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# Implementation of a methodology to analyse cylindrical 5-g sample by neutron activation technique, $k_0$ method, at CDTN/CNEN, Belo Horizonte, Brazil

Maria Ângela de B. C. Menezes · Radojko Jaćimović

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**Abstract** Neutron activation analysis (NAA) is routinely applied to geometrical point-source or small samples because there are technical and theoretical difficulties to analyse larger samples weighing more than 0.5 g. The analysis of larger samples is very advantageous, because the analytical procedure will be less time consuming, it may be possible to reach lower detection limit for several elements, it decreases cost and overcomes the difficulties related to the representativeness of the sample when dealing with inhomogeneous volume or several small samples. Thus, increasing the amount of sample is a way to compensate for low flux of neutrons. This paper is about the establishment of a method at Laboratory for Neutron Activation Analysis, CDTN/CNEN, to determine the elemental concentrations in 5 g-samples, 25 times larger than usual samples analysed by neutron activation,  $k_0$  method, keeping the current irradiation and gamma spectrometry facilities. To develop this method, several aspects were evaluated such as detector efficiency over the volume source, neutron self-shielding during neutron irradiation, axial neutron flux gradient and gamma ray attenuation within the sample during counting. The results suggest that if an appropriate adjustment of the above mentioned parameters is done, the  $k_0$  method of NAA can provide

satisfactory results also for larger samples than the samples typically used in NAA. The KayWin software proved to be a robust program analysing the larger samples weighing 5 g and cylindrical geometry as if it were a small cylindrical sample, producing reliable results. It was successfully implemented at Belo Horizonte, Brazil, fully following the basic principles of the  $k_0$  standardization method.

**Keywords**  $k_0$  method · Large sample · Cylindrical 5-g sample · Neutron activation analysis

## Introduction

Every analytical technique requires a sample preparation and it is often an obstacle for chemical analysis [1]. To apply the instrumental neutron activation technique, a usual requirement for the sample is to be in geometrical point-source, with a maximum mass of around 0.5 g [2, 3]. The reason is that several simplifications can be made, for instance, regardless the neutron self-shielding, neutron-flux gradients over the sample and self-absorption of gamma rays. In case of a point source, they can be considered negligible, with insignificant impact to the degree of accuracy of the results.

However, the representativeness of the sample has been a challenge when dealing with inhomogeneous volume or several small samples. Analysing larger samples can be a way to overcome this problem [2–8].

Analysing larger sample is very advantageous, because the analytical procedure will be less time consuming since several small samples can be replaced by one large sample to reach lower detection limit for several elements and to decrease cost. In addition, when low-power reactor is used

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increasing the amount of sample to be exposed to irradiation is a way to compensate for low neutron flux.

Neutron activation technique is routinely applied to geometrical point-sources or small samples—up to some milligrams and dimensions of few millimetres [3, 9]. There are technical and theoretical difficulties in exploiting the possibility to analyse samples weighing more than 0.5 g, considered large samples.

The expression “large sample activation analysis” itself is not very precise, because every sample which cannot be described as a point sample requires some unconventional treatment. The theoretical approximate calculations for multi-component samples used in activation analysis have not been largely tested. On the other hand, for geometrical point-sources or small samples, several simplifications can be done because the neutron self-shielding, neutron-flux gradients over the sample and self-absorption of gamma rays are considered negligible [4]. It means that for a sample, which is not considered a geometrical point-source, these parameters should be determined to obtain reliable analysis results. It is necessary to correct for neutron flux depression due to absorption and scattering and the relative attenuation of gamma-rays that originate from different positions within the sample.

To evaluate the detector efficiency over the volume source, it is essential to determine the reference full-energy peak efficiency,  $\varepsilon_p$ , of the detector in order to apply the  $k_0$  method, using the KayWin software [10]. It is a specific program to calculate the elemental concentration for so-called small cylindrical samples—routine procedure—including the efficiency and coincidence correction calculations. It also calculates the values of efficiency for each energy based on the experimental full-energy peak efficiency determined previously for point-source geometry aiming at point sample analysis. The detector efficiency can also be determined by other software, ANGLE V3.0 [11, 12], that is specific to calculate the full energy peak efficiency of semiconductor detector to several source geometries as point shape, cylindrical, Marinelli, etc. The ANGLE program is successfully installed at Nuclear Technology Development Centre/Brazilian Commission for Nuclear Energy, CDTN/CNEN, and its validation was established via the analysis of various reference materials. Both software require the detector characteristics, container and geometry dimensions, composition of the sample and reference efficiency curve to determine its efficiency. The final calculations will provide the full-energy peak efficiency,  $\varepsilon_p$ , and the effective solid angle ( $\bar{\Omega}_{\text{eff}}$ ). It is worth mentioning that ANGLE software makes efficiency calculations only for coincidence free gamma lines.

