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Comparison of microwave-assisted acid leaching techniques for the determination of heavy metals in sediments, soils, and sludges

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Abstract Microwave-assisted EPA method 3051 for nitric acid leaching of environmentally key elements from sediments, soils, and sludges was tested, and the influence of leaching temperature and time on element recovery for an estuarine sediment (CRM 277) was investigated. The extraction efficiencies for four certified reference materials applying EPA method 3051, an optimized nitric acid procedure, and an *aqua regia* (HCl/HNO_3 3:1) procedure were compared. Digestions were carried out in a high-pressure microwave system offering simultaneous temperature and pressure control for all digestion vessels employed. Eight elements (Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn) were determined by ICP-AES and ICP-MS. Extraction efficiency strongly depended on the applied leaching parameters and varied for certain elements among different materials when a nitric acid procedure was applied. In general, element recoveries obtained from the *aqua regia* procedure were superior to those obtained from nitric acid procedures and showed good agreement with the 95% confidence interval of the certified value for most of the elements investigated.

Introduction

Environmental pollution is one of the most effective factors in the destruction of the biosphere components. Among all chemical contaminants trace elements, especially heavy metals, are believed to be of a specific ecological, biological and health significance. Elements considered to be of great environmental risk include Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn [1]. The occurrence and cycles of trace elements in the environment as well as pathways in plants, food and animals are subject of investigation [2]. Especially the heavy metal content of sediments, soils and sludges poses possible contamination of the human food chain. As a result, the number of environmental samples and the importance for their analysis is growing continuously.

The major compounds of sediments and soils are clay and carbonate minerals, oxides, and organic matter. In general, trace metals are bound by sorption mechanisms such as organic complexation, specific adsorption, precipitation, and ion exchange [3]. For the exact determination of trace elements using the most common analysis methods such as flame- and graphite furnace atomic absorption spectroscopy (FAAS, GFAAS), inductively coupled plasma-atomic emission and -mass spectrometry (ICP-AES, ICP-MS), transforming the solid sample into a solution is usually necessary. Hence, a sample digestion carried out in a heated mixture of mineral acids [4–6] or by a fusion [4, 5] followed by dissolution in dilute acids has to be applied.

In environmental analytical chemistry acid leaching has become a common procedure to extract metals from various sample matrices. In general, leaching methods employing HNO_3 or $HCl+HNO_3$ mixtures do not extract total quantities of heavy metals from geological materials, because wet digestion methods excluding HF do not attack the alumosilicate matrix [7–14]. However, for a number of environmental studies extractable rather than total element concentrations give better information on the mobility of heavy toxic metals and their bioavailability [1]. Furthermore, leaching procedures are rapid, easy to perform, and avoid handling hazardous HF solutions. Additionally, HF may degrade glass ware and adulterate analytical results. Therefore, removal of HF or its complexation with H_3BO_4 is required, causing additional digestion steps.

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To improve the time-consuming, conventional hot plate techniques, microwave heating was introduced successfully in wet digestion procedures. Considerable reduction of decomposition time for various matrices [8, 15–17] and an improvement in precision [9, 14] were reported. The application of closed pressurized vessels in combination with microwave heating offers a number of advantages and thus, is state of the art for wet digestion [18].

In this paper we report acid leaching techniques for the determination of heavy metals in sediment, soil, and sludge certified reference materials using a high-pressure microwave digestion system, offering simultaneous pressure and temperature control for each of the six digestion vessels [19]. With 50 mL, thick-wall silica vessels reaction pressures up to $72 \cdot 10^5$ Pa can be achieved, resulting in a maximum leaching temperature of approximately 250 °C. Thus, compared to the EPA method 3051 [20] recommended leaching temperature of 175 ± 5 °C for nitric acid, considerably higher temperatures can be achieved. The influence of applied leaching temperature and time on element recoveries for an estuarine sediment was investigated. Following this, an optimized nitric acid and an *aqua regia* procedure were established (defined in Table 1). Element recoveries for four certified reference materials (CRM) were compared for the slightly modified EPA method 3051, optimized nitric acid, as well as the *aqua regia* procedures. Finally, spike recoveries were determined for two certified reference materials applying slightly modified EPA method 3051.

