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Development of the k_0-based cyclic neutron activation analysis for short-lived radionuclides

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Abstract The k_0-based cyclic neutron activation analysis (k_0-CNAA) technique has been studied to explore the applicability at the Portuguese research reactor (RPI). In particular, for the determination of elements which form short-lived radionuclides, particularly fluorine (^{20}F, 11.16 s half-life) and selenium (^{77m}Se, 17.36 s half-life) in polymer, biological and environmental samples. The detection limits obtained for F and Se were about 50 and 0.01 mg kg^{-1}, respectively, in the investigated materials. The timing parameters for the procedure were 10 to 20 s for irradiation, 5 s decay, 10 to 20 s counting, 5 s waiting and performed with eight cycles. The k_0-IAEA program was modified to use millisecond time resolution for irradiation, decay and counting times as needed for interpreting k_0-CNAA data in terms of concentration, accuracy and detection limit. The quality control of the procedure was performed by preparing a standard solution containing fluorine with different contents as well as using the certified reference materials containing selenium from which the bias between the results and the certified values were within 15% for most elements at the investigated content ranges. The analytical results for several other elements producing short-lived or detectable radionuclides, e.g., Al, Ca, Cl, Cu, Dy, I, Mg, Mn, Ti, and V were also obtained by the k_0-CNAA procedure with accuracy within 12%.

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Introduction

Cyclic neutron activation analysis (CNAA) is a NAA technique for the determination of elements forming short-lived radionuclides by the repeated process of irradiation, decay and counting. By this process, the counts of a short-lived radionuclide of interest are considerably increased and the detection limit is significantly improved [1, 2]. In addition, one advantage of using CNAA is a drastic reduction of high radioactive activities formed after irradiation, therefore decreasing pulse loss due to dead time and pile up in the gamma-ray spectrometer [2, 3]. Although CNAA is normally optimized for a single element, other elements forming radionuclides with comparable half-lives will be enhanced along with the targeted element which means that one could aim for a whole group of elements. This has been routinely carried out for analysis of samples in any NAA laboratory. Even if some elements are not of interest they may still needed to correct for interferences. Moreover, researchers often want to know the concentrations of more elements than they initially thought, so it's always better to be calibrated for all elements in any NAA procedure. Nowadays, an increasing need for multi-element concentration determination of a large number of samples has enhanced the value of purely instrumental and non-destructive NAA. The implementation of the so-called "k_0-standardization" method of NAA (k_0-NAA) is now commonly accepted as the best way to achieve multi-element capability [4]. The k_0-NAA method is based on k_0-factors available in the

literature, accurate calibration of the detector response function, and a parameterization of the neutron spectrum. Using the assumption that the absolute neutron flux may vary, but the shape of the neutron spectrum is consistent, the mass fractions of an element in a sample can be calculated by co-irradiating the sample together with a flux monitor (commonly Au), then counting the samples on the calibrated detector. Therefore, the main objective of this work is to explore, and possibly expand the applicability of k_0-NAA with cyclic irradiations (k_0-CNAA) for determination of elements forming short-lived radionuclides. In the present paper, we demonstrate the topics related to k_0-CNAA: (i) the mathematical basic for calculating elemental concentrations; (ii) the establishment of an experimental protocol using k_0-IAEA software; and (iii) the evaluation of applicability of the technique to the elements of interest particularly fluorine (^{20}F, 11.16 s half-life), selenium (^{77m}Se, 17.36 s half-life) as well as the other elements forming short-lived or detectable radionuclides. Table 1 displays a list of elements which induce short-lived or detectable radionuclides and related nuclear data for use in k_0-CNAA, i.e., half-lives, Q_0—ratio of resonance integral to 2,200 m s^{-1} (n,γ) reaction cross-section, $\overline{E}_r$—effective resonance energy and main γ-ray energies.

