ACTIVATION ANALYSIS IN GOLD INDUSTRY

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Introduction

Nuclear techniques and methods were, are, and will be very important for many fields of science, agriculture, industry, etc. Among other examples one can remember role of the nuclear medicine (radiotherapy and radiodiagnostic methods) or semiconductors (communication, computing, information, etc.) which industrial production has been on initial stage based on activation analysis.

One of very illustrative examples is application of nuclear methods in gold industry. This is given by favorable nuclear properties of gold.

Uzbekistan is one of the main producers of gold. Open-cast mining and hydrometallurgic extraction (using leaching by cyanide and sorption by ion-exchange resin) is the mostly used technology. The typical gold ores are sulfide and contain elevated concentration of As and Sb. That needs special technology of gold extraction. Importance of gold for Uzbekistan economy is a reason why for many years there are carried out studies concerning to gold production. These studies include also nuclear methods and their results are successfully used in gold industry.

The present paper gives a brief overview for period of 25 years. For many reasons most of these studies were not published before completely. Despite some results are obtained decades ago we decided to present the overview as an example how nuclear methods can cover requirements of the whole process. We are trying to sort these studies according to methods and applications.

Methods

One of the most important requirements to analytical methods for gold industry is analysis of representative samples. That means that gold concentration in the sample to be analyzed has to be the same as in studied (proceed) ore. Gold is usually distributed in the ore very inhomogeneously. Representativity depends on type of ore and grade of milling. The classic fire assay to obtain reliable results foresees grinding of up to 25 kg of ore, then reduction this sample by divider to 2-4 kg, then milling to about 50 mesh and reduction to two subsamples 50 g each. For size of particles less than 1 mm the representative sample for our ores is 200 g. Many nuclear methods allow to analyze bulk sample up to 25 kg. This advantage together with other advantages (sensitivity, no necessity of sample decomposition, productivity, etc.) makes nuclear methods very convenient for gold industry.

Instrumental Neutron (n,□) Activation Analysis using Nuclear Reactor. Determination of gold using reaction ^{197}Au(n,□)^{198}Au ($T_{1/2}$=2.7 d., $E_{□}$=412 keV) is extremely sensitive. To reduce interferences samples are usually irradiated by epithermal neutrons (using shielding by cadmium or/and boron). Depending on matrice composition detection limit is about 0.001 □g/g.

Radiochemical Neutron (n,□) Activation Analysis using Nuclear Reactor. For radiochemical separation of gold different methods may be used - precipitation by gold reduction, ion exchange, extraction, etc. Detection limit in this case is close to the theoretical value - up to about 10^{-12} g. Radiochemical separation is necessary in of gold analysis to separate elements to be determines from high radioactivity of ^{198}Au. Usually required efficiency of gold removal has to be 10^{6} or more.

Neutron (n,□) Activation Analysis with Preconcentration using Nuclear Reactor. Preconcentration allows to reach sensitivity better than in INAA but lower than in RNAA. Usually sorption processes are applied for preconcentration - activated charcoal, anion exchangers, etc. The most important advantage is possibility to prepare the samples in field conditions (in sea expeditions) in case of water analysis when sample storage is connected with possible loses of gold by adsorption on the flasks surface, in application of nuclide neutron sources when large samples are to be analyzed, etc.).

Instrumental Neutron (n,n') Activation Analysis using Neutron Generator. Next possible reaction is ^{197}Au(n,n')^{197m}Au. ($T_{1/2}$=7.2s, E_g=279 keV). This reaction is hardly acceptable using reactor or nuclide neutron source because of low yield of ^{197m}Au at the fission neutron energy. Yield is growing when neutron energy is more than 2 MeV. But at neutron energy more than 4 MeV interferences from (n,p) reactions on matrix elements grow significantly and do not allow to increase gold determination sensitivity.