The perturbation of the neutron field during absorption and scattering inside the sample, called neutron self-

shielding [13–15] is an effect during the irradiation. This problem can be overcome by experimentally determining the neutron flux distribution in real samples in a defined volume for a matrix [14–16]. In a point-sample, the gradient of neutron flux during irradiation is considered negligible, but in a cylindrical sample it should be determined.

The degree of gamma self-attenuation depends on a number of factors such as sample geometry, linear attenuation coefficient, material density, sample composition, and photon energy [9, 17]. When a gamma photon passes through any material, it undergoes, with a given probability, specific interactions, including the sample in which it is generated. In these interactions, the gamma is either absorbed or scattered, losing energy. In any case it cannot contribute to the peak count-rate.

The laboratories that have been applying the neutron activation to large samples (LS-INAA) [2–9] analyse samples in a range of kilograms and for this procedure special facilities are required, for the activation as well as for the detection. For instance, in Delft, The Netherlands, a facility was constructed to irradiate and measure samples from 2 to 50 kg [2–5]. However, in other institutions due to some local limitations it is not allowed. This is the case of the Laboratory for Neutron Activation Analysis, CDTN/CNEN, that applies the nuclear technique following the usual procedure—small cylindrical sample—using the carousel facility of the TRIGA MARK I IPR-R1 reactor that operates at 100 kW with an average thermal flux of  $6.35 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ . The Laboratory has an expressive demand of analysis, answering the clients' request, analysing several kinds of samples.

At this Laboratory, it is frequently necessary to overcome the difficulties associated to unknown sample like inhomogeneity, time consuming, costs and low neutron flux. Therefore, to analyse larger samples would be an interesting possibility, as well as deeper studies of self-shielding effects on sample size and irradiation site [18, 19] or experimental validation of some thermal self-shielding calculation methods for cylindrical samples in INAA [20, 21].

In this scenario, a study was developed aiming at verifying the possibility to determine the elemental concentrations in 5 g-samples, 25 times larger than usual samples analysed, by  $k_0$  method of neutron activation analysis, keeping the current irradiation and gamma spectrometry facilities. In this study, the small cylindrical sample, around 200 mg is referred to as *small sample* and the larger cylindrical sample, around 5 g-sample, as *large sample*.

In order to establish the methodology to analyse a larger sample at Laboratory for Neutron Activation using the KayWin software it was necessary to verify the three parameters: detector efficiency over the volume source, neutron self-shielding during neutron irradiation and gamma ray attenuation within the sample during counting [3, 9, 14].

## Materials and methods

### Samples and analysis

The reference material IAEA/Soil-7 [22] was analysed using different mass aliquots:  $\sim 200$  mg and  $\sim 5$  g. In this study, the smaller cylindrical sample was called small sample (SS), while sample about weighing 5 g called large cylindrical sample (LS).

For the experiment, three vials (5 cm high, 1.3 cm diameter) were prepared as follows:

- Vial 1: The small-sample (SS), an aliquot of about 200 mg, was sealed in polyethylene ampoule (diameter of 9 mm and 5 mm high), stacked together with neutron flux monitors (Al-0.1 %Au alloy, IRMM-530R, a 6 mm diameter-disc and 0.1 mm high and inserted in a 5-cm-high vial. Air space between sample and top of ampoule was filled with cellulose paper.
- Vial 2: The large sample (LS), aliquot of about 5 g was sealed in a polyethylene ampoule of 1.3 cm diameter and filled up to 3.6 cm high. The first monitor (Al-0.1 %Au disc) was placed below ampoule, the second inside the ampoule on the top of sample and the third outside the ampoule. Air space between sample and top of ampoule was filled with cellulose paper.
- Vial 3: Six polyethylene ampoules (9 mm in diameter and 5 mm high) were stacked with Al-0.1 %Au discs in sandwich forms and inserted into a 5 cm high polyethylene ampoule.

The irradiations were carried out in the carrousel facility of the TRIGA MARK I IPR-R1 reactor at CDTN/CNEN, at 100 kW, average thermal neutron flux of  $6.35 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ . Vials 1–3 were inserted in polystyrene container for irradiation during 8 h. The vials were irradiated in the carousel in the IC-7 channel and adjacent channels, IC-6 and IC-8 ( $f$  and  $\alpha$  parameters are 22.3 and  $-0.0022$ , respectively [23]). After suitable decay, the gamma spectroscopy was performed on an absolute calibrated HPGe detector with 50 % relative efficiency, called D4. The absolute calibration of the HPGe detector was done following recommended procedure in the  $k_0$ -standardization method [17, 23, 24]. For the spectra analysis—peak area evaluation—the HyperLab program [25] was used and for the calculation of elemental concentrations, a software package called KayWin [10] was applied.

