REFERENCE MATERIALS

Suitability of NAA for certification of reference materials for multielements

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Certifications of trace elements in existing CRMs, especially biological CRMs, are far from satisfactory. Neutron activation analysis (NAA) for its inherent advantages combined with newly established parametric standardization, may contribute to improve this situation. The continuing progress of the hybrid extended *k* 0-relative NAA technique developed in our laboratory is discussed. Examples are given to show the reliability of the method in certification of multielements. NAA is still one of the best methods, or even the method of choice, in analysis at sub-μg/g concentration levels. The suitability of the technique for this purpose has been studied through the determination of rare earth elements at ng/g concentration level in two Chinese biological CRMs using both RNAA and ICPMS. Sampling behaviors of multielements in CRMs have been studied by RNAA in an effort to develop CRMs suitable for analysis with small sample sizes.

Introduction

A review of an IAEA compilation of 175 biological CRMs from all over the world shows at least 40% (34 out of 83) naturally occurring elements (most of which are NAA determinable) are not, or only poorly certified. Although NAA has an excellent record in RM certifications of multielements (40 to 70% usage frequency of all techniques) it has not been recognized as a reference method for its insufficient accuracy and relative nature. This hinders the certification of some elements determined accurately by NAA alone. The *k* 0 standardization and its extension combined with traditional relative comparison methods provide a self-validation function, thereby reducing systematic uncertainties relative to standardization and improving accuracy. The parametric nature of the method also satisfies the traceability requirements set by ISO Guide 35.

Certification of elements at ultra trace concentration level is still one of the major challenges in modern inorganic analysis. As an example, the uncertified rare earth elements have been determined in two Chinese CRMs GBW08503 Wheat Flour and GBW09101 Human Hair for certification purpose using RNAA. Results from ICPMS are also given for comparison. Merits and drawbacks of each technique have also been analyzed for both these CRMs. The two methods are found to be complementary to each other for such measurements.

CRMs certified at sample size smaller than 100 to 200 mg (currently given in certificates of solid CRMs and SRMs as minimum sample size) are required for many modern analytical techniques and analytical problems. The sampling representativeness becomes more important when the concentrations of analytes are extremely low. NAA is a method of choice in dealing with determinations of sampling constants for multielements in CRMs, for its relatively definite, and in many cases small, uncertainties in analysis. That makes it possible to isolate sampling uncertainties accurately from the standard deviation of a group of random subsamples of the above mentioned sizes. In present work, a series of CRMs has been studied on Ingamells' sampling constants for multielements by RNAA of groups of 1 to 3 mg subsamples. The results provide the users with information on sampling uncertainty as a function of sample size for given elements in given RMs.

Experimental

Extended *k* 0-relative NAA

The *k* 0 standardization developed by a Belgium-Hungary group has been adopted in our laboratory and further extended. A brief summary for each extension item is given below. Most of them have been detailed in respective references. Meanings of all parameters in Eqs (1) to (11) below are given in corresponding references.

Parametric prediction/correction for neutron flux self-shielding effect.3 The Zweig equation for the calculation of the neutron flux self-shielding factor, *F*, was tested experimentally by extrapolation of the sample weight to zero. NAA of two Chinese deep sea Mn-nodule was used in this experiment.

\[ F = 1 - (0.923 + \ln(1/Z))Z/2 \]  

(1)

Determination of working *k* 0 values for non-1/v reactions:151Eu, 176Lu, 191Ir (n,γ) 152Eu, 177Lu, 192Ir.4

These values were determined under the following conditions: Reactor channel: the 15 MW heavy water research reactor (HWR) in China Institute of Atomic Energy (CIAE); heavy water reflector channel; samples: typical geological/biological/environmental samples (without extreme heat release during irradiation); irradiation time: 6 to 16 hours. These conditions are typical for the large majority of Chinese NAA laboratories.

$I_0$ method for parametric corrections for fission interferences:

A neutron spectrum independent $I_0$ factor was proposed for each fission interference reaction, as in Eq. (2):

$$I_0 = (M^{*}/\partial^{*}\sigma_0)/(M^{*}/\partial^{*}\sigma_0)^* \text{ (theory)} = (A_{sp}^{*} p^{*}(f^{*}Q_{0})^{*})(A_{sp}^{*} p^{*}(f^{*}Q_{0})) \text{ (experiment})$$

$I_0$ values for seven major fission interference reactions have been determined in six irradiation channels with $f$ values 13.7 to 134 of three reactors in CIAE. $I_0$ values for 66 NAA-related fission interference reactions have been tabulated.