Photoactivation (□,□') Analysis. For photoactivation the linear accelerators, microtrons, betatrons, and cyclotrons may be used. The most convenient reaction is $^{197}Au(□,□')^{197m}Au$. ($T_{1/2}$=7.2s, E_g=279 keV). Analysis is made by □-irradiation at about 5-8 MeV because at higher energy grows interference from photo-fission and activation of some interfering elements. It is also possible to use reaction $^{197}Au(□,n)^{196}Au$ ($T_{1/2}$=6.2 d., $E_□$=354 keV) but this reaction needs long time of irradiation.

Analysis with Nuclide Neutron Sources. Using nuclide neutron sources - Po-Be, ^{252}Cf, ^{124}Sb-Be, etc. the (n,□) reaction is realized. Of course, the sensitivity is much lower than using neutron reactor but the main advantage is possibility to use the NAA in field and in small laboratories. Very important is possibility to use these sources in field or in small laboratories.

Prompt □-ray Analysis and Neutron Adsorption.. Analysis using prompt □-irradiation MeV) from n,□ reaction can not be used for gold determination but can be used for some elements, which concentration has to be known to control technological process. Most important for sulfide ores processing is determination of sulfur to modify process depending of this element concentration. Very high neutron absorption cross-section for gold allows to determine elevated concentrations of gold in bulk samples. Very useful for these tasks are nuclide neutron sources.

Activation Autoradiography. When the condition of analysis (irradiation and cooling time) are chosen properly there are possibility to make the ^{198}Au irradiation predominant after irradiation of ores (or rocks) sections in nuclear reactor. In this case contact of section with photographic emulsion allows to obtain the spatial distribution of gold. As an example on Fig. 1 is given distribution of gold in gold ore section[1].

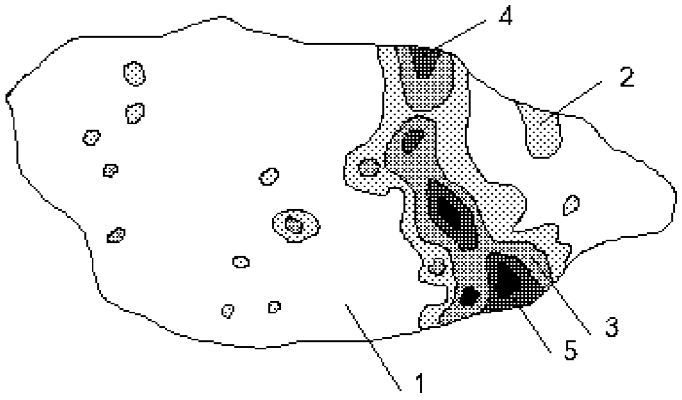

Fig. 1. Photometry of gold ore section autoradiography in gold content (g) on 0.02mm^2 area, 1-less than 10^{-6}, 2-(1-2.5)x10^{-6}, 3-(2.5-10)x10^{-6}, 4-(10-15)x10^{-6}, 5-more than 15x10^{-6}.

Combination of this method with fluorescence photography, analysis using laser microamounts of material transfer from irradiated by neutrons section with subsequent □-spectrometry, track detecting methods (boron, uranium, etc.), etc. allows to obtain very important data about gold distribution and correlation of geochemical behavior of gold and other elements.

X-Rays Methods. Registration of spectra of characteristic X-rays excited using X-ray tubes or sealed nuclide sources allows to determine many elements with detection limit about 1□g/g. It is enough to determine accompanying elements an to analyze gold technological samples.

Radiotracers Technique. Gold isotopes of high specific activity be produced using nuclear reactor or cyclotron. Their application is very fruitful in laboratory conditions on stage of elaboration or modification of technological process as well as in factory condition for monitoring of gold production.

Other methods. Obviously, other nuclear methods are also applicable to gold industry - isotope dilution, activation analysis using charged particles, etc. but at present these methods did not find wide practical application.

