Modern Nuclear Analytical Techniques and Their Applications in China

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Received: October 13, 1999

The earliest activities of nuclear analytical techniques (NATs) in China were much later than those in the developed countries, but since the late fifties a vast progress in the development of NATs has been made. This paper will describe some latest achievements in the field of modern nuclear analytical techniques, including molecular activation analysis, scanning proton microscope, accelerator mass spectrometry, synchrotron radiation-based X-ray analytical techniques, and positron sensitive spectrometry, etc. and their applications in environmental, biological, geological, and material science. The analytical quality assurance and related topics, like new type reference materials for microbeam analysis, biological and environmental specimen banking, and biological monitor for environmental quality survey, will be outlined as well.

The earliest activities of nuclear analytical techniques (NATs) in China can be traced back to the early fifties, much later than in the developed countries. However, since the first nuclear research reactor and low energy accelerator was put into operation in 1958, the NATs in China experienced a rapid growth stage, which was characterized by establishment of various NAT methods and their extensive applications in interdisciplinary fields. Recently, the Chinese government has defined six national goals, i.e., agriculture, environment, human health, energy and resources, materials, and information, as a guideline of major research direction, which are becoming strong impetus to the development of NATs, because NATs can play a significant role in the above 6 aspects. In this paper, the latest achievements of NATs and their applications in China will be described.

1. Hardware

Nowadays there are 10 research reactors available in the mainland China (one high flux reactor with neutron flux of $1 \times 10^{14}$ n/cm$^2$/s, one heavy water reactor with $8 \times 10^{13}$ n/cm$^2$/s, 4 swimming-pool type reactors with $2 \times 10^{13}$ n/cm$^2$/s and 4 miniature neutron source reactors (MNSR) with $1 \times 10^{12}$ n/cm$^2$/s. It should be mentioned that five MNSRs have been exported to foreign countries. Hou et al. discussed the application of the MNSR in neutron activation analysis (NAA), especially in epithermal NAA. The project to establish a new high flux reactor with $5 \times 10^{14}$ n/cm$^2$/s has been approved, which, hopefully, will be completed until 2003. In addition, 2 synchrotron radiation machines, 3 accelerator mass spectrometers (AMS), 3 scanning proton microprobes (SPM) and 2 intensive beam currency and low energy positron spectrometers are available. Also, over 100 low energy accelerators have been providing the routine service for PIXE and other nuclear analytical tasks.

2. Molecular Activation Analysis (MAA)$^{14}$

The MAA is a variety of activation analysis methods that is able to provide the information on chemical species of elements of interest in a studied specimen, although its exact definition remains to be assigned.$^{14}$ The so-called MAA is, in fact, a combination of conventional NAA with physical, chemical or biological separation procedures in order to meet the ever-increasing need for chemical species study. Recently, study of the chemical species of a number of trace elements in biological, environmental and geological samples have been extensively performed by MAA at Institute of High Energy Physics (IHEP). The typical examples in this aspect are as follows:

a) Platinum Group Elements.$^{5-12}$ The chemical species of anomalous iridium at the geological boundary sediments, mainly at the Cretaceous-Tertiary, were analyzed by MAA based on a step by step dissolution procedure and phase isolation technique combined with radiochemical NAA.$^{5-7}$ Interestingly, almost 50% of iridium at the K-T boundary clays exist in an acid-insoluble phase regardless to their continental or marine sedimentation origin, which imply that this part of Ir was likely originated from the extraterrestrial matters. The related work can refer to References 8-12.

b) Rare Earth Elements (REEs).$^{14-17}$ REEs have been widely applied as fertilizer and feed in China to enhance the output of agricultural products, like rice, wheat, corn, sugarcane, tea and tobacco, etc. and animal husbandry, e.g., pig, chicken, fish and shrimp, etc. However, the knowledge about the real mechanism of biological effect of REEs is scarce, although a lot of in vitro simulation experiments were done. The critical point lies in whether REEs can be combined with biological macromolecules, e.g., proteins, polysaccharides and DNA, in natural samples. Wang et al.$^{13,14}$ have successfully identified two new REEs-bound proteins mainly containing two subunits with molecular weight of 14000 and 38700 and 5 new REEs-bound polysaccharides with small molecular weights (10000 to 20000) in a natural plant, a species of fern (Dicranopteris Dichotoma). The latest finding in this aspect is that an experimental evidence about the existence of DNA-binding REE compound has been obtained.$^{17}$ The molecular weight of the REE-DNA band was about 22 kb in agarose gel electrophoresis and the REE contents of the REE-DNA compounds account for 0.087% of the total REEs in the fern leaves.

