

3.7 RESEARCH IN THE FIELDS OF RADIOCHEMISTRY AND ACTIVATION
ANALYSIS USING THE LENA TRIGA NUCLEAR PLANT, V. Maxia, S. Meloni,
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In the past two years most of the research effort at the Radiochemistry Laboratory and National Research Council Center for Radiochemistry and Activation Analysis has been devoted to research and development of activation analysis using the TRIGA Mark II LENA reactor of the University of Pavia.

Fast neutrons have been used both in steady state and pulse mode, in the determination of oxygen in non ferrous materials. Oxygen has been determined (1) in OFHC copper through the reaction $^{16}\text{O} (n, p) ^{16}\text{N}$ ($t_{1/2} = 7.4$ sec) by irradiating samples and standards in the pneumatic system of the TRIGA.

The copper specimens were obtained by mill machining the initial cylindrical sheet and keeping under carbon tetrachloride. In the F-ring of the TRIGA reactor core, that may be reached by the pneumatic system, a fast neutron flux (energy greater than 6 Mev) of about 2.10^{10} n cm⁻²sec⁻¹ is available. To reduce thermal activation, samples and standards were inserted into cadmium containers. Irradiations lasted 6.5 sec and countings, started 8 sec after the end of the irradiations, lasted 20 sec.

Samples of hydrated copper sulphate, oxalic acid and succinic acid have been used as reference standards.

Radioactivity measurements have been carried out by gamma spectrometry using NaI(Tl) crystal 7.6 x 7.6 cm, connected to a multichannel analyzer.

Only gamma rays above 4 Mev were detected and counted. Countings started 8 sec after the end of the irradiation and lasted 20 sec.

First trial analyses have shown an oxygen content of about 2.500 ppm; samples were then cleaned by repeated machining up to constant oxygen content of 318 ± 33 ppm.

Oxygen was determined through the same nuclear reaction in a cylindrical rod of lead ⁽²⁾ sent to this laboratory by Eurisotop Office. Specimens weighing 15-25 g were prepared by cutting the rod with a steel saw and finishing them with a file. Lead acetate aliquots have been used as reference standards and inserted into lead samples weighing as much as the lead specimens to be analyzed. Irradiations took place in the F-ring of the reactor core and lasted 22 sec. Only gamma rays above 4 Mev were detected and counted. Countings started 8 sec after the end of the irradiations and lasted 20 sec. Results have been evaluated by taking into account the oxygen content of the lead containers used to hold the standards. The mean value of the oxygen content in 4 lead samples resulted 138 ± 12 ppm.

Trial analyses were carried out by operating the reactor in pulse mode. In this case the neutron flux was increased by a factor of 10^3 for 200 msec. Strong matrix interferences were encountered and no improvement was obtained by using pulsed neutrons.

Several tests have shown that the oxygen determination in aluminum by pile neutron activation analysis is strongly affected by the thermal activation of the matrix and no acceptable data can be obtained. Thereafter research on this subject was not continued.

Neutron activation has been applied to the determination of some atmospheric particulate pollutants, ⁽³⁻⁴⁾ such as Al, As, Br, Mn, Sb, Si e V. Together with gaseous pollutants such as CO, CO₂, SO₂ and SO₃ they are usually found in the urban and industrial areas. The solid pollutants dispersed in the air were collected on filter paper by air filtration using vacuum pump. A preliminary investigation was carried out on the filtering materials degree of purity: glass fiber and cellulose membranes, polytene and filter paper Schleicher-Schull N° 589¹ were tested. The latter was found to have the lower impurities content and thus the most suitable to our purposes.

Aluminum and manganese content was anyhow quantitatively determined in order to make blank corrections on actual samples.

Air filtrations were carried out up to about 150 m³ and this required 24 hours. A one tenth portion of the filter of 19.5 cm² total area was always used both in the short and long irradiations. Short irradiations of samples and standards took place in the F-ring and lasted three minutes.

They allowed the quantitative determinations of manganese, vanadium, and the sum of aluminum plus silicon through the formation of ^{28}Al ($t_{1/2} = 2.3$ min) ($^{28}\text{Si} (n, p) ^{28}\text{Al}$, $^{27}\text{Al} (n, \gamma) ^{28}\text{Al}$).

By a subsequent 6 min irradiation in the thermal column the aluminum content was determined, thus allowing also the silicon evaluation by difference.

More prolonged irradiations up to two hours were carried out in order to measure the Sb, As and Br content. The resolution of the three metals was made simply by instrumental technique. Radioactivity measurements have been carried out by gamma spectrometry using a 20 cm³ Ge-Li crystal connected to a 4096 channels pulse analyzer LABEN correlatron after a 2 min cooling time in the case of ^{28}Al and ^{56}Mn and 24-36 hours in the case of ^{122}Sb , ^{76}As and ^{82}Br .

Experiments run during July showed a sharp decrease in vanadium content in the air by a factor of four with the respect of winter time content: this must be related to the domestic heating contribute to air pollution (0.02 - 0.08 $\mu\text{g}/\text{m}^3$). Aluminum content ranged from 1.44 to 0.80 $\mu\text{g}/\text{m}^3$, manganese from 0.24 to 0.38, bromine from 0.06 to 0.12, while arsenic stayed almost constant at 0.01 $\mu\text{g}/\text{m}^3$, antimony at 0.07 and silicon at 85.

Another field in which activation analysis has been applied is forensic research. Methods have been developed for the determination of antimony, barium and copper in gunpowder residues (5).

