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Contribution of detection efficiency to the uncertainty budget in NAA

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Abstract In neutron activation analysis the sample to be analysed is counted with the same detection efficiency as the standard or else a correction factor is determined to correct for the difference. The components contributing to the uncertainty of the detection efficiency correction factor were identified and evaluated by using ^{182}Ta gamma-rays for typical NAA samples counted 1 and 100 mm from the detector. Uncertainties as high as 20 % were found due to coincidence summing and gamma attenuation. It was shown how to incorporate these components into the NAA uncertainty budget.

Keywords Uncertainty · Detection efficiency · Neutron activation analysis · Gamma-ray spectrometry

Introduction

It is now recognized [1–5] that the uncertainties reported with neutron activation analysis (NAA) results must include the individual uncertainty components from all sources of uncertainty. The numerous sources of uncertainty include: statistical uncertainty of the peak area, uncertainty in the peak area calculation method, the uncertainty in the concentration of the element in question in the standard, the non-representativity of the sample for inhomogeneous materials, uncertainty in weighing, difference in neutron fluence between standard and sample, neutron self-shielding, correction of difference in decay

between standard and sample, interferences, counting losses, and difference in counting geometry between standard and sample. Each of these contributions to the total uncertainty should be evaluated for each material analysed and combined by statistical means.

NAA measurements generally have uncertainty due to the difference in counting geometry between standard and sample. In the ideal case, the standard would match the sample to be analysed in size, shape, density and chemical composition. In practise this is never possible, but in favourable cases the differences can be made small enough so that, with the high penetrating power of high-energy gamma-rays, the difference in detection efficiency between the two may be quite small, even less than 1 % [6]. Quite often though, the differences in size, shape and density are large and in some cases the activity of a sample may be high enough that one is forced to count it at a greater distance from the detector than the standard. In these cases, the difference in counting efficiency is large and an important correction factor is needed. The required correction will be carried out using an efficiency model. In k_0-NAA the situation is more complex as the analyte and comparator are different elements and an elaborate model is needed to compare efficiencies for gamma-rays of two different energies with different coincidence summing. In this work we evaluate the uncertainty remaining in the analysis result after the necessary corrections are made.

We separate the uncertainty of the efficiency correction into its different components and we estimate the magnitude of each component for typical NAA samples and counting geometries. The components identified are: the variation of efficiency with sample-detector distance, the integration of the efficiency over the sample volume, gamma attenuation and coincidence summing. A fifth and final factor is the accuracy with which the sample is

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positioned in the geometry specified in the correction algorithm. These components are combined statistically to give the total uncertainty of the efficiency correction.

We designate as U_ε the total standard uncertainty in the NAA result due to the uncertainty of the determination of the ratio of detection efficiencies of the sample and the standard, $\varepsilon_{sam}/\varepsilon_{std}$. The correction of the analysis result is carried out by dividing the result by the determined value of $\varepsilon_{sam}/\varepsilon_{std}$. U_ε is determined by combining the contributions from the various components: u_d for sample-detector distance, u_v for integration over the sample volume, u_γ for gamma attenuation, u_c for coincidence summing and u_p for the uncertainty associated with positioning the sample in the geometry specified in the correction algorithm. Then U_ε can be determined from the equation:

$$U_\varepsilon^2 = u_d^2 + u_v^2 + u_\gamma^2 + u_c^2 + u_p^2 \qquad (1)$$

It is expected that u_d, u_c and u_p will be larger for samples counted close to the detector, u_v and u_γ will be larger for large samples and u_γ will be larger for low-energy gamma-rays. Measurements were carried out to quantify these components for typical types of samples analysed at the Polytechnique NAA Laboratory.

Experimental

Test sample preparation

^{182}Ta was chosen as the gamma-emitting nuclide for this study because it has a long half-life, 114.4 days, and it emits a number of gamma-rays over a wide energy range, from 68 to 1221 keV. Metallic tantalum fine powder was activated by neutron irradiation in the Polytechnique Montreal SLOWPOKE reactor. Two batches of powder were activated: one was irradiated for 30s at a neutron fluence rate of $5 \times 10^{11} \mathrm{cm}^{-2}\mathrm{s}^{-1}$ to be used for measurements close to the gamma-ray detector and the other for 300s at the same fluence rate to produce higher activity for measurements farther from the detector.

