



Water as a mild extractant of metals and metalloids from the samples of the selected certified reference materials and subsequent multi-elemental quantification by ICP-AES

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Abstract An assessment of mobility and bioavailability of trace elements present in the soil requires the determination of these elements in soil samples by an appropriate methodology. In such a context, the use of mild extraction reagents—such as water—is considered to be appropriate. On the other hand, performing an analysis of a reference material together with real samples is recommended in order to control the quality of analytical procedure. The quantification of 27 analytes in aqueous extracts of the soil CRMs samples is described. The methodology consisted of single-step extraction of analytes by deionized water ($m/v = 1/10$) with their subsequent direct determination by inductively coupled plasma–atomic emission spectrometry (ICP-OES). Three certified reference materials (CRM) for soils have been selected as model samples: NCS DC 77302 (alias GBW 07410), Metranal-31, and Metranal-33. Although the recoveries of the selected elements obtained by water extractions are very low (i.e., the values usually do not exceed 1%), the results obtained in this study reveal the elements that by means of ICP-OES can be quantified in the water extracts of unpolluted soils are as follows: Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, S, Sr, Ti, and V. However, ICP-OES is not sensitive enough to quantify the elements As, Be, Cd, Co, Pb, Sb, Se, Tl, and Zn that are present in the

water extracts of clean soil samples in too low mass fractions. The results obtained in this paper are useful for future uses of the three tested CRMs, in the cases of the extraction of the analytes by deionized water at room temperature.

Keywords Certified reference materials · Heavy metals · Trace elements · ICP-AES · Soil · Water extraction

Introduction

Soil is a very complex component of an ecosystem and is highly exposed to potential input of the toxic substances. Soil is also a very powerful reservoir of such substances due to its ability to bind various chemicals onto the surface of the soil particles (Dube et al. 2001). Trace metals and metalloids are amongst such substances. Potential hazard of an elevated presence of toxic elements in soil lies in the fact that chemical elements, in their various chemical forms, can enter food chain. The main input of the toxic elements into food chain is through their uptake by plants (Chojnacka et al. 2005; Kabata-Pendias 2011).

An assessment of mobility and bioavailability of trace elements that are present in soil requires determination of those elements in soil samples by an appropriate methodology. Most of the methods for trace metals and metalloids analysis in the soil samples described in the literature and widely present in the professional practice consist of transferring the analytes into solution with subsequent quantification of elements in the

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prepared solutions (extracts or digestates) by means of some of the atomic spectrometric techniques. The development and a choice of methodology for quantification of the “heavy metals” in the soil samples were a consequence of the characteristics (i.e., capabilities) of analytical techniques (Houba et al. 1996). Namely, a more aggressive digestion method yields higher analyte concentrations in the digestates, allowing to apply a less sensitive analytical technique for their measuring in the solutions.

In the context of the analysis of trace and major elements in soil samples, the most used method of transferring of the analytes into solution state consists of digesting the samples by aqua regia (Kingston et al. 1997). Such an aggressive digestion medium does not simulate natural conditions in soil and consequently, yielding concentrations of the elements in the digestates that are too high, does not allow drawing reliable conclusions about the mobility of the analyzed elements in the soil. Therefore, many researchers are trying to develop and characterize methods that would be more appropriate in terms of assessing bioavailability of elements of ecological interest and in these terms the use of mild extraction reagents is found to be much more appropriate (Lebourg et al. 1996; Scheckel et al. 2009; Kumpiene et al. 2017; Vasile et al. 2018; Tariq et al. 2019; Alan and Kara 2019). In the literature, there have been documented many different extraction reagents and described numerous one-step mild extraction methods that were developed with the aim to assess the mobility and bioavailability of metal, semi-metal, and non-metal ions from the soil. A detailed review of such methods would be beyond the scope of this paper, but it has to be mentioned that some of the most often described mild extractants used for the characterization of soil (or sediment) samples are (i) deionized water (Füleky and Czinkota 1993; Heltai et al. 2000), (ii) unbuffered salt solutions (MgCl_2 , CaCl_2 , BeCl_2 , NH_4Cl , NH_4NO_3 , ...), (iii) buffered salt solution ($\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$, ...), (iv) chelating agents (EDTA, DTPA, ...), and (v) diluted or weak acid solutions (HCl , CH_3COOH , HCOOH , ...) (Houba et al. 1996; Lebourg et al. 1996; Rauret 1998; Sahuquillo et al. 2003; Aydinalp and Katkat 2004; Chojnacka et al. 2005). Along with the methods based on a single-step extraction, sequential (multi-step) extraction procedures are also used for the characterization of soil samples. Sequential extraction procedures allow to differentiate and quantify elements bonded to different

