Prospects of non-ferrous metals detecting in samples with use of nuclear physical and *X*-ray fluorescence methods

UDC 669.2:621.039

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There were carried out theoretical and experimental grounds of possibility of the nuclear physical and *X*-ray fluorescence methods usage for detecting non-ferrous metals and its compounds (including ultradispersed form) in different samples. It was experimentally shown a principal possibility of estimation of the gold (including its ultradispersed form) content in samples in amounts up to 10–11 g/sample with the use of the IR-8 (*ИР*-8) research nuclear reactor with the average flux density of thermal neutrons equaled to $3 \cdot 10^{12}$ n/(cm^2·s). Considering existing limitations of the maximum sample mass up to 0.5 kg, it is possible to estimate the gold content in samples in concentrations substantially smaller than the commercially profitable value. The experiment on fast neutrons and fast protons of the U-150 (*У*-150) isochronous cyclotron of the National Research Center (NRC) "Kurchatov Institute" has showed possibility of detecting titanium content in samples in the form of the TiO$_2$ powder in the ultradispersed form or rutile. Nuclear reactions of titanium nuclei interactions with fast neutrons generate ^{46}Sc and ^{47}Sc radioactive isotopes of scandium and interactions with fast protons generate ^{48}V isotope of vanadium, which possess characteristics acceptable for gamma spectroscopy analysis. There are also examined application prospects of the *X*-ray fluorescence analysis version which use not roentgen but synchrotron radiation — bremsstrahlung of electrons, moving along the curved trajectory. This allows to significantly raise the limits of elements detection (by 1–2 order when compared to *X*-ray tubes) and to analyze samples of extremely small volume and mass (about units of mg). The proposed set of methods gives principal possibility to detect several tens of non-ferrous metals.

Key words: non-ferrous metals, nuclear physical methods, charged particles, *X*-ray fluorescence methods, ultradispersed particles, nondestructive detection methods, nanoparticles, gold content, heterophasis dispersed systems.

***DOI:** 10.17580/nfm.2016.02.04*

Introduction

Development of innovation technologies and increase of non-ferrous metals production stipulate the need of non-ferrous metal detecting in different mediums: in geological rocks, environmental and biological objects etc. Among other factors, technical progress in the sphere of non-ferrous metals mining and processing, expressly or by implication results in the changes of ecological state of the environment and forming of new sources of potential danger for the human health [1]. Questions of registration of non-ferrous metals and their compounds in different samples in the ultradispersed form (including nanoparticles) make up a special category of concern.

The most-used methods of estimation of non-ferrous metals content in samples are connected with the sample breakdown and its conversion into the other aggregative state. Nuclear physical and *X*-ray fluorescence methods of chemical elements registration, including non-ferrous metals, are actually free of this shortcoming [2—5]. With the optimum choice of conditions of radiation in the flux of thermal neutrons or fast charged particles, atoms of non-ferrous metals may be activated and their content in the investigated sample may be estimated by the induced activity [2, 3]. The *X*-ray fluorescence methods are based on the investigated nuclei electron shells excitation by *X*-ray or synchrotron radiation with further photon emission [4, 5]. The main advantage of the methods under consideration is an ability to carry out quantitative

measurements of content for individual chemical elements (including ultradispersed form) in complex, multicomponent, heterophasis dispersed systems, such as samples of soil, water and ore, tissues of living organisms etc.

Neutron activation analysis application for non-ferrous metals detecting in the investigated samples by the use of nuclear reactor

The neutron activation analysis (NAA) is one of the best known and commonly used nuclear physical methods of detecting individual non-ferrous metals and their compounds [2]. It is reasonable that this method doesn't allow to estimate content of all non-ferrous metals in the sample. It's fundamental restriction is the limited set of neutron capture nuclear reactions, as a result of which the target isotope turns into the radioactive isotope with characteristics suitable for activity measuring by the highly sensitive spectrometric equipment. So, with some limitations the method may be applied to the following non-ferrous metals: Zn, Ag, Au, Na, Mg, Co, Sc, Al, Ga, Rb, Zr, Mo, Cd, Sn, Cs, Ba, Sm, Eu, Tb, Ho, Ta, W [2, 6].

