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Determination of gold in Romanian auriferous alluvial sands and rocks by 14 MeV neutron activation analysis

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Abstract

In this work a complex study of the nuclear and spectral interferences which appear in gold determination by 14 MeV neutron activation analysis of Romanian auriferous alluvial sands and rocks has been accomplished. The contribution of the nuclear interfering elements – Hg and Pt – to the concentration of gold in the samples is minimum in the case of the nuclear reactions $^{197}\text{Au}(n, 2n)^{196}\text{Au}$, $^{197}\text{Au}(n, 2n)^{196\text{m}}\text{Au}$ and $^{197}\text{Au}(n, n')^{197\text{m}}\text{Au}$. As regards the spectral interferences, these are minimum in the case of using the reactions $^{197}\text{Au}(n, n')^{197\text{m}}\text{Au}$ and $^{197}\text{Au}(n, 2n)^{196}\text{Au}$ and are due to Rb, Ti and V for the short irradiation and to Se for the long irradiation. We propose two methods of gold determination in auriferous alluvial sands and rocks in the range 20–2500 ppm – the minimum value of 20 ppm being at the level of an economic extraction – in the optima conditions established by us so that the systematic errors of analysis due to the gold accompanying elements should be considerably diminished: a method using short irradiation (25 s) and NaI(Tl) spectrometry for the measuring of the induced gamma radioactivity in the samples and a method using long irradiation (3000 s) and Ge(Li) spectrometry. The data presented in this paper can be adapted by other analysts to the rapid determination of gold in a variety of alluvial sands and rocks.

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Keywords: Gold determination; Analysis of auriferous alluvial sands and rocks; Neutron activation analysis; 14 MeV neutrons; Interference effects

1. Introduction

Many world laboratories have developed analytical methods of determining the chemical and isotopic composition of rocks, minerals, ores and

other natural materials. They include classical chemical techniques and atomic or nuclear spectrometric techniques such as atomic absorption spectroscopy (AAS) and emission spectroscopy (ES), inductively coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS), X-ray fluorescence (XRF), particle-induced X-ray emission (PIXE), neutron activation analysis (NAA) using thermal and 14 MeV

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neutrons, photon activation analysis (PAA), etc. Gold has been determined in geological materials by AAS [1]; ICP-MS [2]; ES [3]; thermal NAA [4,5]; PAA [6]; AMS [7]; PIXE [8], etc.

Gold is most commonly found in Romanian alluvial sands in the form of auriferous mineralisations related by the Neogene eruptive and hydrothermal deposits which contain complexes of andesite, rhyolite and dacite rocks [9]. Alluvial deposits are formed by the mechanical accumulation of grains, derived from the pre-existing rocks alteration, in streams and lakes. Gold is usually found with varying amounts of silver, copper, iron and lead as selenides; in gold and/or silver tellurides; with heavy minerals such as magnetite, cassiterite, zircon, monazite, garnets, tourmaline, ilmenite, staurolite or sphalerite; as microscopic and submicroscopic particles included in sulphide minerals, particularly pyrite, chalcopyrite, arsenopyrite, pyrrhotite and galena; in metamorphic polymetallic deposits or within veins related by crystalline schists, associated with quartz, chalcedony, carbonates (calcite, rhodochrosite), sulphates (baryte), etc. [10–12].

In the detection and exploitation of gold from auriferous alluviums and rocks it is very important the choosing of a rapid and sufficiently sensitive method for the determination of gold traces so that its results should be influenced as little as possible by the presence of the other elements in the samples. The minimum concentration of gold required for an economic extraction is 20 ppm. The accuracy which can be obtained with an analytical spectrometric technique largely depends on the extent of the spectral interferences and matrix effects and on how well these can be controlled or corrected for. Instrumental NAA using thermal neutrons provided by reactors is one of the preferred methods in geochemistry because it provides accurate results without any chemical manipulation or pretreatment, it is non-destructive, multielemental, reproducible and very sensitive, having the lowest matrix effects [13,14]. For gold determination, the disadvantages of the technique include waiting seven days for the decay of sodium prior to the analysis. Occasionally very high levels of certain elements like As or Sb (>500 ppm), rare earths (>5000 ppm), uranium (>500

ppm) may cause an elevation in background under the 412 keV photopeak of ^{198}Au from the reaction $^{197}\text{Au}(n, \gamma)^{198}\text{Au}$ and hence an increase in detection limits [14]. The final disadvantage is that only certain design of nuclear reactors can be used for commercial NAA and these reactors have limited availability in the world.

14 MeV neutron activation analysis does not compete in sensitivity with NAA using thermal neutrons but is quite widely useful in circumstances where nuclear reactors are unavailable, having the advantage of rapidity of analyses and that particle accelerators are safer and they may be set up in any industrial or research laboratory. The reactions of the fast neutrons with the target nuclei are of type (n, p), (n, 2n), (n, α), (n, n') and, with a smaller probability, (n, γ). The determination of gold in auriferous alluvial sands and rocks by 14 MeV NAA followed by gamma spectrometry is influenced by the systematic errors due to the great number of chemical elements with different concentrations existing in the samples. The systematic errors are due to the nuclear interferences, instrumental interferences and the interaction phenomena between the fast neutrons or gamma-rays and the sample material. The variation of the sample composition can determine variations of the interest peak area if the choosing of the photopeak is not appropriate or the correction of the area with the contribution of the interfering element is not done. In [15] gold was determined in galena and pyrite ores using the 188 keV gamma-ray from the reaction $^{197}\text{Au}(n, 2n)^{196\text{m}}\text{Au}$, without taking into consideration the interferences.

The experimental sensitivity obtained in 14 MeV NAA – defined as the quantity of a substance, in μg , which would give a photopeak with 100 counts – calculated for pure gold target irradiated at a neutron flux of $5 \times 10^9 \text{ neutrons s}^{-1} \text{ cm}^{-2}$ was 250 counts per 100 μg [16]. This sensitivity was determined using the 279 keV gamma-ray from the reaction $^{197}\text{Au}(n, n')^{197\text{m}}\text{Au}$, without taking into account the interferences which appeared when samples with variable chemical composition were analyzed. In [17] a sensitivity of 200 counts per 1.2 μg of gold was reported for a neutron flux of $3 \times 10^{10} \text{ neutrons s}^{-1} \text{ cm}^{-2}$, using the same nuclear reaction.

