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HEVESY MEDAL AWARD LECTURE

Pushing the limits of NAA: Accuracy, uncertainty and detection limits

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This paper describes some highlights from the author's efforts to improve neutron activation analysis (NAA) detection limits through development and optimization of radiochemical separations, as well as to improve the overall accuracy of NAA measurements by identifying, quantifying and reducing measurement biases and uncertainties. Efforts to demonstrate the metrological basis of NAA, and to establish it as a "Primary Method of Measurement" will be discussed.

Introduction

Neutron activation analysis (NAA) is a mature analytical method, and remains an extremely valuable tool for many applications. NAA offers excellent multielemental capabilities, has characteristics that inherently provide few sources of error compared to most other analytical techniques, and provides intrinsic quality assurance characteristics that often allow measurement results to be internally evaluated and cross checked. It has great advantages for the certification of reference materials, and has been used at the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS), for this purpose for the last forty years.

Over the last 15 years, NAA has faced increasing competition from other analytical techniques for many of the applications normally well suited to NAA, such as multielemental environmental and geological studies. Much of the competition has been from inductively coupled plasma mass spectrometry (ICP-MS), which can successfully compete in multielemental capability and detection limits in solid samples. However, NAA has the potential for superior accuracy, at least for trace analysis, since ICP-MS is more subject to matrix effects and interferences. In addition, ICP-MS requires that samples be in solution (for most implementations) and thus dissolution problems can add an important source of error for complex matrices. Most NAA measurements are performed non-destructively, and even when dissolutions are required for radiochemical separations, the blank-free nature of the method, as well as the ability to add carriers of the same elements under investigation, provide significant dissolution advantages for the method. In view of NAA's capability for accurate measurements, additional opportunities for the certification of reference materials, and for other high-accuracy applications should be explored.

This paper will focus on some highlights of the author's efforts at NIST to improve NAA detection limits through development and optimization of radiochemical separations, to improve the accuracy of NAA measurements by identifying, quantifying and reducing measurement biases and uncertainties, and to demonstrate the method's metrological basis and establish NAA as a "Primary Method of Measurement".

Results and discussion

Improving NAA detection limits with chemical separations

Although instrumental neutron activation analysis (INAA) is a very powerful technique, detection and determination of many elements are often limited by the levels of the other elements present in a sample under investigation. Pre- or post-irradiation chemical separations can greatly improve the detection limits, precision and accuracy of the determination of some important elements that are often not measured well by INAA. With INAA the analyst is limited to those radionuclides that can be seen above the background level of radiation produced by the matrix, but with radiochemical or preconcentration NAA (RNAA/PNAA), specific elements of interest can be targeted. Examples of some extremely low levels of important elements determined by the author using various RNAA procedures[1,2] are listed in Table 1.

Single element separations are ideal in terms of improving detection limits and precision, however, separating each element individually requires a great deal of the analyst's time, and is therefore expensive.

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Table 1. Elemental concentrations (in μg/kg)* in NIST Milk Powder, SRM 1549 and NIST Bovine Serum, SRM 1598 via RNAA

Element	Separation procedure	Milk Powder*	Bovine Serum*
Al	Group-Chelex 100	–	4.5 ± 0.7
Ag	Group-HMD	<0.3	–
As	Group-HMD	1.77 ± 0.11	0.148 ± 0.016
Cd	Single-DDC	0.47 ± 0.09	0.093 ± 0.024
Cr	Group-HMD	2.6 ± 0.7	–
Cr	Single-TBA	2.65 ± 0.17	0.177 ± 0.021
Cu	Single-DDC	606 ± 10	722 ± 22
Cu	Group-Chelex 100	–	705 ± 19
Hg	Single-DDC	0.164 ± 0.016	–
Mn	Group-Chelex 100	–	3.72 ± 0.15
Mo	Group-HMD	322 ± 17	11.2 ± 0.6
Sb	Group-HMD	0.25 ± 0.03	–
Se	Group-HMD	110 ± 3	–
Sn	Single-SnI_4	1.9 ± 0.7	–
V	Group-Chelex 100	–	0.055 ± 0.034

* Uncertainties approximate expanded uncertainties (k=2).

