

## Progress in the $k_0$ -IAEA program

Matthias Rossbach<sup>a,\*</sup>, Menno Blaauw<sup>b</sup>

<sup>a</sup>Industrial Applications and Chemistry Section, NAPC, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, IAEA, Wagramer Str. 5, P.O. Box 100, A-1400 Vienna, Austria

<sup>b</sup>Reactor Institute Delft, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

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### Abstract

The single-comparator instrumental neutron activation analysis ( $k_0$ -INAA) has been introduced in the late 1970s and since then remarkable progress has stimulated the acceptance of this methodology from the NAA community. A large number of publications are referring to  $k_0$  standardization in a variety of analytical fields of applications. About half of the existing NAA laboratories are currently working on the basis of monostandard, or single-comparator technique. The need for harmonization of the applicable software tools has triggered the development of a user-friendly and versatile programme supported by the IAEA to assist Member States in their quality output from nuclear analytical laboratories.  $k_0$ -IAEA software, available since the beginning of 2005, has now been updated by the incorporation of a peak area evaluation routine to facilitate its use from different spectrum accumulation platforms. For  $k_0$ -IAEA, version 2.0 only the raw channel input is needed for obtaining reliable quantitative results. This paper describes the changes being implemented for version 2.0 of the  $k_0$ -IAEA program.

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### 1. Introduction

Neutron activation analysis (NAA) is a unique analytical technique as it is entirely based on well-understood physical principles and can be completely mathematically described. This particular property has led already in the late 1950s to attempt a procedure for ‘absolute’ standardization [1]. However, it became obvious that the quantification of elemental concentrations based on nuclear data obtained from the literature only was prone to systematic errors due to the uncertainties associated with these constants. Even today, after appreciable refinement of these data, the resulting overall uncertainty of absolute NAA cannot compete with the accuracy and uncertainty obtained in relative standard NAA.

The single-comparator method, introduced by Girardi et al. [2] based on the experimental determination of

$k$ -factors depending on nuclear constants by irradiating known weights of single elements with a neutron flux monitor proved to be more reliable and compared well with the level of accuracy and uncertainty of the relative standardization method. The overwhelming disadvantage of that approach was directly related to its applicability to a strictly defined irradiation and counting situation.

The ultimate flexibility of the ‘single-comparator’ concept was introduced only after 1974 when the idea of the  $k_0$ -standardization was developed in Budapest and Gent [3]. “The  $k_0$ -standardization method was intended to be an absolute technique where the uncertain nuclear data are replaced by compound nuclear constants—the  $k_0$ -factors—which are experimentally determined with high accuracy. Basically, this determination is done as for  $k$ -factors, which are then transformed into  $k_0$ ’s by lifting out the experimental parameters.  $k_0$ -factors are thus generally applicable on condition that the activation analyst recombines them with the parameters of the local irradiation and counting conditions, in this way generating ‘his’  $k$ -factors; from this point of

\*Corresponding author. Tel.: +43 1 2600 21750;  
fax: +43 1 26007 21750.

E-mail address: [m.rossbach@iaea.org](mailto:m.rossbach@iaea.org) (M. Rossbach).

view, the  $k_0$ -method is a flexible single-comparator technique.” [4].

A lot of effort was devoted to the determination of accurate  $k_0$ -factors in the past. This work also triggered a review and refinement of existing nuclear data such as cross-sections, half-lives, and decay schemes. Other phenomena like true coincidence, burn-up or contributions of epithermal activation were also investigated intensely and accounted for. Today,  $k_0$ -INAA is a widely accepted and flexible technique for routine and panoramic nuclear analysis producing results comparable to accurate and precise relative standard NAA without the tedious preparation of synthetic standards from pure substances.

A literature search using the INIS data base (The International Nuclear Information System), Chemical abstracts (CA), and Analytical abstracts (AA) revealed that between 1990 and 2003, 172, 68 and 54 publications reporting on various applications of the  $k_0$ -standardization method were published and referenced, respectively (see Fig. 1). The doubling rate of  $k_0$  related publications in this period according to INIS seems to be 3.5 years.

Apart from the numerous applications of  $k_0$ -INAA this standardization method can also be used to investigate nuclear parameters and nuclear reaction rates. However, for its applicability to large data sets and measurements computerization of the routines is mandatory. At the first  $k_0$ -users workshop in Astene, Belgium, 1992, the KEY-ZERO/SOLCOI software was introduced and demonstrated [5]. Although this programme was commercially advertised it did not reach too many laboratories and, hence, several laboratories designed their own software tools being more or less sophisticated. This large spread in computational approaches contributed to a relatively wide

variability in the  $k_0$ -based INAA results. The need for harmonization of software and associated nuclear data resulted in the development of the  $k_0$ -IAEA software, which is available for free distribution since beginning of 2005 [6]. A few training courses have been held and starting kits comprising of a few cm of Al/Au wire, Al/Lu wire, a piece of Zr foil and Ni foil together with the software on a CD were distributed to more than 50 laboratories in 36 countries. Version 2.0 is now available for distribution, which incorporates a spectrum deconvolution routine that will eventually facilitate the application in more laboratories as it is more flexible and independent of different commercial spectrum evaluation software.

