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INVITED PAPER

A BRIEF INTRODUCTION TO NEUTRON ACTIVATION ANALYSIS IN CHINA

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The history, the major achievements in both methodology and applications, the current trends and future perspectives of neutron activation analysis (NAA) in China are briefly described.

Keywords : Neutron Activation Analysis (NAA), Reactor NAA, Fast NAA (FNAA), Prompt Gamma NAA (PGNAA), Speciation NAA (SNAA or MNAA)

1. Introduction

In broad sense, NAA refers to a family of techniques for elemental analyses utilizing the information provided by neutron bombardment of an unknown sample. Practically, however, NAA in "narrow sense", i.e., reactor neutron activation reactions combined with the measurement of characteristic radiations emitted by the decay of product nuclides, is the commonest and most powerful version of NAA. This review focuses mainly on the latter version -reactor NAA, with its general principle given below. Other versions of NAA, such as PGNAA, FNAA (14 MeV NAA), and NAA using isotope neutron sources, will be touched upon only very briefly.

When a sample is bombarded by reactor neutrons, the following "neutron capture" reaction occurs on many elements (one or more isotope(s) of each element) contained in the sample,

$$^{A}Z + n \rightarrow {}^{A+l}Z + \gamma$$

where, ^{A}Z refers to an isotope of an element, Z, in the sample. If the product nuclide, ^{A+l}Z, is radioactive, the properties and intensities of the characteristic radiations emitted from its decay can be used for qualitative and quantitative determination of the element Z (on condition that the isotopic abundance of the target nuclide, ^{A}Z, is the same (or known) for sample and standard).

The first NAA is generally believed to be conducted by Geog Hevesy in 1936, using a Ra-Be neutron source to determine Dy in Y_20_3 samples. The availability of research reactors in late 1940s made NAA a prominent tool for the determination multiple trace elements, thanks to the high thermal neutron fluxes provided by reactors and the large cross-sections of (n, γ) activation reactions on majority of naturally occurring elements. The invention of high resolution Ge γ-ray detector in 1960s (especially the high performance, large volume high purity Ge detectors in early 1980s) is the second milestone in the development of NAA, that made NAA truly non-destructive and multielemental. Since then, NAA has been applied to a large variety of scientific and industrial fields for its unique position in the inorganic trace analysis family.

The earliest activities of NAA in China can be traced back to the early 1960s, soon after the establishment of the heavy water research reactor (HWRR) in China Institute of Atomic Energy in 1958. In 1960, a group of Chinese pioneer nuclear scientists analyzed high purity UO_2 samples for four rare earth elements, Gd, Eu, Sm and Dy, with reactor NAA using radiochemical separation. NaI(Tl) scintillation detectors and GM counters.

Modern NAA based on computerized Ge gamma-ray spectrometry was established in early 1970s. Since then, the technique has been developing rapidly. The first National Conference on Activation Analysis (NCAA) was held in 1978. After the meeting, a national coordinated organization, the Activation Analysis Working Group (AAWG), was established. The AAWG is responsible for organizing national meetings,

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which were held once every 2-3 years. So far, 11 NCAAs have been held in Beijing (1978), Shanghai (1981), Qingdao (1984), Mianyang (1987), Beijing (1990), Shenzhen (1993), Chengdu (1996), Nanjing (1999), Xiamen (2001), Dali (2003), and Mianyang (2006), respectively. Topical meetings dedicated to specific areas of NAA applications were also held aperiodically.

A series of 6 review articles were presented at the 1st NCAA covering applications of NAA in life [l], geo- and cosmo-sciences [2], and material science [3]; the history, current situation and future perspectives of reactor NAA [4]; activation analysis using neutron generators and neutron sources [5]; and CRMs and their applications in activation analysis [6]. These review articles provided Chinese NAA community with fundamental and comprehensive information at the early days of NAA research and applications in our country. Among the following reviews in relation to NAA in China are "Recent Development of Reactor NAA" covering the period of 1978-1981 by Tian [7], "Activation Analysis Activities in China" for upto 1991 by Tian [8], "Activation Analysis" for 1991-1994 by Chai [9], "Activation Analysis" for 1994-1996 by Hou and Chai [10], "Activation Analysis" for 1996-2003 by Zhang and Chai [11], "Activation Analysis" for 2003-2005 by Zhang and Chai [12], "Modem nuclear analytical techniques and their applications in China" in 2000 by Chai [13] and "Neutron Activation Analysis in China: Present Status and Future Perspectives" for 2000-2006 by Zhang and Chai [14], in which original publications are quite comprehensively covered upto 2006. In this review, original papers already referenced in the above-mentioned reviews are generally not individually cited, instead, only relevant reviews are given, to reduce the size of the paper. Selected books, book chapters and review articles are listed in Table 1.

In the following sections, major Chinese contributions to the field of NAA are to be briefly described on a randomly selected basis.

2. Methodological Research

2.1. Development of hardware

One of the most important Chinese contributions to NAA is the development of the Miniature Neutron Source Reactor (MNSR) by China Institute of Atomic Energy (CIAE) in 1984 [15]. The MNSR is specifically dedicated to NAA, training and production of some short-lived radionuclides. Its unique features include fully microcomputer-controlled reactor operation, absolute safety, reasonably high neutron flux ($\Phi_{max}=10^{12}$ n.cm^{-2}.s^{-1}), low temperature (suitable for biological samples), automated pneumatic sample transport system, high epithermal proportion (Φ_{th}/Φ_e = 13.5, conducive to improving detection limits for many elements by relatively reducing interferences from ^{24}Na, ^{32}P, ^{46}Sc, etc., often encountered in activated biological and geological samples) and highly automated software for data collection and reduction. Some NAA work on a prototype of MNSR in CIAE was summarized by Wang, et al. and Hou, et al. [16-18]. There are now 4 MNSRs in operation in China (Beijing, Shanghai, Jinan (Shandong province), and Shenzhen (Guangdong province). Five MNSRs have already been exported to 5 developing countries [13]. Five large (normal scale) research reactors are now operational in the mainland of China, i.e., a high flux reactor with a maximum thermal neutron flux of 6.2 x 10^{14}, and 4 swimming pool-type reactors with maximum neutron fluxes of (l-3) x 10^{13}. A Pulse Reactor was built and put in use in Jan. 2001 in Institute of Xi'an Nuclear Technology [19]. Both stable and pulsed modes of operations are provided for NAA and other purposes [20]. The 15 MW Heavy Water Research Reactor (HWRR) at CIAE ceased operation in Sep. 2008 and is now under decommissioning, after exactly half century of service.

Table 1. Selected books, book chapters and review articles.

Topic	Reference
Neutron activation analysis in general	4, 7-14, 32, 38, 61, 62
Non-reactor NAA	5
Delayed neutron counting for U	57
Molecular NAA	33 – 37
NAA for platinum group elements (PGEs)	41
Activable tracer in biomedical studies	58
Applications in geo- and cosmo-sciences	2, 63 - 65
Applications in life and environment sciences	1, 52, 43, 44, 66
Applications in materials science and Industry	3
Applications in forensic and archaeo-logical sciences	59, 60
Applications in chemical metrology	6, 55, 46 - 49

Pneumatic sample transport systems have been installed for reactor NAA [8], delayed neutron counting (DNC) [8] and 14 MeV NAA [8]. A fully computer-controlled system for U determination by DNC was established by Song at HWRR in CIAE [8]. The device can handle 70-80 samples per hour for routine determinations of U in geological matrices by DNC with typical detection limits of 10 and 0.7 ng for single and cyclic activations, respectively. A computer controlled automatic sample changer developed by Ni, et al., is able to count activated samples continuously without human attendance [21]. A ^{252}Cf NAA on-line analyzer was established by Liu, et al., and used in some Aluminum Works [8]. This automatic system has been proven to be efficient and reliable. ^{252}Cf (and other isotope neutron sources) and 14 MeV neutron generator based on-line NAA Analyzers have been commercially available [14] and applied for neutron logging, as well as the analyses of coal, limestone, cement, glass, explosives and other materials [11, 12, 14].

