



Losses of Cr content in plant samples using digestion procedures with acids

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Received: 31 October 2017
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Abstract

In the WEPAL IPE 2009.2 proficiency test, Jožef Stefan Institute (JSI) participated by measuring Cr by k_0 -INAA; it was the only laboratory providing data by an instrumental technique. The JSI Cr result was about 38% higher than the assigned value in plant sample 124 (Lucerne/Medicago sativum). The same sample was again studied in 2012. This time, more labs, including JSI, used instrumental techniques and the average Cr result was higher and consistent with the 2009 and 2012 JSI results. From the results obtained in the present study, involving four INAA labs, it is confirmed that Cr losses in this sample occurred during the chemical digestion required by the techniques applied by other laboratories, illustrating the inherent advantage of nuclear techniques to be almost matrix independent and independent of the chemical state of the element under study.

Keywords Losses of Cr · Digestion · Plant samples · k_0 -INAA

Introduction

In the year 2009 Wageningen University, Wageningen Evaluating Programs for Analytical Laboratories (WEPAL), Department of Soil Quality, The Netherlands, organized the International Plant-analytical Exchange Program, IPE 2009.2 [1]. The WEPAL organisation is accredited for the organisation of Interlaboratory Studies by the Dutch Accreditation Council RvA since April 26, 2000. The accreditation is based on the ILAC-requirements

(Guidelines for the requirements for the competence of providers of proficiency testing schemes, ILAC-G13: 2007). The scope of the WEPAL IPE program for Inorganic Chemical Composition in study materials is to analyse the following parameters: Ag, **As, B, Ba**, Be, Bi, Br, **Ca, Cd, Cl, Co, Cr**, Cs, **Cu**, F, **Fe**, Ga, **Hg**, I, **K**, Li, **Mg, Mn, Mo, N-Kjeldahl**, N-NH₄, N-NO₃, **Na, Ni, P, Pb**, Pd, Pt, Rb, Rh, **S**, Sb, **Se**, Sn, SO₄, **Sr**, Ti, **V, Zn** (bold signed parameters are in the scope of the accreditation).

In the IPE 2009.2 proficiency test (PT) Jožef Stefan Institute participated by k_0 -instrumental neutron activation analysis (k_0 -INAA) for the determination of Ag, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hg, K, Mo, Na, Rb, Sb, Se, Sn, Sr and Zn in four plant samples 192 (String bean (pods)/Phaseolus vulgaris), 950 (Melon/Cucumis melo L.), 124 (Lucerne/Medicago sativum) and 168 (Sunflower/Helianthus annuus) [1, 2]. The PT study shows that the result obtained by k_0 -INAA at JSI for Cr only in sample 124 was higher by about 38% compared to the assigned value and consequently the JSI result had a high Z-score parameter ($Z = 3.00$). It was seen in the WEPAL report that JSI was the only participating laboratory using an instrumental technique for Cr determination, while all other participants used destructive methods (FAAS, ETAAS, ICP-AES, ICP-MS).

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The objective of this work was to determine the total content of Cr in sample 124 (Lucerne/Medicago sativum) in the IPE 2009.2 program (WEPAL) in several laboratories (Belgium, Brazil, Canada and Slovenia), which use k_0 -INAA. The reason for this study was to confirm that the assigned value of Cr given by WEPAL in plant sample 124 is not correct. In addition, other elements were determined at the four laboratories using k_0 -INAA in order to compare with WEPAL data.

Method

The k_0 -instrumental neutron activation analysis (k_0 -INAA) was applied in four institutes: Jožef Stefan Institute (JSI) in Slovenia; CDTN/CNEN in Brazil, Polytechnique Montreal (Polymtl) in Canada and SCK-CEN in Belgium. The institutes established and validated the method following the basic recommendations of the k_0 -standardization method explained elsewhere [3–5]. Relevant nuclear data for Cr used in the calculation by k_0 -INAA are given in Table 1.

Experimental

Sample preparation

Aliquots of plant sample (about 210–240 mg) 124 Lucerne/Medicago sativum (WEPAL IPE 2009.2 exchange program) obtained from WEPAL were prepared at the JSI in pellet form (10 mm in diameter and about 2.5 mm high) using a SPECAC press (United Kingdom), wrapped with polyethylene foil, fixed in a polyethylene vial and distributed to the colleagues in Belgium, Brazil and Canada. The dry matter content of studied sample was determined at the JSI by drying about 1 g of the sample in a ventilated oven at 105 °C until constant mass was attained. Dry matter content of 91.24% was obtained and used for correction of the results in all labs. The analyses were carried

out at all institutes over a similar period, from December 2010 to February 2011.

Jožef Stefan Institute (JSI), Slovenia

The samples (about 210–240 mg) and standards (Al-0.1% Au IRMM-530RA foil 6 mm in diameter and 0.1 mm thick) were stacked together and fixed in a polyethylene ampoule in sandwich form and irradiated for 20 h in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the JSI at a thermal neutron flux of $1.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

Each sample was measured three times after 3, 10–13 and 30–35 days cooling time. Measurements were performed on an absolutely calibrated HPGe detector (Canberra, USA) with 45% relative efficiency. Measurements were carried out at such sample-detector 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).

