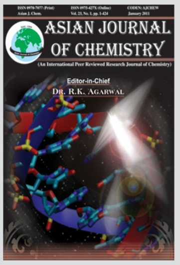
Asian Journal of Chemistry; *Vol. 23, No. 12 (2011), 5213-5216*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Comparison of Three Digestion Methods for Heavy Metals Determination in Soils and Sediments Materials by ICP-MS Technique

E.I. GEANA[1], A.M. IORDACHE[2], C. VOICA[2], M. CULEA[3] and R.E. IONETE[1,*]

[1]Research and Development Department, National R & D Institute for Cryogenics and Isotopic Technologies-ICIT Rm, Valcea, 4 Uzinei St., 240050 Rm. Valcea, Romania
[2]National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, Cluj-Napoca 400293, Romania
[3]Babes-Bolyai University, 1 M. Kogalniceanu St., Cluj-Napoca 400084, Romania

*Corresponding author: Fax: +40 250 732746; Tel: +40 250 733890; E-mail: irina.geana@icsi.ro; roxana@icsi.ro

(*Received*: 20 August 2010; *Accepted*: 4 August 2011) AJC-10256

The measurement of elements concentration in soil and sediment is generally a combination of a digestion procedure for dissolution of elements and a subsequent measurement of the dissolved elements. It is important to evaluate different digestion methods to accurately determine the metals concentration. Therefore, three digestion procedures have been tested on soil standard reference material and Romanian soils and sediments samples for determination of heavy metals by inductively coupled plasma mass spectrometry (ICP-MS). The first is an open-vessel digestion with concentrated acids: HNO_3 + HF and the others two are microwave-assisted concentrated acids digestion A: HNO_3 + HF, B: HNO_3 + HF + HCl. Owing to the multi-elemental capabilities of the ICP-MS technique, in these materials eight elements were determined, at mg/kg concentrations. In general, the microwave acid digestion with HNO_3 + HF + HCl was overall the best procedure for determining concentration of most metals in SRM and Romanian soils and sediments.

Key Words: Heavy metal, Microwave digestion, Certified material, ICP-MS.

INTRODUCTION

The problems associated with heavy metals in the environment have been well documented and studied. Heavy metals are widespread pollutants of great environmental concern as they are non-degradable, toxic and persistent.

Different natural and artificial sources of pollution can pollute the soil and sediments with heavy metals. The most important sources of heavy metals in the environment are the following: the stationary incinerators for urban residues, the metallurgical industry, chemical industry, the construction industry, the mines, traffic, agriculture as well as domestic activities. Chemical and metallurgical industries are the most important sources of heavy metals in soils and sediments[1].

The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity and plant growth[2]. Since sediments play an important role in physico-chemical and ecological dynamics, any change in toxic concentrations of heavy metal residues on the sediments will affect the natural aquatic life support systems[3].

The total analysis of heavy metals such as V, Cr, Mn, Co, Ni, Zn, Pb, U in sediments and soils, is commonly done to evaluate the degree of contamination of aquatic and terrestrial environments. Sample digestion is often a necessary step before determining total element mass concentrations in soils and sediments. A safe dissolution method that provides an analytical recovery of at least approximately 90 % of elements is required. Various digestion methods are used to determine the mass concentration of trace elements in solid matrices[4]. Open beakers heated on hot plates, digestion tubes in a block digester and digestion bombs placed in microwave ovens are the most commonly used equipment to digest solid sample matrices. If open systems are used during digestion, there are risks of atmospheric contamination and volatilization losses of volatile compounds during the extraction procedure[5].

In particular, since the 1980s, the microwave-assisted sample digestion technique has become popular and presently it is widely used due to its safe, rapid and efficient performance[6]. In addition, it reduces the risk of external contamination and requires smaller quantities of acids, thus improving detection limits and the overall accuracy of the analytical method[7].