Taking into account the variation of the gold concentration (20–2500 ppm) and the great number of elements (Si, Al, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zr, Zn, Ga, Se, Rb, Sr, V, Nb, Mo, Ag, Hg, Pb, Sb, Sm, Te, Pt, Na, As, U, Th) which accompany gold in the Romanian auriferous samples [18], whose concentrations were determined by different laboratories by non-activation methods (Table 1), in this paper we have accomplished a complex study of nuclear and instrumental interferences in the gamma-ray spectra, besides a study concerning the optimal choice of activation, cooling and measuring times in order to assure a maximum peak-to-background ratio for gold, with the aid of an original computer program. In earlier work [19] the optimum counting time was calculated for different half lives for signal and background, using simple gamma-ray spectrometry, assuming that the radioactive matrix is composed of one element. In real situations, many radionuclides from matrix elements, not just one, will contribute to the underlying background of the peak of the nuclide of interest after activation. In the case of cyclic activation, for example, for calculating these contributions and the optimum irradiation and counting time (or number of cycles), many computer programs have been developed [20,21]. In the program described

in [20] by entering the total experiment time, transfer time, the mass and relevant nuclear data for matrix elements contributing to the background activity, and the half-life of the nuclide of interest, the background due to individual matrix elements and the total background can be calculated. In the program described in [21], in addition to the contribution to the background of the photopeaks of nuclides produced by matrix elements, the Compton continuum, single and double escape peaks, and bremsstrahlung were also considered.

2. Theory

2.1. Nuclear interferences

In this work we present a calculus relation of the nuclear interferences which appear in gold determination from alluvial sands and auriferous rocks using the nuclear reactions of 14 MeV neutrons on gold: $^{197}\text{Au}(n, 2n)^{196}\text{Au}$, $^{197}\text{Au}(n, 2n)^{196m}\text{Au}$, $^{197}\text{Au}(n, p)^{197m}\text{Pt}$, $^{197}\text{Au}(n, p)^{197}\text{Pt}$, $^{197}\text{Au}(n, \gamma)^{198}\text{Au}$, $^{197}\text{Au}(n, n')^{197m}\text{Au}$ (Table 2). The nuclear interferences are present when an indicator radionuclide is produced by more than one nuclear reaction. Considering that the radionuclide resulted from an isotope j of the element of interest e emits γ -rays with the energy E , the photopeak area in the γ spectrum, $S(E)$, is given by

$$S(E) = g\varepsilon p\Phi M \frac{B_{sc}}{\lambda} c_e (1 - e^{-\lambda t_a}) e^{-\lambda t_c} (1 - e^{-\lambda t_m}), \quad (1)$$

$$B_{sc} = \frac{F_s N_A a_{ej} \sigma_{ej}}{A_e}, \quad (2)$$

where $g = \frac{\Omega}{4\pi} f_p f_a$ is the geometrical factor (Ω – the solid angle subtended by the detector; f_p , f_a – the correction factors for the attenuation of neutrons in the sample and air); ε – the absolute detector efficiency for the given energy E ; p – the peak-to-total ratio; Φ – the neutron flux; M – the sample weight; c_e – the concentration of the element of interest; λ – the decay constant; t_a , t_c , t_m – the activation, cooling and measuring times; N_A – the Avogadro's number; F_s – the absolute intensity of the considered gamma-ray; a_{ej} – the fractional

Table 1
Maximum concentrations of the elements determined in the Romanian auriferous samples by non-activation methods

| Element | Concentration (ppm) | Element | Concentration (ppm) |
|---------|---------------------|---------|---------------------|
| Si | 440 000 | V | 270 |
| Fe | 260 000 | Zr | 7900 |
| K | 90 000 | Nb | 65 |
| Ca | 58 000 | Mo | 50 |
| Al | 35 000 | Ag | 170 |
| Mn | 5300 | Au | 2500 |
| S | 16 000 | Hg | 800 |
| Ti | 23 000 | Pb | 1600 |
| Cu | 1300 | Th | 140 |
| Zn | 3400 | U | 50 |
| Ni | 50 | Te | 5000 |
| Cr | 630 | Na | 10 000 |
| Ga | 30 | Pt | 50 |
| Se | 120 | As | 100 |
| Rb | 340 | Sb | 100 |
| Sr | 240 | Sn | 50 |