The tantalum powder was mixed to ensure good activity homogeneity and was used to prepare samples of known relative activity of ^{182}Ta. Disk samples, with diameter of 14 mm and thicknesses ranging from 2.5 to 15 mm were made by mixing the Ta powder, typically 30 mg, with SiO_2 powder. They were weighed and mixed in 14 mm diameter polyethylene counting vials. Weighed amounts of PbO_2 were added to some of the samples to give a higher gamma-ray attenuation at low energies. Solid samples are often received by the laboratory as small pieces or powders and they are irradiated and counted in small polyethylene vials. When standards are prepared the vials are filled completely but for the received samples there is often not

enough material to fill the vials. To study the uncertainty of the geometry correction in these cases, samples were also prepared by adding SiO_2 powder to the Ta powder to partially fill the 10 mm diameter, 20 mm long polyethylene sample vials.

Counting geometries

The 14 mm diameter disk samples were counted at 1 and 100 mm from a germanium detector with 33 % relative efficiency at 1332 keV. The partially filled 10 mm diameter, 20 mm long polyethylene sample vials were counted on their sides, with their axis perpendicular to the detector axis, as is commonly done at the Polytechnique NAA Laboratory. They were placed on the support 1 or 100 mm from the detector either by hand or using an automated sample changer. All the peak areas were calculated by the Ecole Polytechnique Activation Analysis software (EPAA), which corrects for dead-time and decay, and were converted to specific activities by dividing by the counting time and the mass of the Ta powder. To compare the specific activities measured with different counting geometries, the specific activities for the various samples were divided by the correction factor $\varepsilon_{sam}/\varepsilon_{std}$, which was calculated for each counting geometry using the available model [7]. The calculation of detection efficiency included a correction for coincidence summing [8], which can be quite important for the gamma-rays of ^{182}Ta. In the case of the partially filled vials counted on their sides, the measured specific activities were corrected by a factor $\varepsilon_{sam}/\varepsilon_{std}$, calculated by a simple linear relation of detection efficiency versus filling fraction. Such a linear relation of sample counting efficiency as a function of filling fraction has also been used successfully by Jodlowski [9].

Results and discussion

Uncertainty of the efficiency correction for partially filled vials

The vials filled to various fractions, from 5 to 100 %, were each counted several times, 1 and 100 mm from the detector, to observe the variation of the measured activities and the possible systematic error of the simple efficiency correction used for vials counted on their sides where it was approximated that efficiency varies linearly with the filling fraction. The results are shown in Figs. 1 and 2 for two of the most intense gamma-rays of ^{182}Ta, 68 and 1121 keV. The activities were normalized to the mean activities measured with the 100 % full vials, which were considered as the standards. The measured relative activity of each sample was corrected for the change in detection

