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Certification of Standard Reference Material[®] 2693a Bituminous Coal (Nominal Mass Fraction 0.5 % Sulfur)

Thomas W. Vetter Colleen E. Bryan Sallee Brian E. Lang Anthony F. Marlow Jennifer M. Ness Rick L. Paul Adam L. Pintar Bruce E. Scruggs Nicholas Sharp John R. Sieber Maria Vega

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> Adam Pintar Statistical Engineering Division Information Technology Laboratory

> > *Retired

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NIST Author ORCID iDs

Vetter TW: 0000-0003-1442-2530 Bryan Sallee CE: 0000-0002-2334-3925 Lang BE: 0000 0002 0772 1420 Marlow AF: 0000-0002-1725-1063 Ness JM: 0000-0002-035-4373 Paul RL: 0000-0002-6366-1901 Pintar AL: 0000-0002-6366-1901 Pintar AL: 0000-0002-5021-2576 Scrugs BE: 0000-0002-0303-4148 Sharp N: 0000-0002-3926-1246 Sieber JR: 0000-0003-1748-3718 Vega M: 0000-0002-3094-7866

Contact Information

Please address technical questions you may have about this SRM to <u>srms@nist.gov</u> where they will be assigned to the appropriate Technical Project Leader responsible for support of this material. For sales and customer service inquiries, please contact <u>srminfo@nist.gov</u>.

Abstract

Standard Reference Material (SRM) 2693a Bituminous Coal (Nominal Mass Fraction 0.5 % Sulfur) is intended for use in the evaluation of techniques employed in the determination of sulfur, mercury, chlorine, and ash in coal and materials of a similar matrix. A unit of SRM 2693a consists of 55 g of bituminous coal ground to pass a 250 μ m (60 mesh) sieve, homogenized, and packaged in an amber glass bottle and then sealed in an aluminized bag. This publication documents the production, analytical methods, and computations involved in characterizing this product.

Keywords

atomic absorption spectrometry (AAS); bituminous coal; CANSPEX; chlorine; instrumental neutron activation analysis (INAA); particle size analysis (PSA); mercury; prompt gamma-ray activation analysis (PGAA); Standard Reference Material (SRM); sulfur; wavelength dispersive X-ray fluorescence (WDXRF).

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1. Introduction

Standard Reference Material[®] (SRM[®]) 2693a Bituminous Coal (Nominal Mass Fraction 0.5 % Sulfur) is one of six related certified reference materials provided by the National Institute of Standards and Technology (NIST) intended use in the evaluation of techniques employed in the determination of sulfur, mercury, chlorine, and ash in coal and materials of a similar matrix.

1.1. SRM 2693 Sales History

The initial version of this material, SRM 2693 Bituminous Coal (Nominal Mass Fraction 0.5 % Sulfur), was issued in 2004 [1]. SRM 2693a is the first replacement material.

The purchase of SRM 2693 by country and/or geographic area is summarized in Fig. 1. Over the nearly 17 years of its sales, 68 % of units were sold within the USA, followed by Colombia, Canada, and Korea each accounting for about 7 % of units. The proportion of units sold to Asian nations has increased over time; the proportion sold to European nations has decreased.



Fig. 1. Location of Customers for SRM 2693.

From left to tight, the three charts display the fraction of sales to various countries or geographic regions during three periods from the first sale in November of 2004 to 12/31/2009, 1/1/2010 to 12/31/2015, and 1/1/2016 thru the last unit sold in July 2021. Slices are shown for individual countries only when they purchased at least 3 % of the units sold during that interval. The area of the circle is proportional to the number of units sold during the interval.

2. Material

2.1. Acquisition

Approximately 600 kg of metallurgical coal was donated by Teck Resources Limited (Vancouver BC, Canada) from their Line Creek Operations located in the Elk Valley of British Columbia, Canada. This coal came from the same mine that was the source of the SRM 2693 material.

2.2. Processing

The gross sample was crushed and subsequently pulverized to pass a 250 μ m (60 mesh) screen by an outside contractor. A portion was used to prepare SRM 2693a with the remainder sealed under argon for future use.

2.3. Packaging: Sublots, Runs and Bottling Order

The SRM 2693a portion was prepared initially as eight spin-riffled [2] nominal 62 kg sublots that were analyzed for moisture, sulfur, and ash. The five sublots having the most similar mean sulfur values were chosen for use in the production of SRM 2693a.

Each of the five sublots was divided by spin-riffling into eight bottling runs (40 runs total) with each run consisting of 108 bottles, which was the number of positions in the bottling spin-riffler. Nominally 55 g were packaged in each of $5 \times 8 \times 108 = 4320$ amber glass bottles.

Prior to packaging bottles as SRM units, the bottles were identified by sublot (2, 3, 4, 5, and 7), run within sublot (1 to 8), and fill order (1 to 108). Bottles from each run were randomly sampled using a NIST Statistical Engineering Division (SED) design to determine moisture, ash, and sulfur. The results of these determinations were evaluated by SED to confirm a lack of evidence of heterogeneity at the 95 % confidence level.

2.4. Selection of Analytical Samples

Subsets of the bottles were packaged for a CANSPEX interlaboratory study (ILS) and NIST analytical determinations using SED designed random sampling. For the CANSPEX ILS, bottles were selected from each of the 40 runs for a total of 135 bottles. For NIST analysis, bottles were selected as follows: 40 bottles (one from each run) for homogeneity analysis by wavelength dispersive X-ray fluorescence (WDXRF), 40 bottles (one from each run) divided into eight subsets of five with each subset containing one bottle from each of the five sublots, and 70 bottles (one bottle from each of the 40 runs and an additional one bottle from 30 of the 40 runs divided into seven subsets of ten bottles each with sets subset containing two bottles from each to the 5 sublots for a total of 150 bottles. After their receipt at NIST, all bottles were purged with argon.

