

Fast Method of Multi-Elemental Analysis of Stream Sediment Samples by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with prior Single-Step Microwave-Assisted Digestion

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A aplicação de procedimentos de digestão por micro-ondas em uma única etapa foi investigada visando obter um método rápido para a análise multielementar em amostras de sedimentos de córrego empregando a espectrometria de massas por plasma indutivamente acoplado (SF-ICP-MS). O material de referência certificado de sedimento de córrego produzido pelo Centro Nacional de Análise para Ferro e Aço, China (NCS CD 73309), foi selecionado como referência. Os reagentes empregados e avaliados para os procedimentos de digestão e extração foram: HNO_3 , mistura de HNO_3/HCl (9:1 v/v), mistura de HCl/HNO_3 (água régia, 3:1 v/v) e mistura de $\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v). Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, Tl, V e Zn foram avaliados, sendo que a maioria puderam ser determinados quando somente HNO_3 foi empregado para a digestão da amostra de sedimento de córrego. Para a determinação de Sb, o uso da água régia foi necessário. Berílio, K, Na, Ti e Tl foram fácil e satisfatoriamente isolados das matrizes ambientais quando água régia foi empregada para a digestão da amostra, embora os valores de recuperação para esses elementos tenham sido melhores quando a mistura $\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v) foi empregada.

One-step microwave-assisted digestion procedures were investigated with the scope to obtain fast method for multi-elemental analysis of stream sediment samples by sector field inductively coupled plasma-mass spectrometry (SF-ICP-MS). As a model, certified reference material stream sediment (NCS DC 73309), produced by China National Analysis Center for Iron and Steel was used. The reagents whose extraction abilities have been examined were: HNO_3 , mixture HNO_3/HCl (9:1 v/v), mixture HCl/HNO_3 (3:1 v/v *i.e.*, *aqua regia*), and mixture $\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v). The list of the selected elements is: Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, Tl, V, and Zn. Most of them could be analyzed when only HNO_3 for digestion was employed. For the determination of Sb, the use of *aqua regia* for digestion of stream sediment samples is required. Be, K, Na, Ti, and Tl can be easily and satisfactorily made available for environmental screening when digestion was performed using *aqua regia*, although the recoveries for these elements were better when the mixture $\text{HNO}_3/\text{HCl}/\text{HF}$ (v/v/v 8:1:1) was applied.

Keywords: rapid multi-elemental analysis, ICP-MS, microwave-assisted digestion, riverine sediment, trace elements

Introduction

Inductively coupled plasma-mass spectrometry is a powerful technique for determination of the trace elements in various environmental samples. This technique usually requires a transformation of a sample into solution. Therefore, investigation of the digestion methods makes an important step of the validation (optimization) of

analytical procedure. More precisely, the results of a digestion procedure depend on various factors such as matrix of the material to be analyzed, reagents applied for decomposition, temperature, duration of the digestion procedure, etc.

Most of the papers published so far deal with the analyses of only a few elements in stream sediment materials at the same time and do not provide the information on the possibilities of simultaneous analysis of larger number of elements. Thus Sastre and co-workers¹

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described the determination of Cd, Cu, Pb and Zn in various environmental materials among which is stream sediment reference material. The authors undertook two multi-step microwave-assisted decomposition procedures: one was total digestion procedure which involved HNO₃, HF, and HClO₄, but the other procedure was based on use of *aqua regia*. Total digestion procedure yielded higher recoveries of the analyzed metals. Pöykiö *et al.*² reported on the analysis of Cr, Cu, and Ni in stream sediment as well as in marine sediment reference material. The procedure described in their work implies a microwave-assisted decomposition of the materials using HNO₃, HCl, HF as well as H₃BO₃. Based on recovery values, Pöykiö *et al.*² determined Cr in higher concentration, while Cu and Ni in lower concentrations than certified ones.

Microwave-assisted digestion procedures for sample preparation are widely applied for decomposition of various types of samples from the environment, for instance soil,^{3,4} coal,⁵ various biological materials,⁶ atmospheric aerosols,⁷ etc. The survey of the literature can be summarized as follows: different authors - different digestion procedures.

