Radioanalytical Methods: Data Quality, Method Validation and Use of Standard Reference Materials (continued)

THE APPLICATION OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS FOR THE CERTIFICATION OF THE NEW NIST FLY ASH SRM

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The National Institute of Standards and Technology (NIST) recently released the second renewal of its "Trace Elements in Coal Fly Ash" Standard Reference Material (SRM 1633b). This new material is currently certified for 23 major, minor and trace elements, and concentrations of an additional 24 elements are provided for "information only" purposes. Current plans are to certify the concentrations of a number of rare earths upon completion of additional analytical work now in progress. Instrumental neutron activation analysis (INAA) has played a major role in the certification of this new material in view of its potential for accuracy, multielemental capability, ability to assess homogeneity, high sensitivity for many elements, and essentially blank-free nature. For an element to be certified in a NIST SRM its concentration is usually determined by at least two independent analytical techniques. INAA has provided analytical information for 15 of the 23 elements certified, as well as for 22 of the 24 elements listed for "information only." In addition, INAA has provided much of the homogeneity information for this SRM. This paper will describe these analytical procedures, and highlight those designed to optimize and assess the accuracy of the INAA measurements.

Instrumental neutron activation analysis (INAA) often plays an important role in the certification of inorganic constituents in many complex-matrix Standard Reference Materials (SRMs) in view of its accuracy, multielemental capability, ability to assess homogeneity, high sensitivity for many elements, and essentially blank-free nature. In addition, INAA requires no chemical dissolution prior to analysis, unlike most other analytical techniques. Since the concentration of an element certified in a NIST SRM is usually determined by at least two independent analytical methods, the use of INAA as one method eliminates the possibility of common error sources resulting from sample dissolution.

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Experimental

Irradiations and Counting: Approximately 2 grams of material from each of twelve bottles of the new Fly Ash were dried for 2 hours at 110 °C. Average weight loss was 0.34 ± 0.02% (1s). Samples weighing approximately 100 mg were taken from each bottle, weighed, and doubly encapsulated in acid-cleaned, conventional polyethylene bags (CPE). Two control samples of the previous Fly Ash (SRM 1633a) were processed identically, as controls. To determine elements with short-lived activation products, samples, standards (described below), blanks and control samples were individually irradiated (each with a Cu fluence monitor) for 15 seconds in the RT-1 facility of the NIST reactor. In this facility the neutron fluence rate is $6 \cdot 10^{13}$ n/cm²-s at a power level of 15 MW. After irradiation, the outer bags were removed, and each sample, standard, blank, and control was counted at least four times on a 35% efficient high purity germanium (HPGe) detector. The sample-to-detector distance (counting geometry) was 20 cm. The samples were subsequently recounted at a distance of 10 cm from a second, 25% efficient, HPGe detector. The relatively large number of replicate counts for each sample provided important quality assurance information and will be discussed below.

For elements having longer-lived activation products, thirteen 100 mg-samples, plus standards, blanks, and control samples were irradiated together in one rabbit for a total of 40 minutes at a fluence rate of $6 \cdot 10^{13}$ n/cm²-s. Midway through the irradiation, the rabbit was removed from the reactor, inverted 180 degrees, and reinserted into the reactor to compensate for the linear drop off of the neutron fluence rate in this facility. After irradiation, the outer bags were removed, and each sample, standard, blank, and control was counted at least four times on a 25% efficient HPGe detector. Two counting geometries, 20 and 10 cm, were used.

Comparator Standards: A number of different standards were used for these analyses including: a series of multielemental standards (pipetted onto Whatman 41 filter papers or into linear polyethylene bags) which have been used during the past 15 years to analyze a wide variety of SRMs for certification[2,3]; a series of new multielement standards prepared from NIST certified SRM solutions, for the rare earth elements plus Sc, Hf and Ta; a number of pure metal foils, and as an additional check a number of multielement standards produced by other analysts at NIST.

