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Results of the determination of As and Hg in EURL-HM-21 kaolinitic clay using k_0-INAA and CV-AAS

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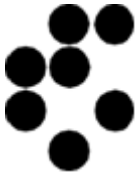

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Content

Results of the determination of As and Hg in EURL-HM-21 kaolinitic clay using k_0-INAA and CV-AAS

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1. Abstract

The objective of this work was to determine the total content of As and Hg in EURL-HM-21 kaolinitic clay, as part of European Union Reference Laboratory for Heavy Metals proficiency test programme. In addition, some typically determined elements using k_0-INAA and long irradiation in the carousel facility of the TRIGA Mark II reactor were presented. The proficiency test (PT) was organized in order to support Directive 2002/32/EC on undesirable substances in animal feed. This PT was opened to National Reference Laboratories (NRLs) and official control laboratories (OCLs). 46 participants from 29 countries registered to the exercise [1]. In this study, for determination of As and Hg in EURL-HM-21 sample the k_0-INAA and CV-AAS were used.

2. Sample description

The material used for PT study was a kaolinitic clay feed additive, which was prepared at Institute for Reference Materials and Measurements (IRMM). Kaolinitic clay is an aluminium silicate mineral, displaying the layered structure of phillosilicates. We registered for the PT study at 7.4.2015 and confirmed the sample receipt at 9.6.2015.

3. Determination of dry matter content

The dry matter content of the studied sample (EURL-HM-21 kaolinitic clay) was determined by drying about 1 g of the sample in a ventilated oven at 105 °C until constant mass was attained. To obtain constant mass, the sample was dried for 4 hours and then dried again to constant mass (about 24 hours). For constant mass a criterion of 1 mg between the successive measurements was applied. Data obtained for the dry mass correction factor are presented in Table 1.

Table 1. Dry matter content and correction factor applied for ERM-HM-21 kaolinitic clay. Correction factor applied was obtained from one replicate.

Bottle no.	Sample mass (g)	Duration time (h)	Net dry mass (g)	Diff. mass (mg)	Dry matter content (%)	Correction factor	Note
22	1.06799	4	1.05504	–	98.7874	1.0123	Not applied
		24	1.05542	-0.38	98.8230	**1.0119**	**Applied**

4. k_0-instrumental neutron activation analysis (k_0-INAA)

The samples (about 130-140 mg) were sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). Samples and standards (Al-0.1%Au alloy IRMM-530R disc of 6 mm in diameter and 0.1 mm thick) were stacked together and fixed in a polyethylene ampoule in sandwich form and irradiated for 12 hours in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute at a thermal neutron flux of 1.1×10^{12} cm $^{-2}$ s^{-1}.

Each sample was measured three times after 3, 7-8 and 22-23 days cooling time. Measurements were performed on an absolutely calibrated HPGe detector (Canberra, USA) with 45 % relative efficiency. Measurements were carried out at such distances that the dead time was kept below 10 % with negligible random coincidences. The detector was connected to an EG&G ORTEC Spectrum Master high-rate multichannel analyzer (zero-dead time (ZDT) mode) with Maestro®-32 Spectroscopy Software.

The HyperLab [2] program was used for peak area evaluation, whereas for determination of f (thermal to epithermal flux ratio) and α (a parameter which represents the epithermal flux deviation from the ideal 1/E distribution), the "Cd-ratio" method for multi monitor was applied [3]. The values obtained for f = 27.11 and α = -0.0042 were used to calculate the element concentrations. The elemental concentrations and effective solid angle calculations were carried out on the KayWin® [4] software package, which is based on the k_0-standardization method of neutron activation analysis.

For QA/QC purposes the certified reference materials BCR-320R Channel Sediment and ERM-CC141 Loam Soil were used.