Table 2

Nuclear data for pertinent reactions in gold determination with 14 MeV NAA

| Nuclear reaction | $T_{1/2}$ | E (keV) | B_{sc} | Interfering reaction | B_{si} |
|---|----------------|--|--|--|---|
| $^{197}\text{Au}(n, 2n)^{196}\text{Au}$ | 6.18 days | 426.1 355.7 333.0 | 5.45×10^{-4} 7.15×10^{-3} 1.88×10^{-3} | $^{196}\text{Hg}(n, p)^{196}\text{Au}$ | 2.09×10^{-9} 2.75×10^{-8} 7.25×10^{-9} |
| $^{197}\text{Au}(n, 2n)^{196m}\text{Au}$ | 9.7 h (8.25 s) | 188.23 168.33 147.77 137.65 285.45 316.15 | 1.61×10^{-4} 3.29×10^{-5} 1.82×10^{-4} 5.64×10^{-6} 1.87×10^{-5} 1.69×10^{-5} | $^{196}\text{Hg}(n, p)^{196m}\text{Au}$ | 1.13×10^{-8} 2.32×10^{-9} 1.28×10^{-8} 3.98×10^{-10} 1.39×10^{-9} 1.26×10^{-9} |
| $^{197}\text{Au}(n, \gamma)^{198}\text{Au}$ | 2.69 days | 675.8 411.8 | 2.35×10^{-7} 2.23×10^{-5} | $^{198}\text{Hg}(n, p)^{198}\text{Au}$ | 1.82×10^{-8} 1.72×10^{-6} |
| $^{197}\text{Au}(n, p)^{197m}\text{Pt}$ | 94.4 m (7.8 s) | 346.5 278.9 346.5 278.9 346.5 278.9 | 3.26×10^{-6} 5.52×10^{-7} 3.26×10^{-6} 5.52×10^{-7} 3.26×10^{-6} 5.52×10^{-7} | $^{196}\text{Pt}(n, \gamma)^{197m}\text{Pt}$ $^{196}\text{Pt}(n, \gamma)^{197m}\text{Pt}$ $^{198}\text{Pt}(n, 2n)^{197m}\text{Pt}$ $^{198}\text{Pt}(n, 2n)^{197m}\text{Pt}$ $^{200}\text{Hg}(n, \alpha)^{197m}\text{Pt}$ $^{200}\text{Hg}(n, \alpha)^{197m}\text{Pt}$ | 2.19×10^{-6} 3.71×10^{-7} 2.23×10^{-7} 3.78×10^{-8} 1.38×10^{-7} 2.33×10^{-8} |
| $^{197}\text{Au}(n, p)^{197}\text{Pt}$ | 18.3 h | 269.2 191.5 269.2 191.5 | 1.22×10^{-8} 1.74×10^{-7} 1.22×10^{-8} 1.74×10^{-7} | $^{198}\text{Pt}(n, 2n)^{197}\text{Pt}$ $^{198}\text{Pt}(n, 2n)^{197}\text{Pt}$ $^{200}\text{Hg}(n, \alpha)^{197}\text{Pt}$ $^{200}\text{Hg}(n, \alpha)^{197}\text{Pt}$ | 3.4×10^{-8} 2.38×10^{-9} 8.5×10^{-8} 5.97×10^{-9} |
| $^{197}\text{Au}(n, n')^{197m}\text{Au}$ | 7.8 s | 278.9 201.8 130.2 | 1.31×10^{-3} 2.06×10^{-5} 5.81×10^{-5} | Groups of reactions (R2) and (R3) | – |

isotopic abundance of the target nuclide j ; σ_{ej} – the activation cross-section of the isotope j ; A_e – the atomic weight of the element e .

In the case that one or more isotopes of other elements existing in the sample give the same radionuclide as the element of interest, the relation (1) becomes

$$S(E) = gep\Phi Mf(t)(B_{sc}c_e + B_{si}c_i), \quad (3)$$

where the factor

$$f(t) = \frac{(1 - e^{-\lambda t_a})e^{-\lambda t_c}(1 - e^{-\lambda t_m})}{\lambda}$$

depends on the experimental times and

$$B_{si} = \frac{F_s N_A a_{ik} \sigma_{ik}}{A_i}$$

is the factor (2) for the isotope k of the interfering element i , having the concentration c_i (in ppm).

Relation (3) can be written as

$$S(E) = gep\Phi Mf(t)B_{sc}(c_e + \Delta c_e), \quad (4)$$

where the expression

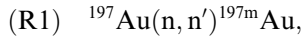
$$\Delta c_e = \frac{c_i B_{si}}{B_{sc}} \quad (5)$$

characterizes the contribution, in ppm Au, of an isotope of the interfering element to the concentration of the element of interest.

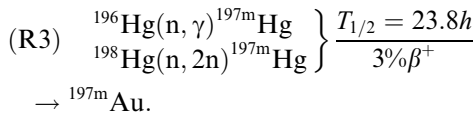
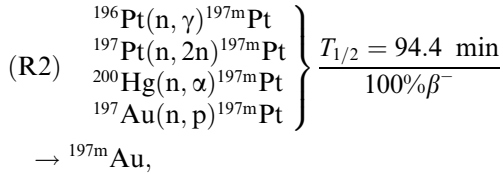
For the evaluation of the nuclear interferences with the aid of the relation (5) we have considered for the interfering elements a concentration two times bigger than the maximum value determined in different auriferous samples of rocks and alluvial sands (Table 1), respectively 1600 ppm for Hg and 100 ppm for Pt. For the gold concentration the minimum value of 20 ppm, considered for an economic extraction, has been considered. Taking into account the relations deduced in the present work and the existing data [22] for the above-mentioned nuclear reactions of Au with 14 MeV neutrons (Table 2), we could evaluate the maxi-

imum absolute errors due to the presence of Pt and Hg in the auriferous samples (Table 3).

In the case of the determination of gold from the direct reaction



the following interferences could appear:



The contribution of the decay of ${}^{197m}\text{Pt}$ (94.4 min) and ${}^{197m}\text{Hg}$ (23.8 h) is totally neglectable when compared to the directly formed ${}^{197m}\text{Au}$ (7.8 s) when short irradiation- and cooling times are applied.

From the calculated values of the relative errors $\Delta c_e/c_e$ given in Table 3, where $c_e = 20$ ppm, it results that from the point of view of the interfering nuclear reactions, ${}^{197}\text{Au}(n, 2n){}^{196}\text{Au}$ and ${}^{197}\text{Au}(n, 2n){}^{196m}\text{Au}$ nuclear reactions can be used for gold determination, with minimum errors, as

well as the reaction ${}^{197}\text{Au}(n, n'){}^{197m}\text{Au}$, where the contribution of the interfering elements is negligible.

2.2. Spectral interferences

Further, using these three nuclear reactions, we have studied the spectral interferences due to the other elements present in the auriferous samples, with the aid of the original field spectrum of gamma-rays emitted by the irradiated sample in the absence of any ambient interaction, considered as a radiation field produced in vacuum by a point source, which maintains the energetic and angular characteristics of the disintegrations taking place in the source. This theoretical spectrum depends on the resulted radionuclides from the nuclear reactions between the fast neutrons and the existing elements in the sample, their concentrations and the experimental times (activation, cooling and measuring). The gamma-ray spectrum of the natural radioisotopes of U, Th and K has not been considered here.