Inductively coupled plasma mass spectrometry, ICP-MS has come to be one of the most attractive detection systems and is routinely used in many diverse research fields such as earth, environmental, life and forensic sciences and in food, material, chemical and nuclear industries[8].

The first objective of this study is to compare the accuracy and precision of three digestion methods of V, Cr, Mn, Co, Ni, Zn, Pb, U (open-vessel hotplate digestion with concentrated acids: HNO_3 + HF and microwave-assisted concentrated acids digestion A: HNO_3 + HF, B: HNO_3 + HCl + HF), using NCS ZC 73006 Certified Reference Material. It is hoped that such information will help us to choose the most appropriate digestion procedure for analyzing trace-metal concentration in soil and sediments. Second we wish to study the variation in soil and sediment samples from Transilvania region.

EXPERIMENTAL

High purity ICP multi element standard solution XXI CertiPUR obtained from Merck (Darmstadt, Germany) was used for external calibration during quantitative analysis. All solutions were prepared and stored in polypropylene vessels, which were cleaned prior to use by soaking in 10 % HNO_3 and then rinsed several times with ultra-pure water, which was produced by a Smart 2 Pure system, TKA (resistivity of 18.2 MΩ cm). Concentrated HNO_3, HF and HCl for ICP-MS determination was used for microwave digestion preparation. The purity of the gaseous argon used to form the plasma in the ICP-MS was 99.9999 % (Messer, Austria).

All calibration solutions were prepared daily, at appropriate mass fractions as the samples to be analyzed and in the same acid matrix as the sample and filter blank solutions. The use of the same matrix for all solution preparations ensured that no additional variability or bias was introduced into the analytical determination from the nitric acid content of the matrix.

A Mars 5 Microwave System (CEM Microwave Technology Ltd., UK) was used for microwave acid digestion of soil samples. Inductively coupled plasma mass spectrometric measurements were performed with a Varian 820 (Varian, Australia).

General procedure: Representative soils and sediments investigated in this experiment were sampled from different areas in Transylvania region: Salaj, Cluj (Tarnita), Somesul Rece. Soils were collected in open areas at 5 cm depths, from fields located at different directions and distances from the steel plant and stored in polyethylene bags for transport to laboratory. The soil and sediments samples were dried, homogenized and then passed through a 20 mesh sieve to obtain very fine particles.

In hot plate open-vessel procedure, an aliquot of samples (0.1 g) were digested in acid mixture HNO_3 : HF = 3:2 and heated at 150 ºC. For microwave acid digestion procedures, an aliquot of samples to be digested (-0.25 g) were placed in the clean Teflon digestion vessel with concentrate acid mixture HNO_3 : HF = 3:1 (A), v/v, for first microwave acid digestion procedure and HNO_3 : HF : HCl = 3:1:0.7 (B), v/v/v in the second microwave digestion procedure. The vessel was closed, placed into the rotor and then increasing the microwave temperature to 200 ºC over a 6 min period and holding the temperature at 200 ºC for 20 min. The digestion was carried out with the following program (Table-1).

The vessels were cooled and carefully opened. After the digestion process, each digest was transferred quantitatively with ultra-pure water to a 100 mL volumetric flask. These solutions were analyzed by ICP-MS after corresponding dilution using external calibration standard. The standard reference materials was digested under the same conditions.

TABLE-1
DIGESTION PROGRAMME

Step	Power (W)	Power (%)	Ramp (min)	Pressure (PSI)	Temperature (ºC)	Hold (min)
1	800	100	6	800	200	20

Detection method: Subsequently, the extracts were analyzed using an inductively coupled plasma/mass spectrometer (ICP-MS) Varian 820 equipped with an SPS-3 autosampler (Varian, Australia). All samples were introduced *via* the autosampler system with a peristaltic pump into the first channel. Each sample was analyzed in duplicate, each analysis consisting of five replicates.

This method allowed us to perform multi-element determination of trace elements. In this method, the extract solution is introduced by pneumatic nebulization into a radiofrequency - generated argon plasma where energy transfer processes causes analyte desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier and the ion information is then processed by a PC-based data handling system.