### Determination of detector efficiency over the volume source

The KayWin software calculates the efficiency for each gamma energy in a spectrum when the elemental

concentration of a real sample is determined. Then, using the reference material IAEA/Soil-7 used as a sample, the following was tested for HPGe detector D4:

- Efficiency obtained by KayWin for cylindrical sample at different distances (2, 5, 10 and 20 cm—reference position) and
- Efficiency differences between KayWin V2.42 and ANGLE V3.0 [11, 12] for different distances sample-detector for cylindrical sample.

To apply the ANGLE V3.0 software, the same reference curve at 20 cm was used in both software, as well as the same detector dimensions, details related to sample-detector distances, dimensions of the vials and sample density.

### Gamma ray attenuation within the sample

The  $k_0$  method of NAA needs an accurate technique to calculate full-energy peak detection efficiency ( $\epsilon_p$ ) of an HPGe detector for various samples and counting geometries. The semi-empirical approach provided by Moens et al. [26] has been introduced in KayWin software via option SOLCOI. Its basic principles are as follows:

- A “reference” counting geometry is chosen to measure a set of calibrated point-sources at large distance e.g. 15–20 cm. Typically, the set cover gamma-energy ( $E_\gamma$ ) range from 60–2,500 keV. This “reference efficiency curve” is obtained experimentally and can be achieved within an accuracy of 1–2 %.
- For an actual sample, the  $\epsilon_{p,\text{geom}}$  for particular gamma-energy is expressed by employing the concept of the effective solid angle ( $\bar{\Omega}_{\text{eff}}$ ):

$$\epsilon_{p,\text{geom}} = \epsilon_{p,\text{ref}} \cdot \frac{\bar{\Omega}_{\text{geom}}}{\bar{\Omega}_{\text{ref}}} \quad (1)$$

with “ref” denoting the reference geometry and “geom” the actual one.

In the definition of the effective solid angle two factors are included: (i) the attenuation effects which gamma-rays undergo outside an HPGe detector active zone,  $F_{\text{att}}$ -factor and (ii) the probability for an energy degradable gamma-ray interaction with the detector material,  $F_{\text{eff}}$ -factor. Both factors can be calculated analytically.

### Calculation of thermal neutron self-shielding factor

For calculation of a thermal neutron self-shielding factor ( $G_{\text{th}}$ ) different software are available. In order to calculate  $G_{\text{th}}$  the sample composition and geometry should be known. In this work KayWin and MATSSF [21] software were tested. For

this purpose, a soil sample in cylindrical geometry with diameter of 13 mm and 36 mm high was used. For soil matrix composition of  $\text{CaCO}_3$  (80 %) and  $\text{SiO}_2$  (20 %) was assumed because those two components are typically major constituents in soil matrices. In principle, the percentage of  $\text{CaCO}_3$  and  $\text{SiO}_2$  in soil may be differing from our assumption, but calculated thermal self-shielding will not change a lot, if at all. The KayWin calculated  $G_{\text{th}}$  equal to 0.997, while for the same configuration the MATSSF obtained  $G_{\text{th}}$  equal to 0.998. Nevertheless, due to the small difference from 1.0 for  $G_{\text{th}}$ , thermal neutron self-shielding was not taken into account for calculation of elemental concentration by KayWin for the large cylindrical sample.

#### Definition of $F_c$ -factor and axial neutron flux gradient

Simplified equation of  $k_0$  method [17] for elemental concentration calculation is written as follows for an analyte (marked as (a)):

$$\rho_a = \frac{A_{\text{sp,a}}}{F_{\text{c,Au}}} \cdot \frac{1}{k_{0,\text{Au}}(a)} \cdot \frac{1}{G_{\text{th,a}}f + G_{\text{e,a}} \cdot Q_{0,a}(\alpha)} \cdot \frac{1}{\varepsilon_{\text{p,a}}}, \quad (2)$$

where:

$$F_{\text{c,Au}} = \frac{A_{\text{sp,m}} \cdot 10^{-6}}{k_{0,\text{Au}}(m)} \cdot \frac{1}{G_{\text{th,m}}f + G_{\text{e,m}} \cdot Q_{0,m}(\alpha)} \cdot \frac{1}{\varepsilon_{\text{p,m}}} \quad (3)$$

is called comparator factor,  $A_{\text{sp,m}}$  and  $A_{\text{sp,a}}$  are the specific activities of monitor (marked as (m)) and analyte,  $k_{0,\text{Au}}(m)$  and  $k_{0,\text{Au}}(a)$  are  $k_0$ -factor of monitor Au (by definition  $\equiv 1$ ) and analyte,  $\varepsilon_{\text{p,m}}$  and  $\varepsilon_{\text{p,a}}$  are the full energy peak detection efficiency of the monitor (Al-0.1 %Au alloy in disc form) and radionuclide of analyte,  $f$  is thermal to epithermal neutron flux ratio,  $G_{\text{th,m}}$  and  $G_{\text{th,a}}$  are the correction factors for thermal neutron self-shielding,  $G_{\text{e,m}}$  and  $G_{\text{e,a}}$  are the correction factors for epithermal neutron self-shielding,  $Q_{0,m}(\alpha)$  and  $Q_{0,a}(\alpha)$  are resonance integral ( $1/E^{1+\alpha}$ ) to 2,200 m s<sup>-1</sup> cross-section ratio and  $\alpha$  is the epithermal flux distribution parameter.

