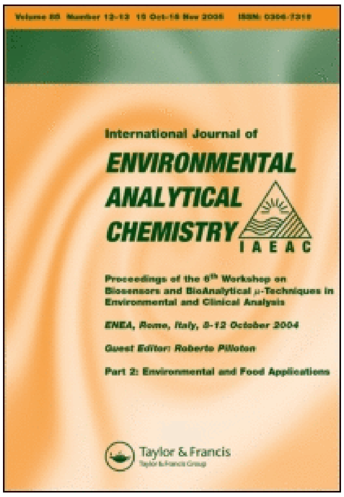

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Väisänen, Ari and Kiljunen, Anne(2005) 'Ultrasound-assisted sequential extraction method for the evaluation of mobility of toxic elements in contaminated soils', International Journal of Environmental Analytical Chemistry, 85: 14, 1037 — 1049

To link to this Article: DOI: 10.1080/03067310500138992

URL: http://dx.doi.org/10.1080/03067310500138992

Intern. J. Environ. Anal. Chem.
Vol. 85, No. 14, 10 December 2005, 1037–1049

Ultrasound-assisted sequential extraction method for the evaluation of mobility of toxic elements in contaminated soils

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(*Received 30 November 2004; in final form 11 March 2005*)

A method for the fast sequential extraction of toxic elements in contaminated soil samples using an ultrasonic water bath, followed by determination with inductively coupled plasma optical emission spectrometry (ICP-OES), was developed and compared with other methods introduced in the literature. The five-step sequential extraction (Tessier scheme) was shortened using ultrasound-assisted sequential extraction (UASE). The optimization of the five-step sequential extraction was based on the analysis of SRM 2710 using Tessiers's method as a reference. Several extracting solutions with different sonication times and temperatures were tested in the optimization procedure. Concentrations of arsenic, cadmium, copper, lead, and zinc were determined in SRM 2710, SRM 2711, and contaminated soil samples with high accuracy and precision. The certified acid-leachable concentrations of the SRM 2710 were obtained for all elements investigated by using an optimized UASE method. Tessiers's method yielded total element concentrations that were too high. The determination of zinc in SRM 2711 yielded concentrations that were too low, whereas arsenic determination yielded concentrations that were too high by the UASE method and analysis by ICP-OES. The analysis of the SRMs showed that the UASE method is highly comparable with the other methods used for such purposes. The major advantages of the UASE method are the high treatment rate (40 samples simultaneously with a sonication time of 54 min) and a low sample and reagent usage.

Keywords: Ultrasound extraction; Toxic elements; Mobility; Contaminated soils

1. Introduction

The increasing industrial use of metals results in the accumulation of trace elements in the atmosphere and the aquatic and terrestrial environment. Potential metal pollutants are mining, metal manufacturing processes, pigment and chemical manufacturing, and combustion of fossil fuels, including the exhaust emissions of motor vehicles [1, 2]. The metal most commonly found at contaminated sites is lead [3]. Toxic elements such as arsenic, cadmium, chromium, copper, mercury, and zinc also play a significant role in soil contamination [2]. It is well known that toxic

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International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online © 2005 Taylor & Francis
DOI: 10.1080/03067310500138992

elements, especially arsenic, cadmium, chromium, and mercury, are potential risks in the environment, even in low concentrations. The most critical areas for the mobility of trace elements in Finland are high permeability sand and gravel formations poor in organic matter [2].

The evaluation of trace-element bioavailability in contaminated soils, which includes risk assessment of their accumulation in plants and animals, is usually carried out with single extraction [4–6] or sequential extraction procedures [7–9]. Column leaching experiments have also been used to study the mobility of trace elements [10, 11] and their bioavailability [11, 12] in soils.

The single extraction procedures are used to produce information about the contamination of topsoil and trace-element availability to plants and animals [13, 14]. This is a very important task because of the higher mobility of trace elements from anthropogenic sources than trace elements from natural sources [2]. The single extractions can be divided into three categories: extraction with ionized water or diluted acid solution such as CH_3COOH, HCl, or HNO_3, neutralized salt solutions, typically $MgCl_2$, $BaCl_2$, $CaCl_2$, NH_4OAc, or NH_4NO_3, and extraction with complexing agents such as EDTA and DTPA [4–7, 14–16]. In single extraction procedures, the total element content in the soil sample is also determined. It should be noted that the single extraction will produce information on the trace-element mobility at the moment in samples analysed. The total element content represents the trace-element concentrations which may leach over a very long period [17].

