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Neutron activation analysis using a modified absolute calibration method

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Abstract In this work a modified absolute calibration method of neutron activation analysis (NAA) was proposed. Reaction rates per atom of elements of interest were calculated by using MCNPX Monte Carlo code with a well established disk surface neutron source. Time dependency of the absolute reaction rate per atom produced during the irradiation was achieved by utilizing a well calibrated neutron monitoring system. Three activation foils with given compositions, namely, Au(1%)/Al, Mn(88%)/Ni and Cu(100%) and a SS304 sample were measured to test the adequacy and performance of this proposed modified absolute calibration method.

Keywords Neutron activation analysis · MCNPX · Neutron monitoring system

Introduction

For NAA both absolute and relative methods of calibration exist. For the relative calibration there are direct comparator method and k_0-comparator method. Direct comparator method is the most popular and accurate method. According to it a calibrator containing a known amount of the element(s) of interest needs to be irradiated together with the unknown sample as reference. For the absolute calibration method the mass of one of the observed elements is determined by directly applying the measurement equation of NAA [1]. The most critical point with the absolute calibration method is the determination of the reaction rate per atom, which strongly depends on several physical and geometrical features of the irradiation neutron field including the intensity, energy and angular distribution. In the derivation of NAA equations reaction rate per atom is divided into two parts, one related to thermal neutrons and the other to epithermal ones. After having considered several parameters and corrections the reaction rate R can be finally re-written as $R = \phi_{th}\,\sigma_{eff}$ [1]. Since each parameter and correction implies the consideration of an additional source of error, final uncertainty can be significant.

At Tsing Hua Open-pool Reactor (THOR), which is located at the campus of National Tsing Hua University in Hsinchu, Taiwan, we have developed an epithermal neutron beam for boron neutron capture therapy (BNCT) and successfully conducted clinical trials for patients with recurrent head and neck cancer since August, 2010 [2]. From the routine QA/QC process for the BNCT beam using activation foils we found that the BNCT beam at THOR can be adequately served also as a facility for conducting some popular NAA works. Since NAA is a side product and not the main task of the BNCT beam, we emphasized on the simplicity and convenience instead of high degree of accuracy. Therefore, a modified absolute calibration method is proposed to (1) avoid the necessity of the preparations of calibrators containing known amount of the element(s) of interest in the direct comparator method and to (2) overcome the difficulties in the determination of the elemental reaction rates per atom in the absolute calibration method. Here we propose a modified absolute

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calibration method, where the reaction rate per atom of the elements of interest is calculated by using MCNPX Monte Carlo code [3] with a well described disk surface neutron source. In addition, time dependency of the absolute reaction rate per atom produced during the irradiation time will be treated by applying the counting rates acquired per second of the well calibrated neutron monitoring system of the BNCT beam.

The Monte Carlo method, a highly powerful tool for the calculation of radiation transport in medium, offers an outlook for standardless absolute NAA [4]. In this work the Monte Carlo method was employed to calculate the reaction rate per atom of samples irradiated in a neutron field. Even in the direct comparator method of NAA, Monte Carlo methods can be used to evaluate the self-shielding factors of calibrator and unknown samples [5, 6]. In addition, since the peak efficiencies of detectors are indispensable data in NAA measurements, Monte Carlo methods can also be utilized to calculate the full energy peak efficiencies of HPGe detectors [7].

Materials and methods

Modification of the measurement equation of NAA

The measurement equation of NAA, which shows how the mass of an element can be derived from the net counts in the corresponding peak of the measured gamma-ray spectrum, can be found in Ref. [1]. In the modified absolute calibration method proposed in this work reaction rates per atom of elements of interest were acquired by Monte Carlo calculations, and the time variation of the neutron fluence rate was taken into account by applying a well calibrated neutron monitoring system. Accordingly the measurement equation of NAA was modified to the following equation.