3. Particle size Analysis (PSA)

The NIST Biorepository and NIST Cryogenic Reference Material Production Facility in Charleston, South Carolina is equipped with a particle size analyzer. The instrument provides detailed information characterizing the particle size distribution (PSD) profiles of materials. The analyzer services the PSD characterization needs of the NIST community for candidate SRMs or research materials as well as provides useful information during the production of reference material and daily cryo-milling operations within the Biorepository.

3.1. Method

Laser-diffraction particle size analysis (PSA) is widely used to characterize the PSD of a variety of materials from cement to pharmaceuticals. The particle size analyzer uses laser diffraction to determine the sizes of particles within the range of (0.01 to 3500) μ m in diameter. It is fitted with a red-light laser ($\lambda = 632.8$ nm) and a blue light laser ($\lambda = 470$ nm). As particles pass through the measurement cell, detection of the angular distribution of scattered light produced by the incident beam and analyzed at the detectors gives the average size distribution represented as an equivalent spherical diameter in an average volume distribution.

The hallmark of quality PSA measurements is a low relative standard deviation expressed in percent (RSD%). In order to conform to ISO Standard 13320:2009(E)[3], the RSD% of the 10th, 50th, and 90th percentiles of the PSD (reported as Dv(10), Dv(50), and Dv(90)) must be as follows: Dv(90) and Dv(10) are < 5 % and Dv(50) is < 3 %. This parameter is used to determine stability and repeatability of the measurement. Measurement stability can be assessed by monitoring the Dv(10) and Dv(90): a consistent decrease over time in Dv(10) typically indicates dissolution of the particles in the dispersant while increases over time in Dv(90) typically indicate aggregation of the sample within the dispersant.

3.2. Analysis

Table 1 lists the critical parameters and their values used in the PSA of SRM 2693a.

Parameter	Value
Dispersant:	Water
Surfactant:	0.01 % Triton X-100
Particle type:	Non-Spherical
Particle refractive index:	1.746
Particle absorption index:	1.0
Particle density:	1.0 g/cm^3
Dispersant refractive index:	1.330
Scattering method:	Mie
Laser Obscuration:	5 % to 10 %
Sonication:	None

Table 1. Laser	Diffraction	Particle Size	Analysis	Parameters	and \	/alues.

The measurement was conducted in water with Triton X-100 at 0.01 % volume fraction. Background measurements were automatically subtracted before sample addition. The sample bottle was mixed by a combination of inversion and rolling 10 to 15 times. Approximately 0.5 g of material was added directly to the measurement cell. The sample was allowed to disperse for 10 s before ten individual measurements at an obscuration of 8.5 %. The mean, standard deviation (SD), and relative standard deviation of the Dv(10), Dv(50), and Dv(90) was calculated. Results were evaluated to determine whether they satisfied the ISO Standard 13320:2009(E). An overall PSD was generated using all measurements.

3.3. Results

Table 2 lists the mean, SD, and RSD% for the Dv(10), Dv(50), and Dv(90) measurements. Results are well within the ISO Standard 13320:2009(E) RSD% levels.

Statistic	Dv(10)	Dv(50)	Dv(90)	Units
Mean:	8.72	51.4	147	μm
Standard Deviation (SD):	0.0705	0.688	2.19	μm
Relative Standard Deviation (RSD%):	0.808	1.34	1.49	%

 Table 2. Final Particle Size Distribution and Statistics.

The PSD derived by averaging the ten individual measurements is displayed in Fig. 2. The PSD ranges from (0.7 to 352) μ m with 10 % of the particles smaller than 9 μ m in diameter and 10 % greater than 147 μ m. The modal (peak) diameter is about 90 μ m; the mass median diameter is 51.4 μ m.



Fig. 2. Average Volume Particle Size Distribution.

4. Homogeneity by Wavelength Dispersive X-Ray Fluorescence (WDXRF)

Wavelength Dispersive X-Ray Fluorescence (WDXRF) analysis was used to assess within-bottle and between-bottle heterogeneity of the packaged SRM 2693a on the basis of X-ray fluorescence intensity variability. The measurements enable comparison of C, O, N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, Zr, Ba, La, Ce, and Nd composition between nominally identical samples but do not provide quantitative information on the mass fraction of these elements in the samples. The measurement results are expressed in thousands of counts per second, kcps.

WDXRF measurements of C, O, N, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Rb, Sr, and Zr were made using their K-L_{2,3} characteristic X-ray lines. The L₃-M_{4,5} line was used for measurements of Ba, La, and Nd. The L₂-M₄ line was used for Ce. Background measurements were obtained for all elements except C, Al, Si, P, S, K, Ca, and Fe, all of which yield count rates greater than 10 times the background rates. This rule-of-thumb, to omit background measurements for elements with high peak kcps to background kcps ratios, reduces measurement times for specimens that are of nearly equivalent compositions, causing background intensity variability among specimens to be very low.

4.1. Equipment

An analytical balance was used for measurement of the mass of coal to be pressed. Briquettes were pressed into aluminum pressing caps using a press run in automatic mode and equipped with a steel 31 mm die set and steel die pellets. Measurements were made using a WDXRF spectrometer using the manufacturer's software and operated in a manner consistent with manufacturer's instructions.