The  $F_{\text{c,Au}}$ -factor as defined in Eq. 3 is proportional to the epithermal neutron flux density and directly indicate a gradient in epithermal flux density. In this study, the  $F_c$ -factors were calculated by KayWin software based on the several Al-0.1 %Au monitors irradiated in Vials 1, 2 and 3 measured at detector D4.

#### Statistical evaluations

The results obtained by  $k_0$ -INAA were expressed through  $E_n$  number [27] in order to evaluate the analytical perfor-

mance of the experiments and the agreement of element contents with certified values. The assigned values for IAEA/Soil-7, i.e. the data given in the Certificate of analysis in 2000 [22] were considered.  $E_n$ -number takes into account the expanded uncertainty of both values with a coverage factor  $k = 2$  (95 % confidence interval).

The following equations were used in the calculations:

$E_n$  number:

$$E_n = \frac{\text{Value}_{\text{Experimental}} - \text{Value}_{\text{Assigned}}}{\sqrt{U_{\text{Experimental}}^2 + U_{\text{Assigned}}^2}}, \quad (4)$$

where  $U_{\text{Experimental}}$  and  $U_{\text{Assigned}}$  are the expanded uncertainties ( $k = 2$ ) of the experimental results and the assigned result, respectively, and

$$U_{\text{Experimental}} = 2 \cdot U_{\text{Lab\_Comb}}, \quad (5)$$

$$U_{\text{Lab\_Comb}} = \sqrt{u_{\text{AREA}}^2 + u_{\text{method}}^2}, \quad (6)$$

where  $u_{\text{AREA}}$  is the uncertainty of the net peak area and  $u_{\text{method}}$  is the overall uncertainty of  $k_0$ -NAA established at the CDTN/CNEN as 3.5 % with a coverage factor  $k = 1$ .

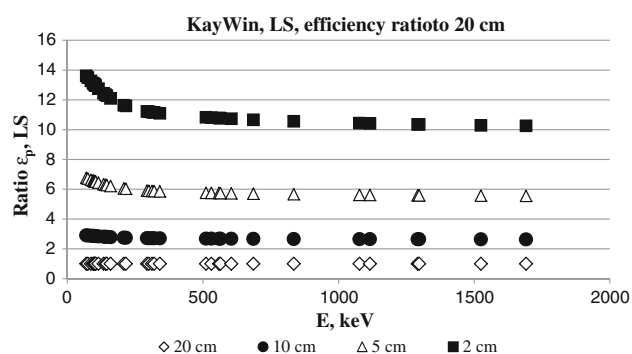
This overall uncertainty was calculated including the uncertainty of the literature values ( $t_{1/2}$ ,  $\bar{E}_r$ ,  $Q_0$ ,  $k_0$ ), the standard uncertainty of the true coincidence correction factors (COI), the Au composition in the Al-0.1 %Au alloy, uncertainty of the previously determined neutron flux parameters ( $f$  and  $\alpha$ ) using the Cd-ratio method, the detector efficiency of a sample, of sample and standard masses and of the net peak area in the measured gamma-line.

To compare the results of the two geometries with reference data, the criterion  $|E_n| \leq 1$  was applied, meaning that the evaluation of the performance of the method was satisfactory and if  $|E_n| > 1$ , the performance was unsatisfactory.

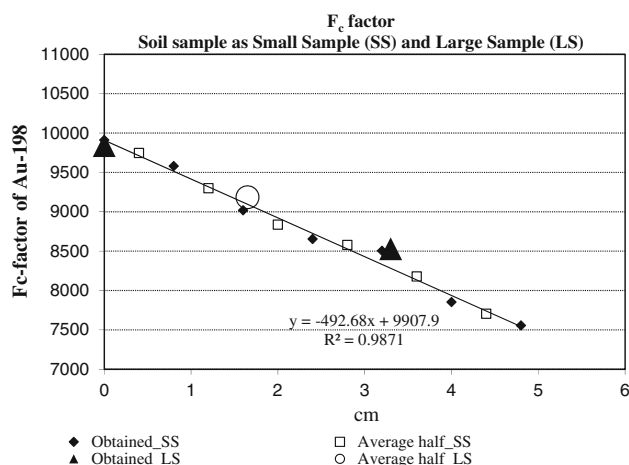
## Results and discussion

#### Detector efficiency over the volume source

The efficiency values at sample-detector distances (2, 5, 10 and 20 cm) related to several gamma lines and respective nuclides were provided by KayWin software, when calculating the elemental concentration of large cylindrical sample. Fig. 1 displays the gamma efficiency calculated for distances sample-detector normalized to 20 cm for HPGe detector D4.



