Fresenius J Anal Chem (1995) 353:3–11

Fresenius' Journal of
Analytical
Chemistry

Comparative study of different digestion procedures using supplementary analytical methods for multielement-screening of more than 50 elements in sediments of the river Elbe

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Received: 14 February 1995 / Revised: 20 April 1995 / Accepted: 24 April 1995

Abstract. The suitability of four different digestion procedures, i.e. i.) an aqua regia digestion according to DIN 38 414–S7, ii.) a pressure digestion using HNO_3/HF in PTFE-vessels, iii.) a HNO_3/HF + HCl-pressure digestion in PTFE-vessels and iv.) a HNO_3/HF + HCl-pressure digestion using microwave induction, has been evaluated with regard to the quantitative determination of about 50 elements in environmental samples. Three sediments of the river Elbe and two standard reference materials (MESS-1 and NIST 1645) have been employed. The analytical results from the dissolved samples, obtained using inductively coupled plasma mass- and optical emission spectrometry as well as total reflection X-ray fluorescence spectrometry, have been compared with those obtained by instrumental neutron activation analysis. Only digestion procedures using HNO_3/HF with a subsequent evaporation to dryness and dissolution in HCl have led to appropriate results for a wide range of elements (more than 50 elements in total). Because of its low contamination risk and its time saving, the microwave digestion is preferred. For this digestion procedure the accordance among the different instrumental methods used is high (better than 15% deviation) in general. A few elements (16) could be determined quantitatively only by a single method.

Introduction

Using modern multielement analytical techniques, such as inductively coupled plasma mass- and optical emission spectrometry (ICP-MS and ICP-OES), total reflection X-ray fluorescence spectrometry (TXRF) and instrumental neutron activation analysis (INAA), it is possible to determine precisely and accurately a wide variety of elements.

Especially the combination of these methods enables to determine elemental distribution patterns, for example in sediments and suspended particulate matter to investigate the water system of the river Elbe. Thus sources, losses, inputs and outflows of a river system can be established in a statistically significant manner [1].

For most of the determination methods, it is necessary to digest the solid samples. The general aspects of this problem and a large number of applications have been recently reviewed in [2]. The main objective of this investigation is to find a suitable digestion procedure for sediments which allows the subsequent determination of a range of approximately 50 elements quantitatively. A widely used procedure is that described in the German Industry Norm specification (DIN) 38 414–S7. It refers to the digestion of sludges and sediments with aqua regia for subsequent determination of the acid soluble part of metals. This digestion procedure has been used in various studies concerning the pollution situation of the river Elbe and her tributaries [3]. One disadvantage of the beforementioned DIN specification is the incompleteness of this digestion especially for main components and elements bound to clay mineral components. Therefore this procedure is only useful for the determination of the acid-extractable fraction of an element and does not represent adequately its total abundance over the entire composition of the sediment.

In this investigation, the results obtained with four different digestion procedures and the appropriate determination of elements using different analytical methods (ICP-MS/ICP-OES and TXRF) are compared to find the most suitable digestion procedure. To evaluate these results the same samples were analyzed by the non destructive INAA-technique. These investigations have been carried out with standard reference materials and sediments of the river Elbe.

Experimental

1 Sample selection

In addition to the standard reference materials (SRM) three nature sediment samples of the river Elbe have been selected, which are assumed to represent the different compositional types of sediments from the river Elbe.

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According to the international agreement within the projects of the International Commission on the Elbe-River Projection (ICEP), only the grain size fraction < 20 µm [4] was employed with the following weight characteristics and nominations:

ES 27: sandy sediment, grain size abundance < 20 µm: 1 weight %

ES 40: silty/clayey sediment, grain size abundance < 20 µm: 30 weight %

ES 38: highly contaminated sediment from the tributary river Mulde, grain size abundance < 20 µm: 2.3 weight %

Apart from real sediment samples, this study also includes two SRM, the highly contaminated NIST 1645 and MESS-1, extremely resistant to digestion, with the following characteristics:

MESS-1: sediment from a Canadian estuary, milled to a grain size < 125 µm

NIST 1645: river sediment, milled to a grain size < 180 µm

2 *Digestion procedures*

Four different digestion procedures were studied to optimize the requirements for the quantitative determination of about 50 elements. As all of them contain oxidative acid steps elements such as Si, C, F cannot be determined from solutions thus digested:

a) aqua regia (HCl/HNO_3 3 : 1) digestion (in line with DIN 38 414–S7)

b) pressure digestion in PTFE vessels with HNO_3/HF (3 : 1)

c) pressure digestion in PTFE vessels with HNO_3/HF (2 : 1), vaporized to dryness and dissolved in 2 ml HCl (6 mol/l)

d) same as c) but with microwave induction under high pressure

The aqua regia digestion (a) was chosen for comparison and for the determination of the extraction rates of elements. A detailed description is given in [5]. The pressure digestion with HNO_3/HF is widely used, e.g. by the ARGE Elbe following the procedure described by Tölg [6, 7]. During runs, following procedure b) it was not always possible to obtain clear digestion solutions. Therefore procedures c) and d) were chosen additionally.