While multielemental procedures may not result in ideal detection limits or precision, their cost per element determined can be significantly better than for single element separations. As an example, a multielemental separation procedure was developed at NIST in 1977[3] that combined the use of an inorganic ion-exchanger (HMD) followed by sequential extraction procedures using bismuth and zinc diethyldithiocarbamates (DDC). This procedure allowed the accurate determination of As, Cd, Cr, Cu, Sb and Se in a wide variety of materials at sub-mg/kg levels. Molybdenum, Ag and Sn were subsequently added to the list of elements that were quantitatively retained on the HMD column, and could be determined in some matrices. Modifications to the original procedure through the use of column preconditioning and elution with dilute phosphoric acid, washing the extracted Cd fractions with aqueous solutions of (unirradiated) Zn holdback carrier, and then back extracting Cd into dilute HCl, allowed the determination of Ag, As, Cd and Sb at sub-μg/kg levels, as well as Cr and Mo at a few μg/kg.[1,2] Variations of the HMD-DDC procedure have been used to provide values that contributed to the certification of more than 30 NIST Standard Reference Materials (SRMs).

Another example of a multielemental separation procedure developed at NIST by the author with H. M. KINGSTON involved the use of Chelex-100 to preconcentrate Co, Cr, Cu, Fe, Mn, Mo, Ni, Sc, Th, U, V, Zn, and others from a saltwater matrix, prior to irradiation. Up to 17 elements were determined via NAA after preirradiation separation.[4,5] Although use of a preconcentration procedure gives up one of NAA's key advantages, i.e., that of being nearly blank free, the high salt content of a marine water sample produces excessive levels of radiation if not first removed.

The Chelex-100 preconcentration procedure also proved to be advantageous for the determination of several elements with relatively short-lived daughter products in biological materials.[6] Chelex-100 effectively retains Al, V, Cu and Mn from biological materials[6] dissolved in HNO_3, HF and $HClO_4$. Separation of Al from a biological matrix prior to irradiation is often important to eliminate the (n, alpha) interference from P. Although rapid separation procedures have been performed for radionuclides with half-lives as short as 3.75 min (^{51}V),[7] separation prior to irradiation reduces the levels of radiation exposure to the analyst. One of the materials analyzed for certification using this procedure was NIST Bovine Serum, SRM 1598. As shown in Table 1, Al and Mn were determined at a few μg/kg, and V was determined at 0.05 μg/kg.

Despite the cost-per-element advantage of multielemental separation procedures, it is sometimes necessary to achieve extremely low detection limits available only by completely separating each element from all others. The author has developed or co-developed single element separation procedures for Hg,[1] Sn,[1] Cr,[8] and Au[9] (with Pt via ^{199}Au), as well as the Cu and Cd procedures mentioned as part of the multielemental procedure. The separation procedures for Cr and Au (with Pt) were developed with R. ZEISLER. Sub-μg/kg determinations of Cr in Bovine Serum and Hg in Milk Powder are listed in Table 1, as well as the determination of Sn at 2 μg/kg in Milk Powder. Table 1 also presents values for Cr determined using both the group separation and the single element separation in the Milk Powder. Although the values are in good agreement, the uncertainty for the single element determination was more than a factor of 4 smaller than that from the multielemental procedure. Furthermore, Cr

could not be determined in the Bovine Serum using the multielemental procedure, but was determined with a relatively small uncertainty using the single element separation. Gold and Pt were both determined using the single element Au separation procedure[9,10] at 8 ng/kg each in NIST SRM 2670 (Toxic Metals in Freeze-Dried Urine), and at similar levels in human liver tissues.

One of the driving forces to develop the separation procedure for Cr was to enable the determination of Cr in human whole-blood samples at natural levels. The ability to determine Cr in blood is limited not only by the background radiation from other radionuclides, but also by the (n, alpha) interference from Fe during the irradiation step. Although RNAA had been successfully used to determine Cr in blood serum at few tenths of a μg/kg,[11] the extremely high levels of Fe in blood produces an average interference equivalent to about 5 μg/kg[11] in a typical light water reactor. Corrections for this interference in a light water reactor would be extremely difficult, even if the natural levels of blood were similar to the interference, since high-accuracy characterization of the Fe interference for each reactor facility would be necessary, as would an accurate determination of Fe in each individual blood sample. Small changes in the fast-to-thermal neutron fluence rates in a facility could make the interference vary as a function of time. Correction for the interference would be impossible if the Cr levels were significantly below the Fe interference level. This problem, however, can be greatly reduced by using a very highly thermalized irradiation facility such as the RT-4 facility[12] at the NIST research reactor. This reactor is D_2O cooled and moderated, and the level of the fast neutron interferences is reduced by a factor of about 100 to 1000 compared to a typical light water reactor. The Cr extraction procedure,[8] combined with the reduced-levels of interferences for RT-4 allowed Cr to be determined at naturally occurring levels of a few tenths of a μg/kg[13] and below. Using non-contaminating collection procedures, Cr was determined in the blood and blood serum of 9 individuals, and the results are listed in Table 2.[13] Note that one person had significantly higher levels of Cr in both whole blood and blood serum when compared to the others. This individual had previously been diagnosed as a diabetic, and had been on medication to control her blood sugar, however, her blood sugar was controlled at the time of sample collection by weight reduction and diet.