4.2. Analysis

Forty bottles of SRM 2693a were chosen by stratified random sampling such that one bottle was sampled from each run of each sublot of coal prepared for bottling. Each bottle was sampled in duplicate for preparation as 31 mm diameter pressed briquettes. Four samples were taken from one bottle of SRM 2693. Sampling was performed by manually rotating each bottle to mix the contents and extracting 3.8 g of powder per specimen using a stainless steel spatula.

Each sample of the coal powder was placed into a pressing cap that had been flared and inserted into the die directly onto the surface of one die pellet. The powder was made approximately level by shaking the die set. The second die pellet was placed on top of the powder, followed by the ram. Pressing was done at 180 N (20 tons) with a hold time of 18 s. Briquettes were stored in a desiccator until all bottles were processed.

Each briquette was evaluated twice, first using a mask that exposed a 29 mm diameter area followed by a mask that exposed a 17 mm diameter area, both areas centered on the briquette. Measuring two different areas yields measurements of two different sample masses per element. Because small particles can be scattered across the measured area, comparison of results between the two areas can help identify some kinds of composition variations.

All measurements were performed in a vacuum environment with the generator operated at 4.0 kW of power. Briquettes were loaded by the sample changer into a single sample cup, which was then loaded into the spectrometer. The mask between the sample and the collimator was set to view a circular area of the sample with a 29 mm diameter for the first batch run and a circular area with a 17 mm diameter for second batch run. Using the 29 mm mask, counting times were chosen to obtain relative counting statistical errors (*CSE%*) ranging from 0.1 % to 1 % depending on the X-ray count rate for each element and the number of measurements of background; however, the *CSE%* does exceed 1 % for some minor XRF signals. Times were not increased for use of the 17 mm mask hence the counting uncertainties are higher. The Rh K-L Compton scatter line from the X-ray tube was measured for use as a drift monitor.

All 80 SRM 2693a briquettes were measured in random order in a single batch for each mask setting. The time required for the measurements was expected to be approximately 100 h for each batch. Therefore, the Rh scatter line and selected background measurements were used to monitor spectrometer drift. Seven count rates, including background measurements for Cl, Mg, N, O, Zn, and Zr and the Rh scatter peak, were used to cover most of the measurement conditions including detectors, crystals and collimators. The monitor count rates for the 29 mm measurements are shown in Fig. 3. The count rates for the 17 mm measurements using the same sets of conditions are shown in Fig. 4.

Although none of the trend lines have zero slope, the slope values are very low and the correlation coefficients, R^2 , are very small. Calculated confidence intervals on the slope values, equal to two times the standard error of the slope, bracket a zero slope value in all cases except for Zn and Zr for the 29 mm mask. The drift is about 0.5 % relative for Zn and 0.8 % relative for Zr. Reviewing the summary statistics for both the 17 mm and 29 mm masks presented later in section 4.3.2 shows this potential minor drift observed for 29 mm mask measurements has no impact on the measured relative standard deviation in comparison to the theoretical relative counting statistical error of the XRF signal for both Zn and Zr. This review indicates that the scatter in each set of count rates is the dominant characteristic of the data variance and long term drift is not a significant source of measurement variability.



Fig. 3. Drift Monitor Count Rates for the 29 mm Mask WDXRF Measurements.



Fig. 4. Drift Monitor Count Rates for the 17 mm Mask WDXRF Measurements.

4.3. Results

Quantitative count rate results were obtained for 30 of the 31 targeted elements. The counts for Br in the SRM 2693a coal were at or below the limit of detection for the measurement conditions used.

4.3.1. Outlier Detection Based on Control Charting Methodology

An outlier detection test based on control chart tests described in ASTM STP15D [4] was used to determine whether there were statistically significant differences between the X-ray line count rates for each of the 30 elements in the replicate samples from each bottle or in the replicate averages between bottles. Statistical differences for within-bottle measurements are determined by the within-bottle variance for a specific bottle as compared to the upper limit of variance as defined by the mean within-bottle variance multiplied by an appropriate control chart factor as defined in ASTM STP15D. Statistical differences for between-bottle measurements are flagged if the average bottle value falls outside of the range of the average as established by the overall measurement average plus or minus the appropriate control chart factor multiplied by the standard deviation of the overall bottle dataset or the range established by instrument stability and measurement statistics, whichever is the larger range. Differences were assessed for each of the 30 elements for each of the 40 bottles.

Table 3 summarizes the numbers of within- and between-bottle differences that were identified as statistically significant at a 95 % level of confidence for each of the 40 bottles. The differences appear widely distributed among the bottles, with no apparent trend among the sublots or runs.

For a 95 % level of confidence and normally distributed data, about 5 % of the differences are expected to be falsely identified as significant if indeed there are no significant differences. The number of flagged within-bottle differences for individual bottles ranges from 0 to 8 with an average of about 3 in the two datasets whereas the expected number of false identifications among the 30 elements evaluated in each bottle is $(30 \times 0.05 = 1.5)$. The overall numbers of flagged within-bottle differences in both the 29 mm and 17 mm mask measurements are twice the expected $(1200 \times 0.05 = 60)$. The 27 flagged differences that were jointly observed (same element in the samples from the same bottle in both the 29 mm and 17 mm data) is much larger than the $(1200 \times 0.05^2 = 3)$ expected for unrelated randomly distributed false identifications. This suggests that there are some bottles for which the two samples have truly different compositions. However, the finding of statistically significant differences between the replicates from a given bottle only indicates that the two briquettes were somehow different, perhaps related to non-uniform thickness or density or chemical composition. This type of statistical testing indicates the number of differences. The magnitude of these differences may or may not need to be accounted for in the uncertainty assessment of the material.