5. Cold Vapour Atomic Absorption Spectrometry (CV-AAS)

About 200 mg of sample was weighed directly in a Teflon digestion vessel, and after addition of 5 mL of mixture of HNO_3/HF (2:1) and 1 mL of HCl, the vessel was closed and the mixture was left to react at the room temperature for an hour. Digestion was finished by heating at 100 °C for 12 hours on a hot plate. When cooled, the sample was diluted with 5% H_3BO_3 to the mark (25.8 mL). The same procedure (reagents without sample) was applied for blank sample. An aliquot of sample is then transferred to the reaction vessel, reduced with $SnCl_2$ and aerated with outside air until equilibrium of mercury vapour is reached. During this circulation, acid gasses leaving the sample solution are removed by acid gas trap containing 10% NaOH solution. After that, the mercury vapour is introduced to the absorption cell by turning the four-way valve and measured by cold vapour atomic absorption spectrometry (CV AAS - Automatic Mercury Analyzer Model Hg-201, Sanso Seisakusho Co., LTD) [5, 6].

For QA/QC purposes the certified reference materials BCR-320R Channel Sediment was used.

6. Statistical analysis by IRMM

The relative standard deviation for proficiency assessment (σ, in %) was set considering the performance of participants in previous PT rounds and taking into account the complexity of

the test item investigated. Therefore, σ was set to 20 % of the assigned value for total As, and to 25 % for ex-Pb and Hg.

6.1. Z- and ζ-scores

For all analytical data a Z- and ζ-scores are calculated according ISO 13528:2005 [7]:

$$Z_{score} = \frac{X_{lab} - X_{ref}}{\sigma} \quad (1)$$

$$\zeta_{score} = \frac{X_{lab} - X_{ref}}{\sqrt{(u_{lab})^2 + (u_{ref})^2}} \quad (2)$$

where

X_{ref} is the assigned value determined in a reference laboratory (IRMM)

u_{ref} is the standard uncertainty of the assigned value X_{ref}

X_{lab} is the laboratory value

u_{lab} is the standard uncertainty of the assigned value X_{lab}

σ is the standard deviation for proficiency assessment.

6.2. Evaluation of results

Unlike other PTs where results are reports related to dry mass, here organizer expected that participants will report the results with the legal requirements set by the feed legislation to 12 % moisture content. Therefore, when participants reported results referring to dry mass these results were systematically corrected to 12 % moisture content to allow a consistent comparison. We reported the results on dry mass basis.

For evaluation of results the absolute value of the Z- and ζ-scores are used. Satisfactory performance **|score| ≤2**, questionable performance **2 < |score| <3** and **|score| ≥ 3** are marked with different colours in the report.

7. Results and discussion

The results of the determination of As and Hg in EURL-HM-21 kaolinitic clay obtained using k_0-INAA and CV-AAS are presented in Table 2 and graphically in Figures 1-3. Results are reported as average values of four independent measurements.

The uncertainty of the average value for the method used is given as:

$$u_{lab} = \sqrt{(St.dev.)^2 + (unc_{method})^2} \quad (3)$$

where *St. dev.* is the standard deviation of three measurements and unc_{method} is the estimated standard uncertainty of the method used (3.5% with a coverage factor k=1).

In addition, data obtained for other elements in EURL-HM-21 kaolinitic clay by k_0-INAA are presented in Table 3.

According to the results of the EURL-HM-21 proficiency test, there was good agreement between the data obtained by k_0-INAA and CV-AAS and assigned data [1].

Table 2. Comparison of data for EURL-HM-21 kaolinitic clay obtained at JSI by k_0-INAA and CV-AAS with IRMM data. Results are given in mg/kg, referring to 12 % moisture content [1].

El.	Dry mass		12% moisture content		k	u_{lab}	Technique	Assigned values			Z-score	ζ-score
	X_{lab}	U_{lab}	X_{lab}	U_{lab}				X_{ref}	U_{ref}	σ		
As	9.71	0.68	8.54	0.60	2	0.30	k_0-INAA	7.93	0.82	1.59	0.39	1.20
Hg	0.051	0.003	0.045	0.003	2	0.001	CV-AAS	0.047	0.004	0.012	-0.15	-0.63