Experimental

Reagents

Nitric acid (69.5%) and hydrochloric acid (37.5%) were obtained from Fisher Chemical (A.C.S. Plus Reagent Grade, Fisher, Pittsburgh, PA). Nitric acid was subboiled distilled before use, using a quartz still. Hydrofluoric acid (48%) was obtained from EM Science (GR Reagent Grade, AWC Inc., Mobile, AL). Standard solutions for Cd, Co, Cr, Cu, Hg, Pb, Rh and Tl were prepared from 1000 µg mL^{-1} (2% HNO_3) standard solutions (SPEX Plasma Standard, SPEX, Metuchen, NJ). For Hg also a 10 µg mL^{-1} (2% HNO_3) solution was used (SPEX Plasma Standard). Standard solutions for Ni and Zn (1000 µg mL^{-1}) were prepared in-house by dissolving 0.6363 g of NiO/500 mL and 0.2500 g of Zn/250 mL in 2% HNO_3, respectively. All solutions were diluted with distilled, deionized (18.2 $M\Omega cm^{-1}$) water. The certified reference materials, CRM 142 (light sandy soil), CRM 144R (domestic origin sewage sludge), CRM 277 (estuarine sediment), and CRM 320 (river sediment), were obtained from the European Commission Joint Research Center (Institute for Reference Materials and Measurements (IRMM), B-2440 Geel, Belgium).

Instrumentation

The high-pressure microwave sample preparation studies were performed using the Multiwave-system (Anton Paar GmbH, Graz, Austria, and Perkin Elmer, Norwalk, CT). This system features a 1000 W magnetron operating at a frequency of 2450 MHz. For the analysis of element concentrations the following instruments were employed: for ICP-AES a Spectroflame ICP D (Spectro Analytical Instruments, Fitchburg, MA), fitted with a glass Meinhard nebulizer and double pass Scott type spray chamber, and for ICP-MS a PE-Sciex Elan 5000a (Perkin Elmer, Norwalk, CT), fitted with a Ryton cross-flow nebulizer and double pass Scott type spray chamber.

Digestion techniques

Temperature-controlled, nitric acid leaching method EPA 3051 was slightly modified (method parameters are listed in Table 1). To achieve elevated reaction temperatures (~250 °C) and pressures ($72 \cdot 10^5$ Pa) 50 mL thick-wall silica digestion vessels were employed. With 50 mL vessels the recommended acid volume of 10 mL (for 120 mL PFA or TFM vessels) was reduced to 5 mL to avoid a considerable decrease of the reaction volume. Maximum reaction pressure (P_{max}) was adjusted to $72 \cdot 10^5$ Pa instead of the recommended value of $7.5 \pm 0.7 \cdot 10^5$ Pa. A simple microwave heating program was applied. The control-temperature was programmed to 175 °C and maximum microwave power was applied from the beginning. If the temperature of one of the six vessels exceeded the programmed value, the power was regulated automatically and temperature was held constant for the remaining digestion time. During the heating period (10 min) the exhaust fan was adjusted to 25% of its maximum power, during the following cooling period (10 min) it was operated at maximum power. Each digestion run included four to five samples and one blank.

The influence of temperature on element recovery was investigated for a nitric acid leaching procedure. The control-temperature was increased stepwise starting at 155 °C to 175 °C, 195 °C, and the highest possible temperature. Consequently, digestion temperature was adjusted to lower as well as to considerably higher values than recommended by EPA method 3051. Digestion time (10 min) was kept constant for all experiments. The maximum temperature (T_{max}) was achieved using the pressure control mode. In this case microwave power was not regulated, unless one of the vessels reached a reaction-pressure of $72 \cdot 10^5$ Pa. The pressure was maintained for the remaining digestion time. In this mode leaching temperatures increased continuously during the digestion and reached up to 250 °C (for t = 25 min).

The influence of leaching time on element recovery was investigated by increasing the digestion time stepwise (5 min, 10 min, 15 min, and 25 min). Again, digestion time was adjusted to lower as well as to considerably higher values than recommended by EPA method 3051. The control-temperature (175 ± 5 °C) was kept constant for all experiments.

An optimized nitric acid and an *aqua regia* procedure were established for the comparison of extraction efficiency among different leaching approaches for four certified reference materials. The operating parameters applied are listed in Table 1.

Table 1 Modified EPA method 3051 and the established acid leaching procedures

Parameter	Modified EPA 3051	Optimized nitric acid procedure	*Aqua regia* procedure
Vessel	50 mL silica	50 mL silica	50 mL silica
(P_{max})	$72 \cdot 10^5$ Pa	$72 \cdot 10^5$ Pa	$72 \cdot 10^5$ Pa
Sample	250 mg	250 mg	250 mg
Acid	HNO_3	HNO_3	$HCl:HNO_3$ 3:1
Acid volume	5 mL	5 mL	4 mL
Heating time	10 min	25 min	25 min
Cooling time	10 min	15 min	15 min
T_{max}	175 ± 5 °C	~250 °C	~250 °C
Control mode	Temperature	Pressure	Pressure

Sample preparation

Certified reference materials were not oven-dried prior to digestion to prevent loss of volatile compounds and possible contamination. The element concentrations measured were based on dry weight after correcting for moisture content determined from separate subsamples dried in an oven for 48 h at 60 °C.

