Demonstration of the Metrological Basis of Instrumental Neutron Activation Analysis

Instrumental neutron activation analysis (INAA) held a unique position in analytical chemistry and trace element research during the 1960s and 1970s and has continued to prosper with applications in environmental sciences, biology, medicine, archaeology, criminology, geo- and cosmo-chemistry, and industry. Its position, nevertheless, has been challenged by increasingly sensitive and versatile elemental analysis techniques, such as atomic absorption spectrometry, inductively coupled plasma emission spectrometry and mass spectrometry, which today are used widely in applications that had been a domain for INAA. However, INAA techniques still occupy a solid niche in analytical chemistry because of the nuclear principle of analysis with its unique advantages, such as the insensitivity to the chemical form, as well as the ability to completely describe the analytical process with mathematical equations of well-determined parameters having known uncertainties. These principles form the metrological basis of INAA; this experimental work explores and demonstrates the seamless integration of the experimental requirements with the nuclear physics principles for highest quality in the results.

In its most common form, the comparator technique, the INAA procedure compares, by means of gamma-ray spectrometry, the neutron-induced activities in an unknown sample with the activities induced in a standard with known composition. This relationship is shown in the equation:

$$C_x = \left(C_z \cdot \frac{A_{0x}}{A_{0z}} \cdot R_\theta \cdot R_\phi \cdot R_\sigma \cdot R_\varepsilon \cdot R_\theta - B \right) \cdot \frac{m_z}{w m_x}$$

where C_x is the analyte amount content in the unknown sample, with C_z the analyte amount content in the primary assay standard, m_x and m_z are the masses of sample and primary assay standard with a dry mass correction factor w if applicable. The decay corrected counting rates for the indicator gamma-ray of unknown A_{0x} and of standard A_{0z} are derived from the measurement. The ratios of isotopic abundances R_θ for unknown and standard, of neutron fluences R_ϕ (including fluence drop off, self shielding, and scattering), of effective cross sections R_σ if neutron spectrum shape differs from unknown to standard, and of counting efficiencies R_ε (differences due to geometry, γ-ray self shielding, and counting effects), are controllable experimental parameters. The highest accuracy is usually attained when the measurement conditions are so designed that the ratio factors R are near unity. INAA can be carried out essentially blank free, but possible contributions from interferences, background, or contamination are considered with the term B. The decay corrected gamma-ray counting rate (A_0) for a measured nuclide is calculated according to $A_0 = N\,\lambda\,\exp(\lambda t_1) / [1 - \exp(-\lambda\Delta)]$ where N is the number of counts measured in the indicator gamma-ray peak, with normalization to the end of irradiation ($t = 0$) calculated using λ, the decay constant for the indicator nuclide, t_1, the decay time to start of count, and Δ, the elapsed time of count.

To illustrate the performance of INAA, we selected the determination of chromium in SRM 1152a Stainless Steel by direct non-destructive comparison with the pure metal in the form of crystalline chromium. The experimental plan was guided by setting a goal of minimizing the uncertainty in the analytical procedure as much as was reasonably achievable; in the case of SRM 1152a, this uncertainty should be comparable or smaller than the uncertainty of the certified value. A review of the uncertainty parameters in the determination of amount content by INAA guided the selection of sample and standards preparation, irradiation, and counting processes to achieve the stated goal.

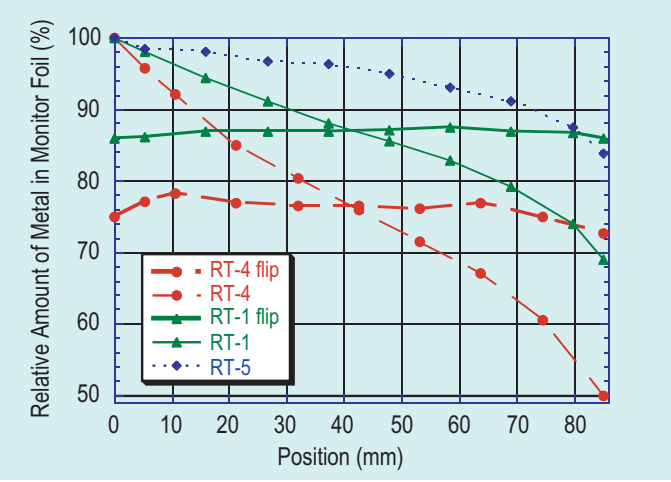

Fig. 1. Plot of the flux gradients found along the axis of the irradiation rabbits in three NBSR irradiation channels depicted by INAA of zinc (RT-4) and nickel (RT-1, RT-5) flux monitor foils, metal amount content based on a foil in position "0 mm" (100 %). When the rabbit is flipped at the irradiation mid point, a nearly linear average flux distribution is found in the center of the rabbit.

