

Evaluation of Atomic Spectrometry Methods for Determination of Some Heavy Metals in Soils, Soil Extracts, Plants, and Biota*

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Three atomic spectrometry methods (FAAS, ETAAS, ICP-AES) for the determination of heavy elements (Cd, Cr, Ni, Pb, V) in soils, soil extracts, plants, and biota were evaluated and compared. The precision and accuracy of spectrometric measurements were checked by certified reference materials. The ETAAS is more suitable for the determination of the elements studied in environmental samples, primarily with respect to convenient determination limits than FAAS and ICP-AES. In this work the following metrological data for ETAAS were obtained: the precision (RSD) values were in the range from 5 % to 10.3 % for Cd; from 6.7 % to 13.3 % for Cr; from 5.4 % to 14.1 % for Ni; from 4.4 % to 14.7 % for Pb, and from 8.5 % to 18.6 % for V; the detection limits – LOD ($3\sigma_{\text{blank}}$ criterion) for Cd were in the range 0.8–1.3 $\mu\text{g kg}^{-1}$; for Cr 1.8–2.3 $\mu\text{g kg}^{-1}$; for Pb 3.0–5.7 $\mu\text{g kg}^{-1}$; for Ni 4.2–5.9 $\mu\text{g kg}^{-1}$; and for V 16.3–23.5 $\mu\text{g kg}^{-1}$. The contents of elements obtained by the tested methods are in good agreement with the certified values of all used certified reference materials.

Various techniques of atomic spectrometry methods, including flame, hydride generation, and furnace AAS, inductively coupled plasma AES and others are usually applied for the determination of element contents in environmental sample solutions [1–3]. The selection of the most appropriate analytical method for the solution of the specific problem depends on the content range of the studied elements in the samples, determination limits as well as on other metrological data (acceptable levels of accuracy and precision of the analytical data) and economic criteria (operating costs). The aim of our work was to statistically evaluate the obtained results by used FAAS, ETAAS, and ICP-AES methods and to select the appropriate analytical method for particular element determinations in individual types of environmental samples.

EXPERIMENTAL

The reliability (accuracy and precision) of the FAAS, ETAAS, and ICP-AES methods was tested by analyzing a wide variety of environmental certified reference materials (CRMs) ten times: soils (CRM SO-2 and SO-4, CANMET); trace elements in water (CRM 1643c, NIST); extractable (EDTA, CH_3COOH) trace elements in sewage sludge amended soil and bovine

muscle (CRM 483, CRM 184, BCR), and lucerne P-ALFALFA (CRM 12-2-03, SIM). The soil CRM samples were decomposed by boiling with acid mixture ($\text{HNO}_3 + \text{HF} + \text{HClO}_4$) and fusion of the solid residue ($\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$). Plant and biota were decomposed with HNO_3 in a microwave oven. The soil extraction procedure (used extracting solvents: 0.05 mol dm^{-3} EDTA and 0.43 mol dm^{-3} CH_3COOH) was designed by *Quevauviller et al.* [4]. The determinations of the total content of elements in soils, plants, biota, and soil extracts (EDTA, CH_3COOH) were performed by FAAS (Perkin–Elmer 1100), ETAAS (Varian SpectrAA-10 with GTA-95), and ICP-AES (KONTRON, PLASMAKON S 35). The total and extractable contents of heavy metals determined in various environmental CRMs by the above-mentioned analytical methods were statistically evaluated (Statgraphics program). The limit of quantitation – LOQ was calculated according to EURACHEM recommendation [5].

RESULTS AND DISCUSSION

The precision and accuracy of analytical results were evaluated by the analysis of environmental CRMs and by comparative analyses using all the

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Table 1. Limits of Quantitation (LOQ), Certified and Found Contents m_r of Cd, Cr, Ni, Pb, and V in Various Environment CRMs Obtained by Different Atomic Spectrometry Methods