The preparation of a new series of filter paper standards containing known quantities of all the rare earths (except Pm, a pure beta emitter) plus Sc, Hf and Ta began with a series of calculations to determine the relative sensitivities of all these elements. Calculations were made using a BASIC program written by one of the authors (DAB) in which all variables of irradiation, decay, isotopic abundance, branching ratios, etc., could be changed in response to screen prompts. The materials used to make the standards were NIST elemental SRM Spectrometric Standard Solutions, which are certified to contain 10.00 mg/ml to $\leq 0.5\%$ uncertainty. Based on results of these calculations, four solutions were produced containing chemically compatible elements which could be determined simultaneously by INAA. The amount of each spectrometric standard required ranged from 50.47 µl to 5.020 ml, depending on isotopic sensitivity. The four solutions and elements contained in each were: Solution 1 - Shorts (Y, Dy, Er, Sm, Nd, and Gd); Solution 2 - Intermediates (La, Ce, Pr, Gd, Yb, Sm, Ho, and Lu); Solution 3 - Longs (Sc, Ce, Nd, Eu, Tb, Tm, and Yb); and Solution 4 - Longs with HF (Hf and Ta). A number of test irradiations were made on individual as well as combinations of elements in order to provide sufficient information to allow the best allocation of elements into their respective solutions. Some elements are in more than one solution because of multiple radioactivation products from thermal neutron irradiation. Finally, 50.47 ± 0.07 µl of solution was deposited onto individual 5.5 cm diameter Whatman #42 filter and allowed to evaporate to dryness inside of a clean hood. These filters containing the rare earths and associated elements were then used as comparator standards for the INAA determinations.

Results and Discussion

The results of the INAA measurements of the new Fly Ash, SRM 1633b, are summarized in Table 1. The mean concentration given for each element was calculated from 13 individual samples, except for Pr, where only 11 samples yielded results above the detection limit. The

Table 1
Summary of Concentrations Determined in Fly Ash, SRM 1633b by INAA

Element	Mean	RSD (%)a	Overall Uncert.b	Element	Mean	RSD (%)a	Overall Uncert.b
Na (µg/g)	2011	0.80	22	Sb (µg/g)	5.10	2.2	0.08
K (%)	1.949	1.0	0.022	La (µg/g)	93.7	0.5	1.0
Rb (µg/g)	145	3.4	4	Ce (µg/g)	192.7	0.6	2.1
Cs (µg/g)	10.74	1.2	0.14	Pr (µg/g)	25	28	5
Ca (%)	1.469	3.3	0.034	Nd (µg/g)	85	8.2	5
Sr (µg/g)	1034	2.9	21	Sm (µg/g)	19.17	0.8	0.22
Ba (µg/g)	720	2.6	13	Eu (µg/g)	4.12	1.0	0.05
Al (%)	14.85	1.3	0.18	Gd (µg/g)	13.3	14	1.7
Br (µg/g)	2.86	9.4	0.16	Tb (µg/g)	2.57	2.3	0.06
Sc (µg/g)	41.22	0.6	0.44	Dy (µg/g)	17.13	1.2	0.36
Ti (µg/g)	7910	1.8	120	Ho (µg/g)	3.57	5.8	0.15
V (µg/g)	294.7	1.4	3.8	Tm (µg/g)	2.14	3.3	0.05
Cr (µg/g)	196.0	0.77	2.2	Yb (µg/g)	7.62	2.0	0.17
Mn (µg/g)	132.0	1.1	1.7	Lu (µg/g)	1.170	2.1	0.027
Fe (%)	7.71	1.0	0.09	Hf (µg/g)	6.82	1.6	0.09
Co (µg/g)	49.6	0.6	0.5	Ta (µg/g)	1.80	3.3	0.04
As (µg/g)	135.0	0.7	1.5	W (µg/g)	5.60	5.5	0.19
Se (µg/g)	10.26	1.8	0.15	Th (µg/g)	25.64	0.6	0.28
In (ng/g)	131	12	10	U (µg/g)	8.61	2.4	0.22

aObserved relative standard deviations in percent
bOverall estimated analytical uncertainties at the 95% confidence level (n=13)

observed relative standard deviations listed in Table 1 (RSDs) reflect a combination of factors including experimental variations due to counting statistics, irradiation/counting geometry differences, peak integration, as well as to material heterogeneity (if significant). Since the uncertainties associated with each of these factors except material heterogeneity are known or can be estimated, the RSDs can therefore provide information regarding any inhomogeneity of the new Fly Ash SRM. The combined experimental variations excluding counting statistics were estimated to be 1% relative (at the 1s level) for those elements determined via the short irradiations, 0.5% relative for those determined from the long irradiation and counted at 20 cm, and 1% relative for those determined from the long irradiation and counted at 10 cm. Using these estimates and counting statistics, no element except Gd showed any excess variation, i.e., possible inhomogeneity. However, the excess variability observed for Gd was most probably due to peak integration problems related to the complex background region around the 103 keV Gd peak, and not to material heterogeneity.