Fewer between-bottle differences than within-bottle differences were flagged as statistically significant, although more than two between-bottle differences were flagged as significant in two bottles of the 29 mm dataset. The average number of flagged between-bottle differences per bottle in the 29 mm dataset is 0.5 and just 0.2 in the 17 mm dataset in comparison to 3.0 and 3.1 average within-bottle differences, respectively. Two bottles had flagged between-

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bottle differences for the same elements (Fe and Al) in both the 29 mm and 17 mm datasets.. This result suggests that, for many elements, the magnitude of within-bottle differences when sampling within the bottle, is greater than the magnitude of between-bottle differences when sampling between bottles, which is the desired general trend analysts would like to see for a candidate test material. The homogeneity of Fe is assessed further in the next section along with the analysis of variance (ANOVA) used to provide a statistical assessment of within-bottle differences compared to between-bottle differences among the total population of bottles for all analyzed elements.

29 mm Mask		17 mm Mask		Joint ^b		
Sample ^c	Within	Between	Within	Between	Within	Between
2-1-082	4	1	4	0	0	0
2-2-058	3	0	4	0	1	0
2-3-082	5	0	2	0	1	0
2-4-007	1	0	3	0	0	0
2-5-078	2	0	3	0	0	0
2-6-002	3	0	3	0	0	0
2-7-024	2	0	4	0	1	0
2-8-096	1	1	1	1	0	1
3-1-029	4	0	4	0	0	0
3-2-027	5	0	2	0	2	0
3-3-082	7	1	7	0	3	0
3-4-007	2	1	1	0	0	0
3-5-048	6	3	4	2	2	0
3-6-076	1	0	2	0	1	0
3-7-096	5	0	6	0	1	0
3-8-016	4	0	2	0	0	0
4-1-012	0	1	3	0	0	0
4-2-056	5	1	2	0	0	0
4-3-015	1	0	2	0	0	0
4-4-087	0	2	4	0	0	0
4-5-088	0	2	5	0	0	0
4-6-074	3	0	5	0	0	0
4-7-104	1	0	1	0	0	0
4-8-077	3	1	0	0	0	0
5-1-007	2	0	7	0	1	0
5-2-044	3	0	5	1	0	0
5-3-033	8	4	5	1	4	1
5-4-034	3	1	2	1	0	0
5-5-067	2	0	7	0	1	0
5-6-098	2	0	3	0	1	0
5-7-075	3	0	1	0	0	0
5-8-078	3	0	1	0	0	0
7-1-081	3	0	1	0	0	0
7-2-040	3	0	6	0	3	0
7-3-036	3	0	5	0	2	0
7-4-083	6	0	1	0	1	0
7-5-038	1	0	1	0	1	0
7-6-088	4	0	2	0	1	0
7-7-064	3	2	2	0	0	0
7-8-069	1	0	1	1	0	0
Total:	118	21	124	7	27	2
Average:	3.0	0.5	3.1	0.2	0.7	0.1

Table 3. Number of Statistically Significant Differences for Each Bottle.^a

а At a 95 % level of confidence.

b

A statistically significant difference observed for the same element in both datasets. Samples identified by sublot (2, 3, 4, 5, and 7), run within the sublot (1 to 8), and fill order (1 to 108). с

Table 4 summarizes the numbers of within- and between-bottle differences that were identified as statistically significant at a 95 % level of confidence for each of the 30 elements. The number of flagged within-bottle differences for individual elements ranges from 0 to 7 with an average of about 4 in the two datasets whereas the expected number of false identifications among the 40 bottles evaluated is $(40 \times 0.05 = 2)$. However, no one element stands out as particularly prone to either within- or between-bottle differences. Only Mg, Al, and Fe are flagged as having significant joint within-bottle differences in more than two bottles. Only Al and Fe are flagged as having significant joint differences between-bottle differences.

29 mm		17 mm		Joint ^b		
Element	Within	Between	Within	Between	Within	Between
С	6	0	4	0	0	0
Ν	4	0	2	0	0	0
0	5	0	4	0	0	0
Na	4	0	3	0	1	0
Mg	5	0	4	0	3	0
Al	5	2	6	1	4	1
Si	5	2	4	0	2	0
Р	6	1	4	2	1	0
S	5	0	5	0	2	0
Cl	4	0	5	0	1	0
K	5	2	3	1	1	0
Ca	3	2	4	1	1	0
Sc	4	0	1	0	1	0
Ti	4	0	5	0	1	0
V	2	0	4	0	0	0
Cr	5	0	4	0	0	0
Mn	3	1	5	0	2	0
Fe	5	3	5	1	3	1
Со	2	0	4	0	0	0
Ni	2	0	3	0	0	0
Cu	5	0	4	0	0	0
Zn	5	1	5	1	2	0
Ga	4	0	4	0	1	0
Rb	4	0	5	0	0	0
Sr	4	0	4	0	0	0
Zr	4	0	4	0	1	0
Ba	5	0	7	0	0	0
La	3	0	3	0	0	0
Ce	0	3	5	0	0	0
Nd	0	4	4	0	0	0
Total:	118	21	124	7	27	2
Average:	3.9	0.7	4.1	0.2	0.9	0.1

^a At a 95 % level of confidence.

^b A statistically significant difference observed for the same element in both datasets.

4.3.2. Summary Statistics

In addition to listing the mean kcps and *RSD*% for each element, Table 5 and Table 6 list summary statistics that provide further insight into the within- and between-bottle variability of the results for the 29 mm and 17 mm datasets. These summaries include three parameters derived using one-factor analysis of variance (ANOVA) for each element assayed and two WDXRF performance parameters.