LOQ ^d /(mg kg ⁻¹)	Certif. value	$m_r(\text{Cd})/(\text{mg kg}^{-1})$ ETAAS		FAAS		ICP-AES	
		0.0015		0.055		0.070	
		Mean	RSD ^e /%	Mean	RSD/%	Mean	RSD/%
CRMs ($n = 10$) ^a							
Soil SO-2	0.130 ^b	0.132	6.8	0.124	7.7	0.115	8.3
Soil SO-4	0.340	0.358	5.0	0.311	5.6	0.326	7.0
Water 1643c	0.012 ± 0.001	0.0116	10.3	< LOQ ^d		< LOQ	
Soil extractants 483 CH ₃ COOH	18.3 ± 0.6	17.5	6.3	18.0	4.3	23.6	5.1
Soil extractants 483 EDTA	24.3 ± 1.3	23.2	7.6	19.0	5.3	26.8	6.1
Lucerne 12.2.03	0.136 ± 0.030	0.138	8.0	0.125	9.2	0.134	10.9
Muscle 184	0.013 ± 0.002	0.020	10.0	< LOQ		< LOQ	
LOQ/(mg kg ⁻¹)		$m_r(\text{Cr})/(\text{mg kg}^{-1})$ 0.010		0.100		0.080	
Soil SO-2	16.0 ± 2.0	14.8	7.8	15.3	4.8	17.9	7.1
Soil SO-4	61.0 ± 6.0	58.5	6.7	56.0	4.1	65.0	5.4
Water 1643c	0.019 ± 0.0006	0.018	13.3	< LOQ		< LOQ	
Soil extractants 483 CH ₃ COOH	18.7 ± 1.0	17.2	8.7	19.8	5.6	19.5	7.5
Soil extractants 483 EDTA	28.6 ± 2.6	25.8	10.5	30.3	8.2	31.2	6.8
Lucerne 12.2.03	(0.900) ^e	0.914	9.6	1.015	11.2	0.921	10.6
Muscle 184	(0.076—0.153) ^f	0.079	10.1	< LOQ		< LOQ	
LOQ/(mg kg ⁻¹)		$m_r(\text{Ni})/(\text{mg kg}^{-1})$ 0.015		0.120		0.080	
Soil SO-2	8.0 ± 2.0	8.3	9.5	7.1	5.9	7.5	6.1
Soil SO-4	26.0 ± 3.0	25.5	8.4	23.0	6.8	28.0	7.9
Water 1643c	0.061 ± 0.007	0.059	9.7	< LOQ		< LOQ	
Soil extractants 483 CH ₃ COOH	25.8 ± 1.0	24.5	8.7	25.6	4.8	26.6	8.5
Soil extractants 483 EDTA	28.7 ± 1.7	28.2	5.4	25.2	4.5	30.7	7.5
Lucerne 12.2.03	2.540 ± 0.080	2.611	9.0	2.586	8.1	2.43	8.7
Muscle 184	(0.270)	0.310	14.1	0.288	11.6	0.29	10.4
LOQ/(mg kg ⁻¹)		$m_r(\text{Pb})/(\text{mg kg}^{-1})$ 0.011		0.300		0.250	
Soil SO-2	21.0 ± 4.0	19.3	8.7	20.8	5.6	23.0	7.5
Soil SO-4	16.0 ± 3.0	14.9	9.1	16.5	4.3	18.4	6.2
Water 1643c	0.035 ± 0.0009	0.034	14.7	< LOQ		< LOQ	
Soil extractants 483 CH ₃ COOH	2.10 ± 0.25	2.24	8.2	2.38	7.8	2.27	8.7
Soil extractants 483 EDTA	229 ± 8.0	240	7.3	171	6.2	223	6.4
Lucerne 12.2.03	1.84 ± 0.08	1.78	8.4	1.55	7.8	1.96	8.2
Muscle 184	0.239 ± 0.011	0.310	8.7	< LOQ		< LOQ	
LOQ/(mg kg ⁻¹)		$m_r(\text{V})/(\text{mg kg}^{-1})$ 0.030				0.020	
Soil SO-2	64.0 ± 10.0	66.4	9.5			60.5	8.0
Soil SO-4	90.0 ± 11.0	84.8	8.5			85.0	6.4
Water 1643c	0.031 ± 0.003	0.035	14.0			0.033	8.5
Soil extractants 483 CH ₃ COOH	n.d. ^g	18.7	10.5			17.2	8.8
Soil extractants 483 EDTA	n.d.	28.6	10.5			25.8	10.2
Lucerne 12.2.03	(0.800)	0.900	18.6			0.840	11.5
Muscle 184	(0.076)	0.079	11.4			0.087	8.7

a) The data are the average of ten determinations on the same sample CRM; b) certified values ± standard deviation; c) relative standard deviation; d) LOQ – limit of quantitation; e) informational values; f) range of results observed; g) not determined.

above presented analytical procedures and methods. The results of CRM analyses are shown in Table 1. The precision of the analysis was expressed by rela-

tive standard deviation (RSD/%) based on ten replicate determinations of individual elements in the CRM samples. The ETAAS method provided I

values in the range from 5 % to 10.3 % for Cd; from 6.7 % to 13.3 % for Cr; from 5.4 % to 14.1 % for Ni; from 4.4 % to 14.7 % for Pb, and from 8.5 % to 18.6 % for V, depending on the magnitude of the measured concentrations. The FAAS and ICP-AES methods give for the same concentrations of all elements, with the exception of Cd similar or slightly lower mean values of RSD in comparison with ETAAS. The accuracy was checked for all methods. Values of monitored elements in CRMs are certified, in a few cases are uncertified (informational values of Cr and V in CRMs of lucerne and bovine muscle) and only for V in soil EDTA and CH₃COOH extractants are not determined. The concentrations of elements obtained are in good agreement with the certified ones for all environmental CRMs (Table 1). The quantitation limits (LOQ) of the methods we used ($6\sigma_{\text{blank}}$ criterion) are shown in Table 1. Of course, ETAAS gives better LOQ for Cd, Cr, Ni, and Pb than FAAS and ICP-AES procedures. Only the LOQ of V is better by using ICP-AES in comparison with ETAAS. According to the presented metrological data (precision, accuracy, quantitation limit), ETAAS is more suitable for the determination of the studied elements

in soils, soil extractants, plants, and biota, primarily with respect to the more convenient detection limit than the one achieved by FAAS and ICP-AES. This is why ETAAS was applied for the next analysis of environmental samples.

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REFERENCES

1. Kubová, J., Streško, V., Čelková, A., Medveď, J., and Agrawal, S., in *CANAS '95, Konstanz 1995* (Welz, B., Editor, Bodenseewerk Perkin—Elmer). P. 621. Oberschwäbische Verlagsanstalt, Ravensburg, 1996.
2. Karadjova, I. and Karadjov, M., *Fresenius' J. Anal. Chem.* 360, 246 (1998).
3. Medveď, J., Kubová, J., Chmielewská, E., and Streško, V., *Turkish J. Chem.* 25, 323 (2001).
4. Quevauviller, Ph., Lachica, M., Barahona, E., Gomez, A., Rauret, G., Ure, A., and Muntau, H., *Fresenius' J. Anal. Chem.* 360, 505 (1998).
5. Fleming, J., Albus, H., Neidhart, B., and Wegscheider, W., *Accreditation and Quality Assurance* 2, 51 (1997).