For procedure c) "Tölg-vessels" were used just as in procedure b) with the above mentioned acid mixture. After 12 h heating under pressure and subsequent cooling, the solutions were vaporized until dryness (about 6–8 h for 6 samples). The residues were dissolved in 2 ml HCl (all acids used were obtained by subboiling of "suprapur" concentrated acids from Merck, Darmstadt, D). After addition of 2 ml ultrapure water, the solutions were heated for 20 min, cooled and diluted to a volume of 25 ml.

For procedure d) the microwave system MLS-1200 from Milestone (Intec Laborgeräte Vertriebs GmbH, Uhingen, D) was employed, using digestion vessels up to 200 bar, which allows digestions under high pressure. The sediment samples were weighed into Teflon-PFA vessels. The acid mixture was added and the following microwave heating program was started: 250 W for 2 min, 0 W for 0.5 min, 500 W for 3 min, 0 W for 0.5 min, 600 W for 3 min, 0 W for 0.5 min, 700 W for 2 min, 0 W for 0.5 min, 800 W for 2 min, 250 W for 5 min. The external infrared temperature control was set to 100° C. After cooling down, the solutions were vaporized until dryness in the same microwave system using the evaporation unit (MCR-6) with the following heating program: 150 W for 75 min, 0 W for 15 min. The residues were dissolved in 2 ml HCl (6 mol/l) and after the addition of 2 ml ultrapure water the following heating program was started: 250 W for 20 min. Finally the solution was diluted to a volume of 25 ml.

For each procedure three parallel digestions were performed, using 70–150 mg of the sediment sample. All solutions were introduced to ICP-MS, ICP-OES and TXRF, whereas pure sediment powders were analyzed directly without any prior dissolution by INAA. A short overview of the operating conditions of these methods will be given in the following section.

3 *Analytical techniques*

ICP-MS and ICP-OES. For ICP-MS, a Perkin-Elmer Sciex Elan 5000 instrument with a quadrupol mass separator and a channel electron multiplier was used. The plasma parameters were optimized for each analysis and varied over a range of common operating conditions [8]. The digested samples were introduced via a peristaltic pump and a cross-flow nebulizer at a rate of about 1.2 ml/min.

For ICP-OES, a Perkin-Elmer Optima 3000 instrument with an Echelle Spectrometer and a segmented-array, charge-coupled device detector (SCD) was employed [9]. The instrument was operated under normal conditions with a plasma argon gas flow of 15 l/min, an auxiliary gas flow of 1 l/min and a nebulizer gas flow of 0.9–1.1 l/min. The RF-power was set to 1100 W and the viewing height was optimized to 12 mm above load coil. The sample uptake rate through the crossflow nebulizer was set to 1.0 ml/min. The integration time varied automatically between 2 and 20 s. All data intensities read from the detector were processed in the peak height mode.

ICP-OES was applied mainly for the determination of the major and minor components. The ICP-results for the elements Na, Mg, Al, K, Ca, S, Fe, and Mn originate from ICP-OES determinations. All other results were obtained by ICP-MS-analysis.

The calibrations for both instruments were performed with standard solutions which were adapted to the elemental concentration range in sediments. The calibration line was fitted through 3 calibration points after blank subtraction.

TXRF. For the TXRF measurements, an EXTRA II Spectrometer from Atomika Instruments GmbH was used. It consisted of a software controlled HV generator, the X-ray tubes, either a Mo-anode or a W-anode, and a QX 2000 analyzing system from Link Analytical with an 80 mm^2 Si(Li)-detector having an energy resolution of 155 eV at 5.9 keV. The X-ray tubes were operated at 50 kV with a variable current from 5 to 38 mA, depending on the count rate of the sample [10].

One drop of the digested sample, typically 25 µl, was transferred to a quartz glass sample carrier, dried and excited by the totally reflected X-rays. Each sample was measured for a period of 3000 s. The quantification was performed very simply by internal standardization. Only one internal standard element, (Co or Ga) in a concentration-range of 3000–7000 µg/g (total concentration in the sample), needed to be chosen which, by its given concentration and together with the instrument response function, allows the conversion of the signal intensities for all elements directly into their concentration values.

INAA. Dry aliquots of the samples were irradiated in the GKSS research reactor FRG-1 at a thermal neutron flux of 2 to 5 × 10^{13} n/cm^2s. For determination of the neutron flux, Fe, Ni- and Au-foils were irradiated together with the samples [11]. This can be regarded as an external standardization. Two irradiations were performed with irradiation times of 1 min and 3 days, respectively. For gamma-ray spectrometry a HPGe-detector, a multichannel-analyzer and a specially designed computer program [12] were used. After different decay times from 6 min to 30 d at least four γ-radiation spectra from the radioactive nuclides were measured. The counting periods varied between 5 min and 8 h. Mg, Al, Cl, Ti, V, Mn and Cu were determined after a short irradiation, the other elements after long term activation.

A detailed description of the above mentioned analytical techniques can be found in the literature [8–13]. A comparison as well as the analytical characteristics, the advantages and disadvantages of ICP-MS, TXRF and INAA are given in [13].