geological phases of the soils (or sediments) (Heltai et al. 2002; Probst et al. 2003; Sahuquillo et al. 2003; Rao et al. 2008; Heltai et al. 2011, 2015).

Regarding the trace element determination in “real” samples, a use of an appropriate certified reference material (CRM) plays an important role. The CRMs allow an analyst to control accuracy and precision of an analytical procedure. The CRM applied in testing of a set of “real” samples has to be similar in terms of matrix and needs to be treated analogously to the tested samples. Many different CRMs of the soils with certified metals and metalloids mass fractions are present in a worldwide use nowadays, but almost always the certified values reflect the total mass fraction of the elements; i.e., the elements get quantified in the digestates prepared using the reagents that contain hydrofluoric acid. There are some soil CRMs (such as Metranal-31, Metranal-33) whose certification sheets present mass fraction values that were determined after the use of less strong digestion reagents (e.g., aqua regia, nitric acid). However, according to our best knowledge, there is no soil CRM that has been certified after extraction with deionized water. We have chosen three soil CRMs for this study: NCS DC 77302 (alias GBW 07410), Metranal-31, and Metranal-33. A survey of the databases *Web of Science* and *GeoReM* (Jochum et al. 2005) reveals that the CRM NCS DC 77302 (GBW 07410) has been multi-elementally characterized only after digestion with strong acid reagents (Roje 2010; Fiket et al. 2017), while there is no reference to characterization of Metranal-31 and Metranal-33. So, we consider this paper to be the first in dealing with multi-elemental analysis of the three cited CRMs for soil by measurement of the analytes in the extracts prepared using deionized water. The results presented in this paper will be useful as information to researchers in the future uses of these CRMs for quality control of analysis, in the context of multi-elemental testings of soil samples with the extraction by deionized water as an extraction reagent.

Experimental

Certified reference materials

Three certified reference materials for soil have been selected for this study:

- NCS DC 77302, China National Analysis Center for Iron and Steel, Beijing, China
- Metranal-31, Analytika, Prague, Czech Republic
- Metranal-33, Analytika, Prague, Czech Republic.

Standards and other chemicals

Standard solutions as well as sample solutions were acidified using nitric acid (v/v 1%, HNO₃, 65%, supra pur, Fluka).

Standard solutions for external calibration have been prepared by appropriate dilution of the Multi-element Standard Solution containing Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, In, K, Li, Mg, Mn, Mo, Na, Ni, Nb, Pb, Rb, Sb, Se, Sr, Ti, Tl, V, U, and Zn (100 ± 0.2 mg L⁻¹, 5% v/v HNO₃), CPACChem, Ltd., Bulgaria. Along with this solution, the Multielement standard solution III for ICP (Ca, Mg, K, Na; 5% v/v HNO₃), Fluka, Switzerland, has been used after being 1000-fold diluted. Furthermore, the standard solutions for calibration of P and S were prepared by dilution of the Multi-element Standard Solution containing P and S (100 ± 0.2 mg L⁻¹), CPACChem, Ltd., Bulgaria.

For the purposes of the control of quality of the instrumental measurement, two certified reference materials (CRM) were used: (i) CRM for water SLRS-6, National Research Council, Canada, and (ii) Multi-element Standard Solution QCCPAWater1.L1, CPACChem, Ltd., Bulgaria.

Ultra-pure water (Siemens Ultra clear, 0.055 µS/cm) was used for dilution and rinsing of the vessels.

All dilutions and the storage of standard solutions as well as sample solutions were made using polypropylene vessels. All vessels were washed in nitric acid, 10% (v/v) (HNO₃, 65%, p.a., Carlo Erba Reagenti, Italy), and thoroughly rinsed by ultra-pure water prior to use.

