

k_0 -INAA method accuracy using Zn as comparator

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Resumen

Se presenta una evaluación de la exactitud del análisis por activación neutrónica según el método del k sub cero, usando zinc laminado como comparador. Se ha encontrado una buena precisión intra e inter analistas, así como un buen grado de veracidad para la mayoría de elementos. Se describe también la determinación de parámetros experimentales importantes, tales como la determinación de la eficiencia de conteo, coincidencias verdaderas γ - γ , preparación del comparador y aseguramiento / control de la calidad.

Abstract

An evaluation of the accuracy in the application of the k_0 -INAA method using Zn foil as comparator is presented. It was found a good agreement in the precision within analysts and between them, as well as in the assessment of trueness for most elements. The determination of important experimental parameters like gamma peak counting efficiency, γ - γ true coincidence, comparator preparation and quality assurance/quality control, are also described and discussed.

1. Introduction

It is well known that the number of users of the k_0 NAA method has been increased in the last years [1-3]. Moreover, many laboratories have contributed to upgrade the method in several ways; e. g. improving or recalculating the values of nuclear constants involved in the method [4-5], developing alternative methods for the determination of f and α parameters, true coincidence and neutron self shielding corrections, development of software, etc. [6-10]. All these efforts have contributed to the accuracy of the method and to enhance its potentiality and world wide acceptance. In addition to the mentioned parameters, the selection and preparation of comparators play an important role, since it is necessary to accurately know the mass and nuclear constants. Some systematic errors could occur in the preparation of the comparator due to the use of impure reagents, non stoichiometry and evaporation losses, imprecision of micropipette, use of non calibrated balances, reagents contamination and instability of standard solutions used. Some of these factors were avoided in many laboratories through the use of the set ^{198}Au - ^{95}Zr - ^{97}Zr - ^{177}Lu [11], where gold is used as flux monitor and comparator.

Other laboratories have already used Zn as comparator in the form of a solution [12]. In our laboratory, since the k_0 method

implementation, a sodium standard solution has been used as comparator, due to its better performance respect to the non-ideal behaviour of the epithermal flux [13].

However considering the time stability, availability, prevention of systematic errors described above, low cost, the possibility of doing measurements at any time with good counting statistics and lower production of waste material, it was decided to explore the use of Zn foil as comparator. Despite the long half-life of ^{65}Zn , all mentioned advantages compensate the practical impossibility to use it again. The performance obtained for the Zn foil as k_0 -based INAA comparator, is reported in the present paper.

2. Experimental

2.1. Sample preparation

To evaluate the fitness for purpose in terms of accuracy (precision + trueness) two analysts participated in the analysis. Each one did six replicate determinations on three reference materials, as indicated in table 1.

200 mg of sample were placed in clean polyethylene vials of 6.6 mm of height and 9.6 mm of diameter, producing a well defined cylindrical disk of a 9.0 mm diameter and 2 mm height. The vial is sealed using heat to be

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conditioned for the irradiation capsule.

2.2. Comparator preparation

Zn foils were prepared from zinc granular 99.9 % purity (Merck pro analysi). The zinc granular was cleaned with diluted nitric acid and pressed using a hydraulic press system to get a first foil of 0.2 mm of thickness and

0.10 g mass approximately. After that and using a small punch drill the foils were cut in small discs of 0.030 g, pressed again and cut once more to obtain foils of 0.10 mm of thickness and 0.010 g of mass. The final discs were 6 mm diameter.

All mass determination were performed using a calibrated balance ($d = 0.01$ mg).

Table 1. Reference material values, in $\mu\text{g/g}$. *, in %.

