Neutron activation analysis of sediments and rocks from two lakes of Romania

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Introduction

Bâlea Lake (Făgărş Mountains) and St. Ana Lake (Harghita Mountains) are two medium size lakes of different origin: Bâlea Lake is a typical high altitude proglacial lake while St. Ana Lal, located in the Ciomadu extinct volcano caldera, is the unique volcanic lake in Romania, Although both lakes have different location and origin, they are characterized by a total absence of any source of industrial pollution in their direct neighborhood. For this reason, and by taking into account the distance of about 115 km between them, these lakes could be chosen as good indicators for an extended screening of industrial pollution. On the other hand, Bâlea as well as St. Ana lakes, due to their picturesque landscape, are visited during summer time by a great number of tourists, so a certain degree of anthropogenic influence is expected to exist. Both lakes collect pluvial water from relative restricted areas (about 234 ha in the case of lake Bâlea and 147 ha for the lake St. Ana lake) so the mineralogical and elemental composition of their sediments will reflect the geochemical characteristics of surrounding geological formations. Accordingly, the sediments of Lake Bale are expected to reflect the mineralogical composition of the Suru Formation, mainly consisting of metamorphic rocks such as amphibolitic schists, quartzo-felspatic gneissic rocks and mylonites as well as limestones. On the contrary, the sediments of St. Ana lake which occupies the bottom of now extinct Ciomadu volcano, mainly consist of fragments of weathered andesite together with an considerable amount of phytodetritus, the last one originated from the coniferous and deciduous forests that cover the caldera walls.

Irrespective of their tourist interest, both lakes have received little attention regarding geochemistry, and particularly, the level of pollution with heavy metals, although their importance as reference systems for zero level industrial pollution cannot be ignored. For this reason, in summer 2008 and winter 2009 we performed two campaigns of a systematic investigation concerning the geochemistry of both sediments and neighbor geological formations by collecting six sediments cores as well as an appreciable number of samples of rocks to be analyzed by instrumental neutron activation analysis (INAA).

Experimental

Sediments collected from the Bâlea Lake consisted, at their upper part, mainly of blackish, seldom green-grayish silt, with fragments of vegetation and few aquatic invertebrates, while the deeper ones contained also sand and fine to coarse gravel. The granulometric analysis showed the predominance of silt up to 80%, with an almost normal distribution, while vegetal fragments, sand as well as gravel or lithic fragments accounted for the rest of 20%. On the contrary, St. Ana sediments were more homogenous, consisting of brownish silt, rich in fragments of vegetation and in some places, exhaling an odor of H_2S.

INAA was carried out at the research reactor of WWR IRT type, at the Moscow Engineering Physics Institute (Moscow). Well homogenized samples weighing 100–200 mg, together with the reference materials: IAEA-433, IAEA 140/TM, IAEA SL-1 and IAEA Soil-7, were irradiated in the vertical experimental channels with a thermal neutron flux density of 10^{12} n $cm^{-2}s^{-1}$ for 15–20 h. All gamma spectra were recorded by using a HPGe detector of ORTEC GEM 25185 type with an energy resolution of 1.85 keV for the 1332 keV of Co^{60} line.

Results and discussion

The results for the seven elements are reported in Table 1.

Investigating the distribution of above mentioned elements in Bâlea and St. Ana lakes, we have been interested to establish to which extent to these elements could be attributed an anthropogenic origin, and, at the same time, to evidence the relationship between sediments and the lithologiy of their, although reduced as surface, drainage basins.

Accordingly, in Table 1 we have reproduced the content of investigated heavy elements, to which, for comparison, we have added also the natural occurring, nonpolluting Sc. As reference systems, we have used the Upper Continental Core (UCC) and Pacific and Indian Oceans MORB as well as Romanian Regulations concerning the content of some heavy polluting elements in soils. The content of these elements in the sediments and rocks in different formations is given by means of box and whiskers diagrams in Fig. 1.

To identify and characterize possible sources of the determined elements Correlation Analysis (CA) and Principal Component Analysis (PCA) (Davies, 2002) were performed by means of StatSoft® Statistica 6.0.

The PCA plot of all seven elements (considering samples as variables and elemental contents as cases) is reproduced in Fig. 2.