An aliquot of 250 ± 1 mg of sample was transferred into each vessel, and 5 mL of nitric acid was added slowly in a fume hood. To allow immediately occurring reaction gases to escape and to provide a homogeneous sample+acid mixture, the vessels were agitated carefully for 5 to 10 s before sealing. Samples were heated following the microwave program established for EPA method 3051. Upon finishing the digestion step, each vessel was carefully opened in a fume hood at ambient temperature to release the reaction pressure. This precaution is important especially for samples such as sludges that contain a high organic fraction. After the escape of the majority of the brown NO_x-vapor, the sample solutions including the solid residuals (alumosilicates) were transferred quantitatively into 10 mL polyethylene (PE) tubes. The solutions were centrifuged for 3 min at 5000 rpm. The supernatants were transferred to 50 mL polyethylene vessels. The solid residuals were washed twice, silica digestion vessel were rinsed three times with distilled, deionized water. The washing solutions were collected and added into the volumetric flasks. Finally, the digests were diluted to 50 mL using distilled, deionized water. Blanks were processed in the same way as samples.

For the investigation of spike recoveries for two certified reference materials, an aqueous multi-element standard solution containing 20 to 80 μg/mL of each element was prepared. To an aliquot of 250 ± 1 mg of sample exactly 250 μL of the aqueous spike solution was added. The mixture was agitated to provide a homogeneous slurry and equilibrated for 1 h prior to digestion by the slightly modified EPA method 3051 (Table 1).

Cleaning

Polyethylene vessels were soaked in HNO_3 1:10 (v/v) for 48 h, rinsed carefully with distilled, deionized water, oven-dried, and stored in clean polyethylene bags. Between digestion runs for the same sample, vessels were rinsed with HF 1:10 (v/v) to dissolve the remaining silica deposits, rinsed several times with distilled, deionized water, 2 mL HNO_3, and again several times with distilled, deionized water. After finishing this treatment vessels were ready for the next digestion run. Between digestion runs for different samples, vessels were cleaned additionally by adding 3 mL of HNO_3 and performing a pressure controlled digestion lasting for 10 min.

Analysis

All analyses were carried out with a matrix solution containing nitric acid diluted 1:10 (v/v). A linear calibration with up to five multi-element standards was prepared. Samples were diluted according to the calibrated range. Measurements were carried out with internal standardization. For ICP-MS rhodium (50 ng mL^{-1} Rh) was used as the internal reference element for Cd, Co, Cr, Cu, Ni, and Zn, and thallium (50 ng mL^{-1} Tl) was used as the internal reference element for Hg and Pb. For ICP-AES yttrium (500 ng mL^{-1} Y) was used as the internal reference element for Cr, Cu, Ni, Pb, and Zn. Reported concentrations for the internal reference elements were final concentrations in the analytical solution. The calibration was verified by measuring control standards periodically.

Results and discussion

Leaching temperature

The results of metal analysis for the investigation of the influence of leaching temperature on element recovery for an estuarine sediment (CRM 277) upon applying a nitric acid procedure are listed in Table 2. Elements could be classified into two groups. One group included elements that were leached almost quantitatively and the other one, elements that showed low recoveries. The concentrations obtained for Cd, Pb, and Zn fell within the 95% confidence interval of the certified values; Cu concentrations fell slightly below. The variation of the applied leaching temperature had no significant influence on the extraction recovery for these elements. The second group included Cr, Ni, and Hg. Particularly for Cr and Ni recoveries were strongly dependent on the applied leaching temperature (significance tests, $\alpha = 0.05$). With increasing temperature considerably higher extraction efficiencies could be achieved. The percent element recovery for Cr increased from 72.4% (for 155 °C) to 87.5% (for 230 °C), and for Ni from 80.4 to 90.1%, respectively. The variation of determined Hg concentrations was more likely caused by random deviation or losses than by the lower recovery. In general, the largest confidence intervals were observed for the highest applied leaching temperature. Therefore, higher temperatures resulted in better recoveries for some elements, but in addition random variation was slightly increased. This indicated that at very high temperatures the alumosilicate matrix was partly attacked by nitric acid and resulted in higher recoveries for Cr and Ni. However, during dilution following the digestion a white precipitate (silicates) occurred. Solid residuals together with the precipitate were removed by centrifugation and did not adulterate analytical results.

Table 2 Element concentration and applied leaching temperature for CRM 277[a] (estuarine sediment)

