J Radioanal Nucl Chem (2014) 300:473–480
DOI 10.1007/s10967-014-2991-7

Verification of k_0-NAA results at the LVR-15 reactor in Řež with the use of Au+Mo+Rb(+Zn) monitor set

Marie Kubešová · Ivana Krausová ·
Jan Kučera

Received: 10 October 2013 / Published online: 6 February 2014

Abstract Long-time experience in neutron flux monitoring on irradiation in the LVR-15 research reactor in Řež proved that Au+Mn+Rb and Au+Mo+Rb(+Zn) monitor sets for short and long irradiation, respectively, are more suitable in our conditions than the most frequently used Au+Zr set. The advantages of the former monitor set have been described previously, in the present work we discuss the advantages of the latter monitor set for long irradiations in varying active core configurations of the LVR-15 reactor. The successful application of the Au+Mo+Rb(+Zn) monitor set has been verified by comparative determination of the neutron flux parameters α (epithermal flux distribution parameter), f (thermal-to-epithermal neutron flux ratio), and $F_{c,Au}$ (comparator factor) using this and the Au+Zr monitor set, and by analyses of certified reference materials, namely NIST SRMs 1547 Peach Leaves, 2711 Montana Soil, and 1633b Trace Elements in Coal Fly Ash.

Keywords Neutron activation analysis · k_0 standardization · Neutron flux parameters · Monitor set for long irradiations

Introduction

For k_0 standardization in neutron activation analysis (k_0-NAA) the determination of neutron flux parameters α, f, and $F_{c,Au}$ has to be performed [1]. The $F_{c,Au}$ parameter is defined and computed in Kayzero for Windows [2] according to Eq. (1)

$$F_{c,Au} = \frac{A_{\mathrm{sp,Au}} \times 10^{-6}}{k_{0,\mathrm{Au}}(\mathrm{Au}) \cdot (G_{\mathrm{th,Au}} \cdot f + G_{\mathrm{e,Au}} \cdot Q_{0,\mathrm{Au}}(\alpha) \cdot \varepsilon_{\mathrm{p,Au}})}. \tag{1}$$

For the determination of the above parameters, several methods were proposed during the development of the k_0 standardization [1, 3]. However in case of reactor LVR-15 of the Research Center Řež, Ltd., and other multi-purpose reactors with often changing neutron flux parameters, only the bare multi-monitor method is recommended (or Cd-covered multi-monitor method for ENAA). It is in fact considered as an in situ neutron flux parameters determination technique, because the monitors can be co-irradiated with the samples analysed. For a long time, the Au+Zr monitor set has been recommended [1] for in situ determination of neutron flux parameters, especially for long irradiations. A few years ago, a new monitor set composed of Au+Mo+Cr was proposed for routine monitoring of neutron flux parameters in k_0-NAA, especially suitable for well-thermalized facilities (a high f value), and its performance has been found comparable with that of the Au+Zr monitor set [4]. However, it has been recently reported that the use of the monitor sets Au+Zr and Au+Mo+Cr leads to considerably different values for the parameters f and α [5, 6]. Therefore, after successful implementation of k_0-NAA in our laboratory employing both Kayzero for Windows [7, 8] and k0-IAEA [9] software packages with the use of the Au+Mn+Rb set for short irradiations (which was developed in our laboratory) [10] and the Au+Zr set for long irradiations, we also tested the Au+Mo+Cr monitor set as well, but with rather unsatisfactory results as described previously [11].

We have also found that the combination of Au+Zr is not fully convenient for our experimental conditions for the following reasons:

M. Kubešová (✉) · I. Krausová · J. Kučera
Nuclear Physics Institute ASCR, 250 68 Řež, Czech Republic
e-mail: mariekubes@centrum.cz; kubesova@ujf.cas.cz

1. Short half-life of ^{97}Zr–^{97m}Nb ($T_{1/2} = 16.74$ h).
2. Problem with photoneutrons from the Be reflector for ^{95}Zr ($\bar{E}_r = 6260$ eV) [12].
3. Low k_0 values for both Zr nuclides.
4. Use of a smaller mass (ca 3 mg) of the IRMM-530RA 0.1 % Au–Al alloy instead of 10 mg for which the value and its uncertainty of 1.003 ± 0.012 mg kg^{-1} has been certified. This may lead to a higher uncertainty of k_0-NAA results, because the relative standard deviation of the gold content of 0.30 %, which was determined for 10-mg samples in the original study [13], may increase. The use of 10-mg alloy aliquots would cause in our experimental conditions (a thermal neutron fluence rate of up to 7×10^{17} m^{-2} s^{-1}) excessive activities of ^{28}Al in short irradiation, and of ^{198}Au in long irradiation.
5. Different mass of individual elements in each monitor set.

