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Accelerating k_0

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Combining the powers of a fast pneumatic transport system and the Automatic Activation Analyzer (AAA) of the Atominstitut in Vienna with the newest version of the IAEA k_0-Software, the application of the k_0-method to the determination of short-lived radionuclides becomes easily possible. By calculating Asp-values with the IAEA software, the often expensive and time-consuming measurement of Asp-values using certified reference materials is reduced to quality control checks. Measurements clearly show that the two approaches are equivalent, especially since both take self-absorption and neutron self-shielding into account. In this way it is possible to expand the library of the AAA with many hitherto unobtainable Asp-values. At the same time, using highly accurate Asp-values already measured for many short-lived radionuclides, k_0-values for those can be produced with a simple procedure.

Introduction

In this study, the compatibility of two different but similar approaches to comparator-type neutron activation analysis, namely the Asp-[1] and the well known k_0-approach are examined. A main objective of this study is the evaluation of the feasibility of experimentally determining k_0-values of short-lived radionuclides via Asp-values as well as the application of k_0-values to quickly and easily produce Asp-values for use with the Neutron Activation Analyzer.

The Asp-approach

The Neutron Activation Analyzer[1–4] made possible by the Preloaded Digital Filter[5,6] offers fully automated, loss-corrected analysis with a high throughput and count-rates of up to 1000 kcps. Since its main strong points rely on the real-time capabilities and memory management of the DOS™ operating system, no port to a Windows™ system is possible. As samples in an automated pneumatic transfer system can only be irradiated sequentially, direct comparison to single- or multi-element standards has to be sequential, too. Thus the Neutron Activation Analyzer uses extensive libraries of so-called Asp-values.

The Asp-value, is an experimentally determined constant that represents the corrected saturation activity by mass:

$$\mathrm{Asp} = \frac{\theta\gamma}{M} N_A \varepsilon c(\sigma_0 \phi_{\mathrm{therm}} + I\phi_{\mathrm{epi}}) \qquad (1)$$

where θ represents the isotopic abundance, σ_0 is the cross section for the capture of thermal neutrons, I is the resonance cross section for epithermal neutrons, γ is the branching ratio, c is the coincidence correction factor, ϕ_{therm} and ϕ_{epi} are the thermal and epithermal neutron flux density, respectively, and ε is the efficiency of the detector and the counting setup. N_A represents Avogadro's constant and M is the atomic mass. It corresponds closely to the B-values introduced in 1993.[7,8]

In principle, the Asp-value could be calculated from known constants but the values found in the literature often carry large errors and thus a direct measurement is more efficient, especially since neutron attenuation and γ-ray self-absorption are automatically accounted for. For the measurement of Asp-values, single- or multi-element standards, both artificially created and certified reference materials are used.

By measuring a sample containing a known amount m of an element, the Asp-value can be calculated by the following equation:

$$\mathrm{Asp} = \frac{A}{m(1-e^{-\lambda t_{\mathrm{irr}}})e^{-\lambda t_{\mathrm{dec}}}\left(\frac{1-e^{-\lambda t_{\mathrm{meas}}}}{\lambda}\right)} \qquad (2)$$

where A represents the measured peak area after an irradiation time of t_{irr}, a decay of t_{dec} and a measurement time of t_{meas}.

As the average sample mass used in the measurement procedures for the Neutron Activation Analyzer comes up to 3 g, the process of creating a library of reliable Asp-values can be not only time-consuming but also very expensive.

The k_0-approach

As an alternative to the process described above, application of the single-standard k_0-method[9] to the Neutron Activation Analyzer shows a lot of promise.

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The k_0-method for activation analysis is implemented in the k_0-IAEA software.[10] This program offers a practical frontend for all users of the k_0-method. By collecting all data necessary (characterization of irradiation facility, detector calibration, certified reference material data, k_0-library) under a single roof, the user can easily access and employ all the assets of the k_0-method while leaving the sometimes rather complex calculations to the software.

While there have been attempts to combine loss-free counting and the k_0-method,[11,12] no implementation has been produced that allows for automatic analysis as well.

