Summary

IAEA Technical Contract No: 13708
Project Time Period: from 15-September-2006 till 15-September-2007
Institut fuer Radiochemie, Technische Universitaet Muenchen, where the project was carried out.
Institute Director: Prof. Andreas Tuerler
Chief Scientific Investigator: Dr. Xilei Lin

Accurate Determination of the k_0-values for Reactions ^{94}Zr (n, γ) ^{95}Zr and ^{96}Zr (n, γ) $^{97}Zr/^{97m}Nb$

Xilei Lin

Institut fuer Radiochemie, Technische Universitaet Muenchen

85748 Garching, Germany

(10-September-2007)

To be used as a flux monitor, zirconium plays a remarkable role in the k_0-NAA. A combination of bare zirconium and gold is known as the only realistic mean for neutron flux characterization in routine basis. Efforts looking for reliable k_0-values and other relevant nuclear parameters for the Zr-monitor are never interrupted since launching of the k_0-NAA in 1975. So far, however, all k_0-determinations were carried out at irradiation positions with low f-values (f - thermal to epithermal neutron flux ratio).

In this work, a Zr-foil and a Au-Al foil (IRMM-530, 0.100% Au) were co-irradiated in a position in the new research reactor FRM-II in Garching, Germany. At this position, the gold Cd-ratio was determined and found to be 1835, corresponding to an f-value of 28580. At this condition, the contribution from epithermal neutrons can be completely ignored in ^{95}Zr k_0-determination. For $^{95}Zr/^{95}Nb$, with the highest Q_0-value in all (n, γ) reactions, influence from

epithermal neutrons decreases so much that no accurate information is needed for these nuclear parameters dealing with epithermal neutron flux (Q_0, Er, and α-factor). Then the k_0-determination is consistent to the definition of the k_0-factor.

The k_0-values from this work are presented in Table S.1, together with the recommended values. It can be seen that, for nuclide ^{95}Zr, the k_0-values from this work are not much different from the recommended values: the k_0-value of the two gamma-rays 724.2+756.7keV from this work is 0.9 % higher, and for the individual gamma-rays, 724.2keV and 756.7keV, the k_0-values from this work are 1.3 % higher. For ^{97}Zr/^{97m}Nb gamma-ray 743.4keV, the k_0-value of 1.275E-5 from this work is apparently higher than the recommended value of 1.237E-5. The difference is 3.1 %.

Table S.1
Zr k_0-values from this work compared to the recommended ones

Reaction and nuclide	**gamma-ray, keV**	**k_0-value (s, %)**	
		from this work	**Recommended[a]**
^{94}Zr (n, γ) **^{95}Zr**	724.2 + 756.7	2.017E-4 (2.3)	2.000E-4 (1.2)
	724.2	9.02E-5 (2.3)	8.90E-5 (1.3)
	756.7	1.114E-4 (2.3)	1.10E-4 (1.3)
^{96}Zr (n, γ) **^{97}Zr/^{97m}Nb**	743.4	1.275E-5 (2.3)	1.237E-5 (0.3)

a - F. De Corte and A. Simonits, Recommended nuclear data for use in the k_0 standardization of neutron activation analysis, Atom. Data and Nucl. Data Tables, 85 (2003) 47

Final Report

IAEA Technical Contract No: 13708
Project Time Period: from 15-September-2006 till 15-September-2007
Institut fuer Radiochemie, Technische Universitaet Muenchen, where the project was carried out.
Institute Director: Prof. Andreas Tuerler
Chief Scientific Investigator: Dr. Xilei Lin

Accurate Determination of the k_0-values for Reactions ^{94}Zr (n, γ) ^{95}Zr and ^{96}Zr (n, γ) ^{97}Zr/^{97m}Nb

Xilei Lin
Institut fuer Radiochemie, Technische Universitaet Muenchen
85748 Garching
Germany
(10-September-2007)

1. Introduction

The k_0-factor[1], as defined below, is a combined nuclear constant, including the isotope abundance θ, the 2200m/s neutron (n, γ) cross-section σ_0, the absolute gamma-ray emission intensity e_γ, and the atomic mass M for an isotope/gamma-line of a (n, γ) reaction under study and the reference one ^{198}Au/412 keV:

$$k_0 = \left(\frac{\theta \cdot e_\gamma \cdot \sigma_0}{M}\right) \Big/ \left(\frac{\theta \cdot e_\gamma \cdot \sigma_0}{M}\right)_{Au} \qquad (1)$$

The k_0-factor was introduced into neutron activation analysis in 1975 for NAA standardization (k_0-NAA, as short)[1]. Since then this method received extensive attention. Nowadays more than 60 laboratories worldwide use this method. This number is increasing because an IAEA k_0-program[2] was developed and is being distributed since 2005, which

makes it possible for all the NAA laboratories in IAEA member countries to be able to enjoy the k_0-NAA benefits.

To be used as a flux monitor, zirconium plays a remarkable role in the k_0-NAA, because the reactions ^{94}Zr (n, γ) ^{95}Zr is sensitive to the thermal neutrons and the other, ^{96}Zr (n, γ) $^{97}Zr/^{97m}Nb$, to the epithermal neutrons. In fact, the resonance integral to 2200m/s cross-section ratio, Q_0, of the first reaction is about 5 while the Q_0-value of the second reaction is about 250, which is the highest in all (n, γ) reactions. One of the other distinguish advantages[3] is that, from the gamma-ray spectrometry point of view, the effective gamma-ray energy of the two gamma-lines of ^{95}Zr, 724.2 and 756.7 keV, is 742.2 keV, which is practically identical to the $^{97}Zr/^{97m}Nb$ gamma-line of 743.4 keV. Moreover, these lines are cascade coincidence fee. These features much facilitate the gamma-ray spectrometry of this flux monitor.

A combination of bare zirconium and gold is known as the only realistic mean for neutron flux characterization in routine basis. This procedure[4] involves activation and gamma-ray spectrometry of bare flux monitors of zirconium and gold (Zr-foil and Al-Au alloy, for instance). From this straightforward experimental work the shape-factor α of the epithermal neutron flux and the thermal to epithermal neutron flux ratio f can be calculated. All the k_0-NAA programs, including the k_0-IAEA program, are implemented with this procedure for neutron flux characterization.

In view of the above mentioned facts, efforts looking for reliable k_0-values and other relevant nuclear parameters for the Zr-monitor are never interrupted since launching of the k_0-NAA in 1975. The development in this issue can be seen from Table 1.

