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Neutron activation analysis of large volume samples: The influence of inhomogeneity

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A large sample neutron activation analysis (LSNAA) facility is under development at GRR-1 research reactor, NCSR 'Demokritos', to perform multi-element, non-destructive, contamination-free analysis of large volume samples. Correction algorithms have been derived to account for thermal neutron and gamma-ray self-attenuation in macroscopically homogeneous samples, as well as the photon detection efficiency to voluminous samples, based on no prior knowledge of the sample matrix composition. In the present study Monte Carlo simulations were performed to estimate the influence of inhomogeneities of major (matrix) and trace element on the accuracy of the technique. Types of inhomogeneities that can lead to severe errors in the analysis were depicted. The potential of including inhomogeneity tests in the measuring procedure to ensure the method's applicability was examined.

Introduction

A large sample neutron activation analysis (LSNAA) facility is under development at GRR-1 research reactor, NCSR 'Demokritos'.[1,2] The facility will be used to perform multi-element, non-destructive, contamination-free, analysis of large volume samples. The procedure includes sample irradiation at the reactor's graphite thermal neutron column and subsequent measurement of the induced activity. However, erroneous results can be obtained in the analysis of large samples (mass in order of kilograms) due to (a) field perturbation related to the presence of the sample during both neutron irradiation and photon counting and (b) the photon detection efficiency from different positions within the voluminous samples. Various methods have been proposed to take into account these factors.[1–7]

TZIKA et al.[1,2] reported that there are relationships between the irradiation correction factor, f_n, (the ratio of the average flux throughout the volume of the sample, $\overline{\Phi}_v$, to the average flux at the surface of the sample, $\overline{\Phi}_s$) and the neutron flux depression factor, h_n, (the ratio of $\overline{\Phi}_s$ to the unperturbed mean flux in graphite over the sample volume prior to its insertion in the graphite column – Fig. 1) in cylindrical homogenous samples of unknown composition, 0.4 to 5 l in volume. The neutron flux depression factor can be determined experimentally by foil activation. Moreover, they proposed the use of a semi-empirical relationship between the detection correction factor f_γ (the ratio of the volume source photopeak efficiency, ε_V, to the point source photopeak efficiency, ε_P, located at the centre of the sample) and the parameter $\mu \cdot r \cdot H(r+H)$, where r and H are the radius and the height of the sample, and μ the apparent attenuation coefficient of photons in the sample. The apparent attenuation coefficient can be determined experimentally by a series of transmission measurements along the long axis of symmetry of the cylindrical samples, using a collimated photon beam from a radioactive source, such as a ^{152}Eu source.[2] The proposed methodology can be applied for the analysis of samples with h_n>0.25 and does not require any prior knowledge of the sample composition. However, it requires uniformity of sample composition at the macroscopic level.

The aim of the present study was to assess the error in the analysis of macroscopically non-homogeneous samples to be analyzed at the GRR-1 LSNAA facility due to non-uniform distribution of either the major (matrix) materials or the trace elements in the sample volume. Monte Carlo simulations were used to determine the inhomogeneity factor, R_i^j, defined as the ratio of f_i values of two samples, an hypothetical homogenous with external dimensions, r and H identical to those of the sample to be analyzed and the inhomogenous (the real sample). The index i accepts values n and γ corresponding to the activation and the counting process respectively, and j values m and t corresponding to major materials and trace element inhomogeneities, respectively.

Method

The GRR-1 LSNAA facility design incorporates sample irradiation at the reactor's graphite thermal column and subsequent measurement of the induced activity. During counting the sample was assumed to be rotated along its long axis of symmetry at a 25 cm distance from the detector end cap. Details on the facility can be found elsewhere.[1,2]

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The MCNP-4C2 code[8] was used to simulate cylindrical samples (10 cm in diameter and 20 cm in height) consisting of two materials with different elemental composition and mass density. The studied major materials were graphite, Cu and SiO_2. These materials differ up to 5 orders of magnitude with regards to macroscopic absorption cross section of thermal neutrons, 2 orders with regards to thermal neutron scattering cross section, and 3 orders of magnitude for photon attenuation coefficients in the energy region of interest (Table 1). The spatial distribution of the major materials was assumed to be either axial or radial (Fig. 2). The effect of both axial and radial inhomogeneities on the irradiation correction factor was estimated for a range of inhomogeneity volume fractions of 10% to 90%, while for gamma-ray measurement one of the materials was assumed to occupy the central 1/3 of the sample volume.

