Original Article

Applied Science

Determination of Trace-Elements in Fingernails of Artisanal Gold Miners Using K0- and Relative Standardization Methods of INAA

Christian K NUVIADENU [1], Benjamin JB NYARKO [2], Godsway K BANINI [2], Amos FORSON [1], Seth K DEBRAH [1], Juanita E AYIVOR [2]

ABSTRACT [ENGLISH/ANGLAIS]

The K_0-method was tested against the routinely used relative-method, two standardizations of Instrumental Neutron Activation Analysis (INAA). Both methods have been used to quantify Gold (Au), Arsenic (As) and Antimony (Sb) contents of fingernails of artisanal *(Galamsey)* miners from Ghana. Geometric mean concentrations of 0.44µg/g, 2.24µg/g and 0.47µg/g were obtained for Au, As, and Sb respectively using the relative-method; whiles 0.48µg/g, 2.26µg/g and 0.42µg/g were also obtained for the same trace-elements using the K_0-method. In the light of the closeness of the two sets of results, it was recommended that the K_0-method be adopted for trace-elements analysis.

Keywords: Instrumental neutron activation analysis, K_0-method, relative-method, trace-elements

RÉSUMÉ [FRANÇAIS/FRENCH]

Le K_0-méthode a été testée contre la routine utilisée par rapport-méthode, deuxnormalisations de l'analyse par activation neutronique instrumentale (INAA). Les deux méthodes ont été utilisées pour quantifier l'or (Au), arsenic (As) et antimoine (Sb) le contenu des ongles de la pêche artisanale (Galamsey) mineurs en provenance du Ghana.Moyenne géométrique des concentrations de 0.44µg / g, 2.24µg / g et 0.47µg / g ont été obtenus pour Au, As, Sb et utilisant respectivement le parent-méthode; Whiles 0.48µg / g,2.26µg / g et 0.42µg / g ont été également été obtenus pour les mêmes oligo-éléments en utilisant le K0-méthode. A la lumière de la proximité des deux séries de résultats, il a été recommandé que la méthode de K0-être adoptée pour l'analyse des oligo-éléments.

Mots-clés: Analyse par activation neutronique, K0-méthode relative par rapport à la méthode, oligo-éléments

Affiliations:

[1] Department School of Nuclear and Allied Sciences (SNAS), University of Ghana, Box AE1 Kwabenya, Accra, GHANA

[2] National Nuclear Research Centre (NNRI), Ghana Atomic Energy Commission (GAEC), Box LG 80 Legon-Accra, GHANA

Address for Correspondence/ Adresse pour la Correspondance: eys@gmail.com

Accepted/Accepté: March, 2011

Citation: Nuviadenu CH, Nyarko BJB, Banini GK, Forson A, Debrah SK, Ayivor JE. Determination of Trace-Elements in Fingernails of Artisanal Gold Miners Using K- and Relative Standardization Methods of INAA. World Journal of Engineering and Pure and Applied Sciences 2011;1(2):77-80.

INTRODUCTION

An important feature of the Instrumental Neutron Activation Analysis (INAA) technique is its methods of standardization. A widely used standard method for determining concentration of elements in an unknown sample is the relative standardization where a standard and a sample of unknown elements (with unknown concentrations) are co-irradiated and measured separately on the same detector, in the same geometry, for the same time [1]. The two peak areas obtained are proportional to the amounts of element in the standard and sample. This method is very accurate with easy error propagation. Its disadvantage is that multi-element analysis is only possible with multi-element standards. It is also quite sensitive to unrecognized interferences [2]. The k_0 standardization is a more accurate method due to its increased applicability to routine work and multi-element analyses with just one single comparator standard needed. However, it requires a lot of initial work with irradiation facility characterization (by thermal-to-epithermal ratio f, and deviation from a perfect epithermal spectrum α) and detector efficiency calibration (ε) before the first sample can be analyzed. This drawback makes it less attractive and it is usually not used for trace-elements determination. The relative and the k_0 methods have been tested by applying them to fingernails carefully collected from local small scale miners *(Galamsey)* from arseno-pyrites gold mines in

Ghana for the purposes of determining their trace-element (TE) levels. Trace-elements have been measured in various biological specimens where they are found to be useful biomarkers for exposure to toxic elements. These include study of finger and toe nails [3], hair analysis [4], urine analysis [5], and study of blood [6]. This work however focuses on the validity of the results obtained using both standardization methods.