- RSD% (within), the within-bottle relative SD expressed as a percentage. RSD% (within) = $100\sqrt{MS}$ (within)/mean, where MS(within) is the between-group mean square estimate from the ANOVA [5].
- RSD% (between), the between-bottle relative SD expressed as a percentage. RSD% (between) = $100\sqrt{max(0, MS(between) - MS(within))/2}/mean$, where MS (between) is the between-group mean square estimate from the ANOVA [5].
- *p*, the probability of observing a larger test statistic than was actually observed when *H*₀, the null hypothesis that the coal in all of the bottles has the same amount of a given element, is true, where *p* is derived from the probability distribution of the *F*-statistic *MS*(between)/*MS*(within). *p*-values less than 0.05 suggest that the differences are statistically significant at a 95 % level of confidence. Like the mean square values, the *p* value is provided by the ANOVA software.
- *CSE%*, the relative Counting Statistical Error expressed as a percentage [6]. This is the theoretical X-ray counting statistical error, a component of observed variability that is not related to within- or between-bottle heterogeneity, divided by the mean XRF signal intensity. For a large signal peak and minor background, this is estimated as $1/\sqrt{N}$, where *N* is the total counts and is equal to the product of the kcps and the counting time (in seconds). When the background becomes more significant, then the background counts must be factored in as well.
- Estimated Sample Mass, derived from the "Total Measured Mass of Sample" determined using the signal X-ray line energy for each particular element [7]. This is the estimated mass of the sample being probed by the measurement based on attenuation depth, estimated sample density, and excitation area. For high energy analyte lines, e.g., from Rb, Sr and Zr, the entire 31 mm diameter pellet thickness is being sampled and the mass shown reflects the geometrical ratio of the 29 mm mask to the 31 mm diameter pellet. Estimated sample masses for the 17 mm mask use the 29 mm mask numbers with the appropriate geometrical correction factor.

		One	Factor ANO	VA			
	Mean		RSD%	RSD%			Estimated
Element	(kcps)	RSD%	(within)	(between)	р	CSE%	Mass (g)
С	35.91	0.366	0.481	0.136	0.32	0.26	0.003
Ν	0.092 55	4.22	7.22	0.000	0.88	3.36	0.003
0	2.222	1.11	0.978	0.874	0.002	0.42	0.005
Na	0.1290	4.50	3.77	3.630	0.001	2.10	0.003
Mg	0.3122	2.05	2.09	1.418	0.022	0.48	0.004
Al	175.5	0.953	0.924	0.695	0.010	0.12	0.007
Si	138.3	0.630	0.620	0.452	0.012	0.13	0.012
Р	9.444	1.05	1.12	0.690	0.040	0.16	0.017
S	99.43	0.196	0.246	0.0904	0.23	0.11	0.026
Cl	0.6196	2.16	2.16	1.527	0.016	1.01	0.048
K	8.345	0.716	0.711	0.511	0.014	0.10	0.077
Ca	20.71	0.654	0.993	0.000	0.67	0.12	0.10
Sc	0.1037	2.07	2.18	1.385	0.033	2.51	0.15
Ti	39.91	0.287	0.393	0.074	0.42	0.16	0.19
V	0.6062	0.443	0.628	0.000	0.50	0.50	0.27
Cr	0.9960	0.836	1.25	0.000	0.63	0.88	0.35
Mn	1.306	2.98	3.74	1.373	0.23	1.40	0.45
Fe	418.5	1.08	1.06	0.770	0.013	0.11	0.58
Co	0.1776	2.20	2.23	1.540	0.019	2.38	0.77
Ni	2.361	0.515	0.884	0.000	0.88	0.83	0.95
Cu	4.355	0.587	0.901	0.000	0.70	0.61	1.2
Zn	5.884	2.08	3.22	0.000	0.706	0.51	1.5
Ga	1.660	1.30	1.94	0.000	0.62	1.88	1.8
Rb	3.073	1.60	2.22	0.328	0.45	1.95	3.6
Sr	39.94	0.428	0.525	0.213	0.19	0.37	3.6
Zr	56.68	0.413	0.700	0.000	0.87	0.45	3.6
Ba	0.066 26	1.93	2.55	0.702	0.33	0.78	0.19
La	0.094 31	2.69	3.76	0.420	0.47	3.80	0.21
Ce	0.081 85	1.86	2.43	0.717	0.31	0.71	0.31
Nd	0.027 85	4.25	5.86	0.960	0.43	6.30	0.31

 Table 5. Summary Statistics for the 29 mm Mask Dataset.