The original field spectrum has been calculated with the relation

$$S(E_{ij}) = \frac{\Omega}{4\pi} f_p f_a \varepsilon_{ij} p_{ij} M \Phi c_i \times \frac{B_{sij}(1 - e^{-\lambda_{ij}t_a}) e^{-\lambda_{ij}t_c} (1 - e^{-\lambda_{ij}t_m})}{\lambda_{ij}}, \quad (6)$$

Table 3
Maximum errors introduced by the reaction interferences

| Nuclear reaction | Interfering element | Maximum absolute error, Δc_e (ppm) | Maximum relative error $\Delta c_e/c_e$ (%) | Remarks |
|---|---------------------|--|---|---|
| ${}^{197}\text{Au}(n, 2n){}^{196}\text{Au}$ | Hg | 6.1×10^{-3} | 3×10^{-2} | Reaction can be used for gold determination |
| ${}^{197}\text{Au}(n, 2n){}^{196m}\text{Au}$ | Hg | 0.11 | 0.55 | Reaction can be used for gold determination |
| ${}^{197}\text{Au}(n, \gamma){}^{198}\text{Au}$ | Hg | 124 | >100 | Reaction cannot be used |
| ${}^{197}\text{Au}(n, p){}^{197m}\text{Pt}$ | Pt | 173 | >100 | Reaction cannot be used |
| | Hg | 68 | >100 | |
| ${}^{197}\text{Au}(n, p){}^{197}\text{Pt}$ | Pt | 2.8×10^2 | >100 | Reaction cannot be used |
| | Hg | 11.2×10^3 | >100 | |
| ${}^{197}\text{Au}(n, n'){}^{197m}\text{Au}$ | Pt | Negligible | Negligible | Reaction can be used for gold determination |
| | Hg | | | |

where $S(E_{ij})$ is the photopeak area in the γ spectrum of the isotope j of the interfering element i which emits γ -rays with the energy E_{ij} ; ε_{ij} – the absolute detector efficiency for the given energy E_{ij} ; c_i – the concentration of the interfering element; λ_{ij} , p_{ij} , B_{sij} are the decay constant, the peak-to-total ratio and the factor (2) of the isotope j of the interfering element i . We have considered the correction factors f_p and f_a equal to 1, the sample mass $M = 8$ g, the neutron flux $\Phi = 10^9$ neutrons $s^{-1} cm^{-2}$ (an easy to reach value with the available generator) and the interfering elements concentrations two times bigger than the maximum values found in the samples by different authors (Table 1). In this way a covering limit favoring the interference has been assured. For gold the maximum concentration of 2500 ppm has been considered. The values of the 90×50 mm² NaI(Tl) detector efficiency and the relative solid angle of the used experimental unit were considered. The relation (6) has been applied to all the peaks of the potentially existing elements in the auriferous samples and all the nuclear reactions that could appear. The calculated values for every peak for a short irradiation ($t_a = 80$ s, $t_c = 3$ s, $t_m = 100$ s) are presented in Fig. 1 and for a long irradiation ($t_a = 3000$ s, $t_c = 1000$ s, $t_m = 3000$ s) in Fig. 2.

For each of the gold peaks we have delimited the gold peak zone considering the energetic resolution for the NaI(Tl) detector $\pm 20\%$ in the energy range 0–500 keV, $\pm 15\%$ in the energy range 500–1000 keV and $\pm 10\%$ for energies bigger than 1000 keV. In the case of using the Ge(Li) detector these energetic resolutions have been diminished with an order of magnitude. The true resolutions of these detectors are smaller. As can be seen from Table 4, the gold peaks are situated in the energy range 118–427 keV and in this domain is possible to find the Compton edges of the photopeaks which appear in the range 484–1214 keV and the double escape peaks of the photopeaks situated in the domain 1140–1449 keV.

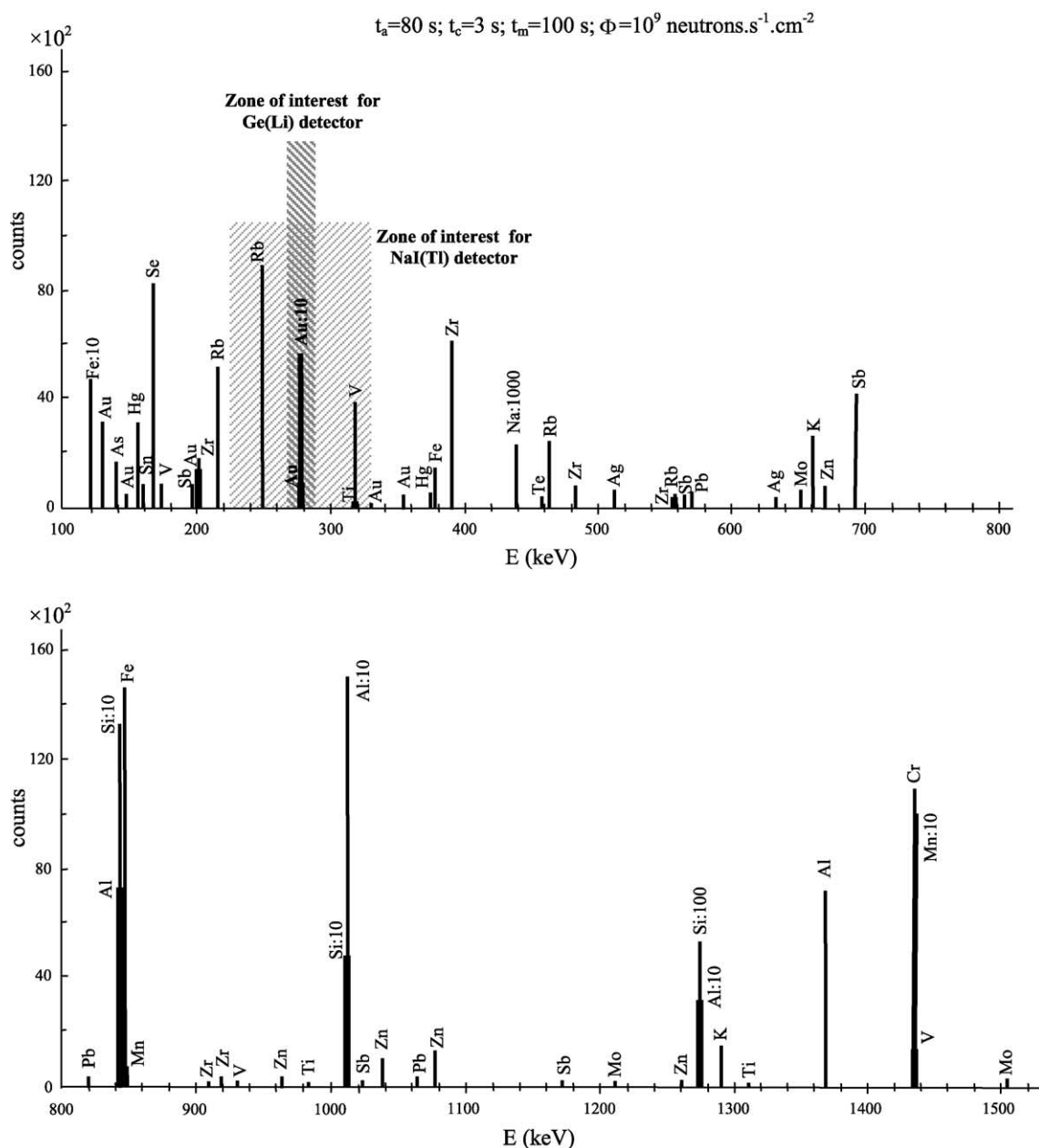
In order to characterize the influence of the different elements upon the results of gold concentration determined in the sample we have calculated for each element an equivalent gold concentration, EGC, defined as the ratio of the

