



Introduction

Heavy metals occur naturally in soils, by geological processes, in addition to contamination from anthropogenic activities. Determination of heavy metals in soils requires sample digestion for most analytical techniques. Numerous methods are available involving mainly a fusion or acid leaching[1]. Although there is no consistent definition for acid leaching it is considered as a wet procedure based on an acid digestion with a heated mixture of mineral acids. There are different heating systems with microwave assisted methods being generally preferred since they are rapid, safe, and efficient with minimal loss of volatiles [2]. The International Organization for Standardisation (ISO) as well as the Environmental Protection Agency (EPA) have recommended the use of HNO₃ and HCl in open vessels on a hotplate [3,4] or in a microwave [5,6]. The extraction capability depends on the type of sample and the element. In this paper, three different digestion procedures using aqua regia and reversed aqua regia for samples extraction were compared using two different soil origin certified reference materials (CCRM SO-2, IAEA SOIL-7). Six elements of environmental interest (Ni, Pb, Cr, Co, Mn, Cu) were measured by ICP-OES. Accuracy, detection limits, repeatability and recoveries of spiked samples were determined for all methods and elements. The combined effect of all potential sources of uncertainty was estimated and standard uncertainty was calculated.

Experimental

Aqua regia extraction – Hot plate digestion (AR-HOT) ISO 11466.3 [4]: The extraction was based on the ISO method. Up to 0.5g of sample was placed in a 250 ml Pyrex beaker with 40 ml of 37% HCl:70% HNO₃ (3:1) mixture. The beaker was heated at 130 °C for about 30 min and evaporated almost to dryness. The residue was re-suspended using HNO₃ 1.6 M. After centrifuging the supernatant was diluted to 25 ml. No pre-digestion step was performed **Aqua regia extraction – Microwave digestion (AR-MW) ISO 12914 [6]:** Up to 0.5g of sample was placed in a Teflon vessel with 12 ml of aqua regia (37% HCl:70% HNO₃ (3:1) mixture). The vessels were heated in a microwave apparatus up to 180 °C within 5.5 min and remained at 180 °C for 9.5 min. **Reversed aqua regia extraction – Microwave digestion (EPA) USEPA 3052 [5]:** Up to 0.5g of sample was placed in a Teflon vessel and treated with 12 ml of 37% HCl:70% HNO₃ (1:3) mixture with the same microwave program. The START D (Milestone) apparatus was used for all microwave assisted digestions. The ICP-OES Optima 7000 DV spectrometer (Perkin Elmer) was used for the determination of metals with a standard calibration method. The wavelengths used were selected according to the ISO 11885:2009 (E), standard applied on water quality determination by ICP-OES [7].

Results and discussion

The two reference soils were treated in triplicate. Detection limits as well as quantification limits were calculated for all wavelengths. Blank spiked solutions were used to estimate the percent recovery. Results are presented in Table 1. The detection limit (LOD) was calculated as three times the standard deviation of the measured blank signals divided by the slope of the calibration curve while the quantification limit (LOQ) was calculated as ten times respectively. Standard deviation of triplicate measurements was used for the precision estimation varying from 0.2 to 2% in all cases. The accuracy was checked using two certified reference materials (RM) which were treated in triplicate while triplicate spiked samples underwent the same digestion procedures. All samples were analyzed for the elements of interest. The results are presented in Table 2a and 2b. The mean values obtained from each digestion procedure were compared to the certified values according to the equation (1). The result is reported as % accuracy.

$$\%accuracy = \frac{measured\ value}{reference\ value} \times 100 \quad (1)$$

Table 1. Detection limits (LOD), quantification limits (LOQ) and recovery of spiked blanks for each procedure. (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

	Ni	Pb	Cr	Mn	Cu	Co
LOD (µg/L)	1.6	4.4	7.8	0.8	1.5	1.3
LOQ (µg/L)	5.3	14.4	25.6	2.6	5.0	4.2
% Recovery (blank spiked)						
AR-HOT	100.9	102.5	96.4	96.8	99.4	96.8
AR-MW	104.5	99.4	102.2	99.3	97.3	104.2
EPA	99.2	97.8	97.7	99.7	97.2	95.6

Table 2a. Analytical results for IAEA Soil-7 reference material. (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