**Fig. 1** Gamma efficiency normalized to 20 cm obtained by KayWin software for detector D4, large cylindrical sample



**Fig. 2**  $F_{c,Au}$ -factors obtained for Al-0.1 %Au monitors in Vial 2 (LS) and in Vial 3 (SS)

### Calculation of $F_{c,Au}$ -factor and axial neutron flux gradient

Figure 2 shows the  $F_{c,Au}$ -factors obtained for Al-0.1 % Au monitors in Vials 1, 2 and 3. The trend of axial gradient is a linear equation. In order to calculate the elemental concentration of large cylindrical sample, it was assumed that  $F_{c,Au}$ -factor value is the correspondent to average height of the sample.

Once verified that KayWin software calculated the efficiencies of cylindrical sample accordingly, the results of elemental concentration determined for the cylindrical sample applying this software are shown on Table 1. The large cylindrical sample was measured at 2, 5, 10 and 20 cm and the elemental concentrations were calculated for each distance and for several distances RP (routine procedure of analysis for customers i.e., suitable distance

sample-detector depending on the activity/dead-time). The results show a good agreement with the recommended values of reference material, IAEA/Soil-7.

In order to verify the influence of distance sample-detector for small and large cylindrical samples, it was calculated the ratio between the concentration values obtained for each distance to reference distance, 20 cm, applying the KayWin software.

The results point out that for small sample, 84 % of the results presented deviations lower than 5 % and 95 % of them was lower than 10 %. For ratios related to 2 and 10 cm, as well as to routine procedure, 99 % of the results presented deviation lower or equal to 10 %. Related to cylindrical sample, 91 % of the results presented deviations lower than 5 %; 96 % of them are related to ratios calculated to 2, 5 and 10 cm. Concerning deviations lower or equal to 10 %, 99 % of all results are within this range.

Table 2 shows the normalised values of small and large cylindrical samples to IAEA/Soil-7 recommended data. These indicate that the  $k_0$  standardization method showed a majority of results within 95 % CI for assigned values. The results, 88 %, presented deviation from the certified values lower than 10 % for small sample and 74 % for large sample. The best performance was observed for point sample measured at 10 cm, and for cylindrical sample, also at 10 cm, both presenting 12 % of deviations. It should be mentioned that similar conclusion was obtained Kennedy and St-Pierre [28] in their work, where 10 cm distance sample-detector shows the best performance.

### Statistical evaluations

Table 3 shows the results of the statistical test using  $E_n$ -number and its criteria. The  $E_n$ -numbers for small and large cylindrical samples were obtained by the KayWin software taking into account uncertainty of the concentration with a coverage factor  $k = 2$ . Only one value for As at 2 cm for the small sample slightly exceeded value  $>1$ , indicating unsatisfactory result. The other  $E_n$ -numbers are satisfactory ( $|E_n| \leq 1$ ) pointing out that the results are in good agreement with the assigned values. The  $E_n$ -numbers for the large sample were  $\leq 1$  for all studied elements except for As, Cr and Zr. These unsatisfactory results may be associated with non-recommended data of  $Q_0$ -factor for As and Cr in the kayzero library [29] or influence of  $f$  and  $\alpha$  to final results for Zr via its analysis using  $^{95}\text{Zr}$  and gamma line at 756.7 keV. Some systematic error for the same elements can be found in work of Kennedy and St-Pierre [28].



**Table 1** Elemental concentration calculated for Small and for Large Cylindrical Sample and the values for the Reference Material IAEA/Soil-7 (mg kg<sup>-1</sup>)