2.2. *Development of software*

Computer programs for the determination of energies and peak areas in Ge γ-ray spectra have been studied by several authors. The one developed by Wang (SPAN) is able to give a reasonable compromise in finding true peaks and rejecting false ones, accurate peak areas for both singlets and multiplets, and fast calculation speed [22]. Softwares for the calculation of elemental concentrations have been established at all NAA laboratories with different levels of automation. The one developed by Ni et al., ADVNAA, has the functions of both k_0 and relative standardizations, parametric corrections for various interferences and normalization for different counting positions, and on-line quality control [21]. It has now been integrated into a fully automatic counting system, as described in the above section. An automatic data processing system for reactor NAA has been designed [11, 12, 14]. The system has functions of radionuclide identification, f and α calculation, k_0 value measurement, quantitative calculation of elemental concentrations, nuclide data management and experimental design, etc. Several programs have been written for elemental correlation evaluation and cluster analysis [8]. Examples on development of hardware and software are listed in Table 2.

Table 2. Examples on development of hardware and software

Topic	Reference
Hardware	
Miniature Neutron Source Reactor (MNSR)	15-18
Pulse Reactor	19,20
HPGe detectors	8
HPGe-NaI(TI) anti-Compton spectrometer	8
Rabbit systems for reactor NAA	8
Rabbit systems for 14 MeV NAA	8
Automated system for DNC and NAA	8,21
^{252}Cf on-line NAA system	8
Mobile 14 MeV NAA system	8
Rabbit system for DNC	8
^{252}Cf and 14 MeV neutron generator on-line NAA Analyzer	11,12,14
Software	
Gamma-ray spectrum analysis	22
NAA programs	8, 21, 11, 12, 14
Cyclic DNC	8
Dead-time corrections	8
Pile-up corrections	8
R-matrix	8
APCP	8
NAA expert system	8
Correlation and cluster analysis	8

2.3. *Development in parametric standardizations*

The advent of high resolution Ge γ-ray spectrometry in 1960s revolutionized NAA. Non-destructive analysis for multielements in various matrices became a commonplace by NAA using Ge detectors. A "nearly absolute" method having the advantages of standardization without multielement standards, determination of unforeseen elements, and computer compatibility with little sacrifice in accuracy has been pursued by many activation analysts since late 1960s. Among the most perfect models is the k_0 expression proposed by Simonits et al. in 1975 [23]. k_0-NAA was mastered and adopted by Chinese activation analysts in late 1970s [24] and early 1980s [25], and fully computerized in late 1980s [21].

Major Chinese contributions to the development of k_0 methodology include (not restricted to) the following five aspects: 1) k_0-NAA for non-l/v analytical reactions. Primary k_0-NAA expression is for l/v reactions only. By using a Lu standard as "neutron thermometer", the effective neutron temperature, T_n, during irradiation can be obtained by using literature g factor. T_n can then be used for calculation of thermal neutron cross sections and k_0 values for all the non-l/v reactions [26]. Lu, Eu, Ir and other elements with non-l/v analytical reactions, originally unsuitable for k_0-NAA, are thus k_0-NAA usable; 2) parametric corrections for fission interferences. An Ik_0 factor was defined for each interference case, and its neutron spectrum-independent nature was verified at different channels of three research reactors for 8 major fission interference cases [27]. The concept and Ik_0 values were later confirmed by De Corte et al. [28] and incorporated in a recent compilation of k_0 and related parameters [29]; 3) parametric corrections for reactor fast neutron induced threshold reactions. Reactor fast neutron energy distributions were found to be close to primary ^{235}U fission neutron spectrum at random channels of three reactors using cross sections averaged over a primary fission neutron spectrum, $\bar{\sigma}_f$ for a series of standard threshold reactions with scattered effective threshold energies. Reactor fast neutron flux (primary fission neutron spectrum equivalent) can be obtained by using a monitor (e.g., ^{54}Fe (n, p)), and the rates of all the threshold interference reactions calculated (using literature $\bar{\sigma}_f$ values) [8, 26. 30]; 4) parametric normalizations for efficiencies at different counting positions. Effective interaction depth (EID) principle was experimentally proven to be usable for quasi-point source and summing effect-free γ-rays with an uncertainty less than 3%. EID as a function of γ ray energy, S_0 (E), was determined for each Ge detector in use [24, 31]; and 5) parametric evaluation and corrections for thermal neutron flux self-shielding. Established equations may be used to evaluate if neutron flux self-shielding factor is smaller than 10%. If yes, these equations can be directly used for corrections on condition that the neutron spectrum is soft enough. Otherwise NAA may not be suitable for the analysis in question [46]. Examples on k_0 method are listed in Table 3.

Table 3. Examples on parametric standardization.

Topic	Reference
Study on k_0 standardization	24,25,8,11, 13,14
Compilation and re–determination of relevant parameters	8, 67
k_0 Extension–correction for fission interferences	27
k_0 Extension–correction for threshold reaction interferences	8, 26, 30
k_0 Extension–efficiency vs counting geometry	24, 31
k_0 Extension–k_0 for non-1/v reactions	26, 61
k_0 Extension–evaluation for neutron flux self-shielding	46

2.4. Chemical procedures involved in NAA

2.4.1. Special chemical standards

The making of Hg standard has long been a difficult task, because of its volatility that may result in a loss of Hg in the standard, or more badly, contamination of unknown samples by Hg. A new kind of Hg standard with sulfhydryl cotton matrix was made for reactor NAA [8]. It proves to be homogeneous, accurate and stable under reactor neutron irradiation. Synthetic phenolic resin based multielement standards have also been developed [8].

2.4.2. Pre-irradiation chemical treatments

Chemical treatments prior to neutron irradiation will lose two unique advantages of NAA - relatively free from contamination of analytes, and relatively low blank. However, these treatments may be necessary in the following situations: 1) substantial neutron flux self-shielding exists due to the high concentrations of elements with large (n, γ) cross sections; 2) unrealistically large size of sample is needed to make the elements of interest detectable; 3) indicator nuclides are short-lived and not detectable by instrumental NAA (INAA); and 4) studies on elemental speciation. For the first three cases, chemical pre-concentration of the elements of interest is usually used before neutron irradiation. The term chemical NAA, or CNAA, will be used for this category of NAA, while speciation NAA, SNAA (or molecular NAA, MNAA), for the last case, throughout this paper.

Studies on CNAA were mainly focused on preconcentration of REE [8] and ultratrace Au from geological samples [8], Hg from environmental samples [8], and REE from high purity compounds [8].

Species analysis, or speciation, is the analysis for the specific chemical forms, states, or valences of given elements. In species analysis, the species of interest are usually separated before their determination by proper established analytical techniques, one of which is NAA. Speciation NAA, SNAA, will be dealt within an independent subsection due to its ever growing significance and the unique contributions made by Chinese analysts in this area. Specifically, in the case of speciation for elements in different chemical forms and/or their distributions in different groups of molecules, the term molecular NAA (MNAA) is often used.

2.4.3. Radiochemical separation

The activated samples sometimes undergo radiochemical separation before counting, to reduce interferences from the co-existed interfering nuclides. This version of NAA is called radiochemical NAA, or RNAA. There are three categories of RNAA schemes: single element separation (SES), group separation (GS), and chemical spectra stripping (CSS).

