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IPEN-CNEN/SP PERFORMANCE IN THE CCQM-P70 PILOT STUDY ON TRACE ELEMENTS IN SEWAGE SLUDGE

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Abstract: Participation in interlaboratory comparison programmes is an important quality assurance tool for the production of reliable measurement results. This paper describes the performance of IPEN-CNEN/SP Neutron Activation Analysis Laboratory (LAN) in the CCQM-P70 Pilot Study on trace elements in sewage sludge. Comparison of LAN results to the CCQM-P70 reference values leads to the z-score values -0.10 for Cr and -0.18 for Zn, demonstrating the suitability of the methods employed and the good performance of the laboratory.

Key words: interlaboratory program, pilot study, uncertainty assessment, trace elements.

1. INTRODUCTION

Participation in interlaboratory comparison programmes is one of the internationally accepted quality assurance tools in order to a laboratory be able to consistently produce reliable measurement results [1] being also one requirement for laboratory accreditation [2]. Other important quality assurance tools are: validation of analytical methods; use of certified reference materials (CRMs) and the employment of routine internal quality control.

The Consultative Committee for Amount of Substance – Metrology in Chemistry (CCQM) is the committee of the Bureau International des Poids et Mesures (BIPM) with the task of ensuring world-wide uniformity of measurements and their traceability to the International System of Units (SI) in the chemical field. Present activities concern primary methods for measuring amount of substance, international comparisons, and establishment of international equivalence between national laboratories [3].

In the field of international comparisons, CCQM organizes the so called key comparisons. Key comparisons participants are the National Metrological Institutes (NMIs) and the goal is to enhance mutual recognition among the various NMIs. The CCQM-K44 key comparison was organized for the analysis of trace elements in sewage sludge.

When besides NMIs, other invited institutes participate on a CCQM interlaboratory comparison, the comparisons is denominated a Pilot Study. CCQM-P70 Pilot Study was issued to analyze the same sewage sludge material of CCQM-K44. The participation on CCQM Pilot Studies allows participants to assess their performance compared not only to the Pilot Study participants but also to NMIs.

The sewage sludge used in CCQM-K44 and CCQM-P70 was also used in an International Measurement Evaluation Programme (IMEP) organized by the Institute for Reference Materials and Measurements (IRMM). IMEP-21 resulted in the certification of the sewage sludge as a reference material for the analysis of trace elements, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PHAs) [4].

The importance of analyzing sewage sludge with internationally accepted quality comes from the fact that this material is recycled to be used in agriculture and harmful effects to the environment are possible due to low levels of trace elements such as Cd, Cu, Hg, Ni, Pb and Zn and organic contaminants such as PCBs and PAHs. Due to this fact, the levels of these contaminants are subject to governmental legislation [4].

This study presents the IPEN-CNEN/SP Neutron Activation Laboratory (LAN) performance in the CCQM-P70 Pilot Study on trace elements in sewage sludge. LAN presented results for Cr and Zn obtained by Instrumental Neutron Activation Analysis (INAA) [5]. Concentration results were submitted to the interlaboratory comparison provider with their combined and expanded standard uncertainties, whose sources are described and estimated in the following sections.

2. EXPERIMENTAL

2.1. Specification of the measurand

The measurand is the concentration C (mol kg^{-1}) of the elements Cr and Zn in a CCQM-P70 sewage sludge sample, determined by the relative method of Instrumental Neutron Activation Analysis (INAA).

In the relative method of INAA, the sample is irradiated simultaneously with standards of the elements of interest, in an appropriate flux of neutrons and the concentration C is determined by means of Equation 1:

$$C = \frac{m\, A_u\, e^{\lambda(t_u - t_s)}}{M\, A_s} \quad (1)$$

where:
m = mass of the element in the standard;
M = mass of the sample;
A_u = activity of the sample;
A_s = activity of the elemental standard;
t_u = sample decay time;
t_s = elemental standard decay time;
λ = decay constant, where $\lambda = \frac{\ln 2}{t_{1/2}}$ and $t_{1/2}$ is the half life of the element.

