

METHOD VALIDATION FOR DETERMINATION OF METALS IN SOILS BY ICP-MS*

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Abstract. In this study a method of quantitative analysis for the determination of metals in soils by ICP-MS was validated and applied. ICP-MS is a multi-element technique characterized by high selectivity, sensitivity and detection limits much lower than other multi-element techniques [4].

Key words: soil, ICP-MS, method validation.

1. INTRODUCTION

Soils represent a matrix with inherent heterogeneity and variable mineral composition leading to analytical complexity. This challenge has been recognized by the soil community and consequently, acceptable precision and accuracy for digestion methods has been reported as typically < 20% [1, 2].

The pollution of the environment increased rapidly during the last years, especially the contamination of soil and groundwater. There is an increasing need to determine concentration of contamination rapidly and precisely, in particular those of toxic heavy metals.

Heavy metals are widespread pollutants of great environmental concern as they are nondegradable, toxic and persistent [3].

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 [4, 5]. Chemical and metallurgical industries are the most important sources of heavy metals in soils and sediments

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[6]. The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organisms activity, plant growth [7, 8]. Heavy metals and some trace elements are biologically toxic and can affect and threaten the health of human being owing to their accumulation and persistence in the compartments of the food chain.

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.

Analytical protocols for the elemental analysis of soil and sediments normally require the partial or total breakdown of the sample matrix. Recoveries and precision of pseudo-total and total digestion methods vary with many factors, including the mineral composition and origin of the soil, the digestion method, as well as the elements of interest. Moreover, the determination of some elements in soil is challenging and may require the development of various specific methods for a complete multi-element analysis [9, 10]. For these reasons, there is an increasing interest in finding alternative and/or complementary solid sampling techniques that provide direct analysis of solid matrices. Soils represent a matrix with inherent heterogeneity and variable mineral composition leading to analytical complexity.

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 [11, 12]. 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.

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 [13].

Inductively coupled plasma mass spectrometry (ICP-MS) are powerful techniques for trace analysis of elements and the latter is preferred for ultratrace levels due to its higher sensitivity [14–16]. Mass spectrometry with inductively coupled plasma (ICP-MS) is a multi-element technique for analyzing liquid samples, characterized by high selectivity, sensitivity and detection limits much lower than other multi-element techniques.

The purpose of this paper is validation of method for the determination of metals and trace rare earth in soil by inductively coupled plasma mass spectrometry (ICP-MS) method. Several parameters have been taken into account and evaluated for the validation of method, namely: linearity, the minimum detection limit, the limit of quantification, accuracy and uncertainty.

2. EXPERIMENTAL

2.1. MATERIALS AND REAGENTS

Ultra-pure de-ionized water ($18 \text{ M}\Omega\text{cm}^{-1}$) from a Milli-Q analytical reagent-grade water purification system (Millipore) and ultra-pure HNO_3 60% (Lot – No B0157318 Merck) were used.

In order to validate the method for determining the concentration of metals, NCS ZC 73006 Certified Reference Material was used. For digestion of this reference material, an acid mixture (3 ml HNO_3 ultrapure 60%, 2 ml HF 40%) was added to 0.1 g of sample in a teflon receptacle, tightly closed. Six such receptacles were inserted in a device made of six stainless steel cylinders mounted between two flanges, to confer pressure resistance. The whole system was put in an oven at 200°C for 12 hours. A colorless solution resulted and ultra-pure water was added up to 50 ml.

Calibration standard solutions and internal standards were prepared by successive dilution of a high purity ICP-multielement calibration standard ($10\mu\text{g/l}$ from twenty-nine element ICPMS standard, item N9300233, Matrix: 5% HNO_3 , PerkinElmer Life and Analytical Sciences).

All plastic labware used for the sampling and sample treatment were new or cleaned by soaking 24 h first in 10% HNO_3 then in ultra-pure water.

2.2. INSTRUMENT

All the determinations were carried out by inductively coupled plasma quadrupole mass spectrometry (ICP-Q-MS). A PerkinElmer ELAN DRC (e) instrument was used with a Meinhardt nebulizer and silica cyclonic spray chamber and continuous nebulization.

The operating conditions are: Nebulizer Gas flow rates: 0.86 l/min; Auxiliary Gas Flow: 1.2 l/min; Plasma Gas Flow: 15 l/min; Lens Voltage: 7.25 V; ICP RF Power: 1100 W; $\text{CeO/Ce} = 0.031$; $\text{Ba}^{++}/\text{Ba}^+ = 0.016$.