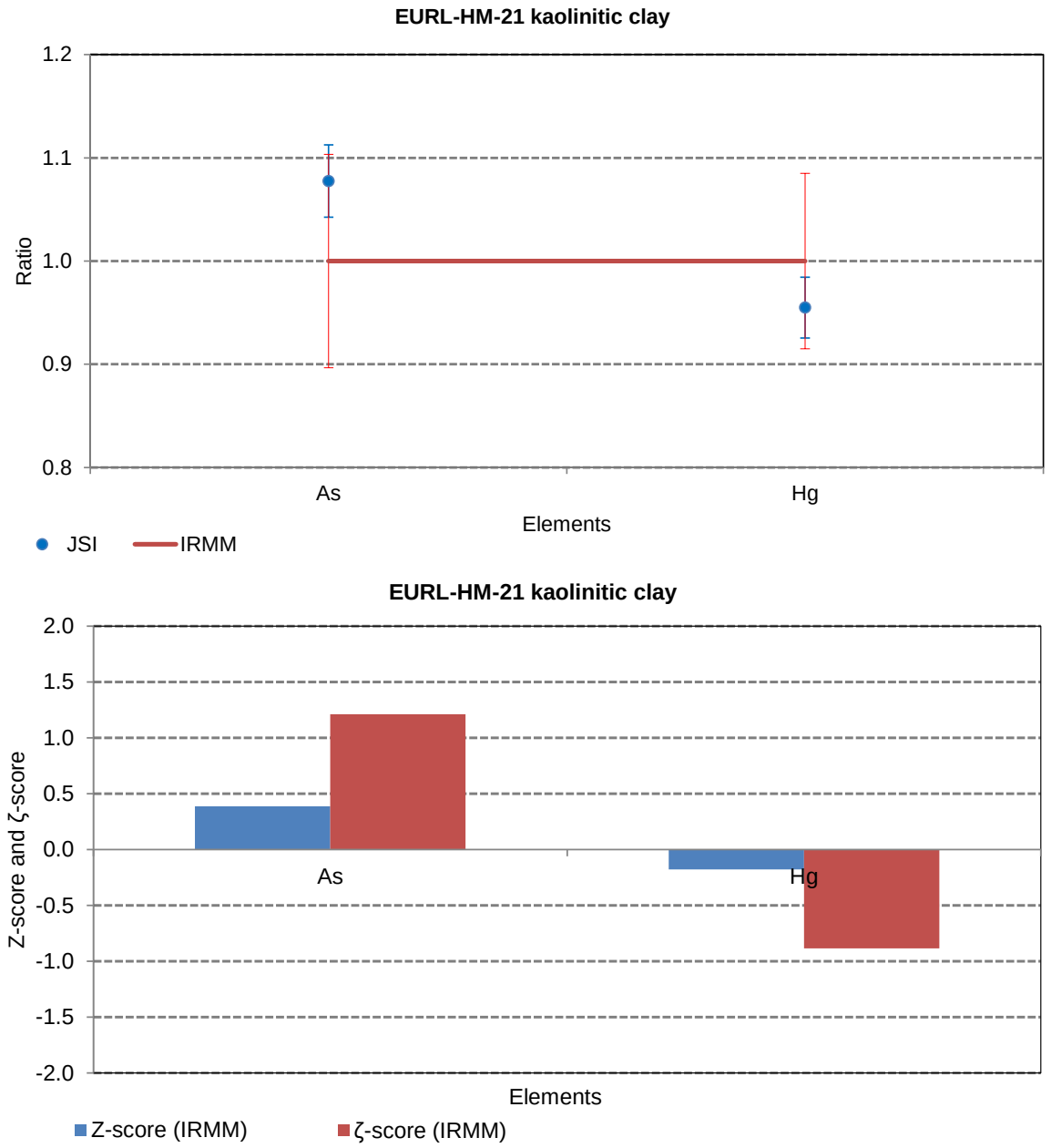

Figure 1. Comparison of data for As and Hg obtained by k_0-INAA and CV-AAS, respectively, with EURL-HM-21 data (referring to 12% moisture content) [1].