Method	IAEA SOIL 7	Ni	Pb	Cr	Mn	Cu	Co
		mg/kg					
reference values		26.0	60.0	60.0	631.0	11.0	8.9
AR-MW values measured		20.6	55.6	36.6	547.5	9.9	6.8
Uncertainty		± 2.4	± 6.5	±4.3	±64.3	±1.2	±0.8
% repeatability		6.4	9.3	3.8	3.4	6.7	4.8
% accuracy		79.2	92.7	61.0	86.8	90.2	75.9
% recovery (spiked sample)		97.3	99.4	98.8	99.3	97.3	99.4
EPA values measured		19.2	54.7	40.4	528.1	9.4	5.8
Uncertainty		±2.3	±6.4	±4.7	±62.0	±1.1	±0.7
% repeatability		3.0	3.8	1.8	2.1	2.2	1.5
% accuracy		74.0	91.2	67.4	83.7	85.6	64.8
% recovery (spiked sample)		96.8	96.5	99.0	99.7	104.6	95.6
AR-HOT values measured		17.8	49.0	32.6	541.0	8.7	6.3
Uncertainty		±2.1	±5.8	±3.8	±63.5	±1.0	±0.7
% repeatability		4.6	9.1	5.1	6.1	3.3	4.4
% accuracy		68.6	81.7	54.3	85.7	79.1	70.3
% recovery (spiked sample)		95.0	96.1	98.2	95.5	99.4	96.4

Table 2b. Analytical results for Canmet Soil-2 reference material. (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

Method	CCRM SO-2	Ni	Pb	Cr	Mn	Cu	Co
		mg/kg					
reference values		8.0	21.0	16.0	720.0	7.0	9.0
AR-MW values measured		4.9	16.0	10.5	413.6	7.1	9.4
Uncertainty		0.6	1.9	1.2	48.6	0.8	1.1
% repeatability		6.4	9.3	3.8	3.4	6.7	4.8
% accuracy		61.6	76.0	65.5	57.4	101.0	104.7
% recovery (spiked sample)		97.3	99.4	98.8	99.3	97.3	99.4
EPA values measured		4.5	16.6	9.2	383.6	7.5	6.1
Uncertainty		0.5	1.9	1.1	45.0	0.9	0.7
% repeatability		3.0	3.8	1.8	2.1	2.2	1.5
% accuracy		56.3	79.1	57.4	53.3	107.4	67.3
% recovery (spiked sample)		96.8	96.5	99.0	99.7	104.6	95.6
AR-HOT values measured		5.0	14.0	9.1	325.3	5.9	7.3
Uncertainty		0.6	1.6	1.1	38.2	0.7	0.9
% repeatability		4.6	9.1	5.1	6.1	3.3	4.4
% accuracy		62.4	66.4	57.2	45.2	83.9	81.1
% recovery (spiked sample)		95.0	96.1	98.2	95.5	99.4	96.4

The repeatability of the method refers to relative standard deviation of three samples treated on different days by the same analyst. Percent recovery is calculated from the average values determined in spiked samples. Recovery of spiked samples varied within the range of 95 to 105% in all cases. Quantification of uncertainty performed for cobalt (Co), was based on the Eurachem Guide for the quantification of Uncertainty of Analytical Measurement [8]. Uncertainty was calculated as relative combined uncertainty $u_{rel}(CON)$ taking into account individual uncertainties of the parameters considered to have affected the final concentration according to equation (2) $u_{rel}(C_A)$ expresses the relative uncertainty of the analyte concentration including the preparation of standard solution its repeatability. $u_{rel}(V_{final})$ is the uncertainty attributed to the dilution of the sample digest solution, of the final volume of the digest, $u_{rel}(m_{sample})$ is the uncertainty derived from the sample weight and finally the $u_{rel}(Rep)$ is the uncertainty for the repeatability calculated from the relative standard deviation of the measurements by the formula: $Rep = RSD / \sqrt{N}$. For the calculation of the uncertainty of standard solution as well as the sample volume, the temperature factor was also estimated according to equation (3), whereas $(Q_{water}) = 2.1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ Expanded uncertainty was obtained by multiplying the combined standard uncertainty by a coverage factor $k=2$, producing an interval with a confidence level of approximately 95%.