Experimental

Establishment of k_0-CNAA basic equation

In order to establish the k_0-cyclic NAA equation, we calculate the reaction and counting rates when a nucleus is exposed in a neutron field then counted on a radiation detector. We can determine the reaction rate (right) and count (left) rates for a cycle:

$$\frac{N_p / t_c}{SDCw} \cdot \frac{M}{N_A \theta \gamma} = [G_{\text{th}} \Phi \sigma_0 + G_e \Phi_e I_0(\alpha)] \varepsilon_p \quad (1)$$

where, specific activity

$$A_{\text{sp}} = \frac{N_p / t_c}{SDCw}, \quad (2)$$

Saturation factor $S = 1 - e^{-\lambda t_i}$, with t_i—irradiation time (s), decay constant $\lambda = \frac{\ln 2}{T_{1/2}}$ and $T_{½}$—half-life; decay factor $D = e^{-\lambda t_d}$, with t_d—decay time; correction factor during counting $C = \left(1 - e^{-\lambda t_c}\right)/\lambda t_c$, with t_c—counting time; Amount of element (g) in sample—$w = \rho W$, with ρ—concentration of element (g/g), W—sample mass (g); G_{th}, G_e—thermal and epithermal neutron self-shielding factors, respectively; Φ_{th}, Φ_e—thermal and epithermal neutron

Table 1 List of short-lived or detectable radionuclides and related nuclear data [16] for use in k_0-CNAA

Element	Radionuclide	Half-life*	Q_0	$\overline{E}_r$ (eV)	Main γ-ray energy (keV)
Ag	^{110}Ag	24.6 s	18.4	6.08	657.8
Al	^{28}Al	2.24 min	0.71	11,800	1778.9
Br	^{80}Br	17.7 min	12.1	69.3	616.2
Ca	^{49}Ca	8.72 min	0.45	1,330,000	3084.4
Cl	^{38}Cl	37.3 min	0.69	13,700	1642.4, 2167.5
Co	^{60m}Co	10.47 min	2.0	136	58.6
Cu	^{66}Cu	5.12 min	1.06	766	1039.4
Dy	^{165m}Dy	1.26 min	0.25	224	108.2
F	^{20}F	11.16 s	2.2	44,700	161.9
I	^{128}I	24.99 min	24.8	57.6	442.3
K	^{42}K	12.36 h	0.87	2,960	1524.7
Mg	^{27}Mg	9.46 min	0.64	257,000	843.8, 1014.4
Mn	^{56}Mn	2.58 h	1.05	468	846.7, 1810.7
Na	^{24}Na	14.96 h	0.59	3,380	1368.6, 2754.0
Se	^{77m}Se	17.36 s	0.77	577	161.7
Sb	^{122m}Sb	4.19 min	33	13.1	61.5
Si	^{31}Si	2.62 h	1.11	2280	1266.2
Sn	^{125m}Sn	9.52 min	60.1	74.2	331.9
Ti	^{51}Ti	5.76 min	0.67	63,200	320.1
U	^{239}U	23.45 min	103.4	16.9	74.7
V	^{52}V	3.75 min	0.55	7,230	1434.1
Au (monitor)	^{198}Au	2.69 day	15.7	5.65	411.8

* Half-lives of several radionuclides are not "short" (e.g., ^{24}Na, ^{42}K, ^{56}Mn, ^{31}Si), nevertheless, their original elements which are normally presented in biological and environmental samples as major elements, so they may be detected along with the short-lived radionuclides

fluxes, respectively; α—factor expressing for epithermal neutron distribution deviation and ε_p—full-energy peak detection efficiency [4].

Replace Eq. 2 into Eq. 1 and re-arrange we obtain:

$$A_{sp} = \frac{N_A\,\theta\gamma}{M}\left[G_{th}\,\Phi_{th}\,\sigma_0 + G_e\,\Phi_e\,I_0(\alpha)\right]\varepsilon_p \tag{3}$$

Replace the above mentioned factors and parameters into Eq. 3 we obtain the activation equation for a cycle:

$$w = \frac{N_p\,/\,t_c}{SDC}\cdot\frac{M}{N_A\,\theta\gamma}\cdot\frac{1}{\left[G_{th}\,\Phi_{th}\,\sigma_0 + G_e\,\Phi_e\,I_0(\alpha)\right]}\cdot\frac{1}{\varepsilon_p} \tag{4}$$

The "Cyclic factor" F_c for n cycles expressed [3]:

$$F_c = \left[\frac{n}{(1-e^{-\lambda T})} - \frac{e^{-\lambda T}\left(1-e^{-n\lambda T}\right)}{(1-e^{-\lambda T})^2}\right] \tag{5}$$

where, $T = t_i + t_d + t_c + t_w$ (t_w—waiting time between two cycles).

