

NEUTRON ACTIVATION ANALYSIS AT THE "INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES"

MARINA B.A.VASCONCELLOS

Radiochemistry Division

Instituto de Pesquisas Energéticas e Nucleares - CNEN/SP

Caixa Postal 11049 (Pinheiros) - 05499 - São Paulo, SP - Brasil

ABSTRACT

A review is made of the work carried out at IPEN using neutron activation analysis.

An introduction is made on the main characteristics of the method, including comments about the general experimental procedures applied.

Methods of neutron activation analysis developed at IPEN in several fields are discussed, involving various types of samples and elements to be determined.

Analysis of geological samples are carried out by using activation with thermal neutrons, epithermal neutrons and delayed neutron techniques (for uranium and thorium analysis).

Mettalic samples are analysed for several minor and trace elements, such as tantalum in niobium, mercury in steel, tin, antimony, arsenic, copper, chromium and silver in a tin-lead alloy.

Environmental pollutants are determined by neutron activation in samples of air, water and hair.

Biological materials, such as tomatoes, animal and human viscera, food, hair, nails are also analysed for several components, such as mercury, sodium, potassium, arsenic, gold and others.

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Marina B.A.Vasconcellos

Radiochemistry Division

Instituto de Pesquisas Energéticas e Nucleares

Comissão Nacional de Energia Nuclear

Caixa Postal 11049 - Pinheiros

CEP 01000 - São Paulo, SP - Brasil

I. INTRODUCTION

Neutron activation analysis (NAA) is an outstanding application of nuclear research reactors. Due to the high neutron fluxes produced, an excellent sensitivity of analysis is attainable and a great number of elements can be determined in the parts per million or parts per billion concentration range. NAA is undoubtedly one of the most sensitive, accurate and precise methods available for trace element analysis.

NAA has remarkable advantage over the other trace analytical methods, due to the fact that it is free from contamination problems, once the material is irradiated. One has to be concerned only with the handling of the samples before irradiation.

The Radiochemistry Division of the Instituto de Pesquisas Energéticas e Nucleares has, since 1957, when the operation of the IEA-R1 nuclear reactor began, been engaged in activation analysis work, with excellent results. Many works have been published by the IPEN group, in Brazilian as well as in the international literature.

The group has always accompanied the developments in the field, by for example, optimizing radiochemical separation methods in order to increase the number of determined elements as well as to improve the precision and accuracy attainable.

As to the electronic equipment employed for radioactivity measurements, the Radiochemistry Group has also accompanied

the more recent developments, by using Ge(Li) or pure Ge detectors coupled to 4096-channel analyzers for multielemental analysis.

II. PRINCIPLES OF THE METHOD

The activation analysis method is based on the formation of radioactive nuclides by means of nuclear reactions, upon exposure of the sample to nuclear particles produced in a nuclear reactor, particle accelerator or other suitable source.

The probability of occurrence of the nuclear reaction, the isotopic abundance of the target nuclide and the half-life of the radioisotope produced should be sufficiently large so that the analysis becomes feasible.

The nature of the emitted radiations as well as their energies and the half-life of the radioisotope produced can be used for performing a qualitative analysis. Depending on the complexity of the matrix analyzed and on the equipment available, the analysis can be made destructive, with radiochemical separation, or non-destructive.

The quantitative determination is based on the fact that the activity of the radioisotope formed is proportional to the mass of the parent element to be analyzed.

II.1. Limits of Detection

Below are tabled the limits of detection for some elements commonly determined by neutron activation analysis.

Limits of Detection at a Thermal Neutron Flux of 10^{13} n/cm².s

(1 h maximum irradiation time)

Element	Radionuclide	Half-Life	Limit of De- tection (μ g) by γ -Ray Spectrometry
Al	²⁸ Al	2.31 m	9×10^{-4}
Sc	⁴⁶ Sc	83.9 d	5×10^{-3}
Mn	⁵⁶ Mn	2.6 h	7×10^{-6}
Cu	⁶⁴ Cu	12.8 h	6×10^{-4}
Ga	⁷² Ga	14.1 h	4×10^{-4}
As	⁷⁶ As	26.4 h	6×10^{-4}
Dy	¹⁶⁵ Dy	2.35 h	4×10^{-6}
Ir	¹⁹² Ir	74.2 d	4×10^{-4}
Ta	¹⁸² Ta	115.1 d	3×10^{-2}
Lu	¹⁷⁷ Lu	6.74 d	5×10^{-4}

II.2. Activation With Neutrons of Different Energies

II.2.1. Thermal Neutrons

The so-called neutron capture or (n, γ) reaction is the most useful for activation analysis, between all the reactions that can be produced in nuclear reactors.

This is due to the high thermal neutron flux available in reactors and to the high cross-section (σ) for thermal neutrons exhibited by many stable nuclides.