_

_			One Factor ANOVA				
	Mean		RSD% RSD%			Estimated	
Element	(kcps)	RSD%	(within)	(between)	р	CSE%	Mass (g)
С	7.480	0.547	0.763	0.091	0.46	0.58	0.002
Ν	0.018 45	8.57	13.77	0.000	0.79	7.75	0.002
0	0.4871	1.49	1.565	0.991	0.034	0.90	0.003
Na	0.027 82	6.51	7.20	4.053	0.063	4.48	0.002
Mg	0.068 09	3.20	3.58	1.966	0.070	1.02	0.002
Al	36.85	1.08	1.31	0.561	0.16	0.26	0.004
Si	29.18	0.762	1.07	0.097	0.48	0.29	0.007
Р	2.046	1.32	1.72	0.508	0.31	0.35	0.010
S	21.45	0.298	0.451	0.000	0.66	0.24	0.015
Cl	0.1388	3.08	4.08	1.071	0.34	2.09	0.028
Κ	1.779	1.26	1.43	0.756	0.082	0.21	0.045
Ca	4.519	1.12	1.82	0.000	0.81	0.26	0.059
Sc	0.022 64	4.28	5.96	0.740	0.46	5.45	0.088
Ti	8.786	0.486	0.778	0.000	0.78	0.34	0.11
V	0.1348	0.857	1.277	0.000	0.63	1.06	0.16
Cr	0.2039	1.87	2.34	0.866	0.22	1.96	0.21
Mn	0.2863	4.55	6.81	0.000	0.64	2.92	0.26
Fe	89.88	1.47	1.79	0.741	0.18	0.24	0.34
Co	0.039 12	3.64	5.45	0.000	0.64	5.10	0.45
Ni	0.5362	1.28	1.68	0.481	0.317	1.70	0.56
Cu	1.307	0.760	1.21	0.000	0.77	0.97	0.70
Zn	1.590	3.13	5.88	0.000	0.96	0.87	0.88
Ga	0.3474	2.86	5.53	0.000	0.97	4.07	1.1
Rb	0.6854	2.62	4.76	0.000	0.94	4.15	2.1
Sr	9.376	0.642	0.973	0.000	0.67	0.78	2.1
Zr	13.61	0.754	1.33	0.000	0.92	0.93	2.1
Ba	0.015 14	3.80	6.54	0.000	0.89	1.63	0.11
La	0.020 82	5.26	7.50	0.000	0.52	8.14	0.12
Ce	0.019 05	3.20	5.02	0.000	0.74	1.48	0.18
Nd	0.006 50	7.79	12.14	0.000	0.73	12.66	0.18

Table 6. Summary Statistics for the 17 mm Mask Dataset.

The *RSD%*, *RSD%*(within) and *RSD%*(between) estimates for both the 29 mm and 17 mm datasets are displayed in Fig. 5 as functions of the X-ray signal mean count. These estimates are inversely dependent on the signal intensity, with smaller values for larger count rates. The 17 mm estimates tend to be larger than those for the 29 mm because of the smaller signal from the smaller area assayed with the same fixed measuring time. The *RSD%*(between) estimates are much smaller than the *RSD%*(within), in accord with the relatively few significant between-bottle differences listed in Table 4.



Fig. 5. Relative Variability Estimates as Functions of Mean Count.

The panel to the left displays total RSD% for all elements in both the 29 mm and 17 mm datasets as a function of the mean count. The center panel displays the RSD%(within) component, and the panel to the right displays RSD%(between).

The *p*-values from Table 5 and Table 6 are plotted in Fig. 6 as functions of the RSD%(between)/RSD% ratios. A RSD%(between)/RSD% ratio of 0.1 or less indicates that the between-bottle component accounts for no more than a chemically insignificant 1 % $(0.1^2 = 0.01)$ of the total variance marked by vertical dashed lines in Fig. 6. The between-bottle differences for the 29 mm dataset that are both statistically and chemically significant are O, Na, Mg, Al, Si, P, Cl, K, Sc, Fe, and Co. Only O in the 17 mm dataset has a between-bottle difference that is both statistically and chemically significant due to the poorer counting statistics of the 17 mm measurements.



Fig. 6. *p*-values from Table 5 and Table 6 as Functions of *RSD*%(between)/*RSD*%.

The panel to the left displays the *p*-values from Table 5 and the *RSD*%(between)/*RSD*% ratio for all elements in the 29 mm dataset for which *RSD*%(between) is greater than zero. The panel to the right likewise displays the ratio for the 17 mm dataset in Table 6. The solid horizontal line denotes the usual 5 % confidence level used for testing the statistical significance of the differences. The vertical dashed line denotes a *RSD*%(between)/*RSD*% value of 0.1, marking the ratio below which the between-bottle component makes little or no chemically significant contribution to the measurement variability.

The within-bottle variability relative to the statistical counting error, *RSD%*(within)/*CSE%*, are displayed in Fig. 7 as functions of the fraction of the sample contributing to the measurement. In analogy with a typical definition of the limit of quantitation as ten-fold the SD of the blank signal, only Fe has a *RSD%*(within)/*CSE%* ratio greater than approximately 9, in the 29 mm dataset although the ratio for Fe in the 17 mm dataset drops to between 7 and 8. The relatively large ratio in the 29 mm dataset for Fe suggests some degree of within-sample heterogeneity arising from the presence of Fe "nuggets."



Fig. 7. RSD%(within)/CSE% as Functions of Fraction Sample.

The panel to the left displays the *RSD*%(within)/*CSE*% ratio as a function of the fraction sample probed by the X-ray line used to for each element in the 29 mm dataset. The panel to the right likewise displays the ratio for the 17 mm dataset. The solid horizontal dotted line marks where the *RSD*%(within) are 10-fold larger than their *CSE*%. The vertical dotted line marks where the measurement represents at least 1 % of the sample volume.

4.3.3. Comparison to SRM 2693

Although the material for SRM 2693a came from the same mine that was the source of SRM 2693, significant differences in composition are possible. Table 7 lists the mean, SD, and RSD% for the four SRM 2693 briquettes; the mean, SD, and RSD% for the 80 SRM 2693a briquettes; and the (SRM 2693a)/(SRM 2693) ratio of the mean and RSD% estimates. All values are for measurements using the 29 mm mask. The results for the two materials are compared in Fig. 8.

