EVALUATION OF K_0 AND $K_{e,0}$ METHODS AS NEW STANDARDIZATION TECHNIQUES IN REACTOR NEUTRON ACTIVATION ANALYSIS

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الخلاصـة :

في هذه الدراسة مقارنة حرجة بين طريقتين حديثتين للتحليل التنشيطي لعينات متعددة العناصر وذلك من حيث الدقة والاتقان بنيت على أساس نظرية "Error Propagation Theory" بجانب أمثلة عددية درست تحت ظروف محددة بالمفاعل .

ABSTRACT

Two recent methods applied to multielement analysis are critically compared regarding their accuracy and precision. The analysis is based on the theory of error propagation. Numerical examples for specific conditions in the "Thetis" reactor (Gent, Belgium) are given.

EVALUATION OF K_o AND $K_{e,o}$ METHODS AS NEW STANDARDIZATION TECHNIQUES IN REACTOR NEUTRON ACTIVATION ANALYSIS

1. INTRODUCTION

Previously [1–8] various methods have been described for the simultaneous determination of a number of trace elements in low weight materials. The conclusion shows that the K_o and $K_{e,o}$ methods while being experimentally simple, versatile, and suited for computerization, offer a potential accuracy which depends mainly on the K_o and $K_{e,o}$ factors. These factors are a composite of nuclear constant containing atomic weights, isotopic abundances, thermal neutron cross-sections and gamma intensities which are often unreliable [9, 10]. Therefore accurate experimental determination of K_o and $K_{e,o}$ can be accomplished by using the following equations:

$$(K_o)_{exp} = \frac{[(A_{sp})]}{[(A_{sp}^*)]} \times \frac{[F + Q_{o(\alpha)}]}{[F + Q_{o(\alpha)}^*]} \times \frac{\varepsilon_p^*}{\varepsilon_p} \tag{1}$$

and

$$(K_{e,o})_{exp} = \frac{[(A_{sp})_{Cd}/F_{Cd}]}{[(A_{sp}^*)_{Cd}/F_{Cd}^*]} \times \frac{Q_o \times Q_{o(\alpha)}^*}{Q_o^* \times Q_{o(\alpha)}} \times \frac{\varepsilon_p^*}{\varepsilon_p} \tag{2}$$

or

$$= \frac{[(A_{sp})]}{[(A_{sp}^*)]} \times \frac{F + Q_{o(\alpha)}}{F + Q_{o(\alpha)}^*} \times \frac{\varepsilon_p^*}{\varepsilon_p} \times \frac{Q_o}{Q_o^*}$$

$$= K_o \frac{Q_o}{Q_o^*} \tag{3}$$

where the asterisk refers to the comparator (power monitor).

In Equations (1–3) it is assumed that: the Westcott g-factor is equal to 1, *i.e.* $\sigma(v) \sim 1/v$, in the thermal neutron region (up to 1 eV) [11]; $E_{Cd} = 0.55$ eV [12]; and A_{sp} is the specific activity of the measured γ-peak $= A_p/SDCW$ (in case of complicated reaction/decay mechanisms, parent–daughter *etc.*, the term has to be replaced by adequate expressions) with A_p = measured average activity of the full-energy peak $= N_p/t_m$ with N_p = measured number of net counts under the full energy. $S = 1 - \exp(-\lambda t_{irr})$, t_{irr} = irradiation time and $T = \ln 2/\lambda$ = half life; $D = \exp(-\lambda t_d)$, t_d = decay time; $C = [1 - \exp(-\lambda t_m)]/t_m$ = measuring time, W weight of the irradiated element; F_{Cd} cadmium transmission factor [5, 13, 14] mostly ≤ 1; ε_p detection efficiency;

Q_o resonance integral to thermal cross-section ratio, where the conversion proceeds as [15]:

$$Q_{o(\alpha)} = (Q_o - 0.429) \bar{E}_r^{-\alpha} + C_\alpha$$

with

$$C_\alpha = 0.429/[(E_{Cd})^\alpha (2\alpha + 1)] ; \tag{4}$$

$\bar{E}_r$ = effective resonance energy [16], and α is a measure for the deviation of the epithermal flux spectrum $(\sim 1/E^{1+\alpha})$ from the $1/E$ law.

This paper presents the results of a comparative study of the accuracy and the precision which can be expected with K_o and $K_{e,o}$ techniques. The mathematical treatment is based on the theory of error propagation with an attempt to group the uncertainties into systematic (accuracy) and random ones (precision). The final goal of this study is to help in a judicious choice of methods for analysis.

THEORETICAL FOUNDATIONS

In both methods, the factors K_o and $K_{e,o}$ have to be calculated usually from an implicit function of the form:

$$F(K, x_i) = 0, \quad i = 1, 2, \dots. \tag{5}$$

where the x_i's are either statistical variables or fixed parameters with an associated uncertainty (*e.g.* nuclear data).

