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# Quality control and performance evaluation of $k_0$-based neutron activation analysis at the Portuguese research reactor

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ABSTRACT

The quality control (QC) and performance evaluation for the $k_0$-based neutron activation analysis ($k_0$-NAA) at the Portuguese research reactor (RPI) has been developed with the intention of using the method to meet the demands of trace element analysis for the applications in environmental, epidemiological and nutritional studies amongst others. The QC and performance evaluation include the following aspects: (1) estimation of the overall/combined standard uncertainty from the primary uncertainty sources; (2) validation of the method using a synthetic multi-element standard (SMELS); and (3) analysis of the certified reference materials from the National Institute of Standards and Technology (USA): NIST-SRM-1633a and NIST-SRM-1648 and the reference material from the International Atomic Energy Agency: IAEA-RM-336, for the purpose of controlling the overall accuracy and precision of the analytical results. The obtained results revealed that the $k_0$-NAA method established at the RPI was fit for the purpose. The overall/combined standard uncertainty was estimated for elements of interest in the intended applications. The laboratory's analytical results as compared to the assigned values with the bias were less than 12% for most elements, except for a few elements which biased within 13–18%. The *u*-score values for most elements were less than $|1.64|$, except for Co, La and Ti within $|1.64|-|1.96|$ and Sc, Cr, K and Sb within $|1.96|-|2.58|$. The NIST-1633a was also analyzed over 14 months for the purpose of evaluating the reproducibility of the method. The quality factors of $k_0$-NAA established at RPI were evaluated, proving that the method meets the requirements of trace element analysis, which is also considering the method's performance for which the $k_0$-NAA affords a specific, rapid and convenient capability for the intended applications.

## 1. Introduction

According to the International Standard ISO/IEC-17025: 2005 requirements [1], the analytical laboratory has to establish the scope of the measurements as well as the necessary equipment, the certified reference materials (CRMs) and the standard operation procedures (SOPs), etc. In particular, the laboratory has to estimate the measurement uncertainty. The necessity of reporting the uncertainties associated with the measurement results has been stated by ISO and EURACHEM [2,3]. This study was performed in order to implement the quality control (QC) and performance evaluation for $k_0$-NAA established at the RPI.

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. The calibration of the HPGe detector is performed by determining the full-energy peak detection efficiency ($\varepsilon_p$) and the correction factors, e.g. true-coincidence (COI) and sample geometry effects. The neutron spectrum parameters describe the deviation from the ideal $1/E$ epithermal neutron distribution ($\alpha$), the thermal to epithermal neutron flux ratio ($f$), the thermal to fast neutron flux ratio ($f_F$) and the neutron temperature ($T_n$). The Au, Lu, Ni and Zr monitors are suitable for use in both theoretical and practical viewpoints to determine the neutron parameters $\alpha$, $f$, $f_F$ and $T_n$. 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 sample and monitor on a properly calibrated HPGe detector [4].

The 34 elements: Al, Ca, Cu, Mn, Ti, V, As, Ba, Br, K, La, Na, U, Ag, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Rb, Sb, Sc, Se, Sm, Sr, Ta, Tb, Th, Yb and Zn that are commonly found in environmental, epidemiological and nutritional samples were used to determine the scope of the $k_0$-NAA method that was established at the RPI reactor. The first six elements in the above list that produce short-lived nuclides were normally analyzed by a short irradiation on SIPRA (a fast pneumatic sample transfer system), and then counted on a coupled-HPGe detector. The elements from As to U in the above list that produce

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medium-lived nuclides can be detected by the use of a Compton suppression system (CSS) with and without anti-Compton modes enabled [5] after allowing the associated decay times to elapse. The elements from Ag to Zn in the above list that produce long-lived nuclides were analyzed by an irradiation for long times at Cell 55 or Cell 56 of the RPI reactor then measured on ORTEC HPGe detector-based automatic sample changers. After allowing the associated decay times to elapse, the medium and long-lived nuclides can be detected by the two measurements, respectively. The elements of the medium-lived nuclide group were determined by both irradiation modes for the purpose of comparison and quality control.

All equipment used for $k_0$-NAA at RPI was determined to be working correctly within the manufacturer's specifications and properly calibrated. The performance of the $\gamma$-ray spectrometers was confirmed by evaluating background and FWHM measurements weekly, and biannually for full-energy peak detection efficiency. The characterization of the irradiation facilities was performed whenever the reactor configuration or fuel was changed (the most recent changes were conducted in 2000 and 2007). The sample preparation devices had detailed instructions on their proper use and operation, in which the analytical balance was of great importance. The $k_0$-IAEA program [6] was used for processing of the experimental data in this study.

The QC and performance evaluation works carried out in this study have included aspects: the estimation of the overall/combined standard uncertainty; the validation of the method using SMELS, a synthetic multi-element standard [7] with three different types of elements that produce short, medium and long-lived radionuclides when irradiated with neutrons; and the analysis of certified reference materials NIST-SRM-1633a (coal fly ash), NIST-SRM-1648 (urban particulate matter) and reference material IAEA-RM-336 (lichen) with the intention of controlling the overall accuracy of the analytical results. Internal quality control at the chemical analytical laboratory, involves a continuous, critical evaluation of the laboratory's own analytical methods and working routines, so the analysis of NIST-SRM-1633a over 14 months were also performed for the purpose of evaluating the reproducibility of the method.

