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VALIDATION OF INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY TECHNIQUE FOR THE DETERMINATION OF TRACE ELEMENTS IN GRANULAR WASTE

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ABSTRACT. The study presents the validation protocol for the determination of Cd, Cr, Cu, Pb and Zn by inductively coupled plasma atomic emission spectrometry in leachate of granular waste with size below 4 mm at liquid-to-solid ratio of 2 L/ kg and in aqua regia digest. The assay was found to be linear for a concentration range between limit of quantitation and 25 mg L^{-1} (R=0.999). The limits of detection in leachate allow the determination of elements at concentration levels for the acceptance of non-hazardous wastes, while in aqua regia digest at values ten times lower than the normal levels in soil. Internal repeatability was in the range 0.8-5.4 %, reproducibility between 2.6 – 12 % and recovery 91-109 %, which fully complied with imposed targets in Romanian regulations. The maximum variance of the method was found for Zn (5.65 %), while the maximum relative expanded uncertainty for Cu (21 %).

Keywords: *method validation, trace elements, atomic emission spectrometry, granular waste, leaching test*

INTRODUCTION

The problem of making rapid and inexpensive determinations in order to evaluate the risk represented by solid wastes is of high concern. Chemical measurements are needed to compare the concentrations of hazardous substances present in solid waste with the limit values imposed by the Romanian legislation complying with that in the European Union. Classification of wastes and their disposal in accordance with the Directive 1999/31/EC (Landfill Directive, Annex II) and Decision 2003/33/EC impose the following types of tests: Level 1. Basic characterization, Level 2. Compliance testing. Level 3. On-site verification.

Romanian legislation establishes criteria and preliminary procedures for waste acceptance in different landfill classes [1]. Certain wastes such as waste glass, concrete, bricks, tiles, ceramics and mixtures thereof free of

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hazardous substances are considered inert and can be landfilled without preliminary testing. All other wastes are subject to testing in order to be categorized as inert/non-hazardous/hazardous. Tests include a range of inorganic determinants in eluate derived from the European standard leaching test ISO EN 12457:2002 and several specific parameters determined on waste it self such as pH, acid neutralization capacity and total organic carbon. Limit values in water leachate for each waste category are given for liquid-to-solid ratios (L/S) of 2 L/kg (2:1), 10 L/kg (10:1) as well as for the percolation test. Indicators refer to the contents of As, some metals (Ba, Cd, total Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Zn), anions (chlorides, fluorides, sulphates), phenol index, organic compounds dissolved and total dissolved solids.

Validation is a matter of great importance as it attests the capability of the laboratory to provide reliable results [2,3]. In agreement with Mermet [4], one of the possible research areas in ICP-AES analysis is method validation for intended purposes as the instrumentation is well implemented. The topic related to method validation by ICP-AES is supported by the scarcity of publication in the field [5-7].

The aim of this study was to validate and extend the application of inductively coupled plasma atomic emission spectrometry (ICP-AES) for the characterization of granular wastes from the non-ferrous industry and soil contaminated with heavy metals. The selection of elements (Cd, Cr, Cu, Pb and Zn) took into account their high levels in these materials. Validation refers to analysis of waste leachate at L/S (2/1) and aqua regia digest of granular wastes with size below 4 mm. The validation protocol combines the existing standards elaborated for the determination of elements by ICP-AES in water and soil [8, 9].

RESULTS AND DISCUSSION

The characteristics considered to be of interest for the procedure proposed for validation were specificity/selectivity, limit of detection, limit of quantification, repeatability, reproducibility, linearity and measurement uncertainty.

Selectivity/specificity. These characteristics assessed confidence in measurement in the presence of interference. The reference standard for this proposed procedure [4] reveals possible interferences, such as that of Fe on Cd, Zn, Cu, Cr and interference of Cu and Ni on Zn. The high resolution of the used spectrometer (9 pm) and the low relative intensity of interfering wavelengths reduced the likelihood of interference. Negative controls gave baseline signal for the analyte. One point or two points approaches were used for background correction provided by the software of the ICP spectrometer.

Limit of detection. Table 1 presents LODs (3 σ criterion) by ICP-AES for the leaching and aqua regia digestion tests on granular wastes expressed as dry mass based on detection limits in solution and sample preparation protocol.