According to the classical theory of propagation of errors, the overall (total) relative uncertainty in K, as a function of the relative uncertainties in the x's, is given by:

$$S_{K,T} = \{\sum_j [Z_K(x_j) S(x_j)]^2\}^{1/2} \tag{6}$$

where the error propagation factor $Z_K(x_j)$ is defined as the multiplier of the relative error on x_j to obtain the associated relative error on K.

When writing the relative uncertainties in terms of differentials, one obtains according to the above definition:

$$Z_K(x_j) = \left| \frac{dK}{K} \middle/ \frac{dx_j}{x_j} \right| . \tag{7}$$

It should be kept in mind that $Z_K(x_j)$ denotes the "partial" error propagation factor for K, caused by the relative error in x_j.

The partial derivation of the F-function (Equation 5) can be written as:

$$\frac{dF}{dK}\,dK + \frac{dF}{dx_j}\,dx_j = 0 .\qquad(8)$$

Utilizing this partial derivative of F into Equation (7) one gets:

$$Z_K(x_j) = \left|\frac{x_j}{K}\frac{dF}{dx_j}\Big/\frac{dF}{dK}\right| .\qquad(9)$$

From Equation (9) it is possible to calculate error propagation factors for the individual variables and parameters in Equation (5). To obtain the overall uncertainty in K, these $Z_K(x_j)$-factors have to be introduced into Equation (6), together with the measured or estimated uncertainties in the x_j-parameters under consideration.

It should be noted that the application of Equation (6), with the introduction of $Z_K(x_j)$-factors according to Equation (9), in principle will only be realistic for moderate $S(x_j)$-values, or, for $K = F(x_j)$ relations which do not deviate dramatically from linearity. Nevertheless, in most practical cases the above expressions can be considered as an acceptable approximation; this has been checked numerically in the present work.

PRECISION, FIXED ACCURACY, AND EXPERIMENTAL ACCURACY OF THE K-DETERMINATION

The x_j and $S(x_j)$-factors of Equation (6) can be classified into the following categories:

1. x_j parameters with a random error (index R), which can be described by the laws of probability $[x_R, S(x_R)]$. These parameters influence the precision of the K-determination.

2. x_j parameters with a systematic error (index S) $[x_S, S(x_S)]$. These parameters influence the fixed accuracy of the K-determination.

3. x_j parameters with a gross error (index G), which normally should be avoided or corrected for $[x_G, S(x_G)]$. These parameters influence the experimental accuracy of the K-determination.

Equation (6) can then be rewritten as:

$$S_{K,T} = (S_{K,R}^2 + S_{K,S}^2 + S_{K,G}^2)^{1/2}\qquad(10)$$

with

$$S_{K,R} = \{\sum_R [Z_K(x_R)\ S(x_R)]^2\}^{1/2}\qquad(11)$$

$$S_{K,S} = \{\sum_S [Z_K(x_S)\ S(x_S)]^2\}^{1/2}\qquad(12)$$

and

$$S_{K,G} = \{\sum_G [Z_K(x_G)\ S(x_G)]^2\}^{1/2}\qquad(13)$$

where $\sum_R$, $\sum_S$, and $\sum_G$ denote a summation over all parameters which are causing random, systematic, or gross errors, respectively.

The K-factor can then be computed from the specific count rates of the irradiated detectors, from the nuclear data involved, and, if occurring, from the appropriate full-energy peak detection efficiencies (ε_p).

Thus Equation (5) can be written explicitly as:

$$F[K,\ A_{sp,j}\,(\text{Nuclear Data}):,\ \varepsilon_{p,j}] = 0 .\qquad(14)$$

Where the index j refers to all isotopes used. Usually a small systematic error on $T_{1/2}$, and the gross uncertainties on t_{irr}, t_d, and t_m, do not contribute significantly to the error in A_{sp} [17]. The standard deviation in A_{sp} is then basically determined by counting statistics, and thus is essentially random. However, other factors may add to the error in A_{sp}, such as time variation in detection equipment stability, or in the case of time fluctuations in the reactor neutron spectrum. Nevertheless, it can be assumed that under well controlled conditions, these contributions as well as that of ε_p are likely to be negligible in the present calculations because they play the same role in K_o and $K_{e,o}$ factors.

The K_o and $K_{e,o}$ values are based on irradiating and measuring a single element (comparator) instead of using standards for the elements to be determined. The ρ_i concentration for a given element can be calculated simply as:

$$\rho_{i(ppm)} = \frac{\dfrac{A_{p,i}}{SDCW}}{K_{anal}\ A_{sp}^*} ,\qquad(15)$$

where W represents the sample weight in grams.