An extreme case of the influence of trace element non uniformity during irradiation was examined. Specifically, a mass of 12 g of gold was assumed distributed within a graphite sample at: (a) the entire surface of the sample in a 1 mm thick layer, (b) its cylindrical surface in a 1 mm thick layer, (c) one of its circular surfaces in a 1 mm thick layer, (d) the central cross-plane in a 2 mm thick disk, (e) its centre as a sphere 1 cm in radius and (f) at the long axis of the sample in the form of a wire 3 mm in radius. The element of interest could either be the Au itself or another element distributed uniformly in the sample volume.

Six uniform activity distributions were examined as shown in Fig. 3 in order to derive the magnitude of their effect on gamma-ray measurement.

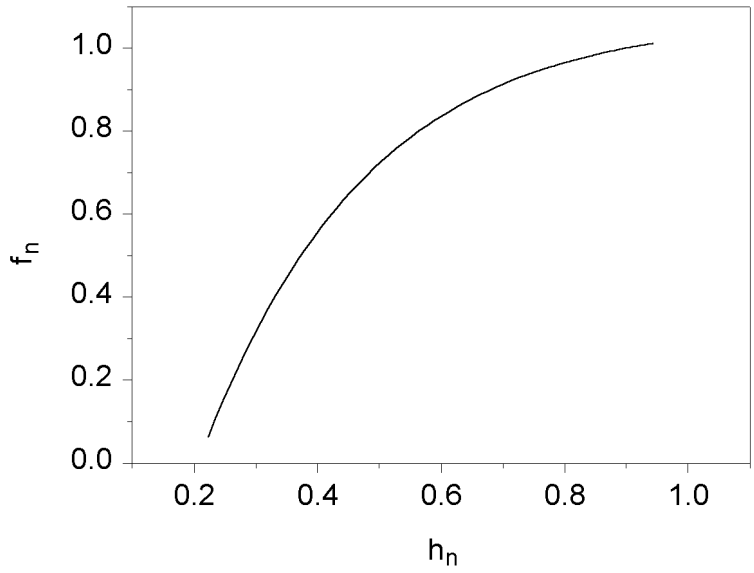

Fig. 1. Irradiation correction factor, f_n, of cylindrical samples ($H = 20$ cm, $r = 5$ cm) as a function of the thermal neutron depression factor (based on data by TZIKA et al.)[1]

Table 1. Some radiological properties of the materials in the simulated samples

Material	Density, g/cm^3	Σ_α, cm^{-1}	Σ_s, cm^{-1}	$\mu_{\gamma,100}$, cm^{-1}	$\mu_{\gamma,300}$, cm^{-1}	$\mu_{\gamma,700}$, cm^{-1}	$\mu_{\gamma,1500}$, cm^{-1}
Copper	8.96	0.326	0.669	4.10	1.00	0.64	0.43
Gold	19.3	5.83	0.428	99.5	7.23	1.96	1.00
Graphite	1.60	0.00032	0.019	0.242	0.171	0.120	0.083
SiO_2	2.32	0.0037	0.226	0.391	0.250	0.129	0.120