Sequential extraction procedures are widely used to produce information for trace-element risk assessment [7–9]. The sequential extraction methods are based on trace-element partitioning and speciation methods for determination of toxic chemical forms of trace elements in air, water, animal, food, soil, sediment, and sewage sludge samples [18–20]. In recent decades, several sequential extraction procedures for soil and sediment samples including from three to eight steps were developed. Most have been reviewed by several authors [21–23]. Tessier's five-step sequential extraction method is one of the most suitable for trace-element partitioning in soil samples [24]. The Standards, Measurements and Testing programme (SM&T), formerly European Community Bureau of Reference (BCR), has standardized the three-step sequential extraction procedure for trace-element partitioning, and the fourth step is dissolution of sample residue [25]. The sequential extraction procedures developed by Geological Survey of Canada (GSC) [26] and Kersten and Förstner [27] are also widely used. Most of the sequential extraction methods available are modifications of Tessier's method [23, 28–30].

Tessier's sequential extraction method is probably the most valuable because it includes a five-step fractionation into (1) exchangeable, (2) carbonate, (3) reducible, (4) oxidizable, and (5) residual element concentrations. The standardized (BCR) three-step extraction method [25] does not contain an exchangeable fraction 1, which represents the highly mobile element content in soil. This fraction is the cation content that can be exchanged between the soil solution and the zone interacting with charged soil colloid surfaces. It is called the cation exchange capacity (CEC) [31].

The sequential extraction always includes several extraction steps, which are time-consuming and require careful laboratory work. Recently, some papers have reported the use of ultrasound for acceleration of the sequential extraction process [32–35]. Most of those sequential extraction procedures were performed with an ultrasonic probe operating with a 100 W power and 20 kHz frequency [32–34].

According to Davidson and Delevoye [35], better results were obtained with the use of ultrasonic water bath than the use of ultrasonic probe. The use of an ultrasonic water bath offers the advantage to use a higher power and frequency with a high sample treatment capacity. In our earlier studies, the ultrasound-assisted extraction with the digestion solution of diluted aqua regia (1 : 1, v/v) was successfully performed in the analysis of arsenic, cadmium, copper, lead, and silver concentrations in contaminated soil SRMs [36]. The 9 min ultrasound-assisted extraction (UAE) procedure followed by an ICP-OES measurement was compared with microwave and reflux methods, and no significant differences were found.

The aim of this study was to develop a fast method for the evaluation of toxic-element mobility in contaminated soils. Special laboratory instruments are not required, and the whole five-step extraction procedure can be carried out in plastic centrifuge tubes. The ultrasound-assisted sequential extraction (UASE) was found to be a powerful tool for the risk assessment of toxic elements in contaminated soils.

2. Experimental

2.1 *Instrumentation*

All the measurements were performed with a Perkin-Elmer Optima 4300 DV ICP-OES. The concentrations of the elements were measured using default parameters of the instrument (nebulizer flow 0.8 L min^{-1}, plasma power 1300 W, auxiliary gas flow 0.2 L min^{-1} and plasma gas flow 15 L min^{-1}). The wavelengths used are shown in table 1. An automatic background correction was used for each wavelength.

2.2 *Reagents*

All the reagents used were of the analytical grade, and only high-purity ELGA water was used. The acids used were nitric acid (65%, p.a.), hydrochloric acid (37%, p.a.), and sulphuric acid (95–97%, p.a.) supplied by Riedel-de-Haën and acetic acid (>90%, p.a.) supplied by Merck. The standard stock solutions (1000 mg L^{-1}) for the ICP-OES measurements were supplied by Merck. The working concentration ranges used are shown in table 1.

The reagents used in the production of the extracting solutions were CH_3COONa (p.a.), $NH_2OH \cdot HCL$ (p.a.), H_2O_2 (30%, p.a.) supplied by Riedel-de-Haën; $MgCl_2 \cdot 6H_2O$ (p.a.) supplied by J.T. Baker; NaOH pellet (p.a.) supplied by Merck and CH_3COONH_4 (p.a.) supplied by FF-Chemicals.

Table 1. Calibration data of the determination of samples by ICP-OES.

Element	Wavelength (nm)	*r*	LOD[a] (mg L^{-1})	LOQ[b] (mg L^{-1})	Calibration range (mg L^{-1})
As	193.696	0.9995	0.080	0.270	0.1–10.0
Cd	214.440	0.9991	0.004	0.014	0.01–1.0
Cu	327.393	0.9998	0.060	0.210	0.2–20.0
Pb	217.000	0.9994	0.150	0.510	0.25–25.0
Zn	213.857	0.9999	0.180	0.600	0.5–50.0

[a] Limit of detection ($a + 3s_a$).
[b] Limit of quantification ($a + 10s_a$).