The HyperLab [9] program was used for peak area evaluation, whereas for determination of f and α , the “Cd-ratio” method for multi monitor was applied [10]. The values $f = 28.63$ and $\alpha = -0.0011$ were used to calculate the element concentrations. The elemental concentrations and effective solid angle calculations were carried out with the KayWin® [11] software package, which is based on k_0 -standardization method of neutron activation analysis.

For QA/QC purposes the certified reference material NIST SRM-1547 Peach Leaves was used.

CDTN/CNEN, Laboratory for Neutron Activation Analysis, Brazil

The samples—pellet form, 222.5–226.6 mg—were inserted in polyethylene vials and intercalated by neutron flux monitors Al-0.1% Au IRMM-530RA disc (5 mm diameter and 0.1 mm high).

The irradiation was carried out in the carousel of the TRIGA MARK I IPR-R1 reactor at CDTN, at 100 kW, for

Table 1 Relevant nuclear data for determination of Cr used in k_0 -INAA [6–8]

El.	Nuclide	Half-life	E_{γ}^a , keV	Q_0^b	\bar{E}_r , eV	$k_{0,Au}^d$
Cr	^{51}Cr	27.70 days	320.1	0.53	$7530 \pm 11\%$	$2.62 \times 10^{-3} \pm 0.5\%$

^aGamma-ray energy

^b $Q_0 = I_0/\sigma_0$, resonance integral to 2200 m s⁻¹ (n, γ) cross-section ratio

^cEffective resonance energy with standard uncertainty in %

^d k_0 factor with standard uncertainty in % of an analyte “a” is defined as: $k_{0,Au} = \frac{M_{Au} \sigma_{0,a} \theta_a \gamma_a}{M_a \sigma_{0,Au} \theta_{Au} \gamma_{Au}}$, where M is the atomic weight, θ is the isotopic abundance, σ is the 2200 m s⁻¹ (n, γ) cross-section, and γ is the absolute gamma-ray intensity (emission probability)

8 h, under a thermal neutron flux of $6.35 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, in IC-7, where parameters f and α are 22.324 and -0.0022 , respectively [12].

After suitable decay and measurement time, the gamma spectroscopy was performed on an absolutely calibrated HPGe detector (CANBERRA) with 25% relative efficiency. The spectrum deconvolution—peak area evaluation was carried out using the HyperLab program [9] and for the elemental concentration calculations, the software package KayWin[®] [11] was applied. The certified reference material GBW 08505, Tea, was also analysed.

Polytechnique Montreal (Polymtl), Canada

Three pellets of sample 124, of approximate mass 210 mg, were sealed in polyethylene bags and irradiated together for 6 h in a polyethylene rabbit in inner irradiation site 3 of the Polytechnique SLOWPOKE reactor at a thermal neutron flux of $5.3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. Each pellet was transferred to a polyethylene counting vial, weighed, and then measured twice after 9 and 16 days cooling time using an HPGe detector (EG&G ORTEC, USA) with 55% relative efficiency. Sample-detector distance was 6 mm and counting time was 15 h with an EG&G ORTEC DSpec Plus multichannel analyzer.

Table 2 Digestion and extraction techniques [1]

Code	Technique
AA	Dry ashing without HF and uptake in HCl
AB	Dry ashing without HF and uptake in HNO ₃
AC	Dry ashing with HF and uptake in HCl
AD	Dry ashing with HF and uptake in HNO ₃
AE	Dry ashing without HF and uptake in H ₂ SO ₄
B	Melt
CA	Schoeniger combustion and uptake in HCl
CB	Schoeniger combustion and uptake in HNO ₃
DA	Wet digestion without HF and final medium H ₂ SO ₄
DB	Wet digestion without HF and final medium HNO ₃
DC	Wet digestion without HF and final medium HClO ₄
DD	Wet digestion with HF and final medium H ₂ SO ₄
DE	Wet digestion with HF and final medium HNO ₃
DF	Wet digestion with HF and final medium HClO ₄
DG	Wet digestion in closed pressurized system and final medium HNO ₃
DH	Wet digestion in closed pressurized system and final medium HCl
EA	Microwave digestion in closed system with HF and final medium H ₂ SO ₄
EB	Microwave digestion in closed system with HF and final medium HNO ₃ /HCl
EC	Microwave digestion in closed system with HF and final medium HClO ₄
ED	Microwave digestion in closed system without HF and final medium H ₂ SO ₄
EE	Microwave digestion in closed system without HF and final medium HNO ₃ /HCl
EF	Microwave digestion in closed system without HF and final medium HClO ₄
EG	Microwave digestion in open system with HF and final medium H ₂ SO ₄
EH	Microwave digestion in open system with HF and final medium HNO ₃ /HCl
EI	Microwave digestion in open system with HF and final medium HClO ₄
EJ	Microwave digestion in open system without HF and final medium H ₂ SO ₄
EK	Microwave digestion in open system without HF and final medium HNO ₃ /HCl
EL	Microwave digestion in open system without HF and final medium HClO ₄
FA	Extraction with water
FB	Extraction with acid(s)
FC	Solubilizers
G	Others
H	Dry combustion (Elementary analysis)

