Matrix-type certified reference materials for quality control of metal determination from solid environmental and vegetation samples

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Abstract
In the context of monitoring environmental factors, metals are one of the major analytical components. Applying appropriate determination methods and obtaining accurate results is a requirement imposed on environmental laboratories that perform quality control of water, soil, waste or vegetation. This study presents some examples of certified reference materials for quality control of the results of toxic metal determination from solid environmental and vegetation samples. The analyzed and verified metals were As, Cd, Cr, Cu, Ni, Pb and Zn. The pre-treatment of the samples, the determination methods of metals and the obtained results are also presented. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-EOS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques are suitable for low metal concentrations, while ICP-EOS and Flame Atomic Absorption Spectrometry (FAAS) methods can be used at high concentrations.

Keywords: *toxic metals, ICP-EOS, Flame AAS, CRMs, environmental matrices*

INTRODUCTION

Due to the advanced industrialization during the last decades of the past century and the first of this century, many areas became contaminated with toxic metals, considerable quantities being found both in soil, sediments, groundwater and surface water.

The monitoring and rehabilitation studies have as a starting point the investigation of the quality of environmental factors affected by anthropogenic activities, such as: mining, metallurgical industry, machine building industry, intensive agriculture, etc. Even if some mines have been closed or abandoned, the surrounding areas remain a potential danger to fauna, flora, the aquatic environment and human health [1-4].

Different types of waste with varied metal content are stored either in specially designed landfills, which over time can produce discharges of toxic substances into the environment, or directly on the ground as long as the content of toxic substances is below certain limits imposed by laws [5, 6].

The high metal content in contaminated soils, sediments, waste, biological sludge must be accurately determined using appropriate analytical techniques, so the composition of the complex matrices must not interfere with the determination [7].

In this context, in several international projects, matrix-type Certified Reference Materials (CRMs) have been developed, containing certified values of toxic metal content and the associated uncertainty.

Several institutions provide such complex matrices for soils (organic rich soil, sandy soil, road dust, industrial soil), sediments (estuarine, coastal, lake or river sediment), waste (fly ash, sewage sludge amended soil), plant tissue (hay powder, clover, lichen, tomato leaves, apple leaves, plankton, rice, etc.) or animal organs (tuna muscle, cod liver, etc.). Among these, we can mention the best known, namely: *European Commission Joint Research Center* - JRC (800 CRMs of the BCR- and IRMM-brands as well as the ERM-branded materials that were produced by the JRC) or *US Department of Commerce* -

National Institute of Standards and Technology NIST. Obtaining such materials implies the application of well-established rules, which ensure the homogeneity and stability of the samples, as well as the assigned value and the uncertainty for each element or compound [8].

The international requirements imposed by the EN ISO 17025/2018 standard enforce accredited laboratories around the world to verify their analytical results for the determined pollutants [9]. Thus, the use of matrix-type certified reference materials has become a common practice in such laboratories (Table 1).

Table 1. Examples of CRMs in environmental analysis

CRMs	Matrix type	Aqua regia extractable content
ERM-CC 141	Loam Soil	As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
ERM-CC018	Sandy Soil	As, Cd, Cr, Co, Cu, Pb, Hg, Ni, V, Zn
RTC SPE-001	Soil	Al, As, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Li, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Sb, Na, Sr, Sn, Ti, V, Zn
WQB-1	Sediment	Al, As, Co, Cu, Pb, Fe, Mn, Hg, Ni, Se, V, Zn
RTC CRM016	Sediment	Al, As, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Li, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Sb, Na, Sr, Sn, Ti, V, Zn
BCR 146R	Sewage sludge from industrial origin	Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
NIST 2782	Industrial sludge	As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Zn
CRM 029	Sewage sludge	Al, As, Ba, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Se, Ag, Sb, Na, Sr, Sn, Ti, V, Zn
BCR 483	Sewage sludge amended soil	Cd, Cr, Cu, Ni, Pb, Zn
BCR 176R	Fly ash	As, Cd, Co, Cr, Cu, Fe, Ni, Pb, Sb, Se, Tl, Zn
ERM-CE464	Tuna fish	Hg total, CH_3Hg^+
BCR 482	Lichen	Al, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn
NIST 1515	Apple leaves	Al, B, Ba, Cd, Ca, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, K, Na, V, Zn
NIST 1573a	Tomato leaves	Al, Sb, As, Ba, B, Cd, Ca, Cr, Cu, Co, Fe, Mn, Hg, Mo, Ni, K, Se, Ag, Na, Sr, V, Zn