	SF	SR	2693a/2693					
Mean SD				Mean	SD		Mean	RSD%
Element	(kcps)	(kcps)	RSD%	(kcps)	(kcps)	RSD%	Ratio	Ratio
С	34.527	0.069	0.2	35.91	0.18	0.50	1.0	2.51
Ν	0.0887	0.0018	2.0	0.0926	0.0061	6.59	1.0	3.25
0	2.212	0.022	1.0	2.222	0.029	1.31	1.0	1.31
Na	0.3339	0.0057	1.7	0.1290	0.0067	5.19	0.39	3.04
Mg	0.2833	0.0066	2.3	0.3122	0.0079	2.53	1.1	1.09
Al	179.9	2.1	1.2	175.5	2.0	1.15	1.0	0.99
Si	143.2	1.1	0.8	138.34	1.1	0.77	1.0	1.00
Р	9.605	0.022	0.2	9.444	0.12	1.31	1.0	5.74
S	134.58	0.33	0.2	99.43	0.26	0.26	0.74	1.07
Cl	4.32	0.02	0.5	0.620	0.016	2.65	0.14	5.71
K	10.066	0.073	0.7	8.345	0.073	0.87	0.83	1.20
Ca	20.58	0.33	1.6	20.71	0.20	0.96	1.0	0.60
Sc	0.0903	0.0039	4.3	0.1037	0.0027	2.60	1.1	0.60
Ti	35.364	0.092	0.3	39.91	0.159	0.40	1.1	1.53
V	0.4719	0.0028	0.6	0.6062	0.0038	0.63	1.3	1.06
Cr	0.7184	0.0078	1.1	0.9960	0.012	1.21	1.4	1.12
Mn	0.617	0.024	3.9	1.306	0.052	3.97	2.1	1.02
Fe	202.4	2.9	1.4	418.5	5.5	1.31	2.1	0.91
Co	0.1248	0.0050	4.0	0.1776	0.0048	2.70	1.4	0.67
Ni	2.269	0.010	0.4	2.361	0.019	0.81	1.0	1.85
Cu	3.956	0.051	1.3	4.355	0.038	0.87	1.1	0.67
Zn	3.10	0.13	4.2	5.88	0.18	3.08	1.9	0.74
Ga	1.671	0.035	2.1	1.660	0.031	1.89	1.0	0.90
Br	5.230	0.081	1.5	0.05 ^a	0.08 a	-	0.009	-
Rb	4.236	0.054	1.3	3.073	0.069	2.24	0.7	1.76
Sr	48.47	0.23	0.5	39.94	0.23	0.56	0.8	1.19
Zr	55.96	0.65	1.2	56.68	0.37	0.65	1.0	0.56
Ba	0.0902	0.0020	2.2	0.0663	0.0018	2.72	0.7	1.23
La	0.0826	0.0040	4.8	0.0943	0.0036	3.82	1.1	0.79
Ce	0.0754	0.0010	1.3	0.0818	0.0021	2.57	1.1	1.94
Nd	0.0233	0.0010	4.3	0.0279	0.0017	6.12	1.2	1.42
Rh Scatter ^b	135.82	0.14	0.1	131.15	0.38	0.29	1.0	2.78

Table 7. Comparison of Summary Results for SRMs 2693 and 2693a.

а

Counts for Br in SRM 2693a were at or below the limit of detection. Count rates for the Rh K-L Compton scatter line from the X-ray tube, used as a drift monitor. b



Fig. 8. Comparison of SRMs 2693 and 2693a Mean and RSD% Results.

The panel to the left displays the SRM 2693a/SRM 2693 ratio between the mean counts for the 31 target elements plus the Rh K-L Compton scatter as a function of the counts in SRM 2693. The panel to the right likewise displays the SRM 2693a/SRM 2693 ratio between the RSD% s as a function of the RSD% for SRM 2693. The solid horizontal lines denote equality between the SRM 2693a and SRM 2693 results; the dashed lines bound the factor-of-two intervals between 0.5 and 2.

The most notable differences between the SRMs are the much lower mean signals for Cl and especially Br in SRM 2693a. The signal for Na is also somewhat lower in SRM 2693a than in 2693; the signals for Mn, Zn, and Fe are somewhat higher. The variability for C, Cl, N, Na, and P in SRM 2693a is at least a factor of two greater than in SRM 2693. However, these estimated ratios are associated with considerable uncertainty since the RSD% for SRM 2693 are estimated from just four replicates. Further, the variability in Rh scatter is also greater for SRM 2693a, suggesting that some of the variability differences may be measurement artifacts. For example, the intensity of the Rh scatter is a function of briquette density and thickness as the Rh scatter is sufficiently energetic to eminate from the entire briquette thickness as are Rb, Sr and Zr as shown in Table 5 which are lower in energy than the Rh scatter.

4.4. Summary

Assessment of material homogeneity is a combination of statistical analyses and subjective judgement, essentially trying to judge if the measured homogeneity is fit-for-purpose. A statistical difference may be identified, but the magnitude of that difference may not be significant with respect to the overall expanded uncertainty of the measurand; or, the certification plan may not require a particular mass fraction to be certified. For example, SRM 2693 only has certified mass fractions for S, Hg and Cl.

In addition to measurement statistics presented in this section, it is also important to note the theoretical counting statistics, CSE%, and estimated sampling size by XRF. Heterogeneity associated with limitations in sampling size may be overcome by using measurement methods with larger sampling sizes. The CSE% provides a limit on the resolution of the XRF heterogeneity measurement. For example, note that almost all analytes have acceptable

p-values (see Fig. 6) when measured with the 17 mm mask, which has a poorer CSE% resolution.