The EPAA software [13] was used for peak area evaluation and concentration calculation by the k_0 method. The thermal neutron flux and the parameters $f = 18.0$ and $\alpha = -0.051$ were determined previously [14] using Al-0.1%Au IRMM-530R wire and the Cd-ratio method for multi-monitor. The relevant nuclear data for Cr used in the calculation by k_0 -INAA are given in Table 1.

SCK-CEN, Belgian Nuclear Research Centre, Belgium

All samples were irradiated in the BR1 reactor at SCK-CEN, Mol at 700 kW in channel Y4 (nominal thermal neutron flux $3 \times 10^{11} \text{ cm}^{-2}\text{s}^{-1}$, $f = 38.1$, $\alpha = 0.065$) for about 7 h [15]. On each sample three measurements were

carried out at cooling times of 2, 10 and 21 days, depending on the isotope to be measured and counting times varied from a few hours to 24 h. For a correct application of the k_0 -INAA protocol the samples were irradiated together with flux monitors IRMM-530R Al-0.1%Au and as QA/QC sample SMELS [16] was used. Acquisition was performed on 40% relative efficiency HPGe detectors equipped with a LFC-module. Peak fitting was performed using HyperLab[®] [9] and calculation of solid angles and coincidence summing corrections were performed using the Solcoi[®] module and elemental concentration calculation was performed using the Kayzero[®] module of the Kaywin code.

Table 3 Methods of detection [1]

Code	Method
AA	AAS-flame without background correction using air-acetylene
AB	AAS-flame with deuterium background correction using air-acetylene
AC	AAS-flame with Zeeman background correction using air-acetylene
AD	AAS-flame with pulsed hollow cathode lamp backgr. corr. using air-acetylene
AE	As AA using N ₂ O-acetylene
AF	As AB using N ₂ O-acetylene
AG	As AC using N ₂ O-acetylene
AH	As AD using N ₂ O-acetylene
BA	AAS-ETA without background correction/without chemical modifier
BB	AAS-ETA with deuterium background corr./without chemical modifier
BC	AAS-ETA with Zeeman background correction/without chemical modifier
BD	AAS-ETA with pulsed hollow cathode lamp backgr. corr./without chem. mod.
BE	AAS-ETA without background correction/with chemical modifier
BF	AAS-ETA with deuterium background correction/with chemical modifier
BG	AAS-ETA with Zeeman background correction/with chemical modifier
BH	AAS-ETA with pulsed hollow cathode lamp background cor./with chem. modifier
CA	Flame emission
CB	ICP-AES (different wavelengths possible; indicate the used wavelength)
CC	Other excitation source
D	ICP-MS
E	Spectrophotometry
F	Hydride technique (similar techniques using analyte volatilization; specify)
G	Cold vapour technique
H	Ion selective electrode
IA	Direct voltammetry
IB	Stripping voltammetry
J	Chromatography
JA	Gas chromatography
JB	Liquid chromatography
JE	Ion chromatography
KA	X-ray fluorescence with material melted
KB	X-ray fluorescence with material pressed
L	Neutron activation analysis

WEPAL new statistics: normal distribution approximation (NDA)

NDA does not rely on arbitrary outlier removal or subjective manual interpretations. This model was chosen to calculate population characteristics (mean and standard deviation) from experimental datasets [17]. This model uses an estimate for the probability density function (pdf) of the measurement processes and calculates a best fit based on all observed values. The implementation of this

model does not require uncertainty estimates for all data points; instead it uses a normal distribution approximation for the pdf of the individual data points. In essence, the pdf's of the individual datapoints are superposed on each other to create a continuous pdf representing the entire distribution (all datapoints).

With the NDA model, mean and standard deviation are calculated using all reported data when at least 8 results are left after removal of reported "lower than" (<) and 0 (= zero) values. No outliers are removed [1].