A method for the transfer of the chemical elements from a sediment sample into solution should be chosen regarding the goals of the investigation, especially when an assessment of the anthropogenic impact on the sediment metal and metalloids content have to be done. That is because too strong digestion condition (*e.g.*, when HF is applied) leads to an over-digestion of a sample with subsequently erroneous conclusion about eventual environmental risks.⁸ It is well known that mobility and potential toxicity depend on the metal-to-sediment binding forms. For most of the environmental testings, digestion of the stream sediment samples using only nitric acid or *aqua regia* yields acceptable results.⁴ On the other hand, the selection of the digestion parameters may depend on the chemical properties of the investigated element(s). For instance, Al or Sb are elements whose recoveries strongly depend on the acid applied as it will be shown later here.

In this investigation, four series of digestion of the CRM stream sediment (NCS DC 73309), China National Analysis Center for Iron and Steel, Beijing, China, 2004 have been performed. In each series different acidic reagent was applied. The digestion of the sediment samples was carried out by closed-vessels microwave-assisted sample preparation system and the content of the selected metals and metalloids in the prepared solutions was determined by sector field mass spectrometry with inductively coupled plasma (SF-ICP-MS). The main objective of this investigation is to establish how a selection of an acid/acid mixture employed for digestion affects the recovery of the selected metals and metalloids from stream sediment samples.

Experimental

Materials and methods

Certified reference material stream sediment (NCS DC 73309, also known as GBW 07311), China National Analysis Center for Iron and Steel, Beijing, China, 2004 has been used for this validation.

For digestion purposes nitric acid (HNO₃, 65%, p.a., Kemika, Zagreb, Croatia), hydrochloric acid (HCl, 36.5%, p.a., Kemika) and hydrofluoric acid (HF, 48%, Mallinckrodt Baker B.V., Holland) were used.

Mass calibration of the SF-ICP-MS was performed using multi-elemental solution that contained B, Ba Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U, and Y in the concentration of 1 µg L⁻¹ (5% v/v HNO₃).

Standard solutions for external calibration have been prepared by appropriate dilution of the standard multi-elemental solution containing Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Sr, Ti, Tl, V, and Zn (100.0 ± 0.2 mg L⁻¹, 5% v/v HNO₃, Analytika Czech) with the addition of the single standard solutions Sb (1.000 ± 0.002 g L⁻¹, 5% v/v HNO₃ + 1% v/v HF, Analytika Czech), Sn (1.000 ± 0.002 g L⁻¹, 5% v/v HNO₃ + 1% v/v HF, Analytika Czech), U (1.000 g L⁻¹, 5% v/v HNO₃, Uranium Atomic Spectroscopy Standard Solution, Fluka). Separate standard solutions of Ag were prepared by dilution of single standard solution Ag (1.000 g L⁻¹, 5% v/v HNO₃, Silver Atomic Spectroscopy Standard Solution, Fluka).

For dilution, Milli-Q water (Millipore purification system, < 18 MΩ cm, Billerica, MA, USA) was used.

Microwave digestion system Multiwave 3000, Anton Paar (Graz, Austria) with high pressure Teflon vessels and the rotor XF-100 was used for wet digestion of the stream sediment CRM samples. Each solid sample (*ca.* 0.10 g) was put in the pre-cleaned vessel and mixed with the reagent(s). Volume of the acid/acid mixture was 10 mL. Since the XF-100 rotor accepts 8 vessels, seven replicas of the CRM stream sediment sample along with one procedural blank have been digested at the same time. The rotor was prepared according to the manufacturer's instructions and the parameters of the digestion procedure have been programmed as follows: T_{max} = 230 °C, P_{max} = 1400 W; t_(ramp) = 20 min, t_(heating at max. temperature) = 20 min, t_(ventilation) = 20 min. The selected heating temperature and power are the maximum for this model of rotor. Since previous studies as well as author's preliminary tests revealed that even small variation of the applied digestion temperature has significant influence on the extraction recoveries for some elements, it has been decided to

perform the investigation by heating the reaction mixtures at maximum available temperature, *i.e.* 230 °C.

When instrumental digestion routine has been finished, each solution was transferred into a plastic 100 mL volumetric flask (Nalgene, Rochester, NY, USA) and diluted to 100 mL. An aliquot of the solution (*ca.* 10 mL) was centrifuged. Centrifuge (Sigma, Sain Louis, MO, USA) was adjusted to 3000 rotations min^{-1} ; 20 min. After centrifugation, the 10-fold dilution (namely, 1 mL of sample solution was diluted to 10 mL solution) and addition of the internal standard (In 1 $\mu\text{g L}^{-1}$) was made prior to measurement on the SF-ICP-MS.