Table 1. The average values, (Aver), and standard deviations, (St. Dev.) of investigated heavy elements in St Ana sediments (12 samples), St. Ana andesites (3 samples), Bâlea lake sediments (6 sampes), Bâlea lake rocks (8 samples). For comparison, the content of the same elements as defined by Romanian Regulations (Anonymous, 1997) together, with UCC (Taylor and McLennan, 1983), as well as Pacific and Indian MORB (ERDA, 2010) contents are reproduced too. Concentration of elements is given in mg/kg.

	Sample		Sc	Cr	Co	As	Se	Br	Sb
St. Ana Lake	Sediments	**StDev**	4.5	31	4.2	4.1	1.7	23.7	2.4
		Aver	0.9	3	0.4	1.0	0.4	7.4	0.9
	Andesite	**Aver**	4.5	29	3.6	2.4	1.2	28.3	1.3
		StDev	1.2	10	1.0	0.7	0.3	16.4	0.0
Bâlea Lake	Sediments	**Aver**	20.0	272	42.3	5.5	3.0	5.7	1.4
		StDev	0.8	39	5.3	1.8	0.5	1.5	0.5
	Paragneiss								
	Paragneiss								
	Paragneiss	**Aver**	24.9	291	39.3	4.3	2.0	0.4	0.2
	Paragneiss + chloritic schists with garnets								
	Amphibolite +amphibolitic schist								
	Paragneiss + amphibolitic schist								
	Paragneiss + chloritic schists	**StDev**	16.0	274	24.5	-	0.8	0.2	0.2
	Paragneiss + chloritic schists								
Reference systems	RR normal		-	30	15	5	1	50	5
	RR alert		-	100	30	15	3	100	12.5
	UCC		11	35	10	1.5	0.05	nd	0.2
	MORB Pacific		31.8	714.3	nd	nd	nd	nd	nd
	MORB Indian		39.1	254.4	nd	nd	nd	nd	nd