The K_{anal} factors in RNAA are defined by:

$$K_{anal} = K_o\,\frac{F+Q_{o(\alpha)}^*}{F+Q_{o(\alpha)}} \times \frac{\varepsilon_p}{\varepsilon_p^*} = \frac{[(A_{sp})]}{[(A_{sp}^*)]} ,\qquad(16)$$

and in ENAA are defined by:

$$K_{anal} = K_{e,o}\,\frac{Q_o^* \times Q_{o(\alpha)}}{Q_o \times Q_{o(\alpha)}^*} \times \frac{\varepsilon_p}{\varepsilon_p^*} = \frac{[A_{sp}/F_{cd}]}{[A_{sp}^*/F_{cd}^*]} .\qquad(17)$$

ERROR EQUATIONS

If the K_o method applied to RNAA the $Q_{o(\alpha)}$-factor (Equation 15) always appear in a term of the following form

$$\frac{F+Q^*_{o(\alpha)}}{F+Q_{o(\alpha)}} .$$

Since all Q_o-values are related to one for Au [18], the errors on $Q^*_{o(\alpha)}$ in the above equation need not be considered here.

The error in ρ_i(ppm) to be determined can be found by differentiating Equation (15) and dividing by Equation (15).

This means that inaccuracies in K_o or $K_{e,o}$ are transferred directly to the final results. According to Equation (2):

$$Z_{k_{e,o}}(Q_o) = Z_w(Q_o)$$
$$= \left| 1 - \frac{Q_o}{Q_{o(\alpha)}} (\bar{E}_r)^{-\alpha} \right| , \quad (18.1)$$

$$Z_{k_{e,o}}(\alpha) = \left| \frac{\alpha}{0.434} \left[\frac{q_{o(\alpha)}}{Q_{o(\alpha)}} \log \bar{E}_r - \frac{q^*_{o(\alpha)}}{Q^*_{o(\alpha)}} \log (\bar{E}_r)^* \right. \right.$$
$$\left. \left. + 0.26\, C_\alpha \left(\frac{1.67}{\alpha + \frac{1}{2}} - 1 \right) \left(\frac{1}{Q_{o(\alpha)}} - \frac{1}{Q^*_{o(\alpha)}} \right) \right] \right| , \quad (18.2)$$

$$Z_{k_{e,o}}(\bar{E}_r) = \frac{q_{o(\alpha)}}{Q_{o(\alpha)}} \left| \alpha \right| , \quad (18.3)$$

$$Z_{k_{e,o}}(E_{cd}) = \left| \frac{1}{Q_{o(\alpha)}} - \frac{1}{Q^*_{o(\alpha)}} \right| \times C_\alpha \times (\alpha + \frac{1}{2}) . \quad (18.4)$$

Also, according to Equation (3):

$$Z_{k_{e,o}}(Q_o) = \left| 1 - \left(\frac{Q_o}{F + Q_{o(\alpha)}} \right) (\bar{E}_r)^{-\alpha} \right| , \quad (19.1)$$

$$Z_{k_{e,o}}(\alpha) = \left| \frac{\alpha}{0.434} \left[\frac{q_{o(\alpha)}}{F + Q_{o(\alpha)}} \log \bar{E}_r \right. \right.$$
$$- \frac{q^*_{o(\alpha)}}{F + Q^*_{o(\alpha)}} \log (\bar{E})^*$$
$$+ 0.26\, C_\alpha \left(\frac{1.67}{\alpha + \frac{1}{2}} - 1 \right)$$
$$\left. \left. \times \left(\frac{Q^*_{o(\alpha)} - Q_{o(\alpha)}}{(F + Q^*_{o(\alpha)})(F + Q_{o(\alpha)})} \right) \right] \right| , \quad (19.2)$$

$$Z_{k_{e,o}}(F) = F \frac{Q_{o(\alpha)} - Q^*_{o(\alpha)}}{(F + Q_{o(\alpha)})(F + Q^*_{o(\alpha)})} , \quad (19.3)$$

$$Z_{k_{e,o}}(\bar{E}_r) = \frac{q_{o(\alpha)}}{F + Q_{o(\alpha)}} \left| \alpha \right| , \quad (19.4)$$

$$Z_{k_{e,o}}(E_{cd}) = C_\alpha (\alpha + \frac{1}{2}) \left[\frac{1}{F + Q_{o(\alpha)}} - \frac{1}{F + Q^*_{o(\alpha)}} \right] . \quad (19.5)$$

According to Equation (6), the overall relative uncertainty in K, as a function of the relative uncertainty on the xs can be calculated.

The data used in this work are listed in Table 1.

As numerical examples for two irradiation positions, $\alpha = 0.015$ and 0.084, Table 2 shows the relevant precisions calculated according to Equation (6).