	155 °C ($n = 4$)[b] mg kg^{-1}	175 °C ($n = 5$) mg kg^{-1}	195 °C ($n = 5$) mg kg^{-1}	~230 °C ($n = 4$) mg kg^{-1}	*Aqua regia* soluble [c] mg kg^{-1}	Certified value mg kg^{-1}
Cd	11.3 ± 0.1[d]	11.6 ± 0.1	11.6 ± 0.3	11.4 ± 0.3	10.8	11.9 ± 0.4
Cr	139 ± 2	146 ± 1	154 ± 1	168 ± 5	145.6	192 ± 7
Cu	96.0 ± 1.0	96.3 ± 1.0	98.0 ± 2.5	97.6 ± 2.6	97.2	101.7 ± 1.6
Hg	1.57 ± 0.05	1.63 ± 0 .03	1.45 ± 0.04	1.53 ± 0.05	na[e]	1.77 ± 0.06
Ni	34.9 ± 0.4	36.1 ± 0.4	37.5 ± 0.6	39.1 ± 1.1	34.9	43.4 ± 1.6
Pb	145 ± 2	145 ± 5	149 ± 2	144 ± 6	137.5	146 ± 3
Zn	544 ± 6	550 ± 9	557 ± 5	555 ± 14	557	547 ± 12

[a] 250 mg sample, 5 mL HNO_3, t = 10 min

[b] Number of replicates

[c] Recommended values, given by IRMM

[d] 95% confidence interval

[e] Not available

Table 3 Element concentration and applied leaching time for CRM 277[a] (estuarine sediment)

	5 min (n = 4)[b] mg kg^{-1}	10 min (n = 5) mg kg^{-1}	15 min (n = 4) mg kg^{-1}	25 min (n = 4) mg kg^{-1}	*Aqua regia* soluble[c] mg kg^{-1}	Certified value mg kg^{-1}
Cd	11.4 ± 0.1[d]	11.6 ± 0.1	11.4 ± 0.2	11.4 ± 0.1	10.8	11.9 ± 0.4
Cr	138 ± 5	146 ± 1	150 ± 1	159 ± 2	145.6	192 ± 7
Cu	94.2 ± 2.9	96.3 ± 1.0	93.3 ± 1.4	96.7 ± 2.2	97.2	101.7 ± 1.6
Hg	1.62 ± 0.03	1.63 ± 0.03	1.60 ± 0.03	1.59 ± 0.01	na[e]	1.77 ± 0.06
Ni	35.5 ± 1.0	36.1 ± 0.4	37.9 ± 0.4	38.7 ± 0.5	34.9	43.4 ± 1.6
Pb	144 ± 4	145 ± 5	144 ± 1	142 ± 2	137.5	146 ± 3
Zn	533 ± 7	550 ± 9	535 ± 6	544 ± 10	557	547 ± 12

[a] 250 mg sample, 5 mL HNO_3, T_{max} = 175° C

[b] Number of replicates

[c] Recommended values, given by IRMM

[d] 95% confidence interval

[e] Not available

Table 4 Element concentrations for 3 leaching procedures, CRM 142 (light sandy soil)

	Modified EPA 3051 (n = 4)[a] mg kg^{-1}	Optimized HNO_3 (n = 4) mg kg^{-1}	*Aqua regia* (n = 4) mg kg^{-1}	*Aqua regia* soluble[b] mg kg^{-1}	Certified value mg kg^{-1}
Cd	0.30 ± 0.01[c]	0.31 ± 0.01	0.30 ± 0.01	0.22	0.25 ± 0.09
Co	9.1 ± 0.1	9.2 ± 0.2	9.3 ± 0.3	na[d]	7.9[b]
Cr	49.1 ± 1.6	71.7 ± 1.8	72.1 ± 4	44.4	74.9[b]
Cu	25.6 ± 0.6	25.4 ± 0.7	26.3 ± 0.7	25.3	27.5 ± 0.6
Hg	0.115 ± 0.016	0.118 ± 0.027	0.110 ± 0.018	na[d]	0.104 ± 0.012
Ni	26.6 ± 1.0	26.2 ± 0.2	28.7 ± 1.0	28.9	29.2 ± 2.5
Pb	28.7 ± 0.4	29.7 ± 1.4	31.7 ± 1.4	30.9	37.8 ± 1.9
Zn	85.7 ± 1.8	86.9 ± 1.5	86.9 ± 2.4	80	92.4 ± 4.4

[a] Number of replicates

[b] Recommended values, given by IRMM

[c] 95% confidence interval

[d] Not available

Leaching time

Results for different leaching times are listed in Table 3. Almost the same effects as for leaching temperature were observed. Elements could be classified into the same groups. Recoveries for Cr and Ni showed a considerable dependence on the leaching time. Again significance tests ($\alpha = 0.05$) showed that recovery rates for Cr (71.9–82.8%) and Ni (81.8–89.2%) were increased by the leaching time. However, the influence of leaching time on element recovery seemed to be less pronounced than that of applied leaching temperature. For the remaining elements a close distribution of recoveries was observed for various leaching times. The concentrations determined fell within the same range as those observed for different leaching temperatures. The random variation for Hg was decreased, whereas that for Cu and Zn were slightly increased. The confidence intervals were not increased with longer leaching times.

