

NUCLEAR-PHYSICAL METHODS OF ANALYSIS OF NOBLE METALS AND RARE-EARTH ELEMENTS

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A summary of the analysis noble and rare metals by combined methods is presented. The electrodeposition of gold at a carbon film and Rutherford backscattering was used for determination its in ores. The sorbents and particle induced X-ray emission was used for determination rare and noble metals in ores. The minimum detectable concentration for ores was 0.1 µg/g.

PACS: 87.58.Ji.

Development of a new method of analysing all metals in the noble metals group and rare-earth elements is a matter of considerable interest. Combined methods reducing minimum detectable concentration and extending significantly the field of application were implemented in electrostatic accelerators NSC KPTI.

DETERMINATION OF GOLD CONTENT OF ORES BY THE RUTHERFORD BACKSCATTERING (RBS) OF HELIUM IONS

The essence of the method lies in analysing the targets obtained by electrodeposition of gold at a carbon base using elastic scattering of accelerated particles. In this case, the energy of scattered ions E_1 is expressed in the following way:

$$E_1 = E_0 \{ [M_2^2 - M_1^2 \sin^2 \theta]^{1/2} + M_1 \cos \theta \} / (M_2 + M_1)^2,$$

where E_0 – energy of incident particle, M_1 , M_2 – masses of the incident particle and target nucleus, θ – scattering angle of the particle with a mass of M_1 . In our case (a thin target of the substance being determined) the energy of scattered particles for a set detection angle will correspond to the atomic weight of elements. Scattering cross-section $\sigma(\theta)$:

$$\sigma(\theta) = (Z_1 Z_2 e^2 / E)^2 (1 / \sin^4 \theta / 2),$$

where Z_1 , Z_2 – charges of the incident particle and target nucleus. The yield Q_d of particles registered by the detector is expressed:

$$Q_d = \sigma(\theta) \Omega Q N_m,$$

where Ω – detector solid capture angle, Q – number of incident ions, N_m – number of atoms per cm^2 . The minimum value N_m , which could be detected with the help of RBS [1] is:

$$N_m = (Q_d Y / \sigma(\theta) d\Omega a)^{1/2},$$

where Y – scattering products yield, a – area of the beam spot. When using helium ions with $E_0 = 2$ MeV, $\theta = 160^\circ$, $d\Omega = 2 \cdot 10^{-2}$ Sr, $Y = 10^{-3}$, $a = 0.1$ cm^2 , with the minimum detection number being equal to 100 (error = 10%), the thickness of the layer for gold is 10^{12} atoms/ cm^2 or 0.3 ng/ cm^2 . Experience shows that the minimum detectable number for gold is $5 \cdot 10^{11}$ atoms/ cm^2 . When using annular semiconductor detectors, the minimum detectable number can reach 10^{11} atoms/ cm^2 .

Fig. 1 shows a typical RBS spectrum for helium ions with energy of 2.87 MeV at carbon target after 30 µg of

gold were deposited in electrolyses. The dose of helium ions was 30 µCl. Energy resolution of the semiconductor detector was 28 keV for alpha-particles with an energy of 5 MeV. The number of counts in peak is $50 \div 100$ counts from 1 µg of gold per µCl. The energy of helium ions was picked to satisfy the condition that the relation of counts in gold peak to total number of counts from carbon should be maximum. It is practically impossible to separate platinum, osmium, iridium and gold. Therefore, gold detection selectivity was achieved by choosing an optimum electrolysis voltage and electrolysis composition.

Gold was concentrated by electrolysis in a quartz cell, with the anode made of the special spectrally pure graphite and the cathode of pyrolytic graphite (total impurities content is less than 1 ppm) [2]. Solution $\text{HCl} + \text{HNO}_3$ at $\text{pH} = 2$ was used as electrolyte. Conditions of electrolysis: voltage 0.76 - 0.9 V, current strength 0.006 - 0.03 mA, target area – 1 cm^2 , electrolysis time – 60 minutes. The standard curve was obtained by method of addition [2].

