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COMPARATIVE STUDY OF DIGESTION PROCEDURES OF SOILS AND WATER SEDIMENTS USING DIFFERENT HCl/HNO_3 RATIOS FOR MULTIELEMENTAL DETERMINATION

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ABSTRACT. The suitability of three digestion procedures using aqua regia (a), Lunge mixture with (b) and without evaporation to dryness (c) was investigated to determine Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn in soils and water sediments. The results for metals determined by ICP-AES in four certified materials digested using the three procedures were compared with the certified values. The dissolution effects for different HCl/HNO_3 ratios are explained and the most adequate digestion methods for the determination of these 12 heavy metals are recommended based on the recovery degree. Cadmium, Cr, Cu, Mn, Ni, Pb and Zn could be determined subsequent any of the three digestion procedures. Aluminium and Fe were quantitatively extracted only in aqua regia, while V and Ti either in aqua regia or Lunge mixture with evaporation to dryness. In the case of As, a volatile element, only the extraction in aqua regia with the collection of gases gave a good recovery degree, while the Lunge procedure without evaporation resulted in an unsatisfactory result.

INTRODUCTION

For most of the determination methods it is necessary to digest the solid samples. The heavy metals like Cd, Cr, Cu, Ni, Pb and Zn in sediments and soils are determined after different digestion procedures including various mixtures of concentrated acids such as HF, HCl, HNO_3, $HClO_4$ and H_2SO_4 [1,2]. Different digestion equipment can be used: open beakers heated on hot plates, block digestors and digestion bombs placed in conventional and microwave ovens [1,2]. The main advantage of the dissolution of sediment and soil in concentrated inorganic acids are low cost and low salt matrix in final solution resulting in a decreased matrix effect on heavy metals determination [3].

The suitability of four digestion procedures for river sediments in aqua regia, pressure digestion using HNO_3/HF, HNO_3/HF + HCl and HNO_3/HF + HCl in microwave oven were investigated by Krause et al. [4]. The analytical results have showed that only the digestion using HNO_3/HF with subsequent evaporation to dryness and dissolution in HCl have led to appropriate results for more than 50 elements. The procedure involving bombs and microwave oven offers the best digestion compared to the total contents of elements determined directly in the solid phase by total reflection X-ray spectrometry (TXRF) and instrumental neutron activation analysis (INAA). Hseu et al. [6] investigated digestion methods for Cd, Cr, Cu, Ni, Pb and Zn in freshwater sediments and soils with aqua regia and different combinations of concentrated acids ($HClO_4$, HNO_3, H_2SO_4, HF), similarly to Burau [1] who used HNO_3-$HClO_4$ or Reisenauer [2], Backer and Amaker [5] who employed HF- HNO_3 -$HClO_4$ - H_2SO_4. The Baker and Amaker procedure is flexible and adequate for the total determination of Cd, Cr, Cu, Ni and Zn in freshwater sediment and soil samples but not recommended for Pb because of its precipitation as sulfate and the greater dispersion of the recovery degree in standard reference materials. The Burau method had proved to be the most appropriate procedure for the dissolution of Pb in both sediment and soil samples. The Reisenauer method is suitable for Cr, while aqua regia can destroy the organic matter, metal oxides and other parts of mineral phases as silicate minerals with higher recovery degree for Cu, Ni and Zn. The most frequently used techniques for the determination of metals in soils and sediments are flame atomic absorption spectrometry (FAAS) [6,7], inductively coupled plasma atomic emission spectrometry or mass spectrometry (ICP-AES/MS) [4], TXRF and INAA [4]. The methods used to collect and digest soil and sediment have been reviewed by Beck and Sneddon [7]. However, it is interesting and necessary to complete the comparison of different digestion ways for the total determination of heavy metals in this kind of samples.

The aim of this study was to investigate the suitability of some digestion procedures based on different HCl/HNO_3 mixtures to determine the contents of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn in soils and sediments. Two certified soils and two certified water sediments were digested using aqua regia and Lunge mixture with and without evaporation to dryness. The analytical results for metals determined in solutions by ICP-AES were compared with the certified values. The best digestion procedure in respect with each element was chosen based on the recovery degree.