Table 4 Participants' data for Cr in sample 124 in the IPE 2009.2 program organized by WEPAL [1]

Lab. code	Content ($\mu\text{g}/\text{kg}$)	Method indicating code (MIC)	Z-score
3	879	EE/D	0.26
32	1166 ^b	G/D	2.91
47	937	G/D	0.80
57	826	EE/BG	- 0.23
61	720	DG/D	- 1.20
70	890	DG/CB	0.36
84	954	G/D	0.95
102	1113 ^a	AC/CB	2.42
112	629 ^a	n.i. ^c	- 2.05
128	< 1500	DB/CB	n.a. ^d
136	755	DC/D	- 0.88
158	794	DB/CB	- 0.52
164	851	EE/CB	0.00
185	891	EE/D	0.37
201	924	DG/CB	0.68
218	791	G/CB	- 0.55
239	800	n.i. ^c	- 0.47
249	1260 ^b	DG/BC	3.78
250	910	EE/D	0.55
264	875	EE/D	0.23
275	874	n.i. ^c	0.22
597	1942 ^b	n.i. ^c	10.07
714	884	n.i. ^c	0.31
855	833	EE/CB	- 0.16
892	850	EE	0.00
905	707	DC/CB	- 1.33
962	605 ^b	EE/D	- 2.27
995 ^e	1176 ^b	L/ k_0 -INAA	3.00
NDA ^f Mean	850.5		
NDA ^f St. dev.	108.4		
NDA ^f N ^g	27		

^astraggler

^boutlier

^cnot indicated

^dnot analysed

^eJožef Stefan Institute's code in the IPE 2009.2

^fnormal distribution approximation (NDA)

^gNumber of results accepted by WEPAL

Table 5 Comparison between k_0 -INAA data obtained in this work for Cr with WEPAL data. All results are given in $\mu\text{g}/\text{kg}$ on dry matter

Institute (Country)	Results			Average \pm St.dev.	n^b	k_0 -INAA u_{method}^c (%)	Average \pm u_{lab}^d	WEPAL NDA ^e \pm St.dev.	N^f	Z- score	ζ - score
	1	2	3								
JSI (Slovenia)	1297	1107	1150	1185 \pm 100	3	3.5	1185 \pm 108	850.5 \pm 108.4	27	3.08	2.18
CDTN/CNEN (Brazil)	1358	1137	2474 ^a	1247 \pm 157	2	3.5	1247 \pm 163			3.66	2.03
Polymtl (Canada)	1205	1260	1271	1245 \pm 35	3	3.5	1245 \pm 56			3.64	3.23
SCK-CEN (Belgium)	1060	970	1170	1067 \pm 100	3	3.5	1067 \pm 107			1.99	1.42
Overall average				1186 \pm 85	4	3.5	1186 \pm 94			3.10	2.34

^aNot taken for average value due to cross-contamination. It was discovered only later that an irradiated Cr-solution with high concentration of ^{51}Cr was counted by another user on the same HPGe detector between the second and third repetitions of sample 124

^bNumber of independent measurements

^cEstimated combined standard uncertainty of k_0 -INAA (u_{method} in %). This systematic uncertainty includes uncertainties of the literature values ($T_{1/2}$, \bar{E}_γ , Q_0 , k_0), the true-coincidence correction factor (COI), the Au composition in Al-0.1%Au alloy, the masses of sample and standard (Al-0.1%Au alloy), dry mass correction factor, the previously determined neutron flux parameters (f and α) using Cd-ratio method and the detector efficiency

^dTotal estimated combined standard uncertainty of k_0 -INAA, calculated as: $u_{\text{lab}} = \sqrt{\text{St.dev.}^2 + u_{\text{method}}^2}$, where St.dev. is the standard deviation of independent measurements in the lab and u_{method} is the estimated combined standard uncertainty of the method used in the lab (3.5%)

^eNew statistic: Normal distribution approximation (NDA)

^fNumber of results accepted by WEPAL

Z-score

For all analytical data a Z-score is calculated according Eq. (1) [1]:

$$Z_{\text{score}} = \frac{X_{\text{lab}} - X_{\text{mean}}}{\text{St. dev.}} \quad (1)$$

in which X_{lab} the reported value; X_{mean} the mean of all values calculated with the NDA model; St. dev. standard deviation calculated with the NDA model.

The sample preparation techniques and methods for detection used by participants in the IPE 2009.2 program are given in Tables 2 and 3, respectively.

ζ -score

For additional evaluation of data quality in proficiency tests, the statistical ζ -score parameter can be used, where the standard uncertainty of the laboratory is taken into account. In our work, the following equation is used in the calculation of ζ -score [18]:

$$\zeta_{\text{score}} = \frac{X_{\text{lab}} - X_{\text{mean}}}{\sqrt{u_{\text{lab}}^2 + \text{St.dev.}_{\text{NDA}}^2}} \quad (2)$$

where u_{lab} is the combined standard uncertainty ($k = 1$) of k_0 -INAA provided by the laboratory and $\text{St.dev.}_{\text{NDA}}$ is the standard deviation calculated with the NDA model.

Results and discussion

The analytical methods FAAS, ETAAS, ICP-AES, ICP-MS require a sample in liquid form. For this reason it is necessary to digest a sample with acids, which have oxidative properties. When plant samples with a high content of fibre (and consequently containing silicates) are analysed and wet ashing using HClO_4 - HNO_3 digestion is applied, substantial losses of Cr due to two effects may be expected: (i) losses of Cr that is bound to silicates and (ii) losses of Cr due to the formation of volatile CrO_2Cl_2 .

