ACTIVATION ANALYSIS IN GREECE

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ABSTRACT

Today Activation Analysis is widely applied to the investigation of medical, environmental, industrial, geological and archaeological problems. In this review the development of activation analysis methods as well as applications of these methods in medicine, environment, geology, and archaeology are described, mainly based on work done by the author's group in the Nuclear Research Center "Demokritos" of Greece.

INTRODUCTION

In the last 35 years there has been a tremendous growth of research, development and applications of neutron activation analysis (NAA) which resulted in a dramatic increase of the relevant literature, showing an exponential growth from 13 papers in 1949 to over 700 in 1971 (1). This represents a doubling time of about three and one half years. From 1971 up to date NAA reached maturity. The annual accretion of papers in the literature kept an exponential growth pattern at a more reduced rate, more or less equal to that of analytical chemistry (2). In 1968 and 1969 two new scientific journals, the Radioanalytical Chemistry and the Radioanalytical Letters were circulated to cover the continuous growth of publications related to NAA.

The increasing international interest for NAA is evident from the number of papers presented at International Conferences of Modern Trends in Activation Analysis (MTAA). In 1961 during the first MTAA Conference about 1/4 of the presented papers were from 6 only countries other than USA (3) while during the 5th and 6th MTAA Conferences in 1976 and 1981 more than 3/4 of the presented papers were from more than 25 countries other than USA.

Several factors contributed to the increasing international interest for NAA some of which are: the establishment of research nuclear reactors in many countries of the world. The use of other nuclear projectiles (charged particles - photons) to the arsenal of activation analysis. The development of radiochemical separation techniques, which, combined with NAA, increased the sensitivity of NAA for some elements to quantities below 10^{-9} grams. However the main factors which contributed most for the international recognition of NAA were the development of multichannel analyzers (4) and Ge(Li) detectors (5) for γ-ray counting and the possibility of γ-ray spectra processing by computer techniques. All these increased the number of trace elements which can be determined by Instrumental NAA, reduced the time of analysis and greatly extended the scope of the method. In many cases NAA can be applied successfully as an Instrumental non-destructive multielement analysis method, based upon multi-channel gamma-ray spectrometry of the neutron activated sample.

Today NAA is widely applied to the investigation of biomedical, environmental industrial, geological and archaeological problems. Due to its great sensitivity precision and accuracy it is considered as an ideal method for the determination of a large number of minor and trace elements in several materials.

In this paper a review of research and development on NAA as well as examples of applications of this method in medicine, environment, geology and archaeology is presented, taken from work carried out over the last 21 years at the Radioanalytical Laboratory of the Department of Chemistry in the Greek Nuclear Research Center "Demokritos". Charged particle activation analysis and delayed neutron counting methods are also mentioned.

DEVELOPMENT OF NAA METHODS AT THE RADIOANALYTICAL LABORATORY

In the last 21 years improved and/or faster radiochemical NAA methods have been developed at our Laboratory for the determination of Au(6), Ni(7), Cl(8), As(11), Cu(14), U(15), V(30), Cr(45), Eu(52), Hg(87) and Mo(88) in several materials as well as for the simultaneous determination of Br and I(9), Mg, Sr and Ni(12), As and Cu(16), As, Sb and Hg(17), Mn, Sr and Ba(19), Cd and Zn(28), Se and As(28), Mo and Cr(28) in biological materials. Instrumental NAA methods have also been

developed for the determination of Ag, Cl and Na in lake waters (6), Al, Ca, Mg and V in wines (100) seven trace elements in biological materials (28), 17 trace elements in sediments (46) and 20 minor and trace elements in ceramics (47). We have also developed a coprehensive computer program for routine activation analysis using Ge(Li) detectors (36).

APPLICATIONS OF NAA IN MEDICAL RESEARCH

In 1971 a review article was written on medical applications of NAA (23) to inform MDs in Greece about the availability of NAA methods in medical research. Cystic Fibrosis is a frequent chronic disease of childhood. Its frequency is 1 in 2000 live births. Early diagnosis followed by the appropriate therapeutic program can help a number of children born with this disease to survive to adult age. The sweat test is an accurate procedure most widely used for the detection of CF. This test however has its limitations. The time, expense and necessity for the patient to visit the laboratory limit the number of people who can be tested. In addition the sweat test cannot easily be performed in newborns, dehydrated and malnourished infants.