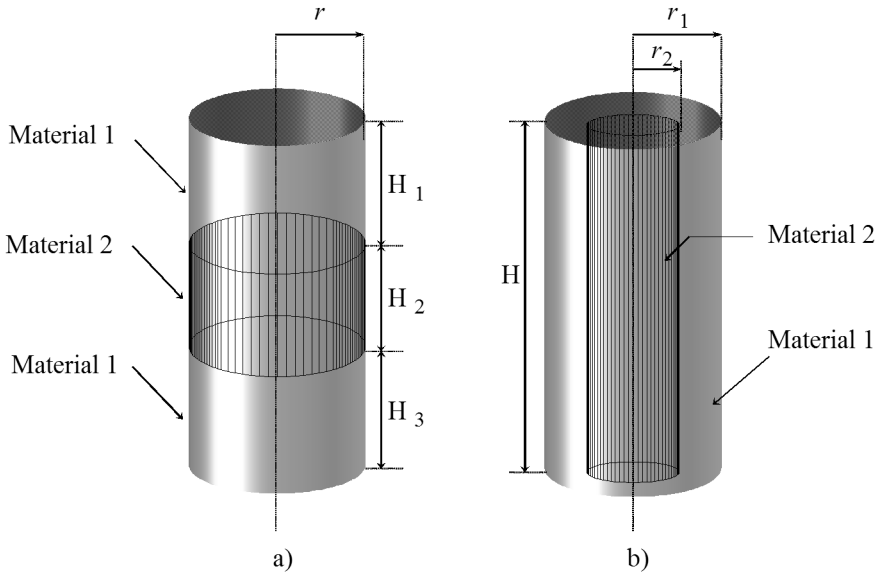

Fig. 2. Inhomogeneities of major materials: (a) axial and (b) radial

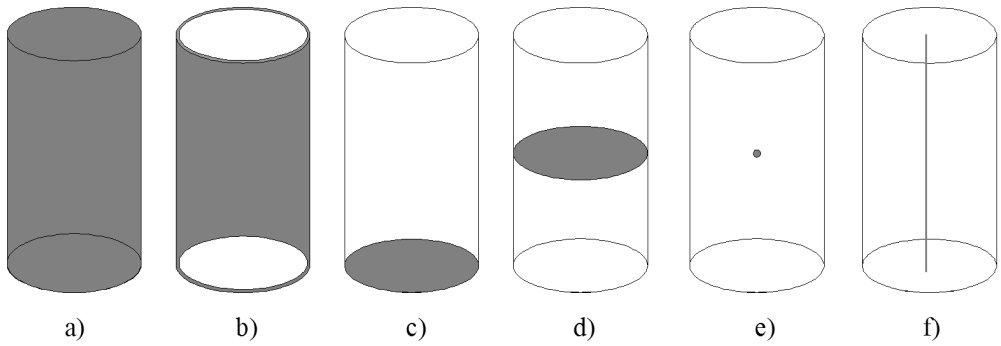

Fig. 3. Activity distributed in a cylindrical sample at: (a) the entire surface of the sample, (b) the cylindrical surface, (c) one of the circular surfaces, (d) the central cross-plane, (e) the center of the sample and (f) the long symmetry axis of the sample

Results and discussion

Axial major elemental inhomogeneities

Figures 4 to 6 show the predicted inhomogeneity factor R_n^m, for the axial matrix inhomogeneity in samples made of graphite, SiO_2, and Cu as a function of the inhomogeneity volume fraction, V_i/V_S. The simulations indicated that R_n^m does not differ statistically from 1.00 for the combinations of SiO_2 with graphite (Fig. 4). However, R_n^m maximum deviations from unity reach the values of 26% and 23% for inhomogeneities of graphite and SiO_2 in a Cu sample, respectively (Figs 5, 6). Figure 7 shows the calculated ratio R_γ^m, as a function of the gamma-ray energy. Small deviations from unity (<4%) were found in combinations of graphite with SiO_2, and high (up to 70% at 100 keV and 18% at 1.5 MeV) in combinations of Cu with either graphite or SiO_2.

Radial major elemental inhomogeneities

Figures 4 to 6 show the calculated inhomogeneity factor R_n^m, for the radial major element inhomogeneity in samples made of graphite, SiO_2, and Cu, as a function of V_i/V_S. The maximum calculated value of R_n^m, 1.24, was observed when the Cu core of 0.7 volume fraction was surrounded by a layer of graphite and the minimal, about 0.62, when the graphite core of 0.5 volume fraction was surrounded by a layer of Cu. Figure 8 shows the calculated R_γ^m, as a function of the gamma-ray energy,

for various material combinations corresponding to an inhomogeneity volume fraction, of 33.4% ($r_2 = 2.89$ cm). Small deviations from unity (<20%) were found in combinations of graphite with SiO_2 over the entire studied range of photon energies, and high in combinations of Cu with either graphite or SiO_2. The factor, R_γ^m, ranges between 0.18 and 0.7 when the inner core is made of Cu in the energy range 100 keV to 1.5 MeV, and between 1.88 and 1.25 in the same energy region when the outer layer is made of Cu.