Water extraction procedure

The extraction of the elements from CRM samples was made using deionized water at room temperature. The reaction mixtures (~ 1 g soil sample/10 mL H₂O) were prepared in 20-mL polypropylene vessels and then shaken on the orbital shaker for 24 h at 200 rpm (Rojc 2008). Immediately after the shaking, the extracts were separated from the solid samples by filtration through syringe-type filters Minisart (pores size 0.45 µm, diameter 28 mm, hydrophilic, non-sterile), Sartorius,

Germany. The obtained extracts were acidified by nitric acid (HNO₃, supra pur, $\psi = 1\%$). All three CRMs were analyzed in ten replicates ($N = 10$) which is notably higher than the number of sample replicates that are usually subjected to similar testings in the environmental analytical chemistry.

Multi-elemental measurement by ICP-OES

The concentrations of the selected elements in the prepared extracts were measured by means of inductively coupled plasma–optical emission spectrometry, ICP-OES (Table 1).

Instrumental detection limits (IDL) were calculated as 3-fold standard deviations of the instrumental blank measurements ($N = 5$). Quality of the instrumental measurement was controlled by measuring the samples of the two CRMs for water: SLRS-6 and QCCPAWater1.L1. The results presented in Table 2 reveal that, in the cases of the elements that could be quantified and for which certified mass concentration values have been provided, measured values are generally in a good agreement with the certified ones. More precisely, a quantitative comparison of the measured values with the certified ones according to the European Commission's recommendations on how to compare measurement results with the certified values (Linsinger 2010) allows a conclusion that only the measured mass concentration of sulfur (S) significantly differs to its certified value. It can be seen that S is overestimated slightly more than 10%.

Method detection limit (MDL) values were determined as 3-fold standard deviations of the procedural blank readings ($N = 15$) including dilution factor. The MDL values are given alongside the results of the CRMs analysis in Tables 3, 4, and 5.

Results and discussion

The results of the quantification of the selected elements in the samples of the certified reference materials for soil, after extraction of the analytes by deionized water, are presented in Tables 3, 4, and 5. As it has been mentioned in the “Experimental” section, MDL values were calculated as three standard deviations of the measurement results of the 15 replicates of the procedural blank, with the calculation using dilution factor; therefore, MDL values are expressed in mg/kg.

Table 1 The main operating parameters of the ICP-OES spectrometer

Parameters	ICP-AES operating conditions
Instrument	Thermo Fisher iCAP6300 Duo
RF power	1150 W
Auxiliary Ar flow	0.5 L min ⁻¹
Sample Ar flow	0.65 L min ⁻¹
Coolant Ar flow	12 L min ⁻¹
Sample introduction system	- auto-sampler CETAC ASX-260 connected by peristaltic pumps - concentric nebulizer with cyclonic spray-chamber
Peristaltic pumps rate	45 rpm
Peristaltic pumps tubes	- sample: orange/white - rinsing: white/white
Flush (take-up) time	45 s
Washing time between samples	60 s
Plasma view	Auto view
Maximum measuring time	- low wavelengths (160–230 nm): 15 s - high wavelengths (230–847): 5 s
Lines measured (nm)	Al-167.079, As-189.042, Ba-455.403, Be-234.861, Ca-393.366, Cd-226.502, Co-228.616, Cr-205.552, Cu-224.700, Fe-238.204, K-766.490, Li-670.784, Mg-279.553, Mn-257.610, Mo-202.030, Na-589.592, Ni-231.604, P-178.284, Pb-220.353, S-182.034, Sb-217.581, Se-196.090, Sr-407.771, Ti-334.941, Tl-190.856, V-311.071, Zn-202.548
Calibration solutions	- 0 µg/L (all elements) - 1 µg/L (all, except Ca, K, Mg, Na, P, and S) - 10 µg/L (all, except Ca, K, Mg, Na, P, and S) - 100 µg/L (all elements, except P and S) - 2000 µg/L Ca, 200 µg/L K, 400 µg/L Mg, 1000 µg/L Na - 50 µg/L (P and S) - 100 µg/L (P and S)
System rinsing solution	Nitric acid, HNO ₃ , supra pur, $\psi = 1\%$