2.2. Uncertainty assessment in INAA

The uncertainty sources for the relative method of INAA are shown in the cause and effect diagram in Figure 1.

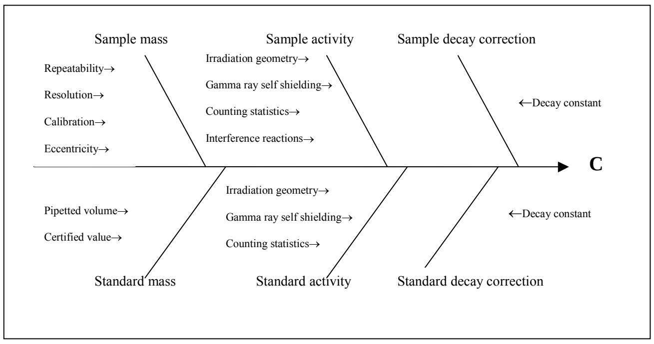

Fig 1. Uncertainty sources in INAA

The uncertainty sources for each of the input quantities were estimated and combined for the assessment of the combined standard uncertainties (u_c) and the expanded uncertainties (U) associated to the measurement of Cr and Zn in sewage sludge by INAA, according to internationally accepted protocols, as described in the Results section [6-11].

2.3. Sample and standards preparation

About 0.050 g of sewage sludge sample was weighed in a properly cleaned polyethylene vial using a Shimadzu AEM-5200 analytical balance. To check the accuracy of the method, about 0.100 g of IAEA EC-TRAP-LRM Lake Sediment certified reference material was also weighed.

Standards with appropriate elemental masses were prepared by pipetting Spex certified solutions onto Whatman filter papers, using an Eppendorf variable volume pipette. After drying, the elemental standards were kept in polyethylene vials with the same geometry of the samples. In Table 1 data on the used standard solutions are presented.

Table 1. Solutions used in the preparation of elemental standards

Element	Certified concentration[1], mg L^{-1}	Pipetted volume, µL	Mass in pipetted standard, µg
Cr	1002.5 ± 3	99.47	98.72
Zn	1000 ± 3	99.06	99.06

[1]Uncertainties are expanded uncertainties, with k = 2.00;

2.4. Irradiation and element determination

Sample aliquots and the reference material were simultaneously irradiated with elemental standards. For element determination, an 8-h irradiation at 10^{12} n cm^{-2} s^{-1} thermal neutron flux of IEA-R1 Nuclear Research Reactor at IPEN was used. After a decay period of about two weeks, the induced radioactivity was measured, using a CANBERRA detector (coupled to a CANBERRA multi-channel system and electronics). Analyses of gamma ray spectra and element concentration were calculated applying in-house software. In Table 2 are presented the used radionuclides, as well as their half lives and gamma ray energies [4]

Table 2. Radionuclides used in sewage sludge determination by INAA

Element	Radionuclide	Energy, keV	Half life, d
Cr	^{51}Cr	320.08	27.7
Zn	^{65}Zn	1115.55	243.9

2.4. Dry-mass correction and conversion to mol kg^{-1} unit

After the determination of element concentration, a dry-mass correction was applied to the results. Moisture content was determined as 5.2 %, according to the CCQM-P70 instructions. Concentration results in mg kg^{-1} were converted to mol kg^{-1} using the appropriate element molar weights.

3. RESULTS AND DISCUSSION

3.1. Uncertainty assessment in INAA

- ***Sample mass***

In Table 3 are summarized the contributions for the sample mass standard uncertainty. The repeatability contribution (Type A uncertainty) was taken from a control chart of 0.1 g measurements, with n = 60. The other contributions were taken from the balance calibration certificate (Type B uncertainty).

