K₀-NAA and its Extension, software as well as Automation

NI BANFE, Tian weizhi, Zhang Yangmei, Zhang Lanzhi, Cao Lei, Wang Pingsheng
China Institute of Atomic Energy, P. O. Box 275-50, Beijing 102413 (P. R. China)

A post-K₀ study of parametric reactor NAA is described including the determination and applications of working K₀s for non-1/v reactions₁₁²Eu(n,γ)₁³⁵Eu and₁⁷⁶Lu(n,γ)₁⁷⁷⁷Lu; parametric corrections for U fission, threshold reaction and γ-spectral interferences; and parametric normalizations for different counting geometries. The analytical significance, the principles, the experimental confirmations, and the application examples of these methods are briefly introduced. The software and automation of hybrid K₀-relative NAA were also introduced.

Working K₀s for₁¹⁵Eu(n,γ)₁³⁵Eu and₁⁷⁶Lu(n,γ)₁⁷⁷⁷Lu

After the publication of K₀ values for 112 1/v nuclides, Eu and Lu are two of the most important elements excluded from K₀ method. Analytical reactions for these two elements are non-1/v ones for which H¹Ogdaž convention should be replaced by Westcott one with σₐ=g(Tₙ)σ₀, where g(Tₙ) is a function of Tₙ. The calculated g(Tₙ) for₁¹⁵Eu(n,γ)₁³⁵Eu and₁⁷⁶Lu(n,γ)₁⁷⁷⁷Lu indicated: under restricted conditions, the range of Tₙ could be relatively narrow and the variations of g(Tₙ)s for₁¹⁵Eu, and even for₁⁷⁶⁷Lu(n,γ) reactions could be small so that working K₀s may be used. Based on this consideration, working K₀s for these two reactions have been determined which shown in Table 1. The agreement between experimental working K₀s and calculated ones for₁¹⁵Eu(n,γ)₁³⁵Eu are fairly good. The effective neutron temperature estimated by Lu reaction is about 60⁰C (g=0.139/0.071=1.947).

<table>
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<th>Nucl.</th>
<th>Eγ</th>
<th>K₀,Au(Can)</th>
<th>K₀(EUS)</th>
<th>Nucl.</th>
<th>Eγ</th>
<th>K₀,Au</th>
<th>K₀(EUS)</th>
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<td>₁³⁵Eu</td>
<td>121.8</td>
<td>11</td>
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<td>₁³⁵Eu</td>
<td>1112.1</td>
<td>5.26</td>
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<td>4945.55d</td>
<td>344.3</td>
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<td>8.04</td>
<td>8.44</td>
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<tr>
<td>778.9</td>
<td>5.03</td>
<td>5.28</td>
<td>177⁷⁷⁷Lu</td>
<td>113</td>
<td>0.0428</td>
<td>0.0834</td>
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<td>964.1</td>
<td>5.64</td>
<td>5.92</td>
<td>6.71d</td>
<td>208.4</td>
<td>0.0714</td>
<td>0.139</td>
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</tbody>
</table>

These working K₀s have been successfully used for three years and on more than 800 samples. The relative differences between values from K₀ and relative method are generally within 3% and 5%, and never succeed 5% and 10%, for Eu and Lu determinations, respectively.

Parametric corrections for₁³⁵U fission interferences

Fission interferences are mainly from fission produced by thermal and epithermal neutrons through₁³⁵U (n, f) reaction. It has been found that in thermal energy region the excitation curve for₁³⁵U (n, f) reaction approximately obeys the 1/v law (only a
small resonance around 0.29 ev). Therefore $^{235}\text{U} (n, f)$ should be considered as $K_0$ method-suitable reaction. Moreover, literature value of $Q_0 (I_{\text{th}}/\sigma_0)$ for $^{235}\text{U} (n, f)$ reaction is only 0.472 and f ($\Phi_m/\Phi_0$) are typically within the range of 10-300. That means that $f+Q_0$ is very insensitive to the variation of $Q_0$.