Therefore, we decided to find another combination of monitors, which would satisfy the following requirements:

1. Content of elements with nuclides that activate readily, with the Q_0 and $\bar{E}_r$ parameters in a wide range of values.
2. Composition of an in situ monitor set optimized for one measurement (ca 30 min.) after a decay time of 4–7 days.
3. Easy preparation with regards to the chemical properties of elements.
4. The same mass of an element in each monitor set (to simplify the data input into calculation programs).
5. The possibility of use of one type of the monitor set for both INAA and ENAA.

Experimental

Candidate elements to form the monitor set were scrutinized according to properties of their long-lived radioisotopes as given in [14]. Several combinations of selected elements were tested. The elements were prepared for irradiation in the form of pipetted aliquots of solutions containing known amounts of elements onto disks of Whatman chromatographic paper. The stock solutions of Rb and Zn were prepared by dissolution of well defined compounds of Rb and Zn ($RbNO_3$, 99.99 %, Aldrich, USA and Zn shots, per analysis, Lachema, Czech Republic, respectively). $RbNO_3$ was dissolved in deionized water, while Zn shots were dissolved in dilute (1:5) sub-boiled HNO_3. For Au and Mo, the NIST SRM-3121 Gold Standard Solution and the NIST SRM-3134 Molybdenum Standard Solution were used, respectively [15], the original solutions being gravimetrically diluted with approx. 10 % HCl as required for pipetting 50 µL aliquots. The aliquots of the above solutions were deposited onto the disks of Whatman chromatographic paper with a diameter of 16 mm using a gravimetrically calibrated 50 µL pipette, carefully dried at a slightly elevated temperature (not exceeding 40 °C) using an infrared bulb and sealed into 25-mm diameter polyethylene (PE) disk capsules made by sealing of two 0.2 mm PE foils. The chemicals used, element masses deposited, and relevant nuclear data are listed in Table 1.

Au+Zr monitor sets were prepared as 6-mm diameter discs of 99.8 % Zr foil (Goodfellow UK, ZR000260 foil, 0.125 mm thickness) and 0.1 % Au–Al foil (IRMM Belgium, Nuclear reference material IRMM-530RA, 0.1 mm thickness) [16, 17], which were weighed and sealed in the centre of two PE discs. Differences in the composition and geometry of the individual types of monitors are taken into account by the Kayzero for Windows software.

Three types of NIST SRMs were used for comparison and verification the results obtained using the monitor sets studied: 1547 Peach Leaves, 2711 Montana Soil, and 1633b Constituent Elements in Coal Fly Ash [15]. Three irradiation containers with two monitor sets of Au+Zr and Au+Mo+Rb+Zn, and one aliquot of each NIST SRM sample were packed for irradiations into disc-shaped polyethylene capsules with a 25-mm diameter, made as described above.

For irradiations, the samples and monitor sets were formed into a column as indicated in Table 2, and hermetically sealed in an Al irradiation container. All PE capsules were wrapped into a thin Al foil to ensure good heat transfer from the samples through the Al container walls during irradiation. No noticeable flux depression has been observed for this irradiation arrangement in preliminary experiments. The Al containers with the samples and monitor sets were irradiated in two channels of the LVR-15 reactor (Fig. 1) as follows:

1. In channel H8 located at the outer perimeter of the LVR-15 reactor active core, in a Be reflector block, with the whole reactor spectrum at an approximate thermal neutron fluence rate of 4×10^{17} m^{-2} s^{-1}, for 3 h;
2. In irradiation channel H6 located next to fuel with the whole reactor spectrum at an approximate thermal neutron fluence rate of 7×10^{17} m^{-2} s^{-1} for 90 min., and
3. With epithermal neutrons (ENAA) in channel H6 using an irradiation container inlaid with a 1-mm thick Cd cover [18] for 2 h.

Prior to activity measurements of the irradiated samples and monitor sets, the cover Al foil was removed and the surface of the PE capsules was cleaned by washing with

Table 1 Nuclear parameters of radinuclides formed upon neutron activation of Au, Mo, Rb, Zn, and Zr [14]

Nuclide	Source of element	Mass of element in monitor (μg)	$T_{1/2}$	E_γ (keV)	k_0 (uncertainty, %)	$\bar{E}_r$ (eV) (uncertainty, %)	Q_0 (uncertainty, %)
^{198}Au	SRM-3121	3.260 ± 0.008	2.695 days	411.8	1 (0)	5.65 (7.1)	15.7 (1.8)
	IRMM-530R	~6					
^{99}Mo–^{99m}Tc	SRM-3134	291.3 ± 1.0	65.94 h	140.5	5.27E−4 (0.5)	241 (20)	53.1 (6.3)
^{86}Rb	RbNO$_3$	325.3 ± 0.5	18.63 days	1,077.0	7.65E−4 (1.0)	839 (6)	14.8 (2.5)
^{65}Zn	Zn shots	992.9 ± 1.8	244.3 days	1,115.5	5.72E−3 (0.4)	2,560 (10)	1.908 (5.0)
^{97}Zr–^{97m}Nb	Zr foil Goodfellow	~16,000	16.74 h	743.3	1.24E−5 (0.3)	338 (2.1)	251.6 (1.0)
^{95}Zr			64.02 days	724.2	8.90E−5 (1.3)	6,260 (4)	5.31 (3.3)
				756.7	1.10E−4 (1.3)		