Identifying, quantifying and reducing measurement biases and uncertainties

Evaluation of uncertainties for INAA: Although, the first use of NAA at NBS/NIST for the certification of elemental content in an SRM occurred about 40 years ago, sources of uncertainty other than measurement precision were not normally considered until a decade later. The first attempt to eliminate all sources of bias and evaluate all uncertainty components for a multiemental INAA measurement of an SRM was by the author about 30 years ago. INAA measurements of 32 elements in SRM 1648, Urban Particulate Matter, were reported[14] with uncertainty budgets that included 10 individual uncertainty components. Many of the combined (relative) uncertainties were about 2–3% at the (estimated) 95% confidence level. These uncertainty budgets were pre-GUM,[15] and did not include every uncertainty component for NAA that subsequently surfaced;[17] however, if all uncertainty components were included, and if GUM-compliant methodology were used, the uncertainly budgets would actually be the same or smaller since the component for measurement replication was not reduced (divided) by the square root of the number of samples analyzed in the evaluations done 30 years ago as is currently recommended.[15]

Table 2. Chromium in human blood and serum (in μg/kg – fresh weight*)[13]

Subject	Sex	Collection date	Whole blood	Blood serum
B1	Male	Mar. 1986	0.159 ± 0.023	0.102 ± 0.012
B1	Male	Mar. 1986	0.160 ± 0.016	–
B1**	Male	Sept. 1987	0.226 ± 0.027	0.193 ± 0.021
B2	Female	Mar. 1986	0.273 ± 0.019	0.378 ± 0.024
B2	Female	Mar. 1986	–	0.445 ± 0.044
B2	Female	Sept. 1987	0.292 ± 0.043	0.454 ± 0.044
M1	Female	Mar. 1986	0.148 ± 0.019	0.117 ± 0.015
T1	Male	Mar. 1986	0.340 ± 0.018	–
D1	Male	Mar. 1986	0.150 ± 0.016	0.182 ± 0.027
W1	Male	Mar. 1986	0.119 ± 0.025	–
J1	Male	Mar. 1986	0.280 ± 0.036	0.258 ± 0.038
R1	Male	Sept. 1987	0.038 ± 0.014	0.077 ± 0.010
T2***	Female	Sept. 1987	1.286 ± 0.048	1.743 ± 0.042

* Uncertainties approximate expanded uncertainties (k=2).
** Cr dietary supplement taken for 1.5 year.
*** This individual had previously been diagnosed as diabetic.

Recently, six samples of this same material have been reanalyzed at NIST by Rolf ZEISLER using INAA as part of the renewal process to produce SRM 1648a.[17] Twenty-seven elements were determined in both sets of measurements. With two exceptions, the average relative difference between the observed elemental concentrations was 2%, demonstrating a remarkable level of stability for the INAA method, even when applied by 2 different analysts separated by 30 years in time, using different irradiation facilities, counting equipment, data-reduction procedures, and comparator standards. The two more significant differences were for La and Hf. The difference for La was due to an error in preparing the original La standards, and was discovered about 15 years ago. Despite using a new/unopened bottle of high purity La_2O_3 to prepare a standard solution for La, much of the La_2O_3 apparently had been converted in air to $La_2(CO_2)_3$, resulting in an incorrect value for the La content of all standards produced from this solution. If the previously calculated La value in the standard was corrected by the actual La content in the standard (as subsequently determined), the resulting La value for the original measurement would differ from the new one by only 2%. The reason for the difference in the Hf results is not currently known, however, a problem in standards preparation is the most probable cause. A comparison of the two sets of INAA measurements with the final certified values is presented in Table 3.