Prior to analysis, the ICP-MS, located in a temperature-controlled laboratory ($20 \pm 2^\circ\text{C}$), was allowed a sufficient period of time to stabilize before optimization procedures were carried out.

3. RESULTS AND DISCUSSION

Several parameters have been taken into account and evaluated for the validation of the analytical methods for quantitative determination of metals in soils, namely: applicability range and linearity, the minimum detection limit, the minimum limit of quantification, repeatability, accuracy, uncertainty.

Linearity domain. Using calibration solutions calibration curves: $y = ax + b$, were determined, where y is the signal intensity and x is the know concentration of the given analyte in the calibration solution. The linearity of the calibration curve was considered acceptable when the correlation factor $R > 0.999$ (Table 1).

Table 1

Parameters of calibration curves ($y = ax + b$) for Ag, As, Mn, Ni, Zn, Sr, Pb, Cd, Co, Ga, V, Rb, U, Li, Cu

Element	a	σ_a	b	σ_b	R
As	1650.55	3.03	-8.41	3.39	0.9999
Ag	5709.43	96.71	0	0	0.9997
Mn	12338.70	152.41	0	0	0.9996
Ni	2478.13	6.11	243.82	75.21	0.9999
Zn	2423.15	30.82	0	0	0.9997
Sr	12602.40	106.72	8.71	53.63	0.9998
Pb	4104.75	43.58	-76.43	48.77	0.9997
Cd	1438.79	18.45	0.31	9.27	0.9997
Co	10485.60	20.13	-39.83	43.39	0.9999
Ga	7396.20	291.93	-141.55	163.36	0.9984
V	8957.89	30.60	-130.10	64.02	0.9999
Rb	9618.81	111.35	-56.30	55.95	0.9997
U	8281.98	249.51	0	0	0.9986
Li	804.87	7.71	3.613	8.633	0.9998
Cu	5187.81	42.00	1459.21	978.68	0.9998

The minimum detection limit (LOD): is the lowest concentration or quantity of analyte which can be measured with reasonable statistical certainty. To determine the limit of detection 3SD a method developed by Perkin Elmer was used. Ultra pure water of $18.2 \text{ M}\Omega\text{cm}^{-1}$ was aspirated and signal intensities for blank were recorded. A solution of $10 \mu\text{g/l}$ As, Ni, Cd, Ag, Pb, Zn, Mn, Sr, Co, Ga, V, Rb, U, Li, Cu was aspirated and the signal intensities for these analytes were recorded (Table 2).

The limit of detection was calculated by Eq. (1):

$$\text{LOD} = 3 \cdot \text{SD}_{\text{blank}} \cdot \text{conc}_{\text{sample}} / (I_{\text{sample}} - I_{\text{blank}}), \quad (1)$$

where: SD_{blank} is the standard deviation for the signal recorded on the blank for the element studied; $\text{conc}_{\text{sample}}$ is the concentration [$\mu\text{g/l}$] of the analyte in the sample, I_{sample} , I_{blank} are the signal intensities recorded for the sample and blank respectively.

Table 2

The limit of detection for As, Ni, Cd, Ag, Pb, Zn, Mn, Sr, Co, Ga, V, Rb, U, Li, Cu

Element	I_{blank}	RSD_{blank}	SD_{blank}	I_{net}	LOD (ng/l)	LOD mg/kg	LMC (ng/l)	LMC mg/kg
As	34.28	25.92	8.88	16100.87	16.60	0.0083	165.62	0.0828
Ag	9.42	4.28	0.40	54582.57	0.22	0.0001	2.22	0.0011
Mn	309.43	5.61	17.37	125038.83	4.17	0.0021	41.68	0.0208
Ni	25.42	11.12	2.82	23374.07	3.63	0.0020	36.29	0.0181
Zn	99.14	9.37	9.29	23722.02	11.80	0.0060	117.53	0.0587
Sr	23.14	8.73	2.02	130811.72	0.46	0.0002	4.63	0.0023
Pb	0.85	141.42	1.21	29396.88	1.24	0.0006	12.36	0.0062
Cd	10.57	34.40	3.63	14359.92	7.60	0.0040	75.96	0.0379
Co	37.14	15.23	5.65	104094.44	1.63	0.0008	16.30	0.0081
Ga	54.00	5.23	2.83	92758.23	0.91	0.0004	9.15	0.0045
V	343.43	1.88	6.46	89781.09	2.20	0.0011	21.61	0.01080
Rb	26.28	21.52	5.65	101952.52	1.66	0.0008	16.64	0.00832
U	0.85	141.42	1.21	75892.64	0.50	0.0002	4.79	0.00239
Li	24.57	3.28	0.80	11036.72	2.20	0.0011	21.96	0.01098