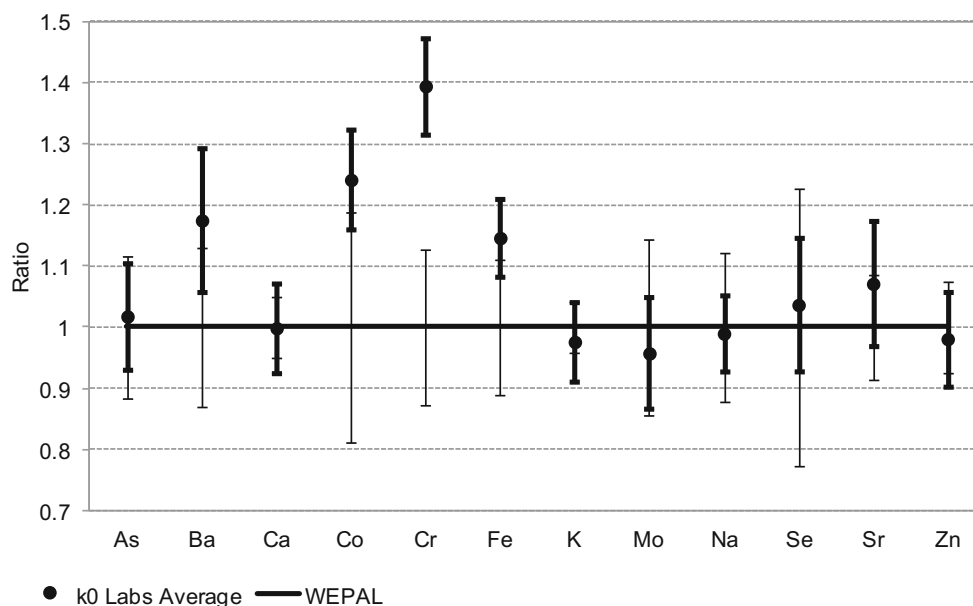
The IPE 2009.2 program included four plant samples. Three of them were with low content of fibre (String bean (pods), Melon and Sunflower) and were not so difficult to dissolve. This was not the case for plant sample 124 (Lucerne), where some losses were likely experienced for the reasons mentioned above. This effect was not very apparent from the proficiency study because almost all participants used destructive techniques (see Tables 2 and 3) and the statistical evaluation provided by WEPAL (New statistic NDA) showed that the result obtained by k_0 -INAA at the JSI (Slovenia) was the outlier. More details are given in Table 4. It is important to stress that the determination of Cr via its radionuclide ^{51}Cr ($T_{1/2} = 27.70$ days) in this particular sample was not especially difficult due to favourable characteristics of ^{50}Cr to NAA, emitting only one single gamma line at 320.1 keV from ^{51}Cr and

Table 6 Comparison between WEPAL data and k_0 -INAA data obtained in this work for elements other than Cr (see Table 5). All results are given in mg/kg on dry matter