High precision, high accuracy measurements of uranium isotopic ratios using gamma-spectrometry: INAA can be thought of as a 3-stage process: sample and standard preparation; irradiation, and gamma-spectrometry (GS). In many INAA measurements, uncertainty components from the GS step are responsible for a large portion of the overall uncertainty. Efforts to evaluate the limits of uncertainty for GS were undertaken as part of a joint project by NBS (currently NIST) and CBNM (Central Bureau for Nuclear Measurements), currently IRMM (Institute for Reference Materials and Measurements) to prepare and certify five sets of uranium Non Destructive Assay standards for nuclear safeguards purposes.[18,19] The materials were certified as NBS/NIST SRM 969 and EC NRM 171, and consisted of U_3O_8 powder at five different $^{235}U/U$ isotope abundance levels sealed in aluminum cans. Gamma-spectrometry was originally intended only to verify the level of homogeneity by analyzing 24 samples from each of the five sets. The desired relative standard deviations (RSDs) for the GS measurements were a few tenths of a percent. However, with careful attention to detail, and an exhaustive search to identify and quantify potential biases, RSDs of 0.05% to 0.11% were actually observed among the 24 or more samples of each set measured. In addition to homogeneity verification, GS was used to determine actual isotope abundances with fully evaluated uncertainty budgets. Corrections were required for counting geometry, pulse pileup, gamma-ray interferences, and gamma-ray self-absorption differences due to changes in sample packing density. Significant uncertainty components were evaluated for each correction applied, as well as for sample replication, counting statistics of the standards, isotope abundances of the standards, and peak-integration method. The relative uncertainty (approximating the 95% confidence level) for each set was 0.08%, and was dominated by the uncertainties of the isotope abundances of the standards used. It was projected that with standards prepared from available separated isotopes, and some slight additional optimization of the measurement process, relative expanded uncertainties of 0.01% to 0.03% could be obtained for similar measurements using GS.

The results of the GS measurements are compared with the certified values in Table 4. As discussed in Reference 18, and indicated in Table 4, there appears to be a slight bias in the GS measurements compared to the certified values. The average of the relative differences for each of the 5 sets is approximately –0.03%. This is actually due to inclusion of one set of data in the certification process that was always biased high compared to the other data used for certification.

Table 3. Comparison of certified and INAA values* determined thirty years apart in NIST Urban Particulate Matter, SRM 1648

Element	INAA Greenberg (1977)	INAA Zeisler (2007)	Certified (1998 Certificate)
Al (%)	3.5 ± 0.1	3.43 ± 0.06	3.42 ± 0.11
As (mg/kg)	117 ± 5	115 ± 4	115 ± 10
Cd (mg/kg)	70 ± 6	–	75 ± 7
Cr (mg/kg)	402 ± 10	404 ± 18	403 ± 12
Fe (%)	3.84 ± 0.08	3.91 ± 0.15	3.91 ± 0.10
K (%)	0.99 ± 0.06	1.001 ± 0.021	1.05 ± 0.01
Mn (mg/kg)	790 ± 20	771 ± 15	786 ± 17
Na (%)	0.40 ± 0.02	0.412 ± 0.009	0.425 ± 0.002
Se (mg/kg)	27 ± 2	26.1 ± 1.0	27 ± 1
V (mg/kg)	130 ± 7	127.4 ± 2.3	127 ± 7
Zn (mg/kg)	0.47 ± 0.02	0.476 ± 0.018	0.476 ± 0.014

* Uncertainties are approximate expanded uncertainties (k=2)

Table 4. Comparison of gamma-spectrometry results for $^{235}U/U$ Isotope Abundances in NIST SRM 969/ EC NRM 171 with certified and other values

Level	Gamma-spectrometry, $\times 10^6$ atom ratio	Certified, $\times 10^6$ atom ratio	Relative difference from certified	Relative difference from UF_6MS
031	3205.3 ± 2.6	3206 ± 2	–0.022%	+0.012%
071	7208.1 ± 5.8	7209 ± 2	–0.012%	–0.021%
194	19660 ± 16	19664 ± 14	–0.020%	+0.010%
295	29830 ± 24	29857 ± 21	–0.091%	+0.044%
446	45158 ± 36	45168 ± 32	–0.022%	–0.020%

Table 5. Uncertainty components for the determination of arsenic implanted in silicon

Type A		
1.	Measurement replication for samples (ν = 9)	0.081%
2.	Counting statistics for standards (ν = 105)	0.073%
3.	Blank (gains) (ν = ≈100)	0.013%
4.	Sample area – measurement precision (ν = 26) (ν signifies degrees of freedom)	0.009%
Type B		
5.	Isotopic abundances (unknowns/standards)	0%
6.	Neutron fluence exposure – irradiation geometry	0.039%
7.	Neutron fluence exposure – self shielding	0.024%
8.	Neutron fluence exposure – scattering	0.015%
9.	Effective cross sections (σ)	0.000005%
10.	Counting efficiency – geometry effects	0.009%
11.	Counting efficiency – gamma-ray self-absorption	0.004%
12.	Effects of half-life	0.056%
13.	Irradiation timing	0%
14.	Count intervals – live-time	0.00003%
15.	Count intervals – clock time	0%
16.	Decay until start of counts – precision	0.000002%
17.	Decay until start of counts – accuracy	0.00007%
18.	Peak integration method	0.019%
19.	Pulse pileup	0.066%
20.	Inadequacy of live-time extension	0.001%
21.	Gamma-ray interferences	0.000004%
22.	Fast neutron interferences	0.0003%
23.	Fission interferences	0%
24.	Irradiation losses	0%
25.	Target isotope burn up	0%
26.	Perturbed angular correlations	0%
27.	Sample area – micrometer accuracy	0.012%
28.	Concentration of standard solutions	0.106%
29.	Amount of standard solutions deposited	0.041%
Type A (combined) = 0.110%		Combined uncertainty = 0.188%
Type B (combined) = 0.153%		Coverage factor = 2.04 (effective ν = 30.8)
Expanded relative uncertainty = 0.384%		Measured value = 91.20 ng/cm^2 ± 0.35 ng/cm^2