calculated number of counts (6) due to $c_i = 1$ ppm of the interfering element, falling in the chosen gold peak zone – corresponding to each detector energetic resolution – and the calculated number of counts (6) corresponding to $c_e = 1$ ppm of gold:

$$EGC = \frac{\varepsilon_{ij} p_{ij} B_{sij} (1 - e^{-\lambda_{ij} t_a}) e^{-\lambda_{ij} t_c} (1 - e^{-\lambda_{ij} t_m})}{\varepsilon p B_s (1 - e^{-\lambda t_a}) e^{-\lambda t_c} (1 - e^{-\lambda t_m})} \frac{\lambda}{\lambda_{ij}}, \quad (7)$$

where ε is the absolute detector efficiency for the gold peak energy E ; λ , p , B_s are the decay constant, the peak-to-total ratio and the factor (2) for the considered isotope of gold.

The obtained results, in ppm Au, for a short irradiation ($t_a = 80$ s, $t_c = 3$ s, $t_m = 100$ s) and for a long irradiation ($t_a = 3000$ s, $t_c = 1000$ s, $t_m = 3000$ s) are given in Table 4. The spectral interferences were calculated for the total absorption peaks, Compton edges and double escape peaks, under the assumption that all calculated counts falling in the gold peak zone contributed to the equivalent gold concentration. The values for the total absorption peaks are maximum equivalent values, taking into account the fact that concentrations two times bigger than the maximum determined ones (Table 1) have been considered. The calculus of the interferences due to the presence of the Compton edge in the interest zone was done only for the 90×50 mm² NaI(Tl) detector, admitting that: (i) the entire Compton distribution was found in the interest peak zone, which is an approximation favoring the interference; (ii) this distribution represented 0.5% from the area of the photopeak corresponding to the radiation energy which had the Compton edge in the interest zone; (iii) 90×50 mm² NaI(Tl) detectors had for the interest domain 90% total absorption of the radiation, from which 50% was by Compton effect. For the calculus of the interferences due to the double escape peak, a pair absorption probability of 15% and an escape probability of 1% were considered for the same type of crystal. These approximations favored the interference, the real contribution of the Compton edge and double escape peak being much smaller. The 511 keV annihilation peaks have not been represented.

Fig. 1. The original γ field for the short irradiation.

The results given in Table 4 or in the original spectra presented in Figs. 1 and 2 could be adapted by other analysts to their studies as function of the concentrations of interfering elements existing in the auriferous sample matrix determined by them

in any type of sand or rock, using both NaI(Tl) and Ge(Li) spectrometry.

From the data presented in Table 4 for the three nuclear reactions $n + \text{Au}$ we have chosen two reactions for gold determination: $^{197}\text{Au}(n, n')^{197m}\text{Au}$