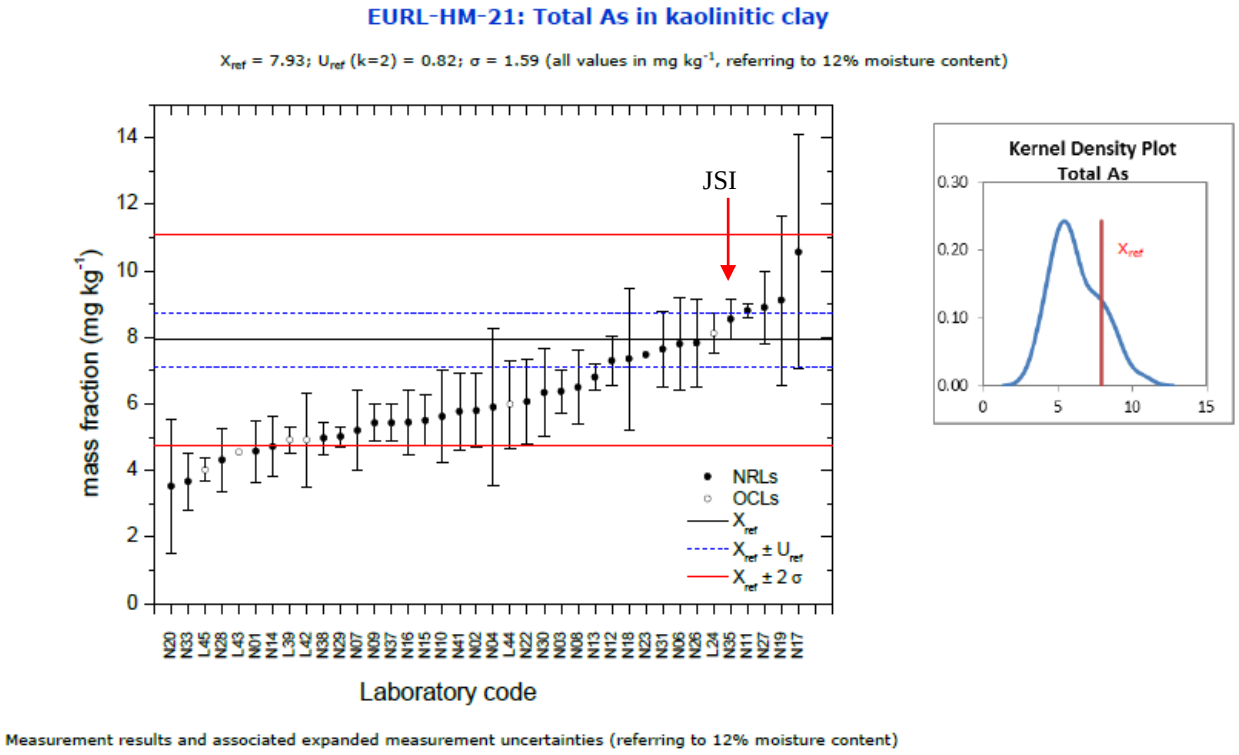

Figure 2. Comparison of data for As obtained by k_0-INAA with EURL-HM-21 data (referring to 12% moisture content) [1].