This bias is dramatically reduced to +0.005% when the GS data is compared with the data determined by UF_6 mass spectrometry with close bracketing of synthetic standards (at each U isotope level). This method was considered the most accurate of all the methods used for certification. The relative differences between the GS and UF_6 mass spectrometry for the individual levels ranged from –0.021% to +0.044%, with a typical difference of 0.021% (average of the absolute values of the relative differences).

Development of complete uncertainty budgets for INAA using the comparator method: By the end of the 1990s, all sources of uncertainty (and bias) for INAA measurements using the comparator method of standardization were known and could be quantitatively evaluated. This was demonstrated in a paper presented at MTAA-12 by GREENBERG, LINDSTROM and SIMONS.[16] Twenty-nine individual uncertainty components were evaluated for the determination of ion-implanted arsenic in silicon (SRM 2134), and the relative expanded uncertainty ($k = 2.04$) for this measurement was 0.38%. The certified value for this SRM is 91.20 ng/cm^2 ± 0.35 ng/cm^2, determined solely by INAA. The 29 individual uncertainty components evaluated for this work were reduced to 19 for the publication, mainly by combining similar ones; for example, fast neutron

interferences and fission interferences were listed as irradiation interferences, and eliminating some that were not applicable to this measurement, such as target isotope burn up since samples and standards were irradiated together. This facilitated apportionment of each uncertainty component to the three main steps in the measurement process: preirradiation, irradiation and gamma-spectrometry. In addition, two of the uncertainty components in the publication were listed as "negligible" because it was clear that they were well below 0.01%. However, the authors subsequently evaluated these uncertainty components quantitatively for completeness, and the complete list of all 29 individual uncertainty components for this measurement is provided in Table 5.

Demonstrating that comparator NAA meets the definition of a "Primary Method of Measurement"

The Consultative Committee on the Amount of Substance – Metrology in Chemistry (CCQM) defines a primary method of measurement as:[20,21]

"A primary method of measurement is a method having the highest metrological properties, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units.

– A primary direct method: measures the value of an unknown without reference to a standard of the same quantity.

– A primary ratio method: measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation."

Rearranging this definition, it appears that a primary direct method of measurement must meet three criteria:

(1) The method's operation can be completely understood, and fully described by a measurement equation;

(2) A complete uncertainty statement can be written in terms of SI units (or ratios);

(3) The method has the highest metrological properties.

Meeting the first two requirements seems relatively straightforward for NAA using the comparator method of standardization. The NAA measurement process can be described by the following equation:

$$m_{unk} = m_{std} \frac{(A_{0,unk})}{(A_{0,std})} R_\theta R_\phi R_\sigma R_\varepsilon - \text{blank}$$

where m_{unk} = mass of an element in the unknown sample; m_{std} = mass of an element in the comparator standard; R_θ = ratio of isotopic abundances for unknown and standard; R_ϕ = ratio of neutron fluences (including fluence drop off, self-shielding, and scattering); R_σ = ratio of effective cross sections if neutron spectrum shape differs from unk. to std.; R_ε = ratio of counting efficiencies (differences due to geometry and γ-ray self-shielding) and:

$$A_0 = \frac{\lambda C_x e^{\lambda t_1}}{(1-e^{-\lambda\Delta})(1-e^{-\lambda T})} f_p f_{ltc}$$

where A_0 = decay corrected count rate; C_x = net counts in γ-ray peak; λ = decay constant = ln $2/t_{1/2}$; t_1 = decay time to start of count; Δ = live time of count; T = irradiation time; f_p = pulse pileup correction; f_{ltc} = live time ext. correction.

Note that the "*R*-values" are normally very close to unity, and all units are either SI-based or dimensionless ratios. Since all units are SI, an uncertainty statement can be written in terms of SI units (or ratios). As previously discussed in the arsenic in silicon measurement described above, all uncertainty components can be completely evaluated.