In order to evaluate the laboratory performance, the $u$-score test [8] was used in which the $u$-score is calculated according to the following equation: $u\text{-score}=(x_{lab}-x_{ref})/\sqrt{u_{lab}^2+u_{ref}^2}$, where $x_{\text{lab}}$ and $u_{lab}$ are the laboratory result and overall/combined standard uncertainty, respectively; $x_{ref}$ and $u_{ref}$ are the reference (assigned) value and standard uncertainty, respectively. The laboratory overall/combined standard uncertainty ($u_{lab}$) of $k_0$-NAA, established at RPI/ITN, is calculated by the law of the propagation of component uncertainties. The consensus/assigned values for which the reference uncertainty ($u_{ref}$) used are the standard uncertainty (=standard deviation/$\sqrt{n}$, with $n$ is the number of replicates). The results of the laboratory are interpreted according to the 5 possible evaluation classes as follows: (1) $u<1.64$, the laboratory result does not differ significantly from the assigned value; (2) $1.96>u>1.64$, the laboratory result probably does not differ significantly from the assigned value; (3) $2.58>u>1.96$, it is not clear whether the laboratory result differs significantly from the assigned value; (4) $3.29>u>2.58$, the laboratory result is probably significantly different from the assigned value; (5) $u>3.29$, the laboratory result is significantly different from the assigned value.

## 2. Experimental

### 2.1. Sample preparation and irradiation

Typically, monitors with masses of 15 mg for Al–0.1%Au and Al–0.1%Lu, 20 mg for pure Ni and Zr were irradiated for 15 min and allowed to decay for 3–5 h, $^{65}$Ni and $^{176m}$Lu, 1 day decay for $^{97}$Zr and 3 days decay for $^{198}$Au, $^{177}$Lu, $^{95}$Zr and $^{58}$Co prior counting. The NIST-SRM-1633a and NIST-SRM-1648 were dried for 2 h at 80 °C, with resulting moisture contents of 2.58% and 2.71%, respectively. The IAEA-RM-336 was dried at 60 °C for 1 h, with a resulting moisture content of 4.16%. The RMs and SMELS were weighed around 150–200 and 100–150 mg, respectively and put into pure polyethylene vials in preparation for irradiation. Short irradiations were conducted for 100 s for each sample on SIPRA at a thermal neutron flux of about $2.7\times10^{12}\ \text{cm}^{-2}\,\text{s}^{-1}$ and allowed to decay for 10 s prior to counting of 200 s. The Al–0.1%Au monitors were irradiated on SIPRA at the starting and ending times of the sample irradiation in order to monitor the flux variation during the period of irradiation. A reactor power display program in real-time mode was also applied in order to observe the neutron flux variation.

For long-term irradiation, the samples together with the Au monitors (usually three Au monitors positioned at top, middle and bottom of irradiation containers) were irradiated for 1 h on Cell 55 or 5 h on Cell 56, with thermal neutron fluxes about $8.4\times10^{12}$ and about $2.4\times10^{12}\ \text{cm}^{-2}\,\text{s}^{-1}$, respectively, and allowed to decay for 3 days and 3 weeks prior to performing the first and second measurements, respectively, for each sample.

In order to evaluate the variation of the flux in the irradiation container, the Cu wires were positioned along the inside wall of the container. The distribution of the neutron flux in the container obtained in this study generally increased along the direction from top to bottom of the irradiation container with a gradient about 1.9% and 2.1% per cm at Cell 55 and Cell 56, respectively.

### 2.2. Gamma-ray spectrum measurement

The monitors and samples were measured on the calibrated HPGe detectors with the FWHM approximately 1.85 keV at 1332.5 keV and the relative efficiency of 30%. The calibration of gamma-ray spectrometers was performed by a series of measurements with point sources $^{137}$Cs, $^{133}$Ba, $^{109}$Cd, $^{60}$Co and $^{152}$Eu at reference positions ($>150$ mm far from detector end cap). The computation of all parameters for the calibration of energy, peak-shape and full-energy peak detection efficiency, and the correction of true-coincidence and sample geometry effects were carried out by $k_0$-IAEA software. The counting time for each monitor ranged 1–5 h to obtain a minimum of 10,000 counts in the peak of interest. After counting each monitor, a combination of selected monitors was re-measured. The long-term irradiated samples were counted with counting times of 1 h for the first measurement (3-day decay) and 3 h for the second measurement (3-week decay).

