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WORKBOOK ON
REACTOR NEUTRON ACTIVATION ANALYSIS (NAA)
OF AIRBORNE PARTICULATE MATTER (APM)

Prepared by

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EDITORIAL NOTE

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Reactor Neutron Activation Analysis (NAA) of Airborne Particulate Matter (APM)

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Reactor Neutron Activation Analysis of Airborne Particulate Matter

1. Brief Introduction to Reactor Neutron Activation Analysis (Reactor NAA)

1.1 Basic principle

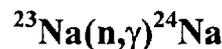
When a sample is bombarded by reactor neutrons, the following “neutron capture” reaction occurs on many elements (one or more isotope(s) of each element) contained in the sample,



where, ${}^A\text{Z}$ refers to an isotope of any element in the sample. If the product nuclide, ${}^{A+1}\text{Z}$, 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, ${}^A\text{Z}$, is the same (or known) for sample and standard).

In qualitative analysis

The use of modern high resolution HPGe γ -ray spectrometer has made it possible to use the energy of a full-energy peak of a characteristic γ -ray to identify a nuclide. For example, the qualitative analysis of Na can be accomplished through the following reaction (called analytical reaction) of ${}^{23}\text{Na}$ (called target nuclide):



The product nuclide ${}^{24}\text{Na}$ (called indicator nuclide of Na) is a β^- - γ radionuclide. The relevant parameters of ${}^{24}\text{Na}$ decay are shown in fig. 1, the simplified decay scheme of ${}^{24}\text{Na}$. In a γ -spectrum of an activated sample, the 1368 keV (or 2754 keV) peak is an indication of the existence of ${}^{24}\text{Na}$.

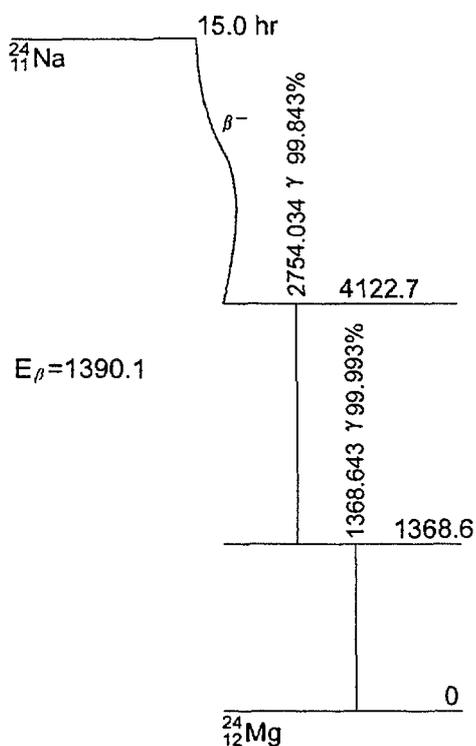


Fig. 1 Simplified Decay Scheme of Na-24

To confirm that the events producing 1368 keV peak are solely from ^{24}Na decay, all possible nuclides emitting γ -rays with energies close to 1368 keV (can not be resolved with 1368 keV peak) should be carefully searched for. If these interferences can not be ignored, corrections are then needed to obtain the intensity of 1368 keV peak solely contributed by ^{24}Na . This is so-called γ -spectral interference correction.

The indicator nuclide ^{24}Na may be produced by elements other than Na via reactor fast neutron reactions, e.g. $^{24}\text{Mg}(n,p)$, $^{27}\text{Al}(n,\alpha)$ or $^{28}\text{Si}(n,\alpha p)$. Some products of ^{235}U fission reactions (e.g. ^{140}La , ^{141}Ce , ^{147}Nd , ^{99}Mo , ^{95}Zr , etc.) are the same as the indicators of some elements, that bring interferences to the determination of relevant elements. All these interference contributions should be determined and necessary corrections made, to obtain the intensity of the indicator nuclide purely from the analytical reaction. This is so-called nuclear reaction interference correction.

In quantitative analysis

The relationship between counting rate of an analytical peak (after all the above-mentioned corrections) and the content of relevant element is expressed in Eq.1

$$W = M.A/(6.02 \times 10^{23} . \theta . \phi . \sigma . \gamma . \varepsilon . S . D . C) \quad (1)$$

Where:

- W = mass of element to be determined in sample, g;
- A = counting rate of analytical peak, s⁻¹;
- M = atomic weight of element to be determined;
- θ = isotopic abundance of target nuclide;
- φ = thermal neutron flux at sample position, cm⁻².s⁻¹;
- σ = effective cross section of analytical reaction, cm²;
- γ = branching ratio of analytical peak;
- ε = detection efficiency for analytical peak;
- S = saturation factor, $S = 1 - \exp(-0.693t_i/t)$;
- D = decay factor, $D = \exp(-0.693t_d/t)$;
- C = measurement factor, $C = (1 - \exp(-0.693t_c/t))/(0.693t_c/t)$.

Where, t_i , t_d and t_c are irradiation time, decay time and counting time (elapse time), respectively; t is the half life of the indicator nuclide.

In practice, relative comparison method is usually used for calculation of elemental content. That is to irradiate and count known amount of element(s) to be determined (called standard(s)) under identical conditions with sample(s) to be analyzed. Equation 1 can then be listed for the relevant element in both the sample and the standard. By taking ratio of the two equations and canceling out factors identical for the two, the following simple relation holds:

$$W = W(st).A(sa)/A(st) \quad (2)$$

where, (st) and (sa) refer to standard and sample, respectively. When any of t_i , t_d and t_c is different for sample and standard, relevant factor(s) S, D, C should be kept uncanceled, as:

$$W = W(st).(A(sa)/A(st)).(S(st)/S(sa)).(D(st)/D(sa)).(C(st)/C(sa)) \quad (3)$$

Apparently, any difference in irradiation and/or counting conditions between sample(s) and standard(s) will violate the prerequisite of Eqs. 1,2 and 3, and thus introduce systematic uncertainties.

1.2 Versions of Reactor NAA

Reactor neutron activation analysis by means of measurement of radiations from the decay of product (indicator) nuclides is classified into three

main versions: non-destructive NAA, radiochemical NAA, and NAA with pre-irradiation treatment.

A) Non-destructive NAA

a) Instrumental NAA (INAA)

It refers to a kind of Reactor NAA in which samples are activated with the whole spectrum of reactor neutrons, and the activated samples are directly counted with a common coaxial HPGe γ -ray spectrometer. Indicator nuclides are γ emitters with γ -ray energies ranging from 60 to 3500 keV and half-lives generally longer than 10 s (It could be much shorter by using fast sample transport systems). It is the commonest version of Reactor NAA.

b) Epithermal NAA (ENAA) [AL85], [TI86]

It refers to a kind of Reactor NAA in which activation is done by reactor epithermal neutrons (thermal neutrons are filtered out by Cd or B), to improve relative sensitivities of nuclides having high I_0 (resonance integral) over σ_0 (thermal neutron cross section) ratios compared to those of major interference nuclides. ENAA is also favorable for elements determined using reactor fast neutron reactions (e.g. $^{58}\text{Ni}(n,p)$ for Ni, $^{29}\text{Si}(n,p)$ for Si, etc.).

c) Cyclic NAA [GR75]

It refers to a kind of Reactor NAA in which the irradiation – decay – counting – decay – irradiation ... cycles are repeated and the analytical peak area from each cycle is added-up, to improve the precision of short-lived nuclides.

d) Measurements with instruments other than single coaxial HPGe spectrometer, for example,

i) planar HPGe or Si(Li) detector measurements for low energy γ/X rays; [ME72]

ii) coincidence techniques, especially HPGe-NaI(Tl) anti-Compton spectrometers; [LA96]

iii) β countings with liquid scintillation or Cerenkov counters; [GU74]

iv) delayed neutron countings by BF_3 or ^3He counters, and nuclear track detection techniques for determinations of U and Th. [AL90]

B) Radiochemical NAA (RNAA) [EH86,88,90,92,94],[FA90]

It refers a kind of Reactor NAA in which the irradiated samples undergo radiochemical separation to remove major interferences and/or isolate indicator nuclides before counting.

C) NAA with pre-irradiation treatment

It refers to a kind of Reactor NAA in which chemical (or biochemical, or physical) separations are carried out before sample irradiation, for

a) Concentration of elements to be determined [LI80], or

- b) Separation of sample into fractions (e.g. different phases, different biological large molecules, etc, depending on particular study objectives), or
- c) indirect determination of an element by chelating with a “surrogate” element (so-called derivative NAA, DNAA) [EH87].