Table 2 Approximate masses of samples and monitor sets and their location in all containers for irradiation

Position	Sample	Mass (mg)
1	0.1 % Au–Al+Zr-1	~ 6 + ~16
2	Au+Mo+Rb+Zn-1	See Table 1
3	NIST SRM-1547	~100
4	NIST SRM-2711	~50
5	NIST SRM-1633B	~50
6	0.1 % Au–Al+Zr-2	~6 + ~16
7	Au+Mo+Rb+Zn-2	See Table 1

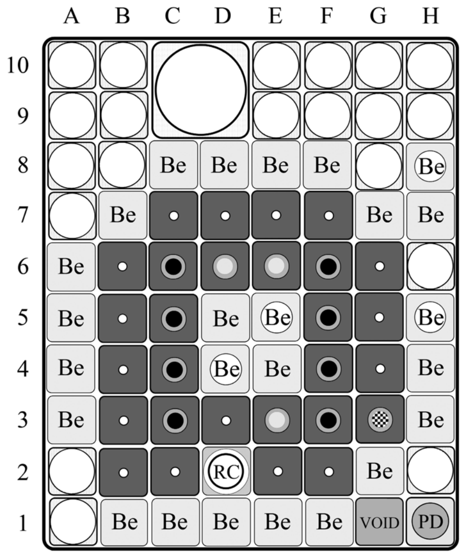

Fig. 1 Layout of the active core of the LVR-15 reactor

dilute nitric acid and deionized water. Gamma-ray spectra of samples and monitors were measured using a coaxial HPGe detector with the following parameters: relative efficiency 77.8 %, resolution FWHM 1.87 keV @1332.5 keV, and peak-to Compton ratio of 82.5:1. The detector was connected to a Canberra Genie 2000 γ-spectrometer through a chain of linear electronics, which contained a loss-free counting module (LFC Canberra 599, dual mode) to correct for pile-up effect and dynamic changes of dead time. Two counts were performed for the NIST SRMs after decay times of 4–5 days and 4 weeks.

Measurement of the monitor sets was carried out considering the methodology of determination of neutron flux parameters using the bare triple-monitor and Cd-covered multi-monitor method [1, 3]. Both Au+Zr and Au+Mo+Rb+Zn monitor sets were measured in reference geometry of 20 cm after a decay time of 3–4 days. In preliminary experiments, a blank correction has been found negligible for counting of both monitors and samples in the PE capsules used for irradiation without transferring them into non-irradiated containers.

Canberra Genie 2000 software was used to control measurements and to evaluate the spectra obtained. Results of k_0-NAA were calculated using the Kayzero for Windows program [2]. In this program, the following values of thermal and epithermal self-shielding factors, G_{th} and G_e, respectively, were used. For the 0.1 % Au–Al foil G_{th} and $G_e = 1$, for the Zr foil $G_e = 0.983$ for the reaction ^{94}Zr(n,γ)^{95}Zr and $G_e = 0.973$ for the reaction ^{96}Zr(n,γ)^{97}Zr [1, 3]. For all other nuclides and matrices the values $G_{th} = G_e = 1$ were used (as calculated in Kayzero for Windows program [2]). The tolerance for peak identification was set to 1.1 keV (one sided).

Results and discussion

The LVR-15 experimental reactor provides irradiation services for more than 20 scientific teams and/or industrial applications. Therefore, the active core configuration is frequently changed, usually after each three-week irradiation campaign or even after short breaks within an operation campaign. These experimental conditions dictate the use of in situ neutron flux parameter monitoring. Results of determination of the neutron flux parameters for different irradiation channels with the use of all monitor sets tested are given in Table 3. Uncertainties of the neutron flux

Table 3 Neutron flux parameters in irradiation channels

Irradiation channel	H6 (INAA)			H6 (ENAA)			H8 (INAA)		
Monitor set	α	f	$F_{c,Au}$	α	f	$F_{c,Au}$	α	f	$F_{c,Au}$
Au+Mo+Zn	−0.007	24.7	823,000	−0.039	0	774,000	0.019	48.9	235,000
Au+Rb+Zn	−0.009	24.7	822,000	−0.026	0	811,000	0.004	49.5	231,000
Au+Mo+Rb	−0.009	25.3	811,000	−0.006	0	833,000	0.022	49.2	234,000
Au+Zr	0.010	25.7	817,000	−0.005	0	824,000	0.032	48.9	228,000