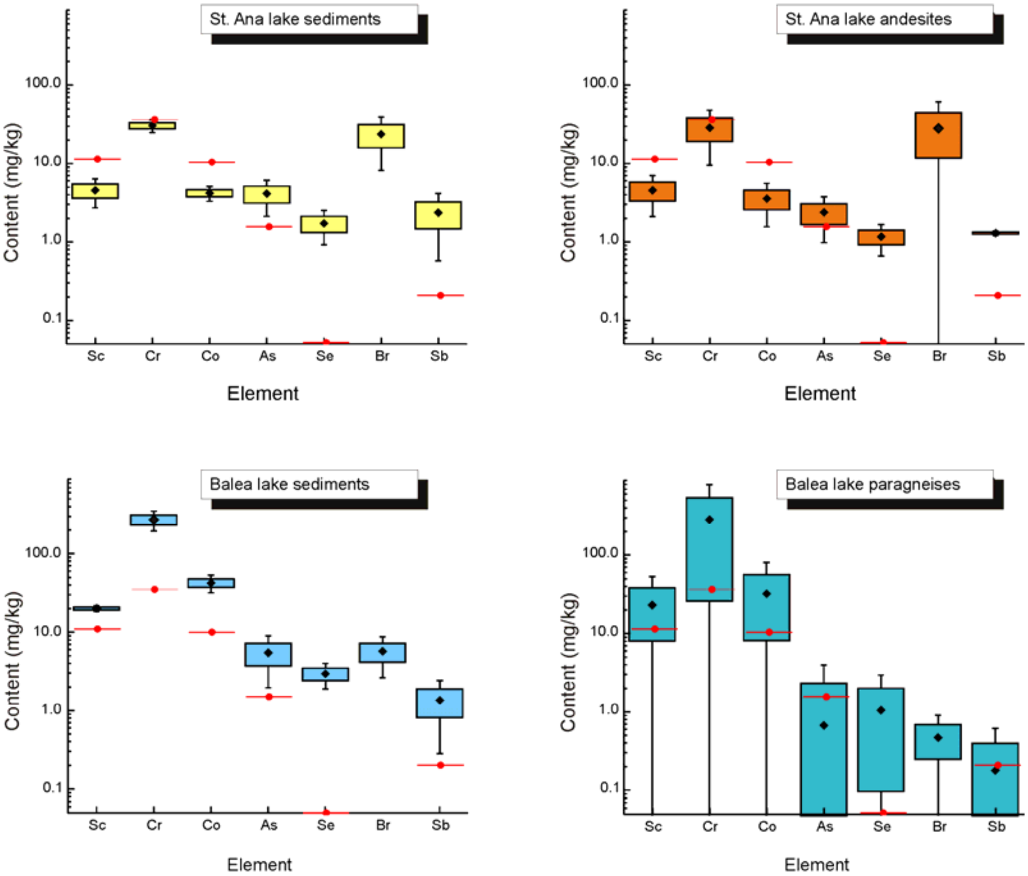

Fig. 1. Box and whiskers diagrams of determined elements in investigated systems

In addition, by means of PCA considering samples as cases, an attempt was made to understand the interrelationship between sediments and adjacent parent rocks (Fig. 3).

In this way, we can consider that observed clusters and sub-clusters, based only on the content of the considered seven elements, reflect with enough precision the differences between investigated samples regarding their natural provenience.

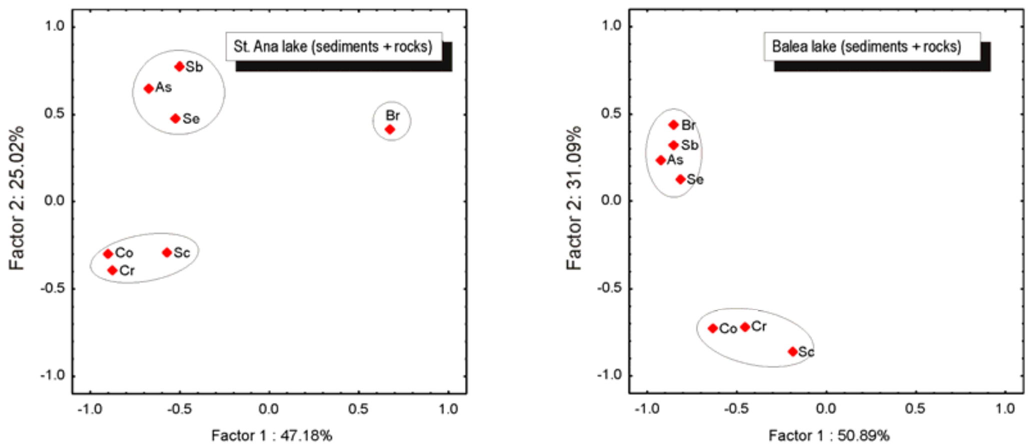

Fig. 2. A bivariate PCA plot illustrating the relative similarity of heavy elements clusters for both lakes (R mode analysis)

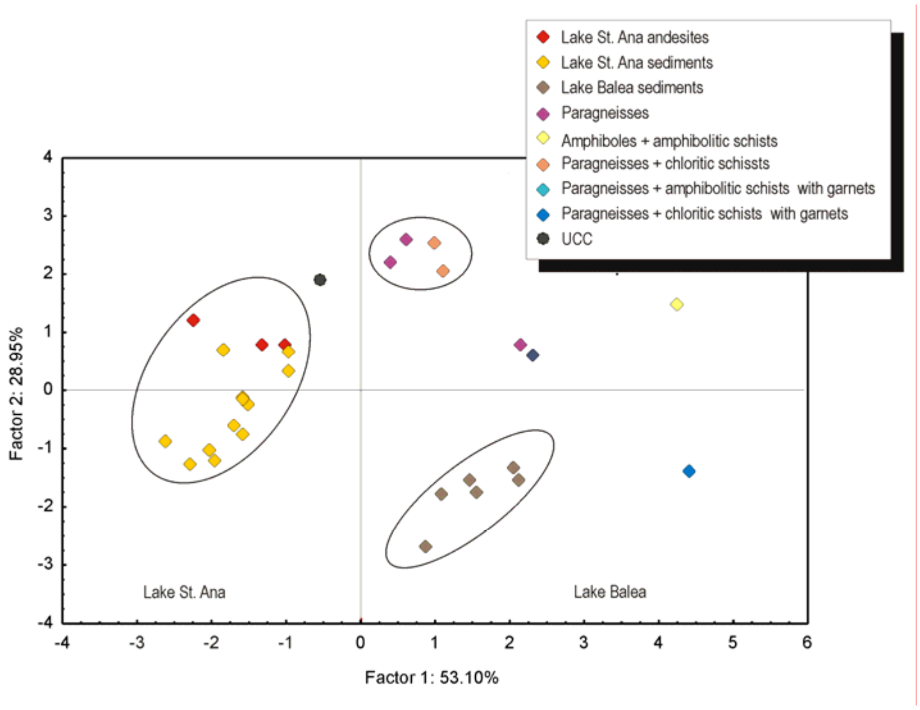

Fig. 3. A bivariate PCA plot illustrating the clusterization of the main lithologic components of investigated systems (Q – mode analysis)