The minimum limit of quantification (LMC) is the lowest concentration that can be quantitatively determined with an acceptable level of repeatability accuracy. The quantification limit is generally considered to be approximately ten times the minimum detection limit (Table 1).

The maximum measurement limit is conditioned by the dynamics of the spectrometer detectors and limited by the requirement that the total amount of the dissolved solid must not exceed 0.2% in the sample solution (unless clogging of the nebulizer nozzels would lead to instabilities and loss of sensitivity).

To test the maximum detection limit, a multielement sample of 1 mg/l was prepared, of which there were determinations for some elements taken into account, using calibration solutions of 0.5, 1, 1.5, 2.5, 3 mg/l.

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.

Repeatability concerns the test results obtained with the same method, on the same sample in the same laboratory, with the same equipment, by the same operator, in short intervals of time. To determine the repeatability the concentration of metals in the certificate materials described earlier was determined. The found standard deviation lies between 0.4–3.94 mg/kg (Table 3).

Table 3
Metals concentrations (repeatability)

Replicates	Metals [mg/kg]											Cu
	As	V	Mn	Ni	Zn	Sr	Co	Ag	Rb	Pb	Li	
1	20.45	103.90	778.15	35.65	75.30	31.10	14.90	1.45	11.80	32.85	36.15	24.40
2	20.35	103.80	790.95	35.50	75.95	31.20	14.85	1.45	11.65	32.80	35.95	24.30
3	20.35	104.65	787.30	36.10	74.50	31.00	14.90	1.35	11.80	33.30	35.70	24.80
4	21.20	103.15	794.70	36.20	75.25	31.65	15.00	1.35	12.10	33.05	36.35	24.30
5	21.20	103.95	793.05	35.45	75.90	30.90	14.90	1.30	12.10	33.55	35.65	24.45
6	20.80	103.50	792.90	35.45	75.45	31.30	15.15	1.35	12.00	33.05	35.80	24.00
7	20.35	103.90	790.70	36.10	75.90	31.30	15.10	1.40	11.90	33.00	35.75	24.50
8	20.85	103.15	799.60	35.60	75.55	31.45	15.30	1.45	11.70	33.30	35.10	24.30
9	20.75	103.95	793.55	35.90	75.15	30.90	15.20	1.45	11.85	32.85	35.70	24.80
10	20.50	104.00	791.80	36.55	75.00	31.40	14.95	1.40	11.75	33.60	35.65	24.60
Average	20.68	103.79	791.27	35.85	75.39	31.22	15.02	1.39	11.86	33.13	35.78	24.44
SD	0.33	0.44	5.58	0.37	0.45	0.24	0.15	0.05	0.158	0.28	0.33	0.24
RSD %	1.61	0.42	0.70	1.05	0.60	0.79	1.02	3.94	1.33	0.87	0.93	1.00

Intermediate repeatability concerns the results obtained with the same method, on the same sample, in the same laboratory, but by different operators and in different days. Standard deviation was found to lie between 0.5–1.4 mg/kg (Table 4).

Table 4
Metals concentrations (intermediate repeatability)

Replicates	Metals [mg/kg]					
	Al	Ni	Mn	Li	U	Ga
1	47994.60	92.10	891.400	37.05	3.55	31.25
2	47619.20	91.10	898.600	37.10	3.60	30.50
3	47405.10	90.60	890.400	37.65	3.60	30.90
4	47962.30	90.80	902.200	37.45	3.50	30.65
5	46998.30	92.20	890.950	37.20	3.55	31.30
6	47503.90	91.50	894.600	36.35	3.50	31.20
7	47748.60	91.70	885.150	37.25	3.55	31.20
8	48166.40	91.10	892.150	36.80	3.50	30.65
9	47858.30	92.15	891.400	35.80	3.50	31.20
10	47467.80	91.30	886.550	37.10	3.50	31.45
Media	47672.45	91.45	892.340	36.97	3.53	31.03
SD	344.99	0.57	5.102	0.54	0.04	0.32
RSD %	0.72	0.62	0.572	1.46	1.16	1.05

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 NCS ZC 73006 Standard Reference Material (SRM NCS ZC 73006) for all elements except Co and Ni for all digestion procedure, and Cr, Pb for hotplate open-vessel digestion procedure.