The overall uncertainties listed in Table 1 are the overall estimated 95% confidence intervals and were calculated by first combining the statistically-evaluated uncertainties (Type A)[4,5] and non-statistically evaluated uncertainties (Type B) in quadrature and then multiplying by the appropriate coverage factor. The significant Type A uncertainties for this set of measurements

are included in measurement replication, and can be found as the RSDs listed in Table 1. The significant Type B uncertainties included: errors in preparing the comparator standards used, counting geometry differences between samples and standards, and peak integration errors. The combined Type B uncertainties were estimated to be 1% relative (at the 1s level) for Dy, Gd, In, Lu, Nd, Tb, Tm and U, and 0.5% for the other elements. The coverage factors varied, depending upon the relative importance of the two types of errors, from 2 to 2.179 (the t-value for 12 degrees of freedom for all elements except Pr, where a t-value of 2.228 (for 10 degrees of freedom) was used.

Quality assurance (QA) is a very important aspect of all NIST measurements. One of the QA requirements usually considered necessary for measurements made as part of an SRM certification is the analysis of control samples of a similar SRM, and the demonstration of agreement with the certified values. However, this can only be accomplished if certified values are available. For this set of measurements, two control samples of SRM 1633a (Fly Ash) were analyzed along with the new Fly Ash and the observed concentrations are compared in Table 2 with the NIST certified values (those values in Table 2 listed with uncertainties), or if certified values were not available, with the recommended literature values from a compilation by Gladney et al.[6]. Good agreement for all elements except possibly Gd (with the literature value) was observed.

Table 2
Concentrations Determined by INAA in Two Control Samples of Fly Ash, SRM 1633a

Element	FA-23	FA-24	Certi-fied/Lit.[a]	Element	FA-23	FA-24	Cert-fied/Lit.[a]
Na (µg/g)	1724	1695	1700 ± 100	Sb (µg/g)	6.38	6.31	6.8 ± 0.4
K (%)	1.902	1.932	1.88 ± 0.06	La (µg/g)	85.8	86.6	84
Rb (µg/g)	140	131	131 ± 2	Ce (µg/g)	177.2	177.6	175
Cs (µg/g)	10.5	10.6	10.5	Pr (µg/g)	15	<31	18.4 (n=2)
Ca (%)	1.11	1.06	1.11 ± 0.01	Nd (µg/g)	80	88	74
Sr (µg/g)	820	780	830 ± 30	Sm (µg/g)	17.25	17.31	17.0
Ba (µg/g)	1390	1433	1420	Eu (µg/g)	3.70	3.73	3.7
Al (%)	14.30	14.16	14.3 ± 1.3	Gd (µg/g)	12.6	14.4	19
Br (µg/g)	2.38	1.95	2.3 (n=2)	Tb (µg/g)	2.27	2.38	2.5
Sc (µg/g)	39.64	39.18	39	Dy (µg/g)	16.6	16.5	15.6
Ti (µg/g)	8420	8450	8230	Ho (µg/g)	3.46	3.36	2.9 (n=1)
V (µg/g)	293	289	297 ± 6	Tm (µg/g)	2.08	2.11	2.4 (n=1)
Cr (µg/g)	189.6	191.3	196 ± 6	Yb (µg/g)	7.79	7.62	7.4
Mn (µg/g)	180.4	179.3	179 ± 8	Lu (µg/g)	1.19	1.20	1.12
Fe (%)	9.56	9.43	9.40 ± 0.10	Hf (µg/g)	7.09	7.23	7.4
Co (µg/g)	45.0	44.4	43	Ta (µg/g)	1.95	1.94	2.0
As (µg/g)	146.9	148.1	145 ± 15	W (µg/g)	5.7	5.7	5.7
Se (µg/g)	10.5	10.0	10.3 ± 0.6	Th (µg/g)	24.97	25.03	24.7 ± 0.3
In (ng/g)	168	110	158	U (µg/g)	9.91	9.71	10.2 ± 0.1

[a]Certified values shown with NIST uncertainties. Other values are average, compiled literature values from Ref 6.