Fig. 1 Corrected relative activities as a function of filling fraction measured for sample vials counted 100 mm from the detector. *Left side*: 68 keV gamma-ray, *right side*: 1121 keV gamma-ray
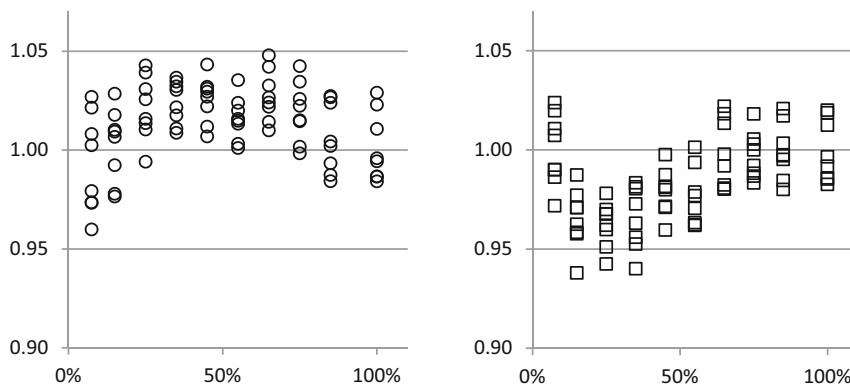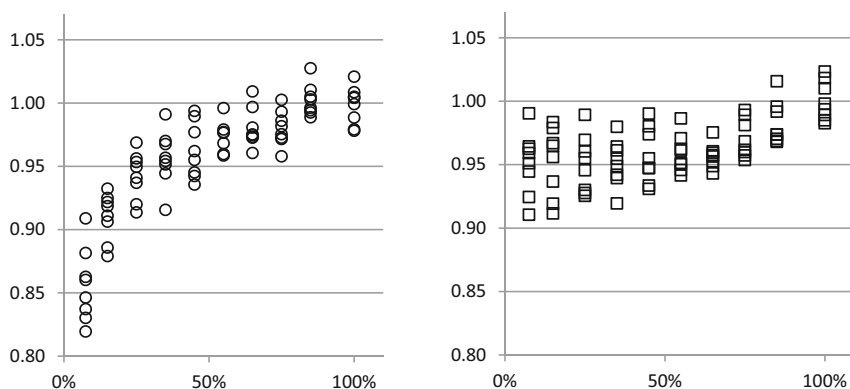
Fig. 2 Corrected relative activities as a function of filling fraction measured for sample vials counted 1 mm from the detector. *Left side*: 68 keV gamma-ray, *right side*: 1121 keV gamma-ray

efficiency due to the filling fraction by dividing by a factor $\varepsilon_{sam}/\varepsilon_{std}$ calculated by the linear relation. Each vial was counted eight times to illustrate the variation from one measurement to another.

For the vials counted 100 mm from the detector, Fig. 1, a random variation in each series of eight measurements is observed with standard-deviation approximately 1–2 %. It is attributed mainly to statistical fluctuations in the peak areas, typically 0.5–1 %. For the vials filled less than 30 % the random variation is slightly greater and it is attributed to changing counting geometry caused by movement of the powder in the vials. Gravity has not perfectly maintained the powder on the bottom side of the vial. This variation is greater at 68 keV than at 1121 keV because, in addition to the variation of the mean distance between sample and detector, there is also a greater variation in gamma attenuation at 68 keV with varying effective sample thickness.

For both gamma-ray energies, a systemic trend is observed due to the inaccuracy of the linear efficiency correction algorithm. For the 1121 keV gamma-ray the mean corrected relative activity decreases to 0.96 at 20 % filling fraction and for the 68 keV gamma-ray it increases to 1.03 at 50 % filling fraction. At 5 % filling fraction the calculated $\varepsilon_{sam}/\varepsilon_{std}$ is 1.08 and it appears to correct the data within 1 % for both gamma-ray energies.

For the vials counted 1 mm from the detector, Fig. 2, the random variation in the measurements has increased. For both gamma-ray energies, the standard-deviation of the eight data points at 5 % filling fraction is now approximately 2.5 % and is attributed to the movement of the powder in the vials. The effect is greater than at 100 mm because the same variation in sample position and mean sample-detector distance causes a greater variation in the counting efficiency when the sample is close to the detector.

Also, for both gamma-ray energies, the systemic trend at 1 mm is greater than that observed at 100 mm. At 5 % filling fraction the $\varepsilon_{sam}/\varepsilon_{std}$ calculated by the linear algorithm is 1.22. As can be seen in Fig. 2, this correction factor over-corrects by 5 % at 1121 keV and by 15 % at 68 keV. The lower than expected peak areas observed for the 68 keV gamma-ray for partially filled vials 1 mm from the detector are due partly to movement of the powder in the vial and also to coincidence summing, an effect not included in the linear algorithm. In any case, the systematic errors in the corrected relative activities are much greater for vials counted at 1 mm compared to those counted at 100 mm, which illustrates that differences in counting geometry between standard and sample cause greater errors in analysis results when samples are counted close to the detector.

