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LIMITATIONS ON ELEMENTAL ANALYSIS OF MATERIALS USING NEUTRON ACTIVATION TECHNIQUES

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Abstract

In this talk, the most important limitations on elemental analysis of different materials using the neutron activation techniques are given. The limitations in the delayed Gamma-ray Neutron Activation Analysis [LDGNAA] as well as the limitations in the Prompt Gamma-Ray Neutron Activation Analysis [LPGNAA] due to the problems appeared in the experimental applications in this field have been discussed. The sources of errors in qualitative and quantitative elemental analysis in the current wide applications including, the samples preparation, neutron irradiation facilities using low and high flux neutron facilities, nuclear data used, gamma-ray detection limits, interfering of nuclear reactions and methods of data analysis are presented. This is to reveal some of the problems facing the user and to get a good accuracy for elemental analysis.

Key words: *limitations, elemental analysis, neutron activation techniques*

INTRODUCTION

Neutron activation analysis [NAA] is one of the most important analytical techniques which can yield very accurate and precise results for trace and ultra-trace elemental determinations in complex materials. In the last several decades, this technique has been applied for determination of a great variety of elements in many disciplines. These include environmental, biological, geological, as well as material science. This technique is considered as a method for qualitative and quantitative determination of elements based on the measurement of characteristic radiation from radionuclides formed directly or indirectly by neutron irradiation of the material [1-22]. The most suitable source of the neutrons is usually the nuclear research reactor. Also, some isotopic neutron sources like (α,n) and Cf^{252} sources are used as well as the neutron generators for high energy mono-energetic neutrons. The high resolution gamma-ray detection systems together with the advanced computer programmes are used for analysis of such complex gamma-ray spectra.

As we know, the gamma-rays emitted by an element after neutron absorption fall into two classes, the prompt gamma-rays (PG) emitted in $\sim 10^{-14}$ s. and the delayed gamma-rays (DG) emitted in the half life time of each irradiated element.

The complete analysis of the data obtained requires a knowledge of the neutron flux parameters at the irradiation position, and the nuclear data of the relevant isotopes such as the thermal neutron capture cross sections, resonance integrals and the gamma-ray emission probabilities of the concerned nuclides. Several special computer programmes should be applied for such analysis.

Under proper conditions the counting systems and the associated programmes have a great influence on the neutron activation analysis methods. However it is important to be aware of their limitations, which may give rise to erroneous results without any warning.

So this paper is made to point out the sources of limitations of NAA techniques and there analytical methods. The concepts of qualitative and quantitative analysis limits will be discussed.

LIMITATIONS AND SUGGETIONS FOR SOLVING SOME TECHNICAL PROBLEMS

It is often difficult to achieve, the high accuracy at the level of few percent, since the parameters such as; sampling, concentration, calibration and detection limits during the various forms of activation analysis. This may severely compromise the results in each form [1-2]. The limitations due to some of these parameters and suggestions for solving such problems will be discussed as follows:

1- Sampling and Pre-irradiation Sample Treatment:

Samples collection from different places in different forms is an important task. The shape of the sample (liquid, solid, powder or granules) is also very important. Cleaning, drying, elimination of interfering elements and well encapsulated in the polyethelene capsules prepared for irradiation (packing) are needed for each sample.

2- Irradiation

A neutron flux in the order of 0.5 to $5x10^{12}$ cm^{-2} s^{-1} is still quite acceptable for many NAA purposes, as has been demonstrated by many laboratories. This low neutron flux reactor facilities offer some addition advantages for NAA, such as, relatively low gamma-ray dose and allowing for relatively long irradiations with samples packed in plastic foils or capsules. However, because of relatively low neutron flux, small reactor types are less suitable for studies of impurities in high purity materials such as Si. For such analysis, a very high neutron dose rate is necessary, often accomplished by many irradiation hours in neutron fluxes greater than $5x10^{13}$ cm^{-2} s^{-1}. The activity of each sample should be calculated which depends mainly on the neutron flux at the irradiation position.

3- Various Forms of Neutron Activation Analysis and Principles of Calculations:

Several forms of NAA are utilized. On the following some notices on each form will be mentioned. For more details, it is recommended to consult the various recent text books [22].