Table 1. Limits of detection (mg kg^{-1}) by ICP-AES for the leaching test (L/S 2:1) of granular waste and aqua regia digestion test

Element	Leaching test	Aqua regia digestion test
Cd	0.004	0.05
Cr	0.036	1.2
Cu	0.018	1.6
Pb	0.042	0.7
Zn	0.010	1.1

LOD was estimated from the calibration function for a signal equal to the net signal of blank and three times its standard deviation. The blank signal included contribution of reagents, microwave digestion system and glass-ware. Standard deviation of blank resulted from the analysis on the same day of 10 independent reagent blank solutions, measured once each.

The performance criteria targeted for the leaching test were the limit values of the selected elements (mg kg^{-1} dry mass) at L/S (2/1) for the acceptance of non-hazardous wastes: Cd - 0.6; Cr- 4; Cu - 25; Pb - 5; Zn – 25 [1]. For the aqua regia digestion test the performance criteria in view were concentrations ten times lower than the normal levels in soil (mg kg^{-1}): Cd – 0.1; Cr – 3; Cu – 2; Mn – 90; Pb – 2; Zn – 10 [10]. Data in Table 1 show that performance targets were largely achieved. Quantitation is possible with reasonable accuracy at concentrations 3 times higher than the limits of detection.

Precision. The most common assays to evaluate precision are internal repeatability and reproducibility [11]. Results obtained in the internal repeatability assay for the leaching test at L/S (2/1) and the aqua regia digestion test conducted on 6 parallel samples and one blank by a single operator using the same equipment are presented in Table 2. The self-imposed targets meeting provisions in [12,13] were standard deviation of repeatability below 9% and limit of repeatability below 25%.

Table 3 summarizes results from the reproducibility study for the leaching test at L/S (2/1) on 10 replicate waste samples from the non-ferrous industry and in the aqua regia digestion test on 6 parallel samples of certified contaminated soil with heavy metals (CRM 025-050). Protocols were carried out by different operators using the same equipment in different days. Blanks were run in each case. Reproducibility characteristics in Table 3 fully correspond to imposed target of 23 % as maximum standard deviation of repeatability [12,13].

Table 2. Results obtained in the repeatability assay by ICP-AES

Element	Leaching test, L/S (2/1)			Aqua regia digestion test		
	$\overline{A}$ /mg kg $^{-1}$	s_r / %	r / %	$\overline{c}$ / mg kg^{-1}	s_r / %	r / %
Cd	0.33	3.4	9.4	18.5	1.4	3.9
Cr	0.43	2.8	7.9	384	3.9	10.9
Cu	22.8	5.4	14.9	592	1.1	3.0
Pb	5.9	2.3	6.5	1311	0.8	2.4
Zn	111	2.7	7.6	2513	4.6	12.6

s_r - standard deviation of repeatability; r - limit of repeatability (s_rx2.8); $\overline{A}$ - average release of constituent in the leaching test; c - average concentration in aqua regia digestion test

Table 3. Results obtained in the reproducibility assay by ICP-AES

Element	Leaching test, L/S (2/1)			Aqua regia digestion			
	($\overline{A}$)/ mg kg^{-1}	s_R/ %	R / %	Cert. conc. ±S.D./ mgkg^{-1}	Found conc. ±S.D/ mg kg^{-1}	s_R/ %	R / %
Cd	0.39	12	34	369±46.3	365±9.3	2.6	7.2
Cr	0.47	12	33	441±50.1	454±14.9	3.3	9.2
Cu	24.43	9	27	7.76±1.68	9.18±0.81	8.8	24.7
Pb	5.98	5	15	1447±203	1523±59	4.0	10.8
Zn	112	8	22	51.8±8.29	59.1±5.09	8.6	24.1

s_R - standard deviation of reproducibility; R - limit of reproducibility (s_Rx2.8); $\overline{A}$ - average release of constituent in the leaching test; S.D.- standard deviation

Recovery. Comparison of found concentration of elements in CRM 025-050 following aqua regia digestion test with the certified values gave recovery in the range of 97-103 % for Cd and Cr, 91-109 % for Cu and Zn and 96-104 % for Pb. Recovery agreed with provision in [13].

Linearity of the calibration function and working concentration range. The target criteria were correlation coefficient of the calibration function (R) above 0.995, homogeneity of dispersion at the limits of the range and variation coefficient of the method (Vox) below 7%. The performance characteristics were estimated according to reference [14].

Linearity of the assay was evaluated from the regression function of calibration using 6 standards, the lowest concentration of which corresponded to the limit of quantitation (3xLOD), while the others were 1; 2; 5; 10; 25 mg L^{-1}element.