Trace element inhomogeneities

The inhomogeneity factor, R_n^t, is close to unity when the element to be analyzed by LSNAA is homogeneously distributed in the sample volume (Table 2). On the contrary, when Au is the element to be assessed, there is drastic reduction in the signal when the trace element is located either close to the long symmetry axis of the sample ($R_n^t = 2.2$) or close to its centre ($R_n^t = 1.6$). Figure 9 shows the calculated ratio R_γ^t, as a function of the apparent attenuation coefficient of photons in the sample. The presence of the trace element has minor influence on counting if located at either the circular surfaces of the phantom or as a thin disk at the central plane of the cylindrical phantom. On the contrary, R_γ^t decreases with increasing μ up to 0.22 at 1.0 cm^{-1} when located either at the entire surface or the cylindrical surface of the sample and increases with increasing μ when located at the remaining locations.

Table 2. R_n^t values for inhomogeneous distribution of Au, 12 g in mass, when the element to be measured is Au or another element

Element to be analyzed	All surfaces	Cylindrical surface	Circular surface	Circular center	Sphere center	Line center
Gold	0.975	1.00	1.10	1.14	1.60	2.21
Other element	0.97	0.97	1.05	0.94	1.00	1.01

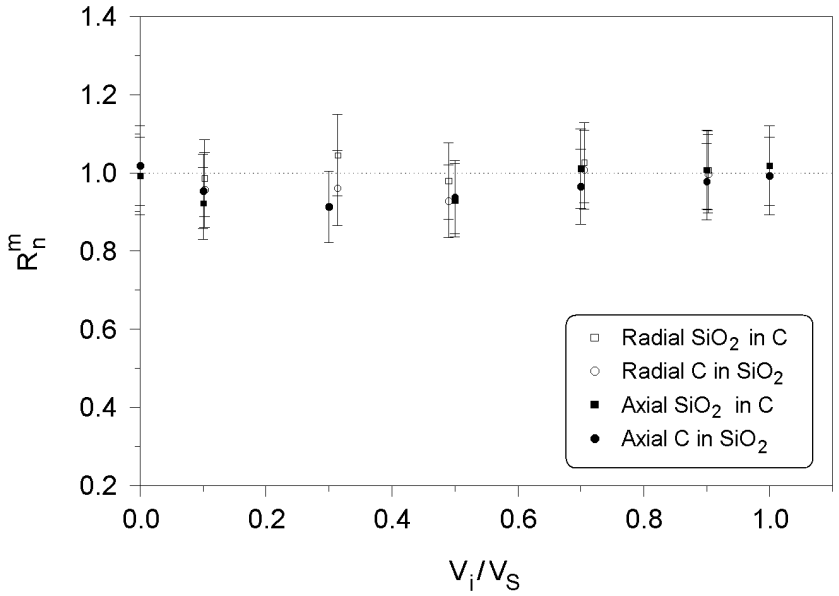

Fig. 4. The ratio of R_n^m as a function of the inhomogeneity volume fraction, V_i/V_S for axial and radial inhomogeneity in the distribution of two major materials, graphite and SiO_2