2.3 *Samples*

Two contaminated soil standard reference materials, SRM 2710 [37] and SRM 2711 [38], both certified by the National Institute of Standards and Technology (NIST), and two metals contaminated soil samples were analysed. The contaminated soil samples S1 and S2 were collected from a warehousing area containing different kinds of metal-containing junk. Those samples can be described as sand and gravel with a low content of humic substances and moisture. Samples were collected from the top layer of soil (0–20 cm). The sample S2 did contain some metallic particles, which were not sieved before analysis so that the sample would be in the same condition as in the environment.

2.4 *Procedure*

About 500 mg of SRM or contaminated soil sample is accurately weighed into a 50 mL plastic centrifuge tube into which an appropriate amount of extracting solution is added. The tube is placed into a 650 W, 35 kHz, Model Transsonic 820/H ultrasonic water bath supplied by ELMA. The sonication times over 3 min are divided into equal steps so that after each 3 min step, the sample centrifuge tube is shaken by hand to prevent sedimentation, and then the sample is placed into the ultrasonic water bath for the next sonication step. Alternatively, Tessier's sequential extraction method with different agitation times and temperatures is used as a reference method [24]. Both sequential extraction procedures (five steps) are carried out progressively on an initial mass of 500 mg of sample material. After each extraction procedure, the sample solution is centrifuged (Heraeus Instruments Megafuge 1.0, 2000 rpm in 10 min) and the solution is pipetted into 25 or 50 mL volumetric flask. After centrifugation, the residue is washed with washing solution, which is centrifuged and pipetted into the same volumetric flask with the sample solution and diluted to volume with water.

The optimized UASE procedure includes extracts and sonication times with the temperatures as follows:

1. Fraction 1 (exchangeable): The soil sample is extracted with the solution of 8 mL of 0.5 mol L^{-1} $MgCl_2$ at pH 7 (pH adjusted with diluted NaOH or HCl) for 3 min sonication in 20°C. After centrifugation, the residue is washed with 5 mL of water.
2. Fraction 2 (bound to carbonates): The residue from the fraction 1 is extracted with the solution of 10 mL of 1.0 mol L^{-1} CH_3COONa at pH 5 (pH adjusted with CH_3COOH) for 15 min (5 × 3 min) sonication in 20°C. After centrifugation, the residue is washed with 5 mL of water.
3. Fraction 3 (bound to Fe and Mn oxides): The residue from the fraction 2 is extracted with the solution of 10 mL of 0.1 mol L^{-1} $NH_2OH \cdot HCl$ at pH 2 (pH adjusted with CH_3COOH) for 18 min (6 × 3 min) sonication in 85°C. After centrifugation, the residue is washed with 5 mL of water.
4. Fraction 4 (bound to organic matter and sulfides): The residue from the fraction 3 is extracted with the solution of 3 mL of 0.02 mol L^{-1} HNO_3 and the solution of 10 mL of 15% H_2O_2 (pH adjusted to 2 with HNO_3) for 9 min (3 × 3 min) sonication in 85°C. After centrifugation, the residue is washed with a solution of 5 mL of 3.2 mol L^{-1} CH_3COONH_4 (CH_3COONH_4 in 20% v/v HNO_3).

(5) Fraction 5 (the residual phase): The residue from the fraction 4 is extracted with the solution 10 mL of $(1+1)$ diluted *aqua regia* for 9 min (3×3 min) sonication in 60°C. After centrifugation, the residue is washed with 5 mL of water [36].

3. Results and discussion

3.1 *Calibration*

All the concentration measurements were carried out using a four-point calibration. The use of ICP-OES instrument equipped with an echelle polychromator and Segmented Array Charge Coupled Detector (SCD) provides a simultaneous measurement with a high analytical sensitivity and low level of interference. According to this, multi-element calibration standards for all five elements (As, Cd, Cu, Pb, and Zn) were used. The backgrounds of calibration standards were produced using the appropriate extracts of all five fractions. The determination of each element was performed by taking the most sensitive emission lines (table 1) to attain the sensitivity required. The possible interferences in the determination of element concentrations were tested with the analysis of synthetic mixtures of matrix elements, and no significant differences were observed.

3.2 *Optimization of the UASE*

The UASE procedure was optimized by the analysis of two replicate samples of about 500 mg of contaminated soil SRM 2710. The optimization was carried out by the determination of the As, Cd, Cu, Pb and Zn concentrations by ICP-OES. These elements were selected because they are common contaminants in metal contaminated areas. Another reason for the selection of those elements is the highly mobile character of arsenic and cadmium, whereas zinc and especially copper and lead are known as the most immobile. The procedure was optimized by comparing the analytical results of each fraction with the concentrations produced by Tessier's method. The UASE was tested with different extraction solutions at different concentrations. Sonication times were 1 min or varied from 3 to 18 min divided into equal 3 min steps. All the element concentrations (figures 1–4) were produced using extracting solutions presented in section 2.4.