### 2.3. Determination of neutron spectrum parameters and calculation of mass fractions of elements

The gamma-ray spectra of monitors and samples were interpreted by $k_0$-IAEA program in which the Au ($^{198}$Au) and Zr ($^{95}$Zr/$^{97}$Zr) spectra were used to calculate for $\alpha$ and $f$, while the Ni ($^{58}$Co/$^{65}$Ni) and Lu ($^{176m}$Lu/$^{177}$Lu) spectra together with $^{198}$Au spectrum were used to calculate for $f_F$ and $T_n$. The mass fractions of elements in sample were interpreted by the gamma-ray spectra of samples using the efficiency curves and the neutron parameters stored in so-called permanent database of the program. The efficiency values for the sample are practically converted from the reference efficiency curve by the correction of true-coincidence and sample geometry effects. The efficiency conversion was performed by Monte-Carlo calculations, for which the option for precision and threshold of interpretation can be changed or turned-off by the user. The monitors Au are usually co-irradiated together with samples to monitor the thermal neutron flux in the irradiation container, with an assumption that the other neutron parameters are constant over time at the irradiation position in reactor. The samples according to $k_0$-IAEA program are categorised into: "Source" for extracting the efficiency values; "Comparator" for dealing with the neutron parameters; "Ordinary" and "Reference Material" are subject to the samples. For "Reference Material" sample, if the permanent database of the program consists of, the certified reference values the program gives the analytical results in terms of mass fractions and accuracy of the sample compared to the certified reference values and the *u*-score values are also calculated and shown. In brief, the $k_0$-IAEA program has worked out the essential tasks required by the $k_0$ methodology, i.e. the calibration of gamma-ray spectrometer, the determination of neutron parameters, the correction of effects (e.g. COI, geometry), the calculation of mass fractions of elements, accuracies, precisions and detection limits as well. In addition, the program can perform the analysis of gamma-ray spectra by a so-called "Holistic" method [9] based-on linear least squares techniques. In this method, the peak areas in a gamma-ray spectrum are considered to be the linear sums of the contributions of the individual components of the sample. These components are radionuclides that are produced from elements constituting the sample.

### *2.4. Calculation of overall/combined standard uncertainty*

The overall/combined standard uncertainty of the $k_0$-NAA method was calculated from the uncertainties grouped into four categories as shown in Table 1: (1) the nuclear data taken from the literature [10,11], i.e. $k_0$-factors, half-life ($T_{1/2}$), resonance integral to thermal neutron cross-section ratio ($Q_0$) and effective resonance energy ($\bar{E}_r$); (2) the calibration of the γ-ray spectrometer (determining $\varepsilon_p$, COI); (3) the characterization of irradiation facility (monitoring $\alpha$, $f$, $f_F$, $T_n$); (4) the operating analysis parameters, e.g. sample mass ($W$), Au monitor composition, irradiation-decay-counting times ($t_i$, $t_d$, $t_c$), flux variation, net peak area ($N_p$), sample geometry, etc. The spreadsheet approach [12] for the calculation of the overall/combined standard uncertainty of $k_0$-NAA was applied for the elements of interest. An example for the calculation of As in the sample is as follows (with uncertainties in parenthesis): for irradiation facility: $f$=105 (10.5%); $\alpha$=0.037 (45%); for monitor Au: mass=0.00671 g (0.1%); composition=0.001003 (0.6%); $t_i$, $t_d$ and $t_c$=5 h, 11 d, 300 s, respectively; $N_p$=47,852 (0.5%); $\varepsilon_p$=1.26E-2 (1.2%); for sample (As): mass=0.02510 g; $t_d$ and $t_c$=4 d and 7 h, respectively; $N_p$=654,560 (0.9%); $\varepsilon_p$=5.45E-2 (1.3%). The calculated mass fraction of As is 147 mg/kg with an uncertainty of 2.9%. In this example, the contribution of components is of 44% for calibration of spectrometry, 33% for nuclear data, 11% for spectrum analysis, 4% for Au composition, 5% for the characterization of irradiation facility and others, for instance, the moisture in sample. The overall/combined standard uncertainties obtained were mostly in the range 2.5–4.3% and this figure may be compared with the overall uncertainty estimated previously by De Corte [4].

**Table 1**
Categories of parameters and corresponding uncertainties in $k_0$-NAA.

| Categories | Parameters | Uncertainties |
|---|---|---|
| Nuclear data[a] | $k_0$ | $u(k_0)$ |
| | $T_{1/2}$ | $u(T_{1/2})$ |
| | $Q_0$ | $u(Q_0)$ |
| | $\bar{E}_r$ | $u(\bar{E}_r)$ |
| Calibration of γ-ray spectrometer | Efficiency $\varepsilon_p$ | $u(\varepsilon_p)$ |
| | COI[b] | $u$(COI) |
| Characterization of irradiation facility | $\alpha$ | $u(\alpha)$ |
| | $f$ | $u(f)$ |
| | $f_F$ | $u(f_F)$ |
| | $T_n$ | $u(T_n)$ |
| Steps of analysis: sample preparation, irradiation, measurement and calculation | Sample mass ($W$) | $u(W)$ |
| | Au composition | $u$(Au) |
| | $t_i$, $t_d$, $t_c$ | $u(t_i)$, $u(t_d)$, $u(t_c)$ |
| | Space flux variation ($F_s$) | $u(F_s)$ |
| | Time flux variation ($F_t$) | $u(F_t)$ |
| | Net peak area ($N_p$) | $u(N_p)$ |
| | Count. geometry ($C_{geo}$) | $u(C_{geo})$ |

[a] The $k_0$-factors and related nuclear data together with their corresponding uncertainties were taken from the literature [10,11] for each element of interest.

[b] The cascade coincidence correction factor (COI) was estimated by De Corte [4]. In this study the real correction factors (COI) were estimated by the conversion of reference efficiency curve to the sample efficiency values. (All uncertainties in the last three categories were taken from the real experimental values e.g. the net peak area, efficiency, COI, geometry, etc.,; however, for several parameters such as space and time flux variation the uncertainties were taken by an estimation by experiment).

## 3. Results and discussion

While evaluating the combined standard uncertainty of the $k_0$-NAA method, in this study, it was observed that the main uncertainty sources from large to small were the calibration of spectrometry, nuclear data, spectrum analysis, monitor composition and characterization of irradiation facility amongst others. It should be noted that the uncertainty of the half-life and irradiation, decay and counting times increased for short-lived radionuclides.