$$m_{\mathrm{x}} = \frac{C\lambda}{\varepsilon \Gamma e^{-\lambda t_{\mathrm{d}}}\left(1-e^{-\lambda t_{\mathrm{m}}}\right) R_{\mathrm{a,s}} F \sum_{1}^{J}\left[FC\left(t_{\mathrm{j}}\right)\left(1-e^{-\lambda \Delta t}\right)e^{-\lambda\left(t_{\mathrm{i}}-t_{\mathrm{j}}\right)}\right]} \times \frac{M_{\mathrm{a}}}{\theta N_{\mathrm{AV}}} \tag{1}$$

where, m_{x}: mass of the irradiated element, g, C: net counts in the gamma-ray peak, λ: decay constant, s^{-1}, M_{a}: atomic mass, g mol^{-1}, ε: full energy peak efficiency of the detector, Γ: branching ratio of gamma ray, t_{d}: decay time, s, t_{m}: time duration of the measurement, s, t_{i}: irradiation time, s, $R_{\mathrm{a,s}}$: reaction rate per atom per source strength, F: fission chamber calibration factor, $FC(t_{\mathrm{j}})$: counting rate of fission chamber at time t_{j}, s^{-1}, Δt: small time interval where the neutron fluence rate is assumed to be constant, 1 s in this work, s, θ: isotopic abundance of the target isotope, N_{AV}: Avogadro's number, $\mathrm{mol}^{-1.}$

Experimental setup

A Polymethylmethacrylate (PMMA) phantom with dimensions of $20 \times 20 \times 20$ cm^3 in direct contact to the exit of the BNCT beam at THOR is served as the irradiation site of NAA. Under normal condition, samples are placed along the central axis of the phantom at a depth of 2 cm, where the thermal neutron fluence rate is the maximum. Of course neighbourhood locations are also adequate for sample irradiation. THOR is a swimming pool type research reactor and can be operated up to a power of 2 MW. The outlet of the BNCT beam has an aperture with a diameter of 14 cm.

The THOR-Y09 disk surface neutron source at the exit of the BNCT beam was applied in the calculation of the reaction rate per atom of elements of interest in the samples placed in the irradiation location in the PMMA phantom. A model of the neutron source was obtained by a Monte Carlo calculation of the reactor core in couple with the beam shaping assembly for the BNCT beam. The calculated result was then adjusted for energy, angular and spatial distribution by deconvolution measurements using multiple activation foils and the indirect neutron radiography [8]. The THOR-Y09 source contains three neutron components: thermal neutron, epithermal neutron, and fast neutron source terms. Although the radius of the BNCT beam aperture is only 7 cm the disk surface source at the beam exit has a radius of 11 cm to take into account radial diffusion of neutrons. Table 1 lists the source strengths of different components of the THOR-Y09 neutron source operated at 1.2 MW. Details of the energy, angular and spatial distributions of the THOR-Y09 source have been presented in our previous work [9]. Figure 1 shows the energy range and energy group distribution of the three neutron source components.

For the gamma-ray spectrum measurements a CANBERRA high purity germanium (HPGe) detector with type GC2520 in a lead cell was applied. The peak efficiencies of the HPGe detector were calibrated by using standard reference sources ^{60}Co, ^{137}Cs and ^{152}Eu. The effect of sample size used in this work on the detector efficiencies was less than 1% estimated by using Monte Carlo calculations [7]. The radioactive samples were placed along the crystal axis at a distance of 6 cm from the top surface of the detector capsule. A DSPEC multichannel analyzer from ORTEC was used for gamma-ray spectrum acquisition. The counting areas associated to the peaks of interest generally exceed ten thousand to get good statistic uncertainty. The constant dead time case for correction of live-time extension loss [1] was adopted in the data analysis.

Table 1 Source strengths of different components of the THOR-Y09 neutron source

Source particle	Energy range (MeV)	Source strength (s^{-1})	
		Beam aperture (radius = 0–7 cm)	Beam leakage (radius = 7–11 cm)
Thermal neutron	1.0E−10 to 4.0E−07	9.312E+09	4.361E+09
Epithermal neutron	4.0E−07 to 7.2E−03	1.261E+11	2.195E+10
Fast neutron	7.2E−03 to 20.0	9.852E+09	1.288E+08
Total neutron	1.0E−10 to 20.0	1.453E+11	2.644E+10