On the basis of the two facts stated above, a parametric method of correcting for interferences caused by fission reactions is proposed and a neutron spectrum-independent factor $K_0$ defined as equations (1) and (2).

$$K_0 = \frac{M^* \cdot \frac{\theta}{\gamma} \cdot \frac{\gamma}{\gamma} \cdot \frac{\gamma}{\gamma} (\text{theory})}{\frac{\mu}{\mu} \cdot \frac{\theta}{\theta} \cdot \frac{\gamma}{\gamma} \cdot \frac{\gamma}{\gamma} (\text{exp})}$$

Where, parameters with asterisk refer to analytical indicators; Parameters without asterisk refer to the corresponding interference fission products.

$$Q_0 = \frac{I_{\text{th}}}{\sigma_0} \cdot \frac{\gamma}{\gamma} \cdot \frac{\gamma}{\gamma} \cdot \frac{\gamma}{\gamma} = \frac{275}{582} \cdot \frac{Y_f}{Y_x} = 0.472 \cdot \frac{Y_f}{Y_x}$$

$I_{\text{th}}, \sigma_0$ -- resonance integral and 2200 m/s cross section for U (n, f) reaction, respectively;

$Y_f, Y_x$ -- $^{235}\text{U} (n, f)$ fission yield for fission spectrum neutrons (an approximation of that for epigrammum neutrons) and subcadmium neutrons, respectively;

Note that each $K_0$ is now for a certain analytical indicator-interference fission product pair.

$K_0$ Values for major fission interferences cases have been determined in six irradiation channals (with $\Phi_m/\Phi_0$ 13.7-134) of three research reactors in CIAE. The $K_0$ values for $^{93,19}\text{Zr}, ^{97}\text{Zr}, ^{99}\text{Mo}, ^{141}\text{Ce}, ^{143}\text{Nd}$ were 10.7±0.3, 176±16, 3.12±0.35, 0.28±0.02, 1.28±0.06, 0.25±0.01, respectively.

The experimental $K_0$ values for major fission interferences show a neutron spectrum-independent nature and general agreement to the calculated ones, which lays the foundations ones, which lays the foundations of the method.

**Parametric corrections for threshold reaction interferences**

Activation equation for reactor fast neutron induced (n, p) and (n, $\alpha$) reactions can be written as:

$$A_n = \theta N_a / (\text{MSDC}_\gamma \varepsilon \sigma \Phi)$$

Where, $\theta, N_a, M$-isotopic abundance of target nuclide, $\varepsilon, \sigma, \Phi$ constant, and atomic mass of target element, respectively; 

$\gamma, \varepsilon$ -- branching ratio and photopeak efficiency of analytical $\gamma$-rays; 

$\sigma_f, \Phi_f$ -- (n, p) or (n, $\alpha$) cross section and fast neutron flux, respectively, over a primary $^{235}\text{U}$ fission neutron spectrum.

Equation (3) is applicable only when the following two prerequisites are met: i) Fast neutron spectrum($E_n>3\text{MeV}$) at irradiation position is close to primary $^{235}\text{U}$ fission one, which makes $\sigma_f$ and $\phi_f$ in eq.(3) meaningful; ii) $\sigma_f$ for relevant reactions are accurate enough. Multi-reactions with scattered effective threshold energies and accurately known $\sigma_f$s can be used for testing the similarity of fast neutron spectrum.
with primary fission one by determining $\Phi_I$ with each reaction and making comparison among them. The uncertainties for most $\sigma_i$ values of NAA interest in literature are less than 15%, adequate for threshold reaction interference corrections.

By integrating eq. (3) with regular $K_o$ expression, We have

$$IK_o = \left[ \frac{\theta \cdot M^* \cdot \sigma}{\theta \cdot M \cdot \sigma_0} \right]_{\text{theory}} = \left[ \frac{A_{\nu^*} \cdot \phi_{A^*}}{A_{\nu^*} \cdot \phi_I} (1 + Q_o / F) \right]_{\exp} \quad (4)$$

Where, again parameters with and without * stand for interfered and interfering reactions, respectively.

Since $t_i = t_i^* = t_i'$, then $A_{\nu^*}/A_{\nu*} = A_{\nu^*}/A_{\nu*}$.

The interference factor $A_{\nu}/A_{\nu^*}$ can therefore be expressed as

$$\frac{A_{\nu}}{A_{\nu^*}} = IK_o \cdot \frac{\phi_I}{\phi_{A^*}} \cdot \frac{1}{1 + Q_o / F} \quad (5)$$

**Parametric corrections for $\gamma$-spectral interferences**

$IK_o$ concept can be used here for $\gamma$-spectral interferences with

$$IK_o = \frac{K_{0,\omega}}{K'_{0,\omega}} = \frac{A_{\nu}}{A_{\nu^*}} \cdot \frac{F + Q_0}{F + Q'} \quad (6)$$

The interference factors $(A_{\nu}/A_{\nu^*})$ obtained from $IK_o$ and traditional relative method are in good agreement.