El.	WEPAL (NDA)			JSI			CDTN/CNEN			Polymtl			SCK-CEN		
	Conc.	St.dev.	N	AVG ^a	u_{lab}	n	ζ -score	AVG ^a	u_{lab}	n	ζ -score	AVG ^a	u_{lab}	n	ζ -score
As	0.4176	0.0484	18	0.471	0.017	3	1.04	0.410	0.035	3	-0.12	0.425	0.034	3	0.13
Au	n.d. ^b			<0.0004 ^c		3		<0.0020 ^c		3		n.d. ^b		3	0.00056
Ba	10.13	1.32	12	12.3	0.9	3	1.36	10.9	1.3	3	0.42	13.7	1.6	3	1.69
Br	n.d. ^b			13.5	0.5	3		12.0	0.5	3		12.9	0.5	3	1.0
Ca	22710	1150	105	22206	854	3	-0.35	24291	2116	3	0.66	n.d. ^b		3	21533
Ce	n.d. ^b			1.04	0.16	3		0.94	0.18	3		1.08	0.15	3	0.92
Co	0.2949	0.0552	26	0.376	0.021	3	1.37	n.d. ^b		3		0.386	0.044	3	1.30
Cs	n.d. ^b			0.049	0.003	3		0.042	0.004	3		n.d. ^b		3	0.041
Eu	n.d. ^b			0.017	0.001	3		<0.010 ^c		3		n.d. ^b		3	0.014
Fe	222.5	24.4	101	257	16	3	1.18	267	38	3	0.99	261	30	3	0.99
Ga	n.d. ^b			<0.69 ^c		3		<0.66 ^c		3		n.d. ^b		3	0.27
Hf	n.d. ^b			0.069	0.006	3		0.055	0.010	3		0.090	0.023	3	0.061
Ho	n.d. ^b			<0.1 ^c		3		<0.1 ^c		3		n.d. ^b		3	0.012
K	26040	1110	108	26750	942	3	0.49	26176	994	3	0.09	25240	1051	3	-0.52
La	n.d. ^b			0.59	0.08	3		0.58	0.09	3		0.60	0.05	3	0.54
Mo	0.3656	0.0530	29	0.365	0.044	3	-0.01	<0.96 ^c		3		0.369	0.062	3	0.04
Na	195.0	23.7	68	200	8	3	0.22	195	7	3	-0.01	199	13	3	0.13
Nd	n.d. ^b			<0.4 ^c		3		<1.2 ^c		3		n.d. ^b		3	0.63
Rb	n.d. ^b			2.14	0.08	3		2.13	0.21	3		2.07	0.10	3	1.73
Sb	n.d. ^b			0.039	0.005	3		0.037	0.008	3		0.035	0.004	3	0.033
Sc	n.d. ^b			0.154	0.010	3		0.140	0.011	3		0.149	0.017	3	0.137
Se	0.1148	0.026	14	0.110	0.012	3	-0.16	<0.24 ^c		3		0.128	0.015	3	0.44
Sm	n.d. ^b			0.091	0.010	3		0.084	0.006	3		0.094	0.013	3	0.075
Sr	55.27	4.77	16	63.4	2.5	3	1.52	56.4	2.7	3	0.22	64.4	4.5	3	1.41
Ta	n.d. ^b			0.012	0.002	3		<0.022 ^c		3		n.d. ^b		3	0.0089
Tb	n.d. ^b			0.0133	0.0006	3		<0.015 ^c		3		n.d. ^b		3	0.0114
Th	n.d. ^b			0.167	0.025	3		0.125	0.012	3		0.154	0.012	3	0.133
Tm	n.d. ^b			<0.04 ^c		3		<0.08 ^c		3		n.d. ^b		3	0.05
U	n.d. ^b			0.061	0.008	3		<0.055 ^c		3		0.057	0.005	3	0.055
W	n.d. ^b			<0.28 ^c		3		<0.21 ^c		3		n.d. ^b		3	0.089
Yb	n.d. ^b			0.042	0.002	3		<0.055 ^c		3		n.d. ^b		3	0.039
Zn	19.78	1.49	99	19.5	0.7	3	-0.17	20.7	1.9	3	0.38	19.9	1.2	3	0.05
Zr	n.d. ^b			<8.6 ^c		3		<25.2 ^c		3		n.d. ^b		3	3.7

^aAverage concentration^bNo data^cLimit of detection

Fig. 1 Comparison between WEPAL and Average values obtained in this work by k_0 Labs for IPE 2009.2 sample 124 (Lucerne/Medicago sativum). Data are taken from Tables 5 and 7 and normalized to WEPAL data (Ratio: k_0 Labs Average/WEPAL). Error bars for k_0 Labs data are given for $k = 1$, while error bars for WEPAL are given as standard deviation calculated with the NDA model



negligible interference from ^{147}Nd ($T_{1/2} = 10.98$ days) from its gamma line at 319.4 keV due to the very low Nd content (about 0.63 mg/kg obtained in SCK-CEN, see Table 6).

In order to prove that the outcome of the WEPAL study concerning Cr data is not correct, we determined total content of Cr in sample 124 (Lucerne/Medicago sativum) using k_0 -INAA in laboratories from Belgium, Brazil, Canada and Slovenia. The results are presented in Table 5. There is very good agreement between the k_0 -INAA laboratories and clear disagreement with the WEPAL data. If Z-score and ζ -score would be recalculated for each of these laboratories unsatisfactory results would be obtained (see Table 5).

For the evaluation of data obtained in this work by k_0 -INAA for other elements and comparison to WEPAL data we used the ζ -score parameter. The results obtained from the four laboratories for 33 elements (As, Au, Ba, Br, Ca, Ce, Co, Cs, Eu, Fe, Ga, Hf, Ho, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Tm, U, W, Yb, Zn and Zr) are presented in Table 6. Establishing the ζ -score as < 2 ($p = 95\%$) it can be seen that all four k_0 labs have passed this criteria. Additionally, it can be seen that there is good agreement among the results of the four laboratories for Br, Ce, Cs, La, Rb, Sb, Sc, Sm, Th and U, which were not reported in the WEPAL report [1]. Furthermore, also good agreement for the other possibly volatile elements (As, Br, Sb, Se and Zn), beside Cr (see Table 5), can be seen. In Fig. 1 a comparison between WEPAL data and average values obtained in this work by k_0 labs for IPE 2009.2 plant sample 124 is given for As, Ba, Ca, Co, Cr, Fe, K, Mo, Na, Se, Sr and Zn. Data are taken from Tables 5 and 7. Error bars for k_0 lab data are given as u_{lab} of the average value

obtained from four results except for Ca, Co, Mo and Se, where three or two results are taken into account (see also Table 7); error bars for WEPAL are given as standard deviation calculated with the NDA model. Good agreement between the four k_0 labs can be seen, where u_{lab} varied from 5.5% for Fe up to 10.5% for Se.