El.	Small sample <sup>b</sup>				Large sample <sup>b</sup>				Recommended values [22]			
	2 cm	5 cm	10 cm	20 cm	RP	2 cm	5 cm	10 cm	20 cm	RP		
As	14.9 ± 0.5	14.1 ± 0.6	14.4 ± 0.5	13.9 ± 0.6	14.6 ± 0.5	15.7 ± 0.6	15.4 ± 0.5	15.4 ± 0.5	15.0 ± 0.5	15.4 ± 0.6	13.4 ± 0.85	
Ba	138 ± 10	142 ± 9	147 ± 8	139 ± 12	141 ± 7	139 ± 10	147 ± 7	147 ± 7	145 ± 9	146 ± 7	(159)	
Br	8.74 ± 0.31	8.27 ± 0.29	8.56 ± 0.31	8.26 ± 0.30	8.67 ± 0.31	8.82 ± 0.32	8.97 ± 0.32	8.93 ± 0.31	8.75 ± 0.31	8.91 ± 0.32	(7)	
Ca <sup>a</sup>	172.9 ± 6.5	166.6 ± 6.2	167.8 ± 6.6	168.1 ± 7.0	169.7 ± 7.2	169.9 ± 6.5	166.4 ± 6.0	168.2 ± 6.1	163.6 ± 5.9	166.4 ± 6.0	(163)	
Ce	60.6 ± 2.2	59.2 ± 2.1	58.1 ± 2.1	58.0 ± 2.3	60.8 ± 2.1	63.2 ± 2.2	60.6 ± 2.1	59.9 ± 2.1	59.3 ± 2.1	61.6 ± 2.6	61 ± 6.5	
Co	9.34 ± 0.33	9.14 ± 0.33	9.12 ± 0.33	9.54 ± 0.35	9.33 ± 0.33	9.48 ± 0.34	9.29 ± 0.33	9.22 ± 0.33	9.09 ± 0.32	9.45 ± 0.34	8.9 ± 0.85	
Cr	76.1 ± 2.7	73.2 ± 2.6	72.0 ± 2.6	73.9 ± 2.8	76.1 ± 2.7	78.2 ± 2.8	75.2 ± 2.9	75.4 ± 2.7	73.4 ± 2.7	77.7 ± 2.8	60 ± 12.5	
Cs	5.69 ± 0.20	5.66 ± 0.20	5.63 ± 0.20	5.69 ± 0.21	5.70 ± 0.20	6.00 ± 0.23	5.88 ± 0.21	5.86 ± 0.21	5.81 ± 0.21	5.92 ± 0.22	5.4 ± 0.75	
Eu	1.03 ± 0.07	1.05 ± 0.06	1.15 ± 0.10	1.05 ± 0.06	1.22 ± 0.28	1.12 ± 0.08	1.17 ± 0.07	1.08 ± 0.06	1.10 ± 0.06	1.12 ± 0.08	1.0 ± 0.2	
Fe <sup>a</sup>	27.69 ± 0.97	27.25 ± 0.96	26.75 ± 0.94	26.99 ± 0.95	27.71 ± 0.97	28.07 ± 0.98	27.49 ± 0.97	27.28 ± 0.96	26.69 ± 0.94	27.77 ± 0.99	(25.7)	
Hf	5.33 ± 0.20	5.22 ± 0.19	5.13 ± 0.18	5.14 ± 0.19	5.33 ± 0.20	5.34 ± 0.21	5.29 ± 0.19	5.30 ± 0.19	5.13 ± 0.18	5.26 ± 0.19	5.1 ± 0.35	
K <sup>a</sup>	12.93 ± 0.46	12.19 ± 0.54	12.22 ± 0.46	12.21 ± 0.45	12.62 ± 0.46	13.30 ± 0.98	12.66 ± 0.50	12.40 ± 0.43	12.51 ± 0.46	12.40 ± 0.45	(12.10)	
La	29.7 ± 1.0	28.4 ± 1.0	28.8 ± 1.0	28.7 ± 1.0	29.0 ± 1.0	29.8 ± 1.0	29.4 ± 1.0	29.2 ± 1.0	28.8 ± 1.0	29.2 ± 1.0	28 ± 1	
Na	2543 ± 89	2394 ± 93	2456 ± 86	2422 ± 86	2483 ± 87	2472 ± 88	2493 ± 88	2484 ± 87	2449 ± 86	2485 ± 87	(2400)	
Nd	28.6 ± 3.8	31.2 ± 2.2	28.0 ± 1.7	28.5 ± 1.9	28.6 ± 3.8	29.5 ± 2.7	32.9 ± 2.1	30.6 ± 2.0	32.6 ± 2.1	32.3 ± 2.1	30 ± 6	
Rb	53.0 ± 2.4	51.4 ± 2.1	50.3 ± 2.1	51.1 ± 2.7	53.0 ± 2.4	55.7 ± 2.3	52.7 ± 2.6	52.7 ± 2.7	52.9 ± 2.3	53.2 ± 3.5	51 ± 4.5	
Sb	1.84 ± 0.07	1.80 ± 0.07	1.79 ± 0.07	1.82 ± 0.09	1.84 ± 0.07	1.82 ± 0.08	1.75 ± 0.07	1.73 ± 0.07	1.75 ± 0.07	1.76 ± 0.08	1.7 ± 0.2	
Sc	9.30 ± 0.33	9.16 ± 0.32	9.02 ± 0.32	9.01 ± 0.32	9.29 ± 0.33	9.35 ± 0.33	9.20 ± 0.32	9.17 ± 0.32	9.02 ± 0.32	9.25 ± 0.33	8.3 ± 1.05	
Sm	4.97 ± 0.18	5.01 ± 0.17	4.84 ± 0.18	4.71 ± 0.17	4.91 ± 0.18	5.26 ± 0.19	5.15 ± 0.18	5.01 ± 0.18	4.92 ± 0.18	5.13 ± 0.18	5.1 ± 0.35	
Ta	0.73 ± 0.03	0.71 ± 0.03	0.73 ± 0.03	0.74 ± 0.04	0.73 ± 0.03	0.76 ± 0.03	0.78 ± 0.03	0.78 ± 0.03	0.77 ± 0.03	0.76 ± 0.03	0.8 ± 0.2	
Tb	0.66 ± 0.02	0.68 ± 0.03	0.66 ± 0.03	0.66 ± 0.03	0.66 ± 0.02	0.73 ± 0.03	0.72 ± 0.03	0.69 ± 0.03	0.69 ± 0.03	0.73 ± 0.03	0.6 ± 0.2	
Th	8.34 ± 0.29	8.23 ± 0.29	8.01 ± 0.29	7.92 ± 0.29	8.35 ± 0.29	8.86 ± 0.31	8.71 ± 0.31	8.63 ± 0.30	8.47 ± 0.30	8.86 ± 0.31	8.2 ± 1.1	
U	2.28 ± 0.10	2.21 ± 0.11	2.28 ± 0.10	2.38 ± 0.14	2.33 ± 0.10	2.57 ± 0.09	2.34 ± 0.11	2.37 ± 0.14	2.31 ± 0.09	2.34 ± 0.11	2.6 ± 0.55	
Yb	2.41 ± 0.09	2.36 ± 0.09	2.32 ± 0.09	2.28 ± 0.10	2.39 ± 0.09	1.52 ± 0.09	1.48 ± 0.09	1.43 ± 0.09	1.51 ± 0.09	1.43 ± 0.09	2.4 ± 0.35	
Zr	207 ± 28	204 ± 36	209 ± 21	207 ± 14	208 ± 17	239 ± 23	211 ± 17	174 ± 15	196 ± 14	241 ± 23	185 ± 10.5	