Table 2 shows the results for the determination of mass fractions of elements in SMELS Types I, II and III by $k_0$-NAA established at RPI. The mean value of six determinations is displayed in the column "$x_{lab} \pm u_{lab}$", where $x_{lab}$ and $u_{lab}$ are the laboratory results and overall/combined standard uncertainties, respectively. The ratio of the laboratory results to the assigned/recommended values and the *u*-score values is displayed in columns "$x_{lab}/x_{ref}$ Ratio" and "*u*-score", respectively. Generally, the biases of the laboratory results as compared to the assigned values in SMELS types I, II and III were less than 5% with the *u*-score values less than $|1.64|$ for most elements, except for Sr in Type III which was equal to 1.64.

The analytical results for NIST-SRM-1633a, NIST-SRM-1648 and IAEA-RM-336 are summarized in Table 3. They revealed that for most elements the laboratory results and the consensus (or assigned/recommended) values were in good agreement (bias within 12% with *u*-score values less than $|1.96|$), except for Ba and Ti in NIST-1633a, which were biased −13% and +15%, respectively, with only *u*-score value for Sc was 2.23. For NIST-1648, most of the elements were biased within 12%, except for Cs, Hf, U and Yb which were biased −17%, −15%, −13% and −13%, respectively. Although the noticeable deviations over 12% for the above mentioned elements were all in negative direction, but the results in Table 3 also show various elements with the deviation in positive direction. The *u*-score values for most elements were less than $|1.96|$, except for Cr, K and Sb which were of 2.50, 2.22 and 2.12, respectively. For IAEA-336, most of the elements were biased within 12%, except for Cs and Rb were biased

**Table 2**
Mass fractions (mg/kg) of elements in SMELS Types I, II and III determined by $k_0$-NAA established at RPI using $k_0$-IAEA software.

| Element | SMELS Type I | | | | SMELS Type II | | | | SMELS Type III | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{lab}$ ($n=6$) | $x_{lab}/x_{ref}$ ratio | $u$-score | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{lab}$ ($n=6$) | $x_{lab}/x_{ref}$ ratio | $u$-score | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{lab}$ ($n=6$) | $x_{lab}/x_{ref}$ ratio | $u$-score |
| As | – | | | | 92.3 ± 1.8 | 91.1 ± 3.7 | 0.99 | −0.30 | – | | | |
| Au | 82.7 ± 0.9 | 80.9 ± 1.8 | 0.98 | −0.90 | 3.93 ± 0.04 | 3.81 ± 0.08 | 0.97 | −1.39 | 0.901 ± 0.008 | 0.921 ± 0.018 | 1.02 | 1.04 |
| Br | – | | | | 157 ± 3 | 154 ± 6 | 0.98 | −0.52 | – | | | |
| Ce | – | | | | 15600 ± 400 | 15918 ± 812 | 1.02 | 0.35 | – | | | |
| Cl | 4330 ± 85 | 4505 ± 161 | 1.04 | 0.96 | – | | | | – | | | |
| Co | – | | | | – | | | | 24.3 ± 0.2 | 23.7 ± 0.4 | 0.97 | −1.49 |
| Cr | – | | | | – | | | | 86.7 ± 1.3 | 89.4 ± 2.4 | 1.03 | 0.98 |
| Cs | 897 ± 19 | 856 ± 43 | 0.95 | −0.87 | – | | | | 20.80 ± 0.17 | 21.8 ± 0.7 | 1.05 | 1.39 |
| Cu | 3930 ± 60 | 3917 ± 119 | 1.00 | −0.10 | – | | | | – | | | |
| Fe | – | | | | – | | | | 8200 ± 95 | 7885 ± 195 | 0.96 | −1.45 |
| I | 152 ± 3 | 155 ± 6 | 1.02 | 0.45 | – | | | | – | | | |
| In | – | | | | – | | | | 462 ± 10 | 486 ± 21 | 1.05 | 1.05 |
| La | 265 ± 5 | 255 ± 11 | 0.96 | −0.83 | – | | | | – | | | |
| Mn | 113.9 ± 1.7 | 112.4 ± 3.6 | 0.99 | −0.38 | – | | | | – | | | |
| Mo | – | | | | 5170 ± 125 | 5442 ± 290 | 1.05 | 0.86 | – | | | |
| Pr | – | | | | 1193 ± 19 | 1147 ± 35 | 0.96 | −1.15 | – | | | |
| Sb | – | | | | 172 ± 4 | 169 ± 7 | 0.98 | −0.43 | 51.2 ± 0.7 | 49.7 ± 1.4 | 0.97 | −0.95 |
| Sc | – | | | | – | | | | 1.140 ± 0.016 | 1.162 ± 0.035 | 1.02 | 0.58 |
| Se | – | | | | – | | | | 131 ± 3 | 137 ± 5 | 1.05 | 1.03 |
| Sr | – | | | | – | | | | 8150 ± 100 | 8490 ± 182 | 1.04 | 1.64 |
| Th | – | | | | 3670 ± 90 | 3851 ± 189 | 1.05 | 0.87 | 26.2 ± 0.5 | 25.7 ± 0.9 | 0.98 | −0.50 |
| Tm | – | | | | – | | | | 23.3 ± 0.4 | 24.0 ± 0.7 | 1.03 | 0.89 |
| V | 39.0 ± 0.8 | 38.0 ± 1.7 | 0.97 | −0.53 | – | | | | – | | | |
| Yb | – | | | | 187 ± 5 | 180 ± 9 | 0.96 | −0.70 | 20.7 ± 0.3 | 21.3 ± 0.4 | 1.03 | 1.28 |
| Zn | – | | | | 6570 ± 100 | 6916 ± 211 | 1.05 | 1.48 | 618 ± 6 | 613 ± 16 | 0.99 | −0.29 |
| Zr | – | | | | – | | | | 4580 ± 50 | 4490 ± 99 | 0.98 | −0.81 |

$x_{lab}$ and $u_{lab}$ – the laboratory results and overall/combined standard uncertainties, respectively; $x_{ref}$ and $u_{ref}$ – the assigned values and standard uncertainties, respectively; $n$—replicate number.