Accurate results (80%–110% recovery) were obtained for microwave digestion procedure, for the element, except Co, Ni and Pb, due to Fig. 1. Comparative with hotplate open-vessel digestion procedure, microwave acid digestion increased elemental recovery for all element except 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.

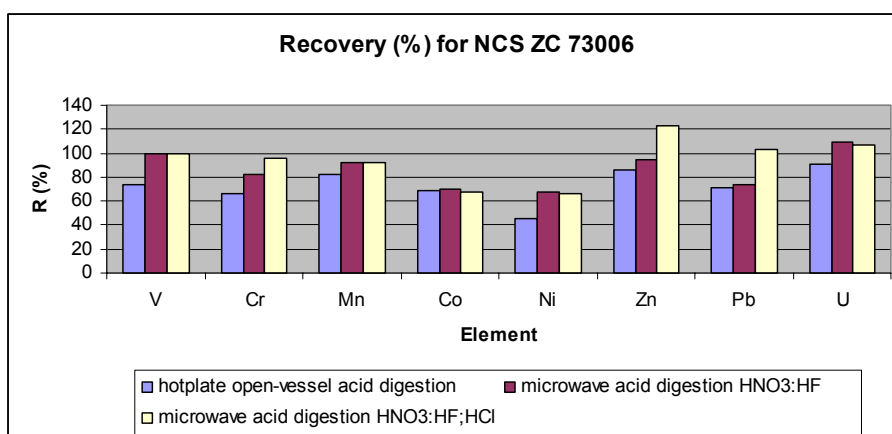


Fig. 1 – Graphical representation of recovery [%] for NCS ZC 73006 ($n = 3$).

Uncertainty estimation. A laboratory has to demonstrate the quality of the results produced and their fitness to the purpose, by giving an estimate of the confidence that can be associated with the result. All the possible sources of uncertainty have to be carefully identified and taken into account.

While measuring the concentrations by ICP-MS with external standard, fluctuations in the measurement of ionic currents occurring as a result of the electrical noise in the detector, instabilities in plasma discharge, instabilities of the electrical parameters of the analyzer, lead to uncertainties in the determination of the parameters of the calibration line. Possible errors in the preparation of the calibration solutions increase these uncertainties.

Let us assume that the calibration line has the form: $y = ax + b$, where y is the signal intensity and x is the concentration of the calibration solution.

The standard deviation of the parameters a and b can be derived as follows (n is the number of points that determine the calibration curve):

$$\sigma_a = \sqrt{\frac{n}{n \sum x^2 - (\sum x)^2}} \sigma_y,$$

$$\sigma_b = \sqrt{\frac{\sum x^2}{n \sum x^2 - (\sum x)^2}} \sigma_y,$$

$$\sigma_y = \sqrt{\frac{\sum (y - b - ax)^2}{n}}.$$

The standard deviation unknown concentration will be:

$$\sigma_x = x \sqrt{\frac{(\sigma_y - b)^2}{y - b} + \left(\frac{\sigma_a}{a}\right)^2} = x \sqrt{\frac{\sigma_y^2 + \sigma_b^2}{(y - b)^2} + \left(\frac{\sigma_a}{a}\right)^2}.$$

It is important to observe that the uncertainty estimation calculated in this manner should be associated with the concentration domain taken into account and, may be, with the analyst skill. Table 5 presents the uncertainty calculation of metals for obtained metals concentrations.