INSTRUMENTATION

The determinations were carried out using the ICP scanning spectrometer SPECTROFLAME and the ICP multichannel spectrometer SPECTRO CIROS^{CCD} (Spectro Analytical Instruments Kleve, Germany). All relevant ICP spectrometer operating parameters such as r.f. power level, gas flows, sample uptake rate and positioning of the torch in the front of the optical plasma interface are controlled by the software. Thus, optimum operating conditions can be easily selected. Details about instrumentation and operating conditions are given in Table 1.

Stock solutions and certified reference materials (CRMs)

All reagents used in this study (65 % HNO_3, 32 % HCl) were purris p.a. quality (Flucka). Stock solution of 1000 μg mL^{-1} As and Cd, 2000 μg mL^{-1} Cr, Ni, V, Ti and 4000 μg mL^{-1} Cu, Zn, Pb, Fe, Mn and Al were prepared starting from oxide (As) or metallic powder. A multielement standard solution of (μg mL^{-1}) 50 As, 20 Cd, 100 Cr, Ni, V and Ti, 160 Pb, 200 Cu, Zn, Al and 400 Fe, Mn was prepared using the single elemental solutions. This solution was used for line selection and to analyze the samples by the multielemental standard addition method. All dilutions were made with 2 % (v/v) HNO_3.

Two certified soils (CRM 025-050, RTC-Laramie New York, USA; LGC 6135 Soil Hackney Brick Works, LGC-Middlessex, UK), a certified river sediment (NSC DC 78301 River sediment, China National Analysis Center for Iron and Steel, Beijing, China) and a freshwater sediment (BCR 701, Institute for Reference Materials and Measurements, Geel, Belgium) were used to evaluate the accuracy of extraction procedures. All CRMs were purchased from LGC Promochem GmbH, Germany.

Table 1

Instrumentation and operating conditions for the ICP atomic emission spectrometers

Equipment	SPECTROFLAME	SPECTRO CIROS^{CCD}
Generator:	Free – running 27.12 MHz, operated at 1200 W	Free – running 27.12 MHz operated at 1400 W.
Plasma torch	Inductively coupled plasma, radial viewing, observation height: 15 mm Argon flow rates: Outer gas 12 L min^{-1}. Intermediate gas 0.6 L min^{-1}. Nebulizer gas 1 L min^{-1}.	Inductively coupled plasma, axial viewing; torch position (mm): X= -3.9; Y=+3.6 ; Z=+2.6. Argon flow rates: Outer gas 12 L min^{-1}. Intermediate gas 0.6 L min^{-1}. Nebulizer gas 1 L min^{-1}.
Sample introduction system	2 channel peristaltic pump, glass concentric nebulizer Meinhardt type K (TR-30-K3), double pass Scott type spray chamber sample uptake rate: 2 mL min^{-1} flushing time: 40 s delay time: 20 s	4 channel peristaltic pump, K2 cross-flow nebulizer, double pass Scott type spray chamber sample uptake rate: 2 mL min^{-1} flushing time: 40 s delay time: 20 s
Optics	160-800 nm double scanning monocrhomator chamber filled with N_2	160 – 800 nm double-grating Paschen-Runge multichannel spectrometer chamber filled with Ar
Detector	9781 R photomultiplier tube supplied at 1000 V (Thorn EMI, Ruislip, Middlesex, UK).	22 CCD detectors
Data processing	Smart Analyzer Software Background correction: linear two points model, integration time 10 s and 3 successive measurements for each parallel sample	Smart Analyzer Software Background correction: linear and square two points models, best SNR strategy, integration time 45 s and 3 successive measurements for each parallel sample

Digestion procedures of the CRMs

Three different wet digestion procedures were investigated to optimize the requirements for the quantitative determination of 12 elements: (i) aqua regia (HCl/HNO_3 3:1); (ii) Lunge mixture (HCl/HNO_3 1:3) without evaporation; (iii) Lunge mixture (HCl/HNO_3 1:3) with evaporation to near dryness. For each procedure 3 parallel digestions were performed. All solutions were analyzed by ICP-AES and the average content and uncertainly as standard deviation has been given.