$$u_{rel}(CON) = \sqrt{u_{rel}^2(C_A) + u_{rel}^2(V_{final}) + u_{rel}^2(m_{sample}) + u_{rel}^2(Rep)} \quad (2)$$

$$u_{temp} = \frac{3(V)(Q)}{1.73} \quad (3)$$

All digestion procedures applied, although based on International protocols, did not result to complete dissolution of the samples. Elements extracted cannot be considered as total, yet they are compared to the reference values. Percent accuracies are plotted for all methods in fig.1. As it is demonstrated, copper and lead showed satisfactory recoveries. Chromium extraction on the other hand, was low in all cases while nickel and manganese did not exceed 60% for CCRM Soil-2. It is evident that the percent release of elements differs according to the element, the soil matrix and the method used. The effect of sample matrix is unambiguous in case of manganese (fig.2), where all methods show approximately 90% accuracy for IAEA Soil-7 but around 50% for CCRM Soil-2. The non-extracted fraction of manganese could be associated with the silicate phase. Elements not released by aqua regia digestion are considered to be mostly bound to silicate minerals[9]. Aqua regia is not suitable for the extraction of elements from refractory compounds, such as SiO₂, TiO₂ and Al₂O₃. CCRM Soil-2 consists of higher silicate phase as was verified by EDX analysis performed by a Fei 200 Quanta SEM/EDAX. The impact of the digestion method applied is elusive in case of lead (fig.3) where microwave assisted aqua regia treatment leads to almost complete recovery of lead. Differences between open vessel heating and sealed vessels used in microwave are expected due to volatilization and/or atmospheric contamination during the oxidation procedure. The impact of the nature of the element is evidently presented in fig.4 for copper and cobalt determination in the same matrix sample. Copper shows excellent extractability for the two microwave assisted methods while cobalt recovery is significantly reduced in case of the USEPA method. The complex behavior of cobalt could be explained assuming that the non extracted fraction is not only associated to the silicate phase but also to iron oxides and hydroxides, which are not completely dissolved by the USEPA method.

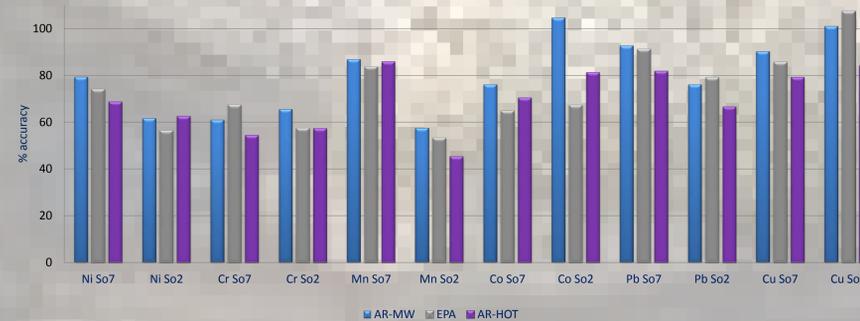


Figure 1. Accuracy of all elements compared to reference values of Soil-2 and Soil-7. (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

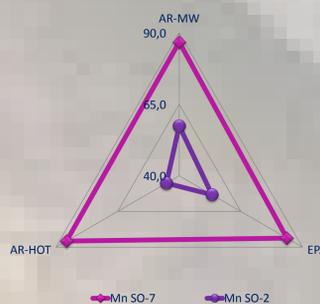


Figure 2. Manganese accuracy for different matrices (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

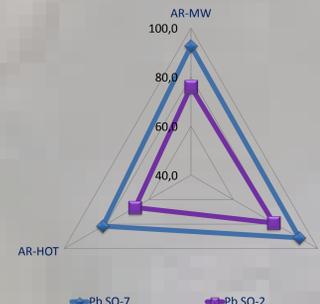


Figure 3. Lead accuracy for different methods (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

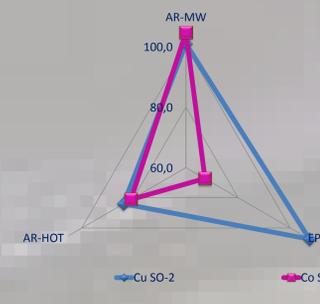


Figure 4. Method accuracy for different elements (AR-HOT: ISO11466.3, AR-MW: ISO12914, EPA: USEPA3052)

Conclusions

Microwave assisted aqua regia extraction (ISO 12914:2012) is an operationally defined method and does not necessarily release all elements completely. Tested on soil reference materials was proven suitable for the release of trace element fractions in soil material. The extractability of the elements depends highly on the soil matrix as well as the element and the compound present. The method can be used for the estimation of element mobility and availability since the contribution of not extracted elements bound to silicate minerals is unimportant. Reference materials characterized for both acid extractable and total concentration of elements are of great value for all laboratories

References

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