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SINGLE-COMPARATOR METHODS IN REACTOR NEUTRON ACTIVATION ANALYSIS

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A critical evaluation of different comparator methods is given. The method based on experimentally-determined and convertible comparison factors (k) is considered to be the most suitable for general use. An alternative method is proposed, introducing generalized k_0 factors which are independent of irradiation and measuring conditions. This approach combines the simplicity of the absolute methods with nearly the same accuracy attained by the relative ones. It is suggested that k_0 factors be compiled in all cases when using single-comparator methods, to allow a continuous re-evaluation.

Introduction

The worldwide interest in the role of trace elements in biology, environmental research, geology and technology has led to an increasing need for multi-element analyses on a large number of samples. In the light of the recent developments in different analytical techniques, and the growing competition between them, this demand has enhanced the value of purely instrumental, non-destructive activation analysis. Indeed, due to its relative simplicity, together with its inherent selectivity and sensitivity (for about 75 elements 0.01 μg can be measured in favourable cases), reactor neutron activation analysis occupies one of the most important positions among the various analytical methods. Although the resulting γ-ray spectra of the irradiated samples are usually very complex (and sometimes can only be resolved after radio-chemical separation), the advent of high-resolution Ge(Li) detectors, 4000–8000-channel analysers and on-line small computers provides the possibility of multi-element analysis without chemical separation in many cases. In the present stage of γ-ray spectrometry, a large

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variety of materials can be analysed non-destructively with only a limited number of irradiations and measurements, thus giving quantitative results for 10–35 elements and detection limits for the remainder. The results of this "preliminary" analysis usually meet the requirements of the user and/or may help to develop additional chemical separations to increase the sensitivity for some elements if it is both necessary and economical.

Multi-element analysis, however, is sometimes not feasible using neutron activation analysis in its classical form: i.e. irradiation and measurement of a standard for each element to be determined. This procedure has some obvious disadvantages, which can be summarized as follows:

(a) The preparation, irradiation and measurement of a large number of standards (usually only for expected elements) is time-consuming and may introduce sources of errors.

(b) Quantitative analysis is impossible for unexpected elements because no standards are provided.

(c) The calculation of detection limits (maximum possible concentrations) is impossible, due to unprovided standards.

(d) It is sometimes difficult to ensure identical irradiation conditions for standards and samples: problems may arise due to flux inhomogeneities along the irradiation can; variation of neutron flux during repeated irradiations; self-shielding effects in the standards; lack of space in the irradiation capsule; etc.

(e) Handling of a large number of standards causes great difficulties in computer-coupled, automated activation analysis.

The difficulties mentioned above can be partially eliminated by using well-characterized materials such as BOWEN's kale or NBS-certified specimens (glass, bovine liver, etc.). The use of these materials as compound standards, however, seems to be advantageous only in limited cases. Their general application is restricted, due to the long time and heavy expenses involved in preparation and intercomparative analysis. In addition, their physical and chemical properties (hygroscopic, strong volatilization for some elements, difficulties in dissolving, etc.) are sometimes such as to make their simple handling not feasible, and the concentration range of trace elements is occasionally far from that of the sample to be analysed. Finally, for the very large variety of samples which can be analysed by reactor neutron activation, this type of standardization – although being continuously improved – can hardly be applied in general.

Due to these difficulties, the use of single comparators has come into prominence in the last few years.[1–3] Several methods have been developed which can be classified according to whether a single, monoisotopic[4] or a single, multi-isotopic element[5] is used as a comparator, or whether a different approach is used to calculate the specific activities of elements to be determined.[6,7] Nevertheless, it is obvious that because of the arbitrarily-defined working procedures employed in the past, the basic experimental data of any one author can be applied only with difficulty or not at all by other possible users. Ultimately this is the result of not correlating these data to the essential working parameters, i.e. irradiation and counting conditions. The present paper deals with a critical examination of the existing comparator methods and leads to the proposal of an alternative, standardized technique enabling the avoidance of overlapping experimental work by different users.

Survey of single-comparator methods

The term single-comparator method refers here to a technique where multi-element analysis can be performed by irradiating and measuring a single element (comparator) instead of using standards prepared from known weights of elements to be determined. The specific activities of the standards (A_{sp}) can be calculated by multiplying the measured specific activity of the comparator (A^*_{sp}) by the experimentally-determined k factors, which can be written as:

$$k = \frac{A_{sp}}{A^*_{sp}} = \frac{M^*}{M} \cdot \frac{\gamma}{\gamma^*} \cdot \frac{\epsilon_p}{\epsilon^*_p} \cdot \frac{\Theta}{\Theta^*} \cdot \frac{\hat{\Phi}}{\hat{\Phi}^*} \cdot \frac{\hat{\sigma}}{\hat{\sigma}^*} \tag{1}$$

with

$$A_{sp} = \frac{A_p}{S\,D\,C\,w} \tag{2}$$

where M – atomic weight of the irradiated element,

Θ – isotopic abundance of the target nuclide,

γ – absolute abundance of the measured γ-ray,

ϵ_p – full-energy peak efficiency of the detector for the measured γ-ray energy,

$\hat{\Phi}$ – conventional reactor neutron flux (WESTCOTT's "total flux"[8]), in neutron $\cdot$ cm^{-2} $\cdot$ sec^{-1},