II.2.2. Epithermal or Resonance Neutrons

In the epithermal region of neutron energies, several nuclides present one or more resonance peaks, that is, for

a certain value of neutron energy the cross section exhibits relatively high values.

Heavier elements, like Eu, Sm, Ir, Ta, Th and others have several resonance peaks higher than 1000 barns. Epithermal Neutron Activation Analysis (ENAA) generally favours the determination of heavier elements in detriment of the lighter ones.

Steinnes⁽¹⁾ has demonstrated clearly the advantage of ENAA for the determination of Rb, Cs, Sr, Sb, Ta and U. Determinations of Ba, Sm, Tb, Hf and Th also appeared to be favourable.

At the Radiochemistry Division of IPEN, ENAA is mainly utilized for U and Th analysis⁽²⁾ and for rare-earth elements determination, both in geological samples⁽³⁾.

II.3. Absolute and Comparative Activation Analysis

By using the activation expression:

$$A = \frac{z \sigma \phi N f m}{M} (1 - e^{-0.693 \text{ ti}/t_{1/2}})$$

it is possible to calculate the unknown mass of a given element, once the values of σ , ϕ , f , t_i and $t_{1/2}$ are known.

Since this absolute method is time consuming and difficult, due to the necessity of measuring absolute activities and since parameters like σ , ϕ , f and $t_{1/2}$ are not always exactly known, it is generally more usual to utilize a comparative procedure.

In the comparative procedure, a standard of known mass and composition is irradiated together with the sample and many of the errors involved in the absolute method are avoided.

II.4. Types of Standards Utilized in the Comparative Method

II.4.1. Synthetic Standards

In this case, the element to be analyzed, or one of its compounds, in the purest form available, is dissolved, generally in water or acids, and pipetted on filter paper, silica gel or quartz ampoules, for irradiation. Standards containing one element or a mixture of elements can be prepared, depending on the number of elements to be determined.

II.4.2. Certified Reference Materials

Some organizations, interested in analytical results for several purposes, like the United States Geological Survey (U.S.G.S.), the International Atomic Energy Agency (IAEA) and the National Bureau of Standards (NBS), prepare certified reference materials, which can be used as standards for analytical methods.

These materials are certified either by being analyzed in a laboratory with very high standards of analysis and of assured reliability, normally by many different methods, or from the results of intercomparisons made all over the world.

III. DETECTORS USED FOR GAMMA-RAY SPECTROSCOPY

Two main types of detectors are used at the Radiochemistry Division of IPEN for γ -ray detection:

- Scintillation detectors
- Solid state Germanium-Lithium detectors.

III.1. Scintillation Detectors

The Radiochemistry Division has in use two Harshaw NaI(Tl) detectors, of 3 x 3 inches, coupled to TMC 400 channel analyzers.

They were very much used for activation analysis

work up to about the 1970s, but due to their not so good resolution, rather complicated radiochemical separations were demanded for multielemental analyses.

Now they are used in cases where one deals with one or only a few radionuclides, or when specially high sensitivity is needed.

One example of the still successful application of this kind of detector is in the epithermal neutron activation analysis of uranium.

III.2. Solid State Ge(Li) Detectors

Two systems for gamma-ray spectrometry are being used at the Radiochemistry Division of IPEN. Both utilize ORTEC Ge(Li) detectors, with about 30 cm³ volume, 2.5 keV resolution for the 1332 keV peak of ⁶⁰Co and 15% efficiency.

One is coupled to a Model 5410A 4096-channel Hewlett Packard analyzer and to a HP 2100 Minicomputer. Data reduction is performed by a program in BASIC language, specially developed for use in this Minicomputer. ⁽⁴⁾

The other is coupled to a Model 6240B ORTEC 4096-channel analyzer coupled to a Digital PDP/11 Computer. The Ge-Li GAM program in ORACL language developed at ORTEC is used for data reduction.

A more powerful program, JANE, in Fortran IV language ⁽⁵⁾ is also available for complete qualitative and quantitative analysis of complex samples.

IV. APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS AT THE RADIO-CHEMISTRY DIVISION OF IPEN

IV.1. Geological Applications

Multielement analysis of minor and trace elements in geological samples, such as rocks and ores, have been performed, using purely instrumental analysis or developing, group radiochemical separations^(6,7,8). Many elements, such as Ga, Zn, Cu, Ho, Sm, Ca, La, Na, K, Sb, Lu, Hf, Ce, Tb, Pa, Cr, Yb, Ba, Sc, Fe, Nd, Ta, Eu, Co have been determined by Thermal Neutron Activation Analysis (TNAA). In the radiochemical procedure, Hydrated Antimony Pentoxide (HAP) was used for the retention of the strong activity of ^{24}Na , anionic ion exchangers were utilized for the retention of the chloro-complexes of Zn, Sb, Fe, Co, Cu, Ga, W. The long-lived ^{46}Sc was retained by extraction chromatography in a column of kieselguhr impregnated with TBP.