The main difficulty associated to an accurate k_0-determination is caused by epithermal neutrons, particularly for reactions with high Q_0-values. By definition, the k_0-factor is relevant to thermal neutrons only (see Eq. (1)). However, all the k_0-determinations for the Zr-isotopes shown in Table 1 were performed at irradiation facilities with f-values less than 300. In other words, the epithermal neutrons played very important role for reaction ^{96}Zr (n, γ) $^{97}Zr/^{97m}Nb$ as particular. For example, if a Zr-monitor was activated at a position in a reactor with f = 300, the induced $^{97}Zr/^{97m}Nb$ activity by epithermal neutrons would be 46 % of the total

activity produced by thermal and epithermal neutrons. For the same reaction, the induced activity by epithermal neutrons would increase to more than 83 % of total activity, when irradiation was taken at a position with f-value less than 50. This was the situation in all the works given in Table 1.

The k_0-value is calculated by using Eqs. (2) and (3). To account for the contribution of epithermal neutrons, the α-factor[5] should be determined and two additional nuclear parameters Q_0 and Er (Er - the effective resonance energy) should be introduced. The α-factor is assumed neutron energy independent[6] but questioned recently[7]. Such calculated k_0-value is not only connected to a larger uncertainty, but also the Q_0- and Er-values dependent.

$$k_0 = \frac{A_{sp}}{A_{sp,Au}} \cdot \frac{\left(G_{th} \cdot f + G_e \cdot Q_0(\alpha)\right)^{Au}}{G_{th} \cdot f + G_e \cdot Q_0(\alpha)} \cdot \frac{\varepsilon_{p,Au}}{\varepsilon_p} \qquad (2)$$

where

$A_{sp} = Np/(w \cdot S \cdot D \cdot t_m \cdot C)$

Np – peak area

w – mass

$S = 1-\exp(-\lambda \cdot t_{irr})$

$D = \exp(-\lambda \cdot t_d)$

$C = (1-\exp(-\lambda \cdot t_m))/(\lambda \cdot t_m)$

t_{irr}, t_m, and t_d – respectively the irradiation, counting, and decay time

$\lambda = \ln(2)/T_{1/2}$, decay constant, $T_{1/2}$ –half-life

f – thermal to epithermal neutron flux ratio

$Q_0(\alpha)$ – resonance to 2200m/s (n, γ) cross-section ratio, corrected for a $1/E^{1+\alpha}$ epithermal neutron flux

G_{th} and G_e – thermal and epithermal neutron self-shielding factors, respectively

ε_p – gamma-ray peak efficiency, after correction for cascade (true) coincidence

Au – standing for the reference reaction/isotope ^{197}Au (n, γ) ^{198}Au 411.8 keV

$$Q_0(\alpha) = \left(Q_0 - 0.429\right) \cdot E_r^{-\alpha} + \left\{0.429 / \left[(2\alpha + 1) \cdot (0.55)^{\alpha}\right]\right\} \qquad (3)$$

Obviously, all the problems caused by the epithermal neutrons may be avoided if zirconium is activated in “pure” thermal neutron flux. In this case, the k_0-factor can be calculated simply by Eq. (8). In this aspect, the first attempt of k_0-determination using the thermal column of

reactor NBSR was reported in 1994[8]. The gold cadmium ration there exceeded 1000, corresponding to 15700 of a thermal to epithermal neutron flux ratio. The k_0-values for ^{122}Sb, ^{124}Sb, ^{110m}Ag and ^{51}Cr were reported.

In this work, zirconium was irradiated in a position Strang-3 in the new research reactor FRM-II in Garching, Germany. At this position, though not "pure" thermal one, the neutron spectrum was found to be highly thermalized with an f-value of 28580. Then the epithermal neutrons contribution to the total produced activity for reaction ^{96}Zr (n, γ) ^{97}Zr/^{97m}Nb would be only 0.89 %. At this favorite condition, it is hoped that accurate k_0-values would be determined.

2. Experimental

2.1. Detector reference efficiency calibration

Three HPGe detectors were used in gamma-ray spectrometry. Information about the instrument set-up and spectrometry conditions is given in Table 2.

The reference efficiencies at 25cm positions from the detectors were established by measuring three gamma-ray standards: NIST/SRM4218F Europium-152 (104.20 kBq with relative expanded uncertainty of 0.78 %, k=2), NIST/SRM4241C Barium-133 (103.09 kBq with relative expanded uncertainty of 0.60 %, k=2), and a home made standard from Amersham QCY48, a mixed radionuclide gamma-ray reference solution. The NIST ^{152}Eu and ^{133}Ba sources are the standards with the lowest uncertainties the author could find.

For the QCY48 standard, gamma-ray activity (gamma-ray per second) and associated uncertainty were given by Amersham in a certificate for each gamma-ray. For the NIST-standards, however, the gamma-ray activities of ^{152}Eu and ^{133}Ba should be calculated from the source activities (kBq given in certificates) and gamma-ray emission intensities. In this work, the emission intensities and uncertainties of nuclides ^{152}Eu and ^{133}Ba were taken from an IAEA report "X-ray and gamma-ray standards for detector calibration"[9]. The uncertainty on gamma-ray activity (gamma-ray per second) was calculated from the uncertainties (k =1) of the source activity and the emission intensity. Results are shown in Table 3, where all the

gamma-ray energies used in the reference efficiency calibration are given, together with the associated uncertainties on gamma-ray activities.

As an example, the determined reference efficiencies at 25cm position from detector "D17" are given in Table 4 and also shown in Fig. 1. The uncertainties (1s) on determined efficiencies in Table 4 were evaluated from the uncertainties of gamma-ray activities in Table 3 and gamma-ray counting statistical uncertainties. It can be seen that, the uncertainties on the determined reference efficiencies are about or better than 1 % for all the gamma-rays with energy higher than 245 keV. At the lower energy range, the uncertainties are worse but not too much.

The emission intensities for gamma-rays 53.15keV, 160.6keV, and 223.24keV of nuclide ^{133}Ba are not recommended values[9], resulted in larger uncertainties on the determined efficiencies. The larger uncertainty on the efficiency at 88.03 keV was due to a larger uncertainty on gamma-ray activity of ^{109}Cd given in the certificate of the QCY48 standard.