Radiochemical procedures developed in pre- and early "Ge era" were characterized by multisteps, single elements or small element groups, and high degree of radiochemical purity. Multielement determinations in high purity Ga [8], Ge [8], Si [8], and soils [8] are good examples. This kind of separation schemes is still being used in "Ge era", especially for elements with pure beta or weak gamma emitters as indicators, for example, P in W wire [8], Ca in high purity Ga [8], Si in various high purity materials [8], Pt in catalys [8], etc.

Separation of individual elements was later no longer necessary in most cases, thanks to the use of the high resolution Ge detectors. Grouping the elements of interest into interference-free groups is often satisfactory. In RNAA of geological samples, attention has been focused on two element groups, the rare earth elements (REEs) and the platinum group elements (PGEs). Two typical REE group separation schemes used in China are based on HEH(EHP) (or HDEHP) extraction chromatography [8] and PMBP-benzene extraction [8], respectively. Chinese contributions to the RNAA of PGEs are the establishment of two unique separation schemes based on thiourea chelate resin [8] and long chain S-alkyl primary amine N_{1923} extraction [8], respectively.

In γ spectral analysis of an activated sample it is often encountered that one or a few nuclide(s) constitute major interference. Multielements can be determined by just selective removal of those nuclides. The CSS schemes were initiated by Girardi, et al. in late 1960s. Examples of CSS schemes developed by Chinese analysts include the use of isotope exchanger $NaBr$-$NaBrO_3$ column for the removal of major interfering nuclides ^{24}Na and ^{82}Br in activated water samples from the Everest [8] and the retention of ^{76}As on the inorganic exchangers TDO [8] and AAO [8]. Examples on RNAA and CNAA are listed in Table 4.

2.5. Speciation NAA (Molecular NAA)

Major progress has been made in MNAA since late 1980s by the NAA group of Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS), led by Prof. Chai Zhifang, as partly summarized in his review papers [33-37]. Compared to an element as a whole, its specific species are more closely related to relevant biological, environmental, and geological functions. In MNAA, NAA is combined with chemical, biochemical, or physical separations prior to neutron activation. In addition to NAA, other nuclear and non-nuclear analytical techniques were also used for post-species separation analyses. The key to species separations is to keep the element species of interest unchanged. The separation techniques frequently used include high speed centrifugation, differential centrifugation, gel-electrophoresis, gel-chromato graphy, chromato-graphy, co-precipitation, sequential dissolution, etc. The achievements made by the IHEP group have greatly developed the technique in terms of the elemental coverage and application fields, and constituted one of the most important Chinese contributions to NAA since 1990s. Among the prominent achievements are the discovery of two kinds of new Se-containing proteins with molecular weights of 335±20 and 249±15 kDa, respectively [35]; the extraction of REE-bond DNA [39]; and the use of MNAA to studies on extractable organic halogen pollutants [40]. Examples on MNAA are listed in Table 5.

Table 4. Examples on RNAA and CNAA

Matrix	Elements	Technique	Reference
Geological / cosmological studies			
Rocks	REE	CNAA PMBP extr.	8
Minerals, rocks	REE	CNAA, HEH(EHP) extr. chrom.	8
and clays	REE	CNAA, ion exch. and precip.	8
	Au	CNAA, activated carbon	8
	$^{235}U/^{238}U$	CNAA, paper-chromat.	8
	Rh	CNAA, Ni matte	8
	REE	RNAA, HDEHP extr. chromat.	8
	REE	CNAA, pressed resin	11
	PGE	RNAA, chelate resin	8
	PGE	RNAA, N_{1925} extr.	8
	PGE	CNAA, Ni matte	8
	PGE	CNAA, fire assay	11
	Re	CNAA, resin	10
	Re	RNAA,Extr	8
	Re, Rb	RNAA, crownether extr	11
	$^{184,190}Os$	RNAA, Distil	8
	Ir	RNAA, Resin	9
	Actinides	RNAA, Multiple	9
	Os, Ru, Ir	RNAA, Distil+extr	9
	Au	RNAA, di-octyl sulfide extr.	8
	Ag	RNAA, chelate resin	8
	Au, Ir, Re, Tc	RNAA	8
	Au, Pt, Pd	CNAA, absorp	11
	PGE	CNAA,Nicklematte fire assay	11,14
		CNAA, resin	11, 14
Granite, lava	Ta, Au, Lu, Sn, etc.	RNAA, TTA extr.	8
Artificial lava	Re, Ir	RNAA, precip., resin	8
Mineral RMs	Au	RNAA, MIBK extr.	8
Ultrabasic rock	REE	RNAA, HDEHP extr. chromat.	8
Jinchuan ores	PGE	RNAA, distil., extr.	8
Lunar sample	36 elements	RNAA, HAP, HDEHP extr. chromat.	8, 42
Meteorites	PGE	RNAA, chelate resin	8
	PGE	RNAA, thiourea resin	8
	Os, Ru	RNAA, distil.	8
	Ga	RNAA, isopropyl ether extr.	8
	$^{184}Os/^{190}Os$	RNAA, distil.	8
	^{53}Mn	CNAA+RNAA, resin, precip.	8
Biological/environmental studies			
Fly ash SRM	Hg	CNAA, sulfhydryl cotton adsorp.	8
Natural water	multielements	CNAA, sulfuydryl cotton adsorp.	8
Biol. environ, mat.	Ga	CNAA, cation resin	8
Water	Hg	CNAA, dithizone extr.	8
Sea water	U	CNAA, Extr	8
Animal organs	REE	RNAA, HDEHP extr. chromat.	8
Blood	multielements	RNAA, HAP, resin	8

	Cu, Mn, Zn, Na, K	RNAA, HAP	8
	Multielements	RNAA, extra (removing Fe)	8
Maize	REE	RNAA, HAP + PMBP extr.	8
Bone	Th	RNAA, anion resin	8
Foodstuffs	Se	RNAA, combustion	8
Skin	Cu, Mn, Zn	RNAA, HAP	8
Wheat	Th	RNAA, cation resin	8
Organs, bones	REE, Th	RNAA, HDEHP extr. chrom.	8
Bioi. Mat.	As, Se, Hg	RNAA, C_{l8} -Si gelatin	8
	As, Cd, Hg, Cu, Zn	RNAA, $Zn(DDTC)_2$ + MIBK	8
	As, Se, Hg, Sb	RNAA, distill. + resin + NaDDTC	8
	As, Cd, Cu, Mo	RNAA, NaDDTC extr. + TDO	8
Ore tailing	REE	RNAA, HDEHP extr. chrom.	8
Ice, snow, river water	multielements	RNAA, NaBr-NaBrO) column	8
Water	multielements	RNAA, HAP	8
Ice, snow	Cu	RNAA, BPHA extr.	8
Water	Hg	RNAA, dithizone extr.	8
Hair, organs	multi elements	RNAA	8
Spring water	mulfielements	RNAA, extr. ^{82}Br, prec. ^{56}Mn	8
Heavy water	Hg	RNAA, toluene extr.	8
Soil	multielements	RNAA, distill. + HAP + resin	8
Soil CRM	Hg, As, Se, Sb, Cu, Zn, Cd	RNAA, distill. + extr.	8
IAEA RM SL-3	45 elements	RNAA, HEH(EHP) extr. chromat.	8
Bioi. CRM	As	RNAA, AAO column	8
Water suspensoid	Cu, Fe, Zn	RNAA, dithizone extr.	8
Blood serum	13 elements	RNAA, AAO + HAP + HMO columns	8
	Cu	RNAA, Precip	9
Sea Water		CNAA, Resin	11,14
Environment		CNAA, Resin	II, 14
Dinosaur egg shell	PGE	RNAA, extraction	II, 14
Hair, Wheat		RNAA, Co-precipitation	II, 14
Materials and industry			
Sc_20_3	multi elements	CNAA+ RNAA, PMBP, HDEHP	8
Y_20_3	multielements	CNAA, HEH(EHP) extr. chromat.	8
Catalyst	Pt	CNAA + RNAA, anion resin	8
Y_20_3	Dy, Tb	RNAA, N-263, TBP extr. chromat.	8
Ga	Ca	RNAA	8
	multielements	RNAA, isopropyl ether extr. of Ga	8
Ge	multielements	RNAA, $GeCl_4$ distil	8
Ga	11 elements	RNAA, distill. + extr. + precip.	8
GaAs	Si	RNAA, butanol extr.	8
UF_6	21 elements	RNAA, TBP, BPHA, PMBP, HDEHP	8
UF_6	Cl	RNAA, AgCl precip.	8
Pearl	multi elements	RNAA, HAP	8
H. P. materials	Si	RNAA, distill as SiF_4	8
W wire	P	RNAA,ion exchanger + precip.	8