Another way of testing the obtained results is by participating in proficiency testing (PT) schemes, where the entire applied procedure is tested (pretreatment, determination, reporting results). There are specialized international organizations that organize annually such schemes, these being diversified according to the pollutants and the matrix type (water, soil, waste, sediment, plant tissue). A database for such PTs in which the topics, the type of matrice and the accreditation of the organization that organizes the scheme are presented is EPTIS database [10].

The aim of this study is to present the results obtained by using various CRMs to check the metal content (As, Cd, Cu, Cr, Ni, Pb, Zn) from different environmental matrices (soil, sediment, fly ash, sewage sludge and vegetable tissues) as well as the applied analytical techniques for metal determination.

EXPERIMENTAL PART

Methods

In order to determine the metal content in solid environmental samples (soil, sediment, fly ash, sewage sludge), FAAS and ICP-EOS techniques were applied.

Table 2 presents the operational parameters for the method that uses ICP-EOS technique [11], while the performance parameters (quantification limit, accuracy and measurement uncertainty) are listed in table 3. The working conditions [12] and performance parameters for FAAS method are presented in table 4.

In the case of vegetation samples, due to their low metal contents, ICP-MS and ICP-EOS methods were applied. The operational parameters, respectively the performance

parameters of the applied ICP-MS method are presented in tables 5 and 6.

Table 2. Operating parameters for ICP-EOS AVIO 500 equipment

Spectrometer parameters		**Plasma parameters**	
		Argon flow rate 15 L/min	RF power 1400 W
Purge gas flow rate: normal Replicates: 3 times	Delay time 40s	Auxiliary agent flow rate: 0.2 L/min Nebulizer flow rate: 0.7 L/min	Plasma view: Axial View distance: 15.0 mm
Processing spectral peaks			
Peak Algorithm: peak area Points per peak: 10 points		Spectral corrections: background correction	

Table 3. Performance parameters of the methods applied with the ICP-EOS AVIO 500 equipment

Element	**Wavelength, nm / matrix**	**LOQ, mg/kg**	**Precision, %**	**Uncertainty, %**
As	188.979 (vegetation) 197.197 (solid samples)	0.75	4.7	14.
Cd	228.802 (vegetation) 214.440 (solid sample)	0.08	3.8	0.9
Cr	267.716	0.04	2.4	13.3
Cu	324,754 (vegetation) 327.393 (solid samples)	0.05	5.3	11.7
Ni	231.604 (vegetation) 341.476 (solid sample)	0.11	4.8	11.7
Pb	220.353 (vegetation) 217.000 (solid sample)	0.33	2.7	9.4
Zn	206.200	0.11	3.2	10.0

Table 4. FAAS - Performance parameters and working conditions

Element	**Wavelength, nm**	**Flame type**	**Background correction**	**LOQ, mg/kg**	**Precision, %**	**Uncertainty, %**
Cd	228.8	air / acetilene	deuterium	2.1	5.56	9.8
Cu	324.8	air / acetilene	deuterium	6.0	3.82	15.0
Ni	232.0	air / acetilene	deuterium	14.0	4.61	9.4
Pb	217.0	air / acetilene	deuterium	16.0	5.21	9.7
Zn	213.9	air / acetilene	deuterium	3.0	2.83	12.8

Table 5. Operating parameters for ICP-MS spectrometer

Delay time: 60s	Purge gas flow: normal
Replicates: 3 times	Peristaltic pump: 1.5mL/min
Tune parameters	
Plasma parameters	
Plasma flow rate: 15L/min	RF Power: 1550W
Auxiliary flow rate: 0.90 L/min	Plasma view: axial
Nebulizer Pump: 0.10rps	RF matching: 1.30V
Plasma mode	
Plasma Mode: General Purpose	Sample Depth: 10 mm
Cell parameters	
He Flow: 4.3mL/min	Octp Bias: -8.0 V
Spectral peak processing	
Peak algorithm: Peak area	Peak pattern: 3 points
Replicates: 3 times	Integration time: 0.2001 sec.