In this booklet, only INAA, the commonest version of Reactor NAA, is to be discussed. The reader is recommended to consult relevant references for details of other versions of Reactor NAA.

1.3 Advantages and disadvantages

Generally speaking, Reactor NAA has low detection limits, high specificity, high precision and accuracy for large majority of naturally occurring elements, and the ability of non-destructive and simultaneous determination of multielements. Relatively low contamination and losses of elements to be determined are the unique and valuable advantages of Reactor NAA. Specifically, some crucial requirements involved in multielemental analysis of airborne particulate matter (APM) samples, such as small sample size (100 µg or less), multielemental capability (for source analysis by statistic methods), and non-destruction (some grains in APM are very difficult to be fully dissolved), can be best met by INAA.

On the other hand, Reactor NAA requires large facilities and sophisticated techniques (reactor, facilities for handling radioactive materials, knowledge and techniques of nuclear research, etc.), that hinders the popularity of the technique. The bombardment of neutrons (and other nuclear particles) alters the chemical binding of elements in the samples. Thus, Reactor NAA alone can not be used for elemental speciation. The inherent property of radioactive decay implies that Reactor NAA is not a “prompt answer” method. Periods of decay are required before countings. This is of course also an advantage in reducing interferences in each counting.

Among the three nuclear and related techniques commonly used for APM analysis, NAA, XRF and PIXE, NAA has the advantages of determining more elements (generally 40 to 45, as indicated in Tables 1 and 2, compared to some 20 for the other two methods) and being much less sensitive to the thickness of the samples. Major drawbacks of NAA include that it can not determine Pb and in most cases S, the two environmentally important elements; the analyzed samples can hardly be reused for other purposes due to the residual radioactivity; and longer turnaround time (4000 to 5000s per sample); etc.

The relatively high accuracy for determination of multielements has made Reactor NAA one of the most important methods in the certifications of reference materials.

1.4 Brief history

The first activation analysis work was published by Hevesy and Lavi in 1936 (determination of 0.1% Dy in Y_2O_3 , using a 200-300 mCi Ra-Be neutron source). However, only when the experimental research reactors were available in 1950s, did NAA become a practical trace analytical technique. The advent of the high resolution Ge detectors in mid-1960s brought Reactor NAA a major breakthrough. Modern Reactor NAA equipped with computerized HPGe spectrometers has made Reactor NAA truly non-destructive and multielemental. The following milestones include: the study on inorganic separators (Girardi, et al. [GI68], and follow-up studies), in an effort to make RNAA systematic; the development of small reactors (SLOWPOKE in 1970s [KA73], Canada; MNSR in 1980s [ZH83], China), in an effort to popularize Reactor NAA; and the development of k_0 method (Simonits, et al., 1975 [SI75], and follow-up studies), in an effort to make Reactor NAA fully parametric and computerized.

Although there have been few major technical breakthroughs since late 1960s, the applications of Reactor NAA have been kept increasing.

Numerous works have been published on Reactor NAA in general and that of APM in particular. For extended readings, the reader is recommended to consult two recent publications and associated references on these topics, [LA99] and [CL98].

2. Procedures of Reactor NAA for APM Analysis

2.1 Sampling and sample handling

Sampling of APM samples for elemental determination has largely been dealt with in a separate booklet. Only procedures carried out in laboratories are included here.

Some of the key points involved in sampling and sample handling are listed below:

- A) Filters used for sample collection should have lowest possible impurities, especially the ones causing substantial background in γ -spectra of activated blank filter samples.
- B) Filters (for both before and after APM sample collection) should be handled in a clean balance room. A Class 100 laboratory or a laminar bench created local Class 100 area is ideal for filter handling. The balance room should keep away any chemicals containing elements to be determined (e.g. those used for standard preparation), to avoid cross-contamination.

- C) The operators should wear clean and dust-free working cloths, caps, and gloves during operation.
- D) Filters should be handled by non-metal forceps (and other tools that may touch filters).
- E) Filters should be equilibrated for 24 hrs. or longer with balance room environment (25 ± 5 °C temperature and 50 ± 5 % relative humidity) before each weighing (both before and after sample collection), to obtain constant and comparable APM weights.
- F) Balance with 1 µg readability should be used for filter weighing, to keep weighing uncertainties as low as possible (for an APM sample, the net weight is sometimes as low as 100 µg or less).
- G) Filters should be kept in a clean and closed vessel (e.g. desiccator) during transportation to and from sampling site, to reduce the chances of contamination.

After weighing, APM samples are wrapped in pre-cleaned PE bags (for short irradiation) or Al foils (for long one) for reactor irradiation.

2.2 Preparation of standards

As described in 1.1, a standard for each element to be determined should be prepared, irradiated and counted under identical conditions with samples to be analyzed.

It is advisable to use certified elemental solutions, either by dilution or as it is, in making standards of relevant elements, so as to satisfy the traceability requirements. In common practice, however, high purity metals or chemicals of elements to be determined are used to make standard solutions. Taking the advantages of the high resolution of HPGe detectors, multielemental standards made of mixed standard solutions have been frequently used to simplify the irradiation and counting procedures. Some of the key points in making elemental standards are listed below.

A) Materials for making standards

Metals or relevant chemicals with high purity (4 9's or purer), especially high stoichiometric purity, should be used for making standard solutions. Some metals, chemicals and standard reference materials (SRMs) suitable for making standard solutions of all naturally occurring elements were recommended by Moody and co-authors [MO88].

B) Material dissolution

Suitable solvent for each starting material may be found in relevant handbooks. Metals should be etched to remove surface impurities and oxide layers, and rinsed with d.d. water, and then immediately dried (better in

vacuum) before weighing. For most metals, the suggested minimum weight of a cleaned, dry piece is ~ 200mg, to minimize the surface area to mass ratio.

C) Dilution and mixture of standard solutions

After dissolution, the concentration and medium of the standard solution need to be adjusted by dilution with suitable solvent (water, dilute acids, or dilute NH_4OH , etc.). It is advisable that gravimetric dilution (rather than volumetric one) be used, to keep lowest possible uncertainty. Diluting solvent should be carefully chosen to make the solution stable in term of the concentration of the relevant element. The recommended concentration of this solution (primary standard solution) is 1 mg (element)/g (solution) or higher, to ensure long-term stability. Working solution (usually in the order of $\mu\text{g/g}$) can be made by diluting primary solution. Plastic vessels are recommended for both primary (or stock) solution and working solution.

For making multielemental working solution, three major error sources should be avoided:

i) improper media

For example, the primary solution of Mo is in basic medium and that of Cd is in acidic medium. A mixture of the two solutions will cause precipitation of one or both elements.

ii) cross contamination

For example, when primary solutions of Fe and Sc are to be mixed, the ratio of Fe/Sc should be 10^4 to 10^5 to keep the intensities of the two analytical peaks in balance (because of the large difference in sensitivities of these two elements). That means the Sc impurity in Fe should be 10^7 or lower to make its contamination being ignored.

iii) γ -spectral interferences

Problems of peak overlapping and very imbalance peak intensities from elements being mixed should be avoided.

D) Blank from backing materials

Although high purity Si chips, quartz vials, Al foil have all been used as backing materials of solution standards, the high purity ashless filter paper is the material of choice for this purpose for its easy handling. Working standard solutions (single element or multielements) can be quantitatively pipetted onto a pad of filter paper (by weighings before and after pipetting). The pad is then dried, packed in Al foil, and irradiated together with samples.

For elements with low cross sections of neutron capture reactions (e.g. Fe, Ni, Zr, etc.), standards can be directly made by weighing relevant high purity metals or compounds.

Special care should be taken when standards of volatile elements (e.g. Hg, I, Br) are to be prepared, to avoid losses of relevant element standards

and/or contamination of samples. A kind of Hg standard with sulfhydryl cotton matrix developed by Chen and co-authors has been proven to be stable under reactor neutron irradiation [CH85]. Weak basic medium is recommended for better stability of I, Br and Cl standards. These problems can be totally avoided in k_0 -NAA.

Preparation of neutron flux monitors and comparator for k_0 -NAA will be dealt with in Appendix 1.

An example of uncertainty budget in standard preparation was given by Greenberg [GR94].

2.3 Reactor neutron irradiation

One short irradiation followed by one to three counting(s) and one long irradiation followed by two countings are common practice for INAA of APM (and most other) samples. A typical irradiation-counting scheme is given in Table 1.