$\hat{\sigma}$ – effective reactor neutron cross-section (also WESTCOTT's definition), in barn,

S = $1 - \exp(-\lambda t_{irr})$, saturation factor dependent on decay constants (λ) and irradiation time, (t_{irr}),

D = $\exp(-\lambda t_d)$, decay factor where t_d is decay period,

C = $[1 - \exp(-\lambda t_m)]/\lambda t_m$, "measurement" factor correcting for decay during measuring period (t_m),

A_p = measured average intensity of full-energy peak (counts/sec),
w – weight of the element (grams).

In practice the comparator is usually a small thin foil or a few millimetres of wire. Due to its low dimensions a comparator can be placed very near to the sample during irradiation, thereby ensuring that $\hat{\Phi}/\hat{\Phi}^* = 1$.

The single-comparator method based on the above-defined k factors was first critically evaluated by GIRARDI et al.[4] In a series of trial runs the accuracy and the precision were found to be similar to those of classical methods. Although very precise and laborious experimental work is needed to determine k factors, once they are available the preparation of standards can be eliminated in any further analysis. It is assumed, however, that the k values are constant, namely that there are no variations in the quantities given in Eq. (1) between the time of determination of the k values and that of the actual analysis. The accuracy of the method, therefore, depends mainly on the constancy of the k values.

In view of this requirement, the set of k values is strictly valid only for one fixed sample – detector distance, so that ϵ_p/ϵ_p^* in Eq.(1) remains constant. Any change in the counting geometry may alter the shape of the efficiency curve of the detector (edge effect) or may result in a change of the measured relative peak intensities, A_p/A_p^*, for some isotopes emitting γ-cascades (coincidence summing effect). It is also assumed that the standards, samples and comparator have constant geometric form during the whole set of experiments, and possible spectrum distortions often encountered in γ-ray spectrometry (e.g. pulse pile-up, effect of varying dead-time during the measurement) are negligible or corrected for.

Because the σ/σ^* effective cross-section ratio depends on the reactor spectrum (i.e. mainly on Φ_{th}/Φ_e, the thermal to epithermal flux ratio), the set of k values is valid only for one selected irradiation position. Although GIRARDI investigated the effect of possible changes of Φ_{th}/Φ_e on the k factors, no correction is given to switch from one irradiation position to another. This can be a significant restriction for laboratories having many irradiation channels. Moreover, if any change occurs in the ratio Φ_{th}/Φ_e, due to reactor core modifications, the whole set of k factors must be remeasured.

In spite of these restrictions, GIRARDI's method can be used extensively by means of steady and well-thermalized reactors with periodic control of the constancy of the irradiation and measuring conditions.

To extend the applicability of the single-comparator method for diverse irradiation channels, DE CORTE et al.[7] introduced the conversion of the k values with respect to the effective activation cross-section. Using the simple approximation of HØGDAHL[9] for reaction rate calculation in a reactor spectrum.

$$R = \hat{\Phi}\,\hat{\sigma} = \Phi_{th}\,\sigma_{th} + \Phi_e\,I_0 \tag{3}$$

and assuming that $\hat{\Phi} = \hat{\Phi}^*$, the k factor in Eq. (1) can be written as:

$$k = \frac{A_{sp}}{A^*_{sp}} = \frac{M^*}{M} \cdot \frac{\gamma}{\gamma^*} \cdot \frac{\epsilon_p}{\epsilon^*_p} \cdot \frac{\Theta}{\Theta^*} \cdot \frac{\sigma_{th}\dfrac{\Phi_{th}}{\Phi_e} + I_0}{\sigma^*_{th}\dfrac{\Phi_{th}}{\Phi_e} + I^*_0} \tag{4}$$

where Φ_{th} = $n(0, E_{Cd}) \cdot v_0$, conventional thermal (subcadmium) neutron flux with $n(0, E_{Cd}) = \int_0^{E_{Cd}} n(v)\,dv$, the neutron density integrated up to the Cd cutoff, and $v_0 = 2200$ m/sec,

σ_{th} – thermal neutron cross-section. This value, when multiplied by Φ_{th}, gives the subcadmium reaction rate per atom. For 1/v-detectors $\sigma_{th} = \sigma_0$, where σ_0 is the "2200 m/sec cross-section",