Unfortunately, it is not apparent how to definitively demonstrate that NAA has the highest metrological properties since objective criteria are not presented. The "highest metrological properties" seems to imply a comparison to other methods of analysis, and may include some or all of the following criteria: (1) freedom from bias (or potential accuracy of the method); (2) measurement precision; (3) completeness and magnitude of uncertainty budgets; (4) traceability, and (5) detection limits. Since a comparison is implied, it is reasonable to compare NAA to the five methods designated by CCQM as potentially primary methods of measurement: isotope dilution mass spectrometry (IDMS); coulometry; gravimetry; titrimetry, and determination of freezing point depression.[20] Of the five methods listed, only IDMS, as ID-ICPMS, is typically used to determine trace elements in complex matrices, as does NAA. Therefore, a comparison between ID-ICPMS and NAA seems appropriate. If we consider the five criteria listed above, the two methods appear to be capable of similar performance. Assuming appropriate implementations, both methods eliminate or minimize potential biases through the use of ratio determinations. ID-ICPMS has the advantage of not requiring quantitative recoveries, however, NAA applied instrumentally, does not require sample dissolution, and thus eliminates any potential problems due to incomplete dissolution, losses, or chemical blank. Even if radiochemical separations are employed, reagent blank is not an issue. Both methods suffer from potential interferences, isobaric and molecular interferences for ID-ICPMS, and gamma-ray, fast neutron and fission interferences for NAA. ID-ICPMS typically has better baseline resolution than NAA, but NAA has greater potential for recognizing and correcting interferences through use of multiple gamma-

lines and by following radioactive decay since it is extremely unlikely that an interfering nuclide has the same half-live as the desired nuclide. ID-ICPMS has the potential for superior precision for elements at high concentrations in aqueous solutions, but the two methods have the potential for relatively similar levels of precision for elements at lower levels, especially in complex matrices. Complete uncertainty statements can be prepared for both methods; however, evaluating the ID-ICPMS uncertainty for dissolution of complex matrices can often be difficult. Both methods are capable of achieving expanded uncertainties of a few tenths of a percent in favorable cases; however, expanded uncertainties of 1–2% would be more typical for trace level determinations in complex matrices. Traceability of both methods is relatively straightforward through measurement equations using comparisons with high purity materials of known purity and stoichiometry (for compounds). Both methods are unable to determine some key elements. IDMS cannot be used for nearly all monoisotopic elements, and NAA cannot measure, or has very poor detection limits for some important elements such as Pb, Si, Bi, etc. ID-ICPMS has better detection limits for many elements in aqueous solutions, but NAA has similar or better detection limits compared to ID-ICPMS for many elements in complex, solid matrices. In both cases, a high level of metrological expertise is required to fully realize the potentials of the methods.

Although both NAA and ID-ICPMS appear to have similar metrological properties in theory, can they both realize them to the same degree in practice? This was initially difficult to evaluate since many of the national metrology institutes (NMIs) routinely apply IDMS at the highest metrological levels, however, relatively few NMIs have in-house NAA capabilities. The vast majority of NAA measurements are performed at a more cost effective, but much lower metrological level, for environmental, biomedical, archeological, or geological studies, etc. However, direct comparison of the performance of NAA and IDMS at the highest metrological levels has become possible through interlaboratory comparisons conducted by the CCQM. Since 2001, 14 laboratories employing NAA have participated in 23 key comparisons and/or pilot studies through the Inorganic Analysis Working Group (IAWG) of the CCQM. Although the data for the pilot studies are often restricted to the participants, results for some pilot studies have been made available on the BIPM web site (http://www.bipm.org). In addition, all data for key comparisons, once finalized, are available to the general public on the BIPM web site. Comparisons of the performance of the two methods in the key comparisons, as well as in available pilot studies, seem to indicate similar levels of performance in terms of magnitude of expanded uncertainty statements and agreement (within uncertainties) of the reported values and the accepted values for the studies. This is clearly illustrated with the publicly available data for Se in CCQM-K43 (Salmon).[22] Selenium values for 5 NMIs using INAA and 4 NMIs using ID-ICPMS are given in the final report, and are shown graphically in Fig. 1.