Applications

Geochemistry of Gold. High sensitivity and productivity of neutron activation analysis is very important for study of gold geochemistry, allowing gold determination beginning from regular gold abundance in rocks (in range of 0.001 - 0.005 mg/g). The main task of geochemical studies is to find the main regularities of gold behavior in Nature and ores genesis. Results of these studies make the scientific background for search for

gold. Preconcentration using coprecipitation on high purity $Fe(OH)_3$ has been used right on scientific ship for study of gold distribution in Atlantic and Pacific Oceans. After expedition concentrates were analyzed using INAA and nuclear reactor. Instrumental and Radiochemical NAA has been used for tens thousands of analyses of rocks, ores, soils, surface and ground water, plants, and airborne particulate matter to modernize existing and develop new methods for search for gold. Very fruitful for desert conditions to detect deposits covered by sand and rocks is biogeochemical method in which sample of plants are analyzed using INAA. The rots are "pumping" gold from levels up to 50 m deep and accumulation factor (gold concentration in plant to soil ratio) for some species reached thousands. High productivity of method allowed to create maps of gold distribution. Similar is hydrochemical method. Samples of surface water (5 l) were acidified by high purity HNO_3 passed through microcolumn (0.4x2 cm) with basic anion-exchange resin and than analyzed using NAA. Simplicity and productivity of this method allowed to make annually up to 5,000 analyses and to trace gold distribution in water.

In geochemistry very important is analysis of monomineral fractions (different minerals are under microscope taken manually from ground sample). Preparation of sample is very labor consuming. Application of INAA because of its high sensitivity allows to reduce required amount of sample many times.

Activation autoradiography allows to determine spatial distribution of gold and some accompanying elements. Using this technique the stepwise growth of gold inclusions has been found. This regularity allows to describe quantitatively the process of ores genesis.

Geology and Prospecting. For gold prospecting acceptable determination limit is 0.01 □g/g. It allows to use radiochemical and instrumental neutron activation analysis on nuclear reactor for productive routine analysis. Such a method was used for analysis of hundreds thousand samples of rocks, ores, soils, water and plants and allowed to detect some new gold deposits. Under rather less productivity can be used nuclide neutron sources (^{252}Cf, ^{124}Sb-Be, ^{210}Po-Be, etc.) with preconcentration.

Typical example bulk samples analysis is determination of gold in ores for its' reserve determination. The number of required analyses on the single deposit amounting to tens of thousands. After preliminary studies of gold distribution, sample homogeneity and acceptable size of ore particles, neutron and gamma-rays in bulk sample, influence of interfering nuclides (elements), etc. the following device and analytical procedure was elaborated[2]. The system optimized for gold-bearing ore samples of up to 300 g mass includes horizontal channel of nuclear reactor, pneumatic transport device with a rabbit collector containing 3,000 samples, □-spectrometry system, system for data accumulation and treatment, and control system. The automated analysis procedure consists in irradiating successively the samples (160-300 g, grinding <3 mm) during short time (25 s) by flux 10^{12} n/cm^2·s, exposing them during 7 days and measuring. During a cycle the rabbit collector is gradually filled up and all the samples having been irradiated on the same day are extracted, each empty cell being filled again by a rabbit irradiated. During measurements samples rotates to eliminate probable inhomogeineities.Productivity of device is about 70,000 samples a year. Many elements are determined simultaneously with following detection limit: Au - 0.01 - 0.02 □g/g, Sc, Eu, Yb, Lu - 1 - 10 □g/g, Co, As, Sb, Cs - 10 - 100 □g/g, Rb, W - 100 - 1000 □g/g, Na, Fe - >1000 □g/g. As a comparator ^{99}Mo has been used. This method has been officially licensed for reserve determination.

On the other hand there are possibility to use nuclide neutron sources like ^{252}Cf with flux 10^{10} n/s which allows to determine by INAA gold in ores with detection limit of 0.1 -0.5 □g/g^3 . Special transporting system allowed to carry out analyses directly on gold fields. Productivity of such method is about 100 samples a day. The most important advantage of this method was reduction of time to obtain analytical data because of elimination of time to transport samples to central analytical laboratory. More rapid data obtaining allowed significantly reduce number of necessary prospecting bore holes.

