Status of NAA in Slovenia: Achievements and Applications

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Abstract

During past decades the accurate determination of trace element concentrations has been a subject of enormous interest for many fields such as nutrition, clinical chemistry and biochemistry, veterinary science, agriculture, environmental sciences, etc.

Among reliable analytical methods for determination of very low concentration levels of essential and toxic elements NAA in both its forms, RNAA and INAA, is very useful, and is also well-known as a reference method /1/.

When using INAA the matrix usually has a negative influence on the ratio between the signal and background. This results in poorer accuracy and higher limits of detection. Such difficulties may be avoided in most cases through application of RNAA methods which, on the basis of carefully chosen experimental conditions, offer selective isolation of the desired radionuclide(s). Further, the addition of carriers and/or radiotracers enables the determination of the chemical yield for each analyzed sample.

In using the Institute's 250 kW TRIGA MARK II Reactor for determination of ultra trace quantities of different elements various radiochemical methods have been developed which are briefly presented in the text below, and have been used to study their levels in human and biological samples, environmental samples and SRMs.

1. Determination of U and Th

For simultaneous determination of uranium and thorium via ^{239}U (23.5 min) and ^{233}Pa(27 d) radionuclides, the so-called LICSIR technique (Long Irradiation, Cooling, Short Irradiation, Radiochemistry) was used. The separation of the induced radionuclides is based on solvent extraction with TBP and TOPO and the chemical yield for the two elements is determined using the radioisotopic tracers ^{235}U and ^{231}Pa /2,3/, respectively.

2. Determination of I and Se

Quantitative determination of both elements in the same sample aliquot via ^{128}I and ^{75}Se after double irradiation (LICSIR technique) of the sample is based on combustion in oxygen followed by solvent extraction (redox cycle for extraction and stripping of iodine, and extraction of the Se chelate 5-nitro-3,1,2-benzoselenadiazole /4/. The chemical yield for I was determined spectrophotometrically and for Se either spectrophotometrically /5/ or by using the radioactive tracer ^{81m}Se /6/.

3. Determination of Pb, Ti and Cd

After fast neutron irradiation of the sample, separation of the induced radionuclides ^{115}Cd (^{115m}In), ^{203}Pb and ^{202}TI was made by the use of ion exchange in bromide media, solvent extraction and gravimetry. The chemical yields were determined by the radioisotope ^{21O}Pb, ^{109}Cd and gravimetrically for TI /7/.

4. Simultaneous determination of Cd, Co and Cu

The radiochemical NAA procedure is based on carbamate extraction of the induced radionuclides ^{115}Cd(^{115m}In), ^{60}Co and ^{64}Cu. The chemical yields of the separation were determined by the use of the radioisotopic tracers ^{109}Cd, ^{17}Co and ^{67}Cu /8/. The latter, ^{67}Cu ($T_{1/2}$ = 62 h), was prepared by irradiation of a ZnO target (^{67}Zn (n,p) ^{67}Cu) and anionexchange separation of Cu from the Zn matrix was employed. This is the first report of the RNAA of Cu using a radioisotopic yield determination.

5. Determination of ultra trace vanadium levels

RNAA of vanadium is based on the only possible reaction ^{51}V (n,γ) ^{52}V ($T_{1/2}$ = 3.75 min), and two complementary procedures were developed /9/: a.) post-irradiation wet ashing, solvent extraction (time for separation is 10-12 min) and b.) preashing in an oven, rapid dissolution and separation after irradiation by solvent extraction (7-8 min). These methods were applied in a study of vanadium levels in blood and hair in exposed and non-exposed persons /10/.

6. Determination of Ni

Nickel can be sensitively determined using the fast neutron reaction ^{58}Ni (n,p) ^{58}Co ($T_{1/2}$ = 71 d). A simple, near quantitative separation based on anion exchange in HCl medium was developed, with the chemical yield being measured by ^{57}Co tracer /11/. Due to the presence of ^{60}Co (produced by ^{59}Co (n,γ) ^{60}Co) in the spectrum, anticoincidence counting to reduce the Compton background under the ^{58}Co peak (810 keV) produced from the two cascade gamma rays (1171, 1332 keV) of ^{6O}Co is very effective for ultratrace determination of nickel.

7. Neutron activation analysis of arsenic species

The total concentration of the element alone gives no reliable information about its possible effects on living organisms, such as toxicity. Ion exchange methods for trace separation of As species (inorganic arsenic, MMA, DMA, arsenobetaine, trimethylarsine oxide, tetramethyl arsonium ion) in various biological samples and the determination of total arsenic in the separated fractions using INAA were developed, involving arsenic speciation in urine, sea-food, mushrooms, etc /12,13/.

8. RNAA of Hg binding to proteins

In order to study the metabolism of Hg we investigated its subcellular distribution in the brains of rats exposed to Hg vapour. The aim of this work was to isolate and partially characterize metallothionein-like proteins with Hg affinity /14/. In a

related study the distribution of mercury in the organs of rats was followed during an exposure (uptake) phase, and its subsequent elimination after the end of exposure. A four compartment model to reproduce the toxics-kinetics of accumulation and excretion was then constructed and the required parameters obtained from fitting the experimental values using an analog computer /15/.

9. Use of the k_0 standardization method of INAA

Apart from RNAA, INAA is also much used in the Nuclear Chemistry Department of IJS where the k_0-based technique has been implemented for multielemental analysis of environmental samples. This technique, which allows determination from 30-50 elements in one sample aliquot, was used in multielement analysis of epiphytic lichens (Hypogymnia physodes L. Nyl) which can be used as bioindicators for air pollution studies with heavy metas /16/. Further, this technique was also used to determine the elemental composition of lignite, electrostatically precipitated fly ash and size fractionated escaping fly ash particles for studies of the influence of the coal-fired Šoštanj thermal power plant on the environment /17/.

According to the nature of NAA (high sensitivity for many elements, negligible matrix influence on analytical results, small probability for sample contamination), which with care allows accurate and reliable results, the Department of Nuclear Chemistry acted several times as a reference laboratory for Hg determination in United Nations Environment Programmes (UNEP) and in International Atomic Energy Agency (IAEA) projects. In addition it has performed the function of external cooperating laboratory for the National Institute of Standards and Technology (NIST) in its certification programmes (trace elements), as well as in many other reference material certification exercises. The results of these analyses are quoted in many of the certificates of analysis.

Conclusions and further trends

Due its relatively high cost NAA, and especially RNAA, should be devoted to projects where its special characteristics (accuracy, freedom from blanks and contamination problems, multielement capacity, sensitivity, matrix independence) are best utilized. These include ultratrace analysis, materials research, panoramic analysis and employment as a reference method.

Further improvements in INAA techniques are likely to emerge with improved and faster electronics for signal processing, better software, and sample changers and other technology for improved throughput or automation. The use of anti-coincidence counters will also increase.

Another trend is undoubtedly the multimethod approach using several different analytical methods for complex problem solving, such as environmental and life sciences studies. In combination with preseparations, INAA can be very useful in speciation studies, an area currently undergoing an explosion of interest.

Thus in spite of some gloomy forecasts about the future of NAA and research reactors, we believe that its unique capabilities will continue to earn it a niche in analytical science and its applications.

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