Results and discussion

The comparison of the analytical results for some salient main components is given in the following figures (Fig. 1, 2). Figure 1 presents the results for MESS-1, which was

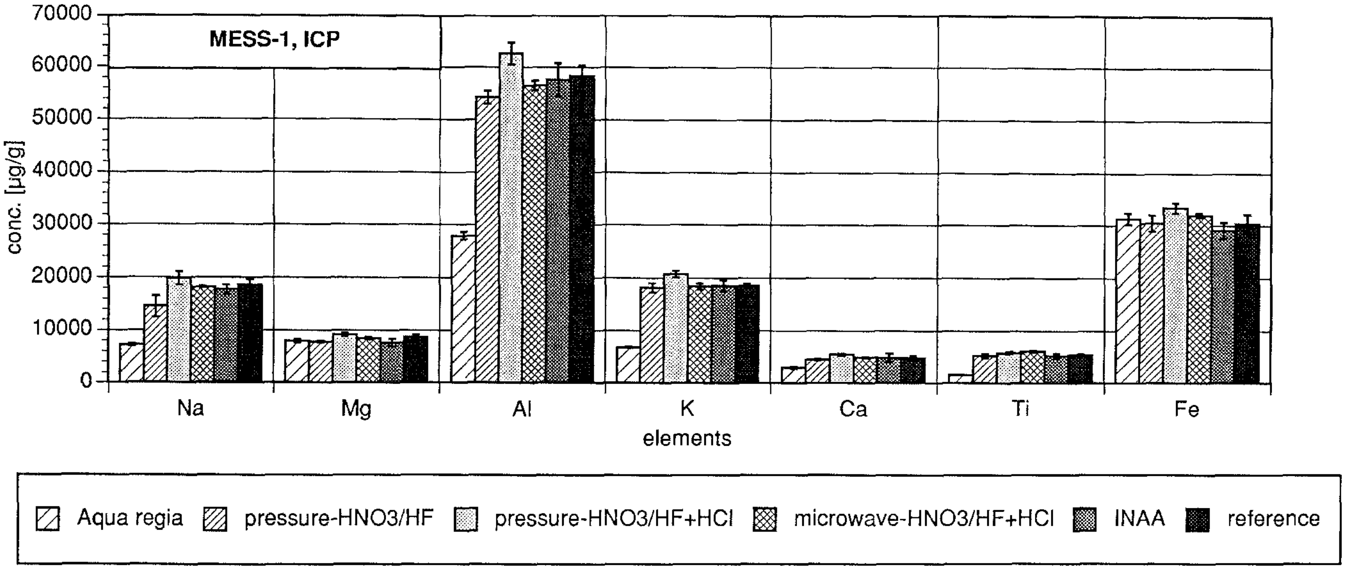

Fig. 1. Comparison of ICP-results of the different digestion procedures with INAA results and reference values for main components in MESS-1; error bar: standard deviation of the total procedure (digestion and determination)

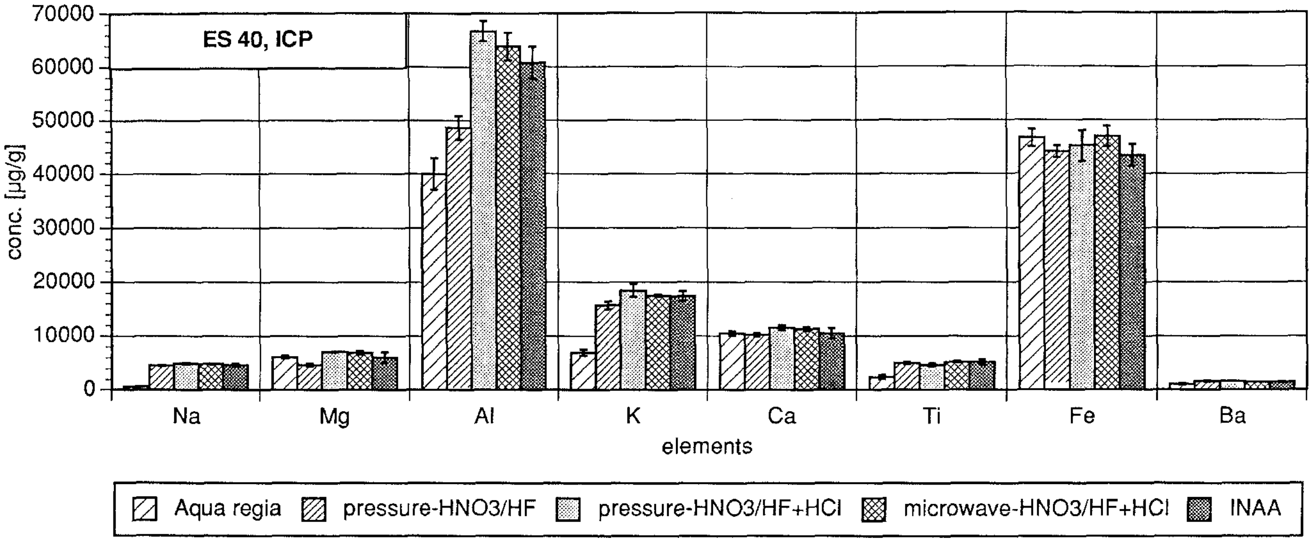

Fig. 2. Comparison of ICP-results of the different digestion procedures with INAA results for main components in ES 40; error bar: standard deviation of the total procedure (digestion and determination)