3-1 Instrumental and Radiochmical Neutron Activation Analysis (INAA) and (RNAA)

INAA is a multielemental method whereby the gamma-ray spectroscopy is applied to radioactivity measurements. The [INAA] technique promises reliable analytical results, because the possible error due to contamination and element loss can be easily avoided. The relatively large samples varying from a several grams to several kilograms could be analyzed by such technique. In case of [RNAA], it involves a post-irradiation radiochemical separation procedure just to isolate one or a group of elements or to element interfering nuclides. Application of a carrier and hold-back carrier makes chemical separation much more convenient. The chemical yield can be calculated from re-determination of the added carrier when it is a stable isotope. When the carrier is a radioactive one, chemical yield can be obtained directly from the sample gamma-ray measurement

3-2 Epithermal neutron activation analysis

In ENAA, a sample is irradiated in an epithermal neutron flux by covering it with cadmium foil or putting it in a borated capsule. Some reactors provide epithermal irradiated facilities by having the irradiation position suitable surrounded by such materials. Q_o is defined as the resonance-to-thermal cross section ratio. ENAA is mainly used to determine a high Q_o nuclide(s) when a low Q_o nuclide(s) is the interference. When irradiated in an epithermal neutron flux, a high Q_o nuclide like $^{114}Cd(n,\gamma)^{115}Cd$ (Q_o = 39.6) will be more activated than a low Q_o nuclide like $^{23}Na(n,\gamma)^{24}Na$ (Q_o = 0.59) if compared to the activation in 'normal' NAA. Consequently, a lower detection limit for Cd determination can be expected.

3-3 Prompt gamma-ray neutron activation analysis

In PGNAA, the prompt γ-rays emitted during the nuclear reaction are measured. It is a non-destructive and multi-elemental method [22]. PGNAA may provide elemental contents and depth profiling for elements H, B, C, N, P, S, Cd, Pd and some rare earth elements, especially Sm and Gd. Most of these elements either cannot, or cannot easily, be determined with normal NAA, so PGNAA is a complementary method. To carry out PGNAA, a neutron beam guide and a γ-ray detector assembly are needed.

3-4 Cyclic neutron activation analysis

This is most frequently used in short half-life NAA. In this method, a sample is repeatedly activated, and the γ-ray spectra after each irradiation are summed. The repetition can continue till the accumulated activity from long lived nuclides is too high. Cyclic NAA is used to improve the counting statistics of the peak-area of short-lived nuclides. To avoid the accumulation of the longer-lived nuclide activity, this cyclic activation can be performed using a series of fresh samples: pseudo-cyclic NAA [22].

In each case of the NAA forms the following calculations are needed:

The neutron flux stability allows the use of the following equation in which the mass m, of a particular element is calculated from the net peak area A,

$$m = A.\left\{K\, e^{-\lambda t_d}\left(1-e^{-\lambda t_i}\right)\left(1-e^{-\lambda t_C}\right)\right\}^{-1} \tag{1}$$

where: $K = Z\,\theta\,N_A\,\sigma\,\varphi M^{-1}/\lambda$

Z = detector efficiency

θ = abundance of the activated nuclide

N_A = Avogadro's number = 6.023 x 10^{23}

σ = isotopic activation cross section

φ = neutron flux

M = atomic weight of the irradiated element

t_b, t_d and t_c are the times of irradiation, decay and counting respectively.

The values of K are determined by the use of suitable standards.

3-5 Photopeak area calculation

In principle each peak within a spectrum is described by three terms, its area, its position (centroid), and its shape (Gaussian-shape). In order to obtain accurate results it is necessary to use a uniform method for calculating peak areas, in the mean time, the net peak area should be assessed for significance using a critical limit. Both parameters will be discussed as follows.

A peak-background correction would be necessary and the uncertainty on the peak area should also be adjusted to take into account uncertainty of correction. The use of partial peak area to obtain optimum precision improve the accuracy when the same peak fraction is used for the comparator of the same element [3]

Kuleff and Kostadinov [4,5] proposed a method for the peak area calculation using only the interference-free half of the overlapping gamma-peaks such as ^{82}Br – ^{76}As, ^{76}As- ^{122}Sb, and 65Zn – 46Sc. This method proved to be very suitable for determination of uranium in phosphate ore samples [6] by the 106.1 keV peak of ^{239}Np. An approaching method proved satisfactory for resolving overlaps [7]

$$A_i = \frac{a_i\, s_i}{\sum_{j=1}^{K} a_j\, s_j} A_{ST} \qquad (2)$$

where:

A_i the count rate of the i'th peak,

A_{ST} the total count rate of the multiplet determined by summing and baseline subtraction,

K the number of overlapping peaks

a_i the net peak height,

s_i the peak width

Peak heights are computed from least squares fit. The error of the i'th count rate is given by

$$\Delta A_i = \pm \sqrt{\frac{(\Delta a_i)^2}{a_i^2} + \frac{\sum_{j=1}^{K} (\Delta a_i)^2}{\left(\sum_{j=1}^{K} a_j\right)^2} + \frac{(\Delta A_{ST})^2}{A_{ST}^2} A_i^2} \qquad (3)$$

The first two terms represent the systematic (bias) errors, the third one contains the statistical (random) error. Peak height errors Δa are generated in the least square fit. If the radioactivities attributed to the identified isotopes are calculated not individually but in a common least squares procedure (called interference correction), the estimated peak area errors must be applied as weight factors in the least squares solution.