Uncertainty of efficiency correction for disks and thick cylinders

Disks 2.5 mm thick and cylinders up to 15 mm thick, all with 14 mm diameter, were counted 1 and 100 mm from the detector, to observe the possible systematic errors of the model which determines the efficiency correction. Each sample was counted four times and the mean activities were calculated for each gamma-ray to reduce the random errors from counting statistics. Each measured relative activity was corrected for the change in detection efficiency due to changing sample thickness by dividing by a factor $\varepsilon_{sam}/\varepsilon_{std}$ calculated by the efficiency model. The model [7] uses an efficiency curve measured at a source-detector distance of 250 mm and calculates the counting efficiency of any sized sample at any distance from the detector by integrating a semi-empirical function of efficiency vs distance over the volume of the sample. It also corrects for gamma attenuation and coincidence summing [8]. The coincidence summing calculation is considered as part of the efficiency calculation. In Fig. 3 the results are shown as a function of sample thickness for the cylinders counted 100 mm from the detector. It is assumed that the standard is a 2.5 mm thick disk. Therefore, all the data are normalised relative to those for the 2.5 mm thick disk and $\varepsilon_{sam}/\varepsilon_{std}$ has zero uncertainty for this disk. For all gamma-ray energies, it is seen that the corrected relative activities become less accurate as the sample thickness increases, with the mean error reaching 2 % at 10 mm thickness and 6 % at 15 mm thickness. The error is greatest for the lowest energy gamma-rays because the correction for gamma attenuation is greatest.

In Fig. 4 the corrected relative activities are shown for the cylinders counted 1 mm from the detector. Again it is assumed that the standard is a 2.5 mm thick disk and the data are normalised relative to those for the 2.5 mm thick disk. The $\varepsilon_{sam}/\varepsilon_{std}$ ratio has zero uncertainty for this disk

Fig. 4 Corrected relative activities measured for cylinders of various thicknesses counted 1 mm from the detector

because any error in the efficiency calculation is the same for the standard and the sample and they cancel. The same trend is observed as at 100 mm but there are now larger differences among the individual gamma-rays. These differences are thought to be due to the coincidence summing correction which is different for each gamma-ray.

In Fig. 5 the corrected relative activities are shown for the same cylinders counted 1 mm from the detector but here it is assumed that the standard is a 2.5 mm thick disk counted 100 mm from the detector. The correction factors $\varepsilon_{sam}/\varepsilon_{std}$ are now very large because of the large difference in source-detector distance between sample and standard. Not only is the correction for source-detector distance quite large but also the coincidence summing correction, which is small at 100 mm, is now quite large at 1 mm. It is seen that even for the thinnest disk the errors are quite large and vary from one gamma-ray to another. These large errors are due mainly to the inaccuracy of the coincidence summing correction. The errors are usually positive because the model usually over-corrects for coincidence summing. As the samples increase in thickness the errors are seen to increase, except for the 152 keV gamma-ray, because for
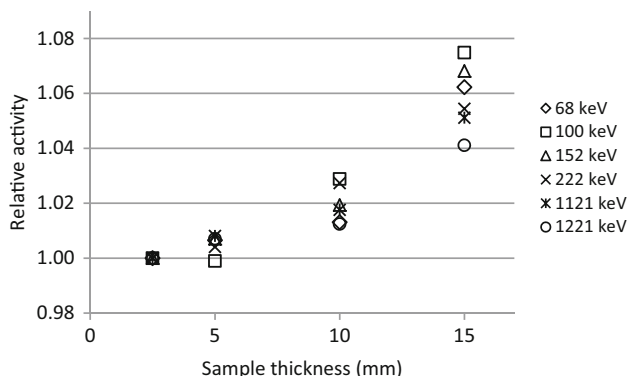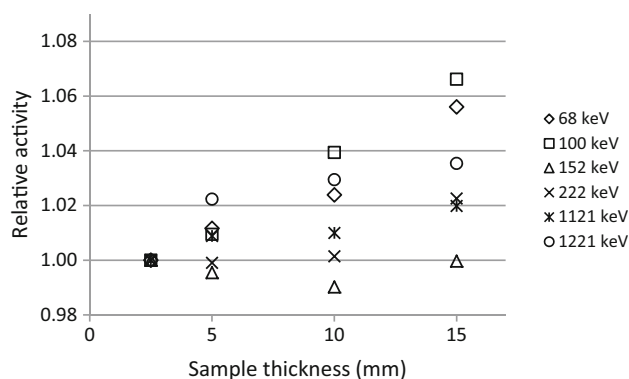