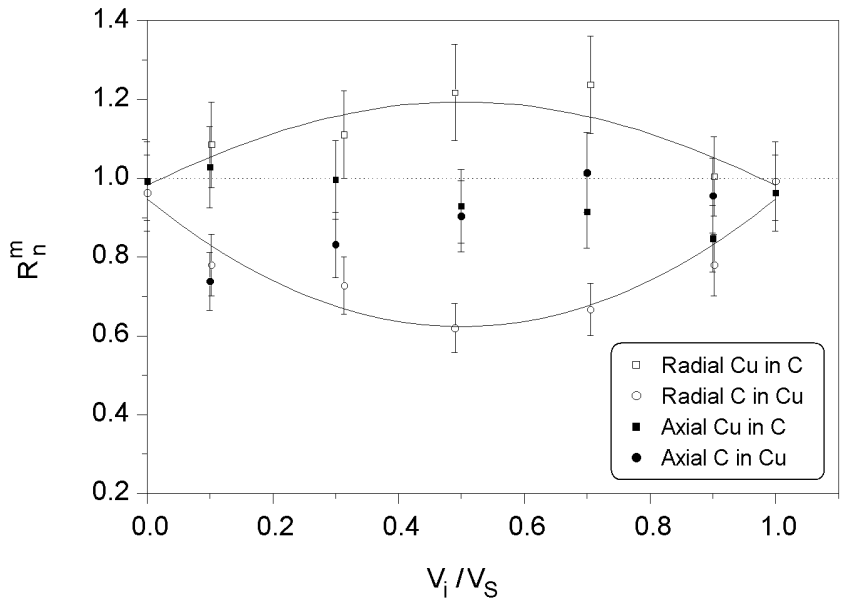

Fig. 5. The ratio of R_n^m as a function of the inhomogeneity volume fraction, V_i/V_S for axial and radial inhomogeneity in the distribution of two major materials, graphite and Cu

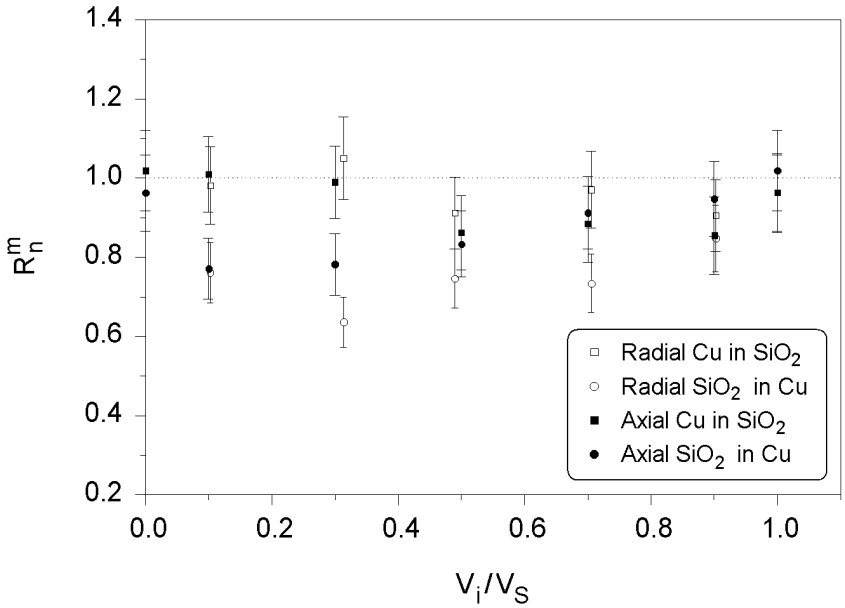

Fig. 6. The ratio of R_n^m as a function of the inhomogeneity volume fraction, V_i/V_S for axial and radial inhomogeneity (Fig. 1) in the distribution of two major materials, SiO_2 and Cu