Insert Eq. 5 into Eq. 4, we obtain the activation equation for n cycles:

$$w = \frac{N_p\,/\,t_c}{SDCF_c}\cdot\frac{M}{N_A\,\theta\gamma}\cdot\frac{1}{\left[G_{th}\,\Phi_{th}\,\sigma_0 + G_e\,\Phi_e\,I_0(\alpha)\right]}\cdot\frac{1}{\varepsilon_p} \tag{6}$$

Monitor for neutron fluence during the irradiation using Eq. 4 with denote "m":

$$w_m = \left(\frac{N_p\,/\,t_c}{SDC}\right)_m\cdot\frac{M_m}{N_A\theta_m\gamma_m}\cdot\frac{1}{G_{th,m}\,\Phi_{th}\,\sigma_{0,m} + G_{e,m}\,\Phi_e\,I_{0,m}(\alpha)}\cdot\frac{1}{\varepsilon_{p,m}} \tag{7}$$

Divide Eq. 6 by Eq. 7, then replace $w = \rho W$ and re-arrange we obtain the basic equation of k_0-based cyclic neutron activation analysis (k_0-CNAA) for an analytical element with denote "a":

$$\rho = \frac{\left(\frac{N_p\,/\,t_c}{SDCWF_c}\right)_a}{A_{sp,m}}\cdot\frac{1}{k_{0,m}(a)}\cdot\frac{G_{th,m}\,f + G_{e,m}\cdot Q_{0,m}(\alpha)}{G_{th,a}\,f + G_{e,a}\cdot Q_{0,a}(\alpha)}\cdot\frac{\varepsilon_{p,m}}{\varepsilon_{p,a}} \tag{8}$$

where, $k_{0,m}(a)$—k_0-factor of monitor "m" (commonly Au) of analyte "a"; $Q_0 = I_0/\sigma_0$ and f—ratio of thermal to epithermal neutron flux [4].

The recursive algorithm for compartmental models with backward branching that applies to all activation-decay-measurement protocols, cyclic or not, as used in k_0-IAEA program for interpretation of k_0-CNAA data was developed by Blaauw [5].

Establishment of k_0-CNAA experimental procedure

Standards were prepared from standard solution containing 1,000 mg/L of sodium fluoride, diluted and doped onto cellulose papers for obtaining the fluorine concentration levels of 10, 100, and 1,000 mg kg^{-1}. Certified reference materials NIST-SRM-1633b (coal fly ash), NIST-SRM-1648 (urban particulate matter), GBW-07406 (soil) and IAEA-336 were prepared with weights of around 30 mg and put into high-purity polyethylene vials in preparation for irradiation. Sheets of polymer materials were cut and washed with alcohol and then weighted and put in pure polyethylene vials for irradiation to determine fluorine content.

An HPGe detector based γ-ray spectrometer (code "G-15") was calibrated for energy, peak-width and full energy peak detection efficiency [6]. "G-15" is using a CANBERRA GC-2018 vertical detector coupled with an ORTEC DSpec-Pro module for acquisition of γ-ray spectra using GammaVision software. The γ-ray spectrometer is connected with SIPRA (fast pneumatic transfer system) installed in the Portuguese research reactor (RPI) at a position with a thermal neutron flux $\sim 2.7 \times 10^{12}$ cm^{-2} s^{-1}. The operation of SIPRA is controlled by PC through a controller and local made software. The characterization of reactor neutron spectrum parameters at SIPRA for use in k_0-NAA was carried out by the determination of α, f, f_F (correction factor for reactions caused by fast neutrons) and thermal, epithermal and fast neutron fluxes [7].

Cyclic irradiations were performed for each sample by using SIPRA which fully automates the irradiation, decay, counting and re-irradiation. After each irradiation, the sample was allowed to decay with a predefined decay time prior to counting on the calibrated "G-15" detector. Au monitors were irradiated at the beginning and at the end of the experiment and measured after 1-day of decay on the same "G-15" detector-based γ-ray spectrometer. A program for monitoring the reactor power during operation was run on a local network to record the power in real time. At the end of the experiment, the data from the reactor power monitoring is used to calculate the variation of the neutron flux [8]. The spectra of the individual cycles of each sample were recorded as well as the accumulated spectra. Mass fractions of elements, accuracies and detection limits were determined by using the k_0-IAEA software [9]. The timing parameters of the cyclic irradiations along with the individual gamma-ray spectra were used by the software, to which three additional steps must be done. Firstly, a series text file containing the timing parameters of cyclic irradiation in milliseconds was prepared and imported in the k_0-IAEA program instead of manually inputting the data using the series database editor. An example of a series text file for k_0-CNAA containing irradiation times in milliseconds is displayed in Table 2. The spectrometer records from the nearest second while photodiodes record the irradiation to the millisecond.