Teflon vessels of the microwave system were accurately cleaned after each digestion procedure. So, after removing the sample solutions, each vessel was rinsed with distilled-deionized water and dried under laminar air flow. Then, 10 mL of the acid reagent that was used in the precedent digestion procedure was instilled in each vessel. Finally, somewhat shortened digestion-like instrumental procedure ($T_{\text{max}} = 230\text{ °C}$, $P_{\text{max}} = 1400\text{ W}$; $t_{\text{ramp}} = 10\text{ min}$, $t_{\text{(heating at max. temperature)}} = 10\text{ min}$, $t_{\text{(ventilation)}} = 20\text{ min}$) was applied in order to remove remaining metal traces from the Teflon vessels. After that, the vessels were carefully (5-7 times) rinsed with water and dried under laminated air at the ambient temperature.

All elements (Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, Tl, V, and Zn) were determined by SF-ICP-MS (Element 2, Thermo Finnigan, Bremen, Germany). The analyzed solutions as well as standard solutions into plasma were transported by the auto-sampler (ASX 510, Cetac Technologies, Omaha, NE, USA) and sample introduction kit consisting of a conical nebulizer (Thermo Finnigan) and Scott-type glass spray chamber (Thermo Finnigan). Before starting the analysis, mass calibration was performed and the measuring conditions of the instrument were optimized (ion sample depth, ion lens setting, auxiliary gas flow, and coolant gas flow) in order to obtain maximum sensitivity.

It is important to pay attention to the selection of the isotopes of the analyzed elements as well as to the instrumental resolution which was employed for measuring certain elements. Regarding to the selection of the isotopes, it is known that one should choose the most abundant isotope of an element whenever it is possible. When possible, more than one isotope of given element should be measured; one for quantification and the other for control of possible interferences. In this study, this strategy was adopted for Cd, Mo and Sb. An isotope cannot be chosen for measuring when subject to a spectral interference. In addition, the isotopes are classified according to the instrumental resolutions in a manner which ensures separation of the analyzed isotope

from interfering ions. It is well known that the sensitivity of the instrument at the medium resolution (MR) is just 10% of the sensitivity at the low resolution (LR), while at the high resolution mode (HR) its sensitivity decreases to only 1% of the sensitivity at LR. Therefore, the rule that governs the selection of instrumental resolution for measurement of some isotope is: "Whenever it is possible one should choose the lowest resolution possible, but higher resolution may be chosen only if necessary." In this research, certain isotopes were measured at the medium resolution mode (MR): ^{47}Ti , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , and ^{86}Sr , because it is well known that these isotopes at low resolution would suffer from interferences such as $^{12}\text{C}^{35}\text{Cl}$, $^{35}\text{Cl}^{16}\text{O}$, $^{40}\text{Ar}^{12}\text{C}$, $^{39}\text{K}^{16}\text{O}$, $^{40}\text{Ar}^{16}\text{O}^1\text{H}$, $^{44}\text{Ca}^{16}\text{O}$, $^{40}\text{Ar}^{23}\text{Na}$, $^{40}\text{Ar}^{26}\text{Mg}$, and $^{75}\text{As}^{11}\text{B}$, respectively. The elements measured at the high resolution mode (HR) and the interferences (in brackets) that one should avoid are: ^{23}Na ($^{7}\text{Li}^{16}\text{O}$), ^{27}Al ($^{13}\text{C}^{14}\text{N}$), ^{39}K ($^{23}\text{Na}^{16}\text{O}$), ^{56}Fe ($^{40}\text{Ar}^{16}\text{O}$; $^{40}\text{Ca}^{16}\text{O}$), and ^{75}As ($^{40}\text{Ar}^{35}\text{Cl}$).⁹

Table 1 summarizes the details of the instrumental operating conditions and the data acquisition parameters.

Table 1. Operating conditions of the SF-ICP-MS and data acquisition parameters for the determination of measured elements