Fig. 3 Corrected relative activities measured for cylinders of various thicknesses counted 100 mm from the detector
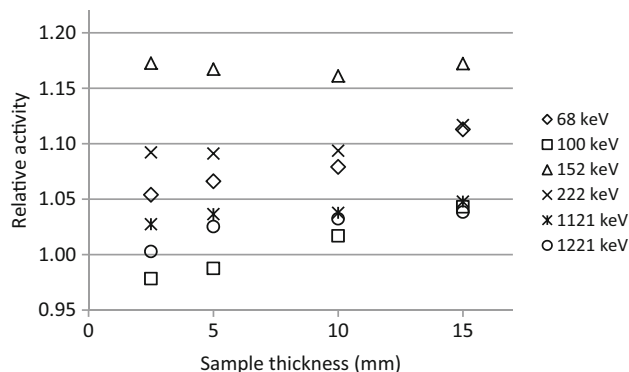

Fig. 5 Corrected relative activities measured for samples counted 1 mm from the detector when the standard is counted 100 mm from the detector

this gamma-ray the error in the procedure for integrating the efficiency function over the volume of the sample is compensated by the error in correcting the coincidence summing.

These data illustrate the inaccuracy when the standard is counted far from the detector and the samples are counted close to the detector. The errors in $\varepsilon_{sam}/\varepsilon_{std}$ seen in Fig. 5 due to coincidence summing would be the same, but in the opposite direction, if the standard was counted 1 mm from the detector and the samples were counted 100 mm from the detector.

Table 1 shows the coincidence summing factors, COI, calculated for the ^{182}Ta gamma-rays in the 2.5 mm thick disk counted 1 mm from the detector. The calculated detection efficiency is corrected for coincidence summing by multiplying by COI. It can be seen that the 1221 keV gamma-ray has less coincidence summing losses than the others; besides having less coincidence summing losses, its COI is also increased by the summing of the 100 and 1121 keV gamma-rays. For the other gamma-rays the COI are generally between 0.6 and 0.7. Thus the correction implies multiplying the analysis result by a factor of the order of 1.5, i.e. a 50 % correction. After application of this correction, Fig. 5 shows that the residual error in the result is generally of the order of 5 %, i.e., a remaining error of 10 % of the applied correction. For all heavy element nuclides which emit gamma-rays and X-rays in coincidence, the calculated coincidence summing correction factors, COI, will generally have 5 % uncertainty for samples counted close to the detector, which is far greater than the 1.5 % uncertainty previously assumed by Kubešová et al. [4] and others. Fortunately, as Fig. 4 shows, the 5 % uncertainty in $\varepsilon_{sam}/\varepsilon_{std}$ due to the coincidence summing correction can usually be eliminated by counting the sample and standard at the same distance from the detector. In k_0-NAA, the analyte and standard are different elements and the uncertainty in $\varepsilon_{sam}/\varepsilon_{std}$ due to the coincidence summing correction cannot be eliminated.

It can be seen in Fig. 5 that the coincidence summing for the 152 and 222 keV gamma-rays is over-corrected by 9–17 %. After these observations, the coincidence summing correction routine [7, 8] was verified and errors were found in the algorithms for these two gamma-rays. After

correction of these errors, the results using the 152 and 222 keV gamma-rays now have uncertainties similar to those obtained with the other gamma-rays of ^{182}Ta.