**Table 3**

The analytical results of NIST-SRM-1633a, NIST-SRM-1648 and IAEA-RM-336 in term of mass fractions in mg/kg (unless shown for Al, Ca, Fe and K in %).

| Element | NIST-SRM-1633a (coal fly ash) | | | | NIST-SRM-1648 (urban particulate matter) | | | | IAEA-RM-336 (lichen material) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{com}$ $(n=15)$ | $x_{lab}/x_{ref}$ ratio | $u$-score | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{com}$ $(n=6)$ | $x_{lab}/x_{ref}$ ratio | $u$-score | $x_{ref} \pm u_{ref}$ | $x_{lab} \pm u_{lab}$ $(n=6)$ | $x_{lab}/x_{ref}$ ratio | $u$-score |
| Ag | (0.076) | – | | | 5.9 ± 0.2 | 6.5 ± 2.3 | 1.10 | 0.26 | – | – | | |
| Al (%) | 14.20 ± 0.05 | 13.6 ± 1.4 | 0.96 | −0.43 | 3.33 ± 0.06 | 3.15 ± 0.25 | 0.95 | −0.70 | (0.068 ± 0.011) | – | | |
| As | 145 ± 1 | 148 ± 5 | 1.02 | 0.59 | 115 ± 1 | 120 ± 3 | 1.04 | 1.58 | 0.63 ± 0.01 | 0.6 ± 0.1 | 0.95 | −0.30 |
| Ba | 1390 ± 13 | 1214 ± 347 | 0.87 | −0.51 | 750 ± 13 | 670 ± 103 | 0.89 | −0.77 | 6.4 ± 1.1 | – | | |
| Br | 2.22 ± 0.05 | 2.35 ± 0.27 | 1.06 | 0.47 | 497 ± 7 | 517 ± 10 | 1.04 | 1.64 | 12.9 ± 1.7 | 11.6 ± 1.6 | 0.90 | −0.56 |
| Ca(%) | 1.12 ± 0.08 | 1.21 ± 0.08 | 1.08 | 0.80 | 5.8 ± 0.1 | 5.7 ± 0.3 | 0.98 | −0.32 | | – | | |
| Cd | 0.98 ± 0.01 | – | | | 73 ± 1 | 70 ± 13 | 0.96 | −0.28 | (0.117 ± 0.015) | – | | |
| Ce | 172 ± 1 | 164 ± 17 | 0.95 | −0.47 | 52 ± 1 | 50 ± 7 | 0.97 | −0.25 | 1.28 ± 0.17 | 1.3 ± 0.2 | 1.02 | 0.08 |
| Co | 44.0 ± 0.4 | 46 ± 1 | 1.05 | 1.86 | 17 ± 1 | 16 ± 5 | 0.94 | −0.20 | 0.29 ± 0.05 | – | | |
| Cr | 194 ± 1 | 210 ± 16 | 1.08 | 1.00 | 390 ± 10 | 429 ± 12 | 1.10 | 2.50 | (1.06 ± 0.17) | – | | \ |
| Cs | 10.4 ± 0.1 | 9.9 ± 1.0 | 0.95 | −0.50 | 3.5 ± 0.1 | 2.9 ± 0.5 | 0.83 | −1.18 | 0.110 ± 0.013 | 0.13 ± 0.01 | 1.18 | 1.22 |
| Cu | 118 ± 1 | – | | | 598 ± 3 | 570 ± 35 | 0.95 | −0.80 | 3.6 ± 0.5 | 4.0 ± 0.5 | 1.11 | 0.57 |
| Eu | 3.60 ± 0.05 | 3.7 ± 0.2 | 1.03 | −0.49 | 0.88 ± 0.04 | 0.78 ± 0.16 | 0.89 | −0.61 | (0.023 ± 0.004) | 0.025 ± 0.003 | 1.09 | 0.40 |
| Fe (%) | 9.36 ± 0.29 | 9.73 ± 0.16 | 1.04 | 1.12 | 3.87 ± 0.04 | 3.87 ± 0.07 | 1.00 | 0.00 | 0.043 ± 0.005 | 0.042 ± 0.001 | 0.98 | −0.20 |