Conclusion

Final results showed that the average content of these elements in sediments was close to these in rocks, and, at the same time, comparable with the normal environmental content of these elements as defined by the Romanian Regulations, such that all elements could be considered as normal, nonpolluting components of investigated lakes. A Principal Component Analysis performed in R-mode showed that Sc, Cr and Co on one hand and As, Sb, Br, and Sb on the other forms two distinct cluster, regardless the lake while Q-mode analysis pointed towards a significant difference between two lakes regarding both sediments and rocks.

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APPLICATION OF SOME MICROORGANISMS FOR SYNTHESIS OF GOLD AND SILVER NANOPARTICLES

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Introduction

Nanobiotechnology is a rapidly advancing area of scientific and technological opportunity that applies the tools and processes of nano/microfabrication to build devices for studying biosystems. The microorganisms (bacteria, microalgae, yeasts, fungi) are often used as possible “nanofactories” for the development of clean, nontoxic and environmentally friendly methods of producing silver and gold nanoparticles (Klaus-Joerger et al., 2001; Li et al., 2011; Mohanpuria et al., 2008; Gericke and Pinches, 2006). Successful collaborative studies of the Sector of NAA and Applied Research of the Division of Nuclear Physics of FLNP with the Institute of Physics, Georgia, in the interaction of metals with microorganisms (Mosulishvili et al., 2002, 2007) were extended to nanobiotechnology (Tsibakhashvili et al., 2011; Kalabegishvili et al., 2011).

Materials and methods

Neutron activation analysis (NAA) is used among the variety of analytical and spectral methods: UV-vis spectrometry, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) with energy-dispersive analysis of X-ray (EDAX), atomic absorption spectrometry (AAS) for investigation of the obtained nanomaterials. The few bacterial strains of actinomycetes *Streptomyces glaucus* 71MD and *Streptomyces* spp. 211A (isolated from the rhizosphere of soybeans grown in Georgia), arthrobacter genera – *Arthrobacter globiformis* 151B and *Arthrobacter oxydans* 61B (isolated from the basalt rocks collected from the Kazreti region of Georgia) and blue-green algae *Spirulina platensis* (strain IPPAS B-256 from the algeological collection of the Timiryazev Institute of Plant Physiology, Russian Academy of Sciences) were used for gold and silver nanoparticles synthesis. Cells of actinomycetes and *Spirulina platensis* were grown as described elsewhere (Tsibakhashvili et al., 2011; Kalabegishvili et al., 2011). The harvested mycelial mass was then resuspended in 250-ml Erlenmeyer flasks in 100 ml of 10^{-3} M aqueous $HAuCl_4$ (chloroauric acid) solution in the synthesis of gold nanoparticles, and in aqueous $AgNO_3$ (argentum nitrate) solution in the synthesis of silver nanoparticles. Time-dependence of nanoparticle formation was studied in different time intervals (several days).

Result and discussion

The gold and silver surface plasmon resonances (SPR) was observed in the UV-vis absorption spectra at ~ 530 nm for gold and at 425 nm for silver, respectively. The presence of SPRs indicate the gold and silver ion reduction and the subsequent aggregation of nanoparticles in the solutions. The intensity of the peaks increased as a function of the reaction time. A single band in all spectra gives evidences for the spherical shape of gold and silver nanoparticles that is also confirmed by TEM images (Fig. 1).