Parameters	SF-ICP- MS operating conditions
Instrument	Element 2 (Thermo Finnigan, Germany)
RF power	1300 W
Auxiliary Ar flow	0.85 L min^{-1}
Coolant Ar flow	1.063 L min^{-1}
Torch	Fassel type, 1.5 mm i.d.
Nebulizer	Micro Mist, AR40-1-F02, 0.2 mL min^{-1} (Glass Expansion)
Spray chamber	Jacketed Twister, 20 mL, quartz (Glass Expansion)
Sample cone	Ni, orifice diam. 1.1 mm
Skimmer cone	Ni, orifice diam. 0.8 mm
Acquisition mode	E-scan (magnetic jump with electric scan over small mass range)
Resolutions (m/ Δ m)	low = 300; medium = 4000; high = 10000
Sample intake	peristaltic pumps connected with the auto-sampler ASX 510, CETAC
Ion sample depth	adjusted daily
Ion lens setting	adjusted daily
Sample uptake rate	1 mL min^{-1}
Take-up time	120 s
Washing time between samples	60 s
Isotopes measured	LR: ^7Li , ^9Be , ^{95}Mo , ^{98}Mo , ^{107}Ag , ^{109}Ag , ^{111}Cd , ^{114}Cd , ^{120}Sn , ^{121}Sb , ^{123}Sb , ^{138}Ba , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{238}U (^{115}In : IS) MR: ^{47}Ti , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{86}Sr (^{115}In : IS) HR: ^{23}Na , ^{27}Al , ^{39}K , ^{56}Fe , ^{75}As (^{115}In : IS)
Acquisition mode	E-scan
Samples per peak	50 (LR), 20 (MR, HR)

Calibration curves were obtained by applying external standardization with series of standard solutions; 0 (*i.e.* blank) and multi-element standard solutions of 1.000 and 10.00 $\mu\text{g L}^{-1}$ as well as standard solutions of Ag (1.000 and 10.00 $\mu\text{g L}^{-1}$) and standard solution containing Na and K at the mg L^{-1} level. Method for calculation of the calibration curve was the weighted regression. High linearity of the calibration curves was obtained; correlation range (r^2) for calibration curves was 0.9850-1.000. One of the important characteristics of the SF-ICP-MS technique is a linear response in the wide range of concentrations. Therefore this technique allows undertaking simultaneous measurements of different chemical elements which in certain samples are present in various concentrations and it guarantees satisfactory results.

Procedural blank solutions and detection limits

Procedural blank solutions were prepared in the same way as sample solutions; equal volumes of an acid or acid mixture, which have been used for sample digestion, were microwave-assisted heated in the same manner that was

applied for the sediment samples digestion. The measured concentrations ($\mu\text{g L}^{-1}$) of the elements in the procedural blank were subtracted from the concentration values measured in the sediment CRM solutions. Table 2 shows the average metal and metalloid concentration values ($\mu\text{g L}^{-1}$) that were measured in procedural blank solutions as well as in the common blank solutions (1% v/v HNO_3 , s.p., 1% v/v HCl , s.p.). The results shown in the Table 2 reveal that the average procedural blank readings, for all measured elements, are far below concentration values measured in the solutions of the stream sediment. The values given in the Table 2 suggest that higher values of some elements (such as Al, K, Na) in the blank solutions are the consequence of the higher concentration of those elements in the stream sediment and their subsequent, somewhat increased, retention in the laboratory equipment. On the basis of the procedural blank values, the values of detection limits (LOD) have been calculated for this method.

The LOD shown in Table 3 represent the lowest concentration value (in mg kg^{-1}) of an element that can be quantified in a stream sediment sample by performance

Table 2. Measured metal concentrations ($\mu\text{g L}^{-1}$) in procedural blank solutions and in calibration blank solution

	Procedural blank ($\mu\text{g L}^{-1}$)				Blank 1% v/v HNO_3 +1% v/v HCl
	HNO_3	HNO_3/HCl (9:1 v/v)	HCl/HNO_3 (3:1 v/v)	$\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v)	
Ag	0.010	0.010	0.001	0.002	0.002
Al	1.25	2.46	8.000	11.7	1.12
As	0.002	0.009	0.445	0.009	0.009
Ba	0.095	0.075	0.055	0.069	0.029
Be	0.001	0.001	0.003	0.001	0.021
Bi	0.007	0.006	0.003	0.005	0.039
Cd	0.005	0.002	0.005	0.010	0.029
Co	0.001	0.001	0.001	0.002	0.009
Cr	0.013	0.024	0.017	0.036	0.021
Cu	0.020	0.015	0.044	0.020	0.013
Fe	0.536	0.600	0.912	1.70	0.537
K	0.150	0.220	0.310	2.43	0.778
Li	0.015	0.027	0.004	0.020	0.040
Mn	0.008	0.010	0.023	0.031	0.037
Mo	0.005	0.003	0.008	0.033	0.054
Na	2.08	1.64	10.0	8.36	0.236
Ni	0.095	0.019	0.041	0.016	0.017
Pb	0.072	0.096	0.026	0.001	0.064
Sb	0.051	0.048	0.039	0.049	0.151
Sn	0.019	0.022	0.113	0.061	0.034
Sr	0.013	0.012	0.005	0.086	0.020
Ti	0.046	0.039	0.064	0.709	0.053
Tl	0.010	0.010	0.042	0.050	0.088
U	0.001	0.001	0.001	0.003	0.029
V	0.003	0.003	0.005	0.009	0.029
Zn	0.540	0.185	0.356	0.048	0.100