Table 6. Performance parameters for ICP-MS spectrometer

Element	LOQ, mg/kg	Precision, %	Uncertainty, %	Element	LOQ, mg/kg	Precision, %	Uncertainty, %
As	0.15	2.14	11.6	Ni	0.21	1.20	13.5
Cd	0.19	1.92	15.4	Pb	0.27	1.95	12.5
Cr	0.24	1.14	14.5	Zn	0.16	1.03	12.8
Cu	0.17	0.95	11.7				

All experimental tests were performed in an accredited laboratory according to EN ISO 17025/2018 [9], respecting the requirements for traceability and quality assurance of the analytical determinations results.

Materials and equipment

Multielements Certified Reference Material ME 21, 100 mg/L (Sigma-Aldrich)
Reference Material (RM) Quality Control Standard 21, 100 mg/L (LGC)
Hydrochloric acid ≥ 30% TraceSelect for trace analysis (Fluka)
Nitric acid ultra trace grade 69% (Scharlau)
Hydrogen peroxide solution, trace select ultra, ≥ 30% for trace analysis (Sigma Aldrich)
Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Perkin Elmer AVIO 500
Flame Atomic Absorption Spectrometer (FAAS) Thermo Scientific M6 Dual
Inductively Coupled Plasma Mass Spectrometer (ICP-MS) 7900 Agilent Technologies
Microwave Oven Ethos Up Milestone

Samples preparation

The content of metals extracted in aqua regia solution from the soil, sediment and sewage sludge samples, was determined. To 1 g of solid sample, 9 mL HCl and 3 mL HNO_3 were added. For the pretreatment of these solid samples (soil, sediment, and sewage sludge), a digestion program was applied (table 7). After cooling, the solutions were filtered and brought quantitatively to a 50 mL volumetric flask with ultrapure water.

Table 7. Microwave program for digestion of soil, sediment and sewage sludge samples

	Power	Time	Temperature T1 (inside vessels)	Temperature T2 (outside vessels)
Stage 1	1800 W	15 minutes	up to 180° C	120° C
Stage 2	1800 W	20 minutes	180° C	120° C
Stage 3	-	30 minutes	cooling	cooling

Vegetation samples (0.5 g) were pretreated with a mixture of 8 mL HNO_3 and 2 mL H_2O_2 and then subjected to the digestion program presented in table 8. The resulting solutions were filtered on low porosity filter paper and brought to the mark with ultrapure water in 25 mL volumetric flask.

Table 8. Microwave program for digestion of apple leave and lichen samples

	Power	Time	Temperature
Stage 1	1800 W	15 minutes	up to 200° C
Stage 2	1800 W	15 minutes	200° C
Stage 3	-	30 minutes	cooling

For each matrix type and each applied digestion program, blank samples were used in order to verify the interference of reagents used during sample preparation.

The metals from the following CRMs: loam soil (ERM-CC 141), sandy soil (ERM-CC 018), sediment (WQB-1), fly ash (176 R), industrial

sludge (NIST 2782) were extracted in aqua regia mixture. The analyzed vegetation CRMs were: apple leaves (NIST 1515), lichen (BCR 482). Each experiment was performed in duplicate, the reported values being the average values.

RESULTS AND DISCUSSION

The results obtained for the analyzed metals (As, Cd, Cr, Cu, Ni, Pb, Zn) in the CRMs are presented in this section. Thus, the obtained data for solid environmental samples (ICP-EOS, respectively FAAS results) are compared to the certified values from the quality certificates of the used CRMs (tables 9 ÷ 13).