For a minimum temperature of 175 °C and a minimum time of 10 min recoveries for all elements except Cu and Zn (recommended leaching value > certified value) were equal to or significantly higher than the *aqua regia* soluble values recommended by IRMM [21]. These *aqua regia* values should give an idea only of the extractable concentration range and were determined with a conventional hot plate technique following the DIN ISO 11466 procedure [22]. Longer leaching times resulted in better recoveries for some elements (Cr, Ni) and did not increase the confidence intervals of any of the investigated elements. Therefore, besides different leaching medium and higher temperature, extended digestion time compared to EPA method 3051 was included in the alternative procedures developed.

Comparison of three different leaching procedures

The analysis results for leaching procedures, described in Table 1, for each certified reference material analyzed are listed in the Tables 4–7. According percent element recoveries for each sample are shown in Fig. 1. Element recoveries were not quantitative for leaching techniques. The best extraction efficiency was achieved with the *aqua regia* procedure for almost all elements and materials investigated. Particularly for Co, Cr, Hg, Ni, and Pb this technique yielded considerably higher extraction recoveries compared to the nitric acid procedures (e.g., Table 7). Concentrations obtained for the *aqua regia* procedure for Cd, Co, Cu, Hg, and Zn fell within or close to the certified range for all sample matrices selected. In general, concentrations for almost all elements were significantly higher (95% confidence level) than the IRMM recommended *aqua regia* soluble values or fell within its certified range (CRM 144R). Confidence intervals were not increased for high temperature digestions when applied leaching times were slightly increased.

Element concentrations obtained by using the optimized nitric acid procedure were equal to or higher than those obtained with modified EPA method 3051. Again higher temperature resulted in much better recoveries for Cr, whereas for Ni this effect was only significant for CRM 277. Depending on the silicate matrix slightly higher element recoveries were also achieved for Co, Pb or Zn (Tables 4, 5, and 7). Concentrations for Cd, Cu, Hg, and Zn fell close to the certified range; those for Cr, Ni, and Pb were considerably lower.

A comparison of the extraction efficiency of EPA method 3051 with that of the *aqua regia* procedure for the

Table 5 Element concentrations for 3 leaching procedures, CRM 144R (domestic origin sewage sludge)

	Modified EPA 3051 (n = 4)[a] mg kg^{-1}	Optimized HNO$_3$ (n = 4) mg kg^{-1}	*Aqua regia* (n = 4) mg kg^{-1}	Certified value *aqua regia* soluble mg kg^{-1}	Certified value mg kg^{-1}
Cd	1.71 ± 0.10[b]	1.73 ± 0.06	1.59 ± 0.07	1.84 ± 0.07	1.82 ± 0.10
Co	14.6 ± 0.2	14.9 ± 0.3	15.6 ± 0.6	13.3 ± 0.5	15.0 ± 0.6
Cr	91.8 ± 3	95.0 ± 3	100 ± 2	na[c]	104 ± 3
Cu	292 ± 7	291 ± 9	294 ± 8	300 ± 11	308 ± 7
Hg	3.25 ± 0.21	3.17 ± 0.18	3.53 ± 0.42	3.12 ± 0.17	3.14 ± 0.23
Ni	39.6 ± 1.1	40.3 ± 2.7	43.0 ± 0.5	44.9 ± 1.5	47.7 ± 1.1
Pb	95.5 ± 2	96.0 ± 2	102 ± 3	96.0 ± 1.5	106 ± 4
Zn	899 ± 12	902 ± 23	896 ± 21	919 ± 16	932 ± 23

[a] Number of replicates
[b] 95% confidence interval
[c] Not available

Table 6 Element concentrations for 3 leaching procedures, CRM 277 (estuarine sediment)

	Modified EPA 3051 (n = 5)[a] mg kg^{-1}	Optimized HNO$_3$ (n = 5) mg kg^{-1}	*Aqua regia* (n = 4) mg kg^{-1}	*Aqua regia* soluble[b] mg kg^{-1}	Certified value mg kg^{-1}
Cd	11.6 ± 0.1[c]	11.5 ± 0.2	11.4 ± 0.1	10.8	11.9 ± 0.4
Co	na[d]	na[d]	16.8 ± 0.3	na[d]	17[b]
Cr	146 ± 1	179 ± 2	177 ± 2	145.6	192 ± 7
Cu	96.3 ± 1.0	98.7 ± 1.2	96.2 ± 1.1	97.2	101.7 ± 1.6
Hg	1.63 ± 0.03	1.56 ± 0.03	1.77 ± 0.02	na[d]	1.77 ± 0.06
Ni	36.1 ± 0.4	39.2 ± 0.6	40.9 ± 1.1	34.9	43.4 ± 1.6
Pb	145 ± 5	142 ± 2	143 ± 2	137.5	146 ± 3
Zn	550 ± 9	556 ± 5	533 ± 9	557	547 ± 12

[a] Number of replicates
[b] Recommended values, given by IRMM
[c] 95% confidence interval
[d] Not available

Table 7 Element concentrations for 3 leaching procedures, CRM 320 (river sediment)