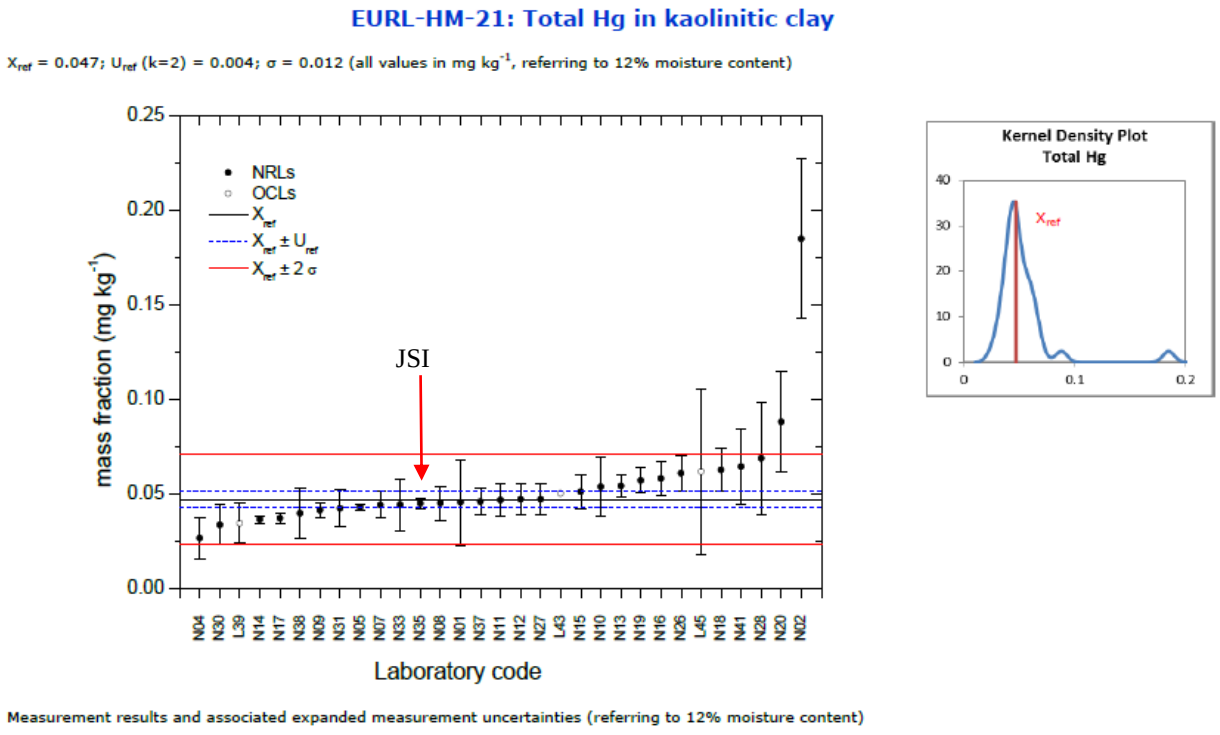

Figure 3. Comparison of data for Hg obtained by CV-AAS with EURL-HM-21 data (referring to 12% moisture content) [1].

Table 3. Results obtained by k_0-INAA for EURL-HM-21 kaolinitic clay. Results are given in mg/kg on dry mass basis.

El.	Average of the mean	St. dev. of the mean	n	u_c (k=1)	LD
Ag			4		0.66
Ba	251	13	4	16	24
Ca			4		3698
Ce	118	1	4	4.3	0.5
Co	3.25	0.04	4	0.1	0.049
Cr	68.7	0.6	4	2	1.1
Cs	6.84	0.05	4	0.24	0.13
Eu	1.81	0.04	4	0.07	0.015
Fe	10640	86	4	330	56
Ga	44.4	0.5	4	1.6	1.2
Hf	8.91	0.04	4	0.31	0.074
K	10574	153	4	400	103
La	65.5	0.4	4	2.3	0.046
Mo			4		0.93
Na	420	4	4	15	0.8
Nd	50.8	1.9	4	2.6	1.9
Rb	86.6	0.6	4	3	2.9
Sb	2.55	0.04	4	0.10	0.041
Sc	15.4	0.2	4	0.6	0.0033
Se			4		0.87
Sm	8.33	0.03	4	0.29	0.009
Sr	66.3	9.3	4	9.5	54
Ta	3.22	0.02	4	0.11	0.029
Tb	1.13	0.02	4	0.046	0.042
Th	21.8	0.2	4	0.8	0.081
U	7.24	0.09	4	0.27	0.078
W	8.31	0.13	4	0.32	0.51
Yb	2.93	0.18	4	0.20	0.067
Zn	39.9	1.2	4	2	1.8
Zr	322	31	4	33	70

Notes:
u_c – combined standard uncertainty; < - limit of detection (LD); n – number of replicates

8. QA/QC for k_0-INAA

For QA/QC purposes for k_0-INAA, the certified reference materials BCR-320R Channel Sediment and ERM-CC141 Loam Soil were used. Results are presented in Tables 4 and 5 and graphically in Figures 4 and 5. There is good agreement with certified values. This was confirmed also by statistical parameter *E_n-number* [7]. The *E_n-number* is calculated according to Eq. 4 using for the uncertainty of the CRM and laboratory with a coverage factor k=2 was applied. *E_n-number* is calculated as:

$$E_n = \frac{X_{lab} - X_{ref}}{\sqrt{(U_{lab})^2 + (U_{ref})^2}} \quad (4)$$

where
U_{lab} and U_{ref} are the expanded uncertainties with a coverage factor k=2 of the laboratory and CRM, respectively.