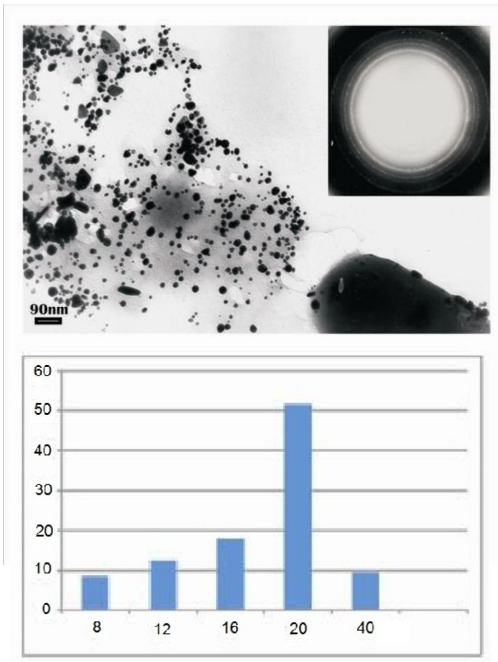

Fig. 1. TEM image and size histogram of Au nanoparticles in biomass of Arthrobacter *61B*

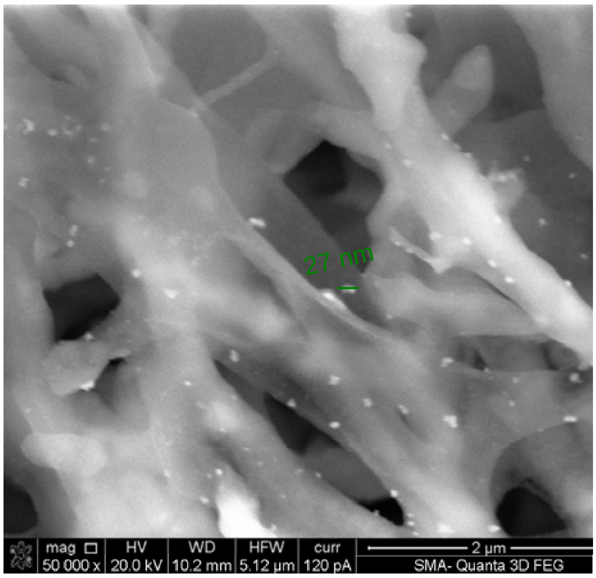

Fig. 2. SEM image of Ag nanoparticles in biomass of *Streptomyces glaucus* 71MD

In all TEM images the diffraction patterns correspond to the face centered cubic (fcc) structure of gold and silver nanoparticles. The particle size histogram for studied samples shows that the size of gold and silver nanoparticles are in the range of 5 to 80 nm, with an average of 25 nm. The XRD data for gold and silver nanoparticles confirm the presence of the fcc structure. As an example, the SEM image of *Streptomyces glaucus* 71MD cells (after interacting with $AgNO_3$ solution for seven days) is given (Fig. 2). The SEM images illustrate that most of the particles are spherical and do not create big agglomerates.

The EDAX X-ray spectra were registered proving the presence of gold nanoparticles in *Spirulina platensis* cells treated with $HAuCl_4$ for 5 days (Fig. 3). Along with the Au peaks, the signals from C, O, Cl and Fe were recorded. Neutron activation analysis (NAA) was carried out in collaboration with the South African Nuclear Energy Corporation (Necsa), Pelindaba, Pretoria, South Africa, at the nuclear research reactor SAFARI-1. The samples were irradiated for 8 s at a neutron flux density of ~ 5.10^{14} n cm^{-2} s^{-1}. Their activities were measured three times, after cooling for 3 and 30 hours and 7 days, respectively. The gold content was determined on the 411.8 keV γ-line of ^{198}Au. Genie 2000 software was used to process NAA data. The data obtained by NAA illustrates that uptake of metals includes two phases: rapid and slower uptake. In the first ‘rapid’ stage, the metal ions are adsorbed onto the surface of the microorganism. The concentration of gold increases rapidly. In the ‘slow’ stage, the metal ions are transported across the cell membrane into the cytoplasm. The total concentration of gold in the samples (extracellular and intracellular) does not change significantly. The data obtained by AAS (Fig. 4) are confirmed by NAA (Fig. 5).