Since its latest version (3.12), the k_0-IAEA software allows export of the Asp-values, making an integration with the Neutron Activation Analyzer possible. By careful characterization of the irradiation facility and calibration of the detectors in use, a direct export of externally created Asp-values is possible which can then be used to expand the existing libraries in use with the Neutron Activation Analyzer.

As the software also produces coincidence correction factors and efficiency factors, the calculation of k_0-values from measured Asp-values is easily possible.

The ratio of two Asp-values, one used as a comparator (Asp_c) and the other one for the analyte (Asp_a), clearly shows its close relation to the k_0-values:

$$\frac{\mathrm{Asp}_a}{\mathrm{Asp}_c} = \frac{M_c \theta_a \gamma_a \varepsilon_a c_a}{M_a \theta_c \gamma_c \varepsilon_c c_c} \left(\frac{\sigma_{0,a}\phi_{\mathrm{therm}} + I_a \phi_{\mathrm{epi}}}{\sigma_{0,c}\phi_{\mathrm{therm}} + I_c \phi_{\mathrm{epi}}} \right) \qquad (3)$$

with the definition of the k_0-value:

$$k_{0,c}(a) = \frac{M_c \theta_a \gamma_a \sigma_{0,a}}{M_a \theta_c \gamma_c \sigma_{0,c}} \qquad (4)$$

and by replacing $\phi_{\mathrm{therm}}/\phi_{\mathrm{epi}} = f$, Eq. (3) can be re-written as:

$$\frac{\mathrm{Asp}_a}{\mathrm{Asp}_c} = k_{0,c}(a) \frac{\varepsilon_a c_a}{\varepsilon_c c_c} \left(\frac{1 + \dfrac{I_a}{f\sigma_{0,a}}}{1 + \dfrac{I_c}{f\sigma_{0,c}}} \right) \qquad (5)$$

Thus, the calculation of k_0-values from Asp-values is possible, as long as the thermal/epithermal flux ratio is known.

Methods and experimental

Detector calibration

For detector calibration, 0.53627 g of the γ-ray reference solution QCY48 (Amersham plc, Solution number R5/19/76) filled up to 5 mL were measured at a fixed position 20 mm from the detector endcap for 50000 seconds. As a single γ-ray source, a ^{137}Cs source (Amersham γ-reference source, Set No. 767) was measured at the same position for 50000 seconds. The resulting spectra were analyzed using the Nuclear Data™ program peak.exe and entered into the k_0-IAEA software.

Characterization of the irradiation facility

For the characterization of the irradiation position in the TRIGA Mark II reactor of the Atominstitut in Vienna, a mixture of the comparators provided with the software were used, containing 431850 μg·g^{-1} Ni, 323682 μg·g^{-1} Zr and 245 μg·g^{-1} Au. Irradiation time was 600 seconds and several spectra were collected at the same measurement position as described above. One spectrum of 7200 seconds after a decay of 8001 seconds, and two spectra of 10000 seconds each after decay times of 25201 seconds and 45201 seconds, respectively was used. Spectra were again analyzed by peak.exe and entered into the k_0-IAEA software.

Measurement of Asp-values

For the determination of Asp-values, the certified reference materials CANMET Reference Soil SO-1 (two samples of 4.703 g and 4.735 g), MC Rhyolite GBW 07113 (two samples of 4.914 g and 4.960 g), NIST 1515 Apple Leaves (one sample of 1.70388 g), and NIST 1573a Tomato Leaves (one sample of 1.79159 g) were used.

The samples were weighed into 5-mL PE-vials and irradiated for 10 seconds. After a decay time of 1 second to ensure arrival of the sample, 10 consecutive spectra of 2, 20, 200, 2000 seconds each were measured. Both corrected and uncorrected spectra were collected at the same time. Automatic analysis using an old existing library and plain text files containing the certified reference values produced Asp-values for all radionuclides found in the spectra with certified values. Error calculation observes correction factors and errors of correction factors.[1,13–15] Out of the Asp-values thus produced, a simple program creates a new library file ready for use where the weighted means of the Asp-values and their uncertainties are automatically collected (Table 1).