Φ_e – epithermal or intermediate neutron flux per unit lnE neutron energy interval (unit lethargy). Φ_e is considered to be independent of the neutron energy. The epithermal flux distribution is assumed to follow the 1/E shape, so $\Phi_e(E) = \Phi_e/E$,

I_0 = $\int_{E_{Cd}}^{\infty} \sigma(E)\,dE/E$, infinitely-dilute resonance integral,

E_{Cd} = 0.55 eV, effective Cd cutoff energy for small 1/v-detectors positioned in a cylindrical Cd box of 1 mm wall thickness.[10] (See also EANDC recommendations.[11])

DE CORTE showed that the k factors determined in one "reference" reactor channel (where the ratio Φ_{th}/Φ_e is well known) can be re-evaluated for any "analysis" channel by the following equation:

$$k_{anal} = k_{ref} \cdot \frac{\left[\left(\dfrac{\Phi_{th}}{\Phi_e}\right)_{anal} + \left(\dfrac{I_0}{\sigma_{th}}\right)_{st}\right]\left[\left(\dfrac{\Phi_{th}}{\Phi_e}\right)_{ref} + \left(\dfrac{I_0}{\sigma_{th}}\right)_{comp}\right]}{\left[\left(\dfrac{\Phi_{th}}{\Phi_e}\right)_{anal} + \left(\dfrac{I_0}{\sigma_{th}}\right)_{comp}\right]\left[\left(\dfrac{\Phi_{th}}{\Phi_e}\right)_{ref} + \left(\dfrac{I_0}{\sigma_{th}}\right)_{st}\right]} \tag{5}$$

where the index-notations are self-explanatory.

From Eq. (5) it is apparent that the method relies on two important parameters: I_0/σ_{th} and Φ_{th}/Φ_e ratios. I_0/σ_{th} can be considered a nuclear constant for a given isotope and should be determined or can be taken from the literature. It is also obvious that in addition to the experimentally-determined factors k_{ref}, an additional procedure is necessary to determine the ratios Φ_{th}/Φ_e in the reference and the other reactor channels.

The applicability of this method was significantly enhanced by the work of VAN DER LINDEN et al.[5], who published measured I_0/σ_{th} values for 122 isotopes. A comparison of I_0/σ_{th} values in the literature, however, has revealed that large discrepancies exist for a number of isotopes. Additional work in this field is still necessary, therefore.

The comparator methods can be further classified according to the flux-ratio determination applied. The simplest and most common procedure is the Cd-ratio measurement for isotopes having well-known nuclear parameters (Au, Co, In, etc.). Irradiation with Cd filters, however, is prohibited in some reactors or certain irradiation channels. Difficulties can arise in compensating the sudden reactivity change when Cd filters are inserted into or withdrawn from the reactor core. Providing appropriate cooling to prevent the melting of Cd in a high-power reactor can also be a problem. Moreover, due to the high flux depression in the vicinity of the Cd cover, the Cd-ratio measurements cannot be carried out simultaneously with the sample irradiation. Consequently, the flux-ratio measurements should be accomplished independently and the constancy of Φ_{th}/Φ_e should be assumed.This is the case, for example, in the "Thetis" reactor of Ghent University, where the flux-ratios (ranging from 20 to 200) in a number of irradiation channels remained constant within 2% during the period 1971–1973.

In an alternative technique, at least two foils with different cross-section curves can be used to eliminate the irradiation of a Cd filter. An important condition to be fulfilled is that the ratios I_0/σ_{th} for the two induced (n,γ) reactions should differ as much as possible. Using this technique, DE CORTE et al.[7] determined Φ_{th}, Φ_e and Φ_{th}/Φ_e values by the irradiating and absolute counting of Au, Co and In flux monitors. However, due to the relatively small differences in the I_0/σ_{th} values, as well as to the inherent difficulties in absolute counting, poor precision was obtained.

The inaccuracies introduced by weighing and absolute counting can be eliminated by making use of an element with two appropriate isotopes, as suggested by MAENHAUT et al.[12] Using 1 and 2 to denote the isotopes in the flux monitor, Φ_{th}/Φ_e can be expressed using Eq. (4) as:

$$\frac{\Phi_{th}}{\Phi_e} = \frac{\frac{\Theta_1}{\Theta_2}\cdot\frac{\gamma_1}{\gamma_2}\cdot\frac{\epsilon_{p,1}}{\epsilon_{p,2}}\cdot\frac{\sigma_{th,1}}{\sigma_{th,2}}\cdot\left(\frac{I_0}{\sigma_{th}}\right)_1 - \frac{A_{sp,1}}{A_{sp,2}}\cdot\left(\frac{I_0}{\sigma_{th}}\right)_2}{\frac{A_{sp,1}}{A_{sp.2}} - \frac{\Theta_1}{\Theta_2}\cdot\frac{\epsilon_{p,1}}{\epsilon_{p,2}}\cdot\frac{\gamma_1}{\gamma_2}\cdot\frac{\sigma_{th,1}}{\sigma_{th,2}}} \tag{6}$$