Kopito and Scwachman (111) first found increased concentrations of sodium in the nail clippings of patients with Cystic Fibrosis (CF). Although their results were very valuable, the method they used was destructive of the sample, time-consuming and unacceptable for large scale applications. Nevertheless their findings prompted several investigators to apply Instrumental NAA of sodium in nail clippings for the diagnosis of C.F. Some of the advantages of INAA to nails as a tool for the detection of C.F. are listed below: a) Small samples (1 mg) are required, b) Simultaneous analysis of many samples per day is possible (over 100), c) Samples are not destroyed. On the other hand nails are very convenient material; they can be clipped by anyone, anywhere and no special storage precautions are necessary. However, there is a problem. Since sodium is abundant in nature, contamination is frequent. Thus, cleaning the nails constitutes a major experimental difficulty. The problem is to remove the surface "contamination" sodium without affecting "intrinsic" sodium.

In the past we have applied INAA for the study of C.F. (24-26,31). We have developed an improved washing procedure for the removal of external sodium contamination from nail clippings which combined with instrumental NAA increased the diagnostic accuracy of the method from ∿75% to ∿90% (25,26). We have developed a simple counting method of sodium-24 in irradiated nail clippings which makes possible the use of inexpensive counting equipment for INAA of sodium in nails. We have successfully applied INAA for the determination of Na in fingernails of 80 patients with C.F. and 2531 controls. The nail sodium ratio of patients to children was 3 to 1 in three pediatric groups examined (newborns, infants, children). We have made a systematic study of 11 more trace elements (Al, As, Br, Ca, Cl, Co, Cu, Mg, Mn, K and Zn) in fingernails of patients with C.F. and controls using NAA. Bromine and chlorine concentrations in nails of C.F. patients of all age groups were found to be 2 to 5 times higher than those of healthy children. Increased potassium and copper concentrations were found only in the nails of infants and children. No significant differences were found for the rest of the elements.

Increased bromine concentrations were first reported by our group (24). Beside Na and Cl values, Br in nail clippings from patients with C.F. can be used as supplementary indicator for C.F. Concentrations of Br, Cl and Na determined by INAA at our Lab. in the sweat of C.F. patients were found to be 2.5, 4.0 and 6.0 times higher respectively than those of controls. This research work was partially supported by the IAEA for 3 years (Research Contracts 689/RB/1969, 689/R1/1970, 689/R2/1971). This work was done in collaboration with the First Pediatric Clinic of Athens University.

Changes of metabolism happen in women's organism during gestation which are probably necessary for the development of the embryo. The concentrations of Zn, Co, Cu, Se, As, Au, Br and Rb have been determined by NAA in maternal and umbilical cord blood sera as well as in healthy non-pregnant women who served as controls (35,39,44,56). The concentrations of Zn and Co were significantly lower, those of Cu and Au significantly higher while levels of As, Se, Br and Rb were similar in sera of pregnant as compared to sera of non-pregnant women. The mean value of Zn in the umbilical cord sera was about two times higher and that of As 1.7 times higher than those in mothers. Toxic levels of As were not found in the studied cases.INAA has been applied for the determination of Co, Rb, Se and Zn in maternal and umbilical cord serum and amniotic fluid of women with normal pregnancy and prolonged pregnancy (89,90). Significantly lower levels of Co, Se and Zn were found in maternal blood serum and cord serum of women with prolonged pregnancy as compared

with those in sera of mothers with normal pregnancy. Zn concentrations were also found significantly lower in amniotic fluid of women with prolonged pregnancy.

Six trace elements (Zn, Co, Se, Rb, Br and Au) were also determined in placental and liver tissue samples at birth (53). The mean concentration of the essential trace elements (Zn, Co, Se) were significantly higher in liver than in placenta, whereas the non-essential trace elements (Rb, Br, Au) were found in significantly higher concentrations in placental than in liver tissue.