Table 2 Example of a series text file for k_0-CNAA containing of irradiation times in milliseconds

"If the first cell on a row of cells does not contain a number, the line is skipped, so you can enter comments"							
Sample _number	Description		Classification matrix reporting		Geometry		Dry/wet ratio Unc
1	AS-2	REFMAT	PE	TRUE powder/liquid	1	0	NIST-1633b

"If the first cell on a row of cells does not contain a number, the line is skipped, so you can enter comments"							
Sample	Action_type	Enabled	Start_date	Start_time	Stop_date	Stop_time	Recipient
1	PACK	TRUE	12-Jan-11	12:00:00.0	12-Jan-11	18:13:27.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:13:28.0	12-Jan-11	18:14:31.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:14:32.0	12-Jan-11	18:15:36.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:15:37.0	12-Jan-11	18:16:41.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:16:42.0	12-Jan-11	18:17:44.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:17:45.0	12-Jan-11	18:18:29.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:18:30.0	12-Jan-11	18:19:46.0	PE Typo C2
1	PACK	TRUE	12-Jan-11	18:19:47.0	12-Jan-11	18:20:00.0	PE Typo C2

"If the first cell on a row of cells does not contain a number, the line is skipped, so you can enter comments"							
Sample	Action_type	Enabled	Start_date	Start_time	Stop_date	Stop_time	Facility
1	IRRAD	TRUE	12-Jan-11	18:11:20.085	12-Jan-11	18:11:29.259	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:12:24.134	12-Jan-11	18:12:33.000	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:13:29.385	12-Jan-11	18:13:38.272	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:14:33.488	12-Jan-11	18:14:42.451	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:15:38.076	12-Jan-11	18:15:46.957	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:16:43.025	12-Jan-11	18:16:51.717	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:17:46.773	12-Jan-11	18:17:55.760	SIPRA_LEU
1	IRRAD	TRUE	12-Jan-11	18:18:50.873	12-Jan-11	18:18:59.609	SIPRA__LEU

"If the first cell on a row of cells does not contain a number, the line is skipped, so you can enter comments"							
Sample	Action_type	Enabled	Start_date	Start_time	Stop_date	Stop_time	Detector
1	MEAS	TRUE	12-Jan-11	18:37:33.0	12-Jan-11	18:36:03.0	Gl5Jan11
1	MEAS	TRUE	12-Jan-11	18:38:49.0	12-Jan-11	18:37:19.0	Gl5Jan11
1	MEAS	TRUE	12-Jan-11	18:38:03.0	12-Jan-11	18:36:33.0	Gl5Jan11
1	MEAS	TRUE	12-Jan-11	18:37:18.0	12-Jan-11	18:36:48.0	Gl5Jan11
1	MEAS	TRUE	12-Jan-11	18:37:18.0	12-Jan-11	18:36:48.0	Gl5Jan11
1	MEAS	TRUE	12-Jan-11	18:37:18.0	18:37:18.0	18:36:48.0	18:36:48.0
1	MEAS	TRUE	12-Jan-11	18:37:18.0	18:37:18.0	18:36:48.0	18:36:48.0
1	MEAS	TRUE	12-Jan-11	18:37:18.0	18:37:18.0	18:36:48.0	18:36:48.0

Secondly, the timing parameters of the packaging and unpackaging of samples must be input into the program. Thirdly, the spectra for the individual cycles are read by the software and then these spectra are accumulated by the k_0-IAEA software. The detection limits reported by k_0-IAEA program are based on Currie's critical level and evaluated as a function of peak width and the local continuum level [10].

k_0-CNAA was performed for the determination of elements that form short-lived and detectable radionuclides in polymer, biological and environmental samples. The timing parameters for the determination of Se were: $t_i = t_c = 20$ s and $t_d = t_w = 5$ s performed with eight cycles. For the determination of F, the timing parameters were: $t_i = t_c = 10$ s and $t_d = t_w = 5$ s with eight cycles. The reasons for choosing these timing parameters are not only based on half-lives of the radionuclides of interest but also on interfering elements (e.g., Cl, Na) as well as on the specifications of SIPRA. The decay and waiting times were chosen at 5 s in order to ensure the transit of the sample as sometimes samples could become temporarily stuck. As shown in Figs. 1 and 2, detection limits and accuracy for the determination of elements were significantly improved after four cycles and close to saturation by eight cycles.