Prior to analysis, the ICP-MS, located in a temperature-controlled laboratory (20 ± 2 ºC), was allowed a sufficient period of time to stabilize before optimization procedures were carried out.

The following instrumental parameters of Varian 820 spectrometer were used: (a) 1 L/min nebulizer gas flow; (b) 1.8 L/min auxiliary gas flow; (c) 18 L/min plasma gas flow; (d) 1400 W ICP RF power; (e) Measuring mode: peek hoping.

RESULTS AND DISCUSSION

A six point calibration with five standards and one blank was used to calibrate all the element of interest. Under the optimized conditions, the resulting calibration curves for all analyte elements are linear. A minimum correlation coefficient of 0.9993 was assigned in the software for quality control check. Prior to analysis of samples, a quality control sample prepared from ICP multi element standard solution VI CertiPUR was analyzed to verify the calibration.

Precision was defined as relative standard deviation (RSD), which was calculated as a percentage using the standard deviation divided by the mean of replicated samples. Accuracy was determined by comparing the measured concentration with the certified values and was expressed as percentage recovery R (%).

The hot plate open vessel and both microwave acid digestion achieved precise analysis using SRM NCS ZC for all elements. The best results are for microwave acid digestion with procedure B (HNO_3 : HF : HCl = 3:1:0,7, v/v/v) (Table-2).

Table-3 reports the results and associated standard deviations, obtained for NCS ZC 73006 with the investigated digestion procedure.

TABLE-2
PRECISION (%) OF THREE ACID DIGESTION PROCEDURE FOR DETERMINATION OF EIGHT ELEMENTS IN NCS ZC 73006 STANDARD REFERENCE MATERIAL (SRM NCS ZC 73006) (THREE REPLICATION)

Element	Precision (%)		
	Hotplate open-vessel digestion	Microwave digestion HNO_3: HF = 3:1	Microwave digestion HNO_3: HF:HCl = 3:1; 0.7
V	1.3	0.9	0.7
Cr	7.2	5.4	4.2
Mn	3.6	2.1	1.8
Co	7.6	5.2	4.4
Ni	8.6	7.3	5.8
Zn	6.5	5.4	3.1
Pb	7.0	3.3	2.5
U	9.2	8,4	5.0

TABLE-3
CERTIFIED CONCENTRATIONS AND ELEMENT MASS FRACTIONS FOR THREE DIGESTION PROCEDURE APPLIED TO SRM NCS ZC 73006

Element	Certified value (mg/kg)	Measured mass fractions (mg/kg) (n = 3)		
		Hot plate open-vessel digestion	Microwave digestion HNO_3:HF	Microwave digestion HNO_3:HF:HCl
V	119 ± 3	88.4 ± 4	118 ± 5.3	118.9 ± 5.4
Cr	130 ± 4	92.7 ± 13.9	106.5 ± 16.0	124.8 ± 18.7
Mn	538 ± 17	413.4 ± 21	498.2 ± 22	497.8 ± 22
Co	17.6 ± 0.7	13.0 ± 1.1	14.3 ± 0.9	15.1 ± 0.9
Ni	88 ± 5	61.4 ± 7.9	64.3 ± 8.2	78.6 ± 7.2
Zn	106 ± 3	57.9 ± 14.3	100.6 ± 4	119.4 ± 3
Pb	18.9 ± 0.5	13.2 ± 3	14.0 ± 3.1	19.6 ± 4.3
U	3.0 ± 0.2	2.7 ± 0.3	3.1 ± 0.3	3.2 ± 0.3

A good agreement with the recommended values has been obtained for the element mass fractions for all digestion methods in the SRM NCS ZC 73006, with better results for microwave acid digestion procedures.

Good recovery (80-110 %) were obtained for microwave digestion procedure, for all the elements, except Ni and Pb for microwave digestion with HNO_3 + HF (Fig. 1).