Element	SRM 679 Brick clay [14] $\pm U$	Ohio red clay [15] $\pm s$	SRM 1633b Coal fly ash [16] $\pm U$
As		14.6 ± 0.6	135.0 ± 1.5
Ba	432.2 ± 9.8	651 ± 51	720 ± 13
Ce	(105)	108 ± 13	192.7 ± 2.1
Co	(26)	22.0 ± 1.3	49.6 ± 0.5
Cr	109.7 ± 4.9	88.0 ± 7.0	196.0 ± 2.2
Cs	(9.6)	10.7 ± 0.6	10.74 ± 0.14
Eu	(1.9)	1.70 ± 0.15	4.12 ± 0.05
Fe*	9.05 ± 0.21	5.24 ± 0.20	7.71 ± 0.09
Hf	(4.6)	7.28 ± 0.39	6.82 ± 0.09
K*	2.433 ± 0.047	3.45 ± 0.49	1.949 ± 0.022
La	NR	52 ± 2	93.7 ± 1.0
Lu	NR	0.62 ± 0.08	1.170 ± 0.027
Na*	0.1304 ± 0.0038	0.142 ± 0.006	0.2011 ± 0.0022
Nd	NR	46 ± 3	85 ± 5
Rb	(190)	176 ± 7	145 ± 4
Sb	NR	1.38 ± 0.19	5.10 ± 0.08
Sc	(22.5)	18.24 ± 0.31	41.22 ± 0.44
Sm	NR	8.9 ± 0.8	19.17 ± 0.22
Ta	NR	1.54 ± 0.36	1.80 ± 0.04
Tb	NR	1.3 ± 0.4	2.57 ± 0.06
Th	(14)	15 ± 1	25.64 ± 0.28
U	NR	3.01 ± 0.28	8.61 ± 0.22
Yb	NR	4.28 ± 0.10	7.62 ± 0.17

NR: not reported.

Results in brackets are non certified values.

2.3. Irradiation, measurement and data processing

Comparators were inserted between samples and piled into a polyethylene capsule, (figure 1) to be irradiated using a pneumatic transfer system of the 10 MW nuclear research reactor at IPEN, as described elsewhere [17]. The irradiation was done during 30 min at 10 MW power of reactor with a nominal thermal neutron flux of $1.9 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and an epithermal neutron flux of $3.2 \cdot 10^{11} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$.

After a decay time of 5 days, a first counting of samples was performed by 5000 – 6000 seconds using the HPGe detector (Canberra GC 1518; relative efficiency = 15%, FWHM

= 1.8 keV at 1332.5 keV ^{60}Co). The comparators were measured by 1000 seconds after 6 decay days. Both measurements were done at a distance of 58.2 mm from the detector cover. Under these conditions the nuclides ^{76}As , ^{42}K , ^{140}La , ^{24}Na , ^{239}Np , ^{122}Sb , ^{153}Sm and ^{175}Yb were determined. A second counting was performed after a decay time of 15 – 17 days by 10000 seconds using the HPGe detector (Canberra GC 7019; relative efficiency = 70%, FWHM = 1.9 keV at 1332.5 keV ^{60}Co). The comparators were counted after a decay time of 10 days by 600 seconds. In this case the distance from the detector was 12.5 mm. The nuclides determined were ^{131}Ba , ^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{152}Eu , ^{59}Fe , ^{181}Hf , ^{177}Lu , ^{147}Nd , ^{86}Rb , ^{46}Sc , ^{85}Sr , ^{182}Ta , ^{160}Tb , and ^{233}Pa .

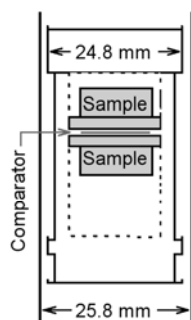


Figure 1. Arrangement of sample and comparator in the polyethylene irradiation capsule.

Gamma spectrum analysis was done using the Canberra software Genie 2000 (v 2.1) and for concentration calculations, an in house developed software application was used, based in a excel spreadsheet and macros written in the Visual Basic for Applications (VBA) tool from Microsoft [18].

2.4. Parameters and corrections factors

The k_0 factors used for concentration calculation as well as the other relevant nuclear data (Q_0 , \hat{E}_r , $T_{1/2}$, isotopic abundance, etc) were adopted from [19].

The flux variation inside the capsule was studied and corrected in the final result. This variation is not more than 1.3%.