Table 5. Examples on MNAA

Sample	Element	Description	Ref
Geo samples	REE	Stepwise dissolution	8
	Ir	Stepwise dissolution	8
Com (proteins)	Se, etc		8
Liver (subcellulars)	20 elements		8
Rat liver subcellular	As	Diff Centrif	11, 14
Human liver cell	17	Diff Centrif	11, 14
Yogurt	CI, Br, I	Extra	11,14
Aerosol	CI, Br, I	Soxhlet, Extra	11,14
Pine needle	CI, Br, I	Soxhlet, Extra	11,14
Air particle	29	sequential extra	11, 14
Wheat root	La	sequential extra	11, 14
Wheat seedling	Se	POD-I enzyme	11
Dicranopteris dichotoma Leaves	REE	Bond Protein, Amylose	10, 11
Algae	I	Species	11
Plant	REE	Species	11
Hair	Hg	Species	10,11
Hair	Tot Hg, Meth Hg	Species	10
Geo sample	Ir	Distrib	10
Soil	REE	Distrib	10,11
Ore	PGE	Distrib	11
Ore	PGE	Distrib	10
Plant	REE	Centrif, extra	14,39
Human liver	Se, etc.	diff centrif, gel chromat	11, 14
Rat organs	Cr	diff centrif, gel chromat	11, 14
Yeast,Cr-enrich	Cr	sequential extr	11,14
Rat liver	As	diff centrif	11, 14
Rat liver	Sm, Yb	diff centrif	11, 14
Plant	REE	diff centrif, sequential-extrac	11, 14
Algae	I	sequential extrac	11, 14
Pine needle	CI, Br, I	soxhlet, extrac	40
Air particle	Multi. Ele.	sequential	11, 14
Milk	CI, Br, I	extraction	11, 14
Rock	PGE	sequential extrac	11, 14
Geo-sample	Au	sequential extrac	11, 14
Coal	As	sequential extrac	11, 14
Water	As	extra, co-precip, resin	11, 14
Geo-sample	Ir		8, 10
Bio-sample	Se		9,10
	REE		9
Bio/Env sample	Hg		9,10
Coal	As	Sequential extraction	9
Water	As	Extr, co-prec, resin	14
Rat liver	As	Centrifuge	14
Milk and yoghourt	CI, Br, I	Extr	14
Cancer tissue	Multiple	Centrifuge	14

2.6. Supplementary techniques in NAA

The term "supplementary" here means NAA using irradiation sources other than the whole spectrum of reactor neutrons and/or measurement techniques other than simple Ge gamma ray spectrometry.

2.6.1. Supplementary activation techniques

Epithermal NAA

Sample irradiation with reactor epithermal neutrons (samples covered by Cd or B boxes) will enhance the relative sensitivities of elements with analytical reactions having higher ratios of resonance integral over thermal neutron cross sections $(Q = I_0/\sigma_0)$, while depress those having lower Q values. When the former is the element of interest and the latter is the interfering one, epithermal NAA (ENAA) will be advantageous.

To judge if ENAA is worthwhile for a concrete analytical case, an advantage factor of ENAA, F_a, has to be defined. Chinese contribution in this aspect is the proposition of a unified F_a by Tian [8], $F_{a,ti} = \surd JG \surd R_j/R_x$, where R_j and R_x are Cd ratios for a major interfering nuclide and the nuclide of interest, respectively, G is an amplification factor of ENAA (by increasing sample size and/or nearing sample counting position). This definition of F_a unified the two conflicting definitions proposed by Brune ($F_{a,br} = R_j/R_x$) [8] and Bern ($F_{a.be} = \surd Ri/Rx$) [8], by indicating that the $F_{a,br}$ and $F_{a,be}$ were nothing but two extreme cases of $F_{a,ti}$ with $G = R_j$ and $G=1$, respectively. Br in geological RMs [8], U, Th [8] and other elements [8] in different matrices are some examples of ENAA.

ENAA performed on MNSR for the certification of Iodine in various biological and environmental matrices [11] is a prominent example for demonstrating the usefulness of both ENAA and its implementation on MNSR (taking the advantages of MNSR in low temperature and high ratio of epithermal over thermal neutron fluxes).

Activation by neutron generators and isotope neutron sources

Applications of 14 MeV NAA have been centered on determinations of elements difficult for reactor NAA, such as O, F, Si, P, S, etc., and other major and minor elements in various samples. Efforts have been made in improving accuracy (e.g., sample spinning during irradiation and measurement [8]), efficiency (60 samples per hour for O, 10 samples per hour for Si [8]) and flexibility (movable 14 MeV NAA [8]). Only scattered papers were published on NAA with isotope neutron sources [8]. ^{252}Cf (and other isotope neutron sources) and 14 MeV neutron generator based on-line NAA Analyzers have been commercially available [14] and applied for neutron logging, as well as the analyses of coal, limestone, cement, glass, explosives and other materials [9, 11,12, 14].

Activation by neutrons from cosmic-rays

An excellent piece of work is the determination of ^{53}Mn by pre- and post irradiation chemical separations [8] and its use in cosmic ^{53}Mn profiling in core samples of Jilin chondrite [8]. A two-stage exposure history was proposed with durations of 10 Mas and 0.5 Ma, respectively. Cosmogenic nuclides ^{22}Na, ^{26}Al, etc. have been determined non-destructively in Ningqiang chondrite with a plastic scintilator shielded NaI (Tl) anti-Compton spectrometer [8].

Activable tracer combined with NAA

The use of stable, however neutron-activable, nuclides as tracers has two major advantages over radioactive tracers in biological and environment studies -no harmful radioactive materials are introduced to the life or environment system studied, and long period of study is feasible (no half-life limits encountered in the case of radiotracers), Examples of work in this aspect include the studies on water flows [8] and the bioavailability of Zn [8] and Fe [11,14].

In-vivo NAA

The advantage of in-vivo NAA is analysis without sampling. Wang Haiying and co-workers initiated the technique in China from late 1980s, and are now continuing the studies on in-vivo determinations of protein, Ca, Na, P, etc. in whole and part bodies of animals [8-11].

2.6.2. Supplementary measurement techniques

Measurement of activated samples by detectors other than simple HPGe

As mentioned above, a device for U determination using delayed neutron counting has been built and automated [8]. Another noble techniques for highly sensitive determination of U, nuclear track detection (NTD), has been used for geological, cosmological and other fields [8]. NTD has also been applied for the determination of B (via ^{10}B (n, α) reaction) in legume forages [8]. HPGe detector has been used for accurate determination of P in typical biological materials by measuring bremsstrahlung from β^- of ^{32}P [8]. Examples on supplementary techniques in NAA are listed in Table 6.