$I_0$ method for threshold reaction interferences:

Fast neutron ($E\geq2 \text{ MeV}$) spectra in different channels of HWR have been proved to have approximately primary $^{235} \text{U}$ fission neutron spectrum by using a series of threshold detectors with scattered effective threshold energies and well-established fission neutron average cross sections. Literature values of the fission neutron average cross sections of relevant threshold reactions are accurate enough. Based on these facts, a neutron spectrum independent $I_0$ factor is defined for each threshold interference reaction by

$$I_0 = (M^{*}/\partial^{*}\sigma_1)/(M^{*}/\partial^{*}\sigma_1)^* \text{ (theory)} = (A_{sp}^{*} \partial^{*})(A_{sp}^{*} \partial^{*})(1+Q_{0}/F) \text{ (exp.})$$

The $I_0$ values for 103 NAA-related threshold reaction interference reactions have been tabulated.

$I_0$ method for $\gamma$-spectral interference corrections:

The $I_0$ concept can also be used here with:

$$I_0 = I_{0\gamma} \text{ for } \gamma\text{-spectral interference corrections}.$$  

$I_0$ values for 163 NAA-related $\gamma$-spectral interference corrections have been tabulated.

Parametric efficiency normalization for different counting geometry:

The effective interaction depth (EID) principle has been verified experimentally using a series of single $\gamma$-energy sources with different intensities as expressed by

$$\varepsilon_1/\varepsilon_2 = ((S(2)+S(E))/((S(1)+S(E))))^2$$

$S(E)$ function for each HPGe detector was determined and used for parametric normalization for different counting positions.

Parametric corrections for summing effect:

Based on simplified decay schemes of indicator nuclides involved in reactor NAA, the following equations were used for parametric corrections for summing effect.

$$C_1 = 1/(1-\varepsilon_1)$$  

$$C_2 = 1/(1-(P_1/P_2)\varepsilon_1)$$  

$$C_3 = 1/(1+(P_1 \varepsilon_1 + P_2 \varepsilon_2))$$

Total efficiency functions, $\varepsilon_i(E)$, have been determined using a series of single energy $\gamma$-sources, based on a clearly defined total response of HPGe detector for single energy $\gamma$-rays (scattering contribution in low energy region included). Fifty ratios of $\gamma$-ray branching ratio values, $P_1/P_2$, have been tabulated for relevant $\gamma$-rays in indicator nuclides of NAA-interest.

A computer software, ADNAA, including all above functions, as well as the relative method, has been written and successfully used for 8 years.

RNA of CRM s GBW08503 Wheat Flour and GBW09101 Human Hair for RRE

Four hundred mg each of seven subsamples each of the two CRMs were irradiated for 80 hr in HWR of CIAE ($\phi_{th}=3.10^{13}$) together with RRE chemical standards, neutron flux ratio monitor Zr foil, comparator Fe wire, and quality control samples NIST SRMs 1632a, 1633a and Chinese CRM GBW07312. After 3 days decay, each irradiated sample was dissolved in HNO$_3$-HClO$_4$ with 100 mg mixed RRE carrier (as La(NO$_3$)$_2$-Lu(NO$_3$)$_3$ solution). The media were converted to 3N HCl. Fifty mg mixed REE(NO$_3$)$_3$ carrier was added to each dissolved sample. By adding HF, (REE)F$_3$ was precipitated, then centrifuged and the precipitation counted for RRE determination. Simultaneously determined were U and Ba, which were used for fission interference corrections.

Characterization of sampling behaviors of multielements in CRMs

Two to three mg each of 12 to 15 subsamples for each of the seven CRMs (or RMs) studied (IAEA RM 396A/S, 396A/M (Urban Air Particulate Matter), SD-M-2/TM (Marine Sediment), IAEA-338 (Lichen), IAEA-413 (Algae), and Chinese CRMs GSPN-2, GSPN-3 (Deep Sea Mn-Nodule)) were irradiated together with relevant chemical standards, Zr foil and Fe wire (for $k_0$-NAA) and NIST SRMs 1632a and 1633a (for quality control). Multielemental NAA was conducted using the hybrid $k_0$-relative method. Ingamells' sampling constants, $K_s$, were calculated for individual elements in