c) Chromium.$^{18-21}$ Chromium is an element which is considered to be related to the glucose and ester metabolism. Ding et al.$^{19}$ applied the MAA to study the chemical species of chromium in a Cr-rich yeast that is used as a supplement for diabetes. The experimental results indicated that Cr can enter the yeast cell through the cell wall during the culture process and about 80% of Cr in the yeast cell exist in the protoplast fraction, which have been converted to the organic chromium. Feng et al.$^{19,20}$ studied the metabolism of physiological amount of Cr (III)
intragastric administration in normal rats by using activable stable isotope $^{59}$Cr compound as a tracer.

d) Selenium. Selenium is one of the essential trace elements to human being. However, up to now almost all research about the biological functions and chemical species of Se was limited to animal test. Chen et al. studied the subcellular distribution of selenium and Se-containing proteins in the nuclei, mitochondria, lysosome, microsome and cytoplasm fractions of human liver samples by MAA. They found 8 kinds of Se-containing proteins with molecular weight of 335, 249, 106, 84.6, 70.5, 45.6, 14.8 and 8.5 kDa, respectively. Among them the 335, 84.6 and 8.5 kDa proteins were individually present in one subcellular fraction, whereas the others coexisted in two, three or four subcellular fractions. The most abundant Se-containing proteins, 70.5 and 14.8 kDa, accounted for 33.6% and 48.5% of the whole-liver soluble Se-containing protein, respectively. The former was enriched in cytosol and the latter in nuclei and mitochondria. Other related researches in the chemical species of Se in environmental and biological samples were also reported.

Besides, iodine in marine algae and human liver, mercury in human scalp hair of pregnant women and their new babies, mercury in urine and blood, and platinum in serum protein of mice, were studied.

3. Scanning Proton Microscope (SPM) [27-40]

Three SPM facilities are located at Shanghai Institute for Nuclear Research (SINR), Fudan University and Institute of Physics. Their proton energies range from 2 to 4 MeV and space resolutions are about 1 to 2 µm. The SPM has been employed to localize the distribution of elements of interest in various matrices. A typical example is to identify an unknown Pt-bearing mineral isolated from ultramafic-mafic rocks at Xinji, Sichuan Province, Southwest China. The experimental results show no any correlation between platinum and nickel or copper, both of which are the main compositions in this mineral. Interestingly, a positive correlation is evident between platinum and arsenic. The correlation coefficient is about 0.80. Further, based on the quantitative calculation, the chemical formula of the unknown mineral can be derived as Pt$_{1.379}$As$_2$.

Another latest work is to identify the source of single atmospheric particle by SPM. The workers at SINR found that the distribution of lead is inhomogeneous in atmospheric particle. In addition, the single particles from different sources, e.g., soil, cement, vehicle exhaust, petroleum, ferrous smelter and coal combustion, etc. possess different fingerprint spectra of chemical element compositions. Based on the artificial nerve network (ANN) method, the contribution rates of various atmospheric pollution sources at winter season in the Shanghai urban region have been estimated.

4. Accelerator Mass Spectrometry (AMS) [41-45]

There are 3 sets of accelerator mass spectrometers, of which two are in Beijing and one in Shanghai. A large number of long-term radioactive nuclides, e.g., $^{14}$C, $^{10}$Be, $^{36}$Cl and $^{137}$I, etc. in various environmental, geological and biological samples have been determined. Liu’s group at Peking University studied DNA adduction with $^{14}$C labeled nicotine and nicotine-derived nitrosamine, 4-(methylnitrosamino)-1-(3-pyridyl)-1-butane (NNK), by AMS in mouse liver at doses equivalent to low-level exposure of humans. A linearly positive correlation between the number of DNA adducts and dose has been observed, which implies that the nicotine is a potential carcinogen. The detection limit of this AMS measurement for DNA adduct was as sensitive as 1 adduct per $10^{11}$ nucleotide molecules, which was $10^{-10}$ better than that of other conventional techniques used for quantitative analysis of DNA adducts. Recently, they used AMS to measure the adduction of mice lung DNA with nicotine and to study the genotoxicity of an insecticide pirimicarb, 2-dimethylamino-5, 6-dimethyl-pyrimidine-4-yl-dimethylcarbamate in mice liver in low dose level.