From Eq. (6) Φ_{th}/Φ_e can be calculated directly knowing the relative full energy peak efficiencies $\epsilon_{p,1}/\epsilon_{p,2}$, the γ-ray abundance ratios (γ_1/γ_2), and the $\sigma_{th,1}/\sigma_{th,2}$ and I_0/σ_{th} values. If these values, particularly γ_1/γ_2 and $\sigma_{th,1}/\sigma_{th,2}$, are unknown or unreliable, the flux-ratio can be determined in a similar way to the k factor conversion technique. With irradiation of the flux monitor in the "reference" and "analysis" channels, and the measurement of $A_{sp,1}/A_{sp,2}$, the full-energy peak intensity ratios, $(\Phi_{th}/\Phi_e)_{anal}$ can be calculated from

$$\left(\frac{\mathrm{th}}{\mathrm{e}}\right)_{anal} = \frac{\left(\frac{A_{sp,1}}{A_{sp,2}}\right)_{ref}\left(\frac{I_0}{\sigma_{th}}\right)_1\left[\left(\frac{\Phi_{th}}{\Phi_e}\right)_{ref}+\left(\frac{I_0}{\sigma_{th}}\right)_2\right]-\left(\frac{A_{sp,1}}{A_{sp,2}}\right)_{anal}\left(\frac{I_0}{\sigma_{th}}\right)_2\left[\left(\frac{\Phi_{th}}{\Phi_e}\right)_{ref}+\left(\frac{I_0}{\sigma_{th}}\right)_1\right]}{\left(\frac{A_{sp,1}}{A_{sp,2}}\right)_{anal}\left[\left(\frac{\Phi_{th}}{\Phi_e}\right)_{ref}+\left(\frac{I_0}{\sigma_{th}}\right)_1\right]-\left(\frac{A_{sp,1}}{A_{sp,2}}\right)\left[\left(\frac{\Phi_{th}}{\Phi_e}\right)_{ref}+\left(\frac{I_0}{\sigma_{th}}\right)_2\right]} \tag{7}$$

Thus, assuming that I_0/σ_{th} and $(\Phi_{th}/\Phi_e)_{ref}$ are well known and that $(A_{sp,1}/A_{sp,2})_{ref}$ is determined, one has only to measure $(A_{sp,1}/A_{sp,2})_{anal}$ to determine $(\Phi_{th}/\Phi_e)_{anal}$ for all other "analysis" channels.

VAN DER LINDEN et al.[5] performed an extensive calculation of the error propagation when using the comparator technique based on Eqs. (5) and (7). They showed that the determination of $(\Phi_{th}/\Phi_e)_{anal}$ is the most likely source of error in the k factors. The accuracy and precision, however, can be markedly improved by an appropriate choice of the comparator isotope, as also noted by GIRARDI.[4] This means that a large error can be allowed for $(\Phi_{th}/\Phi_e)_{anal}$ in Eq. (5), that is flux monitors with a small difference in I_0/σ_{th} values can still be used if the I_0/σ_{th} values for the comparator and for the elements of interest do not differ significantly. In any case, the overall error of the final result can always be calculated via the derived expressions, thereby providing a simple "built-in" check, especially in computer evaluation.

Considering the result of the theoretical treatment, VAN DER LINDEN suggested the use of the multi-isotopic element Ru as a single comparator. Table 1 shows the nuclear data of the three Ru isotopes, together with the three relevant groups of elements which can be determined preferably with each of them. It can be seen that for flux-ratio determinations the ^{96}Ru–^{102}Ru couple is the best possible choice, and each of the three isotopes can be used as a comparator for only a single group of elements selected with respect to their I_0/σ_{th} values.

This method has a unique feature to enable instantaneous flux-ratio determination for every irradiation, and thus, in principle, slow changes in $(\Phi_{th}/\Phi_e)_{anal}$ during repeated irradiations can be eliminated. Unfortunately, the difference in the I_0/σ_{th} values for the selected Ru isotope pair is not sufficiently large for $(\Phi_{th}/\Phi_e)_{anal}$ to be measured with adequate precision, especially in highly-thermalized channels where $\Phi_{th}/\Phi_e > 50$. An interesting consequence is that the use of a Ru comparator generally gives better precision in "not so well" thermalized channels and no advantage in cases where the once-determined Φ_{th}/Φ_e remains stable. However, when applying it in remote irradiations where no a priori knowledge is available about the flux parameters, it has a distinct advantage.