To check homogeneity of dispersions, the standard deviations (s_1) and (s_2) were calculated for series of 6 information values for (3xLOD) and 25 mg L^{-1} element respectively, and the ratio (s_1^2/s_2^2) was compared with the critical value $F_{5;5;0,99}$=10,97. The values for R, Vox and (s_1^2/s_2^2) ratios as well as the working concentration range for the determination of Cd, Cr, Cu, Pb and Zn by ICP-AES are presented in Table 4. Data reveal R values higher than 0.999 over the considered working concentration range, a random difference between checked variances and a maximum Vox value of 5.65 % (Zn).

Table 4. Working concentration ranges, variance ratio at the limits of the range, correlation coefficients (R) and variation coefficients of the method (V_{ox}) in the analysis of wastes by ICP-AES

Element	Concentration range/mg L^{-1}	s_1^2/s_2^2	R	V_{ox}
Cd	0.005 - 25	6.53	0.9997	3.51
Cr	0.05 - 25	6.12	0.9996	3.95
Cu	0.03 - 25	6.19	0.9999	1.71
Pb	0.06 - 25	7.35	1.0000	1.42
Zn	0.02 - 25	6.90	0.9993	5.65

As the target criteria were met, the liquid samples were appropriately diluted before analysis, when necessary, such that the analyte concentrations lie in the linear range.

Standard uncertainty. The protocol to estimate uncertainty followed the classical steps of specifying the measurand, identifying the uncertainty sources, quantifying uncertainty components and calculus of combined uncertainty [15]. The potential sources of uncertainty for the leaching test and aqua regia test on granular waste < 4 mm and analysis by ICP-AES are shown in a cause-effect diagram (fishbone diagram) in Fig. 1.

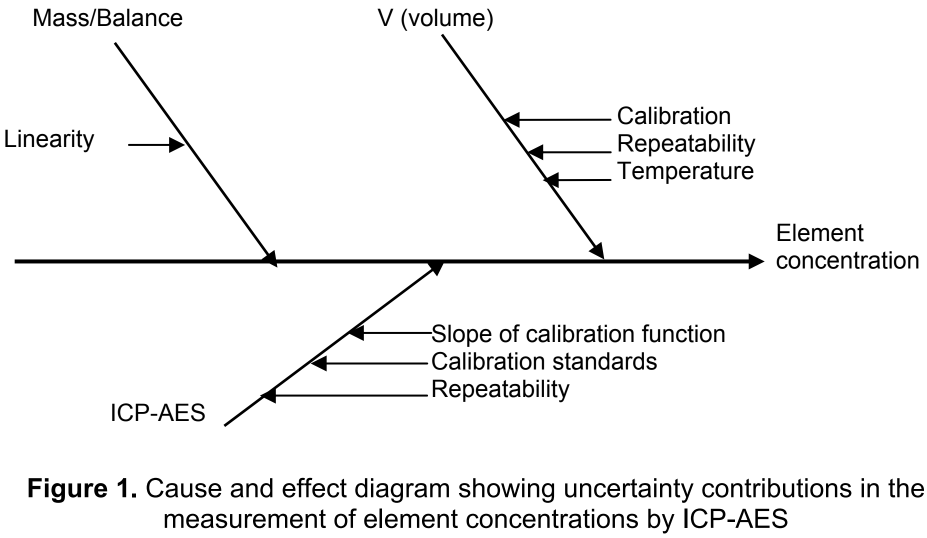

Figure 1. Cause and effect diagram showing uncertainty contributions in the measurement of element concentrations by ICP-AES

The combined standard uncertainty (u_c) was calculated as square root of squares of individual standard uncertainties, according to the specific protocol. The expanded uncertainty (Uc) resulted by multiplying (u_c) by the coverage factor (2) and provided a confidence interval expected to encompass 95% of results attributable to the measurand. The relative expanded uncertainty (U_{rel}) was expressed as $U_{rel} = U_c \times 100$. Results from the uncertainty study in the two tests are given in Table 5.

Table 5. Uncertainty in the analysis of granular waste leachate at L/S (2/1) and aqua regia digests for 1 mg kg^{-1} contaminant by ICP-AES

Element	Leaching test			Aqua regia digestion test		
	u_c/ mg kg^{-1}	U_c/ mg kg^{-1}	U_{rel}/ %	u_c/ mg kg^{-1}	U_c/ mg kg^{-1}	U_{rel}/ %
Cd	0.073	0.147	15	0.044	0.088	9
Cr	0.070	0.140	14	0.056	0.112	11
Cu	0.103	0.206	21	0.073	0.146	15
Pb	0.062	0.124	12	0.029	0.059	6
Zn	0.076	0.151	15	0.068	0.135	14

u_c – standard uncertainty; U_c –combined standard uncertainty; U_{rel} –relative expanded uncertainty.