Finally, in Table 7 we summarize the average results for 33 elements (As, Au, Ba, Br, Ca, Ce, Co, Cs, Eu, Fe, Ga, Hf, Ho, K, La, Mo, Na, Nd, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Tm, U, W, Yb, Zn and Zr) obtained from four institutes. The Z-score and ζ -score parameters for elements for which it was possible are presented. It can be seen that for As, Ba, Ca, Co, Fe, K, Mo, Na, Se, Sr and Zn both scores are relatively low and show the good agreement of our data with WEPAL data. Additionally, it can be seen that there is also good agreement among the results of all four laboratories especially for As, Br, Ce, Fe, K, La, Na, Rb, Sc, Sm, Sr and Zn, where the relative standard deviation did not exceed 10%. A similar conclusion can also be made for Ba and Th, where the variation is between 10.5 and 13.1%. However, this study shows relatively high variation for the data of Hf of about 22% (see Fig. 2), which can be explained by the low content of Hf in the studied material. Nevertheless, it should be stressed that, as INAA is an instrumental technique it would be very unlikely that if results for 20 elements are coherent for four labs and coherent with WEPAL, that the result for Cr would not be coherent for WEPAL.

The WEPAL strategy is that the code of the samples given to a participant does not allow identifying which sample is which material because each sample is named only by SAMP 1, SAMP 2, SAMP 3 and SAMP 4. Decoding of the sample is given by WEPAL only in the

Table 7 Comparison between average k_0 -INAA data obtained in this work from four institutes to WEPAL data. All results are given in mg/kg on dry matter

El.	WEPAL new statistics NDA			This work (averaged data of four institutes)						
	Conc.	St.dev.	<i>N</i>	AVG	St.dev.	<i>n</i>	u_{lab}	Z-score	ζ -score	
As	0.4176	0.0484	18	0.425	0.034	4	0.037	0.14	0.11	
Au	n.d.			0.00056	0.00007	1	0.00007			
Ba	10.13	1.32	12	11.9	1.4	4	1.4	1.36	0.92	
Br	n.d.			12.6	0.7	4	0.9			
Ca	22710	1150	105	22677	1438	3	1642	- 0.03	- 0.02	
Ce	n.d.			1.00	0.08	4	0.08			
Co	0.2949	0.0552	26	0.366	0.028	3	0.030	1.28	1.12	
Cs	n.d.			0.044	0.004	3	0.004			
Eu	n.d.			0.016	0.002	2	0.002			
Fe	222.5	24.4	101	255	13	4	16	1.35	1.13	
Ga	n.d.			0.27	0.02	1	0.02			
Hf	n.d.			0.068	0.015	4	0.015			
Ho	n.d.			0.012	0.002	1	0.002			
K	26040	1110	108	25416	1421	4	1677	- 0.56	- 0.31	
La	n.d.			0.58	0.03	4	0.03			
Mo	0.3656	0.0530	29	0.350	0.030	3	0.032	- 0.30	- 0.26	
Na	195.0	23.7	68	193	10	4	12	- 0.07	- 0.07	
Nd	n.d.			0.63	0.09	1	0.09			
Rb	n.d.			2.02	0.19	4	0.21			
Sb	n.d.			0.036	0.003	3	0.003			
Sc	n.d.			0.145	0.008	4	0.009			
Se	0.1148	0.026	14	0.119	0.013	2	0.013	0.16	0.15	
Sm	n.d.			0.086	0.008	4	0.009			
Sr	55.27	4.77	16	59.2	5.7	4	6.1	0.82	0.51	
Ta	n.d.			0.010	0.002	2	0.002			
Tb	n.d.			0.012	0.001	2	0.001			
Th	n.d.			0.145	0.019	4	0.020			
Tm	n.d.			0.047	0.042	1	0.042			
U	n.d.			0.058	0.003	3	0.004			
W	n.d.			0.089	0.006	1	0.007			
Yb	n.d.			0.041	0.002	2	0.003			
Zn	19.78	1.49	99	19.4	1.3	4	1.5	- 0.23	- 0.17	
Zr	n.d.			3.7	0.9	1	0.9			

final report with all results. In 2012, the JSI participated in WEPAL round proficiency test IPE 2012.1, when plant sample 124 (Lucerne/Medicago sativum) was studied once again as SAMP 2. In this study, JSI reported data for Cr as 1258 $\mu\text{g}/\text{kg}$ and WEPAL evaluation for this sample was $1038 \pm 408 \mu\text{g}/\text{kg}$ (St.dev. of NDA) obtained from 48 accepted values from the participants. Z-score for JSI was 0.54 meaning satisfactory result [19, 20]. Comparing results for plant sample 124 (Lucerne/Medicago sativum) obtained in IPE 2009.2 and IPE 2012.1 it can be seen that the relative St.dev. by NDA model is 12.7 and 39.3%, respectively. All participant laboratories using different methods reported relatively big differences in results and in IPE 2012.1 more participants applied INAA technique (12