All the previous comparator methods are based on the experimentally-determined k factors which could be converted for a given irradiation condition. In order to

Table 1
Compilation of nuclear data for Ru isotopes used as a single comparator with the group of most suitable elements to be determined

Comparator element and nuclear data	Target isotope	Θ, abundance,^{24} %	I_0/σ_{th}^{5}	Isotope formed	T half-life^{24}	Main γ-energies and abs. intensities,^{24} %	Range of appropriate $I_0/\sigma_{th}$$^+$	Isotopes formed in the given I_0/σ_{th} range	Notes
	^{96}Ru	5.46	23.1	^{97}Ru	69.1 h	215.2 (89.6) 324.2 (10.6)	$18.2 < \frac{I_0}{\sigma_{th}}$	^{85}Sr, ^{101}Mo, ^{104m}Rh, ^{111m}Pd, ^{113m}Sn, ^{122}Sb, etc.	
Ru $M = 101.07$ $\sigma_{abs} = 2.6$ barn	^{102}Ru	31.6	3.3	^{103}Ru	39.5 h	497.1 (89.0)	$0 < \frac{I_0}{\sigma_{th}} < 8.2$	^{24}Na, ^{27}Mg, ^{28}Al, ^{38}Cl, ^{42}K, ^{49}Ca, ^{46}Sc, ^{52}V, ^{51}Cr, ^{56}Mn, ^{59}Fe, etc	Possible interference from $E_\gamma = 499.3$ keV (3%) of ^{105}Ru while measuring ^{103}Ru
$I_{abs} = 42$ barn^{++}	^{104}Ru	18.87	13.0	^{105}Ru	4.44 h	326.1 (10.1) 469.4 (19.2) 724.2 (44.5)	$8.2 < \frac{I_0}{\sigma_{th}} < 18.2$	^{77}Ge, ^{76}As, ^{80}Br, ^{82}Br, ^{86}Rb, ^{110m}Ag, ^{115}Cd, ^{116m}In, ^{128}I, ^{185}W, ^{198}Au, etc.	^{105}Rh ($T = 35.5$ h) can also be used (daughter of ^{105}Ru)

$^+$ Isotopes having I_0/σ_{th} values in this range can be determined with the best possible precision by the selected comparator isotope.

$^{++}$ Epithermal self-absorption can be appreciable in the case of thick Ru foils.

further simplify this procedure KIM and BORN[6] determined the factors k_{anal} directly by calculation, taking all the nuclear data in Eq. (4) from the literature. (N.B. In their original work KIM and BORN used slightly different notations, i.e. WESTCOTT's $r\sqrt{T/T_0}$ and s_0 instead of Φ_{th}/Φ_e and I_0/σ_{th}, but this has no significance in the comparison of different methods.) Experimental work is needed only for the determination of the parameters $(\Phi_{th}/\Phi_e)_{anal}$ and ϵ_p/ϵ_p^*, which describe the experimental conditions that are considered stable, and for the irradiation and measurement of a single comparator (gold).

The unique characteristic of their approach is its simplicity, eliminating the experimental work in determining the k factors. Furthermore, there is the possibility of entirely numerical handling of γ-spectra, giving immediate analytical results if well-known irradiation channels and calibrated γ-spectrometers are provided. A few investigators have already developed instrumental activation analysis of the same type, using a single comparator with the aid of computer-based nuclear data libraries.[13–15] The introduction of absolute M, Θ and especially γ and σ_{th} values in Eq (4), however, makes the method itself also "almost absolute"; therefore, all the difficulties eliminated by the previous relative methods appear again. Although the above-named authors believe that existing nuclear data are accurate enough to accomplish reliable analysis for most of the elements, it seems that, in fact, this is not yet the case. In a recent survey concerning the present state in nuclear data compilations, KRIVAN[16] pointed out that the typical scattering of decay-scheme values as γ-abundances is 2–15% (max. 80%), while for thermal neutron cross-sections this range is 5–40% (max. 100%). Further inaccuracies can occur in correcting γ-ray abundancies for internal conversion at small γ-energies. Moreover, the accuracy in γ and σ_{th} is transferred directly to the final result, e.g. a 10% error in σ_{th} will represent the same error in the k factors. This means that the error multiplication factor is 1, whereas for the previous methods, using only Φ_{th}/Φ_e and I_0/σ_{th} values, the error multiplication factor is typically 10^{-1} – 10^{-2}. It is felt, therefore, that at the moment this method is not generally competitive with the other single-comparator methods, where an overall accuracy of 3–5% can reasonably be assumed. The continuously-improving accuracy of nuclear data, however, will certainly enhance the importance of "almost absolute" methods in the future.