of the analytical procedure described in the previous section. The LOD values are calculated as 3 standard deviation values (3σ) of the concentrations measured in the procedural blank (*i.e.* in the appropriate acid/acid mixture for digestion), multiplied by the dilution factor. The obtained values reveal that the established procedure is appropriate for stream sediment analysis, because these LOD values are far from the expected values of the concentrations of the elements in stream sediment samples.

Table 3. LOD of metals in solid environmental samples obtained by SF-ICP-MS after microwave-assisted digestion of samples in closed-vessels

	LOD (mg kg ⁻¹)			
	HNO ₃	HNO ₃ /HCl (9:1 v/v)	HCl/HNO ₃ (3:1 v/v)	HNO ₃ /HCl/HF (8:1:1 v/v/v)
Ag	0.08	0.02	0.02	0.04
Al	3.82	6.96	18.9	16.3
As	0.08	0.28	0.11	0.17
Ba	4.41	0.04	0.21	1.17
Be	0.02	0.02	0.02	0.02
Bi	0.02	0.02	0.00	0.15
Cd	0.02	0.02	0.02	0.04
Co	0.02	0.02	0.19	0.04
Cr	0.04	0.32	0.49	0.40
Cu	0.06	0.06	0.87	0.89
Fe	3.69	1.27	8.08	1.89
K	4.60	13.5	3.00	33.7
Li	0.13	0.13	0.28	0.49
Mn	0.06	0.13	0.42	1.00
Mo	0.02	0.02	0.02	0.02
Na	27.9	5.30	4.20	110
Ni	2.80	0.11	5.66	0.28
Pb	1.42	0.11	2.42	0.40
Sb	0.25	0.06	0.36	0.32
Sn	0.06	0.11	0.64	0.25
Sr	0.21	0.13	0.78	3.39
Ti	0.15	0.04	4.52	19.4
Tl	0.05	0.06	0.34	0.42
U	0.02	0.02	0.04	0.08
V	0.02	0.02	0.23	0.15
Zn	1.34	0.98	7.36	2.31

Results and Discussion

This paper studied analytical procedures for determination of selected metals and metalloids in stream sediment with prior microwave-assisted digestion procedure using four different acidic media. The main purpose of the work is the comparison of the extraction abilities of the acid or acid mixtures and the possibility of their application in fast multi-elemental analyses of the stream sediment samples. The results of the trace elements

determination in the stream sediment certified reference material, obtained after the analyses of seven replicates are shown in Table 4.

Investigation of the extraction of the metals and metalloids from various types of solid samples at different extraction conditions is important, because such results show how a change of the reagent and/or conditions of sample digestion (temperature, use of open or closed vessels) can greatly affect the recovery of an analyte. When a scientist decides to determine a metal content in stream sediment sample, the extraction conditions have to be chosen concerning the goal of the investigation. Namely, if geological characterization of the sample is to be performed - *i.e.*, if total digestion of the samples is required - what should be undertaken is an aggressive extraction procedure. On the other hand, determination of biologically available metal content should be made using milder digestion or extraction conditions.^{1,10}

The results shown in Table 4 have been obtained after analysis of seven replicates, which is significantly more than the number of replicates usually employed in environmental studies. It can be noticed that recovery of the greater part of the selected metals and metalloids increased when *aqua regia* or mixture HNO₃/HCl/HF (8:1:1 v/v/v) was applied instead of HNO₃ alone. The recovery values of some metals (Be, K, Na, Ti, and Tl) were largely increased by employing hydrofluoric acid along with hydrochloric and nitric acid, because partial digestion of the silicate matrix took place. The main exception to this pattern is Al: in solutions that contained HF, Al was determined in lower concentration due to precipitation of aluminium fluoride. It is important to mention that low recovery values obtained for K and Na as well as for Al in HNO₃ and HNO₃/HCl mixtures are due to binding of these metals in silicate core of the stream sediment. The recovery of Sb was significantly increased in *aqua regia* in comparison with the digestion procedures undertaken by nitric acid or by mixture of nitric and hydrochloric acid (9:1 v/v). It is known that in nitric acid Sb transforms into mixture of insoluble oxides (Sb₂O₃, Sb₂O₅, Sb₄O₄(OH)₂(NO₃)₂),^{11,12} but in the presence of hydrochloric acid Sb changes into chloro-complexes¹¹ and in the presence of hydrofluoric acid Sb exists as [SbF₆]⁻.¹¹ These facts about analysis of Sb in the solid samples have to be taken into consideration; Sb is an element of increasing environmental scientists' interest mainly due to anthropogenic emission of this metalloid in the environment.¹³ The results of the analyses of Sn show that recovery values of this element are low in all four applied digestion reagents. Since, according to the author's previous experience, a recovery of Sn usually greatly increases when stronger reagent for digestion is