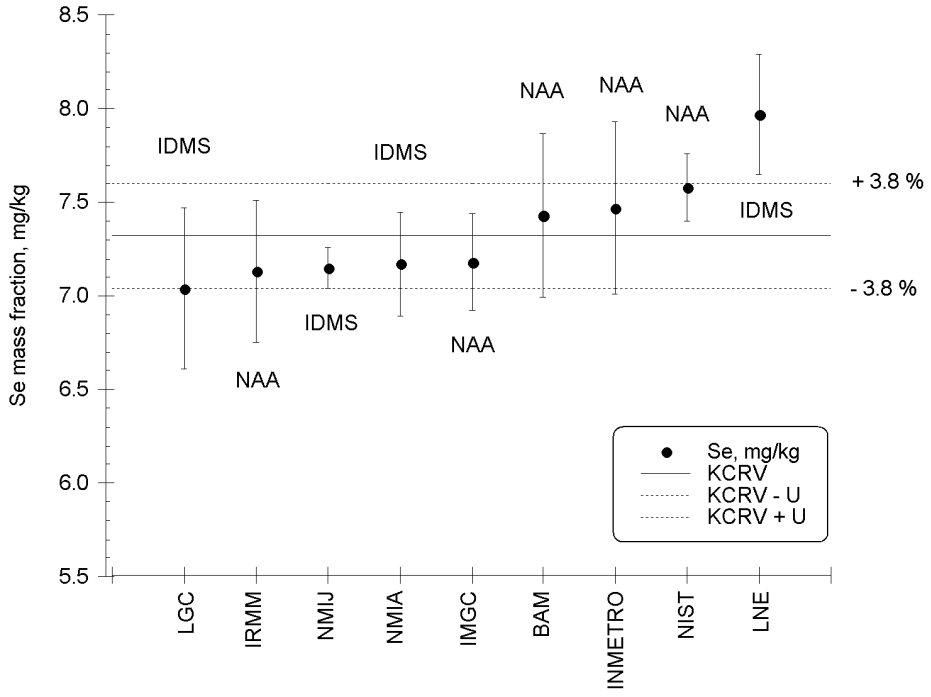

Fig. 1. IDMS and NAA results reported for Se in CCQM-K43, salmon

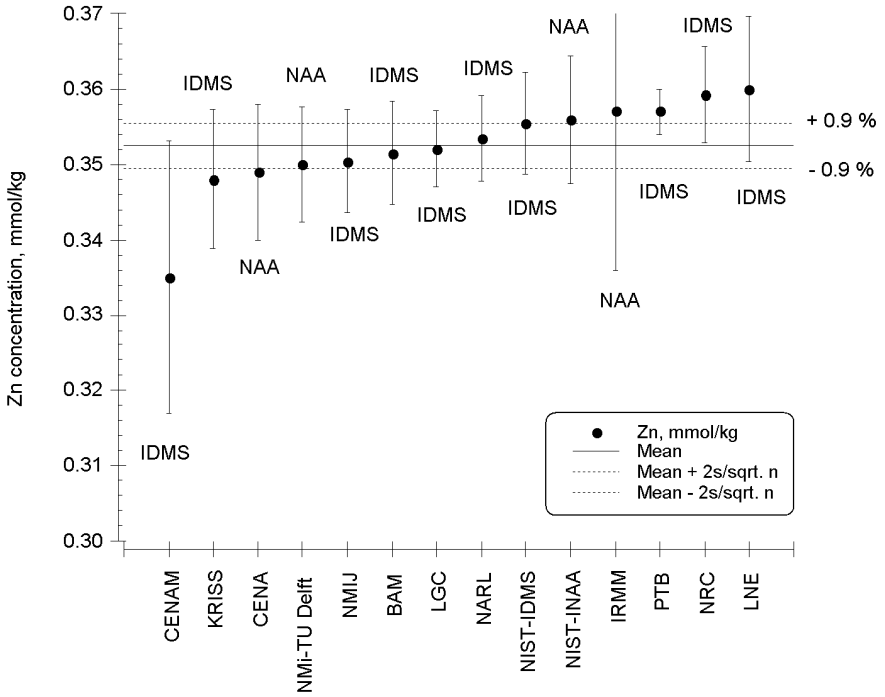

Fig. 2. IDMS and NAA results reported for Zn in CCQM-P29, rice

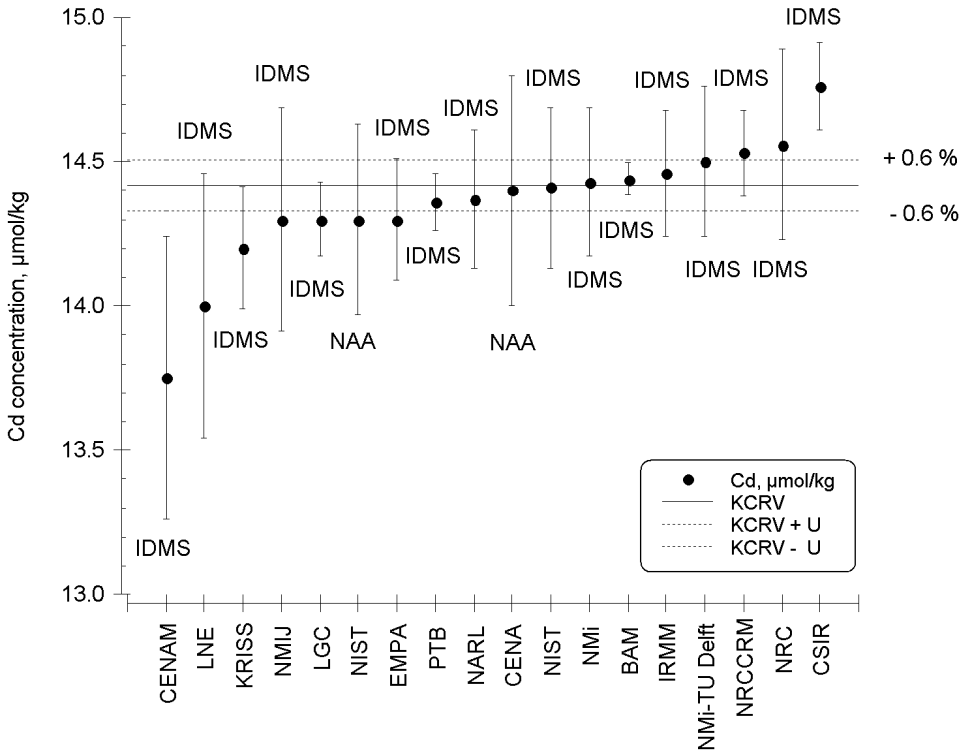

Fig. 3. IDMS and NAA results reported for Cd in CCQM-K24/P29, rice

Another example using publicly available data is for Zn in CCQM-P29 (Rice).[23] Data from 4 laboratories using NAA and 10 laboratories using IDMS are presented in the final report, and are shown in Fig. 2. All data agree well within the stated uncertainties. Although there were notable differences between the magnitudes of the reported uncertainties, the magnitudes of the expanded uncertainties typically reported were similar for NAA and IDMS laboratories. In a similar manner, three INAA results for Cd in the combined key comparison[24] and pilot study[23] CCQM-K29/P29 appear similar, and could not be distinguished from the IDMS values, despite the fact that Cd is a relatively difficult element to determine by NAA in most materials without a chemical separation. Data for this comparison are shown in Fig. 3.

Although results for all pilot studies may not be generally available, comparisons of the NAA and ID-ICPMS results for the following studies indicated similar performance of the two methods: Cd and Zn in Rice Flour, CCQM-K24/P29, Se in Tuna Fish, CCQM-P39; Se in Salmon, CCQM-K43/P39.1; Zn in Sewage Sludge, CCQM-K40/P70; Fe and Zn in Soybean Powder, CCQM-P64; K, Ca and Fe in Clay, CCQM-P65; Se in Yeast, CCQM-P86, and Fe, Zn, Se, Cd, Cr in Bovine Liver, CCQM-K49/P85. In addition, there have been a number of studies including monoisotopic elements for which IDMS measurements are not possible. Multiple NAA labs have demonstrated good agreement among themselves and with the accepted study values for: As in Oyster Tissue (CCQM-P11); As in Oyster Tissue (CCQM-K31); As in Tuna Fish (CCQM-P39); As in Salmon (CCQM-K43/P39.1), and As and Co in Fertilizer (CCQM-P66).

