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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 (ε_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 (α), 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 α, 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 γ-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_{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 2.7×10^{12} cm^{-2} 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 8.4×10^{12} and about 2.4×10^{12} cm^{-2} 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 α 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