The gamma-ray efficiencies for actual Zr and Au-Al monitors (Zr-foil and Au-Al foil) were calculated by using an semi-empirical method based on effective solid angle calculation[10]. The used Zr-foil and the Au-Al foil were very thin, had the same shape and size, and were counted at a far distance of 25cm position. Details on these can be found in the following chapter. At these conditions, the efficiencies of used Zr-foil and Au-Al foil were found to be nearly the same, with only 0.06 - 0.07 % difference in the energy range from 400 keV to 900 keV. Consequently, the induced additional uncertainties from the efficiency conversion to the $\varepsilon_p^*/\varepsilon_p$ calculation should be not much more than 0.1 %.

2.2. Determination of Cadmium ratio and thermal to epithermal neutron flux ratio f

Cadmium ratios were determined to calculate the thermal to epithermal neutron flux ratio f. To do so, a group of flux monitor pairs was made by sticking together Au-Al (0.2 % Au, 35 mg) wire with Zr-foil (Goodfellow, 0.125 mm of thickness, 45 mg). A balance Mettler AT261 with a legibility of 0.01 mg was used to weigh the monitor mass. Dual irradiation was performed in each irradiation position, once with and once without Cd-box. The Cd-box had cylinder shape with inner-diameter, length, and wall-thickness of 1.0 cm, l.5 cm, and 0.1 cm,

respectively. All irradiations were carried out at a much reduced thermal power of 300kW (full power 20MW) in reactor FRM-II. Due to security regulation, Cd-covered irradiation is not allowed at higher thermal power in this reactor. Six pneumatic irradiation positions (see Table 6) were calibrated. Irradiation duration varied from 15 to 60 minutes, depending to the irradiation position. Seven hours after irradiation, the flux monitors were measured at 1cm or 0cm position from detector. No nuclide ^{95}Zr was detected in all Cd-covered irradiations except in the irradiation performed at Strang-4.

Eight months later, the same experiments were repeated at the positions Strang-3 and Strang-6 to check the reproducibility of the results.

The Cd-ratio was calculated by using Eq. (4)

$$R_{Cd} = \frac{A_{sp}\left(\text{without Cd} - \text{box}\right)}{A_{sp}\left(\text{in Cd} - \text{box}\right)} \tag{4}$$

The used nuclear data in calculation of the Cd-ratios are summarized in Table 5, the results are shown in Table 6. Uncertainty evaluation was made by following the EURACHEM Guide[11]. The uncertainty sources and associated uncertainty values for Cd-ratio are shown in Table 7 for an irradiation performed at position Strang-3.

The thermal to epithermal neutron flux ratio f was calculated by using Eq. (5), but after setting $\alpha = 0$.

$$f = \left(F_{Cd} \cdot R_{Cd} - 1\right) \cdot G_e \cdot Q_0(\alpha) \,/\, G_{th} \tag{5}$$

with

F_{cd} – Cd transmission factor for epithermal neutrons

The used nuclear data in calculation of f-values can be found in Table 5, the f-values are shown in Table 8.

2.3. Determination of k_0-values for zirconium isotopes

At the full reactor power of 20MW, a piece of Zr-foil (27 mg) was co-irradiated with a piece of Au-Al foil (37 mg) at irradiation position Strang-3 (Φ_{th} = $5 \cdot 10^{12}$ n·cm^{-2}·s) for 30 or 60 minutes. The co-irradiated Zr and Au-Al foils had a same shape (square) and size (12mm x 12mm). A few hours after irradiation, the Zr-foil was measured at 25cm position from a detector. Some days later, the Zr-foil was re-placed at the same position to measure the nuclide ^{95}Zr. The co-irradiated Au-Al foil was counted at the same position. The data about the used Zr and Au-Al foils were as follows:

Au-Al foil - IRMM-530, (1.00 ± 0.02 g Au)/kg, k=2; 0.1 mm of thickness
Zr-foil - AlfaAesar, 99.9+ % of purity; 0.025 mm of thickness

The above mentioned experiments were repeated several times in a time period of 10 months. In some experiments, 15cm position from detector was used in gamma-ray measurements. One more irradiation was performed at position Strang-6 (Φ_{th} = $9 \cdot 10^{12}$ n·cm^{-2}·s), where the f-value was lower than the position Strang-3 (see Table 8).

Though burn-up loss of ^{198}Au was found to be nearly negligible (less than 0.04 %), due to short time irradiation at low flux, corresponding corrections were applied in k_0-determination, anyhow.

The k_0-values of Zr-isotope ^{95}Zr were calculated by using Eq. (2) (after setting $\alpha = 0$) and presented in Table 9.

The k_0-value of ^{97}Zr/^{97m}Nb was also calculated by using Eq. (2) (after $\alpha = 0$) and presented in Table 9. For the reaction ^{96}Zr (n, γ) ^{97}Zr $\rightarrow$ ^{97m}Nb and gamma-ray 743.4 keV, however, the specific activity Asp was calculated by using Eq. (6). Its k_0-factor is defined[12] as shown by Eq. (7) to account for the decay branching.

$$A_{sp}(3) = Np,_3/(w \cdot t_m) \cdot (\lambda_3 - \lambda_2)/(\lambda_3 \cdot S_2 \cdot D_2 \cdot C_2 - \lambda_2 \cdot S_3 \cdot D_3 \cdot C_3) \quad (6)$$

where

3 – ^{97m}Nb 743.4 keV, $T_{1/2}$ = 52.7 sec

2 – ^{97}Zr, $T_{1/2}$ = 16.74 h

$$k_0 = \left(\frac{\theta \cdot e_\gamma \cdot F \cdot \sigma_0}{M} \right) \Big/ \left(\frac{\theta \cdot e_\gamma \cdot \sigma_0}{M} \right)_{Au} \qquad (7)$$

with

F = 0.968, fractional decay factor of the nuclide ^{97}Zr decaying to ^{97m}Nb

Uncertainty sources in the k_0-determination are given in Table 10. All the k_0-determinations were performed at same or similar conditions in sample preparation, irradiation and gamma-ray spectrometry, resulted in similar uncertainties on individual k_0-values.

3. Results and discussion

3.1. the k_0-values of Zr-isotopes

The k_0-values of Zr-isotopes from this work are presented in Table 11. The recommended k_0-values are shown, together with the actual determined values from three investigators from which the recommended values were derived. These values were calculated from irradiations in reactors with low f-values from 17.3 to 162.

It can be seen that, for nuclide ^{95}Zr, the k_0-values from this work are not different much from the recommended values: the k_0-value of the two gamma-rays 724.2+756.7keV from this work is 0.9 % higher, and for the individual gamma-rays, 724.2keV and 756.7keV, the k_0-values from this work are 1.3 % higher.