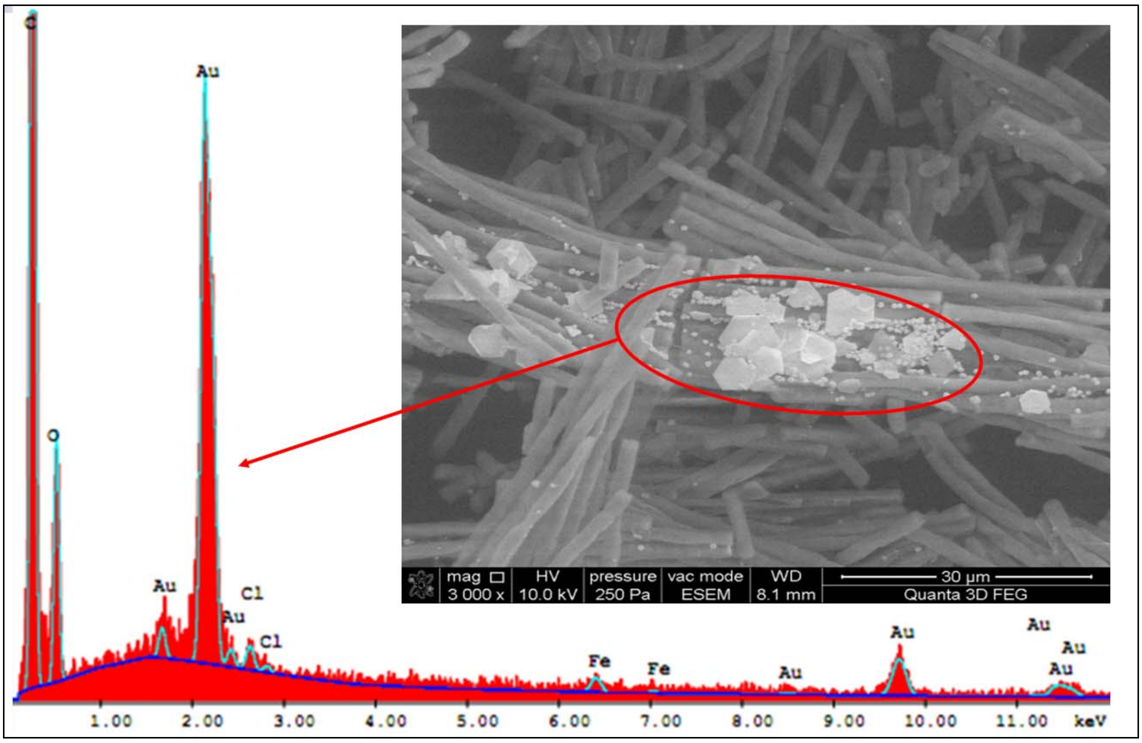

Fig. 3. EDAX spectrum of *Spirulina platensis* exposed to $HAuCl_4$ (10^{-2} M)

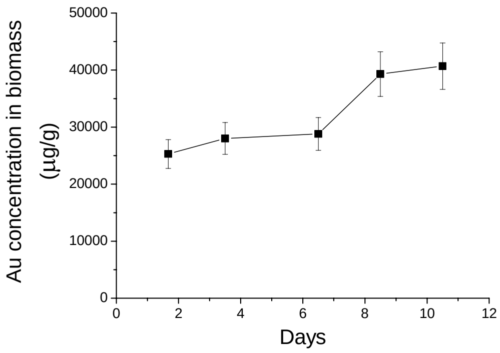

Fig. 4. The gold concentrations in biomass of *Arthrobacter globiformis* 151B versus the time of exposure gold cloroaurat determined by AAS

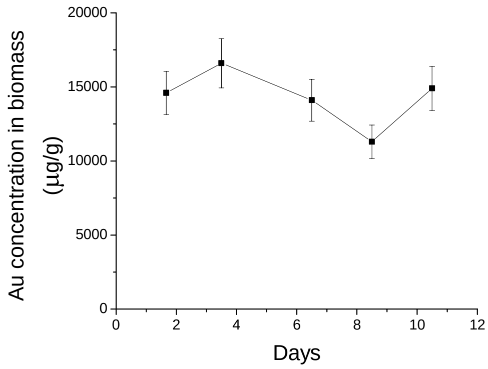

Fig. 5. The gold concentrations in biomass of *Arthrobacter globiformis* 151B versus the time of exposure gold cloroaurat determined by NAA

Conclusions

The results of the performed investigations show that the studied microorganisms are capable of producing nanoparticles extracellular when exposed to the gold and silver compounds. The shape of the majority of the nanoparticles is spherical and the average size is 25 nm. The biosynthesis of nanoparticles is simple, economically viable and an eco-friendly process.

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