Introduction of generalized k_0 factors

In addition to the reviewed single-comparator methods, a new approach is suggested, using a generalized k_0 factor. This alternative method, explained in detail below, combines the simplicity of the "almost absolute" methods with nearly the same accuracy attained in the relative methods.

In Eq. (4) the approximation of HØGDAHL was used for reaction rate calculations. Replacing this by the more accurate STOUGHTON-HALPERIN convention,[17] the total reaction rate for an isotope at infinite dilution is given by

$$R = \Phi_M \sigma_M + \Phi_e I_0' \tag{8}$$

where $\Phi_M = n_M v_0$, conventional thermal flux for Maxwellian neutrons, with

$n_M = \int_0^\infty n_M(v)\,dv$, the total Maxwellian neutron density,

$\sigma_M = g\sigma_0$, neutron cross-section, where WESTCOTT's g factor[18] corrects for the non-1/v cross-section, for use with Φ_M,

$I_0' = \int_{\mu kT}^\infty \sigma(E)\,dE/E$, infinitely-dilute resonance integral, where the integration is taken from μkT, a cutoff point between the Maxwellian thermal and the 1/E epithermal flux,

$\mu = 5$ for most reactors,

$E_T = kT$, the most probable neutron energy at temperature T. At room temperature $T = T_0$, $E_0 = 0.0253$ eV and $\mu kT = 0.165$ eV.

Introducing the STOUGHTON-HALPERIN convention in Eq. (4), the new k_0 factor can be derived from

$$k_0 = \frac{M^*}{M} \cdot \frac{\Theta}{\Theta^*} \cdot \frac{\gamma}{\gamma^*} \cdot \frac{\sigma_M}{\sigma_M^*} = \frac{A_{sp}}{A_{sp}^*} \cdot \frac{\epsilon_p^*}{\epsilon_p} \cdot \frac{\dfrac{\Phi_M}{\Phi_e} + \dfrac{I_0'^*}{\sigma_M^*}}{\dfrac{\Phi_M}{\Phi_e} + \dfrac{I_0'}{\sigma_M}} \tag{9}$$

For any "analysis" case, k_{anal} can be calculated simply from the following expression:

$$k_{anal} = k_0 \cdot \frac{\left(\dfrac{\Phi_M}{\Phi_e}\right)_{anal} + \dfrac{I_0'}{\sigma_M}}{\left(\dfrac{\Phi_M}{\Phi_e}\right)_{anal} + \dfrac{I_0'^*}{\sigma_M^*}} \cdot \frac{\epsilon_p}{\epsilon_p^*} \tag{10}$$

It can be seen from Eq. (9) that k_0 is independent of the reactor spectrum and of the detector characteristics, because it contains only well-defined, invariable nuclear constants. The k_0 values can therefore be measured and used as compound nuclear constants for reactor neutron activation analysis if Maxwellian thermal and 1/E epithermal flux distributions are present. Because this is usually the case for many reactors, the authors feel that experimenters should publish not only k_{ref} or k_{anal} but also

k_0 values. Continuous updating would make it possible to establish k_0 values with good accuracy. With the condition of being measurable under the given experimental circumstances, any type of element or isotope can be used as a comparator, because it is very simple to switch from one comparator to another when using k_0 values. This fact can be advantageous in practical work because it has turned out to be hard to find a single element which would be an appropriate comparator for largely different irradiation conditions.

The k_0 factors can be transformed into k_{anal} via Eq. (10); one need only measure the relative efficiency curve of the detector, determine $(\Phi_M/\Phi_e)_{anal}$ and use the tabulated I_0'/σ_M values. Even if k_{anal} was determined as an experimental result, the transformation into k_0 is recommended as this would save the experimenter from the tremendous work of remeasuring all the k factors if the uncalibrated detector is no longer available.

A survey of published k factors shows that some kind of standardization is necessary. In Table 2 reported k values are given for 10 isotopes. It can be seen that due to the different detectors, geometries and conventions used, the k factors differ considerably even in the case of the same comparator. In an attempt to demonstrate the usefulness of the k_0 factors conception, all the k factors listed in Table 2 have been converted into k_0 values in Table 3. Gold was chosen as a common comparator for the calculations. The theoretical k_0 values were also computed, using the nuclear data from recent compilations. In spite of the lack of accurate data describing the applied experimental conditions in some of the selected papers, the "measured" k_0 values show reasonable agreement with the exception of a few cases. Obviously, extensive work is needed to establish accurate k_0 values.

It should be emphasized that the k_0 factors are valid, and therefore should be determined using point-source geometry. When using different sample and comparator shapes such as a bulky sample with a small comparator wire, appropriate corrections should be introduced. This is also true for classical activation analysis, and therefore the use of point-source referenced k_0 factors imposes no extra difficulties.