**Parametric efficiency normalizations for different counting geometric**

In reactor NAA, it is frequently encountered that the radioactivity differences between samples and standards irradiated in a same batch are so large that they can not be counted at the same position. Thus a geometry normalization is needed.

Many mathematical models have been published dealing with the calculations of Ge detector full-energy peak efficiencies. A general solution was given by Moens, et al in their program SOLANG for calculating full-energy peak efficiencies of cylindrical Ge detectors, taking account of near- and extended-geometric and $\gamma$-ray absorptions before reaching the sensitive volume of a detector. Common problems in all these studies are the requirements for: i) accurate dimensions of detector sensitive volume, which is hardly available; ii) detailed knowledge of dimensions and compositions of the source and absorbing materials between source and detector; and therefore iii) complex mathematical expressions. In fact, what concerns activation analysts most is efficiency ratios between different geometries instead of efficiency values themselves.

According to EID law, a cylindrical Ge detector can be considered a point at certain depth (dependent of $\gamma$-ray energy, $E$) of Ge crystal axis, the full energy peak efficiency $\varepsilon$ is inversely proportional to the square of the distance from source (point source at the extended line of Ge crystal axis) to that point. The EID law can be
briefly illustrated in Following diagram and expressed in Eq.7.

\[
\frac{\varepsilon_1(E)}{\varepsilon_2(E)} = \frac{(S_2 + S_0(E))^2}{(S_1 + S_0(E))^2}
\]

(7)

Where, \(\varepsilon_1(E), \varepsilon_2(E)\) – full energy efficiency of E at counting positions 1 and 2, respectively;

\(S_1, S_2\) – distances from source rack supporter to source positions 1 and 2, respectively;

\(S_0(E)\) – effective interaction depth for E, measured from source rack supporter.

The relative deviations of EID calculated efficiency ratios between different measurement positions from experimentally measured ones are less than 4%, generally within the range of counting statistics. Thus, each of samples and standards irradiated in the same batch with great disparity in gross activities can be measured at a position suitable for its own, without restriction of “counting at the same position”. Normalization can then be made by inputting only the rack heights to EID equations.

In the case of cascade-crossover decay scheme, true coincidence effect corrections may be needed. Since the analytical lines used in NAA are usually the major \(\gamma\)-rays of indicator nuclide, the simple model and equations as shown in Figure 2 and equations 10 and 11 are adequate for large majority cases. The correction factors

\[
C_1 = \frac{N_{1,}}{N_{2,}} = \frac{1}{1 - \varepsilon_{f2}}
\]

(8)

\[
C_2 = \frac{1}{1 - (\frac{P_1}{P_2})\varepsilon_{f1}}
\]

(9)

\[
C_3 = \frac{N_{3,}}{N_{3,}} = \frac{1}{1 + \frac{P_1\varepsilon_1\varepsilon_2\varepsilon_{f3}}{P_3}}
\]

(10)

where, \(N_{1,}, N_{2,}, N_{3,}\) – measured counting rates of full-energy peak for \(\gamma_1, \gamma_2, \) and \(\gamma_3,\) respectively;

\(N_{1,}, N_{2,}, N_{3,}\) – summing effect-corrected peak count rates for \(\gamma_1, \gamma_2, \) and \(\gamma_3,\) respectively;

\(P_{1,}, P_{2,}, P_{3,}\) – branching ratios for \(\gamma_1, \gamma_3, \) and \(\gamma_3,\) respectively;
\[ \varepsilon_1, \varepsilon_2, \varepsilon_3 \text{ --- full-energy peak efficiencies for } \gamma_1, \gamma_2, \text{ and } \gamma_3, \text{ respectively;} \]
\[ \varepsilon_{T1}, \varepsilon_{T2} \text{ --- total efficiencies for } \gamma \text{ and } \gamma_1, \text{ respectively.} \]

An overall error of 5% (maximum) for the combined EID normalization and summing effect correction is estimated for the worst situation (several mm S-D distance, \( \Phi 12 \times 3 \text{ mm bulky source and cascade-crossover decay scheme}), acceptable for most practical \( K_o \) NAA.

**Software**

A hybrid \( K_o \)-relative NAA program, ADVNAA, is established for calculation of elemental concentration and production of analytical report. A block diagram of ADVNAA is shown in Fig. 2. There are three options for standardization: 1) \( K_o \) method alone, 2) relative method alone, and 3) both \( K_o \) and relative methods.