Table 1. A typical irradiation-counting scheme for APM analysis

Counting #	N. Flux, n/cm ² /s	T _i	T _d	T _c	Elements determined
1	1×10 ¹³	300s	300s	300s	Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Cu, Br, Sr, In, I, Ba, Dy, S
2			1 hr	500s	Na, K, Sr, In, Ba, Dy, Mn
3			10hr	1000s	Na, K
4	3×10 ¹³	16 hr	4 d	1500s	Na, Ca, Ga, As, Br, Mo, Cd, Sb, Ba, La, Nd, Sm, Yb, Lu, W, Au, U, Rb
5			15d	4000s	Sc, Cr, Fe, Co, Ni, Zn, Se, Rb, Sr, Zr, Ag, Cs, Ce, Nd, Eu, Tb, Lu, Hf, Ta, Hg, Th

Note: T_i, T_d, and T_c refer to irradiation time, decay time, and counting time, respectively.

While higher neutron flux is usually preferred, it should also be considered to ensure the filter samples not being damaged or melt during irradiation.

Neutron flux gradient over the whole sample/standard package should be measured by flux monitors (e.g. Fe wire), and necessary corrections made. Neutron flux self-shielding is usually not a problem for small size, silicate matrix APM samples. However, materials containing elements with high

neutron absorption cross sections should be avoided nearby sample irradiation positions.

A package for long irradiation should therefore include: APM samples to be analyzed, standards of elements to be determined, proper certified reference materials (CRMs) or standard reference materials (SRMs) for quality control (as detailed in the next chapter), and 3 to 5 pieces of blank filters randomly chosen from each pack used for APM sample collections, for blank corrections. For short irradiation, the above items should also be irradiated, but usually not in the same package. If k_0 -NAA is used, neutron flux ratio monitor(s) and comparator(s) should also be added in the package.

2.4 Counting of activated samples

Coaxial HPGe γ -ray spectrometers with relative efficiency of 20 to 35% and resolution of 1.8 to 2.1 keV are commonly used in Reactor NAA. Major performances of HPGe spectrometers should be continuously monitored for normal working conditions. It is recommended that energy calibrations and background measurement be conducted before each time of use, resolution checked weekly, and efficiency checked monthly.

The timing and position for each counting should be decided by the experimenter, to optimize the analytical quality.

In practice, samples may be placed at positions nearest possible to the detector, on condition that the dead times are smaller than 5% for the first counting after short irradiation, and smaller than 10% for all the other countings, using life-time timer. Efficiency normalizations for different counting positions should be carried out either experimentally by using sources of relevant nuclides with known activity ratios, or parametrically by using effective interaction depth (EID) principle [TI93].

The following experience in the timings for the five countings listed in Table 1 may be of some help.

Counting 1 may be carried out when the ratio of the heights of 1779 keV (^{28}Al) over 847 keV (^{56}Mn) peaks is about 0.7 to 1.

Counting 2 may be carried out after 0.5 to 1.5 hrs decay. Decay time usually should not be longer than 2 hr, since nuclides to be determined in this counting are all have half-lives shorter than ^{56}Mn , the most intense activity in this counting.

Decay time for counting 3 may be centered at about 10 hrs for a batch of samples, to substantially reduce the intensity of ^{56}Mn while keep ^{42}K still determinable.

Counting 4 may be carried out when the ratio of the peak heights of 1368 keV (^{24}Na) over 554 keV (^{82}Br) is about 0.5 to 1, to optimize the determinations

of indicators with half lives between the above two intense nuclides (15 hr and 35.5 hr), such as ^{76}As (559 keV, 26.3 hr) and ^{187}W (686 keV, 24.9 hr).

Counting 5 may be carried out after 10 to 20 days' decay, depending on the results from counting 4. If elements listed in both countings 4 and 5 have been determined in counting 4 with satisfactory results, longer decay time for counting 5 may be preferred, and vice versa.

Relevant nuclear parameters and major interferences involved in Reactor NAA for 66 elements are listed in Table 2.

With the increasing popularity of PC, sample change, data acquisition, and data reduction can be controlled and accomplished by a PC. An automated NAA system is briefly introduced in Appendix II.

2.5 Calculation of elemental concentrations

Two steps are involved in the calculations of elemental concentrations: peak analysis and elemental concentration calculation.

A) Peak analysis

In a γ -ray spectrum from a high resolution HPGe detector, all the useful information is contained in peak regions. Peak energies are used for nuclide (then element) identification, and peak areas are the basis for calculating elemental concentrations.

Peak analysis includes the following steps: i) peak search (eye search method, first derivative method, second difference method); ii) determination of peak position (maximum of peak fitting function, peak centroid); iii) determination of peak energy (calibration by multi- γ emitters with precisely known γ energies, e.g. ^{152}Eu , ^{75}Se , ^{166}Ho , etc.); iv) determination of peak area (channel-by-channel addition, integral of peak fitting function) and its uncertainty.

B) Determination of elemental concentrations

Equation (2) or (3) can be used for this calculation, based on relevant peak areas in sample and standard γ spectra.

Table 2. Relevant nuclear parameters for Reactor NAA

Ele	Nucl	T _{1/2}	E	γ-spec. interf.	Reaction interf.
Na	²⁴ Na	14.96h	1368.6	¹²⁴ Sb(60.2d, 1368.2)	²⁴ Mg(n,p), ²⁷ Al(n,α), ²⁸ Si (n, αp)
Mg	²⁷ Mg	9.458m	843.8	⁵⁶ Mn(2.579h, 846.8)	²⁷ Al(n,p), ³⁰ Si(n, α)
Al	²⁸ Al	2.24m	1778.9		²⁸ Si(n,p), ³¹ P(n, α)
Si	³¹ Si	2.62h	1266.2		³¹ P(n,p)
S	³⁷ S	5.05m	3103.8		³⁷ Cl(n,p), ⁴⁰ Ar(n, α)
Cl	³⁸ Cl	37.21m	1642.4		⁴¹ K(n, α)
Ar	⁴¹ Ar	1.83h	1293.6	⁵⁹ Fe(44.63d,1291.6), ^{116m} In (54.15m,1293.5)	
K	⁴² K	12.36h	1524.7	¹²⁴ Sb(60.2d,1526.4)	⁴² Ca(n,p), ⁴⁵ Sc(n, α)
Ca	⁴⁷ Ca	4.54d	1297.1		⁵⁰ Ti(n, α)
	↓				
	⁴⁷ Sc	3.35d	159.4	¹⁹⁹ Au(3.15d,158.3)	
	⁴⁹ Ca	8.72m	3084.4		
Sc	⁴⁶ Sc	83.82d	889.3		⁴⁶ Ti(n,p)
Ti	⁵¹ Ti	5.752m	320.1	⁵¹ Cr(27.69d,320.1)	⁵¹ V(n,p), ⁵⁴ Cr(n, α)
V	⁵² V	3.75m	1434.0	^{117m} Cd(3.31h,1432.0)	⁵² Cr(n,p), ⁵⁵ Mn(n, α)
Cr	⁵¹ Cr	27.69d	320.1	¹⁴⁷ Nd(10.98d,319.4)	⁵⁴ Fe(n, α)
Mn	⁵⁶ Mn	2.5785h	846.8	²⁷ Mg(9.458m,843.8)	⁵⁶ Fe(n,p), ⁵⁹ Co(n, α)
Fe	⁵⁸ Fe	44.63d	1099.2	^{116m} In(54.2m,1097.3)	⁶² Ni(n, α), ⁵⁹ Co(n,p)
			1291.6	⁴¹ Ar(1.83h,1293.5)	
Co	⁶⁰ Co	5.271y	1173.2	Sum (554+619, ⁸² Br)	⁶⁰ Ni(n,p), ⁶³ Cu(n, α)
			1332.5	Sum (554+776, ⁸² Br)	
Ni	⁵⁸ Co	70.8d	810.8	¹⁵² Eu(13.3y,810.8)	
Cu	⁶⁴ Cu	12.701h	511.0	E _γ >1022keV, ann 511,0	⁶⁴ Zn(n,p), ⁶⁷ Ga(n, α)
	⁶⁶ Cu	5.10m	1039.2		⁶⁶ Zn(n,p), ⁶⁹ Ga(n, α)
Zn	⁶⁵ Zn	244.0d	1115.5	⁴⁶ Sc(83.82d,1120.5)	
	^{69m} Zn	13.76h	438.6		⁶⁹ Ga(n,p), ⁷² Ge(n, α)
Ga	⁷² Ga	14.1h	834.0	⁵⁴ Mn(312.5d,834.8)	⁷² Ge(n,p)
Ge	⁷⁷ Ge	11.3h	264.6	⁷⁵ Se(119.77d,264.7)	
As	⁷⁶ As	26.32h	559.1	^{114m} In(49.51d,558.4)	⁷⁹ Br(n, α)
Se	⁷⁵ Se	119.77d	264.7	¹⁸² Ta(114.43d,264.1)	
	^{77m} Se	17.5s	161.8	^{179m} Hf(18.7s,160.7)	
Br	⁸⁰ Br	17.68m	616.3		
	⁸² Br	35.3h	554.3		⁸⁵ Rb(n, α)
			776.5	⁹⁹ Mo(66.02h,777.9), ¹⁵² Eu (13.3y,778.9)	
Rb	⁸⁶ Rb	18.68d	1076.6		⁸⁶ Sr(n,p)
Sr	⁸⁵ Sr	84.84d	514.0	E _γ >1022keV, ann.511.0	
	^{87m} Sr	2.805h	388.4	^{71m} Zn(3.92h,386.3)	
Y	^{90m} Y	3.19h	202.5		