Certified reference material for soil NCS DC 77302

NCS DC 77302 (that used to be called GBW 07410) is a certified reference material for which a large number of certified (along with a few information) mass fraction values are provided. In this study, 27 chemical elements were measured in its water extracts and 17 elements

Table 2 Instrumental detection limit (IDL) values (µg L⁻¹) and the results of the CRMs analysis, expressed as mass concentration (µg L⁻¹)

Element	IDL*	Certified SLRS-6	Measured**
Al	19.3	33.8 ± 2.2	32.0 ± 5.2
As	2.48	0.57 ± 0.08	< LOD
Ba	0.794	14.28 ± 0.48	14.3 ± 0.3
Be	0.121	0.0066 ± 0.0022	< LOD
Ca	0.602	8760 ± 200	8283 ± 102
Cd	2.01	0.0063 ± 0.0014	< LOD
Co	2.39	0.053 ± 0.012	< LOD
Cr	1.81	0.252 ± 0.012	< LOD
Cu	0.923	23.9 ± 1.8	26.7 ± 0.1
Fe	11.2	84.3 ± 3.6	88.0 ± 5.9
K	31.2	651 ± 54	624 ± 62
Li	2.36	–	< LOD
Mg	0.179	2133 ± 58	2161 ± 91
Mn	1.03	2.12 ± 0.10	2.14 ± 0.42
Mo	4.69	0.215 ± 0.018	< LOD
Na	11.6	2760 ± 220	2709 ± 108
Ni	1.66	0.616 ± 0.022	< LOD
P	13.4	–	< LOD
Pb	20.0	0.170 ± 0.026	< LOD
S	30.3	–	1895 ± 146
Sb	8.39	0.3372 ± 0.0058	< LOD
Se	7.81	–	< LOD
Sr	0.11	40.66 ± 0.32	40.9 ± 0.7
Ti	1.79	–	< LOD
Tl	22.4	–	< LOD
V	8.96	0.351 ± 0.006	< LOD
Zn	0.773	1.76 ± 0.12	1.44 ± 0.45
QCCPAWater1.L1			
P	13.4	500 ± 2	500 ± 27
S	30.3	1993 ± 8	2200 ± 199

* $N = 5$ ** Average ± standard deviation, $N = 6$

were quantified above their method detection limit values. Amongst these 17 analytes whose mass fractions were determined in the water-extractable fraction of this CRM, relative standard deviation (RSD) values of the six analytes—Al, Fe, Li, Mo, Ni, and V—are somewhat higher than 10%. Other 10 elements have been determined with less uncertainty. Generally, a lower difference between method detection limit (MDL) and mass fraction of an analyte in the water-extractable fraction produces a higher uncertainty (higher RSD) of the

Table 3 Results of the determination of the selected elements in the water extracts of the certified reference material for soil NCS DC 77302

	MDL mg/kg	Certified	Found		
		Average ± Std. dev.	Average ± Std. dev.	RSD %	Recovery %
Al	0.136	77003 ± 953	1.52 ± 0.254	17	0.002
As	0.146	10.5 ± 0.8	< 0.146	/*	/
Ba	0.005	623 ± 27	0.097 ± 0.004	3.8	0.016
Be	0.004	2.6 ± 0.3	< 0.004	/	/
Ca	0.036	10150 ± 715	130 ± 5	3.7	1.28
Cd	0.029	0.090 ± 0.030	< 0.029	/	/
Co	0.033	12.8 ± 1.1	< 0.033	/	/
Cr	0.020	66.0 ± 4.5	< 0.020	/	/
Cu	0.021	23.2 ± 2.2	0.171 ± 0.011	6.7	0.736
Fe	0.075	32174 ± 909	1.37 ± 0.17	13	0.004
K	0.490	21501 ± 581	37.8 ± 1.7	4.5	0.176
Li	0.021	33.2 ± 1.5	0.035 ± 0.005	15	0.105
Mg	0.007	2955 ± 241	41.9 ± 1.6	3.9	1.42
Mn	0.007	706 ± 33	1.24 ± 0.05	4.1	0.176
Mo	0.022	0.84 ± 0.12	0.060 ± 0.009	16	7.14
Na	0.097	14095 ± 668	56.8 ± 2.2	3.8	0.403
Ni	0.015	27.6 ± 2.8	0.044 ± 0.007	15	0.160
P	0.098	439 ± 16	3.75 ± 0.21	5.7	0.855
Pb	3.40	29.2 ± 3.2	< 3.40	/	/
S	0.198	174	42.0 ± 1.6	3.8	24.1
Sb	0.093	0.93 ± 0.32	< 0.093	/	/
Se	0.070	0.28 ± 0.06	< 0.070	/	/
Sr	0.002	188 ± 9	0.521 ± 0.020	3.9	0.277
Ti	0.021	2500 ± 200	0.105 ± 0.010	9.2	0.004
Tl	0.234	0.62 ± 0.16	< 0.234	/	/
V	0.037	82.7 ± 3.7	0.063 ± 0.016	26	0.076
Zn	0.013	72.8 ± 4.5	< 0.013	/	/