Table 6. Examples on supplementary techniques in NAA

Special activation techigues	
ENAA	
Newly defined advantage factor	8
ENAA of geo-RMs for Br	8
U, Th in geological samples	8
Multielements in geo-samples	8
Multielements in meteorites	8
ENAA of RMs for I on MNSR	8
14 MeV NAA	
Major elements in minerals, rocks, meteorites	8, 11, 14
Ba in geological samples	8
Ce, Cr, Si, Na, Cl, F in geological samples	8
Petroleum logging	8, 11, 14
Protein in plant	8
N, P and K in plant	8
F in cotton	8
Al, Si in tea leaves	8
O in minerals	8
P and Si in resin	8
Detecting explosives	8
Multielements in ancient pottery, coins, mirror	8
S in perfluoropolymer	8
NAA with neutron sources	
Al in soil by ^{241}Am-Be source	8
N, H in tumor patients by ^{241}Am-Be, Pu- Be sources	11, 14
Au ore survey	8
On-line analysis using ^{252}Cf source	8,9, 11, 14
Determination of cosmogenic nuclide	
^{53}Mn by CNAA+RNAA	8
^{22}Na, ^{26}Al, etc by anti-Compton detection	8
Special neutron sources	
Determination of T	8
Multielements in granites and lava	8
Activable tracer-NAA	
Study on water flow	8
^{70}Zn for Zn bioavailability	8
^{58}Fe for Fe bioavailability	11, 14
In-vivo NAA	
Background for N amd Whole body protein	8
whole body protein in small animals	8
Ca, Na, P, protein in animals	9,10,11
Special measurement techniques	
Delayed neutron counting (DNC) for U	8
Nuclear track detection (NTD) for U	8
NTD for B in legume forages	8
14 MeV NAA- X-ray spectrometry	8
Reactor NAA -Si(Li) X-ray spectrometry	8
Reactor NAA -planar Ge gamma/X-ray analysis	8
Beta counting for Ca and P	8
HPGe detector for P	8

3. Applications

In the following sub-sections, applications of NAA in several major areas, mostly by instrumental NAA, INAA, the most frequently used and the least technically changed version of NAA, are introduced, since other versions of NAA (on both methodology and applications) have been dealt within previous sections.

3.1. Geo- and cosmo-sciences

The high sensitivities for most elements and the advantageous matrices of typical geological materials (e.g., silicates) have made NAA a powerful tool in these fields. One of the most impressive Chinese contributions is the continuous study on Ir (and other PGEs) anomalies in geological boundaries. In a topical review entitled "NAA of PGEs as indicators of extraterrestrial materials" by Chai [41], 30 Chinese papers were listed in references. Kong and Chai have studied Ir distributions in different mineral phases of clay samples from K- T boundaries, in an effort to further clarify the hotly disputed problem -the origin of the Ir anomaly [8]. The geo-boundary anomaly in other PGEs [9] and isotopic abundance [9] were also studied. An Apollo-17 lunar mare sample donated by US was analyzed by INAA and RNAA for 36 elements [42]. An innovative application developed by Chinese scientists is the NAA of geogas from certain hidden ore deposits for marker elements [8, 9.10,11,14]. Ore bodies as deep as hundreds meters can be detected with this technique. Studies on Loess profiling for multielements may provide information on paleoclimate [9]. The numerous publications on REE geo- and cosmo-chemistry are other major Chinese contributions in these fields. Examples on the applications of NAA in geo- and cosmo-sciences are listed in Table 7.

Table 7. Examples on INAA in geo- and cosmo-sciences.

Sample	Element	Description	Reference
Apollo-17 lunar sample	36 elements	lunar research	42
Boundary rocks, clays	PGE, REE, etc.	earth's evolution	8
Spherules	PGE, REE, etc..	rare events, cosmic dust ident	8
Deep sea cosmic dust	PGE, REE, etc.	Origin id.	8
		Au-Ir correlation	8
Inclusion Fe-Ni grain	PGE, etc.	meteorite evolution	8
Chondrite	multielement	element distribution	8
Rocks, meteorites	PGE	Au ore formation, rare events	8
Antarctic icy rocks	multielement	antarctic environmental	8
Drilling core sediment	multielement	retention time and EF	8
Dongting lake sediment	multielement	background values	8
Biogenic apatite	10 REE	evolution in K/O system	8
Basaltic rocks	REE, etc.	trace element geochem	8
Antarctic rocks	multielement	element distribution	8
Metabasites, skarns, gneiss, Ophiolite, volcanic rocks	multielement	Petrology	8
Monominerals	Au, REE	Au distribution	8
	Sc, Cr	Petrogenesis	8
Fossil salt	multielement	formation of a basin	8
U ores	U	Methodology	8
Coals	multielement	formation of coal	8
Antarctic rocks	8 REE	weathering process	8
Fe-Mn nodules and sed.	Multielement	possible formation	8
Trench floatstones	multielement	lava origin, evolution	8
Oil, organic extracts	multielement	organic geochem	8
Shallow sea sediments	multiemenet	sedimentary environment	8
Geogas	multielement	gold ore exploration	8, 10, 14
Rocks	U, Th, K	oil well calibration	8
Rock leaches	REE	element migration history	8
Kimberlites	REE	Petrology	8
Sed. in edge of eddy	multielement	sedimentary process	8
Loess	multielement	Pedogeochem	8
U-bearing granites	multielement	U prospecting	8
Granites	multielement	Petrogenesis	8
Zircon	multielement	U prospecting	8
Au ores	Au	Au evaluation	8
V- Ti magnetite	Sc	comprehensive use	8
Plants	multielement	searching for minerals	8
Sediment	multielement	sediment movement	8
Rock	Multiple	Geochem	9
Single mineral	Multiple	Meteoritics	9
Inclusion	Multiple	Ferruginous rock	9
Rock	Multiple	Metamorphite	9
Basalt	Multiple	Antarctic	9
Lava	Multiple	Ophiolite	9
Sampler	Multiple	Exploration	9
Crude oil	Multiple	Origin	9

Clay	Ir	Calamity	9
Plant	Au	Au exploring	9
Geo-sample	PGE	Distrib, geochem	10
Geo-boundary	PGE	Calamity	9, 10, 14
Geo-boundary (loess)	Ir	Calamity	9, 10
Geo-boundary	Ru, Os	iso abund	10
Tektite	multiple	Geochem	10
Meteorite	multiple	Cosmochem	10
Cosmic dust	multiple	micro-grains	10
Basalt	multiple	isotope geochem	10
Volcanic rock, basalt	multiple	Geochem	10
Inclusion	REE	Geochem	10
Gabbroite	REE	Geochem	10
Mafic rock gas	multiple	Geochem	10
Geo-micrograin	multiple	origin id	10
Ophiolite	multiple	Geochem	10
Metamorp olivinfels	REE	special distr	10
Mantle rock	multiple	Geochem	10
Granite	multiple	Geochem	10
Ultrabasic rock	multiple	Geochem	10
Tuff	REE	Au ore	10
Carbonatite	multiple	chem. Explor	10
Geo-sample	multiple	strata sequence geo	10
Soil, rock	multiple	Au ore	10
Siliceous rock	REE	Ce anomaly	10
Geo-sample	PGE	Geochem	11,14
Geo-boundary	PGE	Calamity	11, 14
Rock, mineral	Multi ele	Geochem	11,14
Jade	Multi ele	Identification	11, 14
Water	Multi ele	Geochem	11,14
Geo-gas	Multi ele	Ele migration	11, 14
Sea water	Ir	Chem states of Ir	14
Hydrothermal sed	Pb, Ag	Ag metallogeny	14
Stratum sample	Co, Ir	Dating	11,14
Water	28	Geochem	11I, 14
Meteorite	13	Classification	14
Cu ore	Re	Methodology	14
Fossil	REE	Calamity	14
Anthraxolite	REE, etc	Org metallogeny	11,14
Black rock series	PGE	Geochem	14
Kupferschiefer	Na, K, Rb, Cs	Geochem	14

3.2. Life sciences

One of the most prominent Chinese characteristics is the wide range in both the kinds of samples and the research objectives. As one example, NAA of human hair samples has been widely used in studies of trace elements related diseases, especially diseases of infants, children and old people [8]. An in-depth investigation on the relationship between trace elements in hair and in organs may lead to more scientific explanations of hair data [8]. Based on analysis for large populations, multielement data for normal Chinese have been established. Routine services on NAA of children's hair for Zn have been offered in Beijing and other major cities in China. Taking the advantages of activable tracer -NAA in non-intrusiveness (no radionuclide is introduced to bio-system) and long period of studies (not limited by radioactive decay), the technique has been used in the study of trace element bioavailability and metabolism, as detailed in previous subsection "activable tracer -NAA ".