Table 4 Results for NIST SRM-1547 Peach Leaves

SRM-1547	NIST Value[a]	H6 (INAA)		H6 (ENAA)		H8 (INAA)	
Element (unit)	$x_{cert} \pm u_{cert}$	$x_{lab} \pm u_{lab}$	E_n	$x_{lab} \pm u_{lab}$	E_n	$x_{lab} \pm u_{lab}$	E_n
As (mg kg^{-1})	0.060 ± 0.018	<0.5	–	<0.5	–	0.086 ± 0.019	0.99
Ba (mg kg^{-1})	124 ± 4	114 ± 15	0.64	–	–	116 ± 8	0.89
Br (mg kg^{-1})	(11)	11.1 ± 0.8	0.07	10.5 ± 0.7	0.38	10.8 ± 0.8	0.15
Ca (%)	1.56 ± 0.02	1.61 ± 0.16	0.34	–	–	1.57 ± 0.12	0.08
Cd, mg kg^{-1}	0.026 ± 0.003	<0.8	–	<0.6	–	<0.5	–
Ce (mg kg^{-1})	(10)	10.9 ± 0.8	0.70	–	–	10.6 ± 0.8	0.47
Co (mg kg^{-1})	(0.07)	0.072 ± 0.007	0.20	–	–	0.073 ± 0.006	0.33
Cr (mg kg^{-1})	(1)	1.40 ± 0.14	2.32	–	–	1.38 ± 0.12	2.43
Cu, mg kg^{-1}	3.7 ± 0.4	<160	–	–	–	<150	–
Eu (mg kg^{-1})	(0.17)	0.19 ± 0.02	0.76	0.18 ± 0.05	0.19	0.184 ± 0.017	0.58
Fe (mg kg^{-1})	218 ± 14	218 ± 16	0.00	–	–	212 ± 15	0.29
Gd (mg kg^{-1})	(1)	<5	–	<4	–	<2	–
K (%)	2.43 ± 0.03	2.34 ± 0.17	0.52	–	–	2.30 ± 0.16	0.80
La (mg kg^{-1})	(9)	9.3 ± 0.7	0.26	–	–	9.1 ± 0.6	0.09
Mo (mg kg^{-1})	0.060 ± 0.008	<0.6	–	<0.3	–	<0.12	–
Na (mg kg^{-1})	24 ± 2	44 ± 3	5.55	–	–	40 ± 3	4.44
Nd (mg kg^{-1})	(7)	7.6 ± 0.9	0.53	–	–	6.9 ± 0.5	0.12
Rb (mg kg^{-1})	19.7 ± 1.2	19.3 ± 1.4	0.22	18.7 ± 1.7	0.48	19.0 ± 1.4	0.38
Sb (mg kg^{-1})	(0.02)	0.052 ± 0.007	4.40	0.059 ± 0.006	6.17	0.044 ± 0.005	4.46
Sc (mg kg^{-1})	(0.04)	0.045 ± 0.004	0.88	–	–	0.044 ± 0.003	0.80
Se (mg kg^{-1})	0.120 ± 0.009	<0.15	–	<0.13	–	<0.2	–
Sm (mg kg^{-1})	(1)	1.11 ± 0.09	0.82	1.08 ± 0.09	0.59	1.06 ± 0.08	0.47
Sr (mg kg^{-1})	53 ± 4	60 ± 6	0.97	59 ± 6	0.83	57 ± 5	0.62
Tb (mg kg^{-1})	(0.1)	0.111 ± 0.009	0.82	0.108 ± 0.008	0.62	0.106 ± 0.008	0.47
Th (mg kg^{-1})	(0.05)	0.058 ± 0.009	0.78	0.059 ± 0.014	0.61	0.057 ± 0.007	0.81
U (mg kg^{-1})	(0.015)	<0.05	–	<0.03	–	<0.04	–
Yb (mg kg^{-1})	(0.2)	0.18 ± 0.03	0.55	–	–	0.176 ± 0.016	0.94
Zn (mg kg^{-1})	17.9 ± 0.4	18.4 ± 1.3	0.37	–	–	18.0 ± 1.3	0.07

[a] Noncertified values without uncertainties given in parenthesis

parameters were studied in our previous work [19]. We concluded that the proposed KRAGTEN-NPI computation tool provides the most appropriate uncertainty values, because the most significant uncertainty sources, including correlations of the relevant parameters, are taken into account. We found that the relative uncertainties of α values determined using the Au+Mo+Rb+Zn monitor set were in the range of 70–120 %, which was in agreement with the De Corte′s statement that “the overall uncertainties are of the order of 5–10 % for high α's ($\alpha \sim 0.1$) to 50 % or more for α's approaching zero ($\alpha \sim 0.01$)” [3]. We also found that for values of f between 25 and 45 the relative uncertainties