Table 4. Determination of metals and semi-metals in the stream sediment CRM by SF-ICP-MS after microwave-assisted digestion with various reagents (mean \pm standard deviation, n = 8)

	HNO ₃			HNO ₃ /HCl (9:1 v/v)		HCl/HNO ₃ (3:1 v/v)		HNO ₃ /HCl/HF (8:1:1 v/v/v)	
	Certified (mg kg ⁻¹)	Found (mg kg ⁻¹)	Recovery (%)	Found (mg kg ⁻¹)	Recovery (%)	Found (mg kg ⁻¹)	Recovery (%)	Found (mg kg ⁻¹)	Recovery (%)
Ag	3.2 \pm 0.2	3.08 \pm 0.10	96	3.01 \pm 0.16	94	3.53 \pm 0.20	> 100	3.95 \pm 0.22	> 100
Al	55000 \pm 270	33100 \pm 3200	60	34200 \pm 2100	62	36400 \pm 1420	66	6420 \pm 7090	12
As	188 \pm 6	167 \pm 10	89	167 \pm 9	89	183 \pm 7	97	181 \pm 9.71	96
Ba	260 \pm 8.6	185 \pm 14	71	183 \pm 10	70	192 \pm 7.2	74	186 \pm 14.4	71
Be	26 \pm 2	13.3 \pm 1.44	51	13.2 \pm 1.40	51	16.4 \pm 1.64	63	28.4 \pm 1.39	> 100
Bi	50 \pm 2	49.3 \pm 2.38	99	48.3 \pm 2.08	97	50.0 \pm 2.11	> 100	52.0 \pm 1.91	> 100
Cd	2.3 \pm 0.5	2.17 \pm 0.10	94	2.13 \pm 0.10	93	2.32 \pm 0.12	> 100	2.24 \pm 0.09	97
Co	8.5 \pm 0.4	7.76 \pm 0.42	91	7.45 \pm 0.34	88	8.11 \pm 0.35	95	7.90 \pm 0.31	93
Cr	40 \pm 2	35.9 \pm 2.71	90	34.8 \pm 1.78	87	37.0 \pm 1.42	93	38.7 \pm 1.32	97
Cu	79 \pm 2	74.4 \pm 3.57	94	72.2 \pm 3.39	91	77.9 \pm 2.95	99	77.7 \pm 2.58	98
Fe	30700 \pm 250	27800 \pm 1700	91	27800 \pm 1600	91	26900 \pm 1200	88	27000 \pm 1400	87
K	27200 \pm 300	13800 \pm 1500	51	14100 \pm 1800	52	13900 \pm 700	51	23500 \pm 1150	86
Li	71 \pm 1	64.5 \pm 3.70	91	64.2 \pm 2.97	90	67.5 \pm 3.89	95	71.6 \pm 3.14	> 100
Mn	2490 \pm 43	2550 \pm 140	> 100	2460 \pm 120	99	2470 \pm 102	99	2500 \pm 92	> 100
Mo	5.9 \pm 0.3	5.85 \pm 0.28	99	5.72 \pm 0.29	97	6.15 \pm 0.28	> 100	5.80 \pm 0.23	98
Na	3500 \pm 120	604 \pm 60	17	600 \pm 55	17	650 \pm 40	19	3370 \pm 132	96
Ni	14.3 \pm 0.51	14.7 \pm 1.91	> 100	13.5 \pm 1.25	95	14.3 \pm 0.65	> 100	14.3 \pm 0.68	100
Pb	636 \pm 11	627 \pm 31.8	99	620 \pm 30	97	610 \pm 28	96	670 \pm 27	> 100
Sb	14.9 \pm 0.61	1.40 \pm 0.26	9	3.56 \pm 0.97	24	13.2 \pm 0.65	89	14.4 \pm 0.76	97
Sn	370 \pm 22	33.1 \pm 4.90	9	50.2 \pm 2.87	14	59.5 \pm 2.88	16	64.7 \pm 4.31	17
Sr	29 \pm 2	12.6 \pm 0.96	43	12.4 \pm 0.79	43	15.0 \pm 0.60	52	17.7 \pm 1.90	61
Ti	2100 \pm 51	450 \pm 45	21	450 \pm 40	21	760 \pm 72	36	2150 \pm 90	> 100
Tl	2.9 \pm .2	1.10 \pm 0.13	38	1.12 \pm 0.09	39	1.41 \pm 0.07	49	2.64 \pm 0.09	91
U	9.1 \pm 0.5	8.64 \pm 0.25	95	8.40 \pm 0.35	92	8.76 \pm 0.51	96	8.84 \pm 0.54	97
V	47 \pm 2	39.7 \pm 2.99	84	39.12 \pm 2.12	83	42.9 \pm 1.90	91	44.1 \pm 1.42	94
Zn	373 \pm 7.1	330 \pm 17	88	320 \pm 15	85	380 \pm 17	> 100	360 \pm 14	96