the material most resistant to digestion, due to its high content of heavy mineral constituents. For the aqua regia digestion, the elements Na, Al, K, Ca and Ti show recovery rates of less than 75% with regard to their certified values. With the exception of aluminum and sodium from the HNO_3/HF-digestion the main components could be determined quantitatively (recovery rate > 85%). Figure 2 shows similar results for an Elbe-sediment (ES 40). Concerning these elements, comparable results were also obtained for the other sediment samples investigated (NIST 1645, ES 27, ES 38) and for the determinations using ICP-methods and TXRF.

In Figs. 3 and 4 the results for the most remarkable elements in the group of minor and trace elements are presented. Again, the results for MESS-1 and ES 40 are shown. The analysis of the other sediment samples leads to similar results. Unsatisfactory recovery rates for all elements with the exception of lead were obtained from the aqua regia extraction. The HNO_3/HF digestion has problems with the elements Rb and Sr, especially when using ICP-methods for determination.

The two digestion procedures with HNO_3/HF and HCl, which differ only in the mode of heating, work smoothly with the exception of zirconium, which could not be determined quantitatively by any of the digestion procedures. For all other elements, which have been determined (more than 50 elements, as shown in Table 1), these digestion procedures lead to very good results in relation to the certified values and the INAA values.

Moreover, as can be seen from these figures, for an incomplete digestion, the recovery rates depend on the applied analytical method. For example, we obtained better