After the peak area has been measured it is important to establish its statistical significance. The basic definitions developed by Currie and others helped to bring a consistent statistical approach to the determination of limits for qualitative detection and quantitative determination with a considerable degree of confidence. Many others [10,11] have elaborated on Currie's definitive work, and today his concepts are generally regarded as the standard approach. He developed an associated concept, critical level, L_c, which is used to assess the statistical validity of a calculated net count. He also gave a symbol, Ld, to the detection limit (minimum detectable activity) with some specified degree of confidence.

In the following the two concepts in relation to the measurement uncertainties are defined as

$$L_C = K_\alpha\, \sigma_o, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$L_d = L_C + K_\beta\, \sigma_d = K_\alpha\, \sigma_o + K_\beta\, \sigma_d \ldots\ldots\ldots\ldots\ldots (5)$$

where

K_α, K_β abscissas of the standardized normal distribution for the corresponding probabilities

σ_o standard deviation of the net measurement result when the sample contain zero radioactivity

σ_d standard deviation when the sample contains radioactivity at the level of the t_d

If α and β are both taken to be 0.05 then $K_\alpha = K_\beta = 1.645$ (for 95% confidence level) and if $\alpha_o = \alpha_d$, then $L_d = K_\alpha^2 + 2K_\alpha\, \sigma_o$. Putting Kα = 1.645 and $\sigma_o^2 = 2\sigma_b$ (where σb is the standard deviation of gross background counts) gives

$$L_d\,(in\,counts) = 2.71 + 4.65\,\sigma_b$$

Although for the peak area case, the expression for σ_o is more complicated, the mathematics is identical except that the final expression [12] becomes

$$L_d = 2.71 + 3.29\,\sigma_b\,\sqrt{1 + n/2m}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

$$L_C = 1.645\,\sigma_b\,\sqrt{1 + n/2m}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where n is number of channel in the peak width and 2m is total number of channels used for the background estimation.

Equations (5) and (8) have typically been referenced to in most procedure manuals and regulatory guidance documents.

4- Detection Limits

The detection limit represents the ability of a given NAA procedure to determine the minimum amounts of an element reliably. The detection limit depends on the irradiation, the decay and the counting conditions. It also depends on the interference situation including such things as the ambient background, the Compton continuum from higher energy γ-rays, as well as any γ-ray spectrum interferences from such factors as the blank from pre-irradiation treatment and from packing materials. The detection limit is often calculated using Currie's formula

However, practically, the INAA detection limits depends on:

4-1 The amount of material to be irradiated and to be counted.

This is often set by availability, sample encapsulation aspects and safety limits both related to irradiation (irradiation containers) and counting (e.g. with Ge well-type detectors), and possibly because of neutron self-shielding and gamma-ray self-absorption effects. For these reasons practically the sample mass is often limited.

4-2 The neutron fluxes.

These are clearly set by the available irradiation facilities [23].

4-3 The duration of the irradiation time.

This is set by practical aspects, such as the limitations in total irradiation dose of the plastic containers because of radiation damage. The maximum irradiation time for polyethylene capsules is usually limited to several hours, for instance 5 hours at 5 x 10^{17} m^{-2} s^{-1}.

4-4 The total induced radioactivity that can be measured

It is set by the state-of-the-art of counting and signal processing equipment, with additional radiation dose and shielding considerations. As an example, the maximum activity at the moment of counting may have to be limited.

4-5 The duration of the counting time.

A very long counting time set limits to the number of samples processed simultaneously in case the radioactivity decays considerable during this counting time. Moreover, it reduces sample throughout.

4-6 The total turn-around time.

Although sometimes better detection limits may be obtained at long decay times, the demands regarding the turn-around time often imply that a compromise has to be found between the longest permissible decay time and customer satisfaction.

4-7 The detector size.

Counting geometry and background shielding. The detector's characteristics may be set in advance by availability but several options exist.