In contrast to the critical values of 2.0 and 3.0 used with Z- and ζ-scores, it is common to use a critical value of 1.0 for E_n numbers. According to this criterion ($|E_n| < 1.0$) the results presented in Tables 4 and 5 are satisfactory except data for Cr in ERM-CC141, which deviated very small from 1. This inconsistency partly can be explained by disagreement between instrumental and destructive techniques used in the certification process, where also slightly higher value of the result obtained by k_0-NAA can be observed [8].

Table 4. Results obtained by k_0-INAA for BCR-320R Channel Sediment during EURL-HM-21 proficiency test. Results are given in mg/kg on dry mass basis.

El.	JSI			IRMM			*E_n-number* (k=2)
	Content	u_c (k=1)	n	Content	U (k=2)	Non-certified	
Ag	0.492	0.034	1				
As	23.0	0.8	1	21.7	2.0		0.51
Ba	265	10	1				
Br	80.2	2.8	1				
Ca	37578	1346	1				
Cd	2.97	0.18	1	2.64	0.18		0.81
Ce	35.5	1.2	1				
Co	10.1	0.4	1	9.7	0.6		0.39
Cr	61.1	2.2	1	59	4		0.35
Cs	4.28	0.15	1				
Eu	0.723	0.029	1				
Fe	26085	913	1	25700	1300		0.17
Hf	4.76	0.17	1				
Hg	0.938	0.039	1	0.85	0.09		0.74
K	12191	440	1				
La	20.2	0.7	1				
Mo	0.81	0.14	1				
Na	9470	331	1				
Nd	19.0	0.8	1				
Rb	64.3	2.4	1				

El.	JSI			IRMM			*E_n-number* (k=2)
	Content	u_c (k=1)	n	Content	U (k=2)	Non-certified	
Sb	1.13	0.04	1				
Sc	5.38	0.19	1	5.2	0.4		0.34
Se	0.675	0.056	1			0.96	
Sm	3.16	0.11	1				
Sr	194	7	1				
Ta	0.502	0.018	1				
Tb	0.428	0.015	1				
Th	5.40	0.19	1	5.3	0.4		0.19
U	1.55	0.06	1	1.56	0.20		-0.03
Yb	1.56	0.06	1				
Zn	331	12	1	319	20		0.38
Zr	199	8	1				

n - number of replicates

Table 5. Results obtained by k_0-INAA for ERM-CC141 Loam Soil during EURL-HM-21 proficiency test. Results are given in mg/kg on dry mass basis.

El	JSI			IRMM			*E_n-number* (k=2)
	Content	u_c (k=1)	n	Content	U (k=2)	Non-certified	
Ag	< 0.30		1				
As	9.55	0.35	1	9.9	1.5		-0.21
Ba	335	12	1				
Br	3.98	0.15	1				
Ca	4430	236	1				
Cd	< 1		1	0.35	0.05		
Ce	70.4	2.5	1				
Co	8.97	0.31	1	8.5	0.5		0.58
Cr	97.0	3.4	1	86	8		1.05
Cs	3.26	0.11	1				
Eu	1.34	0.05	1				
Fe	23009	809	1				
Hf	16.6	0.6	1				
Hg	< 0.15		1	0.083	0.017		
K	17316	618	1				
La	34.6	1.2	1				
Mo	0.66	0.23	1				
Na	8308	291	1				
Nd	37.7	1.4	1				
Rb	77.6	2.8	1				
Sb	0.830	0.030	1				
Sc	8.20	0.29	1				
Se	< 0.4		1				
Sm	6.44	0.23	1				
Sr	83.8	4.0	1				