Transporting container for ^{252}Cf had special flexible tube (25 m in length) which allowed to transport source through the hole and to determine gold in hole. Special □-spectrometry bore hole tool (Ge(Li) detector, liquid nitrogen cooler, and preamplifier) has been created for bore hole 10 cm in diameter. Rather low neutron flux was a reason that velocity of hole logging was about 1 m per hour. It is hardly acceptable for prospecting, but using more powerful source there is possible to reach quite acceptable productivity.

Mining and Ores Sorting. Processing of poor ores or gangue rocks is expensive and economically unacceptable as well as wasting by mistake the rich ores. That means that ores have to be sorted on various stages of ores excavation and conditioning. For sulfide gold ores optical methods of sorting (applied for quartz gold ores) are not reliable. For some types of ores sorting may be carried out on the base of correlation of concentration of gold and some accompanied elements (e.g. As). But found correlations are not enough strong to be completely reliable. At present only sorting according to gold concentration is fruitful.

For routine analyses of ores (especially to select ores into processing or tailings) various nuclear methods may be used but rapid methods are, obviously, most preferable.

One of the very successful method of ores preliminary sorting uses □,□' reaction. Excavation foresees explosive demolishing of blocks of ore in size approximately 10x10x5 m. That means that there are drilled blast holes in 10x10 m grid. Dispersed material (slime) is extracted from blast holes and analyzed using photoactivation. Then, according to the analyses results ore is transporting to the factory or to poor ore pile.

For high enough productivity of analyses special automated system has been installed[4] This system consists of linear accelerator, transporting system, double-channel □-spectrometer, system of data accumulation and treatment, and control system. Weight of sample is 500±100 g. Detection limit is 0.4±0.1 □g/g. Reproducibility less than 10% at concentration 2 □g/g. Duration of single analysis is 20 s and productivity more than 400,000 a year. This system is working for several years and similar systems are installed at other gold deposits of FSU.

It should be noted that system used microtron is also successfully used in the East Siberia.

As a next step at present is ready the project of sorting system in trucks. In this project the sample of about 25 kg of ore is taken from the tracks and analyzed using □,□' reaction on linear accelerator. During the time of ore transportation to the factory results of analysis allows to direct the track to factory or to poor ores pile.

The following step is sorting of pieces of ore after rough grinding (size 20 - 150 mm). The preliminary experimental studies have shown than for this purpose the reaction n,n' using powerful neutron generator should be very promising.

Gold Refining. The typical process is ore milling, cyanide leaching, absorption on ion exchange resin, desorption, and refining to 99.999%.

To select proper conditions of process ore is analyzed for sulfur. Samples about 5 kg in mass are irradiated by ^{252}Cf neutron source (10^8 n/s) and simultaneously using Na(I)-detector is detected photopeak 4.4 MeV from neutron capture by sulfur.

After milling on ball mill fraction of ball debris is removed using gravitation and magnetic separation. This fraction contains significant amount of gold and analyzes using neutron absorption. Samples about 25 kg in mass are irradiated by ^{252}Cf neutron source (10^6 n/s). Analysis duration is 10-20 min. with determination limit about 20 □g/g. This fraction is treated separately.

Efficiency of milling has been studied using neutron activation autoradiography. Portions of pulp after various time of milling have been taken. Dry powder has been irradiated by nuclear reactor neutrons and distributed on flat surface as a thin layer. This layer has been contacted with photoemulsion. Changes of sizes and distribution of gold containing particles allowed to conclude that milling process can be reduced in duration at least on 20%. This, obviously, reduced cost of milling.

Sorption process is carried out in five large absorbers. Ore pulp and ion exchange resin are transported in this system oppositely. After the final absorber pulp is transported to tailing pile and resin to desorption.