| Hf | 7.2 ± 0.1 | 6.4 ± 0.8 | 0.89 | −0.99 | 4.7 ± 0.2 | 4.0 ± 0.8 | 0.85 | −0.85 | | – | | |
| Hg | 0.148 ± 0.005 | – | | | 4.0 ± 0.3 | 3.7 ± 0.5 | 0.93 | −0.51 | 0.20 ± 0.04 | – | | |
| K (%) | 1.89 ± 0.01 | 1.95 ± 0.17 | 1.03 | 0.35 | 1.00 ± 0.02 | 1.08 ± 0.03 | 1.08 | 2.22 | 0.18 ± 0.02 | 0.19 ± 0.02 | 1.06 | 0.35 |
| La | 83 ± 1 | 80 ± 3 | 0.91 | −0.95 | 40 ± 2 | 36 ± 1 | 0.90 | −1.79 | 0.66 ± 0.10 | 0.6 ± 0.1 | 0.91 | −0.42 |
| Mn | 182 ± 2 | 166 ± 13 | 0.91 | −1.22 | 823 ± 8 | 754 ± 37 | 0.92 | −1.82 | 63 ± 7 | – | | |
| Na | 1740 ± 14 | 1757 ± 32 | 1.01 | 0.49 | 4300 ± 106 | 4404 ± 110 | 1.02 | 0.68 | 320 ± 40 | 338 ± 28 | 1.06 | 0.37 |
| Rb | 134 ± 1 | 143 ± 16 | 1.07 | 0.56 | 56 ± 1 | 51 ± 9 | 0.91 | −0.55 | (1.76 ± 0.22) | 2.0 ± 0.5 | 1.14 | 0.44 |
| Sb | 6.7 ± 0.1 | 6.3 ± 0.6 | 0.94 | −0.66 | 42 ± 1 | 45 ± 1 | 1.07 | 2.12 | 0.073 ± 0.010 | 0.07 ± 0.01 | 0.96 | −0.21 |
| Sc | 39.0 ± 0.3 | 40.7 ± 0.7 | 1.04 | 2.23 | 6.9 ± 0.1 | 6.3 ± 0.3 | 0.91 | −1.90 | (0.17 ± 0.02) | 0.18 ± 0.01 | 1.06 | 0.45 |
| Se | 9.6 ± 0.2 | – | | | 24 ± 1 | 22 ± 2 | 0.92 | −0.89 | 0.22 ± 0.04 | – | | |
| Sm | 16.5 ± 0.2 | 17.6 ± 1.2 | 1.07 | 0.90 | 4.4 ± 0.2 | 3.9 ± 0.4 | 0.89 | −1.12 | 0.106 ± 0.014 | 0.10 ± 0.02 | 0.94 | −0.25 |
| Sr | 820 ± 7 | 794 ± 159 | 0.97 | −0.16 | 270 ± 35 | – | | | 9.3 ± 1.1 | – | | |
| Ta | 1.89 ± 0.03 | 1.86 ± 0.55 | 0.98 | −0.05 | 7.5 ± 0.6 | 7.1 ± 1.5 | 0.95 | −0.25 | | – | | |
| Tb | 2.47 ± 0.04 | 2.30 ± 0.35 | 0.93 | −0.48 | (1.2) | – | | | (0.014 ± 0.002) | – | | |
| Th | 25.0 ± 0.2 | 24.5 ± 1.3 | 0.98 | −0.38 | 7.4 ± 0.1 | 7.1 ± 0.5 | 0.96 | −0.59 | 0.14 ± 0.02 | – | | |
| Ti | 8100 ± 52 | 9300 ± 1044 | 1.15 | 1.15 | 4080 ± 44 | 3814 ± 150 | 0.93 | −1.70 | | – | | |
| U | 10.1 ± 0.1 | 10.4 ± 1.5 | 1.03 | 0.20 | 5.4 ± 0.1 | 4.7 ± 0.6 | 0.87 | −1.15 | | – | | |
| V | 294 ± 2 | 315 ± 27 | 1.07 | 0.78 | 126 ± 2 | 131 ± 8 | 1.04 | 0.61 | (1.47 ± 0.22) | – | | |
| Yb | 7.6 ± 0.1 | 7.2 ± 0.3 | 0.95 | −1.26 | (2.3) | 2.0 ± 0.7 | 0.87 | | (0.037 ± 0.012) | – | | |
| Zn | 228 ± 2 | 229 ± 27 | 1.00 | 0.04 | 4680 ± 29 | 4503 ± 189 | 0.96 | −0.93 | 30.4 ± 3.4 | 31 ± 3 | 1.02 | 0.13 |