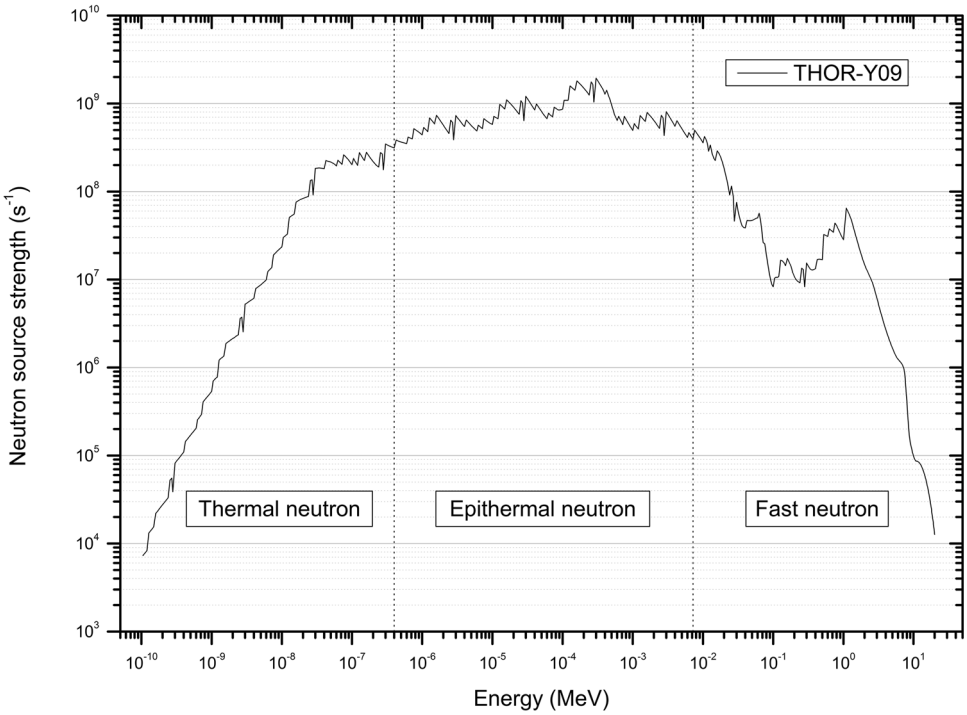

Fig. 1 The energy group distribution of the three source components of the disk surface neutron source at the exit of the BNCT beam

Results and discussion

Test measurement of activation foils

For a test of the proposed modified absolute calibration method we conducted three NAA measurements of activation foils with given element weight percent. The first sample was a Au/Al foil with 1% Au, and the second one was a Mn/Ni foil with 88% Mn. The third sample set was the same Au/Al foil mentioned above followed by a 100% Cu foil. All the foils have dimensions of 1.2 cm in diameter and the thickness of Au/Al, Mn/Ni and Cu are, respectively, 0.2, 0.1 and 0.1 mm. The foil samples were irradiated in the PMMA phantom along the central axis at a depth of 2 cm. The reaction rates per atom of the elements of interest were calculated using MCNPX Monte Carlo code describing the whole system, i.e., samples, the irradiation site and neutron source. Figure 2 shows the counting rates of one of the fission chambers of the neutron monitoring system as a function of time during the irradiation of Mn/Ni foil. Table 2 lists the results of the test measurement. In the estimation of the uncertainty of m_x, which was calculated from Eq. (1), only the uncertainties of net counts in the gamma-ray peak, C, full energy peak efficiency of the detector, ε, reaction rate per atom per source strength, $R_{a,s}$, fission chamber calibration factor, F, and time-dependent counting rate of fission chamber included in the brackets, $FC(t_j)$, were taken into account in this work. In Table 2 the standard uncertainty of peak counts was taken from the multichannel analyzer for gammy-ray spectrum acquisition. In the measurements of this work, the uncertainty of full energy peak efficiency of the HPGe detector was around 2% dominantly due to the uncertainties of the intensities of the standard reference sources used in the efficiency calibration. For the evaluation of the combined standard uncertainty of m_x according to the uncertainty propagation formula, the uncertainty of the full peak efficiency of the HPGe detector was divided by $\sqrt{3}$ since it is assumed to be a uniformly distributed Type B uncertainty [10]. The reaction rate per atom