RP routine procedure

<sup>a</sup> g kg<sup>-1</sup><sup>b</sup> Uncertainty is given with a coverage factor  $k = 1$ 

() Data in brackets are information values

**Table 2** Normalised values of Small and Large Cylindrical Samples to IAEA/Soil-7 on recommended data

El.	IAEA/Soil-7 Certified Values (date of issue: 2000)	Normalised values on IAEA/Soil-7 recommended data									
		Small Sample					Large Sample				
		2 cm ratio	5 cm ratio	10 cm ratio	20 cm ratio	RP cm ratio	2 cm ratio	5 cm ratio	10 cm ratio	20 cm ratio	RP cm ratio
As	13.4 ± 0.85	1.11	1.05	1.07	1.04	1.09	1.17	1.15	1.15	1.12	1.15
Ce	61 ± 6.50	1.00	0.97	0.95	0.95	1.00	1.04	0.99	0.98	0.97	1.01
Co	8.9 ± 0.85	1.05	1.03	1.02	1.07	1.05	1.06	1.04	1.04	1.02	1.06
Cr	60 ± 12.5	1.22	1.18	1.16	1.15	1.15	1.30	1.25	1.26	1.22	1.30
Cs	5.4 ± 0.75	1.05	1.05	1.05	1.05	1.05	1.11	1.09	1.09	1.08	1.10
Eu	1.0 ± 0.2	1.02	1.07	1.10	0.85	0.95	1.12	1.17	1.08	1.10	1.12
Hf	5.1 ± 0.35	1.04	1.02	1.01	1.01	1.04	1.05	1.04	1.04	1.01	1.03
La	28 ± 1	1.06	1.01	1.02	1.01	1.04	1.07	1.05	1.04	1.03	1.04
Nd	30 ± 6	0.87	0.94	0.92	0.95	0.88	0.98	1.10	1.02	1.09	1.08
Rb	51 ± 4.5	1.04	0.99	0.97	0.97	1.04	1.09	1.03	1.03	1.04	1.04
Sb	1.7 ± 0.2	1.08	1.06	1.08	1.07	1.08	1.07	1.03	1.02	1.03	1.03
Sc	8.3 ± 1.05	1.12	1.10	1.08	1.08	1.12	1.13	1.11	1.10	1.09	1.11
Sm	5.1 ± 0.35	0.96	0.98	0.93	0.92	0.96	1.03	1.01	0.98	0.96	1.01
Ta	0.8 ± 0.2	0.91	0.94	0.93	0.93	0.91	0.95	0.98	0.98	0.97	0.95
Tb	0.6 ± 0.2	1.10	1.13	1.10	1.10	1.10	1.22	1.19	1.14	1.15	1.21
Th	8.2 ± 1.1	1.02	1.01	0.98	0.97	1.02	1.08	1.06	1.05	1.03	1.08
U	2.6 ± 0.55	0.90	0.85	0.87	0.85	0.85	0.99	0.90	0.91	0.89	0.90
Yb	2.4 ± 0.35	1.00	0.98	0.95	0.94	1.00	1.06	0.99	0.99	0.98	0.99
Zr	185 ± 10.5	1.12	1.11	1.13	1.12	1.13	1.29	1.14	0.94	1.06	1.30