Table 5 Results for NIST SRM-2711 Montana Soil

SRM-2711	NIST value[a]	H6 (INAA)		H6 (ENAA)		H8 (INAA)	
Element (unit)	$x_{\text{cert}} \pm u_{\text{cert}}$	$x_{\text{lab}} \pm u_{\text{lab}}$	E_n	$x_{\text{lab}} \pm u_{\text{lab}}$	E_n	$x_{\text{lab}} \pm u_{\text{lab}}$	E_n
Ag (mg kg^{-1})	4.63 ± 0.39	4.7 ± 0.5	0.11	4.6 ± 0.3	0.06	4.8 ± 0.4	0.30
As (mg kg^{-1})	105 ± 8	108 ± 8	0.27	96 ± 6	0.90	101 ± 7	0.38
Au (mg kg^{-1})	(0.03)	0.022 ± 0.008	0.94	0.032 ± 0.003	0.47	0.032 ± 0.007	0.26
Ba (mg kg^{-1})	726 ± 38	700 ± 50	0.41	–	–	680 ± 50	0.73
Br (mg kg^{-1})	(5)	5.0 ± 0.5	0.00	5.39 ± 0.11	0.76	5.0 ± 0.5	0.00
Ca (%)	2.88 ± 0.08	<3	–	–	–	<4	–
Cd (mg kg^{-1})	41.70 ± 0.25	41 ± 6	0.12	23.0 ± 1.9	9.76	38 ± 7	0.53
Ce (mg kg^{-1})	(69)	77 ± 5	0.94	–	–	76 ± 5	0.82
Co (mg kg^{-1})	(10)	10.4 ± 0.7	0.33	–	–	9.8 ± 0.7	0.16
Cr (mg kg^{-1})	(47)	49 ± 4	0.32	–	–	48 ± 3	0.18
Cs (mg kg^{-1})	(6.1)	7.1 ± 0.8	0.99	6.0 ± 0.4	0.14	6.6 ± 0.5	0.63
Cu (mg kg^{-1})	114 ± 2	<3,000	–	–	–	<900	–
Eu (mg kg^{-1})	(1.1)	1.21 ± 0.17	0.54	1.2 ± 0.2	0.44	1.20 ± 0.13	0.59
Fe (%)	2.89 ± 0.06	2.9 ± 0.2	0.05	–	–	2.9 ± 0.2	0.05
Ga (mg kg^{-1})	(15)	<110	–	<30	–	<150	–
Hf (mg kg^{-1})	(7.3)	8.2 ± 0.7	0.89	6.2 ± 1.1	0.83	8.3 ± 0.7	0.99
Ho (mg kg^{-1})	(1)	<8	–	<2	–	<6	–
In (mg kg^{-1})	(1.1)	<3	–	<1.8	–	<1.7	–
K (%)	2.45 ± 0.08	2.44 ± 0.18	0.05	–	–	2.34 ± 0.17	0.59
La (mg kg^{-1})	(40)	37 ± 3	0.60	–	–	36 ± 3	0.80
Mo (mg kg^{-1})	(1.6)	<10	–	<2	–	<12	–
Na (mg kg^{-1})	1.14 ± 0.03	1.21 ± 0.08	0.82	–	–	1.15 ± 0.08	0.12
Nd (mg kg^{-1})	(31)	33 ± 3	0.46	–	–	32 ± 3	0.23
Rb (mg kg^{-1})	(110)	121 ± 9	0.77	97 ± 9	0.91	117 ± 8	0.88
Sb (mg kg^{-1})	19.4 ± 1.8	20.5 ± 1.5	0.47	17.5 ± 1.1	0.90	19.4 ± 1.4	0.00
Sc (mg kg^{-1})	(9)	9.8 ± 0.7	0.70	–	–	9.4 ± 0.7	0.35
Se (mg kg^{-1})	1.52 ± 0.14	1.23 ± 0.12	1.57	1.0 ± 0.2	2.13	1.1 ± 0.2	1.72
Sm (mg kg^{-1})	(5.9)	5.7 ± 0.4	0.28	5.4 ± 0.3	0.76	5.3 ± 0.4	0.84
Sr (mg kg^{-1})	245.3 ± 0.7	280 ± 40	0.87	240 ± 30	0.18	270 ± 30	0.82
Th (mg kg^{-1})	(14)	14.7 ± 1.0	0.41	13.3 ± 0.8	0.43	14.8 ± 1.0	0.46
U (mg kg^{-1})	(2.6)	2.6 ± 0.3	0.00	2.50 ± 0.18	0.32	3.0 ± 0.7	0.54
W (mg kg^{-1})	(3)	3.4 ± 0.7	0.53	2.7 ± 0.2	0.83	3.2 ± 0.4	0.40
Yb (mg kg^{-1})	(2.7)	3.1 ± 0.4	0.83	–	–	3.0 ± 0.4	0.62
Zn (mg kg^{-1})	350.4 ± 4.8	360 ± 30	0.32	–	–	350 ± 20	0.02
Zr (mg kg^{-1})	(230)	<400	–	<400	–	<400	–