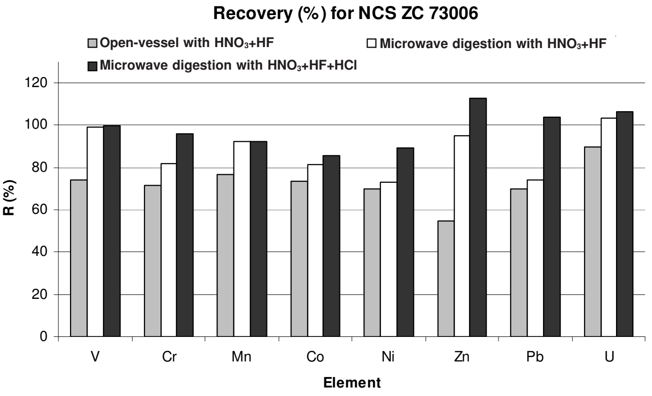


Fig. 1. Graphical representation of recovery (%) for NCS ZC 73006 (n = 3)

Comparative with hot plate open-vessel digestion procedure, microwave acid digestion increased elemental recovery for all element (with little differences for Co and Ni) and that has been attributed to fragmentation of solid material due to the high pressure, which exposed finer portion of the sample to acid attack[5].

For better understand how elemental concentrations vary with soil properties and digestion method, concentrations of 8 elements in 3 soils and 3 sediments samples from three different location in Transylvania region (Salaj, Cluj-Tarnita, Somesul Rece) were determined using the three digestion methods (Figs. 2 and 3).