MATERIALS AND METHODS

Data collection

Fingernail clippings from all ten (10) fingers were collected from each of the 28 identified artisanal miners using a nail cutter. The fingernail specimens were carefully placed in pre-labeled transparent sealable plastic bags. The samples were kept under freezing conditions, and brought to the laboratory. *Galamsey* mining camps from different parts of the Tarkwa and its surroundings in the Wassa-West District of Ghana were almost equally taken into account in the study. The fingernails were washed in de-ionized water to remove dirt, air-dried for 24 hours, weighed into polypropylene pouches and heat sealed. Finally gold, arsenic, and antimony single-element standard reference material solutions were prepared for analysis under the same conditions as the samples.

Sample Irradiation and Analysis

The prepared samples were concealed into irradiation capsules and irradiated through the pneumatic Rabbit System, operating at a pressure of 0.6 MPa within the inner channel of a 30 kW Miniature Neutron Source Reactor (MNSR) for 1 hr at a neutron flux of $5x10^{11}$ neutrons/cm^2/s. The irradiated samples were left to decay for 24 hours in order to minimize exposure risk and also to eliminate all interferences from short-lived radionuclide since the elements of interest in this study are medium-lived. Each sample was counted for 10 min on a liquid nitrogen cooled High Purity Germanium detector connected to a computer system operating at a negative bias voltage of 3kV running Maestro© software. From the energy spectra obtained, the peak areas (P_A) corresponding to the concentrations of the trace-elements of interest were acquired and recorded for use in the calculations.

Finally Gold, Arsenic and Antimony single-element standard solutions were prepared, irradiated and counted under the same conditions as the samples. The peak areas of interest were measured and recorded for use in concentration calculations by using:

$$\rho_{sam} = \frac{\left[\left(P_A/t_c\right)CD\right]_{sam}(\rho W)_{std}}{\left[\left(P_A/t_c\right)CD\right]_{std} W_{sam}} \quad (1)$$

for the relative standardization, where $(P_A/t_c)_{std}$ and $(P_A/t_c)_{sam}$ are the counting rates for standard and sample respectively, ρ_{std} and ρ_{sam} are the concentrations of the element of interest in the standard and sample respectively, C_{std} and C_{sam} are the counting factors for standard and sample D_{std} and D_{sam} are decay factors for the standard and sample respectively; and

$$\rho = \frac{\left(\frac{P_A/t_c}{SCDW}\right)_a}{\left(\frac{P_A/t_c}{SCDW}\right)_{Au}} \cdot \frac{1}{k_0} \cdot \frac{[f + Q_0(\alpha)_{Au}]}{[f + Q_0(\alpha)_a]} \cdot \frac{\varepsilon_p(E_{Au})}{\varepsilon_p(E_a)} \quad (2)$$

for the Hogdahl formalism of the k_0-standardization where k_0 is the k_0-factor and α-dependent $Q_0(\alpha)$ is expressed as:

$$Q_0(\alpha) = \frac{Q_0 - 0.429}{E_r^{\alpha}} + \frac{0.429}{(2\alpha+1)E_{cd}^{\alpha}} \quad (3)$$

Irradiation Facility and Detector Calibration

The irradiation facility was already calibrated by previous works, where the thermal-to-epithermal flux ratio f =18.8 and the non-ideal epithermal neutron flux distribution parameter (*alpha*) α = -0.104 were obtained [7]. These values were readily available for use in concentration calculations. The detector efficiency was also expressed as:

$$\begin{cases} \varepsilon = 19634 \times 10^{-8} \times E^{(1.0484)} & \text{for } 0 \le E \le 121.78KeV \\ \varepsilon = 1.0708 \times E^{-(0.79795)} & \text{for } E \ge 121.78KeV \end{cases} \quad (4)$$

With the k_0-method, the k_0-constants and corresponding parameters for arsenic, antimony and gold isotopes were extracted from the basic nuclear data for activation analysis following [8]. These, together with all other parameters (i.e. f, $Q(\alpha)$, ε, K_0, S, D, C, t_c, and P_A) were substituted into equation (2) to compute the trace-elements concentration of interest.