$x_{ref}$ and $u_{ref}$ – for NIST-SRMs are the consensus values and standard uncertainties [13] (informational values in parenthesis) – for IAEA-RM-336 are the recommended values and standard uncertainties taken from the IAEA Certificate of IAEA-RM-336 (1999); $n$—replicate number.

+18% and +14%, respectively, and all the *u*-score values were less than $|1.96|$. In this study, it should be noted that the obtained results using all radionuclides produced by the $(n,\gamma)$ reactions for determination of Eu by $k_0$-IAEA program, i.e. $^{152m}$Eu ($T_{1/2}=9.31$ h), $^{152}$Eu ($T_{1/2}=13.54$ y) and $^{154}$Eu ($T_{1/2}=8.80$ y) in terms of medium- and long-lived isotopes assigned to the first and the last two radionuclides, respectively, were considerably biased up to +25% for NIST-1648. The interpretation by $k_0$-IAEA program based-on the only long-lived radionuclides, for determination of Eu was established, for which the obtained results were improved with biases shown in Table 3 were +3%, −11% and +9% for NIST-1633a, NIST-1648 and IAEA-336, respectively.

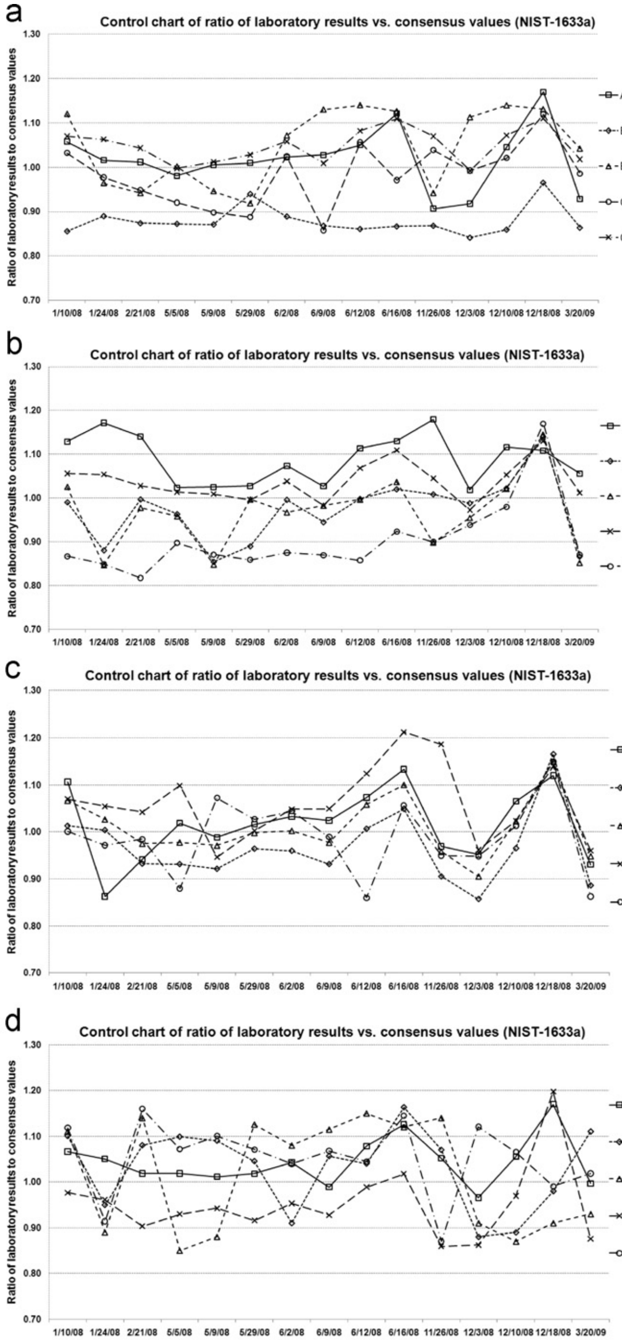

**Fig. 1.** Control chart of the ratio of laboratory results to the consensus values for the determination of mass fractions of elements by $k_0$-NAA established at RPI/ITN over 14 months for NIST-SRM-1633a.

In order to control the reproducibility of the analytical results using $k_0$-NAA, the NIST-1633a was analyzed over 14 months during the period from January 2008 to March 2009. The CRM was put into the irradiation containers together with real samples (in this study, the real samples were the Teflon membrane filters used for collecting of an airborne particulate matter with a Partisol air sampler). Then the CRM and samples were processed in the same manner in all the steps of the analysis, i.e. irradiation, measurement and data interpretation. The control charts of the ratio of the laboratory to consensus values ($x_{\text{lab}}/x_{\text{ref}}$-ratio) and the