RP calculations carried out according to usual procedure to the customers

**Table 3**  $E_n$ -number for small and large cylindrical samples for IAEA/Soil-7 for recommended values

El.	Small sample (~200 mg)					Large sample (~5 g)				
	2 cm	5 cm	10 cm	20 cm	RP	2 cm	5 cm	10 cm	20 cm	RP
As	<b>1.09</b>	0.47	0.75	0.35	0.89	<b>1.59</b>	<b>1.46</b>	<b>1.45</b>	<b>1.16</b>	<b>1.44</b>
Ce	0.03	0.24	0.38	0.38	0.03	0.28	0.05	0.14	0.22	0.07
Co	0.40	0.22	0.20	0.58	0.40	0.53	0.37	0.30	0.18	0.51
Cr	0.98	0.79	0.72	0.50	0.60	<b>1.32</b>	<b>1.11</b>	<b>1.13</b>	0.98	<b>1.29</b>
Cs	0.35	0.30	0.30	0.32	0.35	0.68	0.56	0.54	0.47	0.60
Eu	0.07	0.27	0.39	0.52	0.24	0.48	0.69	0.36	0.44	0.48
Hf	0.43	0.22	0.06	0.08	0.43	0.44	0.36	0.39	0.06	0.30
La	0.74	0.08	0.30	0.18	0.44	0.79	0.61	0.51	0.34	0.54
Nd	0.60	0.30	0.33	0.21	0.57	0.06	0.39	0.08	0.36	0.32
Rb	0.31	0.09	0.22	0.17	0.31	0.73	0.24	0.25	0.29	0.26
Sb	0.58	0.39	0.43	0.45	0.54	0.47	0.21	0.13	0.20	0.22
Sc	0.81	0.70	0.57	0.57	0.80	0.85	0.73	0.71	0.59	0.77
Sm	0.42	0.18	0.67	0.82	0.44	0.31	0.09	0.17	0.37	0.05
Ta	0.33	0.21	0.28	0.26	0.33	0.17	0.08	0.08	0.12	0.17
Tb	0.30	0.38	0.29	0.30	0.30	0.65	0.56	0.42	0.43	0.61
Th	0.11	0.03	0.16	0.20	0.12	0.52	0.40	0.34	0.21	0.52
U	0.45	0.66	0.55	0.66	0.64	0.05	0.45	0.37	0.50	0.45
Yb	0.01	0.13	0.27	0.38	0.03	<b>0.36</b>	0.07	0.07	0.15	<b>0.07</b>
Zr	0.39	0.29	0.56	0.74	0.65	<b>1.14</b>	0.73	0.34	0.37	<b>1.18</b>

RP calculations carried out according to usual procedure to the customers; in bold, values  $|E_n| > 1$ , unsatisfactory



## Conclusions

The efficiency values calculated by KayWin V2.42 for large cylindrical sample at sample-detector distances (2, 5, 10 and 20 cm) and normalized to reference distance, 20 cm, showed good agreement.

The ratios between elemental results calculated using KayWin software at 2, 5 and 10 cm sample-detector distances, as well as applying the routine procedure for customers (several distances) pointed out that for point sample, 84 % of the results presented deviations lower than 5 % and 95 % of them were lower than 10 %. For ratios related to 2 and 10 cm, as well as to routine procedure, 99 % of the results presented deviation lower or equal to 10 %. Related to cylindrical sample, 91 % of the results presented deviations lower than 5 %, 96 % of them are related to ratios calculated to 2, 5 and 10 cm. For deviations lower or equal to 10 %, 99 % of all results are within this range.

Concerning the normalised values for small and large samples to IAEA/Soil-7 recommended data, they indicated that the  $k_0$  standardization method showed a majority of results within 95 % CI for assigned values. The results, 88 %, presented deviation from the certified values lower than 10 % for small sample and 74 % for large cylindrical sample. The best performances were observed for small sample measured at 10 cm, and for large sample, also at 10 cm, both presenting 12 % of deviations.

The statistical test  $E_n$  number pointed out that the  $k_0$  method applied using KayWin software presented satisfactory performance, except for arsenic (2 cm, small sample and all distances, large sample), chromium (2, 5 and 10 cm and RP) and zirconium (2 cm and RP). These exceptions should be investigated using other reference materials.

The KayWin software proved to be a robust program calculating the elemental concentration of larger samples producing reliable results.

This investigation has confirmed that any other laboratory applying  $k_0$ -instrumental neutron activation analysis is able to establish this methodology without having to modify its facilities, since the neutron self-shielding, gamma attenuation and efficiency are established, thus defining the technical analysis condition.

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