A notable Chinese contribution in this field is the development of SNAA (or MNAA), as detailed in previous relevant subsection. Examples on the applications of NAA in life sciences are listed in Table 8.

Table 8. Examples on applications of NAA in life sciences

Sample	Element	Description	Reference
Hair	multielement	contamination in REE mine areas	8
		gallstone	8
		malformation of newly born infants	8
		infants and children	8
		nearsightedness	8
		diabetes and breathing excereise	8
		thyropathy patients	8
		elderly hypertensives	8
		normal persons	8
		effectiveness of Chinese medicine	8
		brain tumour	8
		aging	8
Gallstone	multielement	gallstone	8
Lens	multielement	cataract	8
Cancer tissues	multielement	cervix cancer	8
Rabbit osteotylus	multielement	fracture	8
Breast milk, cow	multielement	nutriology	8
Milk, milk powder, nail	multielement	rheumatoid arthritis	8
Ginseng	multielement	effectiveness of Chinese medicine	8
Bezoar	multielement	effectiveness of Chinese medicine	8
Animal feather	multielement	thyroid enlargement	8
Animal tissues	Na, K	side-effects of contraceptives	8
Blood	multielement	Chinese medicine for leukemia	8
Hair, Feces	Multi	Wiltson's disease	9
Animal	Ca, Na, P, protein	Biopsy	9
Hair	Multiple	Env Poll	9
Brain tumour	Multiple	Subcellular	9
Liver	Multiple	Subcellular	9
Hair, organ	Multiple	Correlation	9
Hair, organ	Multiple	Correlation	9
Yeast	Cr	Species	9
Yeast	Se	Se yeast	9
Rat organ	Multiple	Tumour	9
Hair	Hg	Mother-child corr	9
Plant	Se	Species	9
Hair, nail	Multiple	Longevity	9
Eye crystal	Multiple	Cataract	9
Tea	Multiple	Background	9
Hair	Multiple	Hypertension, respire disease	9
Eye crystal	19	Cataract	10
Dinosaur bone	Multiple	Distr	10
Rabbit	Ca	Abs & distr	10

Hair	Hg, Se	Correlation	10
Animal organ	REE	Correlation	10
Human organ	I, Br	Ref value	10
Saussurea	33	Herbal med	10
Pearl	Multiple	Nutrients	10
Wheat, rice, Fruit, Plant	REE	Physiology	10
Meal	I	Intake	10
Meal	Multiple	comp, variat	10
Eatable	Fe	Bioavail	10
Foodstuff	Multiple	Nutrients	10
Human hair	23	Endemic	11, 14
Human liver	19	Correl	14
Water, foodstuff, soil	25	Endemic	11,14
Fish	18 (incl Se, Hg)	Correl	14
Rat brain and liver	10	Hg nerve toxicity	14
Rat brain	12	La nerve toxicity	14
Rat Bone	6	Estrogen / osteoporosis	11, 14
Blood, urine	Pt	Methodology	11, 14
Food, cosmetics	As	Methodology	11,14
Cr-enriched yeast	Cr	Cr content	11, 14
Fern	REE	Distri	11,14
Coal	As, etc	Pollution	11, 14
Coal	U, Th	Paleo-env	14
Aerosol	Multiple	Atm Env	11, 14
Sediment, plant	27	Pole env	14
Marine sed core	REE	Origin	11, 14
Soil core	REE	Erosion	14
Rat organs	Multiple ele.	Diabetes	11,14
Human tissue	Na. Cl. K. Ca. P	Cancer	11,14
Thyroid gland	I	Content	11,14
Tooth	F	Content	11,14
Excreta	Fe, Zn	Fe, Zn bioavailability	11,14
Rabbit brain	Multiple ele.	Cerebral ischemia	11, 14
Rat organs	REE	Distribution	11,14
Rat hypothyroid	I	Keding Disease	11, 14
Egg	Ir	Metabolism	11,14
Dinosaur egg	Multiple ele.	Content	11, 14
Crops, fruits	REE	Absorption, distribution	11, 14
Cr-enriched yeast	Cr	Chemical species	11, 14
Rabbit iliac crest	Multiple	osteoporosis	14
Human liver	Multiple	elemental correlation	14
Rat brain	Multiple	Neutrotoxicity of La	14
Crop, fruit	REE	Absorp, distrib	14

3.3. Environment science

Background values of multielements in airborne particulates, natural waters and soils have been investigated nationwide, in an effort to establish scientific bases for formulating environmental laws and regulations. NAA has played an important role in this aspect. In a nationwide survey on agricultural soils, 29 out of 60 elements determined were reported by NAA, and 10 of them were solely provided by NAA [43]. An IAEA workbook, "Reactor NAA for Airborne Particulate Matter", by Tian gives a brief description on various aspects of NAA for APM studies [44]. Determination of size distributions of multielements in airborne particulate matter [8] and the states of multielements in natural water [8] are two examples reflecting the new trends in deepening our knowledge on the origins and mechanisms of air and water pollution by means of SNAA. Ecological circulation of toxic element Cr^{6+} has been studied by using NAA [8]. Study on SNAA of environmental materials for extractable organic halogens (EOX), especially one of the most baneful pollutants -persistent EOX (PEOX), is an outstanding Chinese contribution to this field [11, 14, 40]. Examples on applications of NAA in environmental sciences are listed in Table 9.

3.4. Material science and industrial applications

The removal of intense radioactivities from matrices, such as Ga [8], GaAs [8], Ge[8], UF_6 [8], etc., in RNAA of these high purity materials to achieve the determination of multiple trace impurities is among the most impressive procedures in this field. Examples are listed in Table 10.

3.5. Archaeological and forensic sciences

The long and rich history of Chinese civilization provides us with abundant archaeological projects to be studied. NAA has been widely applied in this field, for its inherent advantages. Unearthed potteries are the samples analyzed most often for the study on provenance [8]. Two papers summarized the use of NAA in forensic science [9,10]. Hair and gun powder have been routinely analyzed by NAA for forensic purposes. In addition to provenance, NAA has been used for dating of the unearthed pottery [11, 14]. The raw materials of the terra cotta warriors of Qin Shi Huang Tomb were proven to be local earth [11, 14]. An effort of establishing multielement fingerprint database for unearthed pottery samples is underway. The database so far accomplished has been used for provenance and dating of unknown samples [14]. Multiple trace element pattern obtained by NAA has been used for the detection of the origin of contraband [14]. A recent achievement of NAA in archaeological and forensic sciences is the clarification for the cause of the death of Guang Xu, a Qing emperor (died on 1908-11-14). NAA of his segmented hair and cloths samples for As revealed that the emperor was died of acute (not accumulated) As poisoning [45]. Examples on NAA in archaeological and forensic sciences are listed in Table 11.