RESULTS AND DISCUSSION

The computed concentrations of trace-elements of interest are shown in Figures 1-3. Gold (Au) concentration levels in the fingernails ranged from 0.06 to

3.33µg/g and 0.08µg/g to 3.39µg/g with the relative and k_0 methods respectively. The corresponding geometric means (geomean) were 0.44 µg/g and 0.48 µg/g, whiles the respective arithmetic means (mean) were 0.78 µg/g and 0.80 µg/g.

For Arsenic (As), the concentrations ranged from 0.24 to 25.88 µg/g and 0.24 to 26.01 µg/g with the relative and k_0 methods respectively. Corresponding geometric means were obtained as 2.24 µg/g and 2.26 µg/g with the respective arithmetic means being 4.43 µg/g and 4.45 µg/g. The analysis of Antimony (Sb) levels in the fingernails was as follows: concentrations ranged from 0.08 to 1.68 µg/g and 0.06 to 1.72 µg/g respectively. A geometric mean of 0.47µg/g and an arithmetic mean of 0.62 µg/g were obtained with the relative standardization; whiles with the k_0-method, 0.42 µg/g and 0.59 µg/g were recorded as geometric and arithmetic means respectively. Comparative statistical data of Au, As, and Sb by both relative and k_0-standardization methods are summarized in Tables 1-3. Concentrations obtained with the k_0-method were in general slightly higher than those with the relative method for Gold (Au-198) and Arsenic (As-76); whiles the opposite was recorded for Antimony (Sb-123). These differences however, are insignificant. It has been observed in this work that the k_0-method results closely matched those obtained with the well-established relative methods.

Table 1: This table shows the summary of Gold (Au) analysis results

Method	Geomean (µg/g)	Mean (µg/g)	S.D.	N
relative	0.44	0.78	0.76	28
K_0	0.48	0.80	0.77	28

Table 2: This table shows the summary of Arsenic (As) analysis results

Method	Geomean (µg/g)	Mean (µg/g)	S.D.	N
relative	2.24	4.43	6.15	28
K_0	2.26	4.44	6.16	28

Table 3: This table shows the summary of Antimony (Sb) analysis results

Method	Geomean (µg/g)	Mean (µg/g)	S.D.	N
relative	0.47	0.62	0.43	28
K_0	0.42	0.59	0.44	28

Geo-mean: geometric mean, Mean: arithmetic mean, S.D: standard deviation, N: population size

Figure 1: This figure shows Gold (Au) concentrations (µg/g)

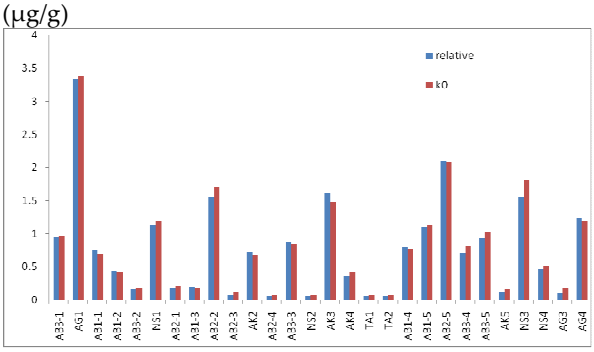


Figure 2: This figure shows Arsenic (As) concentrations (µg/g)