## 2. Spectrum deconvolution in the $k_0$ -IAEA program

The peak-search algorithm, peak shape function and fitting methods now implemented in the  $k_0$ -IAEA program are not new. In fact, they are so well known that it is difficult to refer to the original publications. We will simply enumerate the relevant aspects.

The first step in the analysis of a spectrum is a search for peaks, performed with a smoothed second derivative Gaussian filter function (the “Mexican hat”). Once a shape calibration has been performed, this width of the filter is adjusted to the local peak width in the spectrum, the very first time the user has to supply an approximate estimate.

A Gaussian function with exponential tails on both sides is then fitted to the highly significant, free-standing peaks. At this point, an energy calibration can be performed, using the peak positions associated with photon energies. A quadratic polynomial is used to this end.

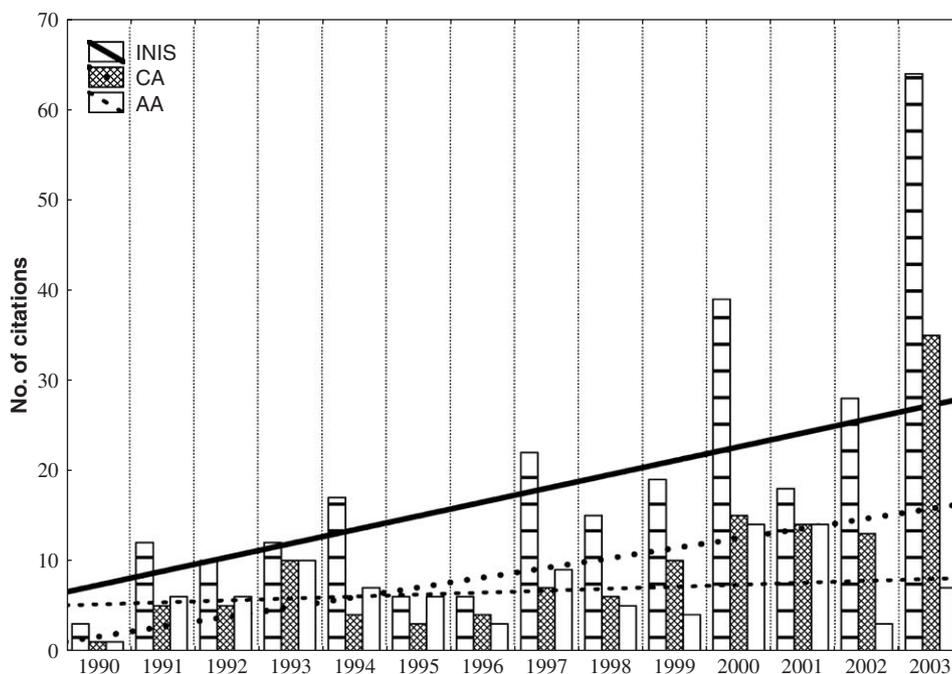


Fig. 1. Number of publications using  $k_0$ -standardization from INIS, CA and AA between 1990 and 2003.

Next, a shape calibration can be performed, where polynomials are fitted to peak width (in keV) and the two tail parameters as a function of peak energy ( $E$ ). For the width curve, the relation  $FWHM^2 = a + bE$  is used, for the two other two simple straight lines suffice. The 511 keV and the pulser peak are treated as exceptions and their parameters values are stored separately.

The calibration curves can be stored in a database, labelled with detector ID and the acquisition time of the spectrum, for future use with other spectra. Calibration of the system ends with the analysis and storage of a background spectrum, to be used for background correction in the analysis of other spectra.

Once the shape and energy calibration curves are available, a sample spectrum can be analysed. Now, all peaks detected are considered, not only the significant and free-standing ones. The peaks are clustered in multiplets if they contribute to each other's channel contents significantly, at a 2 s.d. level. If one peak contributes to the other, in this sense, but not vice versa, the unperturbed one is dealt with first, its contribution is stripped off from its neighbour's fitted region, and then the neighbouring peak is considered.