[a] Noncertified values without uncertainties given in parenthesis

were between 15 and 18 %, while the relative uncertainties of $F_{c,Au}$ were between 10 and 14 %. The data given in Table 3 show no significant differences among the f and $F_{\text{c,Au}}$ values (within their uncertainties) in the individual irradiation channels which were determined with the use of all the monitor sets tested. Slightly lower $F_{\text{c,Au}}$ values evaluated in channel H6 (irradiation with epithermal neutrons) using the monitor sets containing Zn compared with those evaluated with other monitor sets are most probably caused by an imperfect Cd-cover, which does not shield all thermal neutrons. Since the ^{65}Zn nuclide has the lowest Q_0-value from all monitor elements tested (1.908), its use for monitoring of parameters of neutron flux in ENAA is feasible only if the thermal neutron shielding is completely effective. Another drawback of the use of Zn is that the concentration of Au is unstable on a long-term storage of a stock solution, in which Zn is also present. Thus, pipetting from two stock solutions is necessary to prepare a neutron flux monitor set, which contains Zn, Au, and other elements. Significant differences of α values exceeding their

Table 6 Results for NIST SRM 1633b Constituent Elements in Coal Fly Ash

SRM-1633B	NIST Value[a]	H6 (INAA)		H6 (ENAA)		H8 (INAA)	
Element (unit)	$x_{\mathrm{cert}} \pm u_{\mathrm{cert}}$	$x_{\mathrm{lab}} \pm u_{\mathrm{lab}}$	E_{n}	$x_{\mathrm{lab}} \pm u_{\mathrm{lab}}$	E_{n}	$x_{\mathrm{lab}} \pm u_{\mathrm{lab}}$	E_{n}
As (mg kg^{-1})	136.2 ± 2.6	132 ± 9	0.45	137 ± 10	0.08	130 ± 9	0.66
Ba (mg kg^{-1})	709 ± 27	740 ± 150	0.20	–	–	710 ± 80	0.01
Br (mg kg^{-1})	(2.9)	3.2 ± 0.4	0.61	2.76 ± 0.14	0.43	3.2 ± 0.3	0.72
Ca (%)	1.51 ± 0.06	<3	–	–	–	<3	–
Cd (mg kg^{-1})	0.784 ± 0.006	<12	–	< 3	–	<11	–
Ce (mg kg^{-1})	(190)	196 ± 14	0.25	–	–	193 ± 14	0.13
Co (mg kg^{-1})	(50)	51 ± 4	0.16	–	–	49 ± 4	0.16
Cr (mg kg^{-1})	198.2 ± 4.7	212 ± 15	0.88	–	–	208 ± 15	0.62
Cs (mg kg^{-1})	(11)	11.0 ± 0.8	0.00	12.4 ± 0.9	0.99	10.6 ± 0.8	0.29
Cu (mg kg^{-1})	112.8 ± 2.6	<2,000	–	–	–	<700	–
Eu (mg kg^{-1})	(4.1)	4.0 ± 0.4	0.17	4.2 ± 0.4	0.17	4.0 ± 0.3	0.20
Fe (%)	7.78 ± 0.23	8.0 ± 0.6	0.34	–	–	7.7 ± 0.5	0.15
Gd (mg kg^{-1})	(13)	<100	–	<40	–	<90	–
Hf (mg kg^{-1})	(6.8)	6.9 ± 0.6	0.11	–	–	6.9 ± 0.5	0.12
Ho (mg kg^{-1})	(3.5)	<7	–	<8	–	<5	–
K (%)	1.95 ± 0.03	1.90 ± 0.14	0.35	–	–	1.86 ± 0.13	0.67
La (mg kg^{-1})	(94)	86 ± 6	0.72	–	–	84 ± 6	0.90
Na (%)	0.201 ± 0.003	0.207 ± 0.014	0.42	–	–	0.200 ± 0.014	0.07
Nd (mg kg^{-1})	(85)	90 ± 8	0.43	–	–	87 ± 6	0.19
Rb (mg kg^{-1})	(140)	147 ± 13	0.37	147 ± 11	0.39	148 ± 11	0.45
Sb (mg kg^{-1})	(6)	5.0 ± 0.4	1.39	5.1 ± 0.4	1.25	5.0 ± 0.4	1.39
Sc (mg kg^{-1})	(41)	42 ± 3	0.20	–	–	42 ± 3	0.20
Se (mg kg^{-1})	10.26 ± 0.17	10.2 ± 0.8	0.07	9.3 ± 1.0	0.95	9.9 ± 0.8	0.44
Sm (mg kg^{-1})	(20)	17.0 ± 1.2	1.29	17.5 ± 1.3	1.05	17.1 ± 1.2	1.24
Sr (mg kg^{-1})	1,041 ± 14	1,100 ± 90	0.64	1,080 ± 100	0.38	1,090 ± 90	0.53
Ta (mg kg^{-1})	(1.8)	1.76 ± 0.14	0.18	1.84 ± 0.13	0.18	1.72 ± 0.13	0.36
Tb (mg kg^{-1})	(2.6)	2.63 ± 0.19	0.09	2.7 ± 0.2	0.30	2.66 ± 0.19	0.19
Th (mg kg^{-1})	25.7 ± 1.3	26.4 ± 1.8	0.32	27.4 ± 1.9	0.74	26.1 ± 1.8	0.18
Tm (mg kg^{-1})	(2.1)	<7	–	<3	–	<7	–
U (mg kg^{-1})	8.79 ± 0.36	9.0 ± 0.8	0.24	8.9 ± 0.6	0.16	8.5 ± 0.7	0.37
W (mg kg^{-1})	(5.6)	5.5 ± 0.6	0.12	5.0 ± 0.4	0.87	5.5 ± 0.5	0.13
Yb (mg kg^{-1})	(7.6)	7.9 ± 0.6	0.31	–	–	8.0 ± 0.6	0.41
Z (mg kg^{-1})	(210)	217 ± 16	0.27	–	–	213 ± 15	0.12