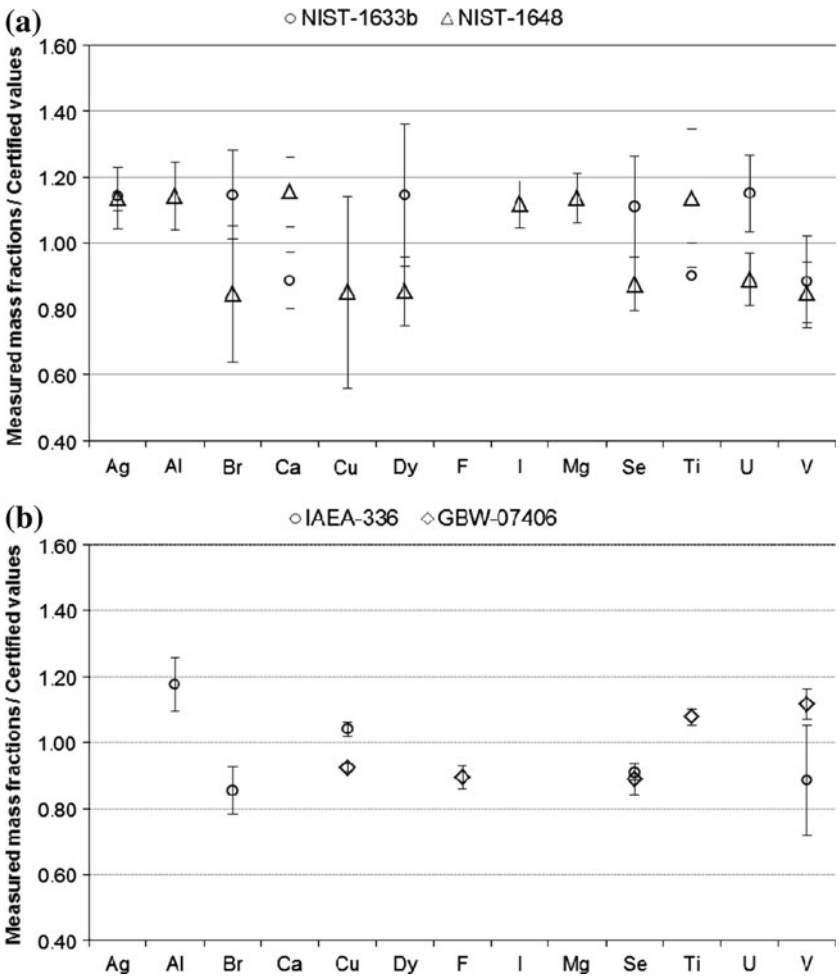

Fig. 1 Ratio of experimental results as determined by k_0-CNAA with eight cycles to certified/assigned values for samples: **a** NIST-SRM-1633b and NIST-SRM-1648; and **b** IAEA-RM-336 and GBW-07406

The digital filter of the peak-search algorithm for γ-ray spectrometry used in k_0-IAEA program has been modeled, resulting in formulas yielding Currie's critical level [11].

Results and discussion

Three replicates for all samples, fluorine standards, certified reference materials (NIST-1633b, NIST-1648, and GBW-07406), reference material (IAEA-336) and polymer materials were analysed by k_0-CNAA with eight cycles. For each sample the average mass fractions and standard deviations were calculated based on the three runs performed. A series text file was generated by a "JOB" file integrated in the ORTEC GammaVision software instead of the use of the series database editing function in k_0-IAEA program. As shown in Table 2, the series text file is divided into three parts: "Package", "Irradiate" and "Measure" in which the second one with the start and stop times were in milliseconds. These timing parameters were recorded by photodiodes installed at external and internal positions of irradiation facility (SIPRA) in the RPI reactor. In fact, the "Measure" part in the series text file makes no sense, because the k_0-IAEA program uses the correct counting time stored in the spectra. So this part is still kept in the text file for program reading but not for use in the real calculation. Although, several input parameters are required for the calculation by k_0-CNAA, however, these parameters along with the calculation are automatically processed by computer software. So, the k_0-CNAA protocol using k_0-IAEA program has still been regarded as suitable for a routine analysis in practical.