For ^{97}Zr/^{97m}Nb gamma-ray 743.4keV, the k_0-value of 1.275E-5 from this work is apparently higher than the recommended value of 1.237E-5. The difference is 3.1 %.

The results shown in Table 11 were determined based on the HØGDAHL convention[13]. It is known that the ^{197}Au (n, γ) ^{198}Au thermal cross-section deviates slightly from the 1/v-law (v – neutron velocity). The temperature of thermal neutron flux was determined by co-irradiation of Au-Al and Lu-Al monitors and found to be 34.0 ^{o}C at Strang-3 and 27.6 ^{o}C at Strang-6. At this condition, the Westcott g(T_n)-factor of ^{198}Au[14] was 1.0073 at Strang-3 and 1.0070 at Strang-6. The Westcott spectral index $r\sqrt{T_n}/T_0$ was calculated from the gold Cd-ratio given in Table 6 and found to be 3.153E-5 and 4.080E-5 respectively for the two irradiation positions. The k_0-factor based on the WESTCOTT convention[15],[16] was then calculated and found that, the k_0-values of ^{95}Zr and ^{97}Zr/^{97m}Nb from Westcott convention were 0.7 % higher than the corresponding values in Table 11.

3. 2. Irradiation in highly thermalized neutron spectra

For reaction of ^{94}Zr (n, γ) ^{95}Zr with Q_0 = 5.31, the epithermal neutrons contribution was negligible (less than 0.02 %) for irradiations performed at position Strang-3. For the reference reaction ^{197}Au (n, γ) ^{198}Au with Q_0 = 15.7, the activity induced by epithermal neutrons would be 0.06 % of the total activity. Consequently, k_0-determination for this reaction does not require accurate information on Q_0 and epithermal neutron flux. Or these parameters relevant to accounting for epithermal neutron flux (Q_0, Er, and α-value) can be simply ignored in k_0-determination. In fact, for nuclide ^{95}Zr, it was found that same k_0-values as that in Table 11 could be calculated by using Eq. (8), where the item $(G_{th}\cdot f + G_e\cdot Q_0(\alpha))^{Au}/(G_{th}\cdot f + G_e\cdot Q_0(\alpha))$ is missing. An example: the k_0-value of ^{95}Zr 724.2+756.7keV in Experiment No.3 was 2.007E-4 (see Table 9), which was calculated by using Eq. (2); when using Eq. (8) the k_0-value was found to be 2.006E-4.

$$k_0 = \frac{A_{sp}}{A_{sp}^{Au}} \cdot \frac{\varepsilon_p^{Au}}{\varepsilon_p} \qquad (8)$$

For reaction ^{96}Zr (n, γ) ^{97}Zr/^{97m}Nb with Q_0 = 251.6, the k_0-value calculated by using Eq. (8) was found to be 0.86 % too high, apparently due to ignoring the contribution from the epithermal neutrons. The difference of 0.86 % is not large, but could be avoided in an accurate k_0-determination when Eq. (2) was used. In this case, however, the k_0-determination

has a large tolerance to the used parameters relevant to accounting for the epithermal neutron contribution. For irradiation performed at position Strang-3, uncertainty on the f-value 28580 is 3.3 % (Table 8), and uncertainty on ^{197}Au (n, γ) ^{198}Au Q_0 is 1.8 % (Table 6) which is believed to be reliable because this reaction/nuclide is a common cross-section standard used in neutron metrology. On the other hand, the published ^{97}Zr Q_0 values differed much, with a maximum value of 282 published in 1984 and a minimum one of 233 in 2003, the difference is 21 % (see Table 1). Kept these in mind and performed a calculation which showed that, the maximum difference on determined k_0-value was 0.33 % in the worst case, namely the Q_0 value of ^{97}Zr would be wrong by 20 %, the Er-values of ^{198}Au and ^{97}Zr wrong also wrong by 20 %, and the α-value would be -0.15, and all the bias in the mentioned parameters were in the direction to cause larger difference in k_0-determination. The reasonable α-value should be in the range of -0.15 and +0.15 in all reactors. In this calculation, the used extreme α-value was -0.15, not +0.15, because the later would reduce the difference. Obviously, this worst case will not happen in real situation, and this example was used to have a figure to show the advantage of applying highly thermalized neutron flux in k_0-determination. In other words, the determined ^{97}Zr k_0-factor in this work is nearly independent of Q_0, Er, and α-value.

3. 3. the thermal to epithermal neutron flux ratio f determined in a low reactor thermal power of 300kW but used at the full reactor thermal power of 20MW

The thermal to epithermal neutron flux ratios were calculated from the gold cadmium rations which were determined in a low reactor thermal power of 300kW, but the k_0-factor determinations were carried out at the full reactor power of 20MW.

The control rod would be at different positions to regulate the reactor thermal power, and the neutron spectra in moderator tank would be influenced. However, the reactor FRM-II has an exceptionally small core with diameter of 24 cm, situated in a large moderator tank with a diameter of 2.5 m, where the thermal neutrons build up. The irradiation position Strang-3 is located far from the reactor core. It is hoped that the neutron spectrum at this remote irradiation position will not change much at different reactor thermal powers, and the thermal to epithermal neutron flux ratio derived from irradiations at a low reactor power is valid also at the full reactor power.

It would be the best to perform a Cd-ratio determination at 20MW but, as already mentioned, it is not allowed to do so in this reactor due to security regulation. The Cd-covered irradiation at 300kW was performed in a special arrangement.

The other way is to determine the k_0-factor at 300kW. This work was performed. After irradiation at 300kW, the monitors were counted at close positions, including the 0cm position from detector, simply due to too low activities. At the low counting positions, it was not possible to evaluate efficiencies accurately for Zr and Au monitors. However, it was demonstrated[17] that, even at 0cm counting position, large uncertainty on gamma-ray counting efficiency ratio $\varepsilon_p^*/\varepsilon_p$ can be avoided by using an internal comparator. This is particularly true if ^{95}Zr 724.2+756.7keV gamma-ray is used as an internal comparator to determine the ^{97}Zr 743.4 keV k_0-value, because the effective gamma-ray energy of the two ^{95}Zr gamma-rays is 742.2 keV, practically identical to ^{97}Zr 743.4 keV, allowing counting the Zr-foil at 0cm position without introducing apparent uncertainty in k_0-value. The ^{97}Zr 743.4 keV k_0-values determined at 300kW are presented in Table 12. Some k_0-values determined at other reactor low powers are also given in this table, which were performed during the reactor start-up procedure in 2004.