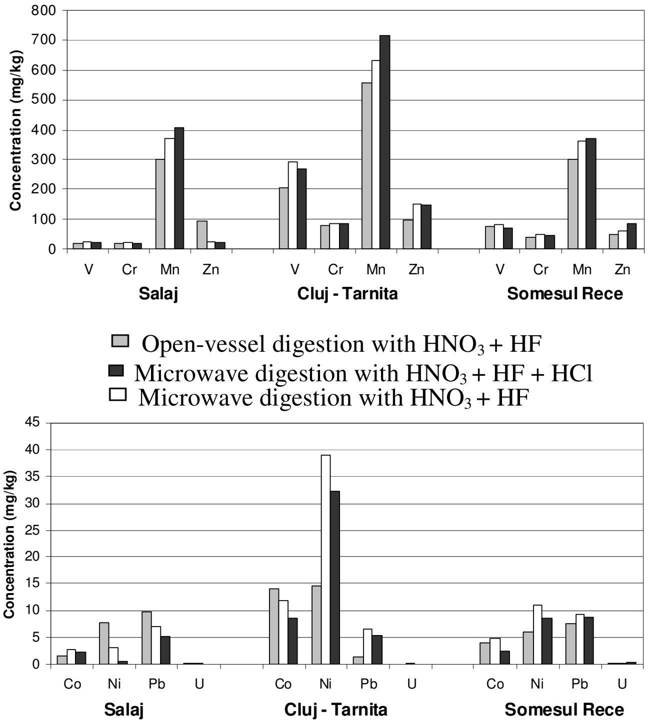


Fig. 2. Metal concentrations in soil samples

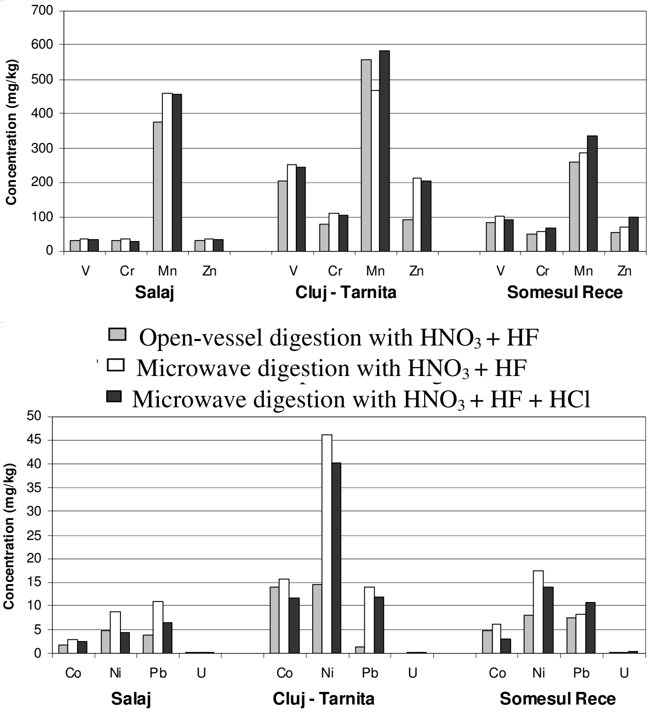


Fig. 3. Metal concentrations in sediment samples

We observed that microwave procedure with concentrated acid mixture was more effective in dissolving these elements from soil and sediment samples than the open digestion. Very good improvement in mineralization process for Mn and Ni, in case of microwave acid digestion methods, was observed.

The obtained results showed that in soil, the concentration of V are between 17.4 and 294.19 mg/kg, Cr between 16.36 and 83.41 mg/kg, Mn between 298.6 and 717.01 mg/kg, Zn between 22.2 and 150.44 mg/kg, Co between 1.68 and 14.0 mg/kg, Ni between 0.51 and 38.96 mg/kg, Pb between 1.44 and 9.88 mg/kg and U between 0.06 and 0.43 mg/kg. In sediment samples the metal concentration are: V between 30.5 and 253.93 mg/kg, Cr between 28.8 and 109.49 mg/kg, Mn between 258.7 and 582.85 mg/kg, Zn between 31.97 and 213.64 mg/kg, Co between 1.7 and 15.7 mg/kg, Ni between 4.38 and 46.16 mg/kg, Pb between 1.44 and 13.9 mg/kg and U between 0.084 and 0.56 mg/kg.

For most identified elements it was found that the concentrations were relatively close, depending of the variability of local collection points. A comparison of the results obtained for the soil and sediment samples from Salaj area revealed that the sediments are richer in Mn, Ni and Pb than soils. The sediment sample from Cluj-Tarnita is richer in Zn, Ni and Pb and the sediment sample from Somesul rece region is richer in Ni and Pb.

According to Romanian legislation, all the metals had normal values for sensitive and less sensitive soil, except V for soil and sediment sampled from Cluj-Tarnita area.

Conclusion

The results reported in this work highlight that the digestion procedure is an essential part of the definition of the measurement procedure in environmental analysis. Both microwave acid digestion achieved precise analysis using SRM, NCS, ZC for all elements. Microwave acid digestion methods reduce the risk of external contamination and require smaller quantities of acids, thus improving detection limits and the overall accuracy of the analytical method. Additional, the hot plate open vessel used in this experiment is time consu-ming procedure and for that we prefer microwave acid digestion for preparation of soil and sediments samples.

REFERENCES

1. H. Lokeshwari and G.T. Chandrappa, *Curr. Sci.*, **91**, 5, 622 (2006).
2. W. de Vries, P.F Romkens and G. Schutze, *Rev. Environ. Contamin. Toxicol.*, **191**, 91 (2007).
3. A.S. Jumbe and N. Nandini, *Am. J. Environ. Sci.*, **5**, 678 (2009).
4. Z. Hseu, Z. Chen, C. Tsai, S. Tsui Cheng, C. Liu and H. Lin, *Water Air Soil Pollut.*, **14**, 189 (2002).
5. M. Chen and L.Q. Ma, *Soil Sci. Soc. Am. J.*, **65**, 491 (2001).
6. F.E. Smith and E.A. Arsenault, *Talanta*, **43**, 1207 (1996).
7. S. Valeria, C.M.M. Smith and A. Donovan, *Talanta*, **60**, 715 (2003).
8. A.A. Ammann, *J. Mass Spectrom.*, **42**, 419 (2007).