The analytical results as determined by k_0-CNAA for fluorine standards (with F content of 10, 100 and 1,000 mg kg^{-1}), GBW-07406 (soil) and polymer (synthetic fiber) are summarized in Table 3. ^{20}F and ^{77m}Se were not detected by conventional INAA in GBW-07406, however, they were detected using cyclic irradiations. Also, ^{77m}Se was not detected by conventional INAA in NIST-1633b, NIST-1648 and IAEA-336 while it was determined in all samples by k_0-CNAA with 8 cycles. The experimental results and the consensus or recommended values for F and Se were in good agreement (bias within 13% for F in NIST-1648 and Se in all samples). Similarly, F was not determined in F standards

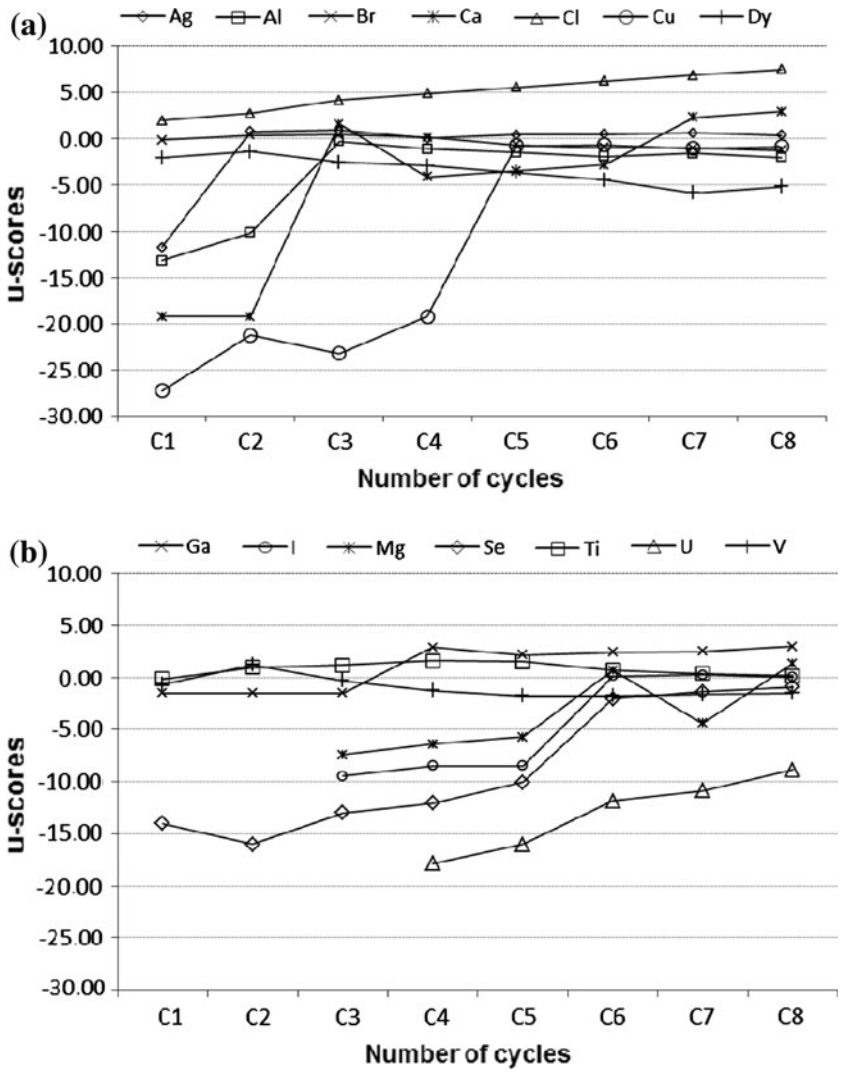

Fig. 2 k_0-CNAA as a function of the number of cycles and the *u*-scores of elements: **a** Ag, Al, Br, Ca, Cl, Cu and Dy; and **b** Ga, I, Mg, Se, Ti, U and V