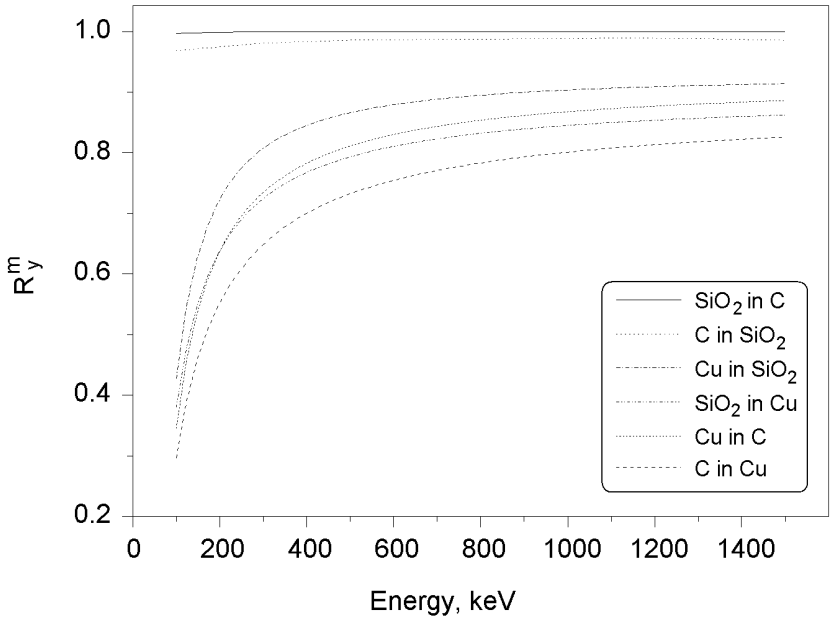

Fig. 7. The ratio R_γ^m as a function of the gamma-ray energy, for the axial matrix inhomogeneity as shown in Fig. 2a ($V_i/V_S = 33.4\%$)

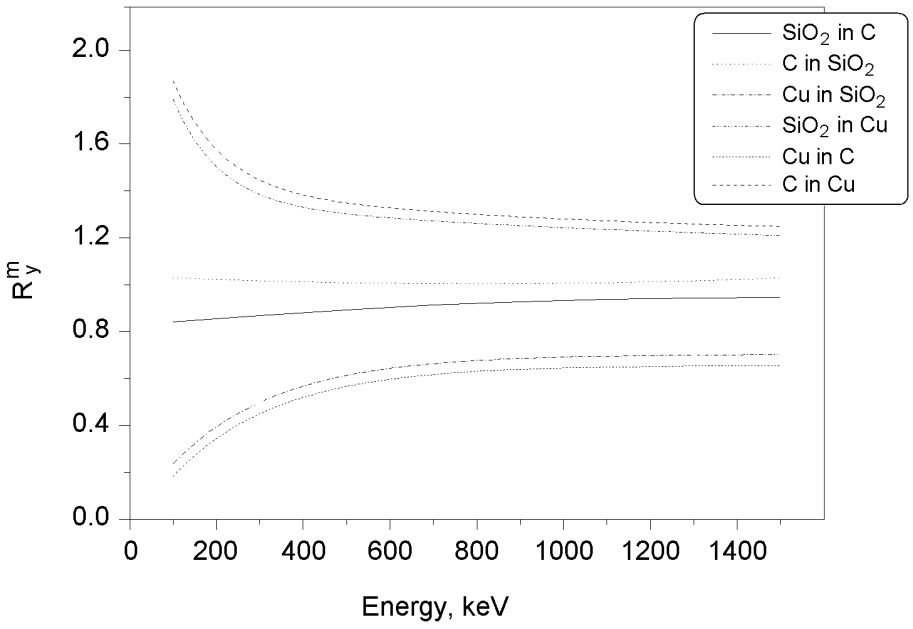

Fig. 8. The ratio R_γ^m as a function of the gamma-ray energy, for the radial matrix inhomogeneity as shown in Fig. 2b ($V_i/V_S = 33.4\%$)