Table 1. INAA results achieved in inter-laboratory comparisons conducted under the auspices of CCQM.

	Matrix	Element	Mass Fraction			
CCQM number			Unit	Value	Expanded Uncertainty	Relative Uncertainty
P-25	Low Alloy Steel	Cr	%	0.4863	0.0031	0.64 %
		Mn	%	0.4478	0.0037	0.83 %
		Mo	%	0.9442	0.0154	1.63 %
P-34	Aluminum	Cr	%	0.4097	0.0025	0.61 %
		Mn	%	0.3892	0.0038	0.98 %
		Fe	%	0.3594	0.0067	1.86 %
		Cu	%	0.2063	0.0049	2.38 %
P-11	Oyster Tissue	As	µg/g	9.645	0.112	1.16 %
K-31	Oyster Tissue	As	µg/g	8.397	0.160	1.91 %
K-24	Rice Flour	Cd	nmol/g	14.30	0.33	2.31 %
P-29	Rice Flour	Zn	nmol/g	355.9	8.5	2.39 %

The neutron fluence distribution over the sample set was determined as one key component in minimizing uncertainties. For this work, flux gradients in all three pneumatic irradiation channels of the NBSR were re-determined with metal foil flux monitors. The 0.1 mm thick, 6 mm diameter foils of Zn or Ni were positioned in the irradiation rabbit along the axis. The thin foils provided an exact axial location for the estimation of the gradients; radial gradients have been found negligible [1]. Figure 1 illustrates the range of fluence drop-off over the length of the irradiation capsule. An INAA determination of the metal amount in Zn or Ni foils, based on the proximal "0 position" foil as the standard, gives directly relative flux values. The steeper gradients towards the ends of the rabbit may be explained by some channeling of neutrons towards the rabbit at the proximal end, and the void of the flight tube at the distal end. The observed linear drop-off in RT-1 and RT-4 between 20 mm and 65 mm provides a nearly homogeneous neutron field for samples placed in this space when the capsule is inverted at mid-point of the irradiation. This is shown with the data from the flipped irradiations. Small deviations from a unity level remain in the center space and are best assayed with flux monitors or sample matrix elements (*e.g.*, iron in steels) in each irradiation set.

Other measures to minimize uncertainty included careful control of neutron self-shielding and gamma-ray self-absorption in samples and standards, correction for remaining small counting geometry differences, and full accounting of dead time and pile-up losses in the gamma-ray spectrometer via the virtual pulse technology [2]. Sufficiently large ($> 10^6$) numbers of counts were acquired for the indicator gamma rays for samples and standards. Applying the discussed measures, an arithmetic mean value of 17.768 % Cr was obtained from eight determinations. This compared very well with the certified value of (17.76 ± 0.04) % Cr. The expanded uncertainty of 0.035 % Cr (0.2 % relative) met the goal of the experimental work.

The Nuclear Methods Group is using this INAA comparator method in highly precise and accurate measurements in the comparisons organized by the Consultative Committee for Amount of Substance (Comité Consultatif pour la Quantité de Matière, CCQM); Table 1 summarizes the recent contributions. This work has provided results in excellent agreement with reported values and has shown that the principle is applicable to the determination of all concentration levels: major elements are determined with similar accuracy as trace elements. The largest components of uncertainty are related to the sample material. In case of the metal analyses, the values of uncertainty in the fluence ratio R_ϕ were larger than in the determinations of SRM 1152a, since the test materials were in form of rather irregular metal chips. In the determinations of the biological materials, the uncertainty in the moisture correction w was the most significant factor that contributed to the reported uncertainty. In all instances, the reported INAA uncertainties were comparable to or smaller than the other techniques' uncertainties.

The measurements are subject to some restrictions that are dependent on the form and composition of the samples provided. High-density materials with high macroscopic neutron absorption cross sections require corrections for the fluence ratio based on measurements of uniform dimensions (thickness) of the samples and knowledge of the complete sample composition. These corrections call for careful experimental design and may limit the applicability of INAA in the analysis of these materials. The applications in light matrix (biological) samples are governed by "unity" ratios with associated small uncertainties. In addition, the non-destructive nature of the INAA procedures offers a true alternative to techniques that require dissolution, a sometimes troublesome process. Direct comparison with primary elemental standards provides desirable traceability of the amount of substance of an element.

References

[1] D. A. Becker, J. Radioanal. Nucl. Chem. **244**, 361 (2000).

[2] G. P. Westphal, J. Radioanal. Chem. **70**, 387 (1982).

R. Zeisler, R. M. Lindstrom, E. A. Mackey, and R. R. Greenberg
Analytical Chemistry Division
National Institute of Standards and Technology
Gaithersburg, MD 20899-8395