with contents being lower or equal to 100 mg kg^{-1}, but the problem was solved by k_0-CNAA and the bias between the experimental results and the assigned values was within 4% for 1,000 mg kg^{-1} and 9% for 100 mg kg^{-1}. Besides the determination of F and Se, k_0-CNAA also allowed for the determination of other short-lived or detectable radionuclides such as Al, Ca, Cu, Dy, I, Mg, Ti, and V. Moreover, in Table 3, it turned out that CNAA allowed for the determination of I, Sr and U, all of which are difficult to measure in the samples by conventional INAA [12].

It should be noted that several radionuclides with complex decay schemes, such as ^{165m}Dy ($T_{1/2}$ = 1.26 m) decays to ^{125}Dy ($T_{1/2}$ = 2.33 h), so the analytical result for Dy determined by CNAA was not as good as when determined by conventional INAA in which the measurements were done after a decay time of several hours so that ^{165m}Dy was completely decayed to ^{165}Dy.

Table 4 shows the analytical results by k_0-CNAA optimized for the determination of F in polymer materials, however, it also reconfirmed, as above, that the same experiment allowed simultaneous determination of several other short-lived or detectable radionuclides such as Cl, Cu, Ti and V. It also should be noted that the high concentration of Al and Cl in polymer material contributes to a high count rate increasing the difficulty of measuring F. Therefore, cumulative mode with lesser sample mass was applied for CNAA in order to decrease the dead time. CNAA has improved the detection limits of F by a factor of 1.9 times and Se by about 1.7 times. The improvement for determination of selenium by k_0-CNAA using ^{77m}Se has proved the study of Hou and Das [13] for which the cyclic INAA enhances the precision and sensitivity with a factor of the square root of the applied number of cycles. The analytical results of the F standards revealed that it was not possible to measure 10 mg kg^{-1} F level with CNAA. However, they were in good agreement with the standard values in levels 100 mg kg^{-1} (bias of 9%) and 1,000 mg kg^{-1} (bias of 4%). Using k_0-CNAA we have

Table 3 Analytical results as determined by k_0-CNAA with eight cycles for fluorine standards, certified reference material (soil-GBW07406) and polymer materials

Elements	F-10		F-100		F-1000	
	x_{ref}	$x_{exp} \pm u_{exp}$	x_{ref}	$x_{exp} \pm u_{exp}$	x_{ref}	$x_{exp} \pm u_{exp}$
F	10	n.d.	100	91 ± 24	1,000	970 ± 150

	Soil (GBW-07406)		Polymer 1	Polymer 2	Polymer 3
	$x_{ref} \pm u_{ref}$	$x_{exp} \pm u_{exp}$	$x_{exp} \pm u_{exp}$	$x_{exp} \pm u_{exp}$	$x_{exp} \pm u_{exp}$
F	906 ± 45	890 ± 90	380 ± 60	630 ± 140	4,300 ± 240
Cl	95 ± 7	103 ± 9	35 ± 4	120 ± 9	115 ± 5
Cu	390 ± 14	377 ± 21	n.d.	n.d.	n.d.
Se	1.34 ± 0.17	1.29 ± 0.36	n.d.	n.d.	n.d.
Ti	4,390 ± 120	4,530 ± 170	650 ± 70	880 ± 80	750 ± 70
V	130 ± 7	135 ± 12	140 ± 8	115 ± 7	165 ± 9

All data in mg kg^{-1}

n.d.—not determined; x_{ref}, u_{ref}—certified and uncertainty values; x_{exp}, u_{exp}—experimental and uncertainty values, respectively; polymer—synthetic fiber

Table 4 The analytical results (three replicates) as determined by k_0-CNAA with eight cycles