It can be seen that the k_0-values from irradiations at low reactor powers are not really different from the irradiations at the full reactor power of 20MW. However, these k_0-values given in Table 12 are for information only, due to larger counting statistics uncertainties (0.5 – 3 %). And more important, the k_0-values were calculated against to the comparator ^{95}Zr, not ^{198}Au. The k_0-factor is defined against ^{198}Au as the comparator with $k_0(^{198}\text{Au}) \equiv 1$.

The results from irradiations at other pneumatic positions with lower f-values (Strang-1, Strang-5, and Strang-4) were also calculated. As expected, the calculated k_0-values are found to be too low, decreasing with decreasing of the f-values. Apparently, the reason is that the contribution of epithermal neutrons was not fully accounted for. Consequently, these pneumatic irradiation positions are not suitable for the ^{97}Zr k_0-determination.

4. Conclusion

New k_0-values for Zr-isotopes were determined and reported. Compared to the recommended ones, the k_0-values of ^{95}Zr are 0.9 -1.3 % higher only; for ^{97}Zr/^{97m}Nb 743.4 keV gamma-ray, the result from this work is 3.1 % higher.

These k_0-determinations were carried out at irradiation positions in reactor FRM-II with an f-value of 28580. The contribution from epithermal neutrons can be completely ignored in ^{95}Zr k_0-determination. For ^{95}Zr/^{95}Nb, with the highest Q_0-value in all (n, γ) reactions, influence from epithermal neutrons decreases so much that no accurate information is needed for nuclear parameters (Q_0, Er, and α-factor). Then the k_0-determination is consistent to the definition of the k_0-factor.

Obviously, the experimental conditions developed in this work is suitable for k_0-determination for all the other (n, γ) reactions, particularly for these with higher Q_0-values but in suspicions[18].

References

[1] A. Simonits, F. De Corte, J. Hoste, *J. Radioanal. and Nucl. Chem.,* 24 (1975) 31.

[2] http://www-naweb.iaea.org/napc/iachem/k0-IAEA.html

[3] A. Simonits, F. De Corte, J. Hoste, *J. Radioanal. Chem.*, 31 (1976) 467.

[4] F. De Corte, S. Jovanovic, A. Simonits, L. Moens, J. Hoste, *Kernenergie-Kerntechnik Supp.*, (1984) 641.

[5] F. De Corte, K. Sordo-El Hammami, L. Moens, A. Simonits, A. De Wisperaere, J. Hoste, *J. Radioanal. and Nucl. Chem.,* 62 (1981) 209.

[6] F. De Corte, L. Moens, S. Jovanovic, A. Simonits, A. De Wisperaere, *J. Radioanal. and Nucl. Chem.,* 102 (1986) 37.

[7] B. Smodis, A. Trkov, R. Jacimovic, *J. Radianal. and Nucl. Chem.,* 257 (2003) 481.

[8] S. O. Yusuf, R. F. Fleming, *J Radioanal. and Nucl. Chem.,* 179 (1994) 105.

[9] IAEA-TECDOC-619, IAEA, Vienna, (1991).

[10] L. Moens, J. De Donder, X. Lin, F. De Corte, A. De Wisperaere, A. Simonits, J. Hoste, *Nucl. Instrum. and Methods,* 187 (1981) 451.

[11] EURACHEM / CITAC Guide CG 4, (2000).

[12] F. De Corte, A. Simonits, *Atomic Data and Nucl. Data Tables,* 85 (2003) 47.

[13] O. T. Høgdahl, Report MMPP-226-1 Dec. 1962.

[14] N. E. Holden, *Pure Appl. Chem.*, *71*, (1999) 2309.

[15] C. H. Westcott, Report CRRP-960 of the AECL, Nov.1, 1960.

[16] F. De Corte, F. Bellemans, P. De Neve, A. Simonits, *J. Radioanal. and Nucl. Chem.,* 179 (1994) 93.

[17] X. Lin and R. Henkelmann, *Anal. Boianal. Chem.,* 379 (2004) 210.

[18] G. Kennedy, J. St-Pierre, *J Radioanal. and Nucl. Chem.,* 257 (2003) 475.