	Modified EPA 3051 (n = 5)[a] mg kg^{-1}	Optimized HNO$_3$ (n = 5) mg kg^{-1}	*Aqua regia* (n = 4) mg kg^{-1}	*Aqua regia* soluble[b] mg kg^{-1}	Certified value mg kg^{-1}
Cd	0.468 ± 0.012[c]	0.498 ± 0.004	0.483 ± 0.023	0.47	0.533 ± 0.026
Co	15.2 ± 0.2	17.5 ± 0.2	18.0 ± 1.0	na[d]	19[b]
Cr	64.1 ± 3	97.0 ± 3	111 ± 6	70.1	138 ± 7
Cu	43.2 ± 1.6	42.7 ± 0.5	44.8 ± 1.9	42.0	44.1 ± 1.0
Hg	0.97 ± 0.03	0.96 ± 0.03	1.13 ± 0.07	na[d]	1.03 ± 0.16
Ni	57.1 ± 1.0	57.3 ± 0.7	65.6 ± 3.5	55.0	75.2 ± 1.4
Pb	29.6 ± 0.4	31.8 ± 1.2	33.2 ± 1.2	30.0	42.3 ± 1.6
Zn	123 ± 1	130 ± 2	138 ± 4	124.4	142 ± 3

[a] Number of replicates
[b] Recommended values, given by IRMM
[c] 95% confidence interval
[d] Not available

four certified reference materials investigated is shown in Figs. 2 and 3. Considerable variation in extraction efficiency occurs from one material to the other for certain elements (e.g., Cr and Pb) with the nitric acid leaching medium (Fig. 2). This effect was decreased only slightly by applying higher leaching temperatures. In comparison, leaching with the highly oxidative and complexating reagent *aqua regia* improved element recoveries and provided a more uniform distribution of the extraction efficiency among different sample matrices for all elements, and particularly for Cr (Fig. 3). Thus, *aqua regia* is the more powerful leaching reagent for the extraction of metals from geological samples compared to nitric acid. Element recoveries of 90 to 120% of the total concentrations were obtained for all materials with exceptions for Cr and Pb (CRM 320). Recoveries for Cd and Hg exceeding 100% still fell within the certified ranges as shown in Tables 4, 5, and 7, respectively. The positive error obtained for Co for CRM 142 might indicate a wrong indicative (not certified) value, based on equal analysis results for three individual leaching procedures (Table 4).

Recently, exact temperature control was found to be paramount for achieving reproducible leaching of elements [14]. The relative standard deviation (RSD) of metal concentrations obtained in this study was less than 3% for all elements with exceptions for Cr and Hg. Since the performed digestions were only leaching procedures this precision was excellent and hence, indicated a uniform temperature distribution among the individually controlled digestion vessels.

Only four materials were investigated in this study, therefore it is rather difficult to link extraction rates to the nature of the matrix. However, the results indicated that recovery rates of certain elements (Cr, Ni, Pb) depended