(1) Fraction 1 (exchangeable): The optimization process showed that the extraction from soil samples by the UASE method will produce concentrations comparable with those produced by Tessier's method. According to the analytical results (figure 1a and b), a sonication time of 3 min was validated for all elements investigated. The extracted concentrations of As, Cu, Pb, and Zn were slightly affected by the sonication time in the SRM 2710, as can be seen in figure 1(a) and (b). The extremely high concentrations of As were obtained when a sonication time of 1 min was used.

(2) Fraction 2 (bound to carbonates): The optimization process showed that the extraction of sample residue from the fraction 1 will produce the concentrations comparable with those produced by Tessier's method. According to figure 2, the highest analytical results were produced for all the elements

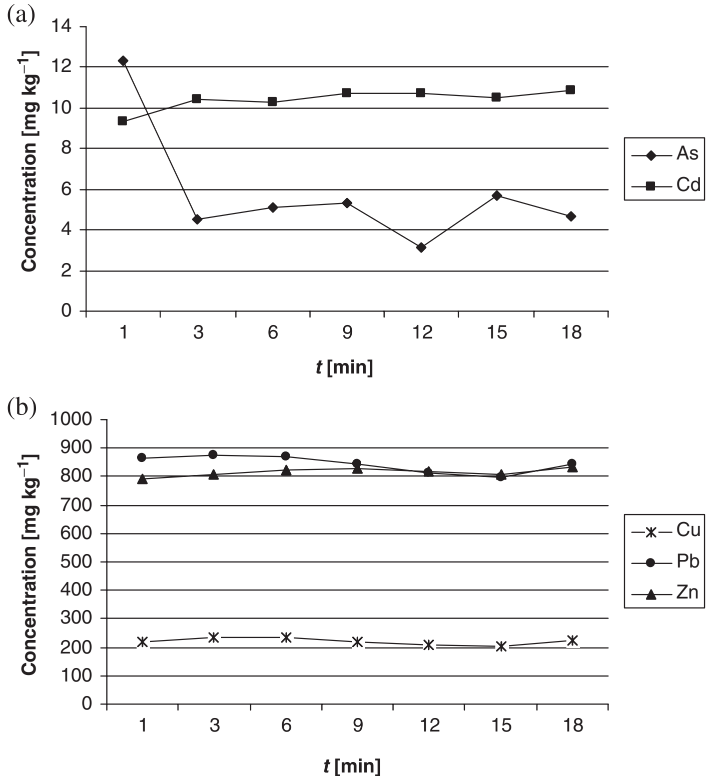

Figure 1. (a) As and Cd and (b) Cu, Pb and Zn concentrations as a function of time, when 0.5 mol L^{-1} $MgCl_2$ solution was tested as an extracting solution at 20°C.

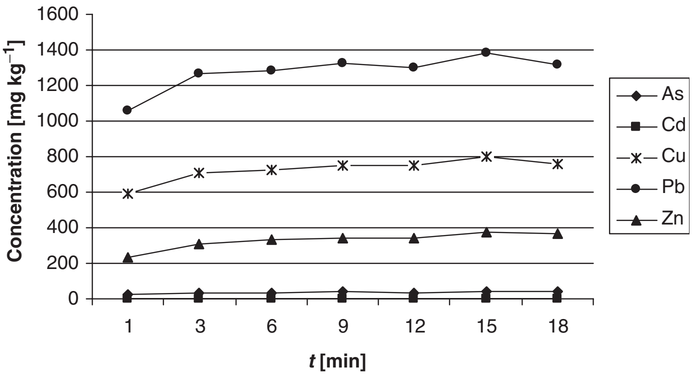

Figure 2. Element concentrations as a function of time, when 1.0 mol L^{-1} NaOAc solution was tested as an extracting solution at 20°C.

investigated when a sonication time of 15 min was used. The extracted concentrations of all five elements were only slightly affected by the sonication time in the SRM 2710, as can be seen in figure 2. Sufficient As and Cd concentrations were produced with a sonication time as low as 1 min. The Cu, Pb, and Zn

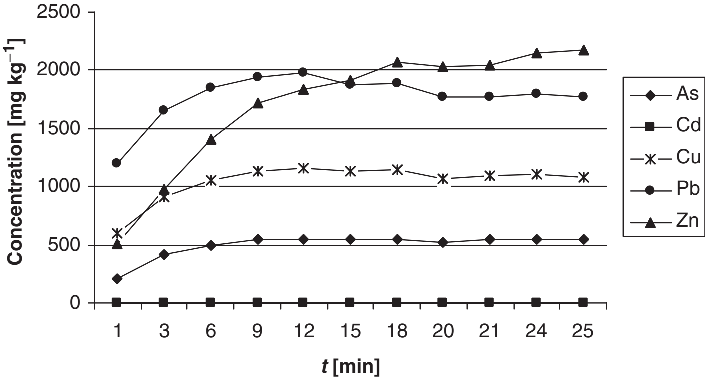

Figure 3. Element concentrations as a function of time, when 0.1 mol L^{-1} $NH_2OH \cdot HCl$ (pH 2) solution was tested as an extracting solution at 85°C.