applied, the observed weak increase of the recovery of Sn could be explained in terms of the nature of Sn binding in the tested stream sediment reference material. Also, high certified value of the Sn content (370 mg kg⁻¹) and RSD of the Sn analyses support this hypothesis. Furthermore, the results obtained by Meeravali and Kumar¹⁴ suggest that the amount of a stream sediment sample could affect Sn recovery. The values obtained for Ba reveal constancy and for Sr a moderate increasing of the recovery when stronger reagent is applied. However, even when the strongest reagent, among investigated acidic reagents, was used (*i.e.*, HNO₃/HCl/HF, 8:1:1 v/v/v), the recovery of Ba was 71% and for Sr was only 61%. This observation could be explained both in terms of the nature of Sr binding in the stream sediment and low solubility of strontium

fluoride.¹² The other one earth-alkaline element selected for analysis was Be. Its recoveries observed in the cases of the digestion processes involving HNO₃ alone or HNO₃ and HCl were quite low. This can be explained in terms of Be chemistry: in HNO₃, Be tends to form covalent compound such as Be(NO₃)₂ that is scarcely soluble¹² or Be₄O(NO₃)₆ which is volatile.¹¹ On the other hand, in the presence of HF, Be forms BeF₂, which is quite soluble; that is why the recovery value of Be obtained when the digestion was carried out with mixture HNO₃/HCl/HF (8:1:1 v/v/v) is high (> 100%).¹² The other metal selected in this work, which shows similar pattern of the recovery is Ti. In the acidic solutions, such as HNO₃ or HCl, Ti forms insoluble oxo-complexes, but reaction of Ti and HF yields soluble fluoro-complex, [TiF₆]²⁻.^{11,12} Finally, the results of

the determination of Tl can also be explained in terms of Tl chemistry. That is, in HNO_3 , Tl forms insoluble oxides. In the presence of HCl, Tl forms TlCl , which is scarcely soluble. In the reaction of Tl and HF, TlF is formed; TlF is well soluble and that results in high recovery of Tl when HF is involved in digestion procedure.¹¹

The relative standard deviation values (RSD) were found to be about 5% or less for most of the elements in all four procedures. The RSD values for some elements that were measured in low concentrations in solutions (such as Sb, Tl) were above 10%. It is important to notice a high RSD value, 110%, for Al in the $\text{HNO}_3/\text{HCl}/\text{HF}$ digestate. This can be attributed to the precipitation of AlF_3 in acid medium and its irregular distribution through the solutions. When comparing the RSD values obtained in this study with those calculated using certified values, it can be noticed that in some cases in this investigation significantly higher RSD values have been obtained. For instance, RSD of the determination of Sb in HNO_3 and HNO_3/HCl (9:1 v/v) leachates are 19 and 27%, respectively, while the certified one is 4.1%. Similar situation occurred with Sn (14 vs. 6%) and Tl (12 vs. 6.9%), both in HNO_3 leachate. Regarding the analyses of two major elements (K and Na), the RSD decreases upon applying stronger digestion condition. Thus, for example, K was determined with the RSD of 11% in HNO_3 leachate, while that in $\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v) leachate was 4.9%. The certified RSD for K is 11%. According to certificate for stream sediment used in this study, the RSD value for Na is 3.4%. Similar to the case of K, also for Na, RSD obtained in the procedure concerning the use of HNO_3 for digestion was 9.9%, while, on the other hand, in the $\text{HNO}_3/\text{HCl}/\text{HF}$ (8:1:1 v/v/v) leachate Na was determined with RSD of 3.9%. On the other hand, for some of the elements, lower RSD values than those calculated from the certified values have been obtained in this study. For Ag the RSD values obtained in this study vary from 3.2 to 5.7%, while 6.3% is calculated from the certified values. The most important case is Cd: RSD calculated from certified values is almost 22%, while RSD in four series of the experiments described in this paper ranged from 4.0 to 5.2%.