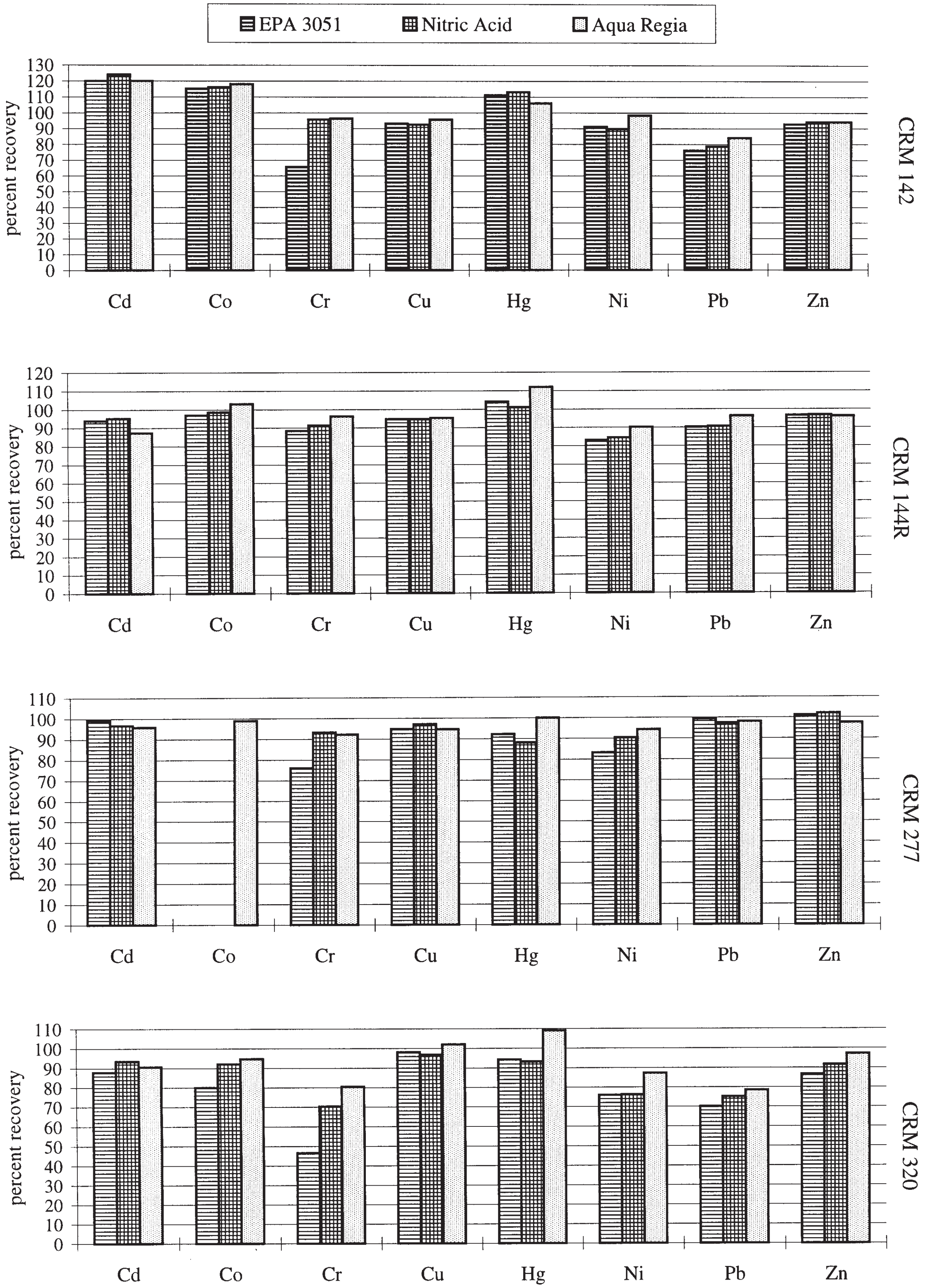

Fig. 1 Comparison of element recovery for three leaching techniques and four different standard reference materials

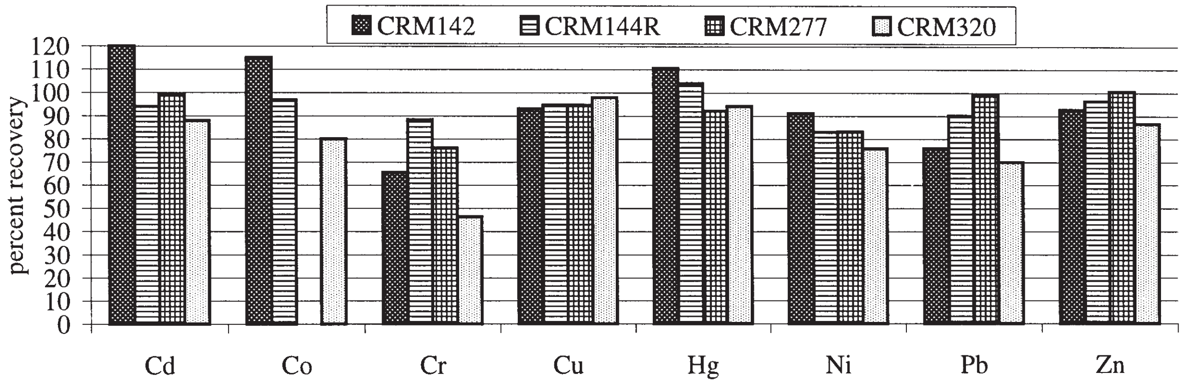

Fig. 2 Comparison of element recovery for four certified reference materials using modified EPA 3051

on the amount and nature of the alumosilicate matrix. The higher this insoluble content, the lower the recoveries for these elements (e.g.; CRM 320). For materials containing a high organic fraction recoveries could be improved (e.g.; CRM 144R). In contrary, elements not necessarily bound to the silicate matrix (Cd, Cu, Hg, Zn) were recovered almost quantitatively and results showed no dependence on the material.