Table 5

Uncertainty estimation for the determination by ICP-MS of As, Ni, Cd, Ag, Pb, Zn, Mn, Sr, Co, Ga, V, Rb, U, Li, Cu

Metals	<i>a</i>	σ_a	<i>b</i>	σ_b	<i>Y</i>	σ_Y	<i>X</i> (mg/kg)	$2\sigma_C$ mg/kg)
U	8281.98	249.51	0	0	59051.58	27.98	3.55	0.206
Li	804.87	7.71	3.61	8.63	58521.76	16.59	36.35	0.670
Cu	5187.81	42.00	1459.21	978.68	417660.7	85.22	40.25	0.653
Ga	7396.2	291.93	-141.55	163.36	475867.60	144.42	32.15	2.440
V	10132.90	47.62	318.37	586.03	2088438.0	195.94	103.05	0.933
Rb	9618.81	111.35	-56.30	55.95	230962.80	175.35	12.00	0.267
Sr	12602.40	106.72	8.71	53.63	787756.70	224.71	31.25	0.509
Pb	4104.75	43.58	-76.43	48.77	273009.50	46.87	33.25	0.679
Cd	1438.709	18.45	0.32	9.27	1601.12	3.22	0.55	0.065
As	1650.55	3.036	-8.41	3.39	67180.42	23.28	20.35	0.120
Ag	5709.43	96.716	0	0	16654.06	21.38	1.45	0.511
Mn	12338.7	152.41	0	0	19202871	1298.36	778.15	18.484
Ni	2478.13	6.111	243.82	75.21	175705.5	5.23	35.45	0.175
Zn	2423.15	30.82	0	0	362049.4	9.83	74.70	1.828
Co	10485.60	20.13	-39.83	43.39	312491.0	87.90	14.90	12.013

* Expanded uncertainty ($k = 2$) represents interval that there is a probability of 95% to be the true value.

3.1. APPLICATION OF THE METHOD TO SOILS SAMPLES

The concern regarding the possible ecological effect of the increasing accumulation of metallic contaminants in the environment is growing. For this reason, the investigation of heavy metals in water, soils and sediments is essential since even slight changes in their concentration above the acceptable level (whether due to the natural or anthropogenic factors) can result in serious environmental harms and subsequent health problems.

In an attempt to characterize some soil sample from the point of view of their metal content, 9 samples were studied. Samples of soils required a process of digestion to be brought into solution. The aliquots were digested in an acids mixture (3 ml HNO₃ ultrapure 60 % + 2 ml HF 40 %) at high pressure and temperature. After cooling, the liquid was transferred quantitatively in a 50 cm³ volumetric flask and was brought to the required volume with ultrapure water. A multi-element stock standard solution 10 µg/l (Perkin Elmer Atomic Spectroscopy Standard – Setup/ Stab/ Masscal Solution Ba, Cd, Ce, Cu, In, Pb, Mg, Rh, U) as external calibration standard.

The analytical method was “Total Quant”: this is a software feature unique to the ELAN ICP-MS systems for quantifying 81 elements in a sample by interpretation of the complete mass spectrum. Total Quant is an ideal tool for semi quantitative analysis during method development; it can also be used for a final material characterization.

Thirty metals were identified with concentrations ranging from 0.0005 mg/l to 300 g/l (Table 6).

Regarding light metals the values were obtained in large limits, exceeding even 11 g/kg. The concentrations were obtained under the limits allowed for soils for Sb, Ag, Ba, Cd, Mn, Mo, Zn [17].

Regarding toxic metals, for some soils from different areas their concentration exceeds the accepted limits, located in sensitive alert thresholds.

Table 6

Metal content of some soils

Element	Metals concentrations [mg/kg]/Soils									
	1	2	3	4	5	6	7	8	9	10
Areal sampling	Salaj			Cluj				Tulcea		
Na	5298.9	5068.7	5003.8	11703.5	8137.0	11231.1	8213.6	1.5	1.5	1.3
Mg	96.1	85.4	111.1	4909.0	4855.3	2453.1	1729.3	0.5	0.5	0.5
Al	10494.8	10542.4	10047.9	12048.9	9942.9	20123.5	21479.5	1.1	1.1	1.09
Si	275547.9	246352.5	281397.0	143985.6	45282.9	199099.9	166766.4	0	0	0
P	242.4	334.5	270.7	483.4	515.8	427.07	380.03	894.4	1046.8	935.6
K	3470.6	3436.6	3126.8	1317.3	1656.8	7767.4	7167.04	0	0	0

Table 6 (continued)