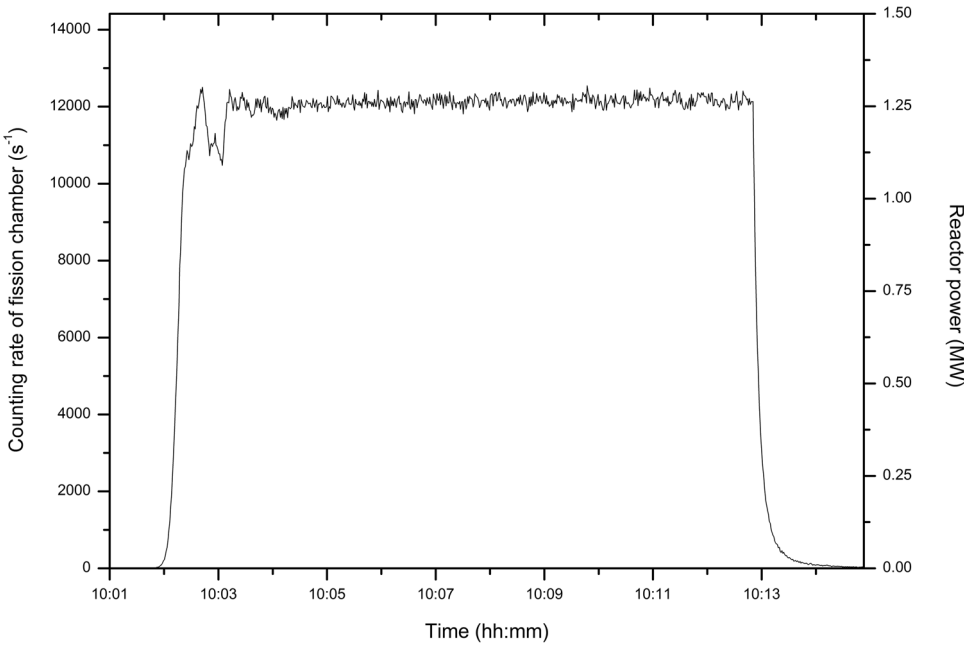

Fig. 2 Typical counting rates of fission chamber as a function of time during the sample irradiation

Table 2 NAA of BNCT QA/QC activation foils

Sample	Weight (mg)	Isotope	Peak energy (keV)	t_i (s)	t_m (s)	Peak counts	Reaction rate per atom (s^{-1})	m_x/weight	m_x/weight (spec.)
Au/Al	70.166	^{198}Au	411.8	600	5400	52,800 ± 200	3.86E−13 (0.7%)	0.988 (14) % of Au	1% of Au
Mn/Ni	77.354	^{56}Mn	846.6	600	1800	77,500 ± 300	2.98E−14 (0.5%)	88.5 (12) % of Mn	88% of Mn
Au/Al[a]	68.526	^{198}Au	411.8	360	1200	11,800 ± 100	3.84E−13 (0.7%)	0.993 (17) % of Au	1% of Au
Cu[a]	104.131	^{64}Cu	511.1	360	180	22,000 ± 200	1.007E−14 (0.2%)	97.9 (14) % of Cu	100% of Cu

All uncertainties are standard uncertainties

[a] Al/Al and Cu foils were stacked together during irradiation

together with percent standard uncertainty in Table 2 was given by the MCNPX calculation. Note that the uncertainty given by the MCNPX only counted the statistic uncertainty of the Monte Carlo calculation based on the given neutron source distributions and cross sections in the data library. That is, the uncertainties of cross sections and neutron source term THOR-Y09 were not taken into account. The uncertainty due to neutron source distributions was estimated to be less than 3% referring to its generation [8]. It is noted, however, that the uncertainty of cross sections itself is often "uncertain" and might have a significant effect on the combined uncertainty of the results. For fission chamber calibration factor and time-dependent counting rate of fission chamber, the standard uncertainties were both less than 1%. In addition, the uncertainties of the other terms in Eq. (1) including decay constant, λ, gamma-ray branching ratio, Γ, and isotopic abundance of the target isotope, θ were not included in the calculation since these uncertainties itself were not considered significant. Nevertheless, note that the deviations of λ, Γ, and θ of ^{198}Au, ^{56}Mn, and ^{64}Cu between various data libraries [11–14] were less than 0.1% except Γ of ^{64}Cu, which was possibly around 10%. It can be seen from Table 2 that the measured weight percent of elements of interest agreed excellently with the specification values with the deviation about 1–2%. From these test measurements it is demonstrated that the proposed modified absolute calibration method is a good and adequate NAA method.