3.6. Study on certified reference materials (CRMs)

3.6.1. NAA in certification of multiple trace elements

NAA has long been one of the backbones in the certification of multielements in various matrices for its advantages in non-destruction, multielement capability, high sensitivity for large number of elements, and its nuclear-based analytical principle unique from those of most other methods, which are mainly based on atomic or molecular properties. Certification of reference materials by intercomparison of international laboratories can be considered analytical "Olympics", where only the number and quality of the reported data count. China has made her contributions in this aspect. As an example, 42 elements were reported in an IAEA intercomparison study on a Lake sediment RM SL-3 by a Chinese lab. with no one single outlier for the certified values of 26 elements and the reference values of 10 other elements [8]. A notable Chinese contribution in this field is the preparation and certification of a human hair CRM (HH-CH-l), which has long been one of very few qualified CRMs of hair matrix in stock in the world [8].

3.6.2. Position of NAA in chemical metrology

In 1995, the Consulting Committee for Amount of Substances (CCQM) (affiliated to CIPM) listed 5 methods, i.e., IDMS, gravimetry, coulometry, titration, and freezing point depression, as "having potential of being primary methods". NAA was not in the list at that time.

A series of four papers by Tian, et al. [46-49] analyzed the traceability and uncertainties of the analytical results by NAA, proved that NAA is qualified as a primary method of measurement, and demonstrated the unique role of NAA in certifications for elemental concentrations of CRMs. These papers were sent to and distributed at the 7th CCQM meeting (Apr. 2001, Paris) as working documents. These are among the Chinese contributions, as part of the common efforts of international NAA community, that led to the eventual recognition of NAA as one of the eight primary methods by Dr. Kaarls, President of CCQM, at the International Symposium on Metrology in Chemistry (Oct. 2004, Beijing).

Table 9. Examples on applications of NAA in environmental sciences.

Sample	Element	Description	Reference
Aerosol, dust	multielement	elemental migration and climate	8
Smoke	multielement	elemental distribution	8
Marine aerosol	multielement	origin identification	8
Aerosol	multielement	in Beijing and Tianjin	8
	multielement	size distribution of multielement	8
Spring water	multielement	assessment of mineral water	8
Drinking water	multielement	seasonal variation	8
Ground water	multielement	environmental contamination	8
Rain water	multielement	environmental contamination	8
Sichuan liquor	multielement	nutritional and toxic elements	8
Soil	multielement	modification of grassland soil	8
	V, Cr	background values	8
Soil solution	multielement	trace element and agriculture	8
Coal, fly ash	multielement	contamination by coal burning	8
Oven coke, slag	multielement	environmental contamination	8
Building mat.	U, Th, K	radiation safety	8
Ore-soil-water	multielement	migration of multielement	8
Water-soil-wheat, rice	Cr	ecological circulation of Cr	8
Hair	Cr, etc	hair as environmental indicator	8
Apple leaves	multielement	environmental indicator	8
Cigarettes	multielement	smoking and health	8
Soil solution	Multiple	Crop Growth	8, 9
Aerosol	Multiple	Sea-air exchange	8, 9
Sea water	U	Background	9,11, 14
Soil	Multiple	Vertical distr	8, 9
Plant, soil	Multiple	Antarctic survey	8, 9
Plant	Multiple	Tibet plateau	8, 9
Coal	Multiple	Air pollution	8, 9
Aerosol	multiple	element influx	10
Aerosol	multiple	air pollution	10
Off-sea aerosol	multiple	sea-atm exchange	9
Env sample	multiple	air pollution	10
Soil	multiple	soil erosion	10
Water	multiple	purity	10
Plant	multiple	background	10
Human hair	Hg (tot, methyl)	river pollution	10
Well water	As	As poisoning	10
Water, Soil	As, etc.	Endemic	11, 14
Human hair	Multiple ele.	Env. pollution	11, 14
Soil	Multiple ele.	Soil erosion	11, 14
Soil	Eu	Soil erosion	11, 14
Soil	Multiple ele.	Background	11, 14
Lichen, moss	Multiple ele.	Atm. pollution	11, 14
Rock, plant (Antarctic)	Multiple ele.	Env. change	11, 14
Water, soil, foodstuff	As, etc.	endemic arsenic disease	14
Coal	As, etc.	pollution	14
Aerosol	As, Au, etc.	air pollution	14

Moss and lichen	multiple	biomonitor for air	14
Natural water	multiple	background	14
Soil	multiple	soil erosion	14
soluble humic acid	Na, Cl	soluble humic acid in soil	14
foodstuff, Plant, Aerosol	Organohalogens	food contamination, air pollution	14
Sediment core	REE	sedimentation	14

Table 10. Examples on NAA in materials science and industy.

Sample	Element	Descriotion	Reference
Activated carbon	multielement	impurity anal.	8
Rubber	multielement	impurity anal.	8
Rh	Ir	impurity anal.	8
Be	multielement	impurity anal.	8
Cu-Au alloy	Cu, Au	ion sputtering mechanism	8
Graphite	multielement	impurity anal.	8
Si wafer	Au	study on defect absorption	8
Si	multielement	impurity anal.	8
	As	profiling of implanted As	8
	P	profiling of implanted P	8
Laser wave guide	multielement	impurity anal.	8
Filter paper	multielement	impurity anal.	8
LiH	Cl, Al	impurity anal.	8
GaAs	B	Crystal	9
Barite	Mo	Identity	9
Sapphire	Ti	Impurity	9
Y_2O_3 etc.	REE	Impurity	9
Quartz, Chip	Multiple	Impurity	9
Ethylen perchloride	U	Impurity	9
Turbine oil	Multiple	Impurity	9
Be	Multiple	Impurity	9
Plastic explosives	N,O	Detection	9
Landmine	N,O	Detection	9

Table 11. Examples on NAA in archaeological and forensic sciences.

Sample	Element	Description	Reference
Ancient pottery	multielement	date and provenance	8
Date, pear, plum	multielement	from a tomb of Han dynasty	8
Hair, paint, bones, blood	multielement	forensic purpose	8
Organic matter	Ni, V, etc.	petroleum origin	8
Palaeozoic rocks			
Bronze battle-axe	Ni, Co, etc.	history of iron production	8
Forensic sample	multielement	summary	9,10
Ancient pottery	multielement	dating	11, 14
Terra cotta warriors	multielement	provenance	11, 14
Ancient pottery	multielement	database	14
Contraband	multielement	detection	14
Hair, cloths	As	cause of death	45

3.6.3. NAA in establishment of microanalysis-oriented CRMs (MO-CRMs) in the future

Minimum sample size specified in certificates of nearly all existing natural-matrix CRMs is 100 mg or larger. Due to the unavailability of the natural-matrix CRMs suitable for quality control of microanalyses (a family of analytical techniques with sample (solid sampling) sizes smaller than, say, I mg (could be down to fg!) and now being increasingly active in various frontier research areas), matrix dependency remains an "Achilles' heel" in laser ablation ICPMS [50] and many other solid sampling microanalyses for accurate quantification.

The idea of specifying minimum sample size for individual certified elements in a given CRM, rather than for the CRM as a whole, was first proposed by Tian in 1981 [7]. This idea was tested on an IAEA marine sediment RM SD-M-2/TM by NAA in 1992 [51]. It was found that many elements are homogeneous (with relative standard sampling uncertainty < 1%) at sample sizes much smaller than 100 mg, and the sampling behaviors are quite different for different elements. A series of international and Chinese CRMs/RMs were studied for sampling behaviors of individual elements by NAA in the following years, as summarized [49]. Sampling behavior of multi elements was also studied by Mao, et al. [53] and Zhang, et al. [54] using SRXRF and μ-PIXE, respectively.