Table 2. Continuation

Ele	Nucl	T _{1/2}	E	γ-spec. interf.	Reaction interf.
Zr	⁹⁵ Zr	64.03d	756.7	¹⁵⁴ Eu(8.561y,756.9)	²³⁵ U(n,f)
Nb	^{94m} Nb	6.26m	871.0		
Mo	⁹⁹ Mo	66.02h	140.5	⁵⁹ Fe(44.63d,142.7)	²³⁵ U(n,f)
Ru	¹⁰³ Ru	39.26d	497.1	¹³¹ Ba(11.8d,496.3)	²³⁵ U(n,f)
Rh	^{104m} Rh	4.34m	555.8		
Pd	¹⁰⁹ Pd	13.7h	88.0	¹⁶⁰ Tb(72.1d,86.8)	
Ag	^{110m} Ag	249.76d	657.8	⁷⁶ As(26.32h,657.1)	
			884.7	⁴⁶ Sc(83.82d,889.3)	
Cd	¹¹⁵ Cd	53.46h	527.9	¹²⁸ I(24.99m,526.6)	
	↓				
	¹¹⁵ In	4.36h	336.2	²³⁸ Np(2.355d,334.3)	
In	^{114m} In	49.51d	190.3	⁵⁹ Fe(44.63d,192.3)	
	^{116m} In	54.15m	1293.5	⁴¹ Ar, ⁵⁹ Fe	
Sn	¹¹³ Sn	115.09d	391.7	¹⁶⁰ Tb(72.1d,392.5)	
	^{117m} Sn	13.61d	158.5	⁴⁷ Sc(3.35d,159.4), ¹⁹⁹ Au (3.15d,158.3)	
Sb	¹²² Sb	2.70d	564.1	¹³⁴ Cs(2.062y,563.2)	
	¹²⁴ Sb	60.2d	1691.0		
I	¹²⁸ I	24.99m	442.9	¹⁴⁹ Nd(1.73h,443.5), ²³³ Th (22.3m,441.0)	
Cs	¹³⁴ Cs	2.062y	604.7	¹²⁴ Sb(60.2d,602.7)	
			795.8	¹⁵² Eu(13.3y,794.7)	
Ba	¹³¹ Ba	11.8d	496.3	¹⁰³ Ru(39.26d,497.1)	
La	¹⁴⁰ La	40.22h	1596.5	¹⁵⁴ Eu(8.561y,1596.7)	¹⁴⁰ Ce(n,p), ²³⁵ U(n,f)
Ce	¹⁴¹ Ce	32.501d	145.4	¹⁷⁵ Yb(4.19d,141.9)	¹⁴¹ Pr(n,p), ²³⁵ U(n,f)
Pr	¹⁴² Pr	19.12h	1575.6		¹⁴² Nd(n,p), ²³⁵ U(n,f)
Nd	¹⁴⁷ Nd	10.98d	531.0		¹⁵⁰ Sm(n,α), ²³⁵ U(n,f)
			91.1	¹³¹ Ba(11.8d,92.3)	
Sm	¹⁵³ Sm	46.7h	103.2	²³⁹ Np(2.355d,103.7)	¹⁵³ Eu(n,p)
Eu	¹⁵² Eu	13.3y	1408.0		¹⁵² Gd(n,p)
Gd	¹⁵³ Gd	246.1d	97.4	²³³ Pa(27.0d,98.4)	
Tb	¹⁶⁰ Tb	72.1d	879.4	⁴⁶ Sc(83082d,889.3)	¹⁶⁰ Dy(n,p)
			1178.0		
Dy	¹⁶⁵ Dy	2.334h	94.7	²³³ Pa(27.0d,94.6)	¹⁶⁵ Ho(n,p)
Ho	¹⁶⁶ Ho	26.8h	80.6	¹⁹⁷ Hg(64.1h,80.2)	¹⁶⁶ Er(n,p)
Er	¹⁷¹ Er	7.52h	308.3	¹⁶⁹ Yb(32.0d,307.7)	¹⁷⁴ Yd(n, α)
Tm	¹⁷⁰ Tm	128.6d	84.3	¹⁸² Ta(114.43d,84.7)	¹⁷⁰ Yb(n,p)
Yb	¹⁷⁵ Yb	4.19d	396.3	¹⁴⁷ Nd(10.98d,398.2)	¹⁷⁵ Lu(n,p)
Lu	¹⁷⁷ Lu	6.71d	208.4	²³⁹ Np(2.355d,209.8)	

Table 2. Continuation

Ele	Nucl	T _{1/2}	E	γ-spec. interf.	Reaction interf.
Hf	¹⁸¹ Hf	42.39d	482.2	¹⁹² Ir(74.2d,484.5)	
Ta	¹⁸² Ta	114.43d	1221.3		
W	¹⁸⁷ W	23.9h	685.7	¹⁴⁷ Nd(10.98d,685.9), ^{110m} Ag (249.76d,687.0)	
Re	¹⁸⁶ Re	90.64h	137.2	⁷⁵ Se(119.77d,136.0)	
Os	¹⁹¹ Os	15.4d	129.4	¹⁶⁹ Yb(32.0d,130.5)	
Ir	¹⁹² Ir	74.2d	468.1		
Pt	¹⁹⁹ Au	3.15d	158.4	⁴⁷ Sc(3.35d,159.4), ^{117m} Sn (13.61d,158.5)	¹⁹⁷ Au(2n,γ)
Au	¹⁹⁸ Au	2.695d	411.8	¹⁵² Eu(13.3y,411.0)	
Hg	¹⁹⁷ Hg	64.1h	68.8	¹⁵³ Sm(46.7h,69.7)	
	²⁰³ Hg	46.612d	279.2	⁷⁵ Se(119.77d,279.5)	
Th	²³³ Pa	27.0d	312.0	⁴² K(12.36h,313.0)	
U	²³⁹ Np	2.355d	277.6	⁷⁵ Se(119.77d,279.5), ²⁰³ Hg (46.612d,279.2)	

Calculations for k₀-NAA will be briefly introduced in Appendix I.

2.6 Expression of analytical results

A) Evaluation and expression of uncertainties

a) Type A uncertainties

Type A uncertainties are defined as uncertainty items evaluated by statistic methods. The commonest expression is standard uncertainty (deviation) and its expansion (at a stated confidence level).

In Reactor NAA, counting statistics is an unavoidable component of type A uncertainty. It is numerically evaluated in most Reactor NAA softwares. Variations in sample weighing, sample homogeneity, neutron flux, counting geometry, chemical yield in radiochemical separation, etc. can all be made type A uncertainties by repeating relevant procedures and calculating standard uncertainties.

Suppose the results of an element from m subsamples of a material are N₁, N₂, N₃, ...N_m, standard uncertainty for single measurement, S_{At}, is expressed in Eq. (4).

$$S_{At} = (\Sigma(N_i - \bar{N})^2 / (m-1))^{1/2} \quad (4)$$

$$\text{Where} \quad S_{At}^2 = S_c^2 + S_n^2 \quad (5)$$

Where S_c and S_n are type A uncertainties from counting and non-counting contributions, respectively. S_{At} is total type A uncertainty

In practice, there are following three situations:

- i) $S_{At} > S_c$, indicating there exist non-counting type A uncertainties;
- ii) $S_{At} \approx S_c$, indicating counting statistics dominates type A uncertainty;
- iii) $S_{At} < S_c$, implying an “unusual agreement” among the results from limited number of subsamples. In this case, S_c , rather than S_{Ab} should be used as total type A uncertainty.

Standard uncertainty for the mean, \bar{S}_{At} , is expressed in Eq (6).

$$\bar{S}_{At} = S_{At} / \sqrt{m} \quad (6)$$

b) Type B uncertainties

Type B uncertainties are defined as uncertainty items evaluated by non-statistic methods.