Uncertainty of the efficiency correction due to gamma attenuation

Efficiency models calculate the gamma attenuation in the sample by integrating over the volume of the sample a model taking into account the sample density and the gamma mass attenuation coefficient, which depends on the chemical composition of the sample. In samples with uncertain chemical composition, such as those with unknown concentrations of heavy elements like Pb, which cannot be determined by NAA, the calculated $\varepsilon_{sam}/\varepsilon_{std}$ will have increased uncertainty. To illustrate this, cylinders 15 mm thick containing up to 100 mg/g PbO_2 were counted. The results are shown in Fig. 6. The measured specific activities were normalised relative to the standard which contained the ^{182}Ta gamma emitter and SiO_2 but no Pb. It can be seen that the additional gamma attenuation at low energy due to the high mass attenuation coefficient of Pb can be as much as 37 %. Gamma attenuation is higher at 100 keV than at 68 keV because 100 keV is just above the k-absorption edge of Pb at 88 keV. Even if the data of Fig. 6 had been corrected for gamma attenuation taking into account the effect of the known concentration of Pb on the mass attenuation coefficients, the corrected results would still have uncertainty due to uncertainty in the correction model used and uncertainty in the Pb concentration.

Summary of uncertainties due to the various components

The above measurements enable us to estimate the uncertainties in $\varepsilon_{sam}/\varepsilon_{std}$ due to each of the components for samples of sizes similar to those used in this work and for

Table 1 Coincidence summing factors for ^{182}Ta gamma-rays in samples counted 1 mm from the detector

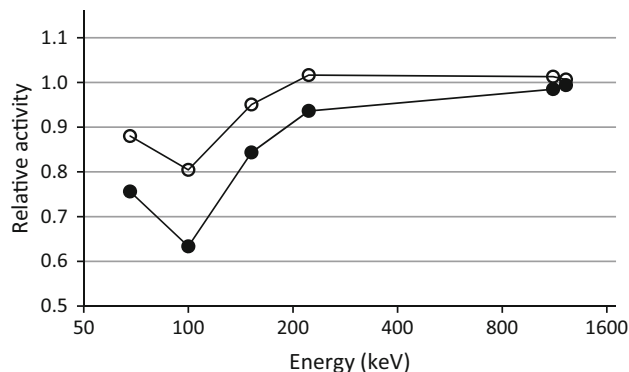| Gamma energy (keV)	COI
68	0.619
100	0.675
152	0.612
222	0.681
1121	0.699
1221	0.801

Fig. 6 Variations in measured relative activities for 15 mm thick samples containing SiO_2 and PbO_2; *open circles*: 50 mg/g PbO_2, *closed circles*: 100 mg/g PbO_2

Table 2 Components of the efficiency correction contribution to the uncertainty of the analysis result for a standard counted 100 mm from the detector and samples counted 1 or 100 mm from the detector

Uncertainty in $\varepsilon_{sam}/\varepsilon_{std}$	
10 mm thick sample 1 mm from detector	
Uncertainty component	Maximum uncertainty (%)
Uncertainty sample-detector distance (model)	6
Uncertainty sample-detector distance (positioning)	3
Integration over the sample volume	6
Gamma attenuation (low energy gamma, heavy element matrix)	20
Coincidence summing (worst cases)	10
2.5 mm thick sample 100 mm from detector	
Uncertainty component	Maximum uncertainty (%)
Uncertainty sample-detector distance (model)	0.5
Uncertainty sample-detector distance (positioning)	1
Integration over the sample volume	0.2
Gamma attenuation (low energy gamma, heavy element matrix)	5
Coincidence summing (worst cases)	0.5

the unfavorable situation where the standard is counted 100 mm from the detector and the sample is counted 1 mm from the detector and for the more common situation where both are counted 100 mm from the detector. These estimates are shown in Table 2.

