SOME ACTIVATION ANALYSES CARRIED OUT AT THE "INSTITUTO DE ENERGIA ATÔMICA"

Alcidio Abrão
Radiochemistry Division,
Instituto de Energia Atômica,
São Paulo, Brazil

INTRODUCTION

"Service function" of the Instituto de Energia Atômica Radiochemical Division included chemical analyses of a variety of materials such as berylium, graphite, uranium and thorium ores, zirconium oxide, etc. Radioactivation analysis was the chosen approach to the problems every time it could simplify the solution of the proposed analysis, especially in the case where material of nuclear purity should be analyzed.

This paper describes, briefly, the procedures used for some of the analyses carried out such as: determination of the hafnium content in samples of zirconium oxide and zirconyl chloride; sodium in demineralized water and in the pool water; non-destructive analysis of sodium in graphite; gold in minerals and ores; uranium in ores from gold mines and in the reactor's pool water; tantalum in ores; chromium in water from dams. Studies are being carried out for analyses of cadmium in uranium oxide of nuclear purity and for a method determining the proportion of the various rare earths elements in a mixture of total rare earths. A systematic study of hair composition has been started in order to verify the possibility of identification of suspect persons in criminalistic investigations.

GOLD AND URANIUM(4)

Minerals of gold from operating brazilian gold mines were analyzed simultaneously for uranium and gold. Uranium was analyzed by the amount of neptunium-239 formed by irradiation and gold by the isotope gold-198. The general technique of standard irradiation was also followed in this case. Radiochemical separations were required in this case since various activities were induced in the ore samples. Gold-198 and Neptunium-239 radioisotopes, were scanned in separate fractions and their amounts calculated by comparing areas in the corresponding photopeaks with the ones obtained with standards. Precision of the analyses were from 1% to 10% expressed as standard deviation, for ore samples containing 20 ppm of gold and 0.1% of U_3O_8.

RADIOCHEMICAL SEPARATIONS

Elements separated: gold and neptunium.

Principle: The method is based on the fact that the strong anionic chloroauric complex is selectively held by an anionic resin (Cl-form). The neptunium and other radioisotopes are eluted with dilute HCl acid.

Irradiated sample: ore samples from Canavieiras Mine, Jacobina, Bahia, containing SiO_2, Fe and S (pyrite) and As, Au, U, Na as minor constituents.

PROCEDURE

0.1 to 0.5 g ore samples are sealed in polyethylene vials and irradiated for two hours in a thermal neutron flux of 10^{12} neutrons/sec.cm^2. Standards of gold (as chloroauric) and uranium (as U_3O_8) were irradiated for the same length of time and at identical geometry. After irradiation a cooling time of 24-72 hours was observed. The irradiated samples were treated with aqua regia, centrifuged, and the residue washed twice with HCl 5M and then with water. The residue was dissolved with HNO_3+ HF acids mixture, fumed with H_2SO_4 acid and finally leached with water. The solutions were collected together and diluted to 100 ml. For analyses, aliquots were taken and the acidity was ascertained to 0.5 M, with HCl.

GOLD DETERMINATION

Small columns of 0.5 cm i.d. x 1.0 cm of height containing 1 ml of anionic resin (Nalcite SAR, Cl-form) were used. The resin was previously conditionated with 5 column volumes of NaOH M, HCl 10M and HCl 0.1M, respectively. The ore solution (20 ml) was percolated with velocity of about 1 ml/min and then the resin washed with 20 ml of HCl 0.5M and water. The resin containing the gold (chloroauric acid complex) was transferred to a polystyrene vial and the Au-198 activity determined. Standards containing both gold and uranium were prepared and the same procedure was applied to them and the gold of the standard solution was sorbed on the anionic resin exactly as described above. The efluents and washings of the columns were collected together and kept for the determination of neptunium (uranium). The identification of gold was made by gamma-ray scanning and its purity was checked by determining the half-life.

URANIUM DETERMINATION

The efluents and washings of the anionic resin column were warmed, neutralized with ammonium hydroxide and treated with hydrochloric acid to a little excess. To the solution, hydroxilamine hydrochloride was added until the yellow colour of ferric iron had fadded, so as to be sure that the reduction of neptunium was complete. The solution was transferred to a platinum crucible and one mililiter of 20 M HF acid and 20 mg of lanthanum (nitrate) were added dropwise. After the lanthanum addition the mixture was stirred during 5 minutes and centrifuged in a polystyrene vial. The precipitate was washed twice with one ml of a HF 1M + HNO_3 1M mixture, centrifuged again and then counted in the gamma scientilometer. The standard containing both gold and uranium after passing through the anionic resin, was submitted to an identical treatment. The identification of neptunium, as in the case of gold, was made by the gamma-ray spectrum and the purity was checked by half-life. The decay of Np-239 was followed by integral gamma activity counting of the precipitate of lanthanum (neptunium) fluoride. The evaluation of neptunium content, consequently U-238, was made by the areas of the peaks, their height, and by the integral gamma activity counting and compared with the corresponding data for the standard.