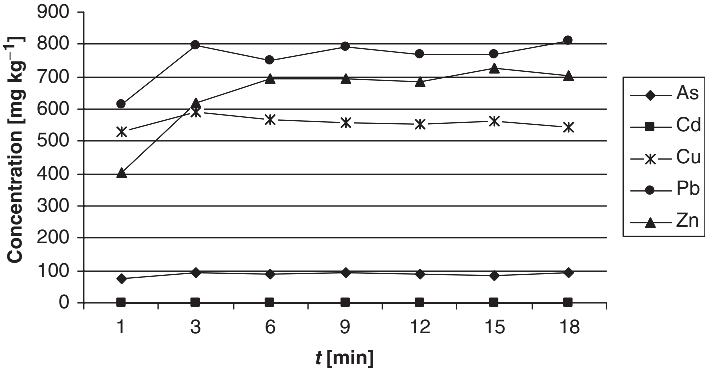

Figure 4. Element concentrations as a function of time, when 0.02 mol L^{-1} $HNO_3 + 15\%$ H_2O_2 (pH 2) solution was tested as an extracting solution at 85°C. The residue was washed with the 3.2 mol L^{-1} $CH_3CO_2NH_4$ solution.

concentrations were increased significantly when the sonication time was extended from 1 to 15 min.

(3) Fraction 3 (bound to Fe and Mn oxides): The optimization procedure showed that the extracted concentrations could be dramatically affected by the temperature used. At temperatures of 20 or 60°C, the recoveries of arsenic, copper, and lead were about 60% compared with Tessier's method. The extracted zinc concentrations at low temperatures were about one-tenth of those extracted with Tessier's method. However, the extracted cadmium concentrations were not affected by the temperature used. When a temperature of 85°C was used, the extracted concentrations of As, Cd, Cu, and Pb compared well with those produced by Tessier's method. Zinc recoveries of about 50% were produced by a sonication time of 18 min. Sonication times up to 25 min were tested without any significant increase in zinc recoveries, as can be seen in figure 3. According to the highest analytical results for arsenic, copper, and zinc, a sonication time of 18 min at the temperature of 85°C was validated.

(4) Fraction 4 (bound to organic matter and sulfides): Only the extraction temperature of 85°C was tested because organic matter is not oxidized using a mixture of diluted nitric acid and hydrogen peroxide at low temperatures [24]. The optimization procedure showed that the extracted concentrations are affected by the sonication time used. It should be noted that significantly higher zinc concentrations were produced. This is due to the low zinc concentrations in fraction 3. When a sonication time of 9 min was used, the extracted concentrations (figure 4) of all the elements investigated except zinc were comparable with those produced by Tessier's method.
(5) Fraction 5 (the residual phase): This fraction was extracted with the UAE procedure optimized for the analysis of toxic elements in contaminated soil samples [38].

According to the optimization procedure, the UASE procedure compares favourably with the well-known Tessier method. The major advantage over Tessier's method is that the extraction time in the optimized five-step UASE method lasts only 54 min, whereas Tessier's method lasts 17.5 h.

3.3 *Analysis*

Two contaminated soil standard reference materials, SRM 2710 and SRM 2711, and two contaminated soil samples were analysed. All results were moisture-corrected so that the concentrations are presented in $\mathrm{mg\,kg^{-1}}$ of dry mass. The UASE method was validated for the fractionation of toxic elements in contaminated soil samples. The elements to be determined, As, Cd, Cu, Pb, and Zn, were selected because of their importance to the environment. Sb was also of interest, but its concentrations in SRMs are too low to be determined by ICP-OES. Cd and As are of major interest owing to their mobility and very high toxicity.

The concentrations (mean of six replicate samples ± confidence limits of the mean) of the five elements (As, Cd, Cu, Pb, and Zn) in SRM 2710 extracted with both UASE and Tessier's methods and SRM 2711 extracted with the UASE method followed by ICP-OES analysis are shown in tables 2 and 3.