El	JSI			IRMM			*E_n-number* (k=2)
	Content	u_c (k=1)	n	Content	U (k=2)	Non-certified	
Ta	1.08	0.04	1				
Tb	0.917	0.032	1				
Th	10.5	0.4	1				
U	2.93	0.10	1				
Yb	3.79	0.13	1				
Zn	60.6	2.4	1	57	4		0.58
Zr	661	26	1				

n - number of replicates

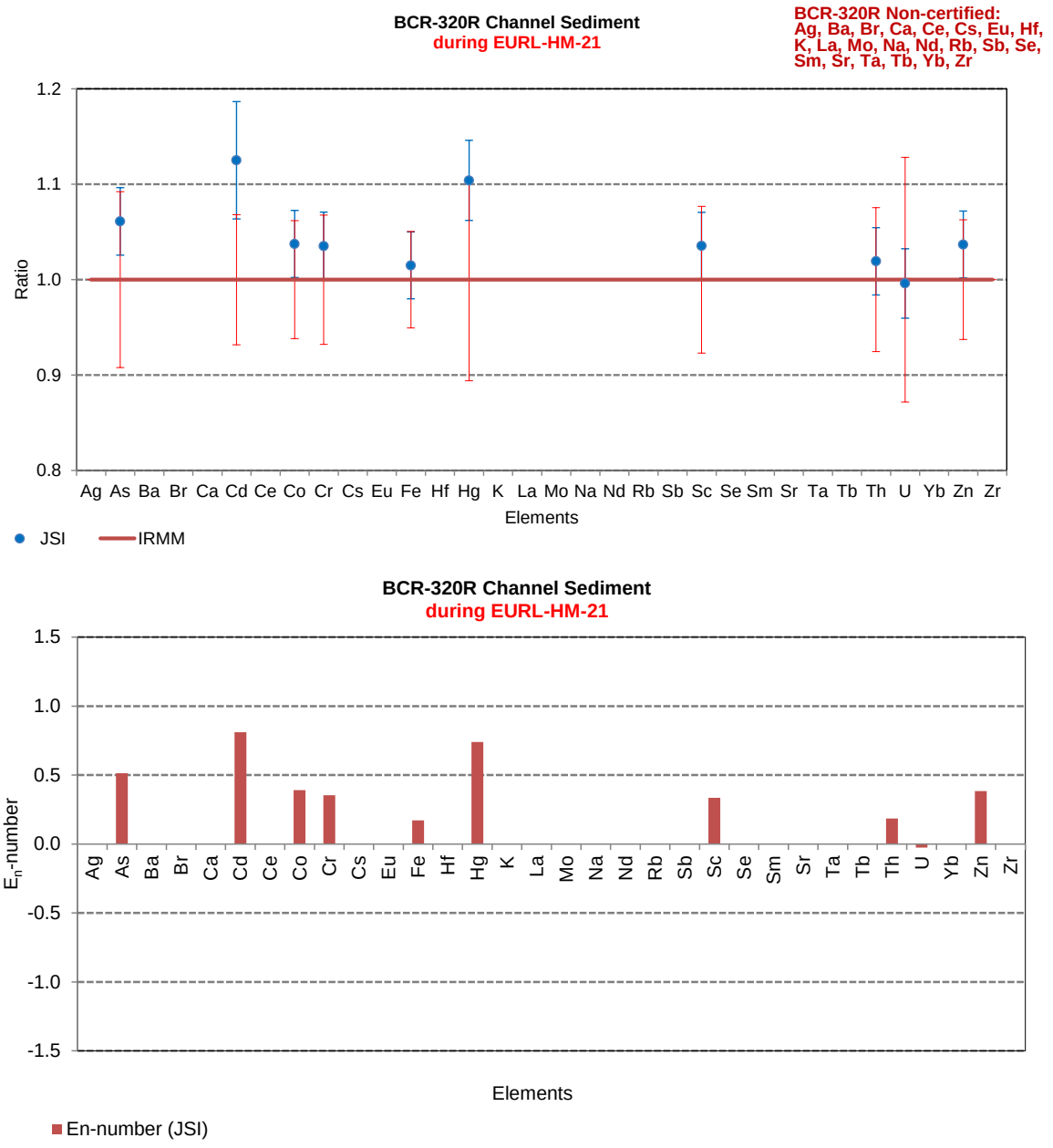

Figure 4. Ratio and *E_n-number* for BCR-320R Channel Sediment obtained by k_0-INAA during EURL-HM-21 proficiency test. Error bars of JSI results are given with a coverage factor k=1, while for CRM they are given with k=2.