Method 1. Aqua regia digestion

A volume of 1 mL water was used to turn 2.5000 g sample into a slurry in a reaction flask, then 21 mL of 32 % (v/v) HCl followed by 7 mL of 65 % HNO_3 were added drop by drop to reduce foaming. A volume of 15 mL 0.5 M HNO_3 was introduced into the absorption vessel connected to the reflux condenser of the reaction flask. The sample was allowed to stand for 16 h at room temperature for low oxidation of the organic matter of soil or sediment. Then the temperature of the reaction mixture was slowly risen until reflux conditions and maintained for 2 h. The content of the absorption vessel was added into the reaction vessel through the reflux condenser and both rinsed with 10 mL of 0.5 M HNO_3. After cooling at room temperature, the sample was transferred in a 100 mL graduated flask with 2 % (v/v) HNO_3. The slurry was filtered through a cellulose based membrane filter with medium pores and the filtrate was used to determine the metals.

Method 2. Lunge mixture without evaporation

The procedure was similar to that using aqua regia but employing in this case 28 mL of Lunge reagent.

Method 3. Lunge mixture with evaporation to near dryness

A volume of 25 mL 1+1 HCl was added to 2.5000 g certified reference material in a 150 mL vessel, then heated on a hot plate to near dryness. After cooling, 25 mL Lunge mixture were added and again the solution was evaporated to near dryness. The residue was dissolved in 25 mL 1+4 HCl and heated for approximately 15 min. The sample was transferred into a volumetric flask and diluted to 100 mL with 2 % (v/v) HNO_3. The contents of metals were determined in the clear solution resulted after filtration.

RESULTS AND DISCUSSION

The comparison of the found analytical results following the three digestion ways with the certified values are illustrated in Tab. 2-5.

Table 2

Comparison of the found content of metals (n=3 parallel samples) with the certified concentrations in CRM 025-050 Soil using ICP-AES.

Element	Certified ($\mu g\ g^{-1}$)		Found ($\mu g\ g^{-1}$)		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
Al	7637±1602	Ciros CCD	8594±1115	8305±1130	8662± 1250
		Spectroflame	8547±870	7842±920	9600±1100
As	339±51.1	Ciros CCD	339±59.4	263±26.2	-
		Spectroflame	329±40.0	263±32.5	-
Cd	369±46.3	Ciros CCD	311±51.0	302±56.4	314±34.8
		Spectroflame	340±45.0	332±42.5	292±41.3
Cr	441±50.1	Ciros CCD	448±41.0	388± 40.4	452±42.9
		Spectroflame	453±39.5	387±51.3	446±50.7
Cu	7.76±1.68	Ciros CCD	8.35±1.68	8.11± 1.27	8.00±1.73
		Spectroflame	8.25±1.25	8.65±1.34	8.65±1.34
Fe	9439±1229	Ciros CCD	10000±1590	10290±1130	8335±1170
		Spectroflame	10027±1450	9240±1520	7577±1168
Mn	173±15.0	Ciros CCD	187± 8.4	178± 7.0	224± 17.0
		Spectroflame	176±11.5	184±7.5	220±18.5

Element	Certified (µg g^{-1})		Found (µg g^{-1})		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
Ni	12.2±3.54	Ciros CCD	12.0±3.25	19.0±4.28	11.3±3.89
		Spectroflame	16.0±4.45	15.2±2.63	10.2±3.29
Pb	1447±203	Ciros CCD	1448±108	1352±237	1458±226
		Spectroflame	1482±227	1370±226	1408±189
Ti[*]	-	Ciros CCD	1004±82	268±12	954± 98
		Spectroflame	955±70	287±45	1000± 80
V	19.3±4.48	Ciros CCD	14.8±2.47	14.3± 3.42	14.2±4.29
		Spectroflame	19.8±3.56	19.0±4.13	17.2±3.89
Zn	51.8±8.29	Ciros CCD	44.4±7.76	48.6± 3.88	46.0± 5.68
		Spectroflame	55.0±8.14	52.1±4.11	56.0±7.34

[*] uncertified value

Table 3

Comparison of the found content of metals (n=3 parallel samples) with the certified concentrations in LGC 6135 Soil Hackney Brick Works using ICP-AES.