Numerical values of type B uncertainties are sometimes difficult to obtain. The hint is to use all the relevant information available, such as:

- previously measured data;
- experience or general knowledge of the behavior or property;
- manufacturer’s specification;
- data obtained in calculation or other reports;
- uncertainties in reference data from handbook.

For combining with type A uncertainties, it is necessary to convert different expression and distribution models of type B uncertainty items to standard uncertainties, by the following methods:

- for normal distribution of different levels of confidence, convert to standard uncertainty (for confidence levels of 95, 99, and 99.73%, divided by 1.96, 2.576, and 3, respectively; for confidence levels of 50 and 68.3%, time 1.48 and 1, respectively);
- for rectangular distribution and “range” expression, divided by $\sqrt{3}$;
- for triangle distribution, divided by $\sqrt{6}$;

The rectangular distribution is a reasonable default model in the absence of any other information. But if it is known that values of the quantity in question near the center of the limits are more likely than values close to the limits, a triangle or a normal distribution may be a better model.

A complete analysis of type B uncertainties in each procedure of the whole process of Reactor NAA is essential for taking measures of eliminating or reducing these uncertainties and evaluating their remaining components.

Possible sources of type B uncertainties in Reactor NAA include

- i) weighing uncertainties in sample and/or standard preparation (e.g. inconstant moisture caused uncertainty in the net weight of an APM sample);

ii) contamination and/or losses of elements to be determined in sample preparation (e.g. fall-off of some APM from filters and/or outside dust falling in the filters during sample handling and transporting);

iii) different isotopic abundance of the target nuclide of an element to be determined in sample and standard (noticeably, U may exist in enriched or depleted form in samples and/or standards. When fission products are used as indicators, uncertainties may occur.);

iv) variations in elemental concentration introduced from preparation, storage and pipetting of standard solution (e.g. adsorption of relevant element(s) and evaporation of solvent);

v) difference in neutron fluxes received by sample and standard/comparator due to flux gradient and/or self-shielding;

vi) poor deconvolution of overlapping peaks and incorrect correction for dead time losses and pulse pile-up.

vii) overlooked or incorrect corrections for interferences from nuclear reactions and/or γ -ray spectra (as listed in Table 2);

viii) incorrect chemical yield corrections in RNAA;

ix) difference in counting geometry for samples and standards (or incorrect normalization for different counting geometry).

An example is given below on the evaluation of type B uncertainty in an Iodine standard preparation by dissolving KI in NH_3 containing water.

1. The purity of KI used for preparing iodine standards, given by the producer (on the label) is >99.5%.

• From this information, the relative uncertainty in the chemical is $\pm 0.25\%$, with a rectangular distribution.

• The content of KI needs to be validated by independent chemicals and CRM(s).

2. Weigh @ 100 mg KI into bottle 1 (@ 80 mg I).

• Relative uncertainty in this step is $\pm 0.2\%$ (balance readability ± 0.1 mg, twice weighings).

3. Weigh @ 16 g water (containing trace amount of NH_4OH to make the solution basic) into bottle 1 to totally dissolve KI.

• Uncertainty in this step is ignored.

4. Shake the solution to make concentration uniform.

5. Transfer @ 750 mg solution 1 into bottle 2.

• Uncertainty in this step is ignored.

6 Weigh @ 19 g water into bottle 2 to dilute solution 1.

• Uncertainty in this step is ignored.

- 7 Shake solution 2 to make concentration uniform.
- 8 Transfer @ 28 mg solution 2 onto each filter paper pad.
- Relative uncertainty in this step is $\pm 0.7\%$ ($0.2/28$) with rectangular distribution.
- 9 Insert each I standard (on filter paper) into a PE bag. Seal the bag. Each I standard contains @ 5.5 μg I.
- 10 The total relative standard uncertainty in each Iodine standard is therefore:
 $((0.25/\sqrt{3})^2 + (0.2/\sqrt{3})^2 + (0.7/\sqrt{3})^2)^{1/2} \% = 0.45\%$

c) Combined standard uncertainty

Now that all type A and type B components have been expressed in standard uncertainty. Overall uncertainty can then be expressed by combining all these components using the law of propagation of uncertainty. In common practice the “root-sum-of-squares” (RSS) method is used, i.e.

$$S_{At} = \sqrt{\sum S_{Ai}^2}; \quad (7) \quad S_{Bt} = \sqrt{\sum S_{Bi}^2}; \quad (8) \quad S_t = \sqrt{(S_{At}^2 + S_{Bt}^2)} \quad (9)$$

Where, S_{Ai} and S_{Bi} are components of type A and type B uncertainty, respectively.

S_{At} , S_{Bt} and S_t are total type A, total type B, and overall standard uncertainty, respectively.

d) Expanded uncertainty

Although standard uncertainty, S_t , can be directly used to express the uncertainties of analytical results, it is sometimes required to give an uncertainty with higher level of confidence (The level of confidence for standard uncertainty is about 68%, depending on the degree of freedom.). In this case, a coverage factor, k , may be used, as

$$S = k S_t \quad (10)$$

Confidence levels are approximately 95% and 99% for k values equal 2 and 3, respectively.

B) Detection limit

Three concepts on detection limits were established by Currie [CU68]:

i) a **decision limit** (L_c) referring to the net instrument response above which an observed signal from a detector can be reliably recognized.

$$\text{In Reactor NAA, } L_c = 2.33 \sqrt{C_B} \quad (11)$$

Where, C_B is the total background counts in the region of an analytical peak of an indicator nuclide of the element to be analyzed.

The physical meaning of L_c is that if the net counts of a “peak” $C_s \geq L_c$, it can be concluded (at 95% confidence level) that the peak is real, and vice versa.

Note that the L_c is the decision limit in counts. It can be converted to decision limit in element weight (or concentration) $L_c(m)$ by just treating it as a peak area.

ii) a **detection limit (L_D)** referring to the true net signal level that may be expected a priori to lead to detection.

$$\text{In Reactor NAA, } L_D = 2.71 + 4.65 \sqrt{C_B} \quad (12)$$

The physical meaning of L_D is that when the net peak area C_s at least equals to L_D , the relevant element can be detected (at 95% confidence level).

Note again that the L_D is the detection limit in counts. It can be converted to detection limit in element weight (or concentration) $L_D(m)$ by just treating it as a peak area. When an element is not detected, $< L_D(m)$ is usually given in an analytical report. If a statistic program requires a completely filled data set, $L_D(m)/2$ or a value between zero and $L_D(m)$ created by a random number generator may be used for the undetected elements.

iii) a **determination limit (L_Q)** referring to the level at which there is adequate precision for a quantitative determination.

$$\text{In Reactor NAA, } L_Q = k_Q^2 (1 + (1 + 8C_B/k_Q^2)^{1/2}) / 2 \quad (13)$$

The physical meaning of L_Q is that when the net peak area C_s equals L_Q , the relevant element can be determined with a relative standard deviation of $1/k_Q$. Suppose 10% is the required relative standard deviation for an element determination, $L_Q = 50(1 + (1 + 0.08 C_B)^{1/2})$.

Again, L_Q in counts can be converted to L_Q in weight, $L_Q(m)$, in the same way as stated above.

3. Quality Assurance and Quality Control (QA/QC)

3.1 Definitions

Quality assurance – A system of activities whose purpose is to provide to the producer or user of analytical data the assurance that it meets defined standards of quality. It consists of two separate but related activities, quality control and quality assessment.

Quality control – The overall system of activities whose purpose is to control the quality of analytical data so that it meets the needs of users,

Quality assessment – The overall system of activities whose purpose is to provide assurance that the quality control activities are being accomplished

effectively. It involves a continuing evaluation of performance of the analytical system and the quality of data produced.

3.2 Internal quality control

A) More than one indicator nuclides for an element to be determined

For example, Ca can be determined using $^{46}\text{Ca}(n,\gamma)^{47}\text{Ca}$ - ^{47}Sc and/or $^{48}\text{Ca}(n,\gamma)^{49}\text{Ca}$ reactions by measuring either ^{47}Ca , ^{47}Sc , or ^{49}Ca . Similarly, indicators ^{65}Ni and ^{58}Co can be used for determination of Ni; ^{64}Cu and ^{66}Cu for Cu; $^{65,69\text{m},71}\text{Zn}$ for Zn; $^{75,77\text{m}}\text{Se}$ for Se; $^{80,80\text{m},82}\text{Br}$ for Br; $^{122,124}\text{Sb}$ for Sb; etc, as can be seen from Table 2.