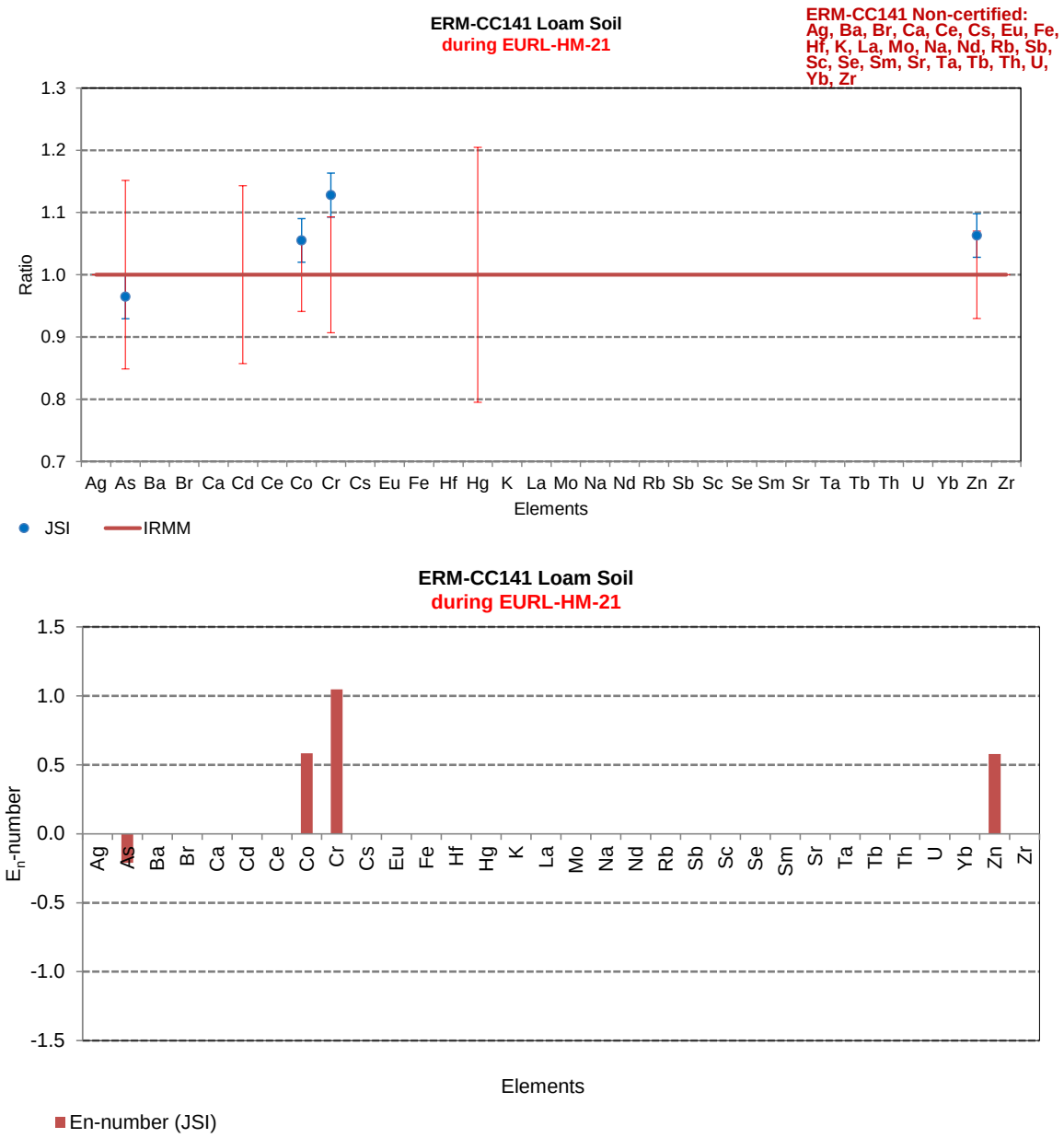

Figure 5. Ratio and *E_n-number* for ERM-CC141 Loam Soil obtained by k_0-INAA during EURL-HM-21 proficiency test. Error bars of JSI results are given with a coverage factor k=1, while for CRM they are given with k=2.

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