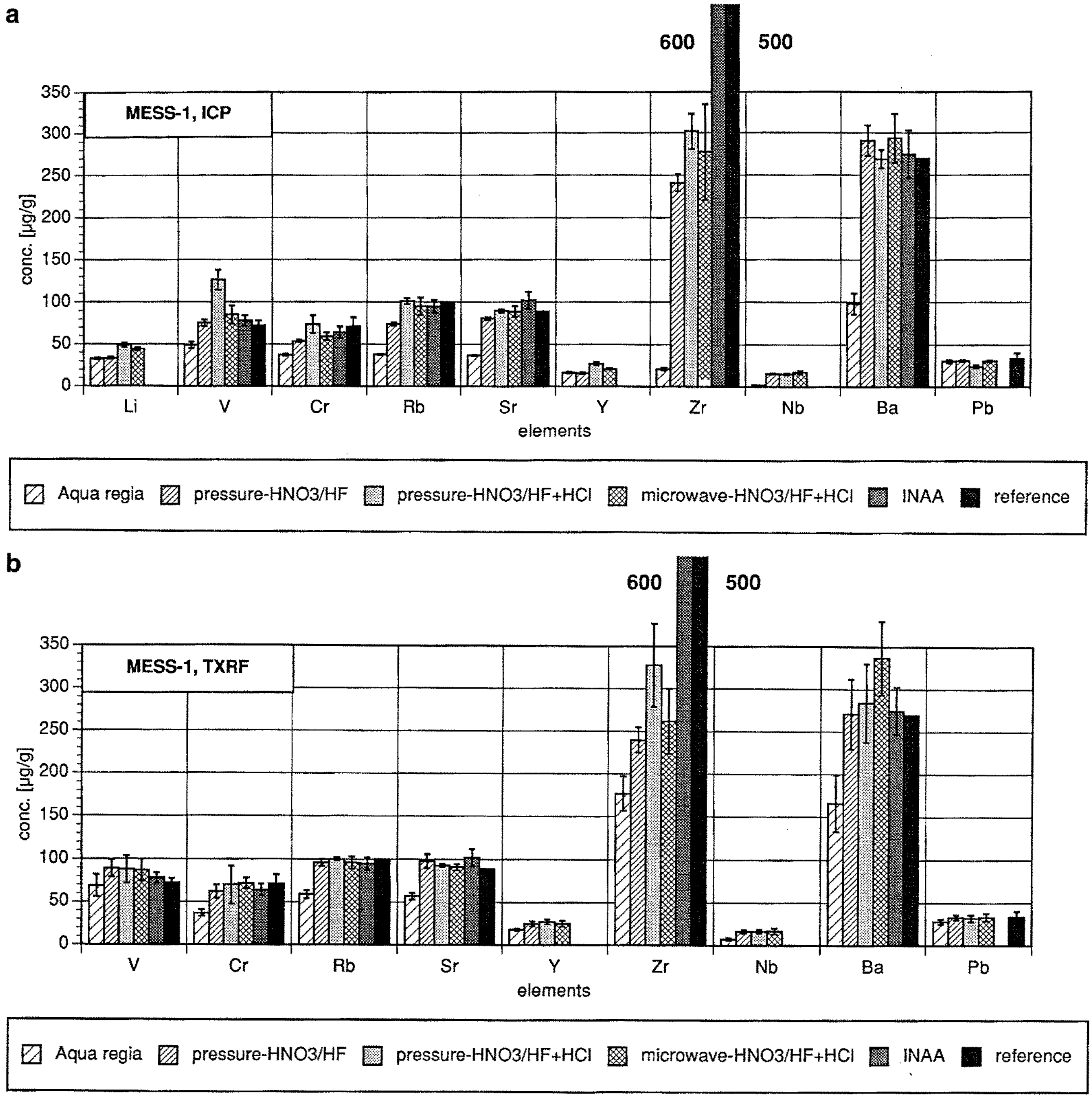

Fig. 3. a Comparison of ICP-results of the different digestion procedures with INAA results and reference values for minor and trace elements in MESS-1; error bar: standard deviation of the total procedure (digestion and determination). **b** Comparison of TXRF-results of the different digestion procedures with INAA results and reference values for minor and trace elements in MESS-1; error bar: standard deviation of the total procedure (digestion and determination)

recovery rates for V, Cr, Rb, and Sr with TXRF as with ICP-MS. The reason is, that the aqua regia and the HNO_3/HF digestion does not yield into clear solutions. The TXRF has less analytical difficulties with solutions containing fine suspended matter, whereas this kind of solutions may cause problems for the ICP-methods.

Furthermore, Figs. 1–4 give evidence of the generally good accordance between the applied analytical methods, i.e. ICP-MS/ICP-OES, TXRF and INAA in the case of a complete digestion procedure. For most elements the results differ in the range of 5–15%. The precision varies between 5 and 20% RSD (obtained by three digestions performed for each procedure and the analytical error). Good reliability of the data were obtained by this approach in combination with measuring five different types of sediment samples and using four different analytical techniques.

These figures show clearly the benefits and advantages of procedures c) and d), because of their high recovery rates for almost all elements and for the different types of sediments. Due to the very low contamination risk of the