A second utility was used to collect the calculated Asp-values from the extensive log-files of the k_0-software, yielding again a usable library in a single step.

To further prove the equivalency of the two methods, k_0-values were calculated using Eq. (5) and the measured Asp-values. As a reference value (Asp_c), the Asp-value of the 1368 keV γ-line of ^{24}Na was used. The resulting k_0-values were then converted to the traditional form, using gold as reference.

Table 1. Comparison of Asp-values produced by the k_0-IAEA software (calculated) and by direct measurement

Nuclide	Energy, keV	Asp-value	
		Calculated	Measured
^{139}Ba	165.8	$1.66\cdot10^{7} \pm 6.3\%$	$1.47\cdot10^{7} \pm 2.9\%$
^{49}Ca	3084.4	$1.27\cdot10^{5} \pm 11.3\%$	$1.29\cdot10^{5} \pm 3.7\%$
^{38}Cl	1642.4	$3.92\cdot10^{6} \pm 1.1\%$	$4.10\cdot10^{6} \pm 3.6\%$
^{38}Cl	2167.5	$4.08\cdot10^{6} \pm 2.3\%$	$4.40\cdot10^{6} \pm 3.6\%$
^{165}Dy	94.7	$5.77\cdot10^{9} \pm 5.3\%$	$6.04\cdot10^{9} \pm 2.6\%$
^{42}K	1524.7	$2.19\cdot10^{6} \pm 4.7\%$	$2.24\cdot10^{6} \pm 3.6\%$
^{140}La	1596.2	$2.86\cdot10^{8} \pm 3.4\%$	$3.01\cdot10^{8} \pm 3.5\%$
^{56}Mn	846.6	$1.81\cdot10^{9} \pm 6.2\%$	$1.89\cdot10^{9} \pm 3.4\%$
^{56}Mn	1811.2	$2.67\cdot10^{8} \pm 5.1\%$	$2.77\cdot10^{8} \pm 3.6\%$
^{56}Mn	2113.1	$1.24\cdot10^{8} \pm 5.4\%$	$1.27\cdot10^{8} \pm 3.6\%$
^{24}Na	1368.6	$1.22\cdot10^{8} \pm 7.6\%$	$1.18\cdot10^{7} \pm 3.5\%$
^{24}Na	2754.1	$6.54\cdot10^{7} \pm 6.4\%$	$6.40\cdot10^{6} \pm 3.6\%$
^{51}Ti	320.0	$2.65\cdot10^{6} \pm 1.1\%$	$3.19\cdot10^{7} \pm 3.3\%$

Results

The efficiency calibration of the detector and the characterization of the irradiation facility was entirely performed within the k_0-IAEA software. The resulting thermal neutron flux density was $2.49\pm0.03\cdot10^{16}$ m$^{-2}\cdot$s^{-1}, fast flux density was $1.18\pm0.01\cdot10^{16}$ m$^{-2}\cdot$s^{-1} at a temperature of 320±5 K. For epithermal neutrons, the f value was 15.6±1.05 and the shape parameter α was 0.0167±0.012.

The weighted means of Asp-values determined from the measurements with standards, as described above, and the values produced by calculation with the k_0-IAEA software and Eq. (1) are compared in Table 1. To further show the usability of the calculated Asp-values, a sample measurement was evaluated twice, once using the original library of Asp-values and once using the calculated Asp-values (Table 2).

Table 3 shows k_0-values that were calculated from the measured Asp-values and the accepted values from literature.

Discussion and conclusions

The main advantage of using directly measured Asp-values is that self-absorption, neutron-attenuation as well as coincidence-correction are implicitly included, as long as the matrices of both sample and certied reference material are reasonably similar. Since all of the above factors are calculated by the IAEA software and included in the Asp-values produced, both ways of creating Asp-values for measurements are in principle equivalent.

In fact, it could be argued that the calculations performed by the software are better able to correct for different matrices as long as all the necessary information about the sample is entered correctly. Tables 1 and 2 clearly show that both approaches yield similar results. There are, however, signicant differences for ^{139}Ba and ^{51}Ti. Those differences are due to resonances of the neutron capture cross section at a neutron energy above 1 MeV,[16–18] which are ignored by the software.