Another typical example of application of the AMS is to study the paleoclimate in China according to radiocarbon dating of a loess profile located at Weinan, Shaanxi Province, northwest China, and of a stalagmite of 1.2 m long taken from Panglongdong Cave at Guilin, Guangxi Autonomous Region. The analytical results indicated that the climate during the Holocene in China was generally warm and damp, but afterwards it experienced a short cold period during 10000-11000 a B.P. A latest major project is to date the archeological relics for the Xia, Shang and Zhou Dynasties chronology.

5. Synchrotron Radiation-based Analytical Techniques [46-50]

In the mainland China there are two synchrotron radiation facilities located at Beijing and Hefei, respectively. A new so-called third generation SR facility will be established in Shanghai. Taking the SR at Institute of High Energy Physics as an example, versatile nuclear analytical techniques have been or are being implemented, mainly SR-XRF (X-ray fluorescence), SR-XD (X-ray diffraction), SR-SAS (small angular scattering), EXAFS (Extended X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy), etc. The SR provides a strong beam intensity of X-ray with microanalysis characteristics to enable the enhancement of analytical sensitivity and the decrease of sampling amount. Feng et al. studied the change of mercury content in pregnant women’s scalp hair during their pregnancy by SRXRF and found that the mercury content in their hair samples decreases in the period of pregnancy. Further, on the basis of analysis of hair mercury contents in their new-born babies, an interesting transformation phenomenon of mercury from mother to infant was revealed. Other related work includes the observation of concentration variation of some essential trace elements in serum protein of mice with and without the cis-platin therapy by the technique of SRXRF. Liu et al. studied the multi-elemental position distribution in some biological tissues by micro-beam SRXRF technique. Shao et al. applied the SRXRF microprobe to observe the change of some elements in human gastric cancer tissue.

EXAFS is a powerful tool to study the structure of compounds. Wang et al. used it to study the local atomic structures of liquid GaSb and InSb.

6. Position Sensitive Spectroscopy (PSS) [51,52]

In order to enhance the energy resolution of conventional X-ray detection, e.g., Si (Li) detector, and to enable the chemical species study of some important elements in systems of interest, a position sensitive spectroscopy has been established with the energy resolution of eV order of magnitude, e.g., 25, 15 and 7 eV for $^{55}$Fe, Ti and Si, respectively. It is based on the dispersive function of flat crystal, which diffracts the X-rays with different energies along a certain space direction. Then, a position sensitive detector with high ability of space resolution is used to record the X-rays at different space positions, which enables the detection of X-ray with high ability of energy resolution. The results of Hu et al. clearly show the satellite spectrum of Si K$_\alpha$. Liu et al. also observed most of the main characteristic X-rays of rare earth elements, which were well-separated for just one time of detection by PSS. The problem of serious overlapping and interference of adjacent line peaks of REEs in the conventional PIXE can be solved.
7. Analytical Quality Assurance of NATs and Related Work

The quality assurance is a critical factor for all analytical techniques. In a certain sense, the NATs are advantage over the non-nuclear techniques, because their error sources are traceable. Chai summarized the Chinese references materials for environmental and biological researches. Mao and Chai examined the change of the distribution homogeneity of elements with different chemical behaviors in a range of sampling amount from milligram to microgram. Other certification work of reference materials by NTAs and related techniques can refer to References 55-57.

Recently, Shao et al. successfully prepared some standard reference materials for microbeam analysis. Metal, alloy and compound films were prepared by vacuum evaporation. Homogeneity of the films was examined by SXRXF and scanning electron microscope, which is comparable with that of similar reference materials prepared in USA. The certified elements include As, Br, Ca, Co, Cr, Cu, F, Fe, Ga, K, Mn, Se and Zn, which can basically meet the requirement for practical sample analysis by microbeam techniques, e.g., SPM or SXRXF.

The biological and environmental specimen banking (BESB) and biological monitoring for environmental pollution are the other two related research topics. Zhang et al. reported a pilot BESB established at IHEP, where 62 normal human liver samples and other biological and environmental samples from different regions in China, which are analyzed by NATs and related techniques. The emphasis is given to monitor the atmospheric pollution of the Beijing city.

8. Perspectives

It is foreseeable that the nuclear analytical techniques with the following advanced characteristics in sensitivity, precision, reliability, accuracy, space resolution, speed, cost, chemical species, dynamics and in situ analysis, are desirable with the tremendous development of science and technology in the next century.

Acknowledgement. This work is financially supported by National Natural Science Foundation of China (NSFC) and Chinese Academy of Sciences (CAS).

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