In those cases where the fit results in a high  $\chi_r^2$ -value, the peak is flagged in the graphical user interface and the user can manually integrate the peak area by indicating where the peak ends on both sides. It was verified that such integration of simple peaks yields the same total area as the area calculated from the Gaussian shape function with its tails.

### 3. Test with the IAEA 1995 test spectra

The  $k_0$ -IAEA program's performance was tested first using the 1995 IAEA test spectra [7]. The shape- and energy calibrations were performed with the CALIB spectrum, and then the STRAIGHT spectrum was analysed. The results were treated just as the results from commercially available programs in the 1995 intercomparison [8]. The STRAIGHT spectrum results are representative for general spectrometry.

The results reveal the quality of the peak areas obtained and the statistical control with the degree to which the areas and their uncertainties agree with the known true values of interest.

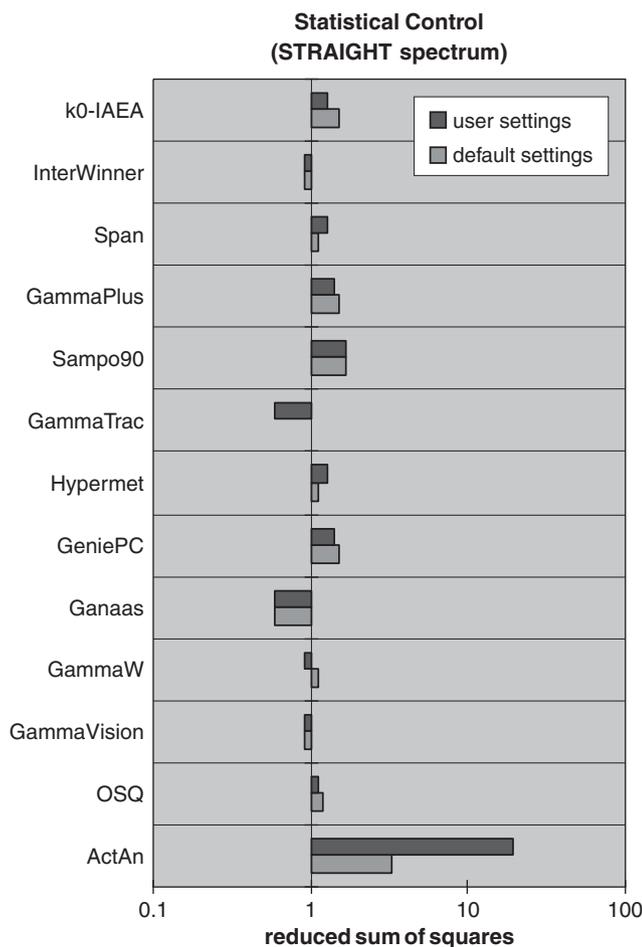


Fig. 2. Statistical control for the STRAIGHT spectrum.

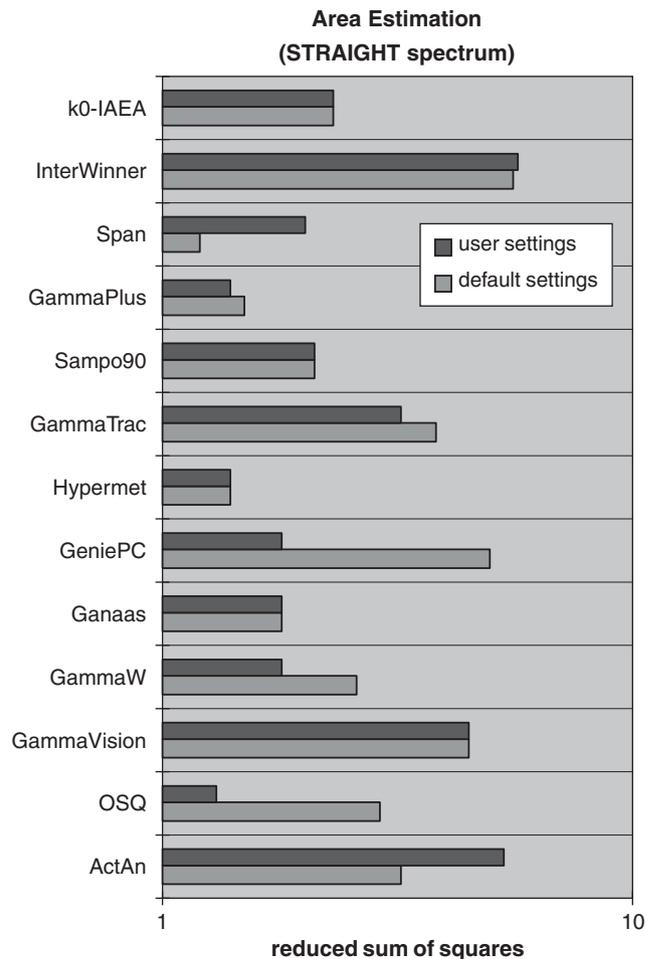


Fig. 3. Quality of peak areas obtained from STRAIGHT spectrum.