Element	Certified (µg g^{-1})		Found (µg g^{-1})		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
Al	22700±4600	Ciros CCD	21000± 1800	2520±2600	6200±800
		Spectroflame	19800±2300	2400±1900	6300±900
As	66±12	Ciros CCD	67±2	57±4	-
		Spectroflame	64±7	62±6	-
Cr	336±28	Ciros CCD	349±12	382±14	340±24
		Spectroflame	315±26	390±22	320±18
Cu	105±5	Ciros CCD	100±5	104±5	118±10
		Spectroflame	108±4	103±8	103±8
Fe	40900±2700	Ciros CCD	39200±2000	7000±800	11625±2300
		Spectroflame	37100±2300	6900±1100	10250±920
Mn	348±18	Ciros CCD	338±21	280±12	338±25
		Spectroflame	348±16	287±22	370±16
Ni	277±13	Ciros CCD	260±30	199±33	310±21
		Spectroflame	240±16	206±24	291±6
Pb	391±16	Ciros CCD	411±31	355±32	355±32
		Spectroflame	400±21	373±32	350±36
Ti[**]	200	Ciros CCD	190±20	50±4	245±18
		Spectroflame	235±28	58±8	203±24
V	78±11	Ciros CCD	70±10	64±6	84±8
		Spectroflame	77±6	58±9	83±6
Zn	316±41	Ciros CCD	316±18	321±27	321±27
		Spectroflame	318±22	318±18	339±23

[**] indicative value

Table 4

Comparison of the found content of metals (n=3 parallel samples) with the indicative values of the supplier in BCR 701 Freshwater sediment using ICP-AES.

Element	Indicative values (μg g^{-1})		Found (μg g^{-1})		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
As*	-	Ciros CCD	41±4	40±3	-
		Spectroflame	56±6	65±7	-
Cd	11.7±1.0	Ciros CCD	12.5±1.0	11.8±0.6	12.3±1.0
		Spectroflame	10.3±1.5	10.9±0.8	10.5±0.9
Cr	272±20	Ciros CCD	275±17	265±18	295±26
		Spectroflame	280±12	271± 22	301±20
Cu	275±13	Ciros CCD	280±18	279±19	279±19
		Spectroflame	276±15	273±10	267±10
Mn*	-	Ciros CCD	604±35	502±18	656±22
		Spectroflame	675±45	560±23	645±20
Ni	103±4	Ciros CCD	100±10	100±6	100±9
		Spectroflame	100±8	98±7	105±4
Pb	143±6	Ciros CCD	144±8	140±10	133±14
		Spectroflame	140±6	148±10	149±9
Ti*	-	Ciros CCD	1529±91	891±42	1530±75
		Spectroflame	1550±80	1093±110	1345±86
Zn	454±19	Ciros CCD	457±20	458±18	458±18
		Spectroflame	458±14	445±12	484±12

* uncertified value

Table 5

Comparison of the found content of metals (n=3 parallel samples) with the certified concentrations in NCS DC 78301 River sediment using ICP-AES.

Element	Certified (μg g^{-1})		Found (μg g^{-1})		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
As	56±5	Ciros CCD	53±2	51±4	-
		Spectroflame	59±5	55±6	-
Cd	2.45±0.2	Ciros CCD	2.50±0.5	2.40±0.5	2.45±0.3
		Spectroflame	2.35±0.3	2.50±0.3	2.31±0.4
Cr	90±4	Ciros CCD	84±6	83±5	93±9
		Spectroflame	88±5	85±7	96±5
Cu	53±3	Ciros CCD	54±5	54±4	51±3
		Spectroflame	52±3	51±3	50±4
Mn	975±17	Ciros CCD	858±50	864±26	821±30
		Spectroflame	920±40	865±30	977±28

Element	Certified (µg g^{-1})		Found (µg g^{-1})		
			Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
Ni**	32	Ciros CCD	34±6	42±7	41±8
		Spectroflame	30±8	30±6	33±6
Pb	79±6	Ciros CCD	78±5	78±4	78±4
		Spectroflame	83±8	81±5	81±6
Ti*	-	Ciros CCD	423±30	199±8	370±15
		Spectroflame	392±28	184±20	400±30
Zn**	251	Ciros CCD	248±38	252±14	285±14
		Spectroflame	245±25	255±12	265±18

* uncertified value

** indicative value

The average recovery degrees considering the found values for the reference materials are presented in Tab.6.