[a] Noncertified values without uncertainties given in parenthesis

uncertainties were observed in all irradiation channels in most cases, when monitor sets of the studied composition were used. However, owing to the low α values being close to zero, the differences found have only a negligible effect on the k_0-NAA results.

From the comparison of the use of monitor sets tested, and the ease of their preparation, it can be concluded the monitor containing a combination of the elements Au+Mo+Rb is the most suitable both for bare and Cd-covered irradiations as a replacement of the traditional Au+Zr monitor. All results presented in this paper were obtained using only this newly composed monitor set, although results were calculated also for other combinations (for INAA) and Au+Zr monitor set with almost identical results. In the case of ENAA only elements forming long-lived nuclides with Q_0-values higher than 3 are presented, as the perturbation of these results using imperfect Cd-shielding is negligible.

Single aliquots of all SRMs were analyzed in each irradiation run, *i.e.*, in channels H6 and H8 (INAA), and channel H6 (ENAA). Agreement of the element contents found in SRMs, x_{lab}, with certified values, x_{cert}, was tested with E_{n} number defined as [20]

$$E_n = \frac{|x_{\mathrm{lab}} - x_{\mathrm{cert}}|}{\sqrt{u_{\mathrm{lab}}^2 + u_{\mathrm{cert}}^2}}. \qquad (2)$$

The uncertainty of a single result, u_{lab}, was evaluated in accordance with the international guidelines [21, 22] employing the approach contained in Kayzero for Windows software [3], i.e., as the square root of quadratic summation of the statistical counting error and the estimated systematic uncertainty of all standard uncertainties of parameters involved in k_0-standardization (3.5 %) and converted to an expanded uncertainty ($k = 2$). The expanded uncertainties of certified values u_{cert} ($k = 2$) were taken from certificates. For non-certified values which are not furnished with their uncertainties, the expanded uncertainties ($k = 2$) were set to 10 % relative of the values given in certificates for the purpose of this work, to be able to use the same criterion as for the certified values. This may be considered as a reasonable estimate of the real uncertainty, because relative expanded uncertainties ($k = 2$) of certified values are frequently in the range of 1–7 % relative and it may be regarded plausible to presume that expanded uncertainties of non-certified values are somewhat larger compared with those of certified values. Using E_{n} number, performance levels are normally determined as follows: $E_{\mathrm{n}} \leq 1$ = satisfactory performance, $E_{\mathrm{n}} > 1$ = unsatisfactory performance.

Results for matrix reference materials NIST SRM-1547 Peach Leaves, NIST SRM-1633b Constituent Elements in Coal Fly Ash, and NIST SRM-2711 Montana Soil (representing matrices of botanical, environmental, and geological samples) obtained by k_0-NAA are shown in Tables 4, 5 and 6 (using the new Au+Mo+Rb monitor set). In most cases, the results were found to be in agreement with certified and/or noncertified values of element contents in all three SRMs ($E_{\mathrm{n}} \leq 1$). However, several discrepancies ($E_{\mathrm{n}} > 1$) were observed for a few elements, for which the following explanations may be offered. Apparently discrepant values of Cr and Sb in NIST SRM-1547 are probably due to incorrectly set uncertainties of the noncertified values, which may be larger than those presumed in this work. A higher Na value than the certified value in this SRM has again been found as in our previous studies [9–11]. The reason for this discrepancy which may be twofold (contamination or biased certified value) is still to be studied. A lower Se value than the certified value in NIST SRM-2711 is most probably due to insufficiently resolved spectral interferences, while the reason for a lower Cd value determined in this SRM by ENAA remains unknown. For somewhat lower Sb and Sm results than noncertified values in NIST SRM-1633b the same reasoning applies as for the noncertified values of Cr and Sb in NIST SRM-1547, i.e., incorrectly set uncertainties of the noncertified values. The discrepancies found in the three various NIST SRMs are obviously not of a systematic nature. Results for Hg have not been presented due to possible volatility losses (depending on Hg speciation) on sample irradiation in the PE capsules.