In view of the similarity of results obtained by NAA and ID-ICPMS, it now seems reasonable to accept that NAA (using the comparator method of standardization) meets all the requirements of a primary method of measurement. The case for INAA as a primary method had initially been made to CCQM by P. BODE and R. R. GREENBERG at a Primary Methods Symposium as part of the CCQM meeting in April 2000. However, CCQM declined to designate any additional primary methods at that time. With the results of the 23 CCQM comparisons described above, the case for NAA as a primary method of measurement was made again by P. BODE, E. FERNANDES and R. R. GREENBERG at a 3-hour workshop held as part of the April 2007 meeting of the IAWG. The IAWG membership agreed that NAA should be considered a primary method, and the case was then presented to the main CCQM body. Although the final recommendations are not yet finalized, it appears that the CCQM has agreed to consider NAA as a primary method of measurement.

Conclusions

NAA is one of the more mature analytical methods currently in use, and yet remains highly competitive with other methods in terms of accuracy, detection limits and multielemental capabilities. Its freedom from chemical blank, ability to analyze most samples without dissolution, and low detection limits for many important elements make it an ideal, and sometimes the only, available choice for many applications. The method's potential for high-precision, high-accuracy determination of trace constituents in solid matrices, and its lack of significant sources of error and uncertainty in common with other (non-nuclear) methods of analysis, make it ideal for use in certifying reference materials. NAA has a sound metrological base, and meets the current definition of a primary method of measurement.

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