The photopeak efficiency curves were determined for both detectors, at two geometries for each detector: one of them is "reference" (G_{Ref}) and the other one is "routine" (G_{Rout}). The G_{Ref} for the used detectors are 210.7 mm for GC1518 and 200 mm for GC7019 detector, distance from the detector end cap. These geometries were evaluated using standard sources with known activities in a range of 88 – 1810 keV: ^{54}Mn , ^{109}Cd , ^{65}Zn , ^{22}Na , ^{60}Co and ^{57}Co , from Canberra Industries and ^{152}Eu , ^{133}Ba , ^{137}Cs from the International Atomic Energy Agency (IAEA). A secondary source of ^{56}Mn was added to the set, which was prepared depositing an aliquot of 0.1000 mL 1000 $\mu g/mL$ standard solution in a polyethylene vial and irradiated. Another set of secondary gamma sources was prepared of ^{198}Au , ^{165}Dy , ^{203}Hg , ^{51}Cr , ^{142}Pr , ^{86}Rb , ^{52}V and ^{28}Al , to obtain the efficiency at G_{Rout} at 58.2 mm and 12.5 mm. Then the efficiency was determined by $\epsilon_\gamma = A_m \cdot \lambda \cdot \exp(\lambda T_d) \cdot T_r/T_v / (1 - \exp(-\lambda T_r)) \cdot P_\gamma \cdot A_0 \cdot COI$, where; A_m = peak area, T_v = live time, T_r = real time T_d = decay time, A_0 = Measure count rate, P_γ = gamma

emission probability and $COI = \gamma\text{-}\gamma$ true coincidence value. The pairs $\ln(\text{energy}) / \ln(\text{efficiency})$ are adjusted to a grade 4° polynomial regression [20].

The f and α parameters, as well as the neutron temperature of the irradiation facility were determined using well characterized standard solutions of Au-Co-Mo Lu [21].

The $\gamma\text{-}\gamma$ true coincidence corrections were also experimentally determined, according to a procedure implemented in the laboratory [22]. It considers the relative difference of counting activities of the photopeak of interest for the used measurement geometry of 12.5 mm respect to the defined reference measurement geometry of 200 mm. An adequate volume of standard solutions was deposited into an irradiation vial containing powder cellulose. After irradiation, these were measured using the GC7019 HPGe detector, long enough to get counting statistics better than 0.5 % for both mentioned geometries.

Neutron self-shielding effects were determined calculating the effective neutron self shielding factor given by the weighted mean of thermal and epithermal factors described by C. Chilian and G. Kennedy and using the spreadsheet developed by the cited authors [8].

Spectral interference corrections were performed in the evaluation of ^{153}Sm , ^{122}Sb , ^{141}Ce and ^{51}Cr . The correction factors were determined performing measurements of an irradiated standard of the interfering nuclide ^{239}Np , ^{76}As , ^{175}Yb and ^{147}Nd , respectively. The interfering photopeak area is evaluated and also the area of the photopeak usually used in the determination of the element. A ratio is obtained from these areas. The photopeak area interfered divided by the correction factor, is subtracted from the photopeak area to be determined.

The correction factors for uranium fission interference were calculated for the three materials [23]. Table 2.

Table 2. Estimation of contributions from uranium fission interference (%).

Element	SRM 679	Ohio red clay	SRM 1633b
Ce	0.74	0.77	1.34
Nd	1.52	1.28	2.45
La	0.04	0.04	0.07

3. Results y Discussion

Figure 2 shows the efficiency curves obtained for GC1518 detector, covering an energy range of 88 keV to 1810 keV. These exhibit a good agreement between the standard and the prepared gamma sources as well as between the fitting curve and the experimental points. However, a relative dispersion of about 2% was observed for the region between 88 keV and 150 keV, that could affect the determination of ^{153}Sm using the gamma peak at 103 keV.

The reason to use two detectors to perform measurements was that GC7019 detector is associated to a sample changer system that allows measurement of 20 samples in an automated way. This fixed system requires location of samples at a distance of 12.5 mm and for medium half-life nuclides the death time exceed the criteria of $\leq 5\%$, adopted in the laboratory. In the other hand, the minimal distance to sample in the GC1518 detector is 58.2 mm, because of the design of its associated sample changer, which restricted the possibility to obtain good counting statistics with low uncertainties for ^{152}Eu , ^{181}Hf , ^{177}Lu , ^{147}Nd , ^{86}Rb , ^{182}Ta , ^{160}Tb and ^{233}Pa .

The values of f , α and neutron temperature parameters at the irradiation position were (60.0 ± 1.2) , (0.0330 ± 0.0037) and $(40.0 \pm 2.0) \text{ C}$ ($k = 1$), respectively.