labs were listed as using INAA in Ref. [19]) providing higher values compared to destructive techniques. In addition, comparing the elemental content for Cr in IPE 2009 and 2012 rounds, we can see a difference in the WEPAL data of about - 18.1% and in the JSI data of about - 6.5%. It is one additional indication that the JSI data obtained by k_0 -INAA are more reliable than WEPAL evaluated data from participants using various analysis techniques. Consistency of the JSI results for Cr was confirmed also by the QA/QC procedure using NIST SRM 1547, where the Cr content obtained during the IPE 2009.2 study was $1.30 \pm 0.07 \text{ mg}/\text{kg}$ ($k = 1$) and during the IPE 2012.1 study $1.28 \pm 0.05 \text{ mg}/\text{kg}$ ($k = 1$) [2, 20].

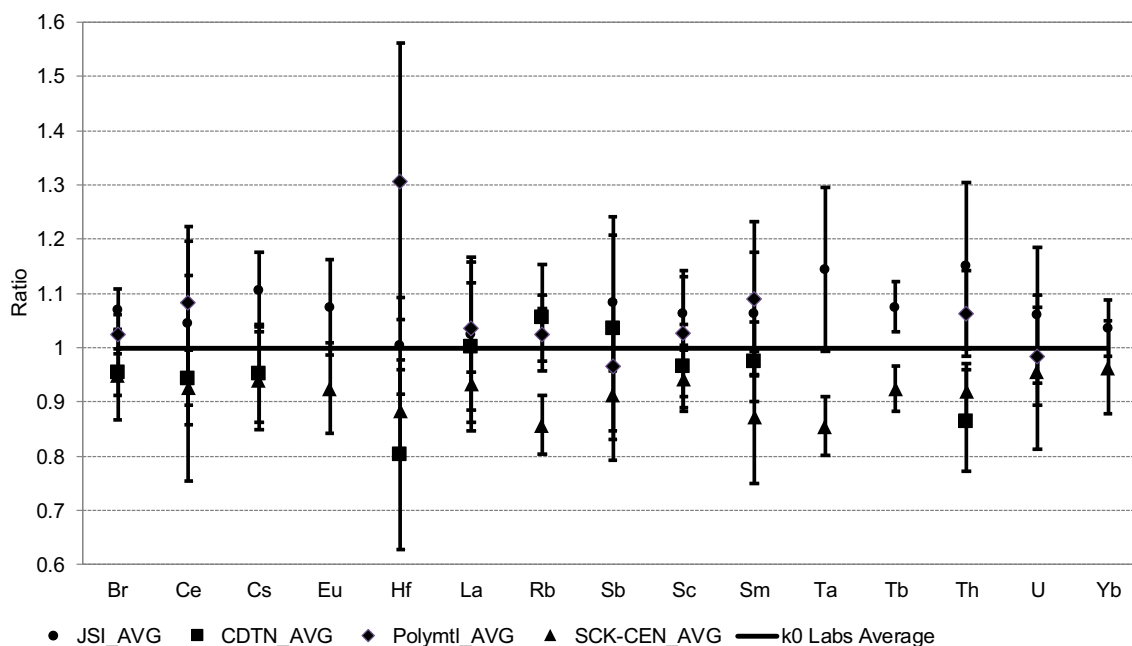


Fig. 2 Consistency of other elemental contents in IPE 2009.2 sample 124 provided by particular k_0 Labs compared to the average value calculated from the four k_0 Labs

Conclusions

In this study four institutes from Belgium, Brazil, Canada and Slovenia applied k_0 -INAA for re-determination of total content of Cr in plant sample 124 (Lucerne/Medicago sativum) from WEPAL IPE 2009.2 proficiency test. The data obtained by four institutes for Cr are in good agreement with each other and in disagreement with WEPAL data evaluated by their NDA model. It was confirmed that the original JSI result included in the first WEPAL report [1] was correct, since it is in good agreement with the results of the present study involving four INAA labs. Additional proof is the good agreement of the result of JSI for this same sample 124 (Lucerne/Medicago sativum) in the WEPAL IPE 2012.1 round, when more participants used non-destructive INAA.

It is concluded from this study that Cr losses in sample 124 occurred during the chemical digestion procedure applied by other participants and we call attention to Cr data obtained by digestion techniques for other plant samples which may contain Cr in silicates.

Acknowledgements The authors thank the IAEA for the initiative to facilitate laboratories to participate in ILC's by WEPAL under project TC-RER1007. The Slovenian author kindly acknowledges financial support of the Slovenian Research Agency (ARRS) through programme P1-0143 and the Metrology Institute of the Republic of Slovenia (MIRS) under MIRS/IJS contract No. 6401-5/2009/27 for activities and obligations performed as a Designate Institute as an etalon (standard of measurement) for amount of substance/chemical trace elements/in the organic and inorganic materials. The work of

this study is part of project ENVCRM, which was funded within the framework of the EMPIR.

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