Table 3. Contributions for sample mass standard uncertainty

Uncertainty source	Uncertainty, g	Probability distribution	Factor	Standard uncertainty, g
Repeatability	0.00002	Normal	1	2.0×10^{-5}
Readability	0.00001	Rectangular	1/2√3	2.89×10^{-6}
Calibration[1]	0.00001	Normal	2.05	
Eccentricity	0.00002	rectangular	1/2√3	

Combined uncertainty				

[1]expanded uncertainty, k = 2.05

- ***Element mass in standards***

The uncertainty in the element mass in standards depends on the certified concentration values for the standard solutions (taken from solution certificates, Table 1), a Type A contribution, and on the volume of the solution pipetted onto filter papers. Volume repeatability (Type A, normal distribution, n = 10), declaration of the pipette producer and uncertainty from volume expansion due to differences in the temperature were considered to obtain the uncertainty in the element mass in standards (Type B, rectangular distribution), as summarized in Table 4.

Table 4. Contributions to the uncertainty in element mass in standards

Element	Element mass, μg	Combined uncertainty, μg
Cr	98.72	0.31
Zn	99.06	0.31

- ***Decay constant***

The contribution of the decay constant to the concentration uncertainty depends on the uncertainty of the half lives of the elements. In Table 5 such contributions are summarized. Half lives were converted to minutes and uncertainties in decay constant were propagated as exponential uncertainties.

Table 5. Contributions for decay constant standard uncertainty

Radionuclide	Half life, min	Uncertainty, min	Decay constant, min^{-1}	Uncertainty[1], min^{-1}	Standard uncertainty, min^{-1}
^{51}Cr	39892	3	1.74×10^{-5}	1.51×10^{-9}	8.69×10^{-10}
^{58}Zn	351734	374	1.97×10^{-6}	2.10×10^{-9}	1.21×10^{-9}

[1]Rectangular distribution, factor : 1/√3:

- ***Sample and standards activities***

There are various sources of uncertainty in sample and standards activities; some are due to the irradiation process and others due to gamma ray spectrometry measurement:

- ***Irradiation***
  - ***Irradiation geometry differences***

This contribution is due to neutron flux differences inside the irradiation capsule. From neutron flux gradient measurements, an uncertainty contribution of 0.12 % in sample and standards activities was estimated.

  - ***Duration of irradiation***

This contribution is negligible as samples and standards were irradiated together.

  - ***Nuclear reaction interferences***

No nuclear reactions were considered for the elements under investigation.

- ***Gamma ray spectrometry measurement***
  - ***Counting statistics***

The counting statistics component to uncertainty is available from the measurement result as the square root of the measured activity, as it follows the Poisson distribution. Usually, this is the most important contribution to activity uncertainty in INAA.

  - ***Gamma ray self shielding***

In a gamma ray self-shielding study, using europium as gamma ray source and biological and metallic reference materials as shielding, it was observed that the shielding is higher for lower gamma ray energies. For the samples under investigation, the uncertainty in the activities were estimated as 1 % for 320 keV (Cr); 0.7 % for 1115 keV (Zn).

In Table 6 the various contributions to sample and standards activities are summarized. All contributions were considered to have a rectangular distribution.

Table 6. Contributions to the combined standard uncertainty of the activities of sample and elemental standards

	Element	Activity cps	Standard uncertainty, cps			Combined uncertainty cps
			Counting statistics	Irradiation geometry	γ ray self shielding	
Sample	Cr	7.402	0.037	0.009	0.074	0.083
	Zn	12.140	0.036	0.015	0.085	0.094
	Cr	77.984	0.156	0.094	0.000	0.182

- ***Determination of combined standard uncertainty and expanded uncertainty for element concentration in sewage sludge by INAA***

The standard uncertainties from the relevant sources of uncertainty were combined, using the relative method, yielding the combined standard uncertainty (u_c), for the concentration of Cr and Zn in sewage sludge. The expanded uncertainty (U) was determined from the combined standard uncertainties using Equation 2, with a coverage factor k = 2, which gives a level of confidence of approximately 95 %. In Table 7 the contributions to the combined standard uncertainties and expanded uncertainties are summarized. As shown in Figures 2, sample activity was the major contribution in the uncertainty assessment for the determination of Cr and Zn by INAA.

$$U = k\, u_c \qquad (2)$$

Table 7. Combined standard uncertainty, u_c, and expanded uncertainty, U, for the determination of Cr and Zn in sewage sludge by INAA