The target values for (U_{rel}) were 25 % of the measured value for the leaching test and 15 % respectively, for the aqua regia digestion test according to [12,13]. Data in Table 5 demonstrate compliance with aimed limits. The main contribution to uncertainty in the leaching test came from the weighing of waste sample and measurement of leaching agent volume, while in the aqua regia digestion test from the determination by ICP-AES.

CONCLUSIONS

The study provided a procedure for the determination of Cd, Cr, Cu, Pb and Zn by ICP-AES in leachate of granular waste with particle size below 4 mm at L/S ratio (2:1) and in aqua regia digest. The estimated parameters within the validation protocol (selectivity/specificity, limit of detection, internal repeatability, reproducibility, recovery, linearity of the working concentration range and uncertainty) were found to meet the imposed performance criteria and the procedure was validated for the intended use.

EXPERIMENTAL SECTION

Reagents and calibration. Acids used were of highest purity (analytical grade): 37 % (m/m) HCl and 69 % (m/m) HNO_3 (Merck, Germany). Calibration standards were prepared starting from the multielement ICP solution IV 1000 mg L^{-1} (Merck, Germany) by dilution with 5 % (v/v) HNO_3. Reagent blanc 1 consisted of 6 mL 37 % HCl + 2 mL 69 % HNO_3 to 100 mL water solution, reagent blanc 2 was distilled water, while calibration blanc was 5 % (v/v) HNO_3.

Distilled water (< 0.5 mS m^{-1}) grade 3 according to EN ISO 3696 was used throughout the experiment. The certified reference material Soil CRM 025-050 (Laramie, New York, USA) was used in the reproducibility assay and recovery assessment.

Instrumentation. Instrumentation used for sample preparation included Kern Balances (Kern&Sohns, Germany) of 0.1 g and 0.1 mg accuracy respectively, Memmert oven with adjustable temperature (Memmert GmbH & Co. KG, Germany), Retsch sieving shaker AS200 (Retsch GmbH, Germany) with mesh size of 4 mm, 10 mm and 250 μm; Heidolph Reax 20/8 Overhead Shaker (Heidolph, Germany), Berghof MWS3 + high-pressure microwave digestion system (Berghof, Germany), Sartorius vacuum filtration unit 0.45 μm pore size filters (Sartorius Stedim Biotech SA, Germany) and Hettich Universal 320 centrifuge (Hettich, Germany). The inductively coupled plasma multichannel spectrometer SPECTROCIROS CCD (Spectro Analytical Instruments, Germany) was used for the determination of metals. The operating conditions were 1400 W, 12 L min^{-1} Ar for plasma generation, 1 L min^{-1} Ar for sample nebulization. Working wavelengths (nm) were: Cd 214.438; Cr 283.563; Cu 324.754; Pb 220.351; Zn 213. 856. Argon (5.0 quality) from Gas SRL Cluj-Napoca, Romania, was used.

Materials. During sample preparation volumetric flasks, graduated and volumetric pipettes of class A, polyethylene bottles for solid samples and solutions, porcelain mortar, exicator were used.

Sample pretreatment for the leaching tests. The test material (waste from non-ferrous industry, contaminated soil) was sieved with a grain size of at least 95% mass below 4 mm. When oversized material exceeded 5 % mass, the entire oversized fraction was crushed. The water content of the samples (MC, %) [16,17] was previously determined and found to be in the range of 0.5 - 2 %. Its determination was necessary in order to correct for the volume of distilled water (L) added for leaching.

Leaching procedure for L/S 2/1 [12]**.** A test portion of total mass of M_W corresponding to 0.175 ± 0.005 kg dry mass (M_D) was weight and put in a 0.5 L volume polyethylene bottle together with a volume of distilled water (L) calculated for L/S=2/1 ratio. The capped bottle was agitated at about 10 rpm for 24 ± 0.5 h at (20 ± 5) ^{0}C. After a decantation time of 15 min, the mixture was centrifuged and filtered through 0.45 micron filters. A volume of 0.44 L distilled water as blank was subjected to the same protocol.

Digestion for subsequent determination of aqua regia soluble portion of elements [9]. A portion of 0.5 – 1 g dried sample sieved at < 250 μm was digested with 10 mL aqua regia in the high-pressure microwave system following a protocol recommended for such samples and diluted to a final volume of 100 mL. A reagent blank was prepared in the same way.

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