The determination of these elements in SRM 2710 and SRM 2711 by ICP-OES was successful, as can be seen in tables 2 and 3. The certified concentrations of As, Cd, Cu, Pb, and Zn in SRM 2710 were obtained with recovery rates of about 87–99% by the UASE method. According to the certificate of the SRM 2710, the element recoveries were in good agreement with the leachable element recoveries, which varied from 85% (zinc) to 94% (arsenic). The results obtained by Tessier's method were too high, as well as most of those introduced by Hall *et al.* [26], Ho and Evans [29], and Li *et al.* [39], when compared with the certified leachable concentrations of Cd, Cu, Pb, and Zn in SRM 2710. The sequential extraction procedures used were the four-step GSC method, three-step BCR method, and five-step Tessier method by Hall *et al.*, Ho and Evans, and Li *et al.*, respectively. According to four- and three-step fractionation, the analytical results of Hall and Ho do not contain an exchangeable fraction (Fraction 1) at all. The concentrations determined in different fractions compared well with those introduced in the literature, although significant differences were observed with fractions 3, 4, and 5 when compared with methods in the literature [26, 29, 39]. The concentrations of As were determined with total recoveries of 98.4 and 122.0% for the UASE method and Tessier's method, respectively.

Table 2. Results (mg kg^{-1}) of SRM 2710 ($n = 6$) produced by the UASE and Tessier methods.

Element	Procedure	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total	Certified	Recovery (%)	NIST (%)
As	Ultrasound	< LOQ[b]	26 ± 4	378 ± 5	91 ± 12	121 ± 4	616 ± 15	626 ± 38	98.4	94
	Tessier	< LOD[a]	25 ± 2	614 ± 14	56 ± 3	69 ± 6	764 ± 16		122.0	
Cd	Ultrasound	10.0 ± 0.2	3.4 ± 0.2	3.4 ± 0.2	1.1 ± 0.1	2.6 ± 0.1	20.5 ± 0.4	21.8 ± 0.2	94.0	92
	Tessier	11.3 ± 0.3	2.8 ± 0.2	5.1 ± 0.3	< LOQ	1.9 ± 0.2	21.2 ± 0.5		97.2	
	Li *et al.*	9.7 ± 0.3	3.0 ± 0.5	3.3 ± 0.3	0.7 ± 0.1	3.9 ± 0.8	20.6 ± 1.0		94.5	
	Hall *et al.*	14.4 ± 0.6		2.9 ± 0.3	2.5 ± 0.2	0.56 ± 0.07	20.2 ± 0.9		92.9	
	Ho and Evans	11.7 ± 0.4		5.1 ± 0.2	1.3 ± 0.2	< 1	18.2 ± 0.5		83.3	
Cu	Ultrasound	241 ± 8	672 ± 11	925 ± 27	608 ± 9	288 ± 11	2735 ± 33	2950 ± 130	92.7	92
	Tessier	229 ± 12	828 ± 15	972 ± 59	710 ± 56	116 ± 4	2856 ± 85		96.8	
	Li *et al.*	147 ± 12	753 ± 48	704 ± 110	657 ± 72	385 ± 30	2650 ± 140		89.8	
	Hall et al.	1501 ± 86		1325 ± 116	96.5 ± 1.6	40.9 ± 2.9	2964 ± 24		100.5	
	Ho and Evans	991 ± 54		850 ± 22	388 ± 23	427 ± 97	2660 ± 130		90.0	
Pb	Ultrasound	917 ± 37	1178 ± 26	1534 ± 45	806 ± 48	610 ± 43	5045 ± 91	5532 ± 80	91.2	92
	Tessier	799 ± 28	1452 ± 74	2123 ± 127	679 ± 41	331 ± 35	5384 ± 159		97.3	
	Li *et al.*	553 ± 20	1300 ± 100	1250 ± 220	900 ± 110	1080 ± 90	5080 ± 280		91.8	
	Hall *et al.*	2797 ± 14		2380 ± 18	63.0 ± 2.3	217 ± 5	5457 ± 17		98.6	
	Ho and Evans	773 ± 79		324 ± 25	2540 ± 130	950 ± 170	4590 ± 180		82.9	
Zn	Ultrasound	820 ± 13	311 ± 5	1721 ± 48	739 ± 18	2412 ± 52	6003 ± 75	6952 ± 91	86.3	85
	Tessier	898 ± 8	455 ± 46	4086 ± 216	428 ± 32	796 ± 40	6664 ± 227		95.9	
	Li *et al.*	743 ± 22	450 ± 40	2010 ± 260	387 ± 26	2860 ± 350	6450 ± 440		92.8	
	Hall *et al.*	1481 ± 10		3210 ± 62	1043 ± 32	556 ± 6	6291 ± 46		90.5	
	Ho and Evans	1211 ± 61		1120 ± 34	519 ± 42	3610 ± 350	6460 ± 350		92.9	

[a] < LOD: Result lower than the limit of detection.