Table 3 shows that the backward calculations to reach k_0-values are also valid. Thus it is possible to use the routines already in place in the AAA to measure Asp-values and easily calculate valid k_0-values for short-lived radionuclides. The values showed here are not intended to replace the established ones, they are to show the validity of the approach.

The two approaches to comparator-type neutron activation analysis are in fact equivalent, as could be shown in this paper. Thus, each method can complement the other, leading to a much faster way of producing libraries of Asp-values on one hand and to a straightforward way of measuring k_0-values for short-lived radionuclides on the other.

Table 2. Comparison of the calculated concentrations in one random sample, analyzed using measured Asp-values and Asp-values produced by the k_0-IAEA software

Nuclide	Energy, keV	Concentration	
		with Asp	with k_0
^{165}Dy	94.7	$7.453\cdot10^{-7}$	$7.120\cdot10^{-7}$
^{139}Ba	165.8	$1.376\cdot10^{-4}$	$1.554\cdot10^{-4}$
^{51}Ti	320.0	$2.571\cdot10^{-3}$	$2.136\cdot10^{-3}$
^{56}Mn	846.6	$8.038\cdot10^{-4}$	$7.698\cdot10^{-4}$
^{24}Na	1368.6	$3.307\cdot10^{-3}$	$3.390\cdot10^{-3}$
^{42}K	1524.7	$1.575\cdot10^{-3}$	$1.540\cdot10^{-3}$
^{38}Cl	1642.4	$1.264\cdot10^{-4}$	$1.208\cdot10^{-4}$
^{56}Mn	1811.2	$7.911\cdot10^{-4}$	$7.625\cdot10^{-4}$
^{56}Mn	2113.1	$7.949\cdot10^{-4}$	$7.761\cdot10^{-4}$
^{38}Cl	2167.5	$8.170\cdot10^{-5}$	$7.577\cdot10^{-5}$
^{24}Na	2754.1	$3.344\cdot10^{-3}$	$3.417\cdot10^{-3}$
^{49}Ca	3084.4	$1.157\cdot10^{-2}$	$1.139\cdot10^{-2}$

Table 3. A comparison of the measured k_0-values with the accepted values in the literature. All values are taken from Reference 19, except for ^{38m}Cl, which are from Reference 20

Nuclide	Energy, keV	k_0-Values	
		Literature	Measured
^{139}Ba	165.8	$1.05\cdot10^{-3}$	$1.13\cdot10^{-3}$
^{49}Ca	3084.4	$1.01\cdot10^{-4}$	$9.36\cdot10^{-5}$
^{38}Cl	1642.4	$1.97\cdot10^{-3}$	$1.73\cdot10^{-3}$
^{38}Cl	2167.5	$2.66\cdot10^{-3}$	$2.28\cdot10^{-3}$
^{38m}Cl	971.3	$7.95\cdot10^{-4}$	$7.44\cdot10^{-4}$
^{165}Dy	94.7	$3.57\cdot10^{-1}$	$3.31\cdot10^{-1}$
^{42}K	1524.7	$9.46\cdot10^{-4}$	$8.54\cdot10^{-4}$
^{140}La	1596.2	$1.34\cdot10^{-1}$	$1.21\cdot10^{-1}$
^{56}Mn	846.6	$4.96\cdot10^{-1}$	$4.37\cdot10^{-1}$
^{56}Mn	1811.2	$1.35\cdot10^{-1}$	$1.21\cdot10^{-1}$
^{56}Mn	2113.1	$7.17\cdot10^{-2}$	$6.44\cdot10^{-2}$
^{24}Na	1368.6	$4.68\cdot10^{-2}$	$4.68\cdot10^{-2}$
^{24}Na	2754.1	$4.62\cdot10^{-2}$	$4.65\cdot10^{-2}$
^{86m}Rb	555.8	$1.13\cdot10^{-3}$	$1.15\cdot10^{-3}$
^{51}Ti	320.0	$3.74\cdot10^{-4}$	$3.03\cdot10^{-4}$

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