The impurities contained in the metallic Zn comparator: Sn (0.001%), Fe (0.002%), Cd (0.0005%), Pb (0.005% and As (0.00001%), do not affect the counting statistics and neither cause any interference.

In view that the granular zinc used to prepare the comparator, has a maximum cadmium concentration of 0.0005%, its contribution to the neutron self shielding was taken into account. The effective neutron self shielding factor obtained was 0.998 which includes the effect of the zinc foil thickness and the presence of cadmium impurities. Thus, it can be concluded that the thickness and mass of the Zn comparator used in the analysis are suitable for the purpose.

It should be noted that the neglecting of the COI factors for the GC 7019 detector could incorporate an error in the measurement from 15% for ^{76}As to 0.3% for ^{233}Pa and from

2.9% for ^{46}Sc to 0.9% for ^{76}As and ^{233}Pa for the GC 1518 detector.

The correction factors from uranium fission interference were not significant for the analyzed reference materials. However in coal fly ash material the uranium content of 8.79 $\mu\text{g/g}$ and 200 mg of sample mass analyzed, cause a significant interference for Nd. The correction factor for La is dependent upon cooling time as the ^{140}Ba ($T_{1/2} = 12.75 \text{ d}$) decays to ^{140}La ($T_{1/2} = 1.68 \text{ d}$) so this interference is avoided [24].

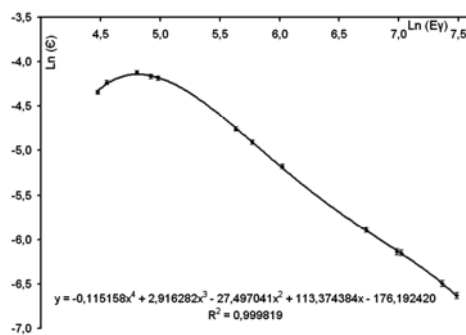


Figure 2. Routine efficiency curve for GC1580 detector at 58 mm distance. Only sources without γ - γ coincidences were used.

All experimental results are expressed in dry weight basis and accompanied with uncertainty to a confidence level of 68% for Ohio red clay ($k=1$) and 95% for brick clay and coal fly ash ($k=2$), to be consistent with the data reported in the correspondent certificates.

The first step in evaluation of the results was the determination of outlier data, applying Grubs test according to ISO 5725-2 [25]. Sb and Rb were identified as outliers in Ohio red clay and brick clay material, respectively, analysed by analyst 1. No outliers were identified in coal fly ash material.

Figures 3 - 5 summarize the results obtained in the analysis. The observed dispersion within analysts (repeatability) was evaluated using the relative standard deviation (RSD %). Most of the elements show a RSD of less than 5%. Exceptions were As (6.8%), Nd (8.2%), Sb (18%) by analyst 1; Nd (9.5%), U (13.9%), Sb (9.1%) and Tb (6.2%) by analyst 2 in Ohio red clay. In brick clay; As (8.6%), U (20%), Sb (8.3%), Tb (7.2%) by analyst 1 and U (12.7%), Sb (7.4%), Tb (8%) and Yb (7.3%) by analyst 2. For coal fly ash material

results obtained for both analysts agreed within a 5% range.

The precision between analysts (reproducibility) was evaluated using the Fisher test ($F_{5,5} = 5.05$; $P = 0.05$) that compares variances and the student-t test (10 degrees of freedom, $P = 0.05$, $|t| = 2.23$) that compares means. It was found that K and U in Ohio red clay, As and Rb in brick clay and Nd in coal fly ash do not fulfill the evaluation criteria for F-test and in the t-test, only Tb in Ohio red clay showed that the observed value is higher than the critical value.

The results of Ohio red clay used as reference values were those published in reference [14] and for coal fly ash material in reference [16]. They were chosen because most of the results of the elements analyzed are expressed with uncertainty values, thus the u-score value could be obtained.

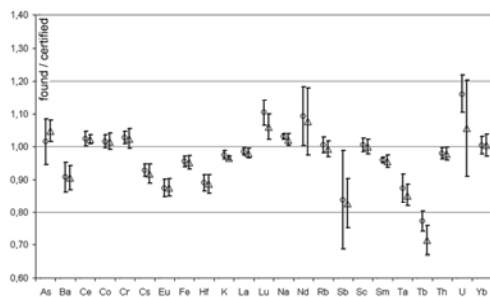


Figure 3. Precision evaluation in Ohio red clay reference material: repeatability and reproducibility. Analyst 1 \circ and Analyst 2 Δ .