Development of the process foresees application of new types of resin. For study of absorption process there are necessary preliminary laboratory studies. Instead of gold determination on various stages (before and after sorption or desorption in pulp and resin) radiotracer ^{198}Au is very successfully used because after complete isotope exchange its activity is proportional of gold content and may detected very simply and rapidly. This allows to check existing ore elaborate new technology more rapidly than using analytical methods.

To check the technological process samples of pulp, liquid phase and resin are taken regularly from absorbers and deserter. For determination of gold in resin is used XRF analysis. For liquid samples has been used isotope dilution method because of low gold concentration in liquid waste. For determination of resin exchange capacity (because of poisoning of resin by accompanied elements) ^{198}Au is added to solution. After contact with resin activity of solution and resin allows to determine the distribution coefficient and exchange capacity.

For total characterization of process the following experiment has been carried out. To portion of pulp of 1 m^3 has been added sufficient amount of ^{198}Au. This mixture has been exposed with mixing for 5 days for isotope exchange an than introduced into process. Then samples of pulp, solutions and resin has been periodically taken from absorbers an desorber. Activity of these samples were proportional to gold content. The main conclusion was that mixing of absorbers in some cases are not enough efficient. This conclusion stipulated changes in mixing of pulp with resin using air-lifting system.

At final stage high concentration of gold is may be determined using XRF analysis. In some cases multielemental radiochemical NAA has been used as an additional method for gold certification.

Fruitful is also multielemental analysis using nuclear methods on various stages of process. These analyses were very important to elaborate technologies of some elements by-production (Ag, Pd, Se, W).

And finally, nuclear are used for analysis of wastes to prevent possible loses. But, because of sophisticated technology, there were never detected elevated amounts of gold in wastes.

Other Fields. For analysis of items made of gold or containing large amounts of gold the non-destructive methods are obviously preferable. The most applicable method is XRF. Analytical system using ^{57}Co source and computed □-spectrometry system is very successively used for analysis of coins and jewels for jewelry, forensic sciences, archaeology and other fields.

Especially for analysis of gold samples of various forms and sizes (rings, chains, plates, medals, ear-rings, coins, etc.) the special simplified system has been elaborated[5]. For X-rays excitation is used ^{57}Co source (0.2-0.5 GBq). System has two Na(I) detectors - one for registration of K-lines of silver and copper and another for L-line gold registration. Samples may be various in form from 0.1 to 100 g. Time of analysis is 0.5-5 min. and accuracy less than 0.2% of three metals (Au, Ag, Cu) concentration.

Neutron absorption method may be used for analysis of bulk samples of gold containing scrap (e.g. from electronic devices) to utilize gold.

In some forensic investigations is necessary to detect the fact that some sample has been contacted with gold (for example - dishes of balances). Traces of gold in case of such a contact are detected very easily using of INAA of cloths or cotton with which the sample has been wiped.

Conclusion

The wide application of nuclear methods (Tab. 1) is given not only by importance of gold but by extremely favorable nuclear properties of gold nuclides. This is why nuclear methods are (or should be) successfully applied in production of uranium, scandium, indium and other elements having nuclides with favorable nuclear properties.

Table 1

Nuclear methods applications in gold industry

Method	Field of Application
INAA	Geochemistry, search for gold, gold field inventory, forensic sciences. Analysis of ores, soils, water, airborne matter, plants, etc.
Radiochemical NAA	Geochemistry, gold refinery. Analysis of ores, soils, water, airborne matter, plants, gold, etc.
NAA with preconcentration	Geochemistry, search for gold. Analysis of ores, soils, water, airborne matter, plants, etc.
Activation autoradiography	Geochemistry of gold and gold extraction process.
Photoactivation analysis	Preliminary sorting of ores
Analysis using $^{197}Au(n,n')^{197m}$ reaction	Conditioning and sorting of ores
INAA with nuclide neutron sources	Works in field, in bore-holes and at factories.
XRF	Perfectioning of the process, jewelry, technology, forensic sciences.
Radiotracers technique	Development of technology, monitoring of the process.

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