REMARKS

1. For gold no isotopic carrier is required.
2. It was observed that neptunium and gold had been separated from silica with relative facility by attacking the ore with aqua regia. After one digestion, all the gold and a considerable fraction of the neptunium were solubilized. So, for the gold determination, the complete solubilization of the residue (SiO_2) with HF is not required and the time of analysis is shortened.
3. Gold is determined by measuring the Au-198 activity directly in the anionic resin column, without any further gold separation.

URANIUM IN THE ION EXCHANGERS TANKS(2),(3)

The radioactivation technique for analyses of traces of uranium fixed on the ion exchangers tanks for the purification of the pool water Reactor of São Paulo, was applied by Lima, Abrão and Pagano(2, 3). After elution of an aliquot of the ion exchanger resin, uranium was extracted by ether (continuous extractor), the ether was evaporated and uranium fraction was irradiated with thermal neutrons. The induced neptunium-239 was detected and determined by the technique of Mahlman and Leddicotte(5). With this analysis it was possible to estimate that about 0.5 gram of uranium was held by the exchanger tank (112 kg of resin) when the new set of fuel elements were put in operation and after the resin had treated 5.7 x 10^6 liters of pool water.

The uranium found in the ion exchanger resin came from external contamination of the aluminum cladding of the elements (3,6).

DETERMINATION OF URANIUM IN THE ALUMINUM CLADDING OF FUEL ELEMENTS.(12)

The aluminum cladding of the fuel elements that are being made by the Nuclear Metallurgy Division is being examined for eventual contamination of the external part of the aluminum. Also the same type of analysis is being carried out for the fuel elements for the sub-critical facility (UO_2 pellets in aluminum tubes).

TANTALUM-NIOBIUM(7)

Tantalum was determined by activation analyses(7) in some ores from the Araxá area, State of Minas Gerais, Brazil. The samples contained phosphorus, niobium, tantalum, titanium, uranium, iron, manganese, thorium, calcium and rare earths. They were opened by acid attack and tantalum was determined in the total oxides (Nb + Ta + Ti) obtained by Schoeller's(8) procedure after burning the tannic acid precipitate. The tantalum content in the ore was determined by comparing the area of its photoelectric peak (Ta-182, half-life 111 days, 0.06 and 1.22 Mev) with that of a tantalum standard irradiated simultaneously in the same geometry, using a single-channel gamma-ray spectrometer. The same procedure was applied for the analyses of various flotation fractions of the same ores. The tantalum content in the original ore was found to be 0.003% to 0.07% in Ta_2O_5.

REMARKS

The Schoeller's procedure applied to those ores gave high results for Nb + Ta when compared with the tantalum results obtained by neutron activation analyses and the niobium results from polarography.

HAFNIUM IN ZIRCONIUM(1)

Samples of zirconium oxides were irradiated at IEA-R1 for periods ranging from three to six hours in thermal neutron fluxes of 10^{12} n/sec.cm^2. Separation of both elements(1) was achieved by applying procedures based upon the complex formation of zirconium and hafnium with sodium triphosphate ($Na_5P_3O_{10}6H_2O$).

HAFNIUM CONTENT IN ZIRCONIUM OXIDE. PROCEDURE.(1)

The hydroxides of zirconium-hafnium were precipitated by adding ammonium hydroxide to zirconium-hafnium sulphates solutions, filtering and washing the precipitate with dilute solution of the precipitant up to a negative test for sulphate. The hydroxides were dried and two aliquots were prepared for irradiation; to one of the samples a known amount of hafnium oxide was added and the samples were irradiated in a thermal flux of 10^{12} n/sec.cm^2 for three hours. The percentage of hafnium oxide was then determined by the relation:

$$\%HfO_2 = \frac{C_1P}{C_2P_1 - C_1P_2}$$

where P_1 and P_2 are the weights of samples 1 and 2 and C_1 and C_2 the activities in counts per minute (cpm) of samples; P is the weight of the standard hafnium oxide added to sample 2. The activities were determined at the Hf-181 photopeaks of 0.133 Mev.

Purity of zirconyl chloride samples for their hafnium content was checked(2) by non-destructive analyses by irradiating the samples and standards of hafnium oxide for the same length of time and at same geometry. Standards and samples were counted, without previous chemical separation, by scanning in gamma spectrometer and comparing the areas for Hf-181 peak at 0.133 Mev. Complete analyses could be made in two to four hours, depending on the irradiation time. Samples of zirconium with a hafnium content of 0.1% to 0.5% were easily analyzed.