To analyse the gold content of ore, the sample was decomposed [3] depending on its constitution. When gold content of water is analysed, gold can be deposited directly after the sample with a volume of 200-500 ml was brought to $\text{pH} = 2$ [4].

DETERMINATION OF NOBLE METALS USING THE METHOD OF PARTICLE INDUCED X-RAY EMISSION (PIXE)

The method of PIXE induced by accelerated particles possesses more universal characteristics for the purposes of elemental analysis. It analyses the source

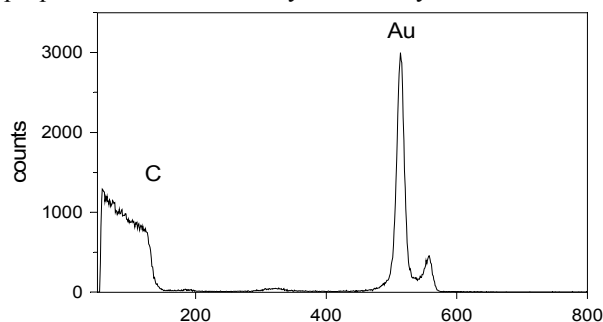


Fig. 1. Backscattering spectrum of helium ions with energy 2.87 MeV from a carbon target

matrix and detects 10 - 15 elements simultaneously. The advantages of the PIXE analysis are especially pronounced when detecting the whole group of noble metals using sorbents. Ore samples can be decomposed and sorbed in field conditions or at a mine, and measurement can be done in laboratory with the help of Van Graaff accelerator. The sorbents containing low-Z elements should preferably be used. This suggests a low level of background braking radiation and PIXE by sorbent atoms (activated carbon, silica-based sorbents, etc.).

The method of proton-induced PIXE with the energy of protons 2 - 3 MeV combination with the use of sorbents produced the lowest minimum detectable concentration when the analysis fell into the following pattern: sample decomposition, sorption, desorption of noble metals by thiourea and their electrodeposition at carbon base followed by analysis using Si(Li)-detector. HCl + HNO₃ solution doped with acetic acid and investigated thiourea sample with noble metals was subjected to electrolysis.

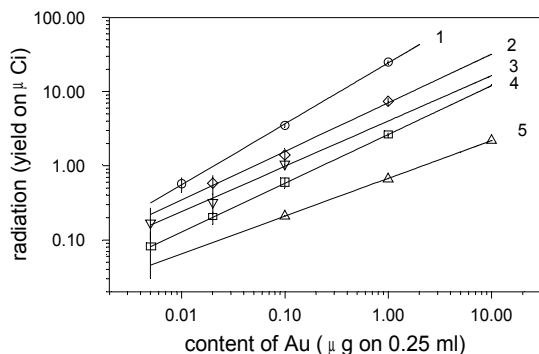


Fig. 2. Dependence of yield of X-rays on gold for various requirements of a cathode, deposition at pH=0.6:

- 1 – HCl+HNO₃+CH₃COOH U=5.0 v,
- 2 – HCl+HNO₃+CH₃COOH+SC(NH₂)₂ U=5.0 v,
- 3 – HCl+HNO₃+CH₃COOH+SC(NH₂)₂ U=4.0 v,
- 4 – HCl+HNO₃+CH₃COOH+SC(NH₂)₂ U=2.6 v,



U=1.1 v

The final analysis was carried out using Van Graaff accelerator with a Si(Li)-detector with the energy resolution of 280 eV for the line of 5.9 keV. The energy of protons was equal to 2 MeV. Fig. 2 represents standard dependencies of gold L-line yield as a function of its content of electrolyte and conditions of cathode deposition.

Deposition is most complete for standard gold solution (curve 1), where the degree of deposition is 70% for 1 μg dissolved in 25 ml, and 100% for 0.01 μg dissolved in 25 ml. In cathode deposition of gold from thiourea in optimum conditions, the degree of deposition made 21% for 1 μg dissolved in 25 ml and 60% for 0.02 μg dissolved in 25 ml. In all cases, the time of cathode deposition was 30 min. The gold minimum detectable concentration of such method was 2 ng/g.