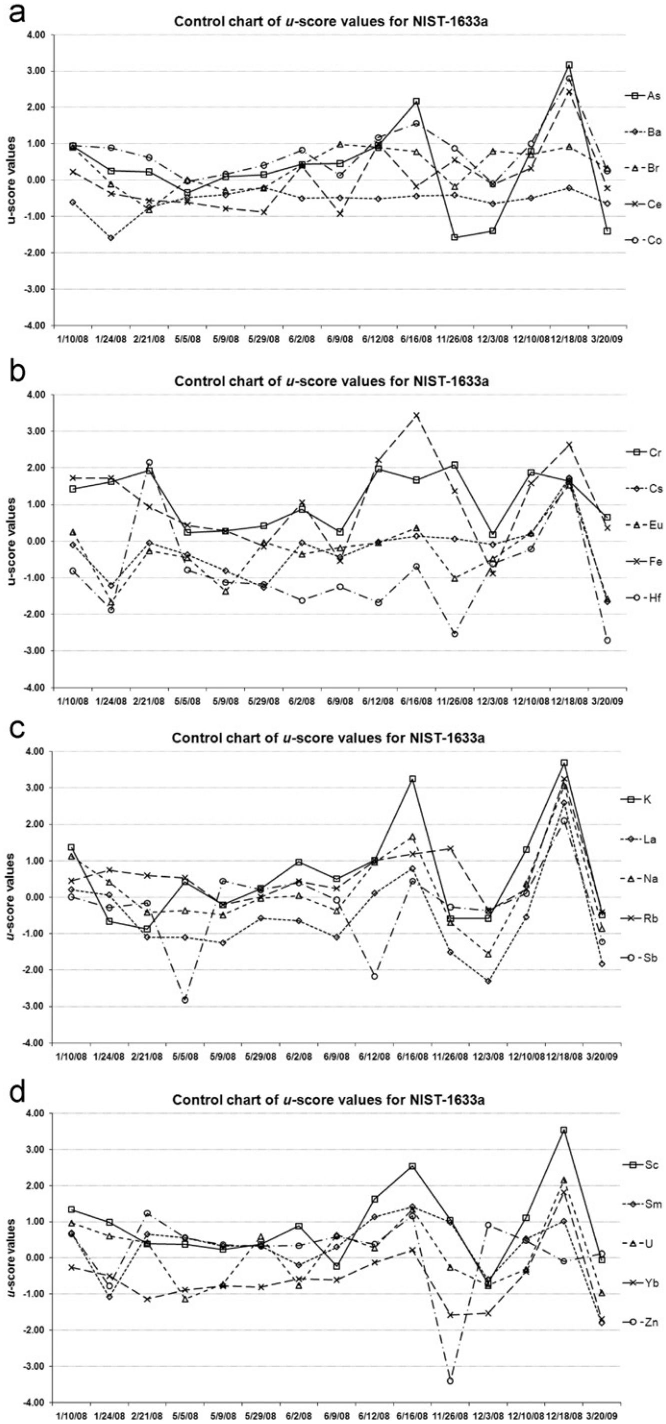

**Fig. 2.** Control chart of the *u*-score values for the determination of mass fractions of elements by $k_0$-NAA established at RPI/ITN over 14 months for NIST-SRM-1633a.

*u*-score values for the determination of mass fractions of elements against times are displayed in Figs. 1 and 2, respectively. The elements that produce medium- and long-lived nuclides were selected to be displayed in the control charts. The control charts show that the $x_{\text{lab}}/x_{\text{ref}}$-ratios were almost within of range 0.90–1.10, i.e. the bias within $\pm 10\%$; however, some cases were less than 0.90 (bias $< -10\%$) for Eu and K (24-January-08), Hf (21-February-08), Sb (20-March-08), U (5-May-08), Cs (9-May-08), Ce (9-June-08), Zn (26-November-08) and Ba, La, Sm and Yb (3-December-08) and greater than 1.10 (bias $> +10\%$) for Br (12-June-08), La (16-June-08), As (12-August-08), Cr (26-November-08) and Ce, Eu, Hf, Rb, Sc and Yb (18-December-08). The *u*-score values were greater than $|1.96|$ for Fe (16-June-08) and As, Ce, K, Na, Rb and Sc (18-December-08). In this context, it should be noted that the analysis done on 18-December-08 gave a noticeable difference of the analytical results as compared to the consensus values and a relatively high estimation of the *u*-score values. There were many causes that might be responsible for unexpected results in $k_0$-NAA as observed on 18-December-08, in which the irradiation time and the mass of sample are questioned firstly, and then the next question should be put on the first measurement of the long irradiation. This is because the elements (As, Ce, K, Na, Rb and Sc) found as biased considerably to the consensus values produce upon neutron irradiation mainly medium-lived nuclides. In such a situation, a check of the counting position of the sample on detector should be done (derived from the number of rings put inside the beaker at below the sample) when using the automatic sample changers. In the above mentioned doubts, the irradiation time is a factor affecting all the co-irradiated samples, while the sample mass and counting position are only affecting to the sample in question. Therefore, if the prior doubt is confirmed the corrective action should be done for all co-irradiated samples, while it is not necessary to do any correction for the co-irradiated samples if one of the later suspects is found. Fortunately, in this study, the counting position (number of rings) was incorrectly recorded and by correcting the right counting position, the analytical results done on 18-December-08 fell within 10% for bias and *u*-score $< |1.96|$ for all the above mentioned elements, except for Rb and Yb where the biases were still greater than 15% and 14%, respectively. It should also be noticed that the biases for Ba and Eu were less than 1.00 (thereby the *u*-score values were negative). The events revealed that the analytical results for these two elements were systematically less than the consensus values, while the other elements have had a normal variation as observed by the biases and the *u*-score values over the controlling period.

## 4. Conclusions

The quality control (QC) and performance evaluation for the $k_0$-NAA at the RPI has been carried out with some aspects: (1) the estimation of the overall standard uncertainty from the primary uncertainty sources, in which the contribution of uncertainty components is typically 35–45% for calibration of gamma-ray spectrometry, 30–35% for nuclear data, 10–15% for spectrum analysis, 3–5% for comparator composition, 5–10% for the characterization of irradiation facility and others. It should be noted that the sample mass for analysis and the determination of moisture are large influential factors to the analytical result as well; (2) the analysis of SMELS, NIST-SRM-1633a, NIST-SRM-1648 and IAEA-RM-336 showed that the analytical results by the $k_0$-NAA were in good agreement as compared to the assigned values with the bias of most elements less than 12%, except for Ba and Ti (NIST-1633a), Cs, Hf, U and Yb (NIST-1648) and Cs and Rb (IAEA-336) which biased within 13–18%. The *u*-score values for most elements were less than $|1.64|$, except for Co (NIST-1633a), La and Ti (NIST-1648) within $|1.64|–|1.96|$, Sc (NIST-1633a), Cr, K and Sb (NIST-1648) within $|1.96|–|2.58|$; and (3) the NIST-1633a that was analyzed over 14 months indicated that the reproducibility of the analytical results was controlled over a long time period. However, the quality assurance (QA) aspect for $k_0$-NAA should be done further in the next stage at the laboratory. Finally, the significant results of the QC works for $k_0$-NAA at RPI were obtained thereby proving that the method meets the requirements of trace element analysis, which is considering the method's performance for which the $k_0$-NAA affords a specific, rapid and convenient capability for the intended applications in environmental, epidemiological and nutritional studies amongst others.

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