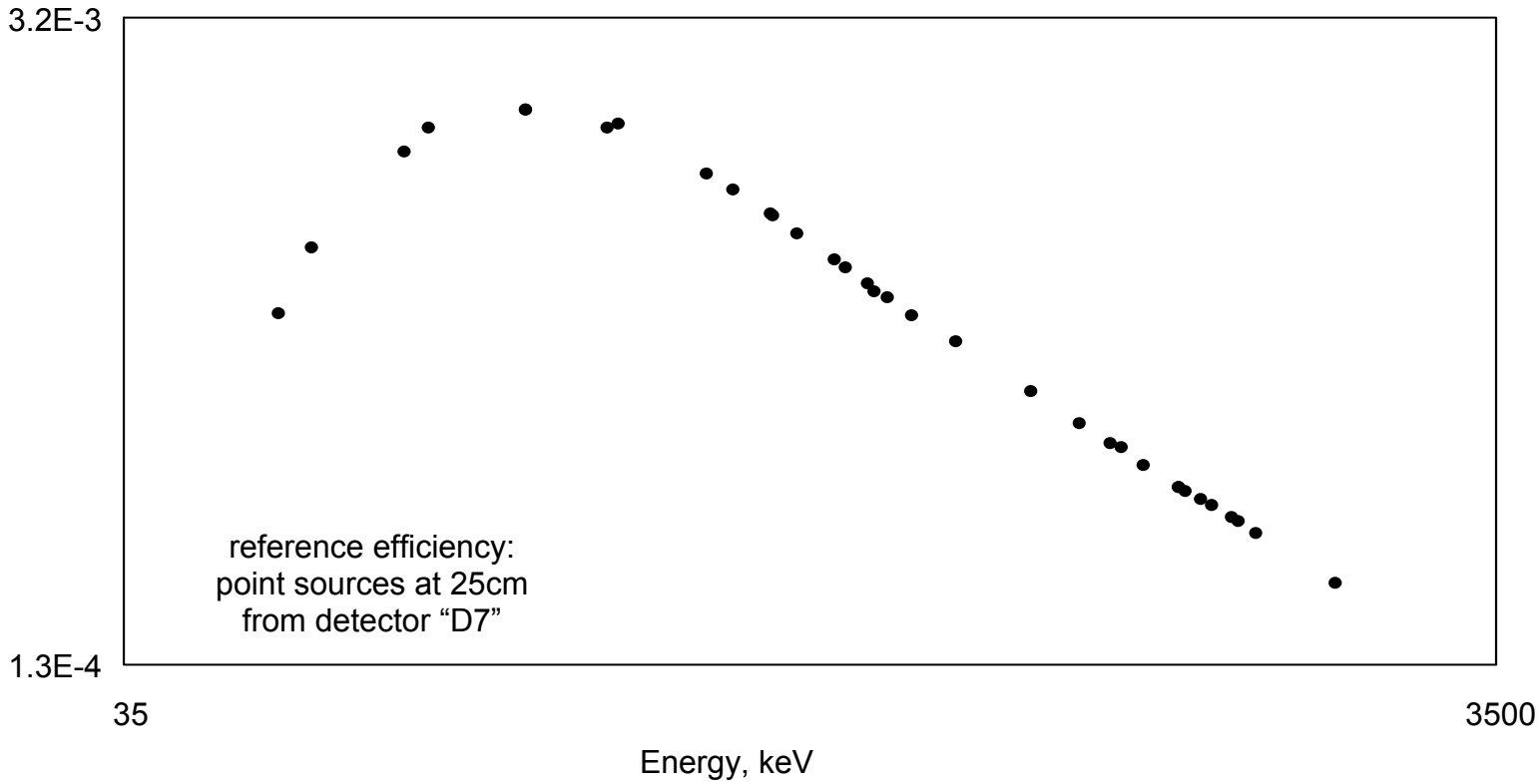

Fig. 1 Reference efficiency for detector “D17”, established by counting standard sources of SRM4241C-Ba133, SRM4218F-Eu152, and QCY48 (Gamma-ray energy, peak efficiency and uncertainty can be found in Table-4)

Table 1

Summary of the k_0-, Q_0-, and Er-values for Zr-isotopes, published since launching of the k_0-NAA in 1975

reaction	parameters	1976/ Simonits[a]	1980/ Simonits[b]	1984/ Moens[c]	1987/ Simonits[d,] 1989/ De Corte[e]	2000/ Simonits[f,] 2003/ De Corte[g]	2003/ Smodis[h]
^{94}Zr (n, γ) ^{95}Zr	k_0 (724.2 + 756.7 keV)	2.14E-04	1.98E-04	2.04E-04	2.094E-04	2.000E-04	2.00E-04
	k_0 (724.2keV)	-	8.86E-05	9.11E-05	9.321E-05	8.90E-05	-
	k_0 (756.7 keV)	-	1.09E-04	1.13E-04	1.149E-04	1.10E-04	-
	$Q_0 = I_0/ \sigma_0$	5.45	5.97	5.88	5.05	5.306	4.98
	Er, eV *	-	4520	4520	6260	6260	14685
^{96}Zr (n, γ) ^{97}Zr/^{97m}Nb	k_0 (743.3keV)	1.16E-05	1.19E-05	1.19E-05	1.296E-05	1.237E-05	1.24E-05
	$Q_0 = I_0/ \sigma_0$	250	280	282	248	251.6	233
	Er, eV *	-	340	340	338	338	382.1

* Er - the effective resonance energy

a - A. Simonits, et. al., "Zirconium as a multi-isotopic flux ratio monitor and a single comparator in reactor-neutron activation analysis", J. Radioanal. Chem., 31 (1976) 467

b - A. Simonits, et. al., "k_0-measurements and related nuclear data compilation for (n, γ) reactor neutron activation analysis (Part I)", J. Radioanal. Chem., 60 (1980) 461

c - L. Moens, et. al., "k_0-mesurements and related nuclear data compilation for (n,γ) reactor neutron activation analysis", J. Radioanal. Nucl. Chem., 82 (1984) 385

d - A. Simonits, et. al., "Neuclear data measurements for zirconium isotopes used for activation analysis and neutron metrology", J. Radioanal. Nucl. Chem., 113 (1987) 187

e - F. De Corte and A. Simonits, "k_0-measurements and related data compilation for (n, γ) reactor neutron activation analysis", J. Radioanal. Nucl. Chem., 1 (1989) 43

f - A. Simonits, et. al., "The k0 and Q0 values for the Zr-isotopes: A re-investigation", J. Radioanal. Nucl. Chem., 245 (2000) 199

g - F. De Corte and A. Simonits, "Recommended nuclear data for use in the k_0 standardization of neutron activation analysis", Atomic Data and Nucl. Data Tables, 85 (2003) 47

h - B. Smodis, et. al., "Effects of the neutron spectrum on the neutron activation analysis constants for ^{94}Zr and ^{96}Zr", J. Radioanal. Nucl. Chem., 257 (2003) 481

Table 2
Gamma-ray spectrometry conditions

HPGe detector	**"D6"**	**"D17'**	**"D19"**
FWHM at 1333keV, keV	1.75	1.64	1.66
Relative efficiency, %	28	20	30
Amplifier	Canberra 2025	Canberra 2026 (digital)	Canberra 2026 (digital)
ADC	ND583	-	-
Software	Canberra VAX/VMS-Genie program		
pile-up/dead-time correction	empirical two-source method implemented in the Genie-program		
gamma-ray counting distance	25cm; 15cm used in 3 k_0-determinations; 1cm or 0cm used in gold Cd-ratio determination		
standard sources used for reference efficiency at 25cm	NIST/SRM4218F ^{152}Eu, NIST/SRM4241C ^{133}Ba, and Amersham QCY48; all "point" sources		
peak-efficience evaluation for actual samples	semi-empirical method based on effective-solid angle calculation[a]		

a - L. Mones, et. al., "Calculation of the absolute peak efficiency of gamma-ray detectors for different counting geometries", Nucl. Instrum. and Methods, 187 (1981) 451

Table 3

Gamma-rays used to establish reference peak efficiencies at 25cm positions and uncertainties on gamma-ray activities of used standards