Whenever the method of analysis involved decomposition of the sample, sorption with subsequent direct Van Graaff accelerator determination of noble metals in sorbent applied on the carbon plate, the obtained detection limit reached 50 ng/g due to the presence of iron, calcium, strontium, bromine, zinc impurities in it, and, hence, their increased background radiation. Fig. 3 gives a typical spectrum of an ore sample containing Au, Pt, Pd, Ag. This variant of analysis proves to be most effective for the elemental analysis of ore with industrial content of noble metals.

USE OF MULTIPLY CHARGED IONS TO DETERMINE GOLD CONTENT OF ORES

The use of multiply charged carbon and nitrogen ions with an energy of 5 - 7 MeV to induce PIXE M-lines in gold provided high content of medium weight metals (A = 40 - 80) deserves special attention. In this case, only gold provided high content of medium weight metals (A = 40 - 80) deserves special attention.

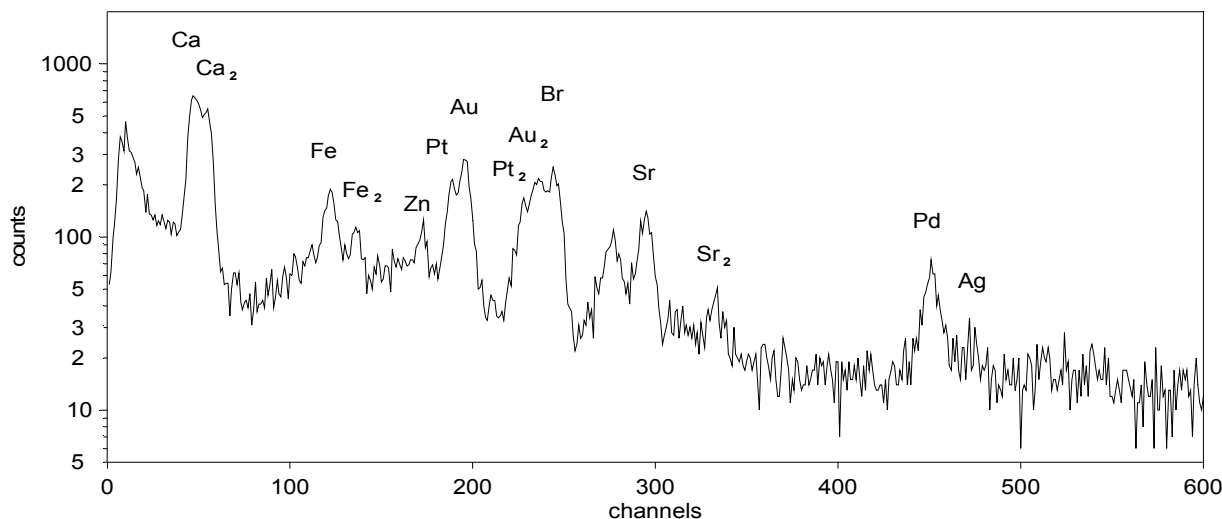


Fig. 3. Spectrum PIXE of sorbent from a sample of auric ore

In this case, only M-lines in elements are excited, which makes it possible to determine gold content at the level of 0.1 ng/g. Ionization cross-section for equal velocities of impinging particles is in proportion to Z^2 (Z – is the charge of incoming particles), the type of ions employed has little effect on the intensity of braking radiation [5]. Therefore, signal/background ratio is higher when multiple charged ions are utilised. The gold M-lines with the energy of 2.12 and 2.20 keV were registered with an X-ray spectrometer. A 1 - 5 mg/cm² thick zircon X-ray

filter protected by a 50 µm thick beryllium film against backscattered particles was used to reduce target background radiation with energy of more than 2.215 keV. Interference caused by phosphorus K-lines, zircon and niobium L-lines was eliminated by applying electrolytic deposition as these impurities do not deposit at the cathode. Optimum gold electrolysis conditions were reducing possible interference from platinum, iridium and osmium.