B) More than one analytical lines for an indicator nuclide

For example, both 1368 keV and 2754 keV lines can be used for determination of ^{24}Na ; 843 keV and 1014 keV lines for ^{27}Mg ; 1642 keV and 2176 keV lines for ^{38}Cl , etc, as also demonstrated in Table 2.

C) An indicator nuclide from more than one countings

For example, ^{56}Mn may be determined from countings 1 and 2 in Table 1; ^{24}Na from countings 1, 2, 3 and 4; ^{42}K from countings 3 and 4, ^{147}Nd , ^{177}Lu , ^{87}Rb from countings 4 and 5; etc.

D) Different peak fitting routines for the same peaks

When peak areas (especially for weak peaks, peaks with complex baselines, or multiplets) obtained from a certain software are in doubt, additional routines may be used for check. Currently available peak fitting routines include commercial ones (e.g. from CANBERA, EG&G, APTEC, etc.) and the ones developed by laboratories (e.g. SAMPO [AA92], SPAN [WA87], etc.).

E) Standardization by both relative comparison and k_0 methods

The internal control procedures listed in A), B), C), D) and E) provide the analysts with abundant measures in detecting and eliminating (or reducing) hidden systematic uncertainties without additional irradiation and counting.

F) Use of different irradiation and/or counting conditions

For example, irradiation at different channels, different reactors or with epithermal neutrons (ENAA); counting by planar HPGe detector, Si(Li) detector (for low energy γ or X rays), or BF_3 for delayed neutrons or nuclear track detector (in determination of U); etc. can all be used either independently or as a measure of internal control.

3.3 Analysis of Certified Reference Materials (CRMs)

A) Definitions

Reference Material (RM) – A generic class of well characterized, stable, homogeneous materials, produced in quantity and having one or more physical

or chemical properties experimentally determined within stated measurement uncertainties.

Certified Reference Material (CRM) – An RM one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

Standard Reference Material (SRM) – A subset of CRMs, issued and certified by the U.S. National Institute of Standards and Technology (NIST, formerly National Bureau of Standards (NBS)).

B) Practical aspects in the use of CRMs

CRMs can be properly used to validate the accuracy of analysis, minimize uncertainties, establish optimum analytical conditions, provide information on the accuracy of an analyst or technique, and validate a newly developed analytical method.

For the validation or quality control of the accuracy of analysis, two or more CRMs with appropriate matrices and with concentrations of the analytes that cover the range expected in real samples should be analyzed together with (or before) the unknown samples.

CRMs should be frequently analyzed (although not necessarily always) with unknown samples and control charts kept for quality control.

Analytical results for CRMs used should always be followed with those for unknown samples in analytical reports and publications. The concentration value for an element in an unknown sample may be validated by comparing analytical and certified (or information) values for the element in the CRMs. The following judgement is recommended.

$$\text{When } |X_e - X_c| < (S_e^2 + S_c^2)^{1/2} \quad (14),$$

the determination of the element concerned is considered validated, and vice versa. In Eq. (14), X_e and X_c are analytical and certified values, respectively, S_e and S_c are associated uncertainties (95% confidence level) of the two values, respectively. This judgement is schematically plotted in Fig. 2.

Cadmium results ($\mu\text{g/g}$) from participant 2

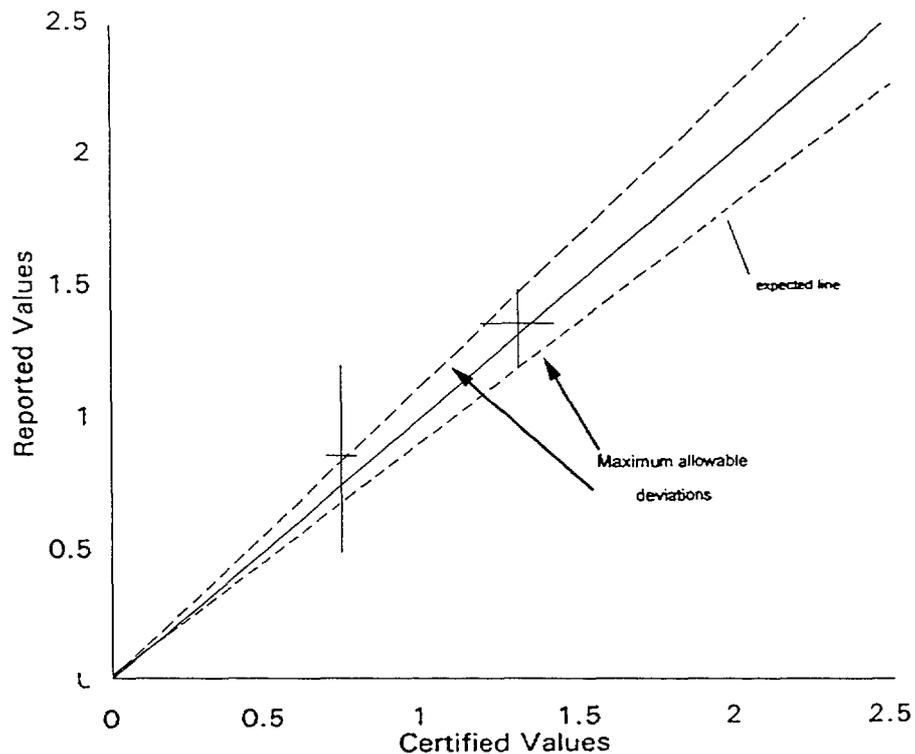


Fig. 2 An example on use of CRM for QC

One of the advantages of Reactor NAA is its relatively independent on the matrices. Hence CRMs proper for APM analysis are not necessarily APM matrix. CRMs with matrices of sediment, soil, coal powder, coal fly ash, etc are all suitable for QC of APM analysis.

The lack of CRMs for microanalysis is one of the major concern for QC in the analysis of APM samples which usually have sample size of about 1 mg or smaller (sometimes even less than 100 μg), while the minimum sample size of all existing CRMs are 100 mg or larger. Development of CRMs suitable for microanalysis and/or re-characterization of some existing CRMs in term of sampling behavior of multielements to identify elements homogeneous at small sample size (1 mg or less) are pressing tasks for analysts [TI98]. Before the above-mentioned tasks are fulfilled, activated APM samples and much larger sized CRM samples have to be counted at different positions, and efficiency normalizations are then made experimentally or parametrically.

It is important to follow all advice contained in the certificates of the CRMs used, including period of validity of the certificate; storage condition;

minimum weight of the material to be taken for analysis; drying conditions; and any other special instructions for use.

Although CRMs can be used as standards for elements having certified values with good accuracy (e.g. uncertainties less than 2%) in routine analysis, they are generally not recommended to be used as multielemental standards because of generally poor uncertainties of certified values (usually 5-10%, compared to 1% or less for synthetic chemical standards), high cost, and especially unsuitable for analysis of candidate CRMs.

Finally, CRMs can not test the whole analytical procedure. Uncertainties in sampling and partly in sample handling normally can not be detected by using CRMs.

3.4 Interlaboratory and multi-method comparison studies

Comparison between analytical methods with different principles has been and is still used for QC. A detailed comparison among XRF, NAA, and PIXE for re-suspended airborne particles was reported by Landsberger and co-authors [LA97]. The results for Al in fine and coarse particles are shown in Fig. 3. Good agreement was found for Cl contents in fine APM samples between NAA and ion chromatography (IC). However in coarse particle samples Cl contents determined by IC are generally 10% lower than those by NAA. It is probably due to the incomplete dissolution in IC. Similar comparison studies were also reported for XRF vs. NAA and XRF vs. ICPMS [WA95], ICPMS vs. NAA vs. PIXE [LA92], etc.