The principal food of infants during the first months of their life is human milk or cow's milk and commercial infant foods. NAA has been applied for the determination of seven trace elements (Co, Cr, Cu, Se, Zn, Rb and As) in colostrum, transitional and mature human milk as well as in powdered cow's milk and commercial infants foods in order to find out whether non-breast-fed infants received the same or different amounts of these trace elements as breast-fed ones. Results have been reported (61). Among them it was found that average concentration of Cu in human milk is about 9 times higher than that of cow's milk.

These works were done in collaboration with the Second Pediatric Clinic of the University of Athens with the exception of the trace element studies in blood sera and amniotic fluid of women with normal and prolonged pregnancies which were performed with the collaboration of the First Clinic of Obstetrics and Gynecology of the University of Athens.

The distribution pattern of Zn, Co, Se, Fe, Cs and Sb has been found by INAA in three parts of myomatus uterus: myoma, endometrium and myometrium. The content of these elements was also determined in submucous, intramural and subserous myoma (41,62). The variation of the content of Zn, Co and Se in myoma and myometrium was found to be very significant statistically compared with the variation of these elements in endometrium. The concentration of the six trace elements determined in myoma, myometrium and endometrium has been correlated with age. This work was done in collaboration with the department of Pathology of the University of Athens.

The distribution of three essential trace elements (Co, Se and Zn) in the eyes of premature and normal newborn babies has been studied (40). This work was done in collaboration with the Second Pediatric Clinic and the First Clinic of Obstetrics and Gynecology of the University of Athens.

Trace elements have been determined in the lens, nail and serum of patients with cataract (67,78). The distribution pattern of Ag, Co, Cr, Cs, Fe, Rb, Sb, Sc, Se and Zn in the human cataractous lenses has been studied using INAA. Differences of concentrations of these trace elements were found in the cataractous lens regarding the concentrations of the same elements in the normal lens (91,92). These works were done in collaboration with the Eye Clinics of the University of Athens.

Active constituents of medicinal plants are products of plant metabolism which is influenced from the variation of the concentration of trace elements. Twenty seven trace elements have been determined in the different parts of the medical plant Helleborus cyclophyllus Boiss and in the soil in which the plant had grown (64,68). The attributed diuretic action in potassium content in some medicinal plants has been studied in correlation with the daily requirement for this element in man (69). Recently simple and rapid NAA methods have been developed and used for the direct and indirect determination of active ingredients in drugs (70,96,103,106) and cosmetics (102,105). These works were done in collaboration with the Department of Pharmaceutical Technology of the University of Athens.

Our Laboratory in collaboration with the Department of Pathology of the University of Athens was participating under a research agreement at a WHO/IAEA Joint Research Program for the study of trace elements in cardiovascular diseases (110).

NAA METHODS IN ENVIRONMENTAL RESEARCH

In the last 21 years in our Laboratory NAA methods have been developed and applied to trace elements research in the environment.

In environmental studies we have determined: seventeen trace elements (Ag, As, Au, Ba, Br, Cl, Cu, I, Mg, Mn, K, Na, Ni, Re, Sr, V and Zn) in surface and bottom waters from 11 most important lakes of Greece (6,12), the arsenic uptake in grapes and plant tissues (20,21) and the uptake of Cu, Mn and Zn in needles of seedlings of Pinus grown under a wide spectrum of soil conditions (18). Bromine in soils polluted with bromine pesticides and in the same soils after treatment

with water (34). Several trace elements in drinking water of the Athens area, in river waters and in water pipes (113). Eleven trace elements (Al, As, Br, Ca, Cl, Cu, K, Mg, Mn, Na and V) in experimental and commercial red and white wines from different wine production areas of Greece (16, 81, 100). Certain inorganic nutrients in natural and artificial food of Dacus oleae larvae (60). Nine trace elements (Ag, Co, Cr, Cs, Sb, Sc, Se, V and Zn) in three edible mollusk species (100). A study of trace elements in greek lignites by INAA has been started (113) in collaboration with the Institute of Geological and Mining Research.