*It is not possible to calculate RSD and recovery values for the elements whose content in the water-extractable phase is below their MDL values

quantification of the analyte. So, it can be noticed that in the cases of almost all seven above-mentioned elements (Fe is an exception) when the found mass fraction value is close (namely, of the same order of magnitude) to the related MDL, the RSD gained higher values. The analytes, whose mass fractions in the water-extractable fraction are at least one order of magnitude higher than the respective MDL, have been quantified with less uncertainty; i.e., their RSD values are lower than 10%. More precisely speaking, since water is a mild extractant, these elements in the prepared extracts were present in the mass concentrations that are close to their limit-of-

detection values of the spectrometer which has been used in this study. Lower concentration of an element in measured solution leads to lower precision of a measurement with the ICP-OES spectrometer; consequently, a concentration of an analyte which is close to its instrumental limit-of-detection value causes higher uncertainty (i.e., higher RSD) of the measurement (Roje et al. 2019).

The recovery values, presented in the last column of Table 3, reflect the presence of the elements in the water-extractable fraction and in most cases, they are a few orders of magnitude lower than recoveries obtained with

Table 4 Results of the determination of the selected elements in the water extracts of the certified reference material for sandy soil Metranal-31

	MDL mg/kg	Certified Average \pm Std. dev.	Found		
			Average \pm Std. dev.	RSD %	Recovery %
Al	0.136	81554	2.51 \pm 0.26	10	0.003
As	0.146	12.3	< 0.146	/*	/
Ba	0.005	970	0.121 \pm 0.004	3.6	0.012
Be	0.004	3.32 \pm 0.26	< 0.004	/	/
Ca	0.036	10720	201 \pm 7	3.4	1.87
Cd	0.029	0.32 \pm 0.05	< 0.029	/	/
Co	0.033	9.66 \pm 0.61	< 0.033	/	/
Cr	0.020	89.6 \pm 4.2	< 0.020	/	/
Cu	0.021	30.8 \pm 0.9	0.293 \pm 0.014	4.7	0.952
Fe	0.075	33083	2.08 \pm 0.24	11	0.006
K	0.490	26233	65.3 \pm 2.2	3.3	0.249
Li	0.021	–	< 0.021	/	/
Mg	0.007	7659	27.7 \pm 1.2	4.4	0.362
Mn	0.007	540 \pm 20	0.613 \pm 0.030	4.8	0.114
Mo	0.022	–	0.064 \pm 0.008	13	/**
Na	0.097	17434	59.2 \pm 2.1	3.6	0.340
Ni	0.015	31.9 \pm 1.6	0.018 \pm 0.009	47	0.058
P	0.098	1484	9.50 \pm 0.34	3.6	0.640
Pb	3.40	43.8 \pm 3.7	< 3.40	/	/
S	0.198	–	30.9 \pm 1.3	4.1	/
Sb	0.093	–	< 0.093	/	/
Se	0.070	–	< 0.070	/	/
Sr	0.002	–	0.492 \pm 0.016	3.3	/
Ti	0.021	3117	0.185 \pm 0.020	11	0.006
Tl	0.234	–	< 0.234	/	/
V	0.037	58.7 \pm 6.3	0.059 \pm 0.010	17	0.100
Zn	0.013	120 \pm 7	< 0.013	/	/

*It is not possible to calculate RSD and recovery values for the elements whose content in the water-extractable phase is below their MDL values