One reason that INAA has become so widely used and valuable in the certification of NIST SRMs is the unique QA characteristics of the method which often allow the analytical values to be internally evaluated and cross checked. In addition, the method itself has characteristics which inherently provide few sources of error[7]. The multiple sets of counts performed in this work provide one means of demonstrating that this series of measurements is in statistical control. Two important sources of error for INAA which are frequently not adequately considered are: losses due to pulse pileup[8,9], and the inadequacy of live-time extension[10]. The latter can be very important when the counting interval approaches or exceeds the half-life of an element of interest. This is especially true when counting at high dead times. In this case, understanding the change in dead time as a function of time is necessary to accurately correct for counts lost due to the inadequacy of live-time extension. One way to demonstrate that corrections for these losses are made accurately is to recount samples at different dead times. Such a series of counts can also be used to verify that corrections due to pulse-pileup losses are made accurately. These two effects can easily be separated by examining data for elements with significantly different half lives since the error due to live time extension is a function of both half life and dead time, while pulse pileup is not dependent upon half life. Sample number FA17 was counted 5 times (on a single detector) following the short irradiation. Tables 3 lists concentration data determined from replicate counts of this sample, and includes data for some elements with half lives which are comparable to the counting times, and data for others with half lives which are significantly longer. In addition, significant

Table 3

Data for Multiple Counts of A Single Fly Ash Sample (FA17) Following a 15 Second Irradiation

Count (DT)[a]	LT[a] (s)	Al (%)[b] $t_{1/2} = 2.24$ min	Ca (%)[b] $t_{1/2} = 8.70$ min	Ti (μg/g)[b] $t_{1/2} = 5.76$ min	V (μg/g)[b] $t_{1/2} = 3.75$ min
#1 (17%)	60	14.90 ± 0.10	1.374 ± 0.137	7895 ± 382	305 ± 7
#2 (10%)	120	15.03 ± 0.11	1.532 ± 0.093	8041 ± 317	294 ± 5
#3 (6%)	300	14.97 ± 0.13	1.535 ± 0.070	8011 ± 238	291 ± 5
#4 (4%)	900	14.48 ± 0.46	1.402 ± 0.059	7872 ± 425	313 ± 9
#5 (3%)	600	-	1.565 ± 0.413	-	-
Red. Chi. Sq.[c]		0.615	0.783	0.056	2.089
Prob. of exc.[c]		60.5%	53.6%	98.3%	9.9%

Count (DT)[a]	Na (μg/g)[b] $t_{1/2} = 15.0$ h	K (%)[b] $t_{1/2} = 12.4$ h	Mn (μg/g)[b] $t_{1/2} = 2.58$ h	Dy (μg/g)[b] $t_{1/2} = 2.33$ h	In (μg/g)[b] $t_{1/2} = 54.3$ min
#1 (17%)	2033 ± 157	-	130.7 ± 2.1	16.4 ± 1.0	-
#2 (10%)	1930 ± 77	-	134.2 ± 1.4	17.4 ± 0.6	157 ± 55
#3 (6%)	1979 ± 39	2.00 ± 0.14	132.8 ± 0.8	16.6 ± 0.3	172 ± 31
#4 (4%)	1994 ± 23	1.96 ± 0.05	133.9 ± 0.5	17.2 ± 0.3	131 ± 14
#5 (3%)	1991 ± 27	1.95 ± 0.06	133.6 ± 0.7	17.3 ± 0.3	140 ± 21
Red. Chi. Sq.[c]	0.196	0.054	0.858	0.989	0.532
Prob. of exc.[c]	94.1%	94.7%	48.8%	41.2%	66.6%

[a]DT signifies percent dead time; LT signifies live time
[b]All uncertainties represent 1 sigma counting statistics
[c]Reduced Chi squared; Probability of exceeding in a normal distribution - see text

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changes in dead times can be observed among the various counts. This table also lists the "reduced-chi squared" values along with the corresponding probability of exceeding this value of chi squared in a normal distribution[11,12]. This "probability of exceeding" indicates the relative probability of observing even more variation in a repeat set of measurements assuming a normal distribution and the same uncertainties (in this case counting statistics). As can be seen from these tables, all variations observed among the replicate measurements can be explained by counting statistics alone.