However most of the trace element environmental research work done in our Laboratory has been concerned with the marine environment. In marine pollution studies we have determined: Br, Cu, I, V and Zn in Pura microcosmus (13). Ten trace elements in the whole body and in ten different parts of the fish Pagellus erythrinus (29), 12 trace elements (Ag, As, Ba, Co, Cr, Cs, Fe, Hg, Mn, Sb, Sr and V) in Cynthia claudicans (30). Toxic trace elements and elements of radioecological importance in mollusk species (27,42) in echinoderm species (43,66) and tunicate species (49) from Saronikos Gulf, Greece. It was found that certain of these marine organisms may be characterized as radioactive and industrial pollution indicators. In NAA of As and Hg in Pagellus erythrinus (33) and of As, Cd, Co, Cu, Fe, Mg, Rb, Sb, Se and Zn in Sargus annularis (54), arsenic concentrations in the flesh of these two fish species were found to be two times higher in samples from polluted areas as compared with samples from the unpolluted areas of the island of Rhodes and Petalion Gulf.

Within the framework UNEP MED POLL II Project, a systematic pollution monitoring of 14 trace elements (Ag, As, Cd, Co, Cr, Cs, Cu, Fe, Mg, Rb, Sb, Se, V and Zn) in Mullus barbatus and Parapenaeus longirostris (58,73,74) has shown increased concentrations of As in the flesh of Mullus barbatus from northern Saronikos Gulf when compared with specimens from other gulfs of Greece. All higher concentrations of arsenic found in fish species of Saronikos gulf are within the "natural background" levels reported for edible fish by other investigators. No significant differences for the rest of the trace elements were found in the flesh of these marine organisms studied in Northern Saronikos Gulf as compared with the same organisms from other gulfs. It seems that these benthic organisms do not reflect the very high trace element concentrations found in seawaters and sediments of the Keratsini bay in the northern Saronikos Gulf.

A study of trace elements (Ag, As, Au, Ce, Co, Cr, Cs, Eu, Fe, Hg, Hf, La, Lu, Rb, Sb, Sc, Sm, Yb, Zn) as an index to pollution in sea sediments (32,37,46,63) from the northern Saronikos Gulf has been made by INAA. It was found that the discharge of industrial and domestic wastes in the Keratsini and Elefsis bays of the upper Saronikos Gulf has led to elevated concentrations of all toxic and other trace elements determined over at least 100 km^2 of seafloor. The 0.5N HCl extraction method (112) of the silt-clay fraction of sediments was used and was successful for the distinction between anthropogenic and residual concentrations of As and Zn in the sediments (95).

Increased concentrations of As, Co, Cs, Cu, Fe, Mg, Rb, Sb, Sc and Zn have been found in seawater samples collected near the main sewage outfall of Keratsini Bay and to a much lesser degree from Faliron Bay (97,113). The affected area however is not very extended since concentration of trace elements fall to natural background levels within 5 km^2 from the outfall.

Six trace elements (As, Co, Cs, Fe, Se and Zn) have been determined by INAA in otoliths of the pelagic fish Scomber japonicus colias from the Aegean Sea (65, 71). It has been found that in general the content of the studied elements in otoliths decreases with increasing age of the fish. Several trace elements have been also determined by NAA methods in skeletal formation of fish species (48) in plankton (50,85) in marine organisms and sediments of the Aegean Sea (51,59,72,75, 76,83,84,86,93,94,99).

Recently the distribution of arsenic in water columns, water particulates and sediment cores from Northern Saronikos Gulf has been studied (109). INAA has been applied for the determination of nine trace elements (Ag, Co, Cr, Cs, Fe, Rb, Sc, Se and Zn) in the medusae Aurelia aurita and Pelagia noctiluca (104) and in muscle, liver and heart of Boops boops and Trachurus mediterraneus (108).

Within the framework of the scientific collaboration between the Activation Analysis Group of the Institute of Nuclear Research and Nuclear Energy (INRNE) of Sofia, Bulgaria and the Radioanalytical Laboratory of the Nuclear Research Center Demokritos, nine trace elements (As, Co, Cr, Cu, Mg, Rb, Se, V and Zn) were determined by NAA in the flesh and liver of the edible fish Gobius niger caught from Varna Bay, Bulgaria and Saronikos and Petalion Gulfs, Greece. No dangerous concentration

- for the human health - of the nine trace elements under investigation were found in all samples of the Gobius niger.