**If a mass fraction of an element is not given in the certificate sheet, its recovery cannot be calculated

aggressive acidic extraction/digestion procedures (Roje 2010; Fiket et al. 2017). Namely, the recovery values obtained in this study range from 0.002 to 24.1%. The lowest recovery values have been found for Al, Fe, and Ti because these elements are amongst main matrix constituents. On the other hand, there are Mo and S, whose recovery values are the highest in this work, that is, 7.14% and 24.1%, respectively. Recoveries could not be calculated for the elements whose mass fractions in this CRM, NCS DC 77302, are below MDL (As, Be,

Cd, Co, Cr, Pb, Sb, Se, Tl, and Zn). The order of the extractability of the selected elements from this CRM by deionized water of the analytes for which the recovery values were calculated is: S > Mo > Mg > Ca > P > Cu > Na > Sr > K = Mn > Ni > Li > V > Ba > Fe > Ti > Al.

Certified reference material for soil Metranal-31

Metranal-31 is a CRM for soil, and is declared as sandy soil. Its certificate sheet presents (certified and

Table 5 Results of the determination of the selected elements in the water extracts of the certified reference material for soil Metranal-33

	MDL	Certified	Found		
	mg/kg	Average ± Std. dev.	Average ± Std. dev.	RSD %	Recovery %
Al	0.136	65095	0.275 ± 0.030	11	0.0004
As	0.146	–	< 0.146	/*	/
Ba	0.005	495	0.173 ± 0.002	1.4	0.035
Be	0.004	2.18 ± 0.16	< 0.004	/	/
Ca	0.036	9863	343 ± 5	1.6	3.48
Cd	0.029	0.32 ± 0.04	< 0.029	/	/
Co	0.033	11.5 ± 0.7	< 0.033	/	/
Cr	0.020	79.8 ± 6.7	< 0.020	/	/
Cu	0.021	29.1 ± 0.8	0.280 ± 0.009	3.3	0.963
Fe	0.075	29027	0.387 ± 0.039	10	0.0013
K	0.490	18350	35.1 ± 0.5	1.3	0.191
Li	0.021	–	0.047 ± 0.005	9.8	/**
Mg	0.007	6151	19.8 ± 0.3	1.7	0.322
Mn	0.007	600 ± 37	1.01 ± 0.02	2.3	0.168
Mo	0.022	–	0.057 ± 0.005	8.0	/
Na	0.097	5490	31.1 ± 0.166	0.53	0.566
Ni	0.015	31.3 ± 1.5	0.084 ± 0.009	10	0.269
P	0.098	698	6.80 ± 0.15	2.3	0.974
Pb	3.40	33.5 ± 2.4	< 3.40	/	/
S	0.198	–	41.9 ± 0.4	0.85	/
Sb	0.093	–	< 0.093	/	/
Se	0.070	–	< 0.070	/	/
Sr	0.002	–	0.805 ± 0.014	1.7	/
Ti	0.021	4076	0.109 ± 0.008	7.6	0.003
Tl	0.234	–	< 0.234	/	/
V	0.037	76.2 ± 6.4	0.045 ± 0.015	34	0.060
Zn	0.013	81.0 ± 7.6	< 0.013	/	/

*It is not possible to calculate RSD and recovery values for the elements whose content in the water-extractable phase is below their MDL values

**If a mass fraction of an element is not given in the certificate sheet, its recovery cannot be calculated

information) values for 13 trace elements and 9 matrix components. In the scientific database *Web of Science*, there is no trace of any reported result of the use or characterization of Metranal-31, so this would be the first one dealing with an analysis of this CRM. In this study, we have quantitatively analyzed 27 chemical elements in the water-extractable fraction of this CRM (Table 4). Amongst these, we have determined mass fractions of 16 elements, while 11 elements were found to have the mass fractions lower than their MDLs. Regarding the uncertainty of this analysis, the RSD

values of the five analytes (Fe, Mo, Ni, Ti, and V) are higher than 10%. In the cases of Mo, Ni, Ti, and V, the obtained mass fraction values are similar to their MDL values. As expected, the elements whose mass fractions that have been determined in this study are one order of magnitude (or more) higher than the respective MDL were determined with less uncertainty; i.e., their RSD values are lower than 10%.