The first part of Table 2 presents a rather pessimistic summary of the uncertainties for the worst case when the standard is counted 100 mm from the detector and the sample is counted 1 mm from the detector. If all these uncertainties are combined according to Eq. (1), then the uncertainty of $\varepsilon_{sam}/\varepsilon_{std}$ and of the analysis result would be 24 %. Let us look at a more realistic case for the same sample and standard counting geometries. The uncertainty of the model for extrapolating the efficiency from 100 mm distance to 1 mm is maintained at 6 % because our experience indicates that most efficiency transfer models in use today are not very good at doing this; they are often developed mainly for samples counted 50 mm from the detector or farther. The 3 % uncertainty assigned to the uncertainty of the positioning of the sample at the specified distance of 1 mm corresponds to an uncertainty in the distance of 0.5 mm. In many cases the sample is positioned with greater accuracy than this and this uncertainty can be reduced to 1 %. Most models in use can integrate over the volume of a 10 mm thick sample 1 mm from the detector with accuracy better than 6 %; let us assume the uncertainty is 2 %. For gamma attenuation, let us assume we do not have a low energy gamma-ray in a heavy element matrix; then the uncertainty would be of the order of 1 %. For coincidence summing, [182]Ta is an extreme case where the emitted gamma-rays are usually in coincidence with two other gamma-rays. For most nuclides, the emitted gamma-rays are not in coincidence or they are in coincidence with only one other gamma-ray. Thus a more

realistic estimate of the uncertainty due to coincidence summing is 2 %. In this more realistic situation the uncertainty in $\varepsilon_{sam}/\varepsilon_{std}$ from the above components is 7 %. If the standard is also counted at 1 mm from the detector, then the uncertainties from the sample-detector distance correction and from coincidence summing can be eliminated and the combined uncertainty in $\varepsilon_{sam}/\varepsilon_{std}$ can be reduced to 2.5 %.

Conclusions

In general, the uncertainty in the efficiency correction factor is greater for large samples and for samples counted close to the detector. For low-energy gamma-rays the uncertainty increases if the sample contains unknown amounts of heavy elements which change the effective gamma-ray mass attenuation coefficient of the sample. The magnitude of the different components of the uncertainty of the efficiency correction factor are different in each laboratory, depending on whether the samples measured are large or contain heavy metals or if they are counted close to the detector, and also on the accuracy of the model used for the corrections and the skill of the analyst in positioning the samples on the detector. The results presented in this work give insight in determining the components of the uncertainty of the efficiency correction factor and how to combine them to give the total contribution to the uncertainty budget of NAA results. The uncertainties can be reduced by preparing standards which match the samples in size, shape, density and gamma attenuation coefficient and by counting sample and standard at the same distance from the detector.

References

1. Robouch P, Arana G, Eguskiza E, Pommé S, Etxebarria N (2000) Uncertainty budget for k_0-NAA. J Radioanal Nucl Chem 245: 195–197

2. Bučar T, Smodiš B (2006) Assessment of the intrinsic uncertainty of the k0-based NAA. Nucl Instr Methods A564:683–687

3. Smodiš B, Bučar T (2006) Overall measurement uncertainty of k0-based neutron activation analysis. J Radioanal Nucl Chem 269: 311–316

4. Kubešová M, Kučera J (2012) How to calculate uncertainties of neutron flux parameters and uncertainties of analysis results in k0-NAA. J Radioanal Nucl Chem 293:87–94

5. Greenberg RR, Lindstrom RM, Mackey EA, Zeisler R (2011) Evaluation of uncertainties for neutron activation analysis measurements using the comparator method of standardization. Spectrochim Acta B 66:208–232

6. Greenberg RR (2008) Pushing the limits of NAA: accuracy, uncertainty and detection limits. J Radioanal Nucl Chem 278:231–240

7. Kennedy G, St-Pierre J (1997) Parameterization of detector efficiency for the standardization of NAA with stable low flux reactors. J Radioanal Nucl Chem 215:235–239

8. van Sluijs R, Bossus D, Blaauw M, Kennedy G, De Wispelaere A, van Lierde S, De Corte F (2000) Evaluation of three software programs for calculating true-coincidence summing correction factors. J Radioanal Nucl Chem 244:675–680

9. Jodlowski P (2007) Correction factors to account for minor sample height variations in gamma-ray spectrometry. Nucl Instrum Meth A580:238–241