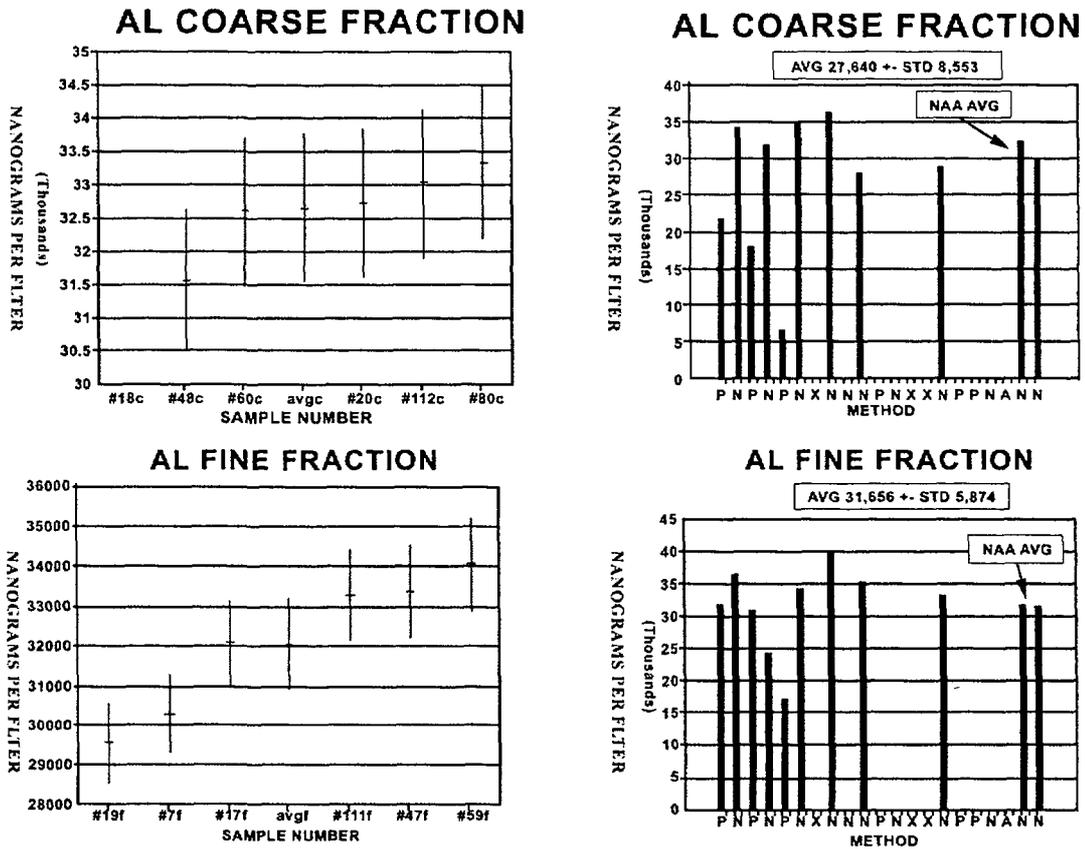


Fig. 3 Comparison among XRF, NAA and PIXE for Al in APM

Numerous intercomparison studies on different materials, including APM matrices, organized by IAEA have greatly improved analytical quality of participating laboratories.

3.5 Control charts

Control charts are plots of relevant parameters with time. They monitor the stability of performances involved in analysis. Among the parameters needed to be monitored are neutron flux gradient, efficiency and resolution of HPGe spectrometer, and most importantly, analytical results for multielements in frequently used CRMs.

Appendix I. Brief Introduction to k_0 -NAA

1. Basic principle [DE87]

Based on Hogdahl convention for $1/v$ reactions, the following equation was deduced for calculation of elemental concentrations:

$$\rho, \text{ ppm} = \frac{\frac{N_p/t_m}{\text{SDCW}}}{\left(\frac{N_p/t_m}{\text{SDCW}}\right)^*} \cdot \frac{1}{k_0} \cdot \frac{f + Q_0^*(\alpha)}{f + Q_0(\alpha)} \cdot \frac{\varepsilon_p^*}{\varepsilon_p} \quad (15)$$

Where k_0 is defined as:

$$k_0 = \frac{M^* \theta \cdot \sigma_0 \cdot \gamma}{M \cdot \theta^* \cdot \sigma_0^* \cdot \gamma^*} \quad (16)$$

In Tables (15) and (16),

M = atomic mass;

θ = isotopic abundance;

σ_0 = $2200 \text{ m}\cdot\text{s}^{-1}$ (n, γ) cross-section;

γ = absolute gamma-ray branching ratio;

N_p = analytical peak area corrected for pulse losses;

W = sample weight in gram;

W^* = comparator weight in microgram;

$S = 1 - \exp(-\lambda t_i)$; t_i -irradiation time; λ -decay constant;

$D = \exp(-\lambda t_d)$; t_d -decay time;

$C = [1 - \exp(-\lambda t_m)] / \lambda t_m$; t_m -measuring time;

f = thermal to epithermal neutron flux ratio;

$Q_0(\alpha) = I_0(\alpha) / \sigma_0$; $I_0(\alpha)$ –resonance integral corrected for a non-ideal (assumed $1/E^{1+a}$) epithermal neutron flux distribution;

ε_p = analytical peak detection efficiency.

Parameters with and without “*” are for comparator and unknown sample, respectively.

2. Parameters needed

A) Parameters to be found in the literature

k_0 [DE86], Q_0 [DE86], \bar{E}_r [JO86], decay parameters [DE86].

B) Parameters to be experimentally determined

i) Efficiency as function of γ -ray energy at a reference counting position.

ii) Instant determination of f using a thin Zr foil (^{94}Zr - ^{96}Zr pair) [DE81].

iii) α determination by “Cd-covered multi-monitor”, “Cd-ratio for multi-monitor” (advance determination), or “bare multi-monitor” (instant determination) methods [DE81]. For the last method, ^{94}Zr - ^{96}Zr - ^{197}Au is an attractive choice in that ^{94}Zr - ^{96}Zr and ^{197}Au can also be served as neutron flux monitor and comparator, respectively.

iv) $Q_0(\alpha)$ calculation from Q_0 , α , and \bar{E}_r by

$$Q_0(\alpha) = (Q_0 - 0.429) / (\bar{E}_r)^\alpha + 0.429 / ((2\alpha + 1) (0.55)^\alpha)$$

v) Calculations for complicated reaction/decay schemes [SI80], [MO84].

vi) P/T (E) determination for summing effect correction [TI93]

C) Extensions to k_0 -NAA

i) Parametric prediction, evaluation and correction for neutron flux self-shielding [NI97].

ii) K_0 -NAA for non- $1/v$ analytical reactions [DE87], [TI94].

iii) Parametric corrections for nuclear reaction interferences [DE87], [TI87], [TI94].

iv) Parametric corrections for γ -spectral interferences [TI94].

v) Parametric normalization for different counting positions [DE87], [TI93].

D) Uncertainty evaluation

An overall uncertainty for k_0 standardization was roughly estimated to be less than 4%, relative [DE87]. The itemized uncertainties were estimated as: the uncertainty propagated from k_0 being 1%, from Q_0 1%, from α 2%, from f 1.5%, from efficiency measurement and conversion 2%, from summing effect correction 1.5%.

E) Role of k_0 method in Reactor NAA

i) Unexpected elements (without standards irradiated) can be determined.

ii) Standard for only one element, i.e. the comparator needs to be certified to satisfy the traceability requirement for the standardization of all elements determined. In practice, high purity Au certified by a definitive method (gravimetry) is easily available to be used as a comparator. In the contrary, for relative method standards of all the elements determined should be certified, which is not easy to be realized.

iii) k_0 method can be combined with traditional relative method to provide an additional measure for internal quality control in detecting and eliminating (or reducing) hidden systematic uncertainties.

Appendix II. Brief Introduction to an Automated Counting System [NI99]

HARDWARE

The PC based automatic sample changer system consists of seven major sections:

- 1) a vertical sample rack, which can hold up to 100 sample rabbits;
- 2) a converter for sending the lowest sample rabbit in the sample rack to the detector each time and holding all the others;
- 3) a tubing system for transporting sample rabbits to and from the detector;
- 4) a compressed air system consisting of an air compressor and a series of electromagnetic valves for driving sample rabbits along the desired directions;
- 5) a measurement system consisting of a HPGe detector and a sample counting terminal with a changeable distance to the detector;
- 6) a control system consisting of an I/O board inserted in a port of a PC;
- 7) a shielding system consisting of a Pb chamber surround the HPGe detector, a reinforced concrete wall separating sample room and counting room, and a separate room for electronics and control board.

A schematic diagram is given in Fig.4.

SOFTWARE

- 1) Three subroutines for peak area calculation are available (integral net counts in peak region, Gaussian fitting, and fitting functions given by the user).
- 2) A hybrid k_0 -relative NAA program, ADVNAA, is used for calculation of elemental concentration and production of analytical report. There are three options for standardization: 1) k_0 method alone, 2) relative method alone, and 3) both k_0 and relative methods.
- 3) Option 1) is usually used in routine analysis of large batch of samples, especially when "comparison analysis" is emphasized (e.g. some archaeological and forensic analysis). Option 2) is usually used when only a few elements are to be determined. In most cases, option 3) is used.