Gamma-ray, keV	Radionuclide of standard[a]	Relative uncertainty on gamma-ray activity, %
53.15	^{133}Ba	5.01
59.54	^{241}Am in QCY48	1.30
80.99	^{133}Ba	0.87
88.03	^{109}Cd in QCY48	3.10
121.78	^{152}Eu	0.60
122.1	^{57}Co in QCY48	0.75
160.6	^{133}Ba	5.01
165.9	^{139}Ce in QCY48	0.85
223.24	^{133}Ba	5.01
244.7	^{152}Eu	0.66
276.39	^{133}Ba	0.52
279.2	^{203}Hg in QCY48	0.70
302.85	^{133}Ba	0.44
344.28	^{152}Eu	0.57
356.0	^{133}Ba	0.38
383.84	^{133}Ba	0.44
391.7	^{113}Tn in QCY48	1.6
411.13	^{152}Eu	0.59
443.96	^{152}Eu	0.59
514.0	^{85}Sr in QCY48	1.3
661.6	^{137}Cs in QCY48	1.0
778.9	^{152}Eu	0.61
867.39	^{152}Eu	0.71
898.1	^{88}Y in QCY48	0.9
964.08	^{152}Eu	0.57
1085.84	^{152}Eu	0.63
1089.77	^{152}Eu	0.65
1112.09	^{152}Eu	0.59
1173.2	^{60}Co in QCY48	0.75
1212.97	^{152}Eu	0.69
1299.15	^{152}Eu	0.78
1332.5	^{60}Co in QCY48	0.75
1408.02	^{152}Eu	0.58
1836.1	^{88}Y in QCY48	0.80

a. ^{133}Ba and ^{152}Eu - NIST/SRM4241C Barium-133 and NIST/SRM4218F Europium radioactivity standards, respectively; QCY48 - Amersham mixed radionuclide gamma-ray reference standard

Table 4
Reference efficiency at 25cm position from detector "D17"

Gamma-ray, keV	Peak efficiency	Relative uncertainty, %
53.15	7.21E-04	5.0
59.54	1.008E-03	1.4
80.99	1.627E-03	0.87
88.03	1.822E-03	3.1
121.78	2.003E-03	0.61
122.1	1.998E-03	0.90
160.6	1.95E-03	5.1
165.9	1.864E-03	1.0
223.24	1.44E-03	5.1
244.7	1.341E-03	0.69
276.39	1.199E-03	0.53
279.2	1.180E-03	0.86
302.85	1.073E-03	0.46
344.28	9.45E-04	0.58
356.0	9.10E-04	0.38
383.84	8.45E-04	0.45
391.7	8.12E-04	1.6
411.13	7.89E-04	0.77
443.96	7.21E-04	0.71
514.0	6.31E-04	1.3
661.6	4.944E-04	1.1
778.9	4.183E-04	0.64
867.39	3.803E-04	0.87
898.1	3.715E-04	0.95
964.08	3.419E-04	0.60
1085.84	3.066E-04	0.70
1089.77	3.056E-04	1.2
1112.09	2.982E-04	0.66
1173.2	2.886E-04	0.85
1212.97	2.796E-04	1.3
1299.15	2.627E-04	1.1
1332.5	2.568E-04	0.85
1408.02	2.430E-04	0.61
1836.1	1.897E-04	0.89

Table 5

Nuclear data used in calculation of Cd-ratio, thermal to epithermal neutron flux ratio f, and k_0-values of Zr-isotopes

Reaction and nuclide produced	**half-life**[a]	**Q_0 (s, %)**[a]	**F_{cd}**[b]	**G_{th}**	**G_e**[c]	**gamma-ray**
^{197}Au (n, γ) **^{198}Au**	2.695d (0.1)[d]	15.7 (1.8)[d]	0.991	1	1	411.8keV
^{94}Zr (n, γ) **^{95}Zr**	64.02d (0.01)[d]	5.31 (3.3)	1	1	0.983 (0.125mm thickness); 0.996 (0.025mm thickness)	724.2keV, 756.7keV; 743.2keV (effective energy of the two gamma- lines)
^{96}Zr (n, γ) **^{97}Zr/^{97m}Nb**	16.74h (0.1)[d]	251.6 (1)	1	1	0.973 (0.125mm thickness); 0.994 (0.025mm thickness)	743.4keV

a - F. De Corte, et. al.; Atom. Data and Nucl. Data Tables, 85 (2003) 47

b - Cd-transmission factor for epithermal neutrons; F_{Cd} = 0.991 for ^{198}Au, adapted from F. De Corte, The k0-STANDARDIZATION METHOD, Rijksuniversiteit Gent, 1987

c - calculated using empirical formula given in: A. Simonnists, et. al., J. Radioanal. Nucl. Chem., 113 (1987) 187

d - uncertainties from F. De Corte, The k_0-STANDARDIZATION METHOD, Rijksuniversiteit Gent, 1987

Table 6
Cadmium ratio values at six pneumatic irradiation positions in reactor FRM-II

irradiation position	experiment date	Cd-ratio value					
		from ^{198}Au	uncertainty (1s)	from ^{97}Zr	uncertainty (1s)	from ^{95}Zr	uncertainty (1s)
Strang-4	24-Aug-2006	83.3	2.1	11.34	0.57	673	46
Strang-5	24-Aug-2006	397	12	48.7	2.4	*	-
Strang-1	23-May-2006	750	23	84.7	4.5	*	-
Strang-2	23-May-2006	1027	31	103.3	6.2	*	-
Strang-6	23-May-2006	1434	52	116.0	9.5	*	-
Strang-6	24-Jan-2007	1418	42	127.0	8.9	*	-
Strang-3	23-May-2006	1794	75	135.4	13	*	-
Strang-3	24-Jan-2007	1835	50	134.0	5.9	*	-

* - no nuclide ^{95}Zr detected in Cd-covered irradiation

Table 7
Uncertainty evaluation on Cd-ratio at irradiation position Strang-3 performed in 24-Jan-2007

Uncertainty source	**Relative uncertainty (1s), %**			
	bare ^{198}Au	**^{198}Au in Cd-box**	**bare ^{97}Zr**	**^{97}Zr in Cd-box**
monitor mass (Au-Al-35mg, Zr-45mg)	0.029	0.029	0.022	0.022
monitor positioning in irradiation container	0.1	0.1	0.1	0.1
irradiation duration	0.17	0.11	0.17	0.11
irradiation situation factor (due to half-life uncertainty)	0.1	0.1	0.1	0.1
neutron flux stability during the dual irradiation (with and without Cd-box), evaluated from reactor operation record	0.1	0.1	0.1	0.1
monitor positioning in gamma-ray counting (causing different efficiency)	1.5	1.5	1.5	1.5
gamma-ray counting statistics	0.1	1.5	0.3	3.8
live-time correction (due to half-life uncertainty)	0.5	0.5	0.5	0.5
decay correction (due to half-life uncertainty)	0.02	0.01	0.02	0.02
combined uncertainty on determined ^{198}Au Cd-ratio		**2.71%**		
combined uncertainty on determined ^{97}Z rCd-ratio				**4.43%**