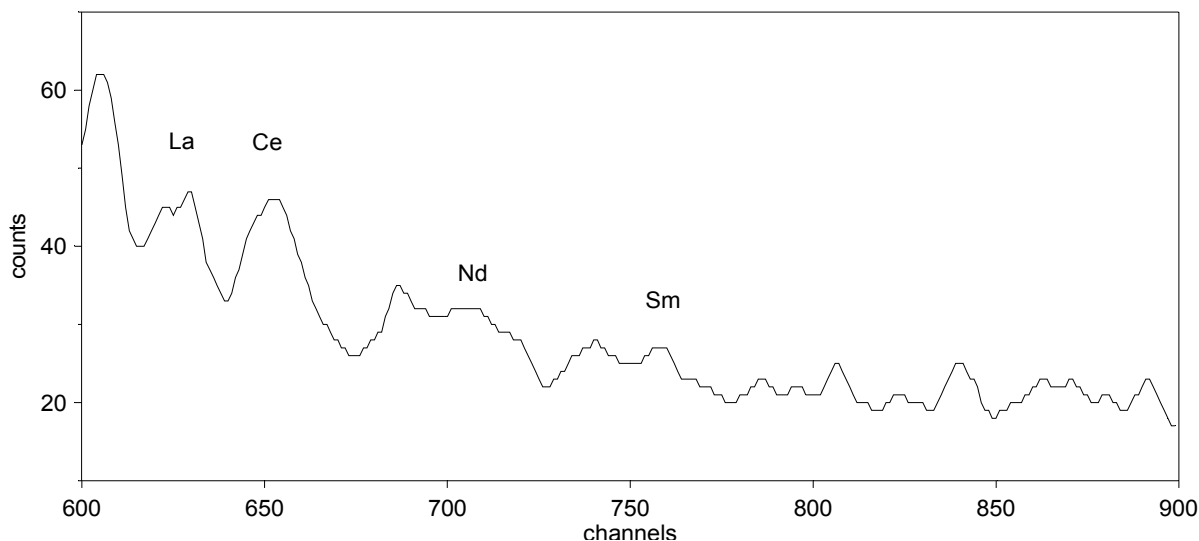


Fig. 4. Spectrum PIXE of a precipitate of ethanedioic acid

DETERMINATION OF RARE-EARTH ELEMENT CONTENTS OF ORES

The increasing demand for rare-earth elements used in production of anticorrosive, heat-resistant, high-temperature alloys calls for development of more sensitive methods of determining their content in ores, mine and dressing mill spoil heaps, etc. Determination of each rare-earth element by methods employed in analytical chemistry presents a challenging task. Chemical group deposition of REE combined with PIXE method makes it possible to effectively solve the problem.

The design of experiment includes sample decomposition, multiple precipitation of rare-earth elements by ammonia solution, dissolution of the precipitate in hydrochloric acid followed by rare-earth elements precipitation by oxalic acid solution. The process of analysis of the manganese ores was modified by including after ammonia precipitation the additional operation of electrolytic deposition on mercury-pool cathode. The resulting precipitate was applied on carbon base and analysed with Van Graaff accelerator using PIXE induced by protons with the energy of 2.3 MeV. As L-lines interfere, K-radiation was used for selective detection of rare-earth elements. When the energy of protons is 2 - 3 MeV, the K-shell ionisation cross section is by 2 - 3 orders of magnitude smaller than that of L-shell in rare-earth elements. The minimum detectable concentration for ores was 0.1 µg/g. It quite satisfies the requirements for exploration and processing of commercial ores [6]. Yttrium is determined at the level of 10⁻⁵ g/g without any sample preparation. It further served as inner bench

mark for oxalic acid complexes. Fig. 4 shows typical proton induced PIXE in oxalic acid precipitate.

Thus, the developed nuclear-physical methods of microanalysis of noble and rare-earth elements can be used in exploration and development of industrial deposits of noble and rare-earth ores, their determination in mine and ore dressing mill spoil heaps, as well as in geology, environment protection and medicine.

In conclusion we would like to thank Mr. V.V. Zolochovsky for his kind assistance in completing this work.

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