Table 6

Average recovery degrees based on the results for the reference materials

Element	Recovery degree / (%)		
	Aqua regia	Lunge mixture without evap.	Lunge mixture with evap.
Al[1]	101±16	56±70	73±65
As[2]	99±1	88±9	-
Cd[3]	95±6	94±7	92±9
Cr[4]	100±3	99±12	104±5
Cu[4]	102±4	103±4	102±6
Fe[1]	100±9	60±61	55±41
Mn[2]	98±7	92±12	108±18
Ni[4]	101±10	99±19	103±12
Pb[4]	102±2	97±4	97±5
Ti[5]	106±17	27±4	112±15
V[1]	95±7	82±6	94±18
Zn[4]	99±2	100±2	104±5

[1] CRM 025-050, LGC 6135

[2] CRM 025-050, LGC 6135, NCS DC 78301

[3] CRM 025-050, BCR 701, NCS DC 78301

[4] CRM 025-050, LGC 6135, BCR 701, NCS DC 78301

The digestion in aqua regia resulted in very good recovery degrees for As, Cr, Cu, Fe, Mn, Pb and Zn. Recoveries (%) were also good for Al, Ni and Ti but the dispersion were large: 101±16, 101±10 and 106±17, respectively. Relatively good results were found for Cd (95±6) and V (95±7).

For the Lunge mixture used as digesting reagent without evaporation, best recovery degrees were achieved for Cu (103±4) and Zn (100±2) and relatively good for Cd (94±7) and Pb (97±4). With regard to Cr, Mn and Ni the digestion method proved to be correct but resulted in a greater dispersion of the results: 99±12; 92±12 and 99±19, respectively. The poor recoveries for As (88±9) and V (82±6) indicated negative systematic errors. For Ti also a very low recovery degree was encountered (27±4). The digestion method was equally unsatisfactory for Al and Fe with recoveries of 56±70 and 60±61. With regard to these two elements in a mineral type of soil, which is the case of CRM 025-050, the digestion using Lunge mixture without evaporation is satisfactory as suggest the found results compared to the certified values in Tab. 2. The procedure was not suitable for clay soil with higher silicate content as LGC 6135 Hackney Brick Works (Tab. 3).

The digestion procedure using Lunge mixture with dryness evaporation led to best recoveries for Cr (104±5), Cu (102±6) and Zn (104±5) and relatively good results for Cd (92±9) and Pb (97±5). Larger dispersions were encountered for Mn (108±18), Ni (103±12),Ti (112±15) and V (94±18). For Al and Fe the results were similar to those found using Lunge mixture without evaporation. The procedure with dryness evaporation proved to be not suitable for volatile elements such as As because of loss during evaporation to dryness.

For the materials with uncertified content of Ti, the ratio of amounts extracted in aqua regia: Lunge mixture with evaporation: Lunge mixture without evaporation were: 1:1:0.28 in CRM 025-050; 1:0.94:0.47 in NCS DC 78301 and1:0.93:0.64 in BCR 701. It can be stated that the extraction degree is generally better in aqua regia followed by the Lunge mixture with evaporation to dryness.

CONCLUSIONS

The digestion procedures using aqua regia, Lunge mixture with and without evaporation were suitable for Cd, Cr, Cu, Mn, Ni, Pb and Zn in soil and sediment. Aluminium and Fe were quantitatively extracted only in aqua regia, while V and Ti either in aqua regia or Lunge mixture with evaporation to dryness. In the case of As, a volatile element, only the extraction in aqua regia with the collection of gases gave a good recovery degree.

Aqua regia or Lunge mixture without evaporation are more suitable for the routine determination of the acid-extractable fraction of the elements from soil and sediment, while the digestion with Lunge mixture with evaporation to dryness is more laborious and time consuming. Only a quantitative digestion with an oxidant mixture of acids resulting in clear solutions guarantees the determination of at least 12 elements. In hot plate digestion procedures, the presence of HNO_3 helps to destroy easily organic species and to convert some elements into the higher, less volatile valence states. A gently pre-digestion with HCl or HNO_3 is also beneficial to avoid overheating through exothermic sample decomposition reactions.

The investigated digesting procedures can be used to determine the acid-extractable fraction of heavy metals in different types of soil from forest regions, industrial parks, residential and commercial areas.

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