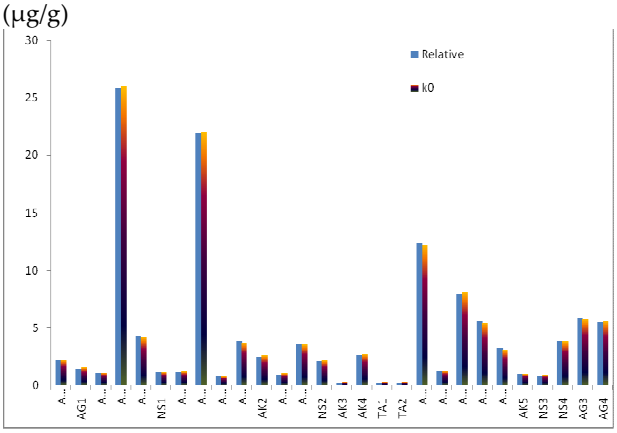
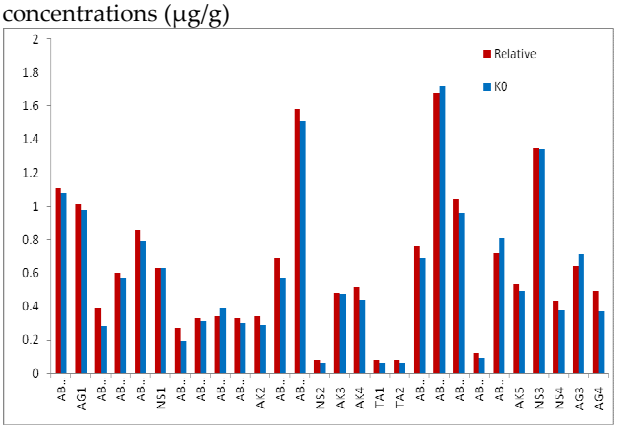


Figure 3: This figure shows Antimony (Sb) concentrations (µg/g)



CONCLUSION

Using the K_0 and the relative standardization methods of Instrumental Neutron Activation Analysis (INAA), concentrations of Gold(Au), Arsenic(As) and s(Sb) in fingernails of artisanal *(galamsey)* miners from Ghana were quantified and compared. Good agreement between the two methods was obtained. Owing to the fact that k_0-method is carried out without the need to prepare standards, it may be prudent to adopt this method for elemental analysis, especially when studying samples with very small mass like fingernails.

REFERENCES

[1] Simonits A, De Corte F, Hoste J. Journal of Radioanalytical Chemistry. 1975;24:31.

[2] Blaauw M. Introduction to K_0-INAA. Nuclear Science and Engineering. 2005;124:431.

[3] Lin TH, Huang YL, Wang MY. Arsenic species in drinking water, hair, fingernails, and urine of patients with blackfoot disease. Journal of Toxicological and Environmental Health A. 1998;53:85-93.

[4] Ewers U, Krause C, Schulz C, Wilhelm M. Reference values and human biological monitoring values for environmental toxins. International Archaeological Occupational and Environmental Health 1999;72: 255–260.

[5] Karagas MR, Morris JS, Weis JE, Spate V, Baskett C, Greenberg ER. Toenail samples as indicator of drinking water arsenic exposure. Cancer Epidemiology Biomarkers Prevalence 1996;5:849-852.

[6] Garland M, Morris JS, Colditz GA, Stampfer MJ, Spate VL, Baskett CK, Rosner B, Speizer FE, Willet WC, Hunter DJ. Toenail trace element levels and breast cancer: a prospective study. American Journal of Epidemiology. 1996;144:653–660.

[7] Osae EK, Nyarko BJB, Serfor-Armah Y. Standardization of GHARR-1 Gamma Spectroscopy System for Instrumental Neutron Activation Analysis. Technical Report: GAEC; 1996. p. 14.

[8] De Corte F, Simonits A. Recommended nuclear data for use in the k_0 standardization of neutron activation analysis. Atomic Data and Nuclear Data Tables 2003;85:47-67.

ACKNOWLEDGEMENT / SOURCE OF SUPPORT

We will like to thank staff of Ghana Research Reactor-1 (GHARR-1) Centre for irradiating the samples used in this work. We will also like to acknowledge training and material support from the International Atomic Energy Agency (IAEA), Vienna and the International Centre for Theoretical Physics (ICTP), Trieste.

CONFLICT OF INTEREST

No conflict of interest was declared by authors