Comparison with other leaching studies

Nitric acid leaching was carried out for soil standard reference materials with different open microwave digestion units by Lorentzen *et al.* [14]. Percent element recoveries obtained for Cd, Cu, Pb, and Zn fell 90% or higher. However, recoveries for Cr (46–59% for NIST 2710 and 32–49% for NIST 2711) and Ni (49–71% for NIST 2710 and 73–83% for NIST 2711) fell considerably lower. Similar results were reported by Hewitt *et al.* [7] when employing a closed microwave system for extraction of NIST 2704. In an investigation of de-Abreu *et al.* [23] *aqua regia*, EPA method 3051, and a $HNO_3/HClO_4$ procedure were compared as leaching media for the metal extraction from agricultural sewage and sediment samples. Correlating to the study presented also *aqua regia* yielded the highest element recoveries. Microwave digestion was based on the method of Nieuwenhuize *et al.* [8]; during a heating period of 65 min a maximum reaction pressure of $8.2 \cdot 10^5$ Pa was allowed. Recoveries for Cr (61%) and Ni (76%) were significantly lower than those reported here. Hence, using a high-pressure digestion device samples could be extracted at elevated temperatures yielding higher recoveries especially for elements embedded in the silicate matrix. Here, decomposition took place at up to 250 °C lasting for 25 min, afterwards digestion vessels were cooled by a fan below 60 °C within 15 min. Compared to other studies [7–17, 23, 24] the small reagent volume (4 mL) reduced the risk of contamination and allowed less dilution after the digestion, resulting in better detection limits. During digestion the reaction temperature was controlled individually for each vessel. The temperature/time graphs recorded by a PC provided useful documentation and quality control for analysis results. As demonstrated in Table 2 recoveries for Cr and Ni strongly depended on the applied leaching temperature. A significant deviation of extraction efficiency was obtained for a temperature difference of 20 °C. Analysis errors due to deviation in leaching temperature among certain vessels will be easily identified by the operator.

Spike recovery

Results for the investigation of spike recoveries for two certified reference materials applying the slightly modified EPA method 3051 are listed in Table 8. Spike recov-

Fig. 3 Comparison of element recovery for four certified reference materials using an *aqua regia* procedure

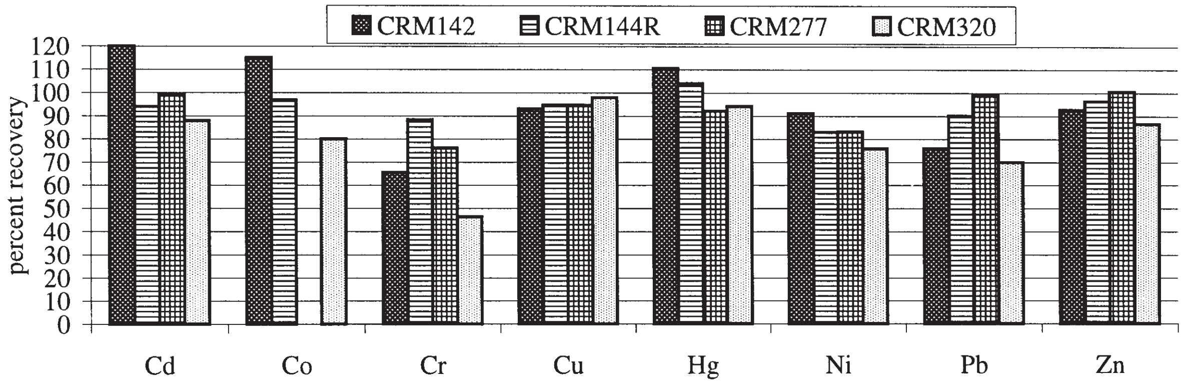

Table 8 Spike recoveries (modified EPA 3051)

	CRM 320 river sediment (n = 5)[a]		CRM 142 light sandy soil (n = 4)	
	Spike (µg)	Recovery (%)	Spike (µg)	Recovery (%)
Cd	5	99 ± 1[b]	10	101 ± 1
Cr	20	100 ± 3	20	98 ± 2
Cu	20	101 ± 1	20	94 ± 2
Hg	5	98 ± 1	10	101 ± 1
Ni	20	99 ± 1	20	96 ± 1
Pb	20	97 ± 1	20	98 ± 2
Zn	20	99 ± 3	20	99 ± 2

[a] Number of replicates
[b] Relative standard deviation

eries were obtained by subtracting the determined mean concentration for each standard reference material (Table 4 and Table 7) from the measured concentration. Excellent spike recoveries and low relative standard deviations were obtained for all elements in both materials. These results indicated the absence of significant bias introduced by matrix interferences. Quantitative recoveries for Hg demonstrate that microwave digestion in closed vessels is an acceptable sample preparation technique for the determination of volatile metals.

Conclusion

High-pressure, microwave-assisted acid leaching methods provided rapid, reliable, and very convenient sample preparation techniques for the screening of hazardous trace metals potentially bioavailable in environmental samples. The dependence of element recovery on applied leaching parameters such as temperature, time, and medium was as expected rather strong. Element recoveries obtained for an *aqua regia* procedure turned out to be superior when compared with an analogous nitric acid procedure and EPA method 3051, especially for elements embedded in the silicate matrix (e.g., Cr, Ni, Pb). Extraction recoveries for different standard reference materials were almost quantitative and close to or within the certified range for the majority of the elements investigated. Precision of analysis results was excellent, an average of 3% RSD was obtained. Finally, the distribution of extraction efficiency among different sample matrices was improved for all elements, and particularly for Cr.

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