An additional demonstration of statistical control for this series of measurements can be obtained by comparing the measurements made between the different counting geometries and between irradiations. Table 4 compares the mean concentrations, with the 95% confidence intervals based upon precision only ($ts/\sqrt{n}$), for the concentrations of Na, K, As, La, Sm and Ho observed at two different counting geometries (10 and 20 cm). Data for Na and K are given

Table 4

Comparison of Mean Concentrations Determined from Different Irradiations and Counts of Fly Ash, SRM 1633b

Geometry	Na (µg/g)	K (%)	As (µg/g)	La (µg/g)	Sm (µg/g)	Ho (µg/g)
Short Irradiations						
20 cm	2000 ± 24[a]	1.942 ± 0.046	-	-	-	-
10 cm	2011 ± 9	1.959 ± 0.015	-	-	-	-
Red. Chi. Sq.[b]	0.577	0.517	-	-	-	-
Prob. of exc.[c]	44.7%	47.2%	-	-	-	-
Long Irradiation						
20 cm	2002 ± 7	1.949 ± 0.011	135.0 ± 0.6	93.5 ± 0.3	19.20 ± 0.09	3.51 ± 0.11
10 cm	1995 ± 7	1.960 ± 0.030	134.3 ± 0.8	93.8 ± 0.3	19.13 ± 0.09	3.64 ± 0.13
Red. Chi. Sq.[b]	0.505	0.418	0.849	0.474	0.499	1.956
Prob. of exc.[c]	47.7%	51.8%	35.7%	49.9%	48.0%	16.2%
Overall (Both Irradiations and Both Counting Geometries)						
Red. Chi. Sq.[b]	0.836	0.388	-	-	-	-
Prob. of exc.[c]	47.4%	76.1%	-	-	-	-

[a] All uncertainties represent $ts/\sqrt{n}$ (precision only) at the 95% confidence interval
[b] Reduced Chi squared values were calculated with calibration uncertainties of 1.0% for Ho and 0.3% for all other elements
[c] Probability of exceeding in a normal distribution - see text

separately for both the short and long irradiations. Reduced chi squared values were calculated based upon a combination of observed precision ($s/\sqrt{n}$) and calibration uncertainties, i.e., counting statistics of the standards (1% relative for Ho and ~0.3% for other elements listed). A comparison of the reduced chi squared values and the associated "probability of exceeding" values for the different sets of data indicates all differences among counts and between irradiations can be explained by the observed precision and calibration uncertainty between each set of measurements.

A final quality check can be made by comparing the values determined by INAA with other analytical values used for the certification of the new Fly Ash. Such a comparison is shown in

Table 5
Comparison of Data used for the Certification of Fly Ash, SRM 1633b

Element	INAA Value[a]	Other Value[a,b]	Other Technique
As (µg/g)	135.0 ± 1.5	137.6 ± 3.1	FIA-HAAS
Al (%)	14.85 ± 0.18	15.23 ± 0.13	XRF
Ba (µg/g)	720 ± 13	701 ± 6	IDMS
Ca (%)	1.47 ± 0.03	1.53 ± 0.04	ICP-AES
Cr (µg/g)	196.0 ± 2.2	202 ± 7.3	FAAS
Fe (%)	7.71 ± 0.09	7.92 ± 0.25	XRF
K (%)	1.949 ± 0.022	1.961 ± 0.043	FES
Mn (µg/g)	132.0 ± 1.6	131.0 ± 4.4	FAAS
Na (µg/g)	2011 ± 22	1995 ± 80	FES
Se (µg/g)	10.26 ± 0.15	10.3 ± 0.4	FIA-HAAS
Sr (µg/g)	1034 ± 21	1041.0 ± 4.7	IDMS
Th (µg/g)	25.64 ± 0.28	25.73 ± 0.65	IDMS
Ti (µg/g)	7910 ± 120	7850 ± 210	XRF
U (µg/g)	8.61 ± 0.22	8.936 ± 0.063	IDMS
V (µg/g)	295 ± 4	296.9 ± 6.5	ICP-AES

[a]Uncertainties represent the estimated, overall analytical uncertainties at the 95% confidence level
[b]Values are from various NIST internal reports

Table 5. The average difference between the INAA values and those reported by other analytical techniques was 1.7% (relative). The estimated 95% confidence intervals for all elements, except Al and U, overlap. The 95% confidence intervals for both Al and U miss overlapping by only 0.5% relative. It should be noted, however, that there was a lack of agreement between INAA and atomic spectroscopy techniques for two of the elements determined in this material, namely Rb and Sb. The concentrations of these elements have not been certified but are given for "information only." The Rb concentration determined by INAA was 9% higher than determined by FES, however, the 95% confidence intervals missed overlapping by only 2% relative. The Sb concentration determined by ETAAS, however, was 40% higher than that determined by INAA, and the 95% confidence levels missed overlapping by more than 20%. Research is in progress to understand these problems.

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Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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