Table 8
The thermal to epithermal neutron flux ratio f, calculated from corresponding gold Cd-ratio given in Table 6

irradiation position	experiment date	f-value from ^{198}Au Cd-ratio	uncertainty[a] (1s)
Strang-4	24-Aug-2006	1283	40
Strang-5	24-Aug-2006	6180	220
Strang-1	23-May-2006	11670	420
Strang-2	23-May-2006	15990	560
Strang-6	23-May-2006	22330	910
Strang-6	24-Jan-2007	22080	770
Strang-3	23-May-2006	28000	1300
Strang-3	24-Jan-2007	28580	930

a - evaluated from uncertainties on Cd-ratio and ^{198}Au Q_0-value

Table 9

k_0-values of Zr-isotopes obtained in this work

Irradiation position	**Experiment No.**	**k_0, (s, %)**			
		^{94}Zr (n, γ) ^{95}Zr			**^{96}Zr (n, γ) ^{97}Zr/^{97m}Nb**
		724.2 + 756.7 keV	724.2 keV	756.7 keV	743.4 keV
Strang-3	1	2.025E-4 (3.1)	9.037E-5 (3.1)	1.120E-4 (3.1)	1.265E-5 (3.1)
	2	2.022E-4 (3.1)	9.046E-5 (3.1)	1.116E-4 (3.1)	1.258E-5 (3.1)
	3	2.007E-4 (2.5)	8.967E-5 (2.5)	1.109E-4 (2.5)	1.269E-5 (2.5)
	4	2.014E-4 (2.5)	9.018E-5 (2.5)	1.112E-4 (2.5)	1.275E-5 (2.5)
	5	2.022E-5 (2.5)	9.048E-5 (2.5)	1.117E-4 (2.5)	1.281E-5 (2.5)
	6	2.027E-4 (2.5)	9.067E-5 (2.5)	1.119E-4 (2.5)	1.280E-5 (2.5)
	7	2.014E-4 (2.5)	9.008E-5 (2.5)	1.112E-4 (2.5)	1.274E-5 (2.5)
Strang-6	1	2.018E-4 (3.1)	9.028E-5 (3.1)	1.115E-4 (3.1)	1.293E-5 (3.1)
	2	2.007E-4 (3.1)	8.974E-5 (3.1)	1.109E-4 (3.1)	1.283E-5 (3.1)
	Mean value	**2.017E-4**	**9.024E-5**	**1.114E-4**	**1.275E-05**
	sdandard deviation	**7.2E-7**	**3.4E-7**	**4.1E-7**	**1.1E-07**
	% sdandard deviation	**0.36**	**0.37**	**0.36**	**0.84**

Table 10
Uncertainty evaluation in k_0-factor determination

Source of uncertainty	**Relative uncertainty on k_0-value (1s), %**		
	^{198}Au	**^{95}Zr (724.2 + 756.7keV)**	**^{97}Zr**
monitor mass	0.027	0.037	0.037
monitor concentration	1	0.01	0.01
irradiation duration	0.06	0.06	0.06
irradiation situation factor (due to half-life uncertainty)	0.1	0.01	0.1
neutron flux stability during irradiation period, evaluated from reactor operation record	0.1	0.1	0.1
from $(f+Q_0)^{Au}/(f+Q_0)$ item in Eq. (2), maximum value	-	0	0.33
monitor positioning at 25cm or 15cm gamma-ray counting position (causing different efficiency)	0.2 (25cm), 0.5 (15cm)	0.2 (25cm), 0.5 (15cm)	0.2 (25cm), 0.5 (15cm)
gamma-ray counting efficiency at 25cm or 15cm position	1.3 (25cm), 2 (15cm)	1.3 (25cm), 2 (15cm)	1.3 (25cm), 2 (15cm)
live-time correction	0.5	0.5	0.5
decay correction (due to half-life uncertainty)	0.13	0.001	0.002
gamma-ray counting statistics	0.1 - 0.2	0.1 – 0.5	0.1 - 0.4
combined uncertainty on ^{95}Zr k_0-values		**2.24 - 3.22 %**	
combined uncertainty on ^{97}Zr k_0-values			**2.27 - 3.22 %**

Table 11

Zr k_0-values from this work compared to the recommended ones

Nuclide	gamma-ray, keV	k_0-value (s, %)				
		from this work	KFKI-AEKI[a]	IRMM/SCK[a]	INW[a]	Grand mean[b]/ Recommended[c]
^{95}Zr	724.2 + 756.7	2.017E-4 (2.3)	2.039E-4 (0.34)	1.959E-4 (0.88)	2.001E-4 (0.38)	2.000E-4 (1.2)
	724.2	9.02E-5 (2.3)	n.r.[d]	n.r.[d]	n.r.[d]	8.90E-5 (1.3)
	756.7	1.114E-4 (2.3)	n.r.[d]	n.r.[d]	n.r.[d]	1.10E-4 (1.3)
^{97}Zr/^{97m}Nb	743.4	1.275E-5 (2.3)	1.238E-5 (0.22)	1.174E-5 (3.2)	1.235E-5 (0.69)	1.237E-5 (0.3)

a - KFKI-AEKI, IRMM/SCK, and INW - three institutions where the k_0-determinations were carried out: A Simonits, et.al., The k_0 and Q_0 values for the Zr-isotopes: A re-investigation, J. Radioanal. Nucl. Chem., 245 (2000) 199

b - the recommended k_0-values were the Grand means of the values shown in this table from investigators KFKI-AEKI, IRMM/SCK.

c - F. De Corte and A. Simonits, Recommended nuclear data for use in the k_0 standardization of neutron activation analysis, Atom. Data and Nucl. Data Tables, 85 (2003) 47

d - not reported

Table 12

k_0-values of $^{97}Zr/^{97m}Zr$ 743.4keV gamma-ray determined from irradiations at low reactor thermal powers

irradiation position	**reactor thermal power**	**k_0-value[a]**
Strang-3	200kW	1.269E-05[b]
Strang-3	300kW	1.278E-05
Strang-3	2MW	1.284E-05
Strang-3	19MW	1.283E-05
k_0-value from irradiations at 20MW (see Table 11)		**1.275E-5 (2.3)**

a - the k_0-values calculated against the internal comparator of ^{95}Zr 724.2+756.7keV with k_0 = 2.018E-4

b - poor gamma-ray counting statistics