[b] < LOQ: Result lower than the limit of quantification.

Table 3. Results (mg kg^{-1}) of SRM 2711 ($n = 6$) produced by the UASE method.

Element	Procedure	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total	Certified	Recovery (%)	NIST (%)
As	Ultrasound	< LOQ[b]	40 ± 2	36 ± 2	22 ± 1	31 ± 1	128 ± 4	105 ± 8	118.5	86
Cd	Ultrasound	10.8 ± 0.4	14.1 ± 0.1	8.35 ± 0.08	2.30 ± 0.10	2.34 ± 0.07	37.9 ± 0.5	41.7 ± 0.25	90.9	96
	Li *et al.*	8.7 ± 0.2	18.7 ± 1.7	8.5 ± 1.2	0.9 ± 0.1	2.1 ± 1.0	38.9 ± 2.4		93.3	
	Hall *et al.*	31.2 ± 1.8		5.6 ± 0.5	0.48 ± 0.03	0.19 ± 0.03	37.4 ± 1.6		89.8	
	Ho and Evans	28.6 ± 1.1		9.3 ± 0.6	2.4 ± 0.9	< 1	40.2 ± 0.8		96.5	
Cu	Ultrasound	2.0 ± 0.1	10.0 ± 0.4	16.2 ± 1.3	39 ± 3	42 ± 2	109 ± 4	114 ± 2	95.8	88
	Li *et al.*	0.9 ± 0.1	7.0 ± 1.0	14.2 ± 1.5	17.7 ± 2.2	66.0 ± 4.0	106 ± 5		93.0	
	Hall *et al.*	15.5 ± 1.8		70.7 ± 4.0	22.2 ± 0.8	5.26 ± 0.40	115 ± 2		100.9	
	Ho and Evans	6.1 ± 1.6		12.4 ± 10.0	13.8 ± 7.2	90.8 ± 17.4	123 ± 18		108.1	
Pb	Ultrasound	< LOD[a]	421 ± 14	393 ± 8	136 ± 5	67 ± 4	1017 ± 20	1162 ± 31	87.5	95
	Li *et al.*	2.3 ± 0.4	506 ± 78	372 ± 54	116 ± 12	90.0 ± 13.8	1090 ± 100		93.8	
	Hall *et al.*	843 ± 12		283 ± 7	3.68 ± 0.16	13.4 ± 0.8	1144 ± 17		98.5	
	Ho and Evans	302 ± 27		349 ± 32	356 ± 85	97.9 ± 19.7	1100 ± 100		95.0	
Zn	Ultrasound	< LOD	33 ± 3	80 ± 2	51 ± 2	99 ± 5	263 ± 7	350.4 ± 4.8	75.1	89
	Li *et al.*	0.5 ± 0.2	29.5 ± 3.4	89.6 ± 16.8	24.9 ± 1.0	171 ± 11	316 ± 20		90.2	
	Hall *et al.*	45 ± 2		187 ± 3	58 ± 2	32 ± 2	322 ± 6		91.9	
	Ho and Evans	41.8 ± 1.2		62.2 ± 7.1	37.1 ± 13.3	206 ± 33	347 ± 34		99.0	

[a] < LOD: Result lower than the limit of detection.
[b] < LOQ: Result lower than the limit of quantification.

Table 4. Results (mg/kg^{-1}) of contaminated soil sample S1 ($n = 6$) produced by the UASE and Tessier methods.

Element	Procedure	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total
As	Ultrasound	< LOD[a]	< LOD	11 ± 3	13 ± 1	< LOD	24 ± 3
	Tessier	< LOD	< LOD	46 ± 4	9 ± 2	< LOD	55 ± 4
Cd	Ultrasound	< LOQ[b]	< LOQ	0.6 ± 0.3	< LOD	< LOQ	0.6 ± 0.3
	Tessier	0.5 ± 0.1	< LOQ	1.1 ± 0.4	< LOD	< LOQ	1.6 ± 0.4
Cu	Ultasound	< LOD	33 ± 2	68 ± 9	22 ± 3	15 ± 4	139 ± 10
	Tessier	< LOD	38 ± 6	67 ± 10	15 ± 4	10 ± 5	129 ± 13
Pb	Ultrasound	< LOD	160 ± 70	200 ± 80	70 ± 70	16 ± 3	440 ± 120
	Tessier	< LOD	240 ± 110	260 ± 80	120 ± 240	7 ± 3	630 ± 270
Zn	Ultrasound	73 ± 4	1500 ± 240	2400 ± 300	95 ± 15	220 ± 40	4300 ± 340
	Tessier	55 ± 3	1750 ± 360	2330 ± 100	50 ± 20	60 ± 40	4200 ± 400

[a] < LOD = result lower than the limit of detection.
[b] < LOQ = result lower than the limit of quantification.