The recovery values (presented in the last column of Table 4) could be calculated only for 13 elements out of 27 that have been analyzed. The recoveries are in the

range from 0.003 to 1.87% and they are in relation to the presence of these elements in the water-extractable fraction of a soil sample. The recovery values could not be calculated for the analytes that could not be precisely calculated due to their low presence in the water-extractable fraction of this soil material (As, Be, Cd, Co, Cr, Li, Pb, Sb, Se, Tl, and Zn) as well as for those analytes (Mo, S, and Sr) for which certified values are not provided on the certificate sheet. In terms of the extractability from the CRM Metranal-31 by deionized water, the order of the analytes for which the recovery values were calculated is:

$$\text{Ca} > \text{Cu} > \text{P} > \text{Mg} > \text{Na} > \text{K} > \text{Mn} > \text{V} > \text{Ni} \\ > \text{Ba} > \text{Fe} > \text{Ti} > \text{Al}.$$

Certified reference material for soil Metranal-33

The CRM for soil Metranal-33 is declared as clay loam soil. Its certificate of quality sheet presents values for 13 trace elements and 9 matrix components. In the scientific database *Web of Science*, just as in the case of Metranal-31, there is no trace of any reported result of the use or characterization of this CRM in scientific papers; therefore, it can be stated that this would be the first paper dealing with an analysis of this CRM. In this study, we have quantitatively analyzed 27 chemical elements in the water-extractable fraction of this CRM (Table 5). Amongst these, we have determined mass fractions of 17 elements, while 10 elements were found to have the mass fractions below the related MDL values of the methodology applied in this study. Regarding the uncertainty of this analysis, the RSD values of two analytes (Al and V) are higher than 10% and it can be noticed that their mass fractions in the water-extractable fraction of this CRM are similar to their MDL values. The elements, whose mass fractions in the water-extractable fractions are at least one order of magnitude higher than the respective MDLs, have been determined with less uncertainty; i.e., their RSD values are notably lower than 10%.

The recovery values (presented in the last column of Table 5) could be calculated for 13 elements out of 27 that have been analyzed. The recovery values are in the range that goes from 0.0004 to 3.48%. The elements that were scarcely extracted by deionized water were Al, Fe, and Ti, and that is according to the fact that these elements are amongst the main constituents of soil matrix, and therefore, their higher recovery is allowed using much stronger

extraction or digestion reagents and methods (Fiket et al. 2017). The recovery values could not be calculated for the analytes that could not be precisely calculated due to their low presence in the water-extractable fraction of this soil material (As, Be, Cd, Co, Cr, Pb, Sb, Se, Tl, and Zn) as well as for those analytes (Li, Mo, S, and Sr) for which certified values were not provided by the producer. The order of the metals and metalloids for which certified values were provided and recovery values subsequently calculated, in terms of extractability from Metranal-33 by deionized water, is:

$$\text{Ca} > \text{P} > \text{Cu} > \text{Na} > \text{Mg} > \text{Ni} > \text{K} > \text{Mn} > \text{V} \\ > \text{Ba} > \text{Ti} > \text{Fe} > \text{Al}.$$

Conclusion

This work has studied the method for multi-elemental quantitative analysis of soil samples by ICP-OES with precedent one-step extraction by deionized water. Three certified reference materials for soil have been used as model samples. It has to be pointed out that the CRMs used in this study represent “clean” soils, namely the soils that contain the analyzed elements in the background mass fractions. The list of the analytes consists of 27 chemical elements: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Sr, Ti, Tl, V, and Zn. Since water is a mild extraction reagent, from the results shown in this paper, it can be concluded that in the water extracts of soil samples, which are not overloaded with metals and metalloids, by means of ICP-OES, it is possible to quantify the following elements: Al, Ba, Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, S, Sr, Ti, and V. Other measured elements could not be quantified exactly, due to their low presence in the water extracts that was under the respective method detection limit values. Relating to the recoveries, their values that were obtained by deionized water extraction procedure were notably (i.e., few orders of magnitude) lower than those that can be obtained by the use of strong acidic digestion reagents. The results presented in this paper can also be useful for future uses of the CRMs that have been herein described, since the mass fraction values that have been determined in this study can be used as information values in the cases of the extraction of the analytes using the deionized water as the extraction reagent.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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