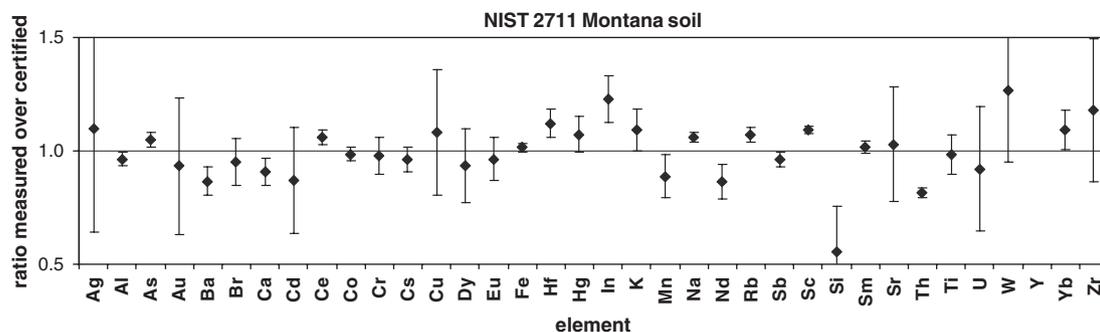


Fig. 4. Concentrations obtained from NIST 2711, Montana soil; divided by the known concentrations. The uncertainties indicated in the figure comprise the GUM's with coverage factor 1 as reported by the  $k_0$ -IAEA program exclusively, not the uncertainties in the certified concentrations or the information values.

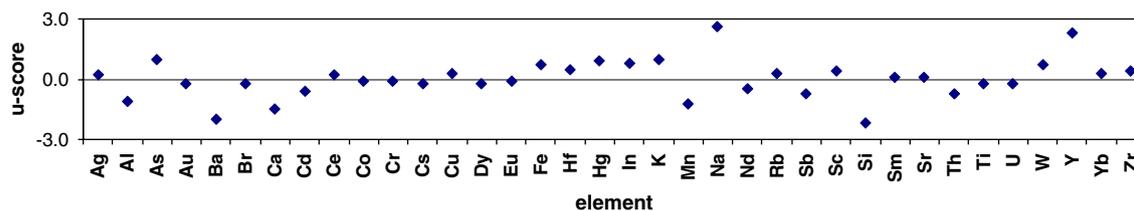


Fig. 5.  $u$ -scores for the measured and certified concentrations of NIST 2711, Montana soil, calculated from the GUM with coverage factor 1 as reported by the  $k_0$ -IAEA program and the uncertainties in the certified concentrations, where a 25% uncertainty was assumed in the information values.

In Figs. 2 and 3, the results for the STRAIGHT spectrum are shown for several programs. The  $k_0$ -IAEA program performance is amongst the best.

#### 4. Test with a real INAA sample

The spectra obtained in the experiment that was used to test the capabilities of the first version of the  $k_0$ -IAEA program [6] were now used again, only this time, obviously, the peak areas and energies were determined with  $k_0$ -IAEA itself, instead of with an external program. The results in terms of elemental concentrations as compared to the certified values are shown in Fig. 4, in terms of ratios, and in Fig. 5, in terms of  $u$ -scores [6]. An uncertainty of 25% was assigned to elemental concentrations that were not certified, but merely information values. The overall  $\chi_r^2$  computed from the  $u$ -scores is 0.91, which indicates good statistical control of the program in conjunction with the  $k_0$ -database. The  $\chi_r^2$ -value would be 1.6 if only the elements with certified concentrations were included, still an acceptable result. The only statistically significant discrepancy is observed in Na, where the  $k_0$ -IAEA result is higher by a factor of  $1.06 \pm 0.02$ , resulting in a  $u$ -score of 2.6. We see this same discrepancy in the Na determinations performed in Delft for NIST 2711, as well as for other NIST reference materials, in spite of the fact that the calibration of the Delft analysis system is independent from the  $k_0$  method. We have no explanation for this fact.

#### 5. Conclusions

The newly implemented peak area determination routines in the  $k_0$ -IAEA program perform as well as those in the commercially available programs. In our test, using NIST 2711, Montana soil, the concentrations calculated from these peak areas obtained using the  $k_0$ -IAEA program agree well with the certified values.

Therefore,  $k_0$ -IAEA program can now be used as a self-consistent unit. The users will still have to use hardware-specific software to acquire the spectra. A comprehensive users' manual is in preparation and will be available soon.

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