Table 9. Loam soil ERM-CC 141(JRC, IRMM brand), mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	FAAS
As	7.5 ± 1.4	8.8 ± 1.3	-
Cr	31 ± 4	30.4 ± 4.0	-
Cu	12.4 ± 0.9	11.6 ± 1.4	11.5 ± 1.7
Ni	21.9 ± 1.6	20.3 ± 2.4	22.1 ± 2.1
Pb	32.2 ± 1.4	30.9 ± 2.9	-

Table 10. Sandy soil ERM-CC 018, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	FAAS
As	22.9 ± 1.3	21.7 ± 3.1	-
Cd	5.4 ± 0.5	5.9 ± 0.5	-
Ni	25.8 ± 1.8	27.3 ± 3.2	24.4 ± 2.3
Pb	289 ± 10	298 ± 28	281 ± 27

Table 11. Sediment WQB-1, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	FAAS
As	23 ± 1.8	24.7 ± 3.5	-
Cu	79.6 ± 16.1	66.4 ± 7.8	63.5 ± 9.5
Ni	61.5 ± 17.6	57.1 ± 6.7	59.7 ± 5.6

Table 12. Fly Ash 176 R, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	FAAS
Cu	1000 ± 70	1013 ± 119	989 ± 148
Pb	5000 ± 500	4572 ± 430	4563 ± 443
Zn	16800 ± 400	17039 ± 1700	16670 ± 2130

Table 13. Industrial sludge NIST 2782, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	FAAS
Cu	2594 ± 52	2626 ± 307	2555 ± 383
Pb	574 ± 11	569 ± 53	573 ± 56
Zn	1254 ± 196	1062 ± 106	1170 ± 150

The reported values for all metals in all solid matrices that were analysed are within the confidence intervals according to the quality certificates data.

Tables 14 and 15 show the results obtained for vegetation samples after metal determination by ICP-EOS, respectively ICP-MS techniques.

Table 14. Apple Leaves NIST 1515, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	ICP-MS
Cd	0.0132 ± 0.0015	< 0.08	0.013 ± 0.0013
Cu	5.69 ± 0.13	5.58 ± 0.88	5.57 ± 0.56
Ni	0.936 ± 0.094	1.025 ± 0.132	1.02 ± 0.10
Pb	0.470 ± 0.024	< 1.5	0.49 ± 0.05
Zn	12.45 ± 0.43	12.75 ± 1.67	12.18 ± 1.22

Table 15. Lichen BCR 482, mg/kg dry matter

Element	Certified value	Determined values	
		ICP-EOS	ICP-MS
As	0.85 ± 0.07	-	0.91 ± 0.09
Cd	0.56 ± 0.02	-	0.57 ± 0.06
Cr	4.12 ± 0.15	5.58 ± 0.88	5.57 ± 0.56
Cu	7.03 ± 0.19	6.87 ± 0.80	7.17 ± 0.72
Ni	2.47 ± 0.07	2.53 ± 0.30	2.44 ± 0.24
Pb	40.9 ± 1.4	41.3 ± 3.9	40.5 ± 4.1
Zn	100.6 ± 2.2	99.6 ± 10.0	98.7 ± 9.9

Table 16 contains the results obtained after participating in an inter-laboratory comparison scheme for a soil sample analysis, the obtained values being compared to the assigned values. The table also presents the Z scores obtained for the reported data, all values falling within the –2 ÷ 2 accepted range of standard deviation.

Table 16. LGC sample 14/2019, results of PTS, mg/kg dry matter

Element	Assigned value	ICP-EOS		FAAS	
		Value	Z score	Value	Z score
As	32.9 ± 4.2	27.9 ± 4.2	-1.44	-	-
Cd	6.28 ± 0.63	5.14 ± 0.51	- 1.72	-	-
Cr	153 ± 15.3	145.4 ± 17.4	- 0.47	145.0 ± 18.7	- 0.49
Cu	112.8 ± 16.8	106.3 ± 16.8	- 0.57	118.3 ± 13.6	- 0.47
Ni	43.9 ± 4.4	37.8 ± 5.3	- 1.39	45.7 ± 4.4	0.44
Pb	226.7 ± 22.7	228.3 ± 31.5	0.07	226.7 ± 22.6	0.00
Zn	815 ± 81.5	898.2 ± 90.2	1.02	935 ± 87	1.47

CONCLUSIONS

The results obtained in the verification of some methods applied for the determination of toxic metals both from solid environmental (soil, sediment, ash waste, respectively sewage sludge) and vegetation samples indicated that the applied ICP-EOS, FAAS, respectively ICP-MS techniques led to good results both on CRM matrices and in the case of participation in a proficiency test scheme.

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