Literature survey reveals that data on similar experiments on the reference material used in this study are quite rare. As mentioned previously, Sastre *et al.*¹ published the results of the determination of Cd, Cu, Pb, and Zn. The recoveries of all four analyzed elements were somewhat above 100%, but also decomposition medium was quite strong: 70% v/v HNO_3 , 40% v/v HF, 70% v/v HClO_4 , as well as 30% m/m H_2O_2 . Valverde¹⁵ undertook wet digestion of the same certified reference material, using *aqua regia* with reflux during 16 h. This author measured only As by ICP-MS and

found it in a concentration of 190.6 mg kg^{-1} , 101% recovery.¹⁵ Stream sediment reference material NCS DC 73309 was used also by Lima *et al.*¹⁶ for method optimization of As, Cd, and Pb determination by electrothermal atomic absorption spectrometry (ETAAS), with prior microwave-assisted digestion of solid samples. The mixture for digestion was composed as follows: 4 mL HNO_3 , 6 mL HCl, as well as 10 mL HF, and maximum temperature was 160 °C. Lima *et al.*¹⁶ undertook a series of experiments which implicated use of seven different permanent modifiers. Therefore the authors obtained a series of seven different results for each element that has been measured. Thus, they determined the recoveries of As, Cd, and Pb in ranges 80-101%, 78-101%, and 86-101%, respectively.

Consequently, one can conclude that elemental concentrations determined in a certain material from the environment, such as stream sediment, are very sensitive to several experimental parameters. Therefore, a comparison of the numerical values is possible when at least one group of parameters, in different experiments that are to be compared, is the same (for instance temperature and duration of digestion, digestion medium or matrix of the analyzed material). One, but not the only one, criterion for estimating the effectiveness of a digestion method is the recovery value obtained for the analyzed element. It is necessary to consider that low recovery does not necessarily imply unsuitability of a method, because the recovery is affected by at least four factors: nature of metal-to-sediment binding, chemical properties of the analyzed element, extraction reagent(s) used, and the temperature of the extraction procedure. On the other hand, a numerically low extraction value does not imply a low concentration of an element and a problem of reaching the method detection limit, *i.e.* analysis of some element can be characterized by low recovery and, at the same time, relatively high concentration in sediment sample and, subsequently, in digestate. Namely, low recovery in such case does not imply an analytical problem.

Taking into consideration the results presented in this paper, it can be concluded that the method employing *aqua regia* as a reagent for wet digestion is the most favorable for simple and fast, ecologically oriented, multi-elemental analysis of stream sediments, for two main reasons: (i) *aqua regia* is a reagent that is not so strong to provide a complete dissolution of a stream sediment samples, and such an analysis generally should not lead to misconceptions about potential ecological risks due to the biologically available metal fraction present in the stream sediment samples, and (ii) *aqua regia* allows chemical change of a large part of the investigated elements into the chemical forms which are soluble in acidic medium and therefore

suitable for measuring by ICP-MS. However, in the cases of more detailed determination of metal contents in stream sediment materials, *e.g.*, when the goal of the investigation is complete geological characterization of the material, multi-step digestion procedures should be carried out.

Conclusions

The subject of this study are the methods for multi-elemental quantitative analysis of stream sediment samples by SF-ICP-MS with previous one-step wet digestion in high pressure microwave system. Among reagents selected for wet digestion of stream sediment samples, *aqua regia* (HNO₃/HCl, 1:3 v/v) was found to be the most favourable digestion medium for fast ecological screenings of the metal and metalloid content (especially those usually anthropogenically disposed in the environment). That is because amongst all digestion methods that have been studied here, *aqua regia* offers the possibility to perform analyses of a large number of ecologically important heavy metals, without over-digesting some of them and, at the same time, by changing the elements to its appropriate chemical forms.

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