The detection of gunpowder on the hands of a person is undoubtedly of great importance in criminal cases. The NAA of antimony, barium and copper, present in the order of submicrograms as residues of fired ammunitions on the hand which fired the weapon, has helped to make obsolete the traditional colorimetric paraffin test.

The removing material is still paraffin but it is dropped from a lighted paraffin-candle on the first interdigital space of the hand. Building maps for gunpowder residues of hands who fired a pistol, the first interdigital space was found to be the most significant. Analyzing the paraffin "blanks" from candles they were found free from antimony, barium and copper. Next a lot of samples from the left and right hands of individuals who did and did not fire a pistol were examined. The results clearly show that from the content of Sb, in first place, and also of Ba, it is possible to identify the person who fired the pistol. Due to the random distribution of copper coming from the skin, this element appears not to be meaningful for the identification of shooters. Some practical cases of suicides and shooters were resolved.

The identification of antimony on the edge of suspected holes and wounds allows also to identify them as induced by fired bullets.

The instrumental antimony, barium and copper radioactivation analysis was carried out by irradiating with the standards in the Lazy Susan position for three hours the paraffin drops that covered 2 cm² of skin. Countings were made using the 20 cm³ Ge-Li crystal, after 1 hour cooling period in the case of Ba and Cu and 24-36 for antimony. Detection limits with the adopted procedure is 0.05 µg for Ba and 0.01 µg for Sb.

By using inorganic materials such as molybdenum dibromide (MDB), zinc ferrocyanide (ZFoc) and cadmium metal in granular form it was possible to set up simple chemical procedures in the activation analysis of trace amounts of noble metals in metallic matrices (high purity nickel and copper), geochemical materials (rocks and meteorites) and biological materials (orchard leaves) (6).

Platinum, palladium, gold, iridium and copper were determined in any sample by irradiating together with standards solutions for 20 hours in the rotating Lazy Susan facility.

Irradiated samples were dissolved in the proper reagents, small amounts of carrier for each element up to 1 mg were added and the solutions brought 0.1 M HNO₃. Carriers were added on account of the adsorption mechanism of the investigated elements on the inorganic adsorbers as the uptake of ions is based mostly on the insolubility of the compound formed with the inorganic adsorber.

The solutions were passed through a cascade of chromatographic columns filled with MDB and Cd metal in the case of nickel and geochemical samples or with MDB and ZFoc in the case of orchard leaves samples. MDB strongly adsorbs palladium, platinum, gold and iridium, copper is adsorbed either on Cd metal or on ZFoc; the latter is used for orchard leaves analysis as it allows also the zinc determination.

Silver determination was accomplished by irradiating the samples for at least 40 hours in the central channel of the TRIGA MARK II reactor; it is strongly adsorbed on both MDB and ZFoc, but in the case of geochemical and copper analysis the former is preferred as it does not hold copper and iron.

Columns were always washed with 1 M HNO₃ to remove the interfering ions and finally dismantled and submitted to gamma spectrometry. The total time required for the separation is about two hours.

Counting on a 20 cm³ Ge-Li crystal lasted 5000 sec.

The lower detection limits are 3 nanograms for Ir and Cu, 5 for Au, 10 for Ag and 100 for Pt and Pd.

Neutron activation analysis was also used to investigate on the extraction from iodide and thiocyanate solutions of the platinum group metals at low concentrations, using tri-n-butylphosphate as extractant.

Spectrophotometric techniques are usually employed in this type of studies to analyze the aqueous phases; they are rather cumbersome and do not apply easily to the organic phases. Neutron activation analysis may well be applied both to organic and aqueous phases and in some cases, rhodium for instance, is very rapid and allows the detection of very small amounts.

Rhodium (III)-iodide system was studied first ⁽⁷⁾ and the extraction efficiency was measured as a function of HClO_4 or H_2SO_4 concentration, rhodium and iodide ions concentration and temperature.

Rhodium extraction yields, regardless its chemical form, were measured by gamma counting from the 44 sec ^{104}Rh formed by irradiating in the rabbit system of the TRIGA reactor the organic and the aqueous phases after the extraction.

The most important factor affecting the rhodium extraction yields is the acid concentration to which the rhodium-iodide complex solution is adjusted before extracting. They rapidly increase up to 1 M HClO_4 and 2 N H_2SO_4 respectively and stay almost constant at 98 - 99% for higher acid concentration values.

In a previous work ⁽⁸⁾ we determined by using radioanalytical techniques the formula of the rhodium iodo complex obtained in the above conditions. The elemental analysis was made on its caesium salt through caesium, rhodium and rhodium/iodine ratio activation analysis and was found to correspond to the dimeric complex $[\text{Rh}_2\text{I}_{10}]^{7-}$. Rhodium (III)-thiocyanate complexes extraction with TBP was investigated in the same way ⁽⁹⁾. As in the iodide system it was found that the extraction yields increase as the HClO_4 or H_2SO_4 concentrations increase: reaching a value of 98% for H_2SO_4 8 N but only 70% for HClO_4 7 N.

It seems possible that two different species are extracted from H_2SO_4 acid solutions, in the 0.5 - 2 N range and 2 - 8 N range respectively. The extraction yields as a function of H_2SO_4 concentration show different slopes in the two ranges and the complex color is also different. Additional chemical studies on this little known subject are thus required.

The iridium (III)-iodide system is very much similar in its behaviour toward extraction with TBP, though the extraction yields are much lower. Researches are in progress on the separation of Rh and Ir mixtures and on the other platinum group metals extraction from iodide solutions.

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