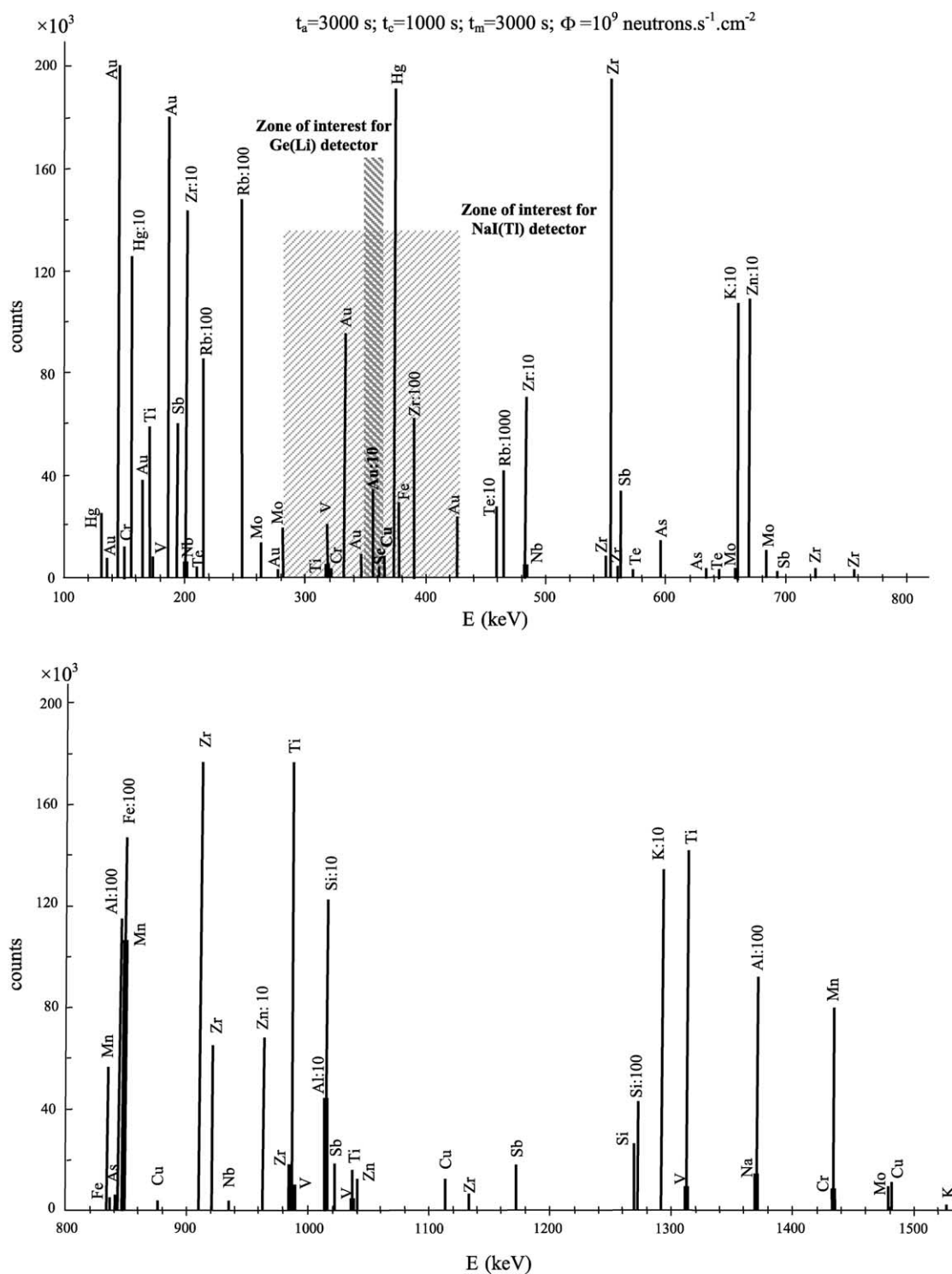
Fig. 2. The original γ field for the long irradiation.

Table 4
Spectral interference, expressed in equivalent gold concentrations

| Nuclear reaction | Experimental times | Detector | Peak energy E (keV) [Peak zone (keV)] | Equivalent gold concentration (ppm)/1 ppm of interfering element | | | | | |
|---|--|----------|--|--|----------------------|--------------|----------------------|--------------------|----------------------|
| | | | | Photopeak | | Compton edge | | Double-escape peak | |
| $^{197}\text{Au}(\text{n}, \text{n}')^{197\text{m}}\text{Au}$ | $t_a = 80$ s $t_c = 3$ s $t_m = 100$ s | NaI(Tl) | 278.9 [223–335] | Rb | 0.56 | Si | 3.6×10^{-3} | Sb | 7.6×10^{-5} |
| | | | | V | 0.28 | Al | 2.3×10^{-3} | | |
| | | | | Ti | 0.002 | | | | |
| | | Ge(Li) | 278.9 [273–285] | – | | – | | – | |
| $^{197}\text{Au}(\text{n}, 2\text{n})^{196}\text{Au}$ | $t_a = 3000$ s $t_c = 1000$ s $t_m = 3000$ s | NaI(Tl) | 333 [266–400] | Mo | 0.9 | Zr | 3.4×10^{-2} | K | 2×10^{-5} |
| | | | | Ti | 2.8×10^{-4} | Zn | 0.26 | Ti | 8.5×10^{-6} |
| | | | | V | 0.78 | Ti | 1.2×10^{-2} | Al | 3.6×10^{-4} |
| | | | | Cr | 1.9×10^{-4} | V | 8.6×10^{-2} | | |
| | | | | Se | 0.04 | Si | 3.8×10^{-3} | | |
| | | | | Cu | 0.02 | Sb | 9×10^{-2} | | |
| | | | | Hg | 0.67 | Cu | 1.1×10^{-2} | | |
| | | | | Fe | 3.2×10^{-4} | | | | |
| | | | | Zr | 2.15 | | | | |
| | | Ge(Li) | 333 [326–340] | – | | – | | – | |
| | | NaI(Tl) | 355.7 [284–427] | Ti | 3.6×10^{-4} | Sb | 0.22 | Ti | 1.1×10^{-4} |
| | | | | V | 0.23 | Ti | 1.5×10^{-2} | Al | 4.6×10^{-4} |
| | | | | Cr | 9.1×10^{-3} | V | 0.1 | Mn | 2.5×10^{-5} |
| | | | | Se | 0.05 | Zn | 0.34 | | |
| | | | | Cu | 0.02 | Cu | 1.3×10^{-2} | | |
| | | | | Hg | 0.85 | Zr | 5.7×10^{-2} | | |
| | | | | Fe | 4.1×10^{-4} | Sb | 0.1 | | |
| | | | | Zr | 2.75 | Al | 0.19 | | |
| | | Ge(Li) | 355.7 [348–363] | Se | 0.05 | – | | – | |
| $^{197}\text{Au}(\text{n}, 2\text{n})^{96\text{m}}\text{Au}$ | $t_a = 3000$ s $t_c = 1000$ s $t_m = 3000$ s | NaI(Tl) | 147.77 [118–117] | Hg | 9.3 | Zr | 6.6×10^{-2} | Zn | 9×10^{-6} |
| | | | | Cr | 0.11 | Sb | 0.3 | Cu | 2×10^{-5} |
| | | | | Ti | 0.01 | As | 0.25 | Zr | 1.8×10^{-4} |
| | | | | V | 0.06 | | | Sb | 1.6×10^{-4} |
| | | Ge(Li) | 147.77 [144–151] | – | | – | | – | |
| | | NaI(Tl) | 188.23 [150–226] | Hg | 9.6 | K | 3.4×10^{-2} | | |
| | | | | V | 0.06 | Zn | 0.89 | | |
| | | | | Ti | 0.02 | Mo | 0.65 | | |
| | | | | Sb | 1.13 | Sb | 1.6×10^{-2} | – | |
| | | | | Nb | 0.42 | Zr | 1.3×10^{-3} | | |
| | | | | Zr | 1.02 | | | | |
| | | | | Te | 0.01 | | | | |
| | | | | Rb | 13.9 | | | | |
| | | Ge(Li) | 188.23 [184–192] | – | | – | | – | |