For choice 1), some extended functions have been developed, including parametric prediction/correction for neutron flux self-shielding; \( K_o \) for non-1/\( \nu \) (n,\( \gamma \)) reactions; \( K_o \) methods for \( ^{235}U \) fission, threshold reaction, and \( \gamma \)-spectral interference corrections; parametric normalization for different counting position; etc., as detailed in corresponding references. Only a piece of weighed high purity Fe wire (comparator) and a piece of Zr foil (neutron flux ratio monitor) are needed for standardization of multielemental determinations (on condition that known \( \alpha \) channels are used). Fe standard is also used as a fast neutron flux monitor (via \( ^{56}Fe(n,p) \) reaction) for the determination of Ni through \( ^{58}Ni(n,p) \) reaction, on condition that the fast neutron spectrum in irradiation position has been proven to be close to a primary \( ^{235}U \) fission neutron spectrum. For choice 2), chemical standards of the elements of interest and relevant "interference standards" are needed for standardization of multielemental determinations. For choice 3), which is a combination of choices 1) and 2), chemical standards, Fe-Zr comparator/monitor and "interference standards" are needed. For any of these choices, appropriate CRMs are needed for analytical quality control.

Option 1) is usually used in routine analysis of large batch of samples, especially when "comparison analysis" is emphasized (e.g. some archaeological and forensic analysis). Option 2) is usually used when only a few elements are to be determined. In most cases, option 3) is used.

A analytical results for QC samples is always given for each batch of samples, as shown in Table 2, in which three values are given in parallel for each analytical line. They are from \( K_o \), relative method, and certified/reference value, respectively. The agreement within uncertainty limits among the three for certain analytical line indicates the reliability of this value.

**Hardware**

The PC based automatic sample changer system consists of seven major sections: 1) a vertical sample rack, which can hold up to 100 sample rabbits; 2) a converter for sending the lowest sample rabbit in the sample rack to the detector each time and...
A batch of irradiated samples is transferred to numbered standard rabbits, which are then arranged in a rabbit rack. A file is prepared for each sample in the batch, including spectrum ID, sample ID, sample weight, and counting position. When a subroutine AUT is started, the I/O board sends and receives signals for controlling the cycle of sample sending (to detector), counting for preset time, spectrum storage, spectrum erasing from the screen, sample returning (from detector to retrieving rack), sending the next sample, .... The stored spectra are automatically analyzed for peak parameters (energy, area, and associated uncertainty). With one command, elemental concentrations in each sample can be calculated and a final report produced by using the hybrid $k_0$-relative NAA program ADVNAA. The retrieving rack loaded with counted samples can be mounted onto the converter for the next round of counting at
The counting cycle can be interrupted manually at any moment (for changing counting time, counting position, or other reasons) and restarted by running AUT.

Summary

A post-K study on parametric reactor NAA has been conducted in an effort to achieve all-round parameterization. The major contents include the determination and applications of working $K_0$s for non-$1/v$ reactions $^{155}$Eu(n, $\gamma$) $^{155}$Eu and $^{176}$Lu(n, $\gamma$) $^{176}$Lu; the parametric corrections for $^{235}$U fission, threshold reactions, and $\gamma$-spectral interferences; and the parametric normalizations for different counting geometries. All these functions have been integrated to our NAA program ADVNAA and successfully used for 3 years.

Table 2 NAA output of NIST SRM 1633a for QA/QC

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy</th>
<th>$K_0$</th>
<th>$Err.$</th>
<th>Relative.</th>
<th>$Err.$</th>
<th>Reference</th>
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<td>Mo</td>
<td>140</td>
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<td>7.2</td>
<td>33.0</td>
<td>6</td>
<td>31.3</td>
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<tr>
<td>Ce</td>
<td>145</td>
<td>163</td>
<td>1.8</td>
<td>160</td>
<td>1.5</td>
<td>168.8±1.2</td>
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<td>Lu</td>
<td>208</td>
<td>1.2</td>
<td>2.6</td>
<td>1.25</td>
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<td>1.15±0.02</td>
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<td>U</td>
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<td>10.3</td>
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<td>Th</td>
<td>312</td>
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<td>Cr</td>
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Note: m means mg/g, all other data are in $\mu$g/g.
Fig. 2 Flow Chart of ADVNAA Software