The k_0 factors are also valid only for monoenergetic γ-lines. Possible coincidence summing effects should be corrected, mainly at high counting geometries. It can be shown[19] that in the case of radioisotopes emitting a cascade of two γ-rays (1 and 2) the correction is:

$$(A_{sp,1})_{corr} = \frac{A_{sp,1} \cdot \omega}{1 - \frac{\epsilon_{p,2}}{P_2} \cdot \omega} \tag{11}$$

or

$$(A_{sp,1})_{corr} = A_{sp,1} \cdot \omega + \frac{A_{sp,sum}}{P_2} \tag{12}$$

where P – peak to total ratio for the measured γ-line,
$A_{sp,sum}$ – specific sum peak intensity,
ω – angular correlation factor, which can usually be ignored ($\omega = 1$).

The correction based on sum peak intensity measurement can be favourably used in the determination of k_0 values. Eq. (11) is convenient in correcting actual sample spectra where the sum peaks are usually hidden. From Eqs (11) and (12) it can be seen that to correct the summing effect, absolute ϵ_p and γ-values and peak to total ratios should be introduced. Fortunately, this correction amounts to a few percent only, and therefore accurate absolute values are not required.

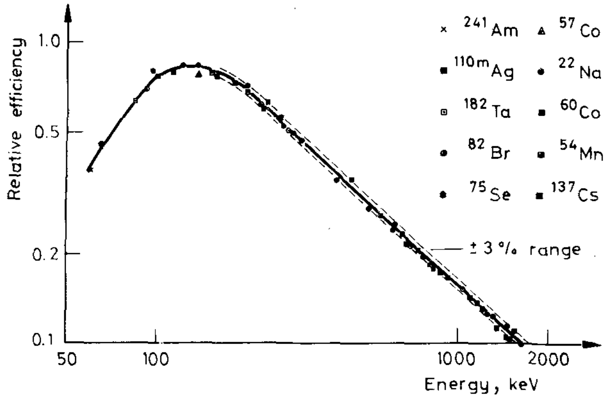

Fig. 1. Relative efficiency curve of a Ge(Li) detector

The determination of relative efficiency curves is especially important in this method, because its accuracy determines the final result directly. Due to the difficulties associated with the theoretical calculation of Ge(Li) detector efficiency, an experimental approach to the problem is usually adopted. A common practice is to use a number of calibrated isotopes. However, the accuracy of the measurements is limited by the accuracy with which the source strengths are known. A more convenient procedure makes use of isotopes which emit a number of γ-rays with well-known relative intensities.[20-21] Fig. 1 shows a relative efficiency curve measured with ^{82}Br, ^{75}Se, ^{110m}Ag and ^{182}Ta isotopes, which can be easily produced by reactor irradiation. It can be seen that 95% of the nearly 60 measuring points fall within a ±3% range. An average accuracy of 1% can therefore be reasonably obtained for relative efficiencies with not too different γ-energies. The once-determined relative efficiency curve can be normalized to the absolute one through the measurement of at least one absolute γ-standard.

Table 2
Experimentally-determined k_{ref} values as reported in the literature

Isotope formed	Measured γ-energy, keV	Experimentally-determined k factors for reactor irradiations measured by				
		(a) GIRARDI[4] comp: ^{59}Co	(b) DE CORTE[25] comp: ^{59}Co	(c) LINEKIN[2] comp: ^{59}Co	(d) VAN DER LINDEN[27] comp: ^{102}Ru	(e) HEURTEBISE[26] comp: none
^{76}As	559.1	$1.055\cdot10^{1}$	$2.23\cdot10^{1}$	–	–	$2.03\cdot10^{-7}$
^{51}Cr	320.1	$1.2\ \cdot10^{2}$	$1.92\cdot10^{-1}$	$1.63\cdot\ 10^{-2}$	$5.09\cdot10^{-1}$	$3.84\cdot10^{-10}$
^{60}Co	1173.2	1.000	$4.17\cdot10^{-1}$ *	1.088	$1.21\cdot10^{2}$ *	$2.60\cdot10^{-9}$
	1332.5	1.103		–	–	–
^{59}Fe	1099.2	$1.315\cdot10^{4}$	$1.71\cdot10^{-3}$ *	$7.6\ \cdot10^{-5}$	$3.62\cdot10^{-5}$	$7.22\cdot10^{-12}$
	1291.6	$2.02\ \cdot10^{4}$		–	–	–
^{46}Sc	889.3	$7.45\ \cdot10^{-1}$	$1.41\cdot10^{-1}$	1.23	$7.15\cdot10^{1}$	–
	1120.5	$9.7\ \cdot10^{-1}$	$1.06\cdot10^{-1}$	–	–	–
^{24}Na	1368.4	$3.1\ \cdot10^{1}$	$1.62\cdot10^{-1}$	$7.46\ \cdot10^{-4}$	1.67	$2.99\cdot10^{-7}$
	2754.1	–	$5.52\cdot10^{-2}$	–	–	–
^{86}Rb	1078.8	$1.46\ \cdot10^{3}$	–	$9.21\ \cdot10^{-4}$	$2.88\cdot10^{-1}$	–
^{117m}Sn	158.4	$1.80\ \cdot10^{4}$	$1.86\cdot10^{-2}$	$3.94\ \cdot10^{-4}$	–	–
^{65}Zn	1115.5	$1.52\ \cdot10^{2}$	–	$4.84\ \cdot10^{-3}$	1.739	–
^{198}Au	411.8	–	$7.33\cdot10^{2}$	$8.26\ \cdot10^{-2}$	–	$1.48\cdot10^{-6}$