In 2004, a three-step roadmap for the establishment of MO-CRMs was proposed by Tian [55], i.e., preliminary MO-CRMs by a combination of nuclear analyses (NAA/PIXE/SRXRF (or μ -PIXE) taking the unique advantages of NAA in quantifiable analytical uncertainties for multielements at weighable sample sizes (> O.x mg) and those of nuclear-based micro-XRF in evaluable sample size and non-elemental fractionation at unweighable sample sizes (sub-ng -O.x mg); upgrade of non-nuclear (and nuclear) microanalytical techniques; and participation of the upgraded non-nuclear (and nuclear) microanalyses in the certification of MO-CRMs. The idea was also presented by Tian at three international conferences ("A call for CRMs used in QC of microanalyses" at the International Symposium on Metrology in Chemistry, Oct. 2004, Beijing; "Nuclear analytical techniques in QC of microanalyses" at NAMLS-8, Apr. 2005, Rio de Janeiro, Brazil; and "Vision of New Generation CRMs for QC of Microanalysis" at APSORC-2005, Oct. 2005, Beijing), and tried by Huang, et al. on a simulated sediment matrix [56].

3.6.4. Biological and environmental specimen banks

A biological and environmental specimen bank and an environmental specimen bank were built at IHEP, CAS, in Beijing [11, 14], and lAP, CAS, in Shanghai [11, 14], respectively. The specimen banks are to archive typical biological/ environmental samples and keep them unchanged in chemical composition and properties for a long time for retrospective studies in the future. Significant new findings are expected by the future's more advanced technologies. Examples on the applications of NAA in studies on CRMs are listed in Table 12.

Table 12. Examples on NAA in study of CRM.

Material	Element determined (or properties studied)	Reference
IAEA sediment SD-N-I/2	23 element	8
Geological SRMs MGI, MGM-01,02	Au, Ag	8
Geological SRMs GAu 1-7	Au, Ag	8
Geological SRMs	Multielement	8
Geological SRMs MGD-01-09	Multielement	8
Geological SRMs	Au, Ag	8
Monomineral SRMs	Multielement	8
Geological SRMs	Au	8
Geological SRMs, (multi-metal ores)	Multielement	8
IAEA marine sediment SD- M/TM	Homogeneity	51
Geological SRM S-CRB	preparation and certif.	8

Tibetan soil	Multielement	8
Tea leaves	Multielement	8
Soil, river sediment	Multielement	8
Fly ash GBCW-1	Multielement	8
River sedim., fly ash, peach leaves	Multielement	8
Beijing soil	multielement	8
Soil	homogeneity	8
Environmental SRMs	multielement	8
IAEA horse kidney	multielement	8
Tomato leaves	multielement	8
Tea leaves	homogeneity	8
Peach leaves	homogeneity	8
IAEA shrimp MA-A-3/TM	homogeneity	8
Fish MA-B-3/fM	homogeneity	8
IAEA-155 Whey Powder	multielement inc. P	8
Pottery KPS-1	multielement	8
Archaeol. SRMs	multielement	8
Hair SRM HH-CH-1	preparation and certif.	8
Geological SRMs	14 REE, Hf, Ta (RNAA)	8
IAEA lake sediment SL-3	45 elements (RNAA)	8
Geological SRM GAu-I- 7	Au (RNAA)	8
Geological SRMs	Br (ENAA)	11,14
Fly ash SRM GBCW-1	Hg (RNAA)	8
Soil SRM	multielement (RNAA)	8
Ultrabasic rock SRMs	multielement (RNAA)	8
Foodstuff SRMs	As (RNAA)	8
Milk powder	multielement	9
BioI, Giol	multielement	9
Spinach	multielement	9
Sediment	multielement	9
Marine sediment	homogeneity	9
Estuary sediment	homogeneity	9
Plant, hair	30	9
Feed	Ca, Mn, Mg, Na	9
Aerosol	23	9
Weeping forsythia	multielement	9
Animal muscle	multielement	9
40 Bio and Env RMs	I	10
20 Bio RMs	I	10
Sediment	Homogeneity	53
Spinach	40 ele	10
Mn Nodule	Multiple	10
Geochem	PGEs	10
Urine	I	10
Rock	Multiple	10
Biological	multielement (RNAA)	14
Bovine liver	homogeneity	54
Sediment	homogeneity	56
Bio- and Env samples	Specimen bank	11, 14

4. Future Perspectives of NAA in China

Since the foundation of modem NAA based on Ge gamma ray spectrometry in China in early 1970s, we have experienced a period of rapid development of NAA in both methodology and applications. Now the technique is no longer in the central position of inorganic trace analytical family as it was during 1960s to mid-1980s in terms of multielemental sensitivity and facility availability, as the rapid development of competing techniques, mass spectrometry of various versions in particular, since late 1980s.

However, we are quite confident for the revitalization of NAA in China in 21st century, based on: 1) the unique inherent advantages of NAA in non-destructive bulky analysis for multielements, relative matrix independence, quantifiable analytical uncertainty, etc.; 2) solid foundation and rich experience in the technique, the facilities, and the trained scientists accumulated during the past 4 decades, as partly reflected in this review; and 3) high flux and quality beams of neutrons to be available from the 60 MW China Advanced Research Reactor (CARR), operational scheduled in 2009.

The following is expected to be among the areas for further development of NAA in China in the near future.

- Non-destructive bulky analysis for multi elements will continue to be the "stronghold" of NAA in inorganic trace analytical field for a long time to come. With the availability of high neutron fluxes (> 1 x 10^{14} n.cm^{-2}.s^{-1}) provided by CARR, NAA will play greater role in all existing (and newly emerging) application fields. Refractory and/or hardly soluble materials (such as Si, silicates, polymers, etc.) are among the most favorable matrices, and special elements / element groups (such as REEs, PGEs, halogens, etc.) are among the most favorable analytes for NAA.
- Species analyses have emerged to be a new trend for materials characterization, and penetrated into many frontier areas of life, environment and material sciences. NAA with strengthened abilities will further contribute to these analyses, as one of the important analytical techniques after species separation.
- There are now only very few CRMs certified for elemental species available, far from satisfied with the quality control for species analyses. Preparation and certification of this category of CRMs are expected to be one of the new trends in CRM development. MNAA techniques very well developed in China will enable us to make greater contributions in this aspect.
- There is so far no bottled natural-matrix CRM certified for multi elements at sub-0.5 mg sample size levels. That hinders the quantification and quality control of solid-sampling microanalyses. We've mapped out a strategy for the establishment of CRMs certified at sample size levels comparable to currently available microanalyses (down to sub-ng), in which NAA will play key role for certification of multielements not only at weighable sample size levels but also at the sample size level "gap" between lowest reached level (say, sub-ng, by micro-XRF) and weighable levels (i.e., 1 μg to 1 mg - unweighable but visible), by taking its advantages in high sensitivity for multielements, non-destruction, and quantify-able analytical uncertainties.
- Reactor-based PGNAA, which used to be weak in China, will be established on both thermal and cold channels of CARR. The strong and high quality neutron beams enable us to setup world class PGNAA systems, with which a series of elements previously unmeasurable can be determined. For example, PGNAA is so far the only non-destructive method for highly accurate determination of trace amount of H in bulky solid samples. The absorption and desorption behavior of H, one of the most promising clean energy sources, in materials is a key area of H energy research, and PGNAA provides a unique tool for this purpose. H and B are also important in materials science. Spacial and temporal information obtained by manipulating cold neutron beams is very valuable in materials characterization and nuclear research.
- NAA by neutron generators has a large potential for further development stimulated by the increasing demand from industries and national security and the increasing supply of high yield neutron generators manufactured

domestically. The high neutron fluxes from CARR may enable us to produce ^{252}Cf for the first time and stronger other isotope neutron sources (^{241}Am-Be, etc.) for on-line or on-site NAA and other applications.

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