Thirty-eight elements (U, Th, La, Ce, Nd, Sm, Eu, Dy, Tb, Yb, Lu, Sc, Ta, Hf, Co, Ni, Cr, Mo, Ti, V, W, In, Ga, Mn, Ba, Sr, Mg, Rb, Cs, K, Cl, Br, As, Sb, Au, Ca, Al and Fe) were determined in Brazilian coals by NAA, using both thermal and epithermal neutron irradiations and a combination of short (~ 10 minutes) and long irradiations (8 to 72 hours).⁽⁹⁾

Vanadium at the ppm level was determined by NAA in petroleum, petroleum fractions and in a silica alumina cracking catalyst⁽¹⁰⁾. Instrumental neutron activation analysis (INAA) using a NaI(Tl) scintillation detector was carried out for the analysis of V in petroleum. For the determination of V in the cracking catalyst, a pre-irradiation treatment was necessary, by fusion with a mixture of K_2CO_3 and Na_2CO_3 . Radiochemical separation of V, after irradiation, was made by solvent extraction with N-benzoyl-N-phenylhydroxylamine in chloroform.

Uranium and thorium analysis has been a major concern at the Radiochemistry Division of IPEN. Several methods are used, such as spectrophotometry with dibenzoylmethane, epithermal neutron activation analysis, with short or long irradiations, and activation analysis followed by delayed neutron counting.⁽¹¹⁾ The

system implanted at IPEN for the analysis of uranium and thorium by delayed neutron counting allows very rapid determinations and is now been used in a routine basis.

Delayed-neutron counting is also being used for the determination of $^{235}\text{U}/^{238}\text{U}$ isotopic ratios. Rock samples from the Northeastern region of Brazil have been analyzed, in search for an "Oklo Phenomenon" in Brazil⁽¹²⁾.

IV.2. Applications to the Analysis of Metallic Samples

Since Brazil has one of the world's largest deposits of niobium, the analysis of impurities in this metal is very important. Tantalum analyses in niobium metal have been performed by TNAA, with irradiation times varying from 8 to 24 hours followed by instrumental analysis in Ge(Li) detectors.

Mercury at the ppb level was determined in Brazilian steel to be exported to the USA, by TNAA, using a radiochemical separation procedure. The gamma-ray peaks of ^{197}Hg and ^{203}Hg suffer interferences from ^{187}W and ^{75}Se , so it was necessary to separate Hg, by means of three distillations in an HBr medium⁽¹³⁾.

Destructive and non-destructive activation analysis methods were applied to the determination of the components of a tin-lead alloy⁽¹⁴⁾. The destructive method was applied to simultaneous determination of Sn, Sb, As, Cu and Ag. A highly selective method of chromatographic retention for Sb using tribenzylamine (TBA) as stationary phase fixed in a silica-gel adsorber has been developed. The non-destructive method was applied to the determination of Sn, Sb and Ag.

IV.3. Applications of NAA in the Analysis of Biological Samples and in Environmental Studies

Hair of arsenic plant workers have been analyzed for arsenic by neutron activation methods⁽¹⁵⁾. Results were also presented for As in nails, whole blood, urine and pubic hair for those workers. Various washing techniques for hair, including ultra-sonics, were applied to the hair, trying to differentiate

arsenic from a systemic origin and arsenic externally deposited on the hair.

Due to the use, in agriculture, of pesticides containing mercury, it is necessary to develop analytical methods sufficiently sensitive and accurate to determine this very toxic element in vegetable foods. In the Radiochemistry Division of IPEN, a radiochemical method was developed for the analysis of mercury in tomatoes⁽¹⁶⁾. Hg is separated from other elements by isotopic exchange on metallic mercury, after attacking the tomato samples with H_2SO_4 , in a reflux system.

The toxic elements: As, Hg, Se, Br and Sb were determined in air samples by radiochemical neutron activation analysis⁽¹⁷⁾. These elements are separated from the rest of the irradiated sample in the form of volatile bromides or Br_2 . This last element is retained in a NaOH solution and As, Hg, Se and Sb were individually separated by ion exchange. Their activities were then measured using a NaI(Tl) scintillation detector.

A research work on the trace analysis of foods, by destructive and non-destructive neutron activation analysis is also under way. Samples of bread and milk powder were analyzed, using short and long irradiations and retaining the high activity of ^{24}Na in a column of hydrated antimony pentoxide (HAP). The elements Na, Cl, Mn, Br, Fe, Rb, Cr, Zn, Sb and Sc were determined in the bread samples and Mg, Al, Mn, Na, K, Ca, Br, Cr, Zn, Rb and Sb in the milk powder, by INAA.

Also under way is a research on the determination of mercury in samples of human hair. This element has been determined in the hair of fishermen, by INAA and now a program is being established for the analysis of dentists' hair.

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