Ca	0	0	0	0	0	0	0	0	0	0
Ti	2404.3	2812.8	2556.9	6867.2	6565.8	2716.9	2965.4	1.1	1.1	1.1
V	22.3	33.8	23.2	220.4	189.2	69.1	73.5	57.6	60.0	42.2
Cr	27.6	34.7	19.7	71.7	90.8	47.0	53.7	0	0	0
Mn	294.7	252.4	278.8	769.6	720.4	306.5	377.8	0.7	0.7	0.7
Fe	6067.6	9440.4	7097.8	33578.6	29300.6	16719.9	17237.0	0	0	0
Co	5.3	4.6	4.4	34.6	31.8	11.3	11.7	12.6	12.3	10.1
Ni	9.9	12.4	7.7	42.3	42.9	18.6	24.3	1.6	1.6	26.5
Cu	4.4	5.9	4.08	49.1	40.3	29.8	18.2	2.0	2.0	6.7
Zn	16.6	21.7	17.7	71.9	76.2	49.0	47.3	61.3	100.0	45.3
As	5.3	7.09	5.9	8.2	11.3	8.5	10.7	28.0	35.5	18.2
Sr	24.4	25.8	26.6	30.5	24.2	24.2	21.8	0.6	0.6	0.6
Rb	11.3	8.5	12.9	2.9	2.4	12.9	12.9	15.9	9.7	14.1
Zr	84.9	90.1	71.6	37.06	32.5	53.9	84.6	83.5	78.1	61.4
Mo	0.3	0.3	0.2	0.4	0.5	0.7	0.7	1.4	1.8	0.7
Ag	0.1	0.2	0.1	0.1	0.1	0.2	0.4	0.4	0.4	0.2
Cd	0.07	0.03	0.02	0.3	0.3	0.2	0.1	0.2	0.5	0.1
In	2.8	0.1	0.09	2.7	0.1	2.8	0.3	0.7	0.3	0.3
Sn	0.9	1.5	0.8	1.3	1.9	4.3	4.2	42.4	22.4	4.8
Sb	0.4	0.6	0.5	1.8	1.1	1.8	0.8	0.9	2.4	0.7
Ba	148.4	157.2	144.1	174.7	73.3	213.1	227.2	0.7	0.7	0.7
La	0.2	0.8	0.3	2.7	1.7	3.7	5.8	7.1	6.8	4.9
Ce	10.8	7.5	12.8	16.0	12.4	12.9	18.1	21.5	23.7	18.4
Pr	0.1	0.4	0.1	1.23	0.7	1.3	2.1	2.3	2.4	1.4
W	1.6	1.2	1.05	0.5	1.2	3.08	3.6	1.6	2.5	1.6
Pt	0.03	0.02	0.01	0.01	0.006	0.02	0.02	0.02	0.01	0.01
Au	0.09	0.09	0	0.07	0.1	0.08	0	1.02	0.2	0.6
Hg	0.05	0.1	0.08	0.07	0.1	0.09	0.2	0.4	0.3	0.1
Tl	0.2	0.2	0.2	0.09	0.09	0.6	0.6	0.3	0.4	0.2
Pb	14.4	16.3	14.6	6.7	37.6	27.1	25.02	17.9	36.2	14.1
Bi	0.05	0.09	0.05	0.04	0.2	0.2	0.2	0.1	0.4	0.1
Th	0.6	0.6	0.6	0.2	0.18	1.01	1.8	2.8	3.3	0.9
U	0	0	0	0	0	0	0	1.8	0	1.3

4. CONCLUSION

In this study a method of quantitative analysis for the determination of some metals (As, Ni, Cd, Ag, Pb, Zn, Mn, Sr, Co, Ga, V, Rb, U, Li, Cu) in soils by ICP-MS was developed and validated.

Several parameters have been taken into account and evaluated for the validation of method: the limit of detection ranged between (0.0001–0.07) mg/kg for the 16 metals studied ensures the minimum limit of quantification required for

quantitative determinations of the concentrations of these elements in soils (0.001–0.7) mg/kg; good linearity (correlation factor $0.9999 \geq R \geq 0.996$) for most elements recommend the method described for determination at trace and ultra-trace level; maximum limit of measurement is limited by the requirement that the total amount of solid dissolved in the sample solution must not exceed 0.2%.

The uncertainty estimation takes into account the uncertainty influence in determining the parameters of the calibration curve. Values determined lies between 0.05–2.0 mg/kg for the most elements (except Mn, Co, where the concentrations are high).

Semiquantitative analysis by ICP-MS has been proven to be a powerful tool for rapid determination of elements and the method is particularly useful for the analysis of unknown samples.

It was characterized semiquantitatively nine samples of soil from different areas country.

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