The surprisingly high concentrations of As in fraction 3 indicate the re-adsorption with iron after fractionation 2. It should be noted that the re-adsorption is noticed as a problem when ultrasound-assisted extraction is performed [23]. High As concentrations may also be due to a precipitation of As with iron oxides and the formation of FeAsS in soils [2]. The results of As in SRMs obtained by sequential extraction methods were not found in the literature.

The analysis of Cu, Pb and Zn in the highly contaminated soil sample S1 resulted in concentrations comparable with the UASE and Tessier's methods, as can be seen in table 4. According to the analytical results, the highest toxic element concentrations were found in fractions 2 and 3. It should be noted that high concentrations of Pb and Zn in fraction 2 are available for plants, whereas those concentrations in fraction 3 are bound to hydrous oxides of iron and manganese with chemisorption and are not so easily available [40]. The low toxic-element concentrations in fraction 4 are due to the low content of humic substances in the sample. The concentrations of As varied with the fraction 3, resulting in significantly higher concentrations when Tessier's method was used. The same effect was observed in the analysis of SRM 2710. The Cd concentrations were too low to be determined with the ICP-OES technique in several fractions. The selected analytical technique is not as sensitive as it should be for this purpose, but according to the measurements, the concentrations of Cd were lower than 1 mg kg^{-1}, which is the target value for Finnish soils [2].

The analysis of the sample S2 was performed with the validated UASE method (table 5). The highest concentrations of Cu and Pb were observed in fractions 3 and 5, although all fractions had measurable concentrations. The low precision of the procedure is probably due to fine metal particles in the sample. This is a common problem when samples are collected from warehousing areas with metal-containing junk. However, the toxic element mobility in contaminated soil samples can be evaluated with the UASE method. The fractions 1 and 2 represent toxic element concentrations that can be easily exchangeable and available to plants, respectively. It should be noted that 12% of the total Pb content was found in fraction 1. This is probably due to a low content of humic substances, which resulted in a poor metal binding capacity in the sample analysed. The other significant trace-element sorbents in soil are hydrous oxides of iron and manganese in the

Table 5. Results (mg kg^{-1}) of contaminated soil sample S2 ($n = 6$) produced by the UASE method.

Element	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total
As	< LOD[a]	< LOD	< LOQ[b]	11.8 ± 0.7	13.0 ± 3.5	25 ± 4
Cd	< LOD	< LOD	< LOQ	< LOD	2.7 ± 0.4	2.7 ± 0.4
Cu	8.2 ± 0.8	16 ± 14	190 ± 340	140 ± 240	200 ± 300	550 ± 520
Pb	680 ± 160	410 ± 200	2700 ± 3500	470 ± 640	1400 ± 2400	5600 ± 4300
Zn	< LOQ	< LOD	< LOQ	< LOD	53 ± 3	53 ± 3

[a] < LOD = result lower than the limit of detection.
[b] < LOQ = result lower than the limit of quantification.

fraction 3 [2, 40]. As can be seen in table 5, almost half of the Pb concentrations were found in this fraction. Owing to a low metal-binding capacity of sample S2, some of the most immobile toxic element Pb has been found in the exchangeable fraction and is readily available. The UASE method showed that Cd and Zn concentrations were found in fraction 5 only, whereas As concentrations were found in fractions 4 and 5. Both As and Cd are quite mobile, so that the most mobile fractions of these elements are probably leached before sampling [2, 40]. Both Cd and Zn resulted in concentrations lower than the limit of detection or quantification in several fractions, which indicates that the concentrations are lower than the target values of soils in Finland [2]. Soil sample S2 should not be handled as it is contaminated by Cd and Zn.

Conclusions

According to the analysis of SRM 2710 and contaminated soil sample S1, the UASE and Tessier's methods produce results that are comparable for the evaluation of toxic element mobility and availability. Tessier's [24] method can effectively be shortened with an ultrasonic water bath. Sequential extractions lasts 54 min, 17.5 h, approx. 26, 51, and 37 h for UASE, Tessier [24], GSC [26], BCR [25], and optimized BCR [30] methods, respectively. The five-step UASE with 10–13 mL of appropriate extracting solution with a sonication time of 3–18 min was suitable for the fractionation of As, Cd, Cu, Pb, and Zn in contaminated soil samples. The certified acid-leachable element concentrations of the SRMs were obtained with high accuracy and precision, as can be seen in tables 2 and 3. The main advantages of the UASE method compared with conventional methods are the high sample treatment capacity (40 samples simultaneously) without the need for any special laboratory instruments. Sample and reagent usage is also at a low level.

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