Conclusions

The accuracy of k_0-NAA results obtained with the use of Au+Zr and Au+Mo+Rb(+Zn) monitor sets for the determination of neutron flux parameters f, α, and F_{c} during long irradiations was tested in the LVR-15 research reactor at Řež. No statistically significant differences of the neutron flux parameters f and $F_{c,Au}$ were found employing the Au+Zr and tested Au+Mo+Rb(+Zn) monitor sets for bare irradiation. In case of ENAA it was found that Zn is not suitable to be used for the determination of neutron flux parameters due to a low Q_0-value of ^{65}Zn. The differences found for the determination of the α parameter with the studied monitor sets turned out to have a negligible effect on the k_0-NAA results owing to the low α values close to zero, in irradiation channels of the LVR-15 reactor. This has been proved by the results of elemental analysis of three NIST SRMs, which were in the majority of cases in agreement with the NIST certified and/or noncertified values. The experiments performed suggest that the most suitable combination of the monitor elements (nuclides) for the determination of α, f, and F_{c} in long irradiations with the use of the bare multi-monitor and Cd-covered methods in our laboratory is the monitor consisting of Au+Mo+Rb.

Acknowledgments This work was supported by the Czech Science Foundation within project P108/12/G108. Measurements were carried out at the CANAM infrastructure of the NPI ASCR Řež supported through MŠMT project No. LM2011019.

References

1. De Corte F, Simonits A (1994) Vademecum for k_0 users. DSM Research, Geleen
2. Kayzero (2005) Kayzero for Windows, Version 2, User's Manual November (2005). http://www.kayzero.com/KfW%20Manual%20V1.pdf. Accessed 1 Sept 2013
3. De Corte F (1987) The k_0-standardization method. A move to the optimization of neutron activation analysis. University of Gent, Ghent
4. Koster-Ammerlaan MJJ, Bacchi MA, Bode P (2008) De Nadai Fernandes EA. Appl Rad Isotopes 66:1964–1969
5. Khoo KS, Sarmani SB, Tan CH, Ti KL (2007) Variation of neutron parameters and neutron flux in an irradiation container at selected irradiation channels by using two neutron flux monitoring sets based on k_0-NAA method. In: Proceedings of the 12th Int. Conference on Modern Trends in Activation Analysis (MTAA-12), Sept 16–21, 2007, Tokyo Metropolitan University, Hachioji, p 124

6. Montoya E, Mendoza P, Bedregal P, Ubillús M, Torres B, Cohen IM (2007) The set Au-Zr-Mo-Cr-Lu as multiple reactor flux monitor. The performance of 96Zr and the analysis of inconsistencies. Informe Científico Tecnológico (ICT) and Instituto Peruano de Energía Nuclear (IPEN), Lima, pp 15–19 ISSN 1684-1662
7. Kubešová M, Kučera J (2010) Chem Listy 105:261–268 (in Czech)
8. Kubešová M, Kučera J (2010) Nucl Instrum Methods A 622:403–406
9. Kubešová M, Kučera J (2011) Nucl Instrum Methods A 654:206–212
10. Kubešová M, Kučera J, Fikrle M (2011) Nucl Instrum Methods A 656:61–64
11. Kubešová M, Kučera J (2012) J Radioanal Nucl Chem 293:665–674
12. Koster-Ammerlaan MJJ, Bode P, Winkelman AJM (2012) J Radioanal Nucl Chem 291:569–572
13. Ingelbrecht C, Peetermans F, De Corte F, De Wispelaere A, Vandercasteele C, Courtijn E, D'Hondt P (1991) Nucl Instrum Methods A 303:119–122
14. k_0-database (2012). http://www.kayzero.com/k0naa/k0naa/News/Entries/2012/3/25_The_IUPAC_databasa.html
15. NIST Certificates of Analysis. http://ts.nist.gov/measurementservices/referencematerials/index.cfm
16. IRMM Certificate of Analysis. http://irmm.jrc.ec.europa.eu/Pages/rmcatalogue.aspx
17. Goodfellow, Certificate of Analysis. http://www.goodfellow.com/catalogue/GFCat4I.php?ewd_token=20huNpDc8E4QioaJUNmiiPfulyESMT&n=Of952yV2Fz5tWw8LKyEz3a4nbvzw7v&ewd_urlNo=GFCat411&Catite=ZR000260&CatSearNum=2
18. Kučera J (1979) Radiochem Radioanal Lett 38:229–246
19. Kubešová M, Kučera J (2012) J Radioanal Nucl Chem 293:87–94
20. ISO Guide 13528 (2005) Statistical methods for use in proficiency testing by interlaboratory comparisons. ISO, Geneva
21. EURACHEM/CITAC Guide CG 4 (2000) Quantifying Uncertainty in Analytical Measurement, Second Edition
22. ISO/IEC Guide 98 (1995) Guide to the expression of uncertainty in measurement. ISO, Geneva