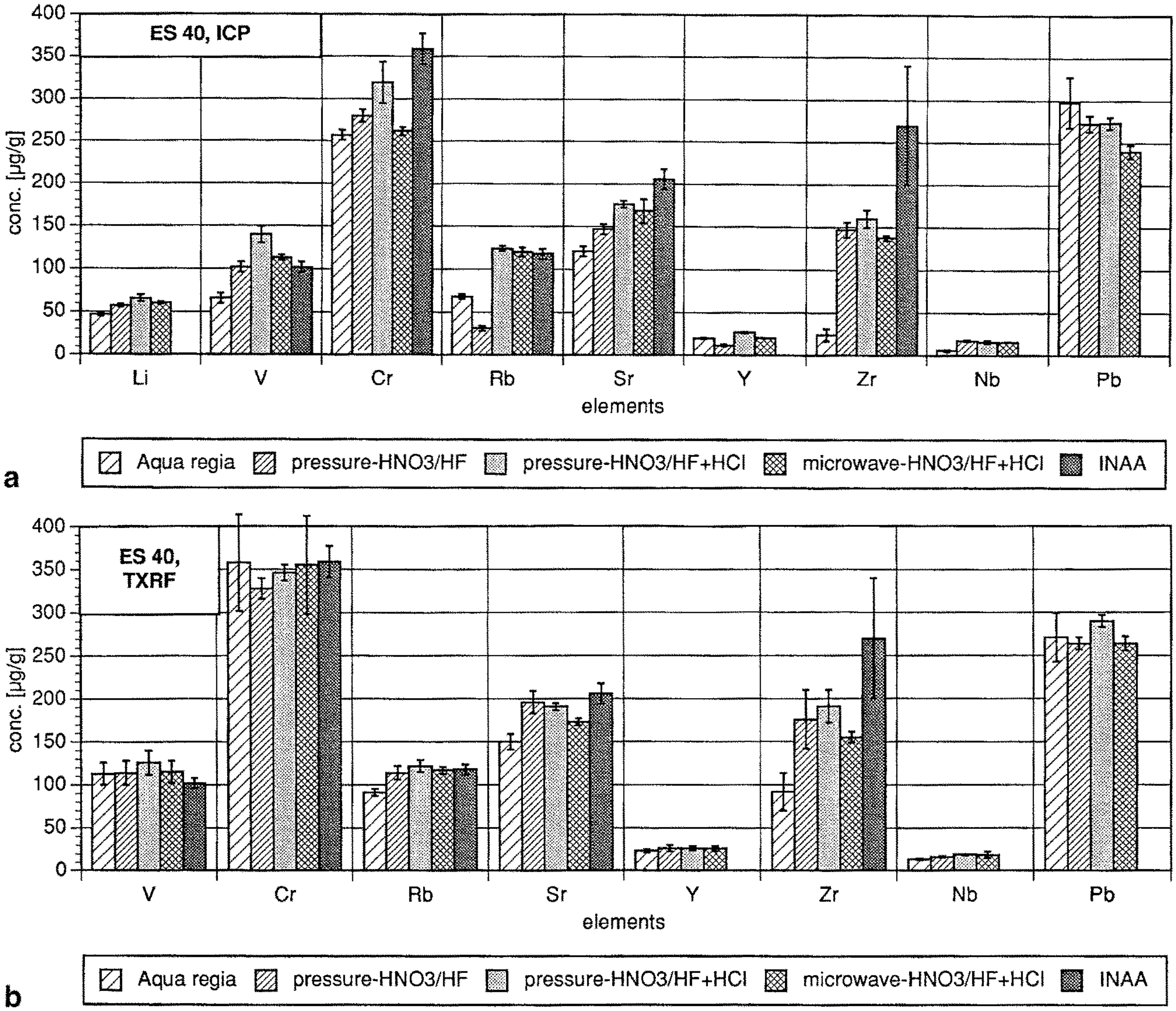

Fig. 4. a Comparison of ICP-results of the different digestion procedures with INAA results for minor and trace elements in ES 40; error bar: standard deviation of the total procedure (digestion and determination). **b** Comparison of TXRF-results of the different digestion procedures with INAA results for minor and trace elements in ES 40; error bar: standard deviation of the total procedure (digestion and determination)

microwave digestion procedure and its time saving, the procedure d), pressure digestion with microwave induction using HNO_3/HF + HCl, is proposed as the preferred digestion procedure for future analysis.

In Table 1 the results for the microwave digestion procedure obtained by the different applied analytical methods for all elements in the Elbe sediment ES 40 are presented in comparison to those obtained by INAA measurements. For allmost all elements the preferred digestion procedures lead to corresponding results for the different applied methods with the exception of Zr (see above). Some rare earth elements, in particular Yb, Lu and sometimes Dy, show variations in the results of ICP-MS and INAA measurements of more than 20%. As no certified values are available for the reference materials until now, it is not possible to decide which are the true results. The variations may be attributed to interferences in the ICP-MS, due to oxide interferences from lighter rare earth elements. A better fitting elemental equation or a correction procedure may compensate for these interferences [14]. This will be addressed in future investigations. Some of the elements could be determined quantitatively only by one of the methods, for example Li, Be, Pr, Gd, Ho, Er, Tm by ICP-MS and Cl, Se, Br, Zr, Ag, Hf, Au and Hg by INAA. For the other elements at least two different methods could be applied satisfactorily.

In Table 2, a summary of all the results from the quantitative determination (recovery rate better than 85% compared to certified values or INAA values) is given. As one can see from this summary, 52 elements could be determined by ICP-MS/ICP-OES and TXRF using the pressure digestion with HNO_3/HF and HCl. Additionally 8 elements could be analyzed by INAA (46 elements by INAA, but very time-consuming for a large series of samples). In total, 62 elements could be determined quantitatively using the combination of these methods. In con-

Table 1. Results for the Elbe-sediment ES 40 obtained after pressure digestion with microwave induction and determination with TXRF and ICP-methods in comparison with INAA-results

AN	ES 40			
	Element	TXRF mg/kg	ICP mg/kg	INAA mg/kg
3	Li		60.4 ± 1.5	
4	Be		4.31 ± 0.09	
11	Na		4810 ± 75	4620 ± 230
12	Mg		6875 ± 350	6000 ± 1000
13	Al		63800 ± 2590	60800 ± 3000
15	P		5050 ± 260	
16	S	4203 ± 183	4870 ± 249	
19	K	17816 ± 148	17500 ± 199	17400 ± 900
20	Ca	11510 ± 85	11350 ± 393	10500 ± 1000
21	Sc		8.87 ± 0.69	10.3 ± 0.5
22	Ti	4640 ± 170	5250 ± 127	5200 ± 500
23	V	115 ± 13	113 ± 3	102 ± 6
24	Cr	355 ± 57	262 ± 5	359 ± 18
25	Mn	1083 ± 16	1145 ± 65	1090 ± 50
26	Fe	42967 ± 378	46950 ± 1909	43460 ± 2000
27	Co			23.5 ± 1.2
28	Ni	93 ± 4	83 ± 3	81 ± 9
29	Cu	296 ± 4	278 ± 7	265 ± 70
30	Zn	1736 ± 10	1553 ± 89	1740 ± 90
31	Ga	15.9 ± 2.3	15.0 ± 0.8	18.5 ± 2.5
32	Ge		2.56 ± 0.08	
33	As	204 ± 4	170 ± 4	204 ± 10
34	Se	4 ± 0.8		3.6 ± 0.5
35	Br			9.7 ± 0.5
37	Rb	117 ± 4	120 ± 5	118 ± 6
38	Sr	173 ± 4	168 ± 14	206 ± 12
39	Y	25.8 ± 3	20.1 ± 0.3	
40	Zr	155 ± 6	138 ± 3	270 ± 70
41	Nb	18.5 ± 3.5	15.6 ± 0.3	
42	Mo		3.99 ± 0.17	2.9 ± 1.5
47	Ag	11.1 ± 4.4		12.0 ± 0.6
48	Cd	15.2 ± 5.6	14.5 ± 0.5	13.9 ± 1.0
49	In			0.42 ± 0.05
51	Sb			8.43 ± 0.43
52	Te		0.26 ± 0.06	
55	Cs		14.1 ± 0.4	14.0 ± 0.7
56	Ba	1669 ± 76	1530 ± 34	1570 ± 90
57	La		38.2 ± 1.4	42.0 ± 2.1
58	Ce		75.9 ± 2.3	77.9 ± 4.0
59	Pr		8.57 ± 0.31	
60	Nd		32.2 ± 0.8	34.4 ± 4.3
62	Sm		5.95 ± 0.21	7.4 ± 0.4
63	Eu		1.58 ± 0.07	1.55 ± 0.08
64	Gd		6.17 ± 0.19	
65	Tb		0.860 ± 0.030	0.92 ± 0.05
66	Dy		4.32 ± 0.10	5.6 ± 0.8
67	Ho		0.694 ± 0.015	
68	Er		2.11 ± 0.04	
69	Tm		0.273 ± 0.010	
70	Yb		2.02 ± 0.01	3.2 ± 0.5
71	Lu		0.286 ± 0.02	0.84 ± 0.09
72	Hf			7.1 ± 0.4
73	Ta		1.33 ± 0.03	1.67 ± 0.15
74	W	28.7 ± 5.1	29 ± 0.9	30.3 ± 1.5
79	Au			0.048 + 0.003
80	Hg			7.9 ± 0.4
81	Tl		1.73 ± 0.07	
82	Pb	264 ± 8	240 ± 8	
83	Bi		5.03 ± 0.2	
90	Th		9.87 ± 0.9	11.3 ± 0.6
92	U	32 ± 4.7	29.8 ± 0.7	31.1 ± 1.6