* Determined for the sum of the two peak intensities.

(a) $k = A^{*}_{sp}/A_{sp}$ for 3" X 3" NaI(Tl) detector; Φ_{th}/Φ_e about 70.

(b) $k = A_{sp}/A^{*}_{sp}$ for different-volume NaI(Tl) and Ge(Li) detectors; $\Phi_{th}/\Phi_e = 23.7$.

(c) $k = A_{sp}/A^{*}_{sp}$ for Ge(Li) detector; Φ_{th}/Φ_e about 80.

(d) $k = A_{sp}/A^{*}_{sp}$ for Ge(Li) detector; $\Phi_{th}/\Phi_e = 23.8$ (unpublished data).

(e) $k = \dfrac{\sigma \lambda \Theta \gamma}{M}$ (for notations see text).

Table 3

k_0^{Au} values calculated from k_{ref} listed in Table 2

Isotope formed	Measured γ-energy, keV	k_0 (theor.) comp: ^{197}Au	k_0^{Au} values calculated on the basis of k_{ref} measured by				
			GIRARDI[4]	DE CORTE[25]	LINEKIN[2]	VAN DER LINDEN[27]	HEURTEBISE[26]
^{76}As	559.1	$5.39 \cdot 10^{-2}$	$5.81 \cdot 10^{-2}$	–	–	–	$5.59 \cdot 10^{-2}$
^{51}Cr	320.1	$2.65 \cdot 10^{-3}$	$3.36 \cdot 10^{-3}$	$2.65 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$2.33 \cdot 10^{-3}$	$2.67 \cdot 10^{-3}$
^{60}Co	1173.2	1.29	1.29	–	1.29	1.28	1.28
	1332.5	1.29	–	–	–	–	–
^{59}Fe	1099.3	$7.34 \cdot 10^{-5}$	$9.3 \cdot 10^{-5}$	$8.6 \cdot 10^{-5}$	–	–	–
	1291.5	$5.66 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$	$6.6 \cdot 10^{-5}$	–	$6.89 \cdot 10^{-5}$	–
^{46}Sc	889.3	1.19	1.38	–	1.08	1.13	–
	1120.5	1.19	1.29	–	–	1.13	–
^{24}Na	1368.4	$4.86 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$	–	–	$4.1 \cdot 10^{-2}$	$4.68 \cdot 10^{-2}$
	2754.1	$4.86 \cdot 10^{-2}$	$4.46 \cdot 10^{-2}$	–	–	–	–
^{86}Rb	1078.8	$6.12 \cdot 10^{-4}$	$7.69 \cdot 10^{-4}$		$8.9 \cdot 10^{-4}$	–	–
^{117m}Sn	158.4	$1.33 \cdot 10^{-5}$	$0.65 \cdot 10^{-5}$	$1.97 \cdot 10^{-5}$	–	–	–
^{65}Zn	1115.5	$6.29 \cdot 10^{-3}$	$7.98 \cdot 10^{-3}$	–	$5.41 \cdot 10^{-3}$	–	–
^{198}Au	411.8	1.000	1.000	–	–	–	1.00

It can be concluded that the detector calibration is of decisive importance in the suggested method. It is felt, however, that the necessary calibrations for a few selected sample detector distances require little effort compared with the disadvantage of handling standards and remeasuring the k factors as well.

It should be mentioned that the conversion of k factors requires the precise definition of flux ratios and I_0/σ_{th} values, which is frequently overlooked. This problem of definition will be dealt with in detail in a forthcoming paper.[22]

Conclusion

The evaluation of different single-comparator methods shows that at present the method based on experimentally-determined and convertible k factors seems to be the most accurate and convenient for general use. In order to simplify the experimental work while maintaining similar accuracy a new approach is suggested, introducing k_0 values which can be considered as compound nuclear data. It is recommended that k_0 factors be published and compared as they are independent of irradiation and measuring conditions. This method can be considered as an alternative to absolute methods, while eliminating many inaccuracies introduced by using ambiguous absolute nuclear data.

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