SODIUM IN WATER(3)

Demineralized water (primary system), water from the pool and recirculating demineralized water (secondary system), were analyzed for their sodium content(3). The amount of sodium remained in the demineralized recirculating water (secondary system) and pool water was determined by evaporation to dryness of 250 ml samples in a platinum crucible, the residue transferred to a polyethylene vial with 1 ml of demineralized water and irradiated in thermal neutron flux of 10^{11} to 10^{12} n/sec.cm^2, for irradiation periods of half to four hours. Standards samples of sodium were also irradiated at the same geometry and for the same length of time. After irradiation, standards and water residues were transferred to counting vials and the activities measured by gamma-ray spectrometry. The average value for various samples was 0.4 ppm in sodium for thé pool water and 0.08 ppm for the demineralized recirculating pool water (repurification system).

REMARKS

1. For both pool water and repurified pool water, no chemical separation was required in the determination of sodium.

2. In the evaluation of the sodium content in water samples, the "internal standard method "(3) was applied. For each type of water three irradiation vials were prepared containing the evaporation residue of the water, the evaporation residue of the water plus an added mass of sodium (internal standard) and the same mass of sodium (external standard) used as internal standard. The results of sodium content of water calculated with the internal standard were in agreement with the ones calculated via external standard.

SODIUM IN GRAPHITE (2)

Non destructive activation analyses of sodium were carried out in samples of some brazilian pure graphites (2). The purity of national graphites samples were compared with the imported "nuclear pure graphite", as for example with the graphite used in the thermal column of the IEA-R1 Reactor. Amounts of sodium varying from 28 to 35 ppm were found in commercial Brazilian graphites while the graphite in the thermal column had a sodium content of 2.5 to 3.4 ppm. Those graphites samples could be analyzed in about two to four hours, including irradiation time, and using 0.1 gram of graphite with a reproducibility of 3%.

CHROMIUM IN WATER FROM DAMS(9)

In order to study the possibility of detecting leakages in dams by adding chromium salts to the water, it was necessary to know the content of chromium in some river waters. The procedure is outlined as follows: after the oxidation of chromium to chromate ion with hydrogen peroxide in hot ammoniacal medium, 3 liters of water are percolated through an anionic resin column (10 ml of Amberlite IR-401, OH-form). The chromate ion is eluted from the resin with 70 ml of 2M ammonium carbonate solution. The eluate is evaporated to dryness over an aluminum foil that acts as container for the residue. Alternatively, it will be tried to irradiate directly the anion exchanger in which chromate was adsorbed. Standards of potassium chromate mounted in the same way are prepared and irradiated at the same geometry and for the same irradiating period. Samples are left to cool for 6 days after irradiation and the chromium content is determined by comparison of the areas under the photopeak of Cr-51 (0.32 Mev) for the samples and the corresponding standards. Preliminary studies indicate that by this procedure it is possible to determine less than 0.04 ppm of Cr in water.

DETERMINATION OF PROPORTION OF RARE EARTHS ELEMENTS IN A MIXTURE OF TOTAL RARE EARTHS(10)

Mixtures of rare earths elements obtained through various steps of rare earths purification are being analyzed for their components using instrumental technique alone for some elements or instrumental technique and fast radiochemical separations in order to analyze the fourteen elements. Dysprosium, lanthanum and europium are elements in the mixture whose determination seems possible without previous chemical separation; for these elements short irradiation periods of from five seconds to five minutes, in a flux of thermal neutrons of about 3×10^{12} neutrons/sec.cm^2, are used. Nylon pneumatic rabbits are used for irradiation and samples can be counted from 30 seconds to one minute after irradiation has stopped.

Presently "library" spectra of pure rare earths radioisotopes is being formed by using a punched-paper tape readout system.

TRACE ELEMENT CHARACTERIZATION OF MATERIAL OF FORENSIC IMPORTANCE(11)

Studies have been started in connection with trace-element characterization in human hair. Later on the study is to be extended to other materials such as fingernails, soil, paint, etc.

EQUIPMENT AVAILABLE FOR ACTIVATION ANALYSES

Presently the available equipment at the Radiochemistry Division is formed by decimal scalers and Geiger tubes, manual and automatic single channel analyzers, multichannel analyzer and NaI (Tl) well scintillation counters. The multichannel analyzer (400 channels) system is provided with readout units: paper tape printer, X-Y recorder, computer typewriter, paper tape punch and reader units and spectrum resolver integrator. A pneumatic rabbit system is located near the counting room in order to allow work with short half-life radioisotopes. The corresponding thermal neutron flux, for this station, is about 3×10^{12} neutrons/sec.cm^2 at 2 Mw reactor power. Irradiations are carried out in nylon or polyethylene rabbits, for short irradiation periods and for work with short half-life radioisotopes, or in aluminum rabbits which are used for long irradiation periods. Usually samples are put in polyethylene envelopes of about one by one centimeter, and the envelopes in the rabbits. Rabbits' travelling time is about three seconds.

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