Measurement of a SS304 sample

Following the test measurement we proceeded to measure a SS304 sample with dimensions of $\sim 1.0 \times 1.0 \times 0.1$ cm^3 and a weight of 741.9 mg. The sample was irradiated at the same location as that for activation foils. After irradiation the gamma-ray spectrum of the sample was acquired at first for 5 h to get the peak counts of ^{65}Ni gamma rays. Following about half day another gamma-ray spectrum of the

sample was acquired for ~3 h to analyze the peak counts for other isotopes. The typical compositions of SS304 [15] were modeled in the MCNPX calculation of the reaction rates per atom of elements of interest. Table 3 lists the measurement results. Similarly, the uncertainties of λ, Γ, and θ itself were also not included in the calculation. However, note that the deviations of λ, Γ, and θ between different data libraries [11–14] were estimated around 1, 0.7, and 10% for ^{59}Fe, and 0.1, 0.4, and 3% for ^{65}Ni. For ^{51}Cr and ^{60}Co all the deviations were less than 0.1%. It was found from Table 3 that the compositions of Cr, Ni and Mn fell within the corresponding ranges of American Society for Testing and Materials (ASTM) specification of SS304 [16]. In addition, 0.236% of Co was found in the sample. It is worthwhile to note that the composition of iron was overestimated by around 10%. The reason was still under exploration, however, it was also inferred that the activation cross section of ^{58}Fe in ENDF/BVII.0 library used in MCNPX calculation may be not accurate enough. Therefore, we performed an additional MCNPX calculation of the ^{58}Fe(n, γ)^{59}Fe reaction rate per atom using the ^{58}Fe activation cross section taken from TENDL-2015 cross section data library [17], and the results are also shown in Table 3. It is interesting to find that the composition of iron derived from the MCNPX calculation using TENDL-2015 library becomes more accurate to provide a total weight percent of the SS304 sample around 100%. The comparison of the ^{58}Fe(n,r)^{59}Fe cross section between ENDF/BVII.1, which is identical with ENDF/BVII.0, and TENDL-2015 libraries can also be found in the Ref. [17]. According to the results in this section, it is clear that the quality of outcome provided by the modified absolute calibration method depends on the quality of cross sections. From the other point of view, however, this dependency can be employed to verify the accuracy of the cross sections in different libraries.

Sensitivity study of sample matrix

One of the key points of the proposed modified absolute calibration method is the calculation of the reaction rate per atom of the elements of interest. As the neutron source is already well described, an accurate reaction rate per atom can be achieved by using Monte Carlo calculation with a detail model consisting of the compositions and geometry dimensions of the sample and the irradiation phantom. However, the compositions of the sample are normally not well known since the weight percent of some elements of interest in the sample is unknown for determination. Therefore, we proceeded to conduct the sensitivity study of the matrix compositions of the samples. Figure 3a shows the variation of total neutron fluence rates at the sample position and reaction rates per atom of ^{197}Au and ^{55}Mn of the Au/Al and Mn/Ni foils, respectively. From Fig. 3a it can be seen that for Au/Al foil, changing the weight percent of Au from 1 to 0 and 2% had essentially no influence on the total neutron fluence rate. Meanwhile, the differences of the reaction rate per atom of ^{197}Au were only around 2%. For Mn/Ni foil, changing the weight percent of Mn from 88 to 50 and 100% had very little influence within the statistical error on both total neutron fluence rate and the reaction rate per atom of ^{55}Mn. Figure 3b shows the variations of total neutron fluence rate and reaction rates per atom of composition elements when the SS304 sample was replaced by SS316, Fe, and PMMA, respectively. The calculation results were essentially the same within the statistical error when the SS304 sample was replaced by

Table 3 NAA of a SS304 sample

Element	Isotope	Peak energy (keV)	t_i (s)	t_m (s)	Peak counts	Reaction rate per atom (s^{-1})	m_x/weight	m_x/weight (ASTM spec.)
Cr	^{51}Cr	320.1	7200	11,437	44,800 ± 200	3.42E−14 (0.4%)	17.55 (24)%	17.5–19.5%
Fe	^{59}Fe	1099.2	7200	11,437	1070 ± 50	2.52E−15 (0.5%)	80 (4)%	N/A
						2.83E−15 (0.5%)[a]	71 (4)%[a]	N/A
Ni	^{65}Ni	1481.8	7200	18,000	2100 ± 200	3.26E−15 (0.4%)	9.5 (11)%	8.0–10.5%
Mn	^{56}Mn	846.6	7200	11,437	42,000 ± 200	2.91E−14 (0.4%)	0.835 (11)%	2%
Co	^{60}Co	1332.5	7200	11,437	1280 ± 50	8.45E−14 (0.5%)	0.236 (10)%	N/A
SS304							108 (4)%	100%
							99 (4)%[a]	