Table 2. Summarized results with recovery-rates (> 85%) obtained for the different digestion procedures and sediment samples using ICP-methods or TXRF in comparison to the capabilities of INAA

AN	Recovery rate > 85 %	Aqua regia = HCl/HNO$_3$ (3 : 1)			Pressure-HNO$_3$/HF (3 : 1)	Pressure-HNO$_3$/HF + HCl (2 : 1 + 2)	Microwave HNO$_3$/HF + HCl (2 : 1 + 2)	INAA
	Element	MESS-1	NIST 1645	Elbe-sediment	All sediment types	All sediment types	All sediment types	All sediment types
3	Li				●	●	●	
4	Be				●	●	●	
11	Na					●	●	●
12	Mg	●	●	●	●	●	●	●
13	Al					●	●	●
15	P				●	●	●	
16	S	●	●	●	●	●	●	
17	Cl							●
19	K				●	●	●	●
20	Ca		●	●	●	●	●	●
21	Sc				●	●	●	●
22	Ti				●	●	●	●
23	V		●	●	●	●	●	●
24	Cr		●		(●)	●	●	●
25	Mn	●	●	●	●	●	●	●
26	Fe	●	●	●	●	●	●	●
27	Co				●	●	●	●
28	Ni	●	●	●	●	●	●	●
29	Cu	●	●	●	●	●	●	(●)
30	Zn	●	●	●	●	●	●	●
31	Ga	●	●	●	●	●	●	●
33	As	●	●	●	●	●	●	●
34	Se							●
35	Br							●
37	Rb					●	●	●
38	Sr					●	●	●
39	Y					●	●	
40	Zr							●
41	Nb				●	●	●	
42	Mo			●	●	●	●	●
47	Ag							●
48	Cd	●	●	●	●	●	●	
49	In							●
51	Sb				●	●	●	●
52	Te							
53	I							●
55	Cs				●	●	●	●
56	Ba				●	●	●	●
57	La	●				●	●	●
58	Ce	●				●	●	●
59	Pr	●	●	●		●	●	
60	Nd	●	●			●	●	●
62	Sm	●	●	●		●	●	●
63	Eu	●	●	●	●	●	●	●
64	Gd	●	●	●	●	●	●	
65	Tb	●	●	●	●	●	●	●
66	Dy	●	●	●	●	●	●	●
67	Ho	●	●	●	●	●	●	
68	Er	●	●	●	●	●	●	
69	Tm	●	●	●	●	●	●	
70	Yb	●	●	●	●	●	●	●
71	Lu	●	●	●	●	●	●	●
72	Hf				●	●	●	●
73	Ta					●	●	●
74	W				●	●	●	●
79	Au							●
80	Hg							●
81	Tl				●	●	●	
82	Pb	●	●	●	●	●	●	
83	Bi				●	●	●	
90	Th				●	●	●	●
92	U				●	●	●	●