Element	C, mg kg^{-1}	Standard uncertainty[1] mg kg^{-1}					u_c, mg kg^{-1}	U, mg kg^{-1}
		u_M	u_m	u_λ	u_{Au}	u_{As}		

Cr	201.1	0.078	0.58	4.1×10^{-4}	2.1	0.43	2.2	4.4
Zn	3046	1.2	9.1	9.5×10^{-3}	22.3	20.5	32	63

[1]u_M, u_m, u_λ, u_{Au}, u_{As} - ,standard uncertainties for sample mass, elemental standard mass, decay constant, sample activity and standard activity, respectively

3.2. Pilot Study participation assessment

Table 8 presents the concentration of Cr and Zn in the CCQM-P70 sewage sludge obtained in this study, as well as the CCQM-P70 mixed model median [12]. There was no significant difference of the estimations of the locations of the CCQM-P70 mixed model median and for the CCQM-K44 key comparison reference values, suggesting that in general, the results in CCQM-P70 are in good agreement with the results obtained by NMIs [12]. From the calculated z scores, it is inferred the suitability of the INAA method used at LAN.

Table 8. Cr and Zn concentration in sewage sludge[1], 10^{-3} mol kg^{-1}

Element	This study	CCQM-P70	Z score
Cr	3.868 ± 0.085	3.875 ± 0.068	-0.10
Zn	46.56 ± 0.96	46.8 ± 1.3	-0.18

[1]uncertainties are: this study: expanded uncertainties (k = 2); CCQM-P70: 95 % confidence interval for the reported results

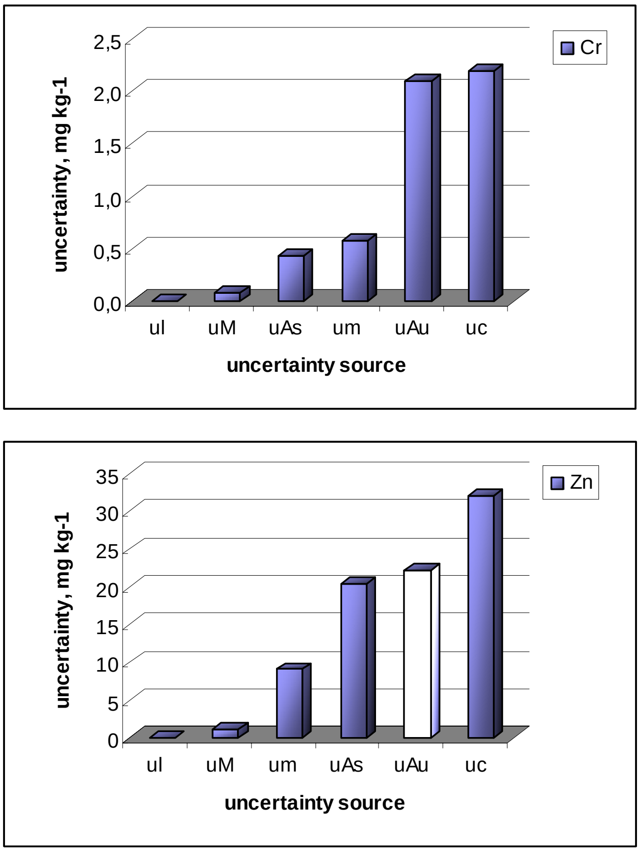

Fig. 2. Sample mass (u_M), elemental standard mass (u_m), decay constant ($u\lambda$), sample activity (u_{Au}) and elemental standard activity (u_{AS}) uncertainties contributions to the combined standard uncertainty (u_c) in Cr and Zn content in sewage sludge by INAA

4. CONCLUSION

This paper describes the well succeeded LAN participation in the CCQM-P70 Pilot Study which was an important contribution to the continuous improvement of LAN quality system. The participation in such interlaboratorial programs is essential for assessment and maintenance of quality assurance systems for analytical laboratories.

5. ACKNOWLEDGEMENTS

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