Research technology of detecting non-ferrous metals (including gold) and their oxides (including ultradispersed form) content has been worked through in experiments with biological samples of nanoparticles of zinc oxide, argentum and gold with the use of neutron activation analysis on the base of the IR-8 research reactor of the NRC "Kurchatov Institute" [7]. Radioactive isotopes ^{65}Zn and ^{110m}Ag, resulting in the reaction of thermal neutrons capture by nuclei of target isotope, have quite large half-value period and are free of registration problems, connected with the Compton scattering of gamma lines of the isotope ^{24}Na, which may present in the investigated sample as well as in packaging (a half-value period equals to 15 h). At the same time, when researching the gold content in the sample by the marker isotope ^{198}Au in the assay, it is required to choose the optimum time of radiation and further aging (to decrease activity of the "interfering" isotope ^{24}Na).

The estimated sensitivity of the gold content in the investigated samples detection method on standard exposition conditions at the IR-8 reactor with a thermal neutrons flux density of $3 \cdot 10^{12}$ cm^{-2}s^{-1} by radioactive markers of the gold isotope ^{198}Au is 10^{-11} g [3, 6]. Since the measured is the content of radioactive isotope induced in the analyzable sample, than increase of the total mass of the sample introduced into the reactor channel up to 1 kg the method in question may ideally allow to measure the gold content in the analyzed sample in concentrations up to 10^{-8} g/t. In real situation, however, presence of some other chemical elements in the investigated sample and interfering Compton scattering effect of these elements after their activation may decrease the sensitivity of the method by 2—3 orders. In any case, the bottom limit of measurement of the gold content in the sample will not be worse than 10^{-4} g/t [6].

The proposed method also allows detecting content in the sample of several elements at once. The estimations were made for the fixed duration of radiation exposure, when it is necessary to measure extremely small levels and (or) concentrations of the investigated material in samples. In the case that the less sensitive method is needed, the duration of radiation treatment in the flux of thermal neutrons of the nuclear reactor may be essentially shortened, as a first approximation, proportionally to the sensitivity of the method required in practice compared to its maximum ability.

NAA application for estimating the superdispersed gold content in soil samples by the use of nuclear reactor

Technology of NAA with californium source neutrons use in order to estimate gold content in ore samples is examined in [8]. Possibility for applying this method to estimate the gold content in assays from silt-settling tanks is investigated in [9]. It was shown the much more correct detection of gold content by this method in comparison with assay analysis. However, isotope ^{252}Cf with a half-value period of 2.65 years is a fissionable material with all the ensuing questions of following the safety measures when working with the source as well as other problems.

We have studied a potential of the NAA method use for estimating superdispersed gold content in the soil samples by the use of model experiment on the base of the IR-8 research reactor [6]. To accomplish this, samples of the soil with addition of different quantity of gold in the form of nanoparticles were prepared. There was used a water suspension of gold nanoparticles of quasispherical form with diameter of 20 nm, concentration of 0.05 mg/ml (made by Nanocomposix company, Canada, ECP1048). The soil samples of approximately equal volume in the eppendorf test-tubes with volume of 2 ml and weight of 1.08 g were added by controlled volumes of the aforementioned suspension of gold nanoparticles with the following thorough mixing. There were prepared 8 samples with different concentrations of gold nanoparticles; in so doing part of the samples has been prepared after preliminary controlled dilution of the origin suspension in distilled water with the following thorough mixing.

Prepared in such a manner samples has been placed into the sealed aluminium container and has been irradiated during 6 h in the channel of IR-8 research reactor with the average thermal neutrons flux density of $3 \cdot 10^{12}$ n/(cm$^2 \cdot$s). After a five-day aging, the samples have been measured on spectrometric apparatus; gold content in each sample has been estimated. Taking into account that the half-value period of activated isotope ^{198}Au equals to 2.7 days, the measurements have been corrected for decay depending on the time of measurement.

Samples activity measurement results showed that there is a principal possibility to estimate gold (including ultradispersed form) concentration in the soil samples with weight of about 1 g with concentration of about

0.01 mkg/g, which corresponds to the concentration in macrosample of about 0.01 g/t. Taking into account that a payload volume of the IR-8 research reactor is about 500 cm^3, the weight of analyzable samples may come to nothing more than 1 kg, which allows to estimate gold concentration in samples (including ultradispersed form) at levels of hundred times less than a commercially profitable value. It should be pointed out that time of radiation treatment (and delay time) of the sample can be essentially lessened because the aim of the fulfilled experiment was a reliable detection of small gold quantities in an assay. Having volume of the irradiated sample increased, real timing data are possible to estimate by calculation (as a first approximation) and (or) by experimental approach.