Element	NIST-1633b (coal fly ash)			NIST-1648 (particulate matter)			IAEA-336 (lichen material)		
	Exp ± Unc	Cert ± Unc	u-score	Exp ± Unc	Cert ± Unc	u-score	Exp ± Unc	Cert ± Unc	u-score
Se	11 ± 3	10.0 ± 0.4	1.53	21 ± 3	24 ± 2	−0.83	0.20 ± 0.07	0.91	−0.25
Ag	0.8 ± 0.2	0.7 ± 0.1	0.45	6.7 ± 0.7	5.9 ± 0.5	0.93	n.d.	–	–
Al (%)	n.d.	–	–	3.8 ± 0.4	3.33 ± 0.22	1.03	0.08 ± 0.01	1.18	0.81
Br	3.3 ± 0.7	2.88 ± 0.09	1.34	420 ± 30	497 ± 22	−2.07	11 ± 2	0.85	−0.72
Ca (%)	1.4 ± 0.3	1.58 ± 0.07	−0.85	6.7 ± 0.8	5.8 ± 0.3	1.05	n.d.	–	–
Cu	n.d.	–	–	509 ± 24	598 ± 19	−2.91	3.7 ± 0.4	1.04	0.22
Dy	19 ± 2	16.6 ± 0.5	2.15	5.2 ± 0.7	6.1 ± 0.5	−1.05	n.d.	–	–
I	n.d.	–	–	19 ± 2	17 ± 2	0.71	n.d.	–	–
Mg (%)	n.d.	–	–	0.84 ± 0.09	0.74 ± 0.10	0.74	n.d.	–	–
Ti (%)	7.11 ± 0.15	7.90 ± 0.5	−1.01	4.63 ± 0.19	4.08 ± 0.18	2.10	n.d.	–	–
U	10 ± 2	8.7 ± 0.5	1.16	4.8 ± 0.7	5.4 ± 0.3	−0.79	n.d.	–	–
V	260 ± 30	295 ± 15	−1.40	107 ± 19	126 ± 9	−0.90	1.3 ± 0.1	0.88	−1.67

"Exp" and "Cert"—experimental results and certified values [14], respectively, (mg kg^{-1}, except Al, Ca, Mg and Ti in %); "Unc"—expanded uncertainty (95% confidence interval)

determined the concentrations of Se and other short-lived or detectable radionuclides in all four samples, the results of which are shown in Fig. 1: NIST-1633b, NIST-1648, IAEA-336, and GBW-07406. The biases between the results and the certified values were within 15%, except for Dy in NIST-1633b (biased 21%), Br, Cu, and Ti in NIST-1648 (biased 21, 29 and 21%, respectively).

The detection limit of F as determined by k_0-CNAA was limited to 50 mg kg^{-1} in polymer (synthetic fiber) due to the presence of Al and Cl, and the detection limit of Se was 0.01 and 0.1 mg kg^{-1} in biological and environmental samples, respectively. A correction for ^{20}F produced by the reaction ^{23}Na(n,α)^{20}F was made by calculating the contribution of fast neutrons and the sodium. Because the reaction ^{19}F(n,γ)^{20}F has a high resonance integral cross-section, the detection limit for determination of F can be improved using epithermal neutrons [15] as observed in Table 1 for elements with high Q_0-values (e.g. Ag, Br, Co, F, I, Sb, Sn, and U).

Figure 2 displays the improvement of the results through the relationship between the u-score, a quantity showing the agreement between the experimental result and the certified value taking into account the uncertainties [17], and the number of cycles.

Conclusions

The k_0-based cyclic neutron activation analysis (k_0-CNAA) has been studied to explore the applicability for determination of elements forming short-lived or detectable radionuclides, in particular fluorine (^{20}F) in polymer material with detection limit about 50 mg kg^{-1} and selenium (^{77m}Se) in biological and environmental matrices with

detection limits of 0.01 and 0.1 mg kg^{-1}, respectively. The k_0-CNAA has lowered the detection limits of Se in comparison with the determination through long-lived radionuclide (^{75}Se) by a factor of 3.1 and 2.5 in biological and environmental samples, respectively. Moreover, the other elements forming short-lived or detectable radionuclides were also determined from the same spectra, i.e. Al, Ca, Cu, I, Mg, Ti, and V. Quality control was carried out by analyzing certified reference materials and fluorine standards in different concentration ranges. The experimental results were in agreement with the certified or assigned values for which the results for determination of F was biased 12% at 1,000 mg kg^{-1} and within 15% at 10–100 mg kg^{-1} range, and the determination of Se was biased within 11 and 13% for biological and environmental samples. The k_0-IAEA software has fully met the needs of the study for k_0-CNAA with the automation of complicated data processing as required by the k_0-NAA method as well as multi-spectra processing of cyclic irradiations.

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