beauchemin D, Berman SS (1987) *J Anal Atomic Spectr* 2:277–281
6. McLaren JW, Beauchemin D, Berman SS (1988) *Spectrochim Acta* 43B:413–420
7. Ross D, Loon JV, Templeton D, Paudyn A (1990) *Fresenius J Anal Chem* 336:99–105
8. Date AR (1991) *Spectrochim Acta Rev* 14:3–32
9. Hall GEM (1992) *J Geochem Explor* 44:201–249
10. Sprengart J, Wagner G (1993) SOP for soil sampling and preparation. Internal report of University of Saarland
11. Schlodot JD, Backhaus F (1988) *Progress in environmental specimen banking*. NBS Special Publication 740: 184–194
12. Lamothe PJ, Fries TL, Consul JJ (1986) *Anal Chem* 58:1881–1886
13. Nakashima S, Sturgeon RE, Willie SN, Berman SS (1988) *Analyst* 113:159–163
14. Rantala RTT, Loring DH (1989) *Anal Chim Acta* 220:263–267
15. Breder R (1982) *Fresenius Z Anal Chem* 313:395–402
16. Stroh A, Völlkopf U (1993) *Atomic Spectr* 14:76–79
17. Vaughan MA, Templeton DM (1993) *Appl Spectr* 44:1685–1689