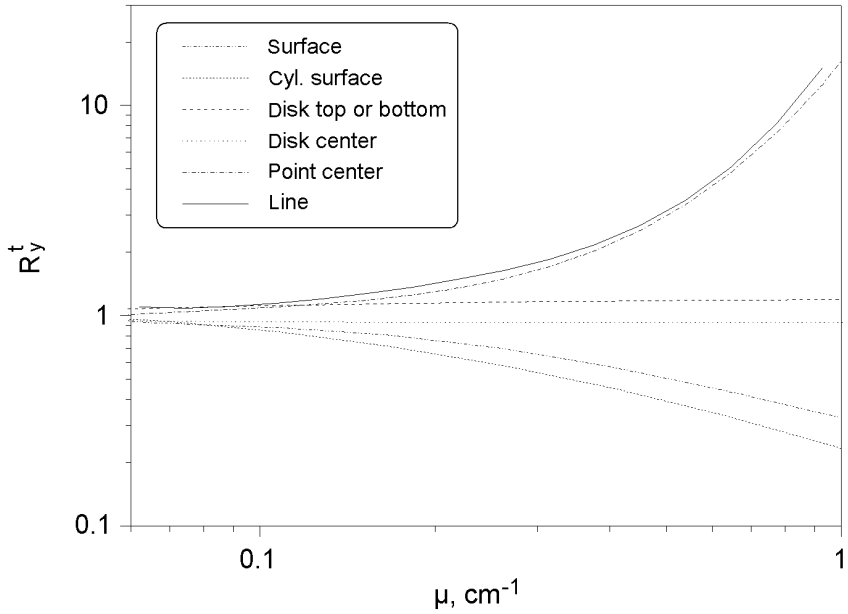

Fig. 9. The ratio R_γ^t as a function of the apparent attenuation coefficient, μ

Discussion

Inhomogeneities in the distribution of either major materials or trace elements in a large sample to be analyzed by neutron activation analysis may lead to severe errors in the measurement. The number of possible types of inhomogeneity is infinite (geometric distribution in macroscopic level, combinations of materials). In the present study we modeled samples consisting of two materials.

Matrix inhomogeneities

Both the photon transmission measurements and the measurements for the assessment of the neutron flux depression factor are expected to reveal the existence of axial inhomogeneity. The product of the inhomogeneity factors R_n^m R_γ^m deviates drastically from unity only for samples with high μ, such as samples containing Cu. The deviation increases, as expected, with decreasing photon energy. On the contrary, such measurements are not expected to reveal the existence on radial inhomogeneities. Whenever sophisticated methods, such as tomographic techniques[7] are not available, simple methods such as the physical inspection of the sample to be analyzed and/or the measurement of its density may reveal that the sample is not homogeneous macroscopically. In addition, the ratio of counted photons from γ-emitters of at least two photon energies may also reveal sample inhomogeneity. In general, the error in the analysis of samples with high μ can be reduced by avoiding counting of low energy photopeaks (e.g., photons with energy less than ~400 keV). For example, as it can be observed in Figs 5 and 8, Cu being in the central region ($r_2 = 2.89$ cm) of the sample results in an increase of the product $R_n^m \cdot R_\gamma^m$ from 0.67 at 500 keV to about 0.76 at 1500 keV. Similarly, when graphite is in the central region ($r_2 = 2.89$ cm) and is surrounded by Cu, $R_n^m \cdot R_\gamma^m$ decreases from 0.88 at 500 keV to 0.82 at 1500 keV.

Trace element inhomogeneities

Table 2 shows that the presence of gold in a graphite matrix is not expected to influence significantly the activation of an element uniformly distributed over the sample volume. On the contrary, if gold is the element to be analyzed factor R_n^t was drastically increased when distributed in a sphere at the sample centre or in a cylindrical volume with long axis of symmetry coincident with that of the sample.

As it can be observed in Fig. 9, when the activity is distributed as a disk at the centre and top or bottom of the cylindrical sample there is only a small dependence of factor R_γ^t on μ. However, when the activity is distributed either at the sample centre or as a linear source along the axis of symmetry factor R_γ^t increases drastically with μ. For example in the latter R_γ^t was found to be 20 at $\mu = 1$ cm^{-1}. Furthermore, when the activity is distributed at the outer surface of the sample, factor R_γ^t decreases with increasing μ. For example R_γ^t was found to be 0.2 at $\mu = 1$ cm^{-1} when distributed at the cylindrical surface of the sample.

Conclusions

The present study confirmed the earlier findings by researchers at Delft University of Technology[3–5,7] that false concentrations may be obtained in LSNAA if macroscopic inhomogeneities are not to be taken into account. The inhomogenous distribution in the sample to be analyzed of either major materials or trace elements may introduce errors in the interpretation of data obtained during both the irradiation and the counting stage. The combinations of materials used for the simulation of samples in the present study were selected to differ drastically with regards to their interaction parameters with thermal neutrons and/or photons. Therefore, the R_i^j values evaluated by Monte Carlo simulations can be characterized as "worst cases" to be met at the NCSR 'Demokritos' LSNAA facility. The application of appropriate correction factors in the experimentally obtained data is expected to provide concentrations with acceptable accuracy even in inhomogeneous samples.

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