5- Interferences

In (1999), we published a paper [21], which include the interference problems due to nuclear reactions. The analysis of the reactions and the resulting isotope concentrations, with the associated errors, leads to a method for considering the interfering isotopes.

A Prior information on the presence or absence of interference in the processing of gamma-spectrum is essential for obtaining accurate results. In some cases the isotope could be the result of an (n,γ), (n,p) or (n,α) reaction. For example the radioactive isotope ^{28}Al is produced by all of the following reactions:

[^{27}Al(n,γ)^{28}Al, ^{28}Si(n,p)^{28}Si and ^{31}P(n,α)^{28}Al]

Both ^{28}Si and ^{31}P are relatively abundant elements and therefore the activity of the ^{28}Al isotope depends on the concentration of ^{27}Al, ^{28}Si and ^{31}P.

Since the (n,γ) reactions are usually induced by thermal energy neutrons, and the (n,p) and (n,α) reactions by fast neutrons, irradiation position with different thermal to fast ratios is expected to provide different activities. Such irradiation are described by Morison et.al. who studied the upper and lower limits of ^{27}Al(n,γ)^{28}Al, ^{26}Mg(n,γ)^{27} reactions which depends mainly on the cross section of each reaction. The error in the concentration values could be estimated using the data analysis mentioned in (refs.14, 15).

6- Reactor Neutron Flux

Reactor neutron activation analysis for most elements is based on their (n,γ) reactions with thermal and epithermal neutrons. The spectrum of the thermal neutrons equals approximately a Maxwellian distribution of the neutron velocity according to the temperature of the irradiation position, whereas the epithermal neutron spectrum is approximately described by a 1/E shape. But usually it deviates and may (according Hafele), better be described by $1/E^{1+\alpha}$. The epithermal neutron spectrum shape factors, α, are different in different reactors and depend also on the irradiation positions. The reactor neutron flux can be described using parameters ϕ_{th}, ϕ_{ep}, ϕ (isotopic abundance) and α, which influences the value of the cross section ratio, Q(α).

Errors of the analytical results depend on those of the flux parameters that in turn depend on those of the activities measured with the flux monitor isotopes. So these parameters have to be measured in the irradiation facility in which the sample shall be activated, before the activation analysis can be carried out by activation methods.

We follow the considerations of Verheijke [17], and use the symbols and notations of Erdtmann [2,18]. So the activity of a monitor nuclide after irradiation in a reactor is obtained from the relation

$$m_x = \frac{A_x\, K_{i,x}}{B_x} . \frac{1}{\phi_x + \phi_{ep} + Q_{0,x}(\alpha)},$$

where

m_x – the amount of an element x present in the sample,

A_x – the activity (absolute decay rate) of the element x,

B_x – build-up factor,

K_i – activation factor

Considering De-Corte Ko standardization method [19]

$$Q_{0,x}(\alpha) = \frac{Q_0 - u}{\bar{E}^{\alpha}_{\gamma,x}} + \frac{u}{(2\alpha+1)E^{\alpha}_{Cd}} \qquad (10)$$

with $u = \sqrt{E_0/E_{Cd}} = 0.429$ and E_{Cd} = 0.55 eV, where Qo is the cross section ratio with α = 0, i.e., for an ideal 1/E spectrum and E_γ is the effective resonance energy. Then

$$Q_{0,x}(\alpha) = \frac{Q_0 - 0.429}{\bar{E}^{\alpha}_{\gamma,x}} + \frac{0.429}{(2\alpha+1)\,0.55^{\alpha}} \tag{11}$$

The error of m_x is

$$\begin{aligned} \Delta m_x(\%) &= 100[1 - \frac{m_{x,error}}{m_{x,true}}] \\ &= [1 - \frac{\phi_{th}(\alpha_{true}) + \iota_{ep}(\beta_{true})Q_{0,x}(\alpha_{true})}{\phi_{th}(\alpha_{error}) + \phi_{ep}(\alpha_{error})Q_{0,x}(\alpha_{error})}] \end{aligned} \tag{12}$$

This equation has been applied to all (n,γ) reactions used in neutron activation analysis. The influence of the errors of the activities of the elements depend, besides the flux and the parameters of the irradiation facilities, on the nuclear parameters of the elements, i,e, on their cross section ratios, $Q_o(\alpha_o)$, and their effective resonance energies, E_γ, more details on this method will be found in ref. (19).

CONCLUSION

It is shown, the great importance of the limitations due to photopeak estimation, nuclear reactions interference, detection limits and neutron flux calculation, also the simples formulas used for error calculations in each case. This improve the high accuracy needed for the applications on the neutron activation analysis techniques.

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