for the short irradiation and NaI(Tl) detector and $^{197}\text{Au}(\text{n}, 2\text{n})^{196}\text{Au}$ for the long irradiation and Ge (Li) detector. In Figs. 1 and 2 the interest zones in both cases of gamma spectrometry are shaded and they are identical to gold peak zones given in Table 4: 223–335 keV for NaI(Tl) spectrometry of 278.9 keV γ -ray of $^{197\text{m}}\text{Au}$ and 348–363 keV for NaI(Tl) spectrometry of 355.7 keV γ -ray of ^{196}Au . In the first case the spectral interferences are due to Rb (1 ppm Rb = 0.56 ppm Au), Ti (1 ppm Ti = 0.002 ppm Au) and V (1 ppm V = 0.28 ppm Au) and in the second case to Se (1 ppm Se = 0.05 ppm Au), besides a small nuclear interference due to Hg (1600 ppm Hg = 0.006 ppm Au), as can be seen from Table 3. The interfering γ -rays in the peak zone chosen by us are the following: 248 keV γ -ray of $^{84\text{m}}\text{Rb}$ ($T_{1/2} = 20.5$ m) from the reaction $^{85}\text{Rb}(\text{n}, 2\text{n})^{84\text{m}}\text{Rb}$; 319 keV γ -ray of ^{51}Ti ($T_{1/2} = 5.8$ m) from the reactions $^{50}\text{Ti}(\text{n}, \gamma)^{51}\text{Ti}$ and $^{51}\text{V}(\text{n}, \text{p})^{51}\text{Ti}$ and 361 keV γ -ray of ^{73}Se ($T_{1/2} = 7.2$ h) from the reaction $^{74}\text{Se}(\text{n}, 2\text{n})^{73}\text{Se}$.

Further, using an original computer program (available from the authors), we have established that the optima conditions for the short irradiation and NaI(Tl) spectrometry of 278.9 keV γ -ray of $^{197\text{m}}\text{Au}$, in order to assure a maximum peak-to-background ratio for gold, in the circumstances of a variable background, were $t_a = 25$ s, $t_c = 2$ s, $t_m = 15$ s. For the calculus of this ratio we have taken into consideration those radionuclides of the matrix which emitted a γ radiation with the energy greater than the energy E of the interest peak and did not give the escape peaks, the Compton edges, annihilation peaks and backscattering peaks in the domain of the interest peak.

For the long irradiation and Ge(Li) spectrometry we have chosen the experimental times $t_a = 3000$ s, $t_c = 1000$ s, $t_m = 3000$ s because the used device did not allow irradiations longer than 3000 s, taking into account the limited life of the tritiated target.

3. Experimental

The analyzed auriferous samples are: alluvial sands (Gilau and Somesul Mic); auriferous sands (Deva); concentrated sands (Cavaran and Rosia

Montana) and auriferous rock (Rosia Montana). Before the irradiations, a gamma-spectrometric analysis has been done in order to detect the natural radionuclides. The peaks of ^{226}Ra (295.2, 352, 609.2 and 1120.3 keV), ^{228}Th (238.6 and 583.1 keV) and ^{40}K (1460 keV) were identified in the auriferous samples, with the exception of the alluvial sand of Somesul Mic and concentrated sand of Rosia Montana, where only the peaks of ^{228}Th and ^{40}K were detected.

The samples weighing 5–7 g were activated in 5 ml polyethylene capsules. The irradiations were performed with a NTA-4B neutron generator (KFKI Budapest, Hungary) based on $^3\text{H}(\text{d}, \text{n})^4\text{He}$ reaction at ISPAT-SIDEX Iron and Steel Works of Galatz (Romania), which provided a neutron flux of 5×10^{10} neutrons $\text{s}^{-1} \text{cm}^{-2}$ for an ion beam current of 1.2 mA. The samples were simultaneously irradiated, transported and measured together with appropriate reference materials used to compensate the variation of the neutron beam: sodium carbonate for the short irradiation and 22 K gold for the long irradiation. The samples and references were uniformly irradiated using a dual sample – biaxial rotating assembly. The induced activities in the samples have been measured with a 90×50 mm² NaI(Tl) detector for the short-lived radionuclides and a Ge(Li) detector for the long-lived radionuclides, both detectors being coupled to PC-based multichannel analyzers having automated dead-time correction. The gamma-rays spectra were recorded and processed off-line with an original computer code. For the references, the photopeaks of 1630 keV of ^{20}F resulted from the reaction $^{23}\text{Na}(\text{n}, \alpha)^{20}\text{F}$ and 333 and 355.7 keV of ^{196}Au from the reaction $^{197}\text{Au}(\text{n}, 2\text{n})^{196}\text{Au}$ have been measured. The induced activities in the references have been measured with 90×50 mm² NaI(Tl) detectors coupled to single-channel analyzers for the energy ranges 1460–1790 and 115–400 keV, respectively. For the monitoring of the neutron flux, a liquid scintillation detector coupled with a single-channel analyzer in integrated assembly having the threshold at 5 MeV was used. In order to minimize the interference effects, the mass calibration curves were plotted using standards prepared with alluvial sand of Somesul Mic, to which known amounts of 22 K gold were added.

The purity of 22 K gold was checked by two steps activation: (1) $t_a = 120$ s, $t_{c1} = 3$ s and $t_{c2} = 90$ s, $t_m = 80$ s and (2) $t_a = 3000$ s, $t_c = 1000$ s, $t_m = 3000$ s. The elements Cu, Ag and traces of Al and Zr were identified but they did not introduce instrumental interferences in gold determination. Although the alluvial sand of Somesul Mic contains Rb, its presence does not modify the considerations from Section 2.2 because the unknown gold represents an equivalent gold for the measurements carried out with the NaI(Tl) detector.