PERFORMANCE

The automatic sample changer system has been successfully operating for more than one year without major unwanted interruption and analytical quality problem. The full capacity of the system is expected to be about 5000 typical geological / biological / environmental samples per year (based on total counting time of 5000 seconds per sample and 300 running days).

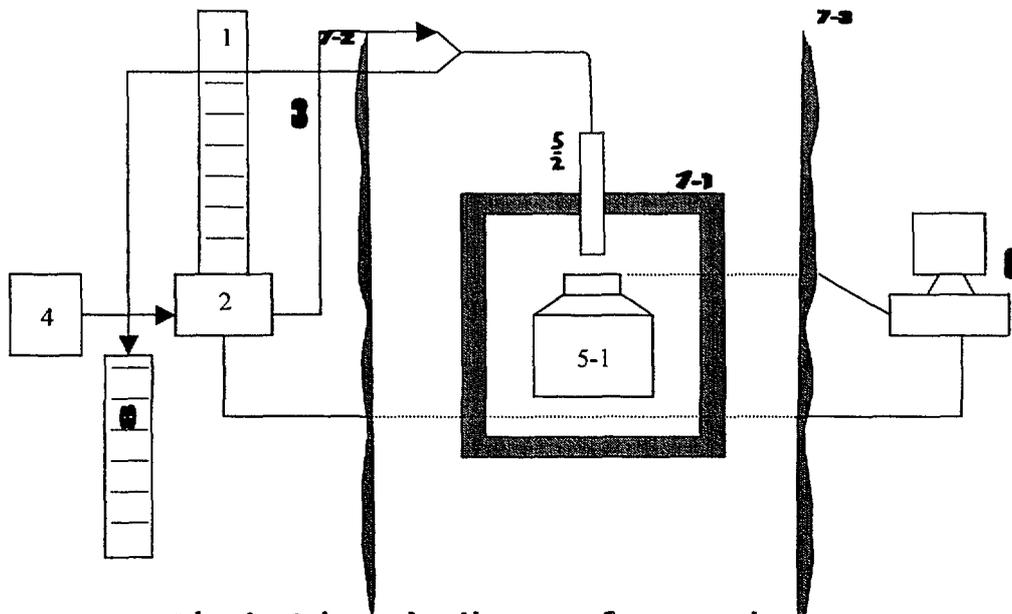


Fig 4. Schematic diagram of automatic MAA system

- | | | | |
|-------------------------------|--------------------------------|----------------------|---------------------------|
| 1. Rack for sample sending; | 2. Converter; | 3. Tubing system; | 4. Compressed air system; |
| 5-1. HPGe Detector; | 5-2. Sample counting terminal; | 6. PC Control system | |
| 7-1. Lead Chamber; | 7-2. Reinforced concrete wall; | 7-3. Common wall | |
| 8. Rack for sample retrieving | | | |

REFERENCES

- AA92 P.A.Aarnio, M.T.Nikkinen, J.T.Routti, *J. Radioanal. Nucl. Chem.*, 160(1992)289
- AL85 Z.B.Alfassi, *J. Radioanal. Nucl. Chem.*, 90(1985)151
- AL90 Z.B.Alfassi, Use of delayed neutrons in activation analysis, in *Activation Analysis, Vol.1*, CRC Press, Boca Raton, 1990, p.97
- CH85 L.Z.Chen, Y.Q.Sha, *Nucl. Techn.*, 8(1985)41 (in Chinese)
- CL98 M.Claes, K.Gysels, R.E. van Grieken, "Inorganic Composition of Atmospheric Aerosols", in *Atmospheric Particles*, R.M. Harrison and R.E. van Grieken, eds., (IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 5), John Wiley and Sons, 1998, p.96.
- CU68 L.A.Currie, *Anal. Chem.*, 40(1968)586
- DE81 F.DeCorte, K.Sordo-El Hammami, L.Moens, et al., *J. Radioanal. Chem.*, 62(1981)209
- DE86 F.DeCorte, A.Simonits, A.DeWispelaere, J.Hoste, A compilation of k₀-factors in NAA, INW/KFK1 Interim Report, 1986
- DE87 F.DeCorte, A.Simonits, A.DeWispelaere, J.Hoste, *J. Radioanal. Nucl. Chem.*, 113(1987)145
- EH86 W.D.Ehmann, S.W.Yates, *Anal. Chem.*, 58(1986)49R
- EH87 W.D.Ehmann, R.C.Young, D.W.Koppelaar, et al., *J. Radioanal. Nucl. Chem.*, 112(1987)71
- EH88 W.D.Ehmann, S.W.Yates, *Anal. Chem.*, 60(1988)42R
- EH90 W.D.Ehmann, J.D.Robertson, S.W.Yates, *Anal. Chem.*, 62(1990)50R
- EH92 W.D.Ehmann, J.D.Robertson, S.W.Yates, *Anal. Chem.*, 64(1992)1R
- EH94 W.D.Ehmann, J.D.Robertson, S.W.Yates, *Anal. Chem.*, 66(1994)229R
- FA90 J.J.Fardy, Radiochemical separation in activation analysis, in *Activation Analysis, Vol.1*, CRC Press, Boca Raton, 1990, p. 61
- GI68 F. Girardi, E.Sabbioni, *J. Radioanal. Chem.*, 1(1968)169
- GR75 F.Grass, *Atomkernenergie*, 25(1975)243
- GR94 R.R.Greenberg, *J. Radioanal. Nucl. Chem.*, 179(1994)131
- GU74 G.Guzzi, R.Pietra, E.Sabbioni, F.Girardi, *J. Radioanal. Chem.*, 20(1974)751
- JO86 S.Jovanovic, F.DeCorte, A. Simonits, L.Moens, et al., *J. Radioanal. Nucl. Chem.*, 113(1987)177
- KA73 R.E.Kay, P.P.Stevens-Guille, J.W.Hilborn, R.E.Jervis, *Int. J. Appl. Radiat. Iso.*, 24(1973)509
- LA92 E.Larsen, A.B.Hansen, L.V.Kristensen, et al., *J. Trace Micro Techn.*, 10(1992)43
- LA96 S.Landsberger, S. Peshev, *J. Radioanal. Nucl. Chem.*, 202(1996)203
- LA97 S.Landsberger, D. Wu, S.J.Wermette, W.Cizek, *J. Radioanal. Nucl. Chem.*, 217(1997)117
- LA99 S.Landsberger, "Trace Element Determination of Airborne Particles by NAA" in *Elemental Analysis of Airborne Particles*, S. Landsberger and M.Creatchman, eds., Gordon and Breach Science Publishers, 1999, p.197.
- LI80 R.Litman, J.Mallet, B.R.Notini, *Radiochem. Radioanal. Letter*, 45(1980)347
- ME72 M.Mental, S.Amiel, *Anal. Chem.*, 44(1972)548
- MO84 L.Moens, F.DeCorte, A.DeWispelaere, et al., *J. Radioanal. Nucl. Chem.*, 82(1984)385
- MO88 J.R.Moody, R.R.Greenberg, K.W.Pratt, T.C.Rains, *Anal. Chem.*, 60(1988)1203A
- NI97 B.F.Ni, P.S.Wang, W.Z.Tian, *J. Radioanal. Nucl. Chem.*, 215(1997)77
- NI99 B.F.Ni, P.S.Wang, H.L.Nie, S.Y.Li, X.F.Liu, W.Z.Tian, *J. Radioanal. Nucl. Chem.*, 1999, in press.
- SI75 A.Simonits, F.DeCorte, J.Hoste, *J. Radioanal. Chem.*, 24(1975)31
- SI80 A.Simonits, L.Moens, F.DeCorte, et al., *J. Radioanal. Chem.*, 60(1980)461
- TI86 W.Z.Tian, *J. Radioanal. Nucl. Chem.*, 103(1986)225
- TI87 W.Z.Tian, *J. Radioanal. Nucl. Chem.*, 111(1987)449
- TI93 W.Z.Tian, B.F.Ni, P.S.Wang, L.X.Peng, *J. Radioanal. Nucl. Chem.*, 170(1993)27
- TI94 W.Z.Tian, B.F.Ni, *J. Radioanal. Nucl. Chem.*, 179(1994)119
- TI98 W.Z.Tian, B.F.Ni, P.S.Wang, H.L.Nie, *Fresenius J. Anal.Chem.*, 360(1998)354
- WA87 L.Y.Wang, *At. Energy Sci, Techn.*, 10(1987)289
- WA95 C.F.Wang, E.E.Chang, P.C.Chiang, N.K.Aras, *Analyst*, 120(1995)2521
- ZH83 Y.M.Zhou, Miniature Neutron Source Reactor, CIAE Report, 1983

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