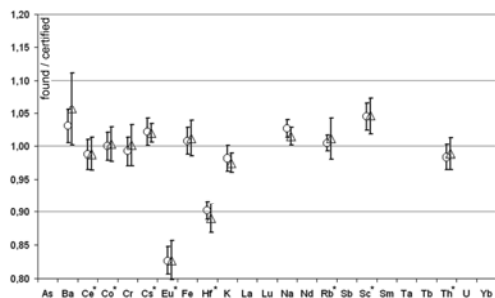


Figure 4. Precision evaluation in SRM 679 BRICK CLAY reference material: repeatability and reproducibility. Analyst 1 \circ and Analyst 2 Δ (* Information values).

Figure 6 show the u-score values obtained for Ohio red clay and coal fly ash materials, which take into account uncertainty values and allow assessing the performance of the laboratory. In this case, all the elements fulfilled the trueness criteria in the three reference materials. The u-score of brick clay

material was not considered because only five elements have uncertainties associated to the results in its certificate.

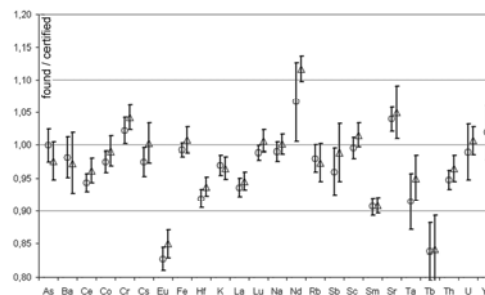


Figure 5. Precision evaluation in SRM 1633b COAL FLY ASH reference material: repeatability and reproducibility. Analyst 1 \circ and Analyst 2 Δ .

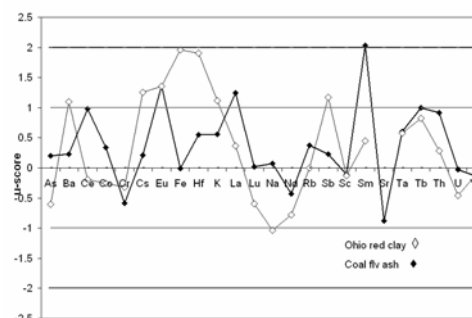


Figure 6. u-score values for Ohio red clay and SRM 1633b coal fly ash reference materials.

Further studies related with correction parameters will be explored to identify the possible errors revealed in the precision evaluation.

Some of the elements analysed e.g. the rare earth elements, Cr, Th, Sc, alkali and earth alkali metals (K, Rb, Cs and Ba), transition metals (Fe, Co, etc.) play an important role in archaeological studies [26]. It is important to ensure the accuracy of the results for the mentioned elements to allow the archaeologist to characterize and discriminate the production centres, involving short distances or intraregional exchange [27].

4. Quality assurance / quality control

The use of Zn as comparator has implied a change in the analysis procedure of clay samples in our laboratory. Following the quality system implemented and as a candidate laboratory for accreditation, care has been taken in all the stages of the analysis: e.g. in samples and comparator preparation; use of calibrated balances, clean material, good housekeeping and clear

labelling. The thickness of each prepared comparator was tested every time to ensure its reproducibility. In the irradiation and measurement stages; the arrangement of comparator and sample in the capsule has been improved, in order to ensure that the error due to neutron flux differences is kept within 0.5%. Measurement equipment has a person responsible for timely fitness and maintenance. The energy resolution is checked systematically and control charts are kept. Personal in charge of measurements have been trained to improve their performance. All these actions have been adequately recorded and documented.

Finally, the evidence found regarding the accuracy of results should guarantee that the whole analytical process is under statistical control.

5. Conclusions

The k_0 -INAA method using Zn foil as comparator was satisfactorily applied for the analysed materials and has been proven that fit for purpose. About 70% of the results fulfil the requirements for precision and 100% for trueness.

The use of zinc foil as comparator is a good choice when relatively short irradiation times (i.e 30 minutes at $1.9 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) are used. Under those conditions, it would be necessary to deposit 10 mg from a zinc standard solution, which is less practical.

6. References

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