The weight of SS304 sample is 741.9 mg

All uncertainties are standard uncertainties

[a] Data with ^{58}Fe activation cross section from TENDL-2015 library

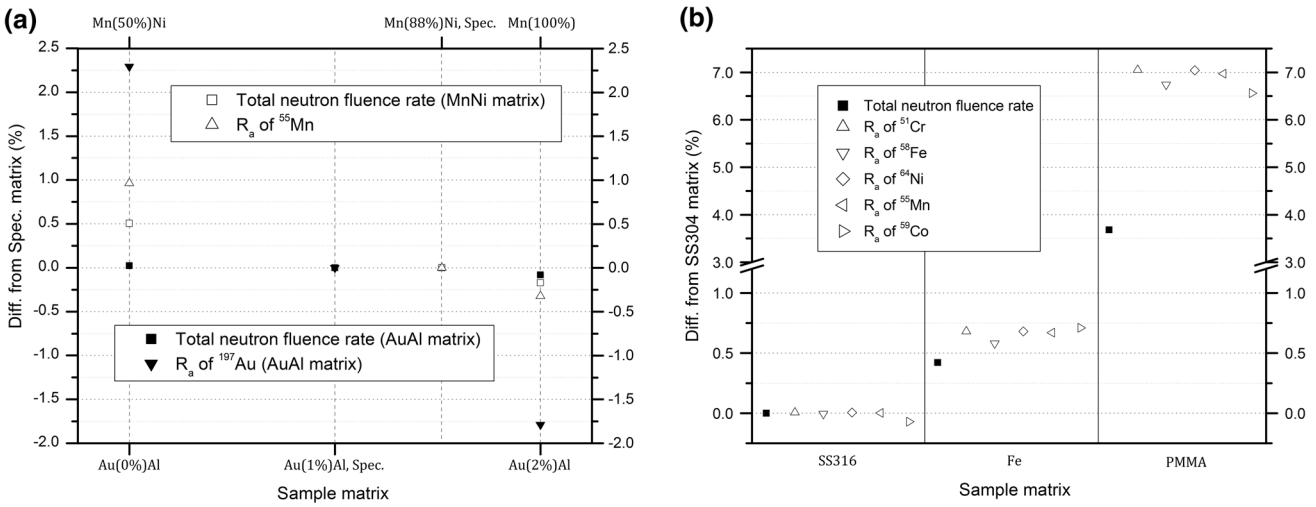

Fig. 3 Sample matrix sensitivity test for **a** activation foils and **b** a SS304 sample

SS316. For the replacement of SS304 sample by pure iron, the difference of reaction rate per atom and the total neutron fluence rate were less than 1%. Even for the replacement of SS304 by PMMA, that is the same material as the surrounding PMMA phantom, the reaction rate per atom of composition elements changed by only about 7.0% and the total neutron fluence rate by around 3.5%. From these sensitivity studies it indicates that for the Monte Carlo calculation of the reaction rates per atom of elements of interest in the sample the information about the compositions of the sample is not sensitive to the calculation results. In the extreme cases without any information, i.e., replacing SS304 sample by pure iron will only cause less than 1% deviation. Even if the SS304 sample is treated as the surrounding PMMA material the deviation is still only about 7.0%. It is worthwhile to note that the mass of an element of interest determined from the modified measurement equation of NAA, where the reaction rate per atom of the element of interest was calculated by the Monte Carlo code with an initial guess of the composition of the sample, can still be improved by applying the measurement equation once again, while the reaction rate per atom of this element of interest is taken from another Monte Carlo calculation with the prior determined mass of the element of interest in the sample.

Conclusion

A modified absolute calibration method of NAA was proposed in this work. With several tests it has been demonstrated that the proposed modified absolute calibration method is a good and adequate NAA method. Meanwhile, it was worthwhile to note that the composition of iron in a SS304 sample was found to be overestimated by around 10% using ENDF/BVII.0 library. This inference was indirectly verified by the calculation using $^{58}Fe(n, \gamma)^{59}Fe$ activation cross section from TENDL-2015 library. The quality of results provided by the modified absolute calibration method obviously depends on the quality of cross sections, but on the other side this dependency is also capable of highlight possible cross-section errors. From the sample matrix sensitivity study it indicates that the calculation of the reaction rate per atom of the elements of interest is not sensitive to the composition of the sample, a rough estimation of the composition is good enough.

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