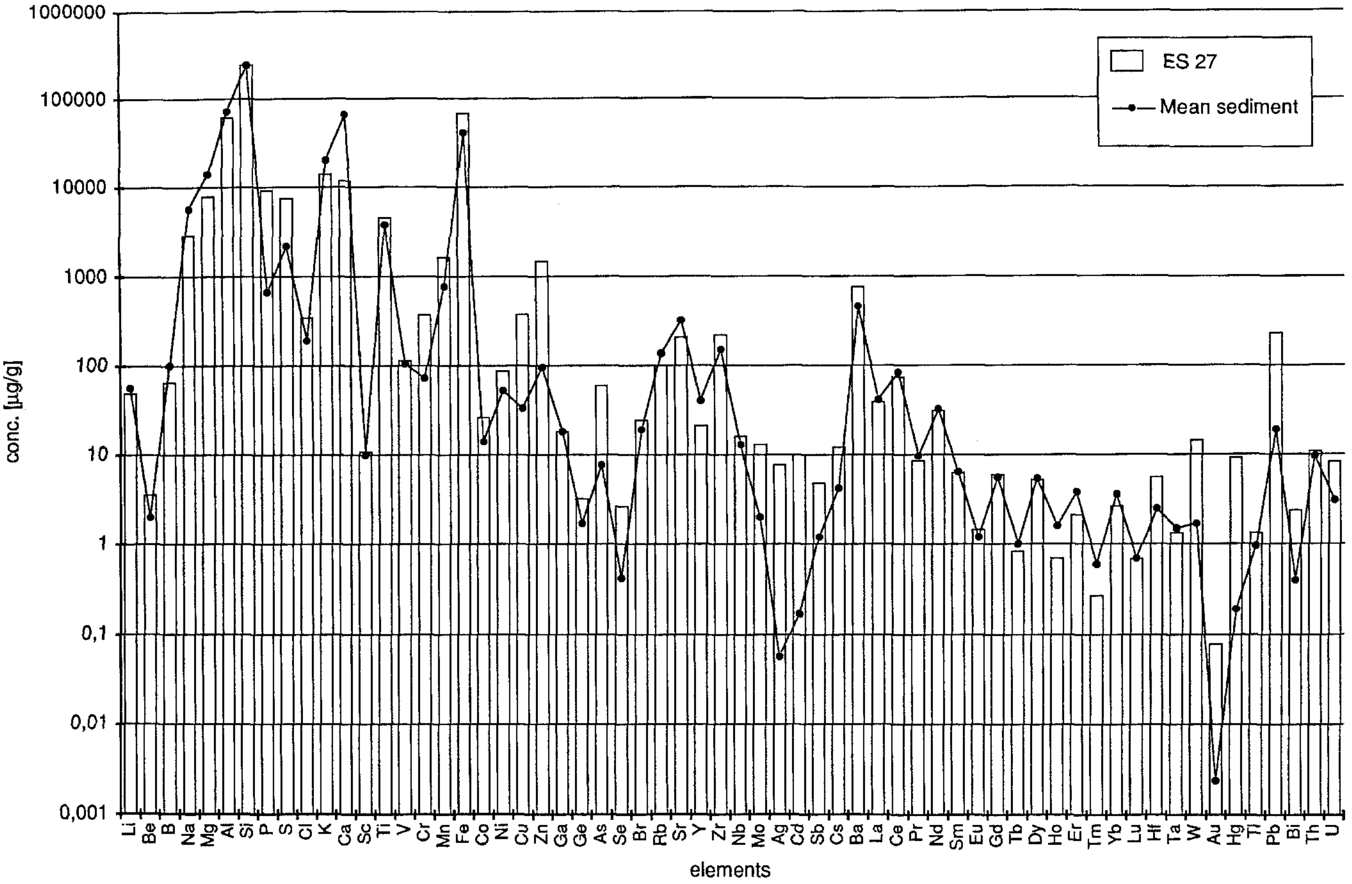

Fig. 5. Elemental pattern for a sediment of the river Elbe (ES 27) in comparison to a mean sediment [15]

trast, only 23 to 29 elements could be determined quantitatively from the aqua regia digestion, depending on the kind of sediment and the analytical method applied.

In Fig. 5 an elemental distribution pattern for the Elbe sediment ES 27 is given as an typical example and outlook for future investigations. To account for large differences in the elemental concentrations from 0.07 µg/g to 235 mg/g, a logarithmic scale has been chosen. This figure shows the comparison between the Elbe-sediment and a mean sediment from [15]. It indicates clearly the great differences for most of the anthropogenic elements, whereas the concentrations of the more geogenic elements, e.g. Al, Sc, Si and Fe are nearly similar. A special pattern can be seen in the group of the rare earth elements, which is characteristic for the distribution in sediments within this group.

Conclusions

The results show that more than 50 elements can be determined using the pressure digestion with microwave induction using $HNO_3/HF + HCl$. The commonly used aqua regia extraction method failed in the quantitative determination of more than 20 elements in sediments. This is especially true for the determination of the main components, like potassium or aluminium and for elements which are bound strongly to clay mineral components. Only a quantitative digestion procedure which results in clear solutions guarantees the determination of almost all elements, which can be determined by an oxidative acid digestion.

A comparison of the analytical methods shows that in general the accuracy for most elements looked at with all applied methods, ICP-MS/ICP-OES, TXRF and INAA is high. In particular, INAA was exhibited to be a useful reference method for direct multielement determinations, however restricted to the availability of special research reactors. The scope of having several methods at hand enables us to determine 62 elements in total. Furthermore the application of different independently working analytical techniques avoids a build-up of systematic errors and ensures the accuracy of the results. This provides us with the proper tools to determine the elemental distribution patterns in the water system of the river Elbe. From these patterns, characteristic tracer and elemental groups representing special sections of the river Elbe will be determined in forthcoming investigations.

Acknowledgements. The authors thank A. Panten, M. Schirmacher and E. Bössow for their helpful assistance within these investigations. Gratefully acknowledged is the financial support of the Bundesministerium für Bildung und Forschung (BMBF) for this work, which is part of the Project "Elbe 2000".

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