Our laboratory has participated at the UNEP MED POLL II and UNEP MED POLL VIII Projects for the protection of the Mediterranean. The partial financial support of our laboratory for these projects by UNEP/FAO as well as for the Research Program "Fates and Pathways of trace elements in the Saronikos Gulf" by the European Economic Communities is gratefully acknowledged.

NAA IN ARCHAEOLOGY

INAA is widely applied to the investigation of archaeological problems. Elemental composition of an object of art besides form, shape and decorative style may give a supplementary indication of the origin of the object. The museum curator will often permit the removal of a specimen from an object for analysis if the amount taken is such a tiny fleck (a few mgs) that its absence is virtually undetectable. In such small quantities of a pottery sample for example more than 20 trace elements can be determined by INAA.

At our laboratory we have applied INAA methods to the investigation of provenance problems of ancient books, ceramics, obsidians, flints, limestones and marbles. We have examined 50 paper samples from old Venetian books (38) in order to correlate the concentrations of trace elements and the age of the books.

INAA has been applied for the determination of 20 minor and trace elements (As, Ce, Co, Cr, Cs, Cu, Fe, Hf, La, Cu, Na, Rb, Sb, Sc, Sm, Ta, Tb, Th, Yb and Zn) in two groups of potsherds (47) which have been excavated at two different sites of Greece, the island of Thasos (Group A) and Delos (Group B). A good agreement for all the elements examined between the pottery specimens of Groups A and B was found. This matching in chemical composition found by INAA between the two groups A and B provides strong support for the archaeologist's hypothesis that the two groups belong to the same major group of "melian" pottery. INAA and X-ray techniques have been applied for the determination of 24 major, minor and trace elements in four different groups of vases (55,77). Protocorinthian, Thapsos Class, Late Geometric Corinthian and Aigion Crater). The matching in chemical composition of the four groups of vases found, strongly suggests the same origin for all of them.

X-ray and NAA and mineralogical examination have been applied to obsidian samples found in the excavation of Kitsos cave at Sounion (82). The trace element concentrations found in Kitsos obsidian match with those of Melos origin found in previous works.

Current research at our Laboratory on Archaeometry deals with provenance studies of ancient pottery from the islands of Naxos and Thera, and Peloponese, as well as ancient marble from different sites of Greece.

Within the framework of collaboration between the AA group of the (INRNE) of Sofia, Bulgaria and the Radioanalytical Lab of NRC Demokritos, Greece a common project started on the development and application of NAA methods to the study of trace elements in flint samples from flint quarries and ores from Bulgaria and Greece as well as in archaeological flint objects found in museums of honey or white honey colour.

CHARGED PARTICLES ACTIVATION ANALYSIS

A rather extended charged particle activation analysis program is carried out for the last 10 years at the Tandem van der Graaff Accelerator Laboratory of the NRC Demokritos, by another group. It includes Particle Induced X-Ray Emission (PIXE) analysis, Particle Induced Prompt Gamma-ray Emission (PIGE), other nuclear reactions and proton activation analysis. It should be noted that the first external beam PIXE technique was established by this group (114,115).

Several papers (116-121) have been reported with applications in the field of biological, environmental sciences in archaeometry etc.

DELAYED FISSION NEUTRON COUNTING

A special neutron activation method, the delayed fission neutron counting method is used for the analysis of fissionable elements, as U,Th,Pu, in samples of the whole nuclear fuel cycle including geological, enriched and nuclear safeguards samples. At NRC Demokritos so far the method has been applied extensively to geological samples for uranium exploration (122).

In conclusion, I would like to add that NAA is another peaceful application of atomic energy. In biomedical and environmental research it may contribute to a higher standard of living. It can also be advantageously used to solve industrial, geological and archaeological problems. However, a close collaboration of clinicians, biochemists, physiologists, environmentalists, ecologists, oceanographers, industrialists, geologists and archaeologists with activation analysis specialists is necessary.

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