4. Results and discussion

By preparing the standards as described in Section 3, the corrections for the attenuation of the neutron beam and gamma rays in the samples were avoided and a linear mass calibration curve was established with an error of 1.5% in the case of the short irradiation and 0.8% in the long irradiation. The concentrations of gold determined by us in Romanian auriferous samples by 14 MeV NAA, together with the gold concentrations obtained for these samples by other laboratories, using non-activation methods, are presented in Table 5. Taking into account the counting statistics errors, the overall uncertainty of gold determination is 10% in the short irradiation and 5% in the long one, the second being more precise because of the lesser influence of the interferences and lower background in the spectra.

For the optimum experimental times $t_a = 25$ s, $t_c = 2$ s, $t_m = 15$ s, the values of EGC for Rb, Ti

and V calculated with the aid of formula (7) are much smaller than those obtained for $t_a = 80$ s, $t_c = 3$ s, $t_m = 100$ s in the theoretical study of the original field spectrum being, respectively, 1 ppm Rb = 0.038 ppm Au; 1 ppm Ti = 1.5×10^{-5} ppm Au and 1 ppm V = 0.0021 ppm Au. We mention that these contributions have been calculated under disadvantageous conditions, in order to cover a large variety of sands and rocks.

From the experimental data given in Table 5, it can be seen that the method of 14 MeV NAA using short irradiation (25 s) and a NaI(Tl) detector for the measuring of the induced gamma radioactivity in the samples, the calculated gold concentrations are in general greater than in the analysis method using long irradiation (3000 s) and a Ge(Li) detector. This situation is explained by the existence of rubidium in the majority of the analyzed samples, which influences the result of analyses in the case of using the NaI(Tl) detector. A significant difference exists in the case of the concentrated sand of Rosia Montana, probably due to the presence of other interfering elements, such as Ti and V and to the sample heterogeneity.

The results obtained in the long irradiation agree typically to within 5% with the values determined by other laboratories with the exception of the alluvial sand of Somesul Mic (7%) and auriferous rock of Rosia Montana (6%). The results obtained in the short irradiation agree to within 5% with the independent determined values only for auriferous sands of Deva and concentrated sand of Cavarán; for the other samples there is a great difference between the results that

Table 5
Gold concentrations determined in the auriferous samples

| Sample type | Gold concentration (ppm) | | |
|-----------------------------------|---------------------------------|--------------------------------|--|
| | Short irradiation, this work | Long irradiation, this work | Determined by other laboratories ^a |
| Alluvial sand (Gilau) | 38 | 27 | 28 |
| Alluvial sand (Somesul Mic) | 34 | 31 | 29 |
| Auriferous sand 1 (Deva) | 79 | 81 | 83 |
| Auriferous sand 2 (Deva) | 735 | 725 | 740 |
| Concentrated sand (Cavarán) | 873 | 850 | 855 |
| Concentrated sand (Rosia Montana) | 286 | 194 | 204 |
| Auriferous rock (Rosia Montana) | 57 | 47 | 50 |

^a Uncertified, information value only.

could be explained by the non-homogeneous distribution of gold in these natural samples.

Because of the differences between the results obtained in the short irradiation using a NaI(Tl) detector and in the long irradiation using a Ge(Li) detector, when choosing between these methods the purpose of the analysis has to be considered. In geochemical exploration where a large number of auriferous samples have to be analyzed at a low cost, the use of the short irradiation and NaI(Tl) spectrometry is justified; care must be taken in this case to small corrections for the interferences due to Rb, V and Ti, as above mentioned. As can be seen from the Table 4 and Fig. 1, in the case of $^{197}\text{Au}(n, n')^{197\text{m}}\text{Au}$ reaction, if available, a Ge(Li) detector can be used for the detection of 279 keV gamma rays of the gold short-lived radionuclides without any interference.

In the case that a few number of samples are to be evaluated or gold must be determined more accurate in a sample, the long irradiation and Ge(Li) spectrometry of the 355.7 keV most intense γ -ray of ^{196}Au from the reaction $^{197}\text{Au}(n, 2n)^{196}\text{Au}$ is clearly the method of choice, taking into account only the small contribution of Se to the gold concentration (1 ppm Se = 0.05 ppm Au). As can be seen from the Table 4 and Fig. 2, in the case of this reaction, the less intense 333 keV γ -ray of ^{196}Au could also be used for gold quantifying, without any interference.

The reaction $^{197}\text{Au}(n, 2n)^{196\text{m}}\text{Au}$ cannot be used, as in [15], because of the low energies of the gamma-rays (148 and 188 keV), the high background in the spectra and, in the case of NaI(Tl) spectrometry, the important interferences (Table 4, Fig. 2).

The limit of detection, defined as the lowest concentration of gold that would give a peak under which the integrated number of counts is equal to three times the square root of the background count [23], was 14 ppm in the case of the short irradiation and 5 ppm in the long irradiation.

5. Conclusions

Taking into account the variation of the gold concentration and the great number of elements

(Si, Al, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zr, Zn, Ga, Se, Rb, Sr, V, Nb, Mo, Ag, Hg, Pb, Sb, Sm, Te, Pt, Na, As, U, Th) which accompany gold in the Romanian auriferous samples, we propose two rapid methods of gold determination by 14 MeV NAA, for concentrations that are at the level of an economic extraction, in the optima conditions established in order to assure minimum errors due to interfering elements and a maximum peak-to-background ratio for gold.

In the short irradiation ($t_a = 25$ s, $t_c = 2$ s, $t_m = 15$ s) the spectral interferences are due to Rb, Ti and V if a NaI(Tl) detector is used, and in the long irradiation ($t_a = 3000$ s, $t_c = 1000$ s, $t_m = 3000$ s) and measurement of the gamma-rays with a Ge(Li) detector – to Se, besides a small reaction interference due to Hg. The use of any of these methods is function of the purpose of the analysis and economic considerations: the short irradiation and high detection efficiency is suitable in geochemical exploration where a large number of auriferous samples have to be analyzed at a low cost; for a limited number of samples and more accurate determination of gold the long irradiation and Ge(Li) detection has to be used.

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