Table 1. Selected Data of 6 Isotopes Used in this Work

Reaction	Q_o Relative error % [18]	$\bar{E}_r$ Relative error % [16]	F Relative error %		α Relative error %		E_{cd} Relative error %
			P_1^*	P_2^{**}	P_1	P_2	
^{94}Zr(n, γ) ^{95}Zr	5.88 (1.7)	4520 (26)					0.55 [15]
^{96}Zr(n, γ) ^{97}Zr	282 (1.9)	340 (37)	25 [3]	72 [3]	0.015 [30]	0.084 [7]	
^{186}W(n, γ) ^{187}W	13.7 (1.1)	19.5 (36)					
^{98}Mo(n, γ) ^{99}Mo	53.1 (1.6)	211 (10)					
^{115}In(n, γ) ^{116m}In	16.8 (1.0)	1.51 (35)					
^{158}Sm(n, γ) ^{153}Sm	14.4 (1.2)	833 (36)					

*P_1 irradiation position No. 1
**P_2 irradiation position No. 2

Table 2a. K_0 Method Using Nuclear Data in Two Different Positions within the Reactor

Isotope		$Z_{k_{e,o}}(Q_{0,st})$	$Z_{k_{e,o}}(\alpha)$	$Z_{k_{e,o}}(F)$	$Z_{k_{e,o}}(\bar{E}_r)$	$Z_{k_{e,o}}(E_{cd})$	$S_{R,T}$
^{95}Zr	P_1	0.80710329	0.01056215	0.20839542	0.002362	0.0034816	1.542840537
^{97}Zr	P_1	0.00889193	0.06473798	0.52842942	0.01360048	0.00882923	2.676049256
^{187}W	P_1	0.64054129	0.00543781	0.03574787	0.00499656	0.00059729	0.75638841
^{99}Mo	P_1	0.27864012	0.04354575	0.28623578	0.00990694	0.00478256	1.6302478
^{116m}In	P_1	0.59695075	0.00847839	0.02042302	0.00585612	0.00034124	0.68325354
^{153}Sm	P_1	0.65815448	0.03896606	0.01999251	0.00523683	0.00017203	1.424579011
^{95}Zr	P_2	0.92347442	0.11395812	0.10584212	0.00293794	0.0005643	1.7909975
^{97}Zr	P_2	0.13639712	0.20171844	0.53782686	0.05840895	0.00286745	3.0555924
^{187}W	P_2	0.39439306	0.1074754	0.02947697	0.0105021	0.00015716	1.2486713
^{99}Mo	P_2	0.49323849	0.00548957	0.16518408	0.02694037	0.00088069	0.97088058
^{116m}In	P_2	0.80952381	0.13250701	0.02453956	0.01506369	0.00013084	1.3412942
^{153}Sm	P_2	0.84138472	0.00433264	0.01462861	0.01175567	0.00004555	1.096067814

Table 2b. $K_{e,o}$ Method Using Nuclear Data in Two Different Positions within the Reactor

Isotope		$Z_{k_{e,o}}(Q_{0,st})$	$Z_{k_{e,o}}(\alpha)$	$Z_{k_{e,o}}(\bar{E}_r)$	$Z_{k_{e,o}}(E_{cd})$	$S_{R,T}$
^{95}Zr	P_1	0.00809066	0.09242595	0.01378959	0.0275454	2.8289318
^{97}Zr	P_1	0.00010905	0.06204253	0.0149747	0.01318189	1.9520326
^{187}W	P_1	0.0007536	0.01847204	0.01452262	0.0235402	0.83970939
^{99}Mo	P_1	0.00048497	0.05449137	0.01487445	0.00973671	1.647979
^{116m}In	P_1	0.00085226	0.01879868	0.014632	0.00115612	0.761986402
^{153}Sm	P_1	0.000331	0.00515082	0.01408999	0.00125887	0.53059083
^{95}Zr	P_2	0.29186713	0.33181722	0.05512924	0.03885986	10.08627191
^{97}Zr	P_2	0.00074217	0.3475978	0.08380522	0.01509862	10.88154495
^{187}W	P_2	0.00477823	0.10266671	0.08099914	0.00444826	4.241905605
^{99}Mo	P_2	0.00032348	0.30456476	0.08306775	0.00996552	9.175842971
^{116m}In	P_2	0.00175197	0.10714232	0.08201344	0.00261411	4.309602070
^{153}Sm	P_2	0.00221977	0.00551107	0.06783596	0.00198072	2.447866494

CONCLUSION

The error analysis together with the corresponding consideration as outlined in this paper, should allow a judicious choice of methods for RNAA analysis. For most analytical cases the K_0-methods provides acceptable precision and accuracy, in which, the use of K_0-factors and of carefully selected Q_0, $\bar{E}_r$, etc. nuclear parameters is strongly recommended.

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