Clearly, the proposed method of estimating the gold content in soil samples is subject to the same restrictions that are considered in [8] with use of californium source of neutrons, adding one more disadvantage such as a need to use a nuclear reactor. However, the problem is theoretically solvable with the availability to use an optimum logistics. The proposed method with the use of nuclear reactor offers greater sensitivity than that with the californium source due to a larger payload volume of the measured sample and quite lengthy reactor's channel. It also has certain prospects of commercial use.

Prospects of nuclear reactions with charged particles application for detecting non-ferrous metals in investigated samples

In principle, list of non-ferrous metals the content of which in different samples can be estimated by using nuclear physical methods may be broadened by means of using nuclear reactions with charged particles [3].

Availability of reactions on fast neutrons and fast protons of the U-150 isochronous cyclotron of the NRC "Kurchatov Institute" for investigating titanium content in samples in the form of the TiO$_2$ powder in the ultradispersed form or rutile has been experimentally verified [6]. When irradiating by secondary beam of fast neutrons in an (n, p) reaction, radioisotopes ^{46}Sc and ^{47}Sc with the nuclear quality required for measurement ($T_{1/2}$ is equal to 83.8 and 3.35 days respectively) are arisen on the natural isotopes of titanium. It was shown that it is impossible to achieve high sensitivity for the method of titaniferrous materials detection because of relatively small section of (n, p) reaction and insufficient power of the secondary beam of fast neutrons. Essentially greater prospects possess a method based on activation of natural titanium isotopes by fast protons with generating radioactive vanadium isotope ^{48}V in (p; n, 2n,...) reactions. Isotope ^{48}V is characterized by a large enough half-value period (15.98 days) and by gamma lines convenient for a gamma spectrometry analysis. Such a method of estimating titaniferrous materials in investigated samples seems to have an actual prospect.

Use of X-ray fluorescence analysis methods for non-ferrous metals detecting in investigated samples

The X-ray fluorescence analysis (RFA) is based on excitation of the investigated nuclei electron shells with further emission of photon radiation [4, 5, 10–14]. This method is a non-destructive one, which is its doubtless advantage. It also guarantees high accuracy and repeatability of results and allows to quantitatively determining large number of elements comprised in the investigated material. Typical bottom detecting limits lie within 0.1 and 10 ppm. Possibility of elements detecting in samples of small volume and mass as well as the rigid binding of non-destructive methods to standard samples may be to some extent treated as disadvantages. Nevertheless, some recent attention has been focused on availability of measurements without comparison samples [15].

In the NRC "Kurchatov Institute" carried out were a series of experiments on application of the RFA method modification with the X-radiation substitution by the synchrotron one or bremsstrahlung of electrons, moving along the curved trajectory. Basics of the method are stated in [16]. An advantage of such a method of radiation generation lies in possibility to vary energy in a wide range for excitation of electrons on K shells (in contrast to X-radiation which excite electrons mainly on L shells of elements' nuclei). Thus, exciting electrons on K shell of argentums requires the X-radiation energy of 28 keV, which is inaccessible when using the X-ray tube. All of this allows to significantly raise the limits of elements detection (by 1–2 order when compared to X-ray tubes) and to analyze samples of extremely small volume and mass (about units of mg).

Due to RFA, the list of non-ferrous metals accessible for detection with the use of nuclear physical methods may be essentially broadened by such elements like K, Ca, V, Sr, Y, Pd, In, La, Ce, Hg, Tl, Pb.

Conclusion

The fulfilled experiment on estimation of gold nanoparticles content in the soil samples by the neutron activation method has allowed to correctly estimate gold concentration in the samples by the use of the IR-8 research rector with the thermal neutrons flux average density of $3 \cdot 10^{12}$ n/(cm$^2 \cdot$s). Fundamental restriction of the method sensitivity by isotope ^{198}Au is about 10^{-11} g/sample, restriction by sample volume is 500 cm^3, which allows to estimate the gold (including its ultradispersed form) content in samples at the levels hundred times smaller than the commercially profitable value.

Possibility of applying the nuclear reactions with charged particles has been experimentally showed by example of the fast neutrons and fast photons interactions with titanium nuclei in rutile powder (titanium oxide in a ultradispersed form).

List of non-ferrous metals detecting of which is possible by the use of nuclear physical methods of thermal neutrons or charged particles activation, may be essentially broadened

by using the X-ray fluorescence methods based on synchrotron radiation. The most important advantages of the enumerated methods are simplicity of sample preparation and absence of destructive effect on investigated sample which may be used for repeated analysis.

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