S and Cl, two analytes certifed in SRM 2693, are sampled by XRF in the range of nominally 40 mg with the 29 mm mask. The measurement statistics for S are excellent in all parameters, better than 0.3 % relative with the 29 mm mask. The measurement statistics for Cl are roughly 10 times worse than S, but the Cl XRF count rates in SRM 2693a are lower by a factor of 10 in comparison to 2693. The lower count rates for SRM 2693a, which indicate the Cl mass fraction is significantly lower than in SRM 2693 material, can lead to a larger uncertainty for a certified measurand.

In reviewing the summary statistics for the 29 mm mask in Table 5, there are a number of analytes with measurement statistics exceeding 1 % relative, i.e., N, Sc, Cr, Co, Ga, Rb, La, and Nd, which appear to be essentially limited by the theoretical measurement program statistics, i.e., CSE%. In this group of analytes, only Sc and Co also failed the *F*-test.

Of the analytes that failed the *F*-test, i.e., O, Na, Mg, Al, Si, P, Cl, K, Sc, Fe, and Co, (see Fig. 6), the measurement statistics for O, Al, Si, P, and Fe are on the order of 1 % relative or less. While it is important to bear this failure in mind for certification, it may be that the level of heterogeneity is not significant compared to the uncertainty generated during consensus of measurement method values. The aspect of nuggets enriched in Fe causing a larger *RSD*%(within)/*CSE*% ratio should also be considered. For the remaining analytes, the assessed heterogeneity will need to be considered against various practical factors, i.e., XRF measurement sample size, uncertainty from consensus of measurement values, and whether the analyte is important to certify.

5. Elemental Analysis for Value Assignments at NIST

Several of NIST's measurement technologies have been used to quantitatively characterize the elemental composition of SRM 2693a. Total C, H, N, and S were determined with combustion analysis and prompt gamma-ray activation analysis (PGAA); Al, Br, Ca, Cl, Dy, Mg, Mn, Na, and V by instrumental neutron activation analysis (INAA), and Hg by atomic absorption spectrometry (AAS).

5.1. C, H, N, and S by Combustion Analysis

A combustion analyzer was used for the analysis of carbon, hydrogen, nitrogen, and sulfur (CHNS), using a thermal conductivity detector (TCD) and/or an infrared detector. Helium was used as the carrier gas and oxygen was added to aid the combustion of the sample. The combustion tube was controlled at 1150 °C for the analysis and the reduction tube was controlled at 950 °C. The method was calibrated for each of the four elements using SRM 143d Cystine [8]. Samples were analyzed in a manner consistent with ASTM methods D4239-18e1 and D5373-16 [9,10].

An analytical balance was used for mass determination in the preparation of samples and standards. The balance is serviced and calibrated annually. Prior to use, calibration was verified using 20 mg and 200 mg standard masses as check masses.

Initially, ten bottles of candidate SRM 2693a were obtained for analysis (set A). Based on an initial concern about stability a second set of ten bottles (set B), and a third set of six bottles (set C) were obtained. Each set of ten bottles consisted of two bottles from each of five lots of the same starting material bottled for the SRM. Four bottles of SRM 2693 were analyzed as a control material. Powdered graphite, determined to be 99.972 % C by a NIST WDXRF analysis, was also analyzed as a control because of its similarity to the coal matrix.

5.1.1. Sample Preparation

For each day of analysis of carbon, hydrogen, and nitrogen (CHN), three nominal 23 mg test portions were taken from each bottle of SRM 2693a. A known mass of each test portion was added to a tared tin foil boat of known mass that contained approximately 30 mg of powdered tungsten trioxide, WO₃. Tungsten trioxide is added to aid combustion during analysis [9,10]. After the test portion was added, the foil boat was then folded and sealed in a manner to minimize entrapment of air (containing nitrogen) and prevent sample loss during further handling. Three analytical samples were taken from each bottle to have a have sufficient sampling for data analysis, and to account for inevitable bad data points that arise because of the inherent challenges of the measurement technique.

Immediately before and after test portions were taken from each bottle, approximately 1 g test portions of known mass were transferred into clean, dry, glass weighing bottles (two test portions total). These samples were used to determine moisture mass fraction in each bottle via loss on drying (LOD), heating the coal samples at 107 °C for 1 hour and determining the resultant mass change. The control samples of SRM 2963 and graphite were prepared in the same manner, except the graphite samples did not need to be analyzed for moisture.

The sulfur mass fraction was too low to obtain enough sensitivity for sufficiently accurate measurements using the TCD. Sulfur was therefore analyzed independently using an infrared detector. The samples were prepared in the same manner as above except that test masses of the SRM were about 50 mg and approximately 60 mg of tungsten trioxide were used as a combustion aid. Nitrogen was analyzed along with S since it was easy to extend the calibration up to the necessary levels.

Calibration samples of SRM 143d Cystine were prepared by transferring a known mass of the SRM into tared tin foil boats of known mass. Nominal test portion masses of the calibrant needed were pre-determined so that the masses of a given element in the standards would bracket the average mass of the element in the test portions. For the nominal 23 mg test portion size used for CHN analysis, between 1 mg and 85 mg of SRM 143d were used for calibration. For the nominal 50 mg test portion size used for S analysis, between 0.1 mg and 10 mg of SRM 143d were used.

5.1.2. Method

Analysis was performed in a series of one-day sessions designed to determine either CHN or nitrogen and sulfur. Two experimental methods were used: one for SRM 143d and one for coal and graphite. The difference between the methods is that more oxygen over a longer time period was introduced to the coal and graphite samples to aid in the combustion of the samples with a very high carbon mass fraction. Table 8 lists the parameter values used.

	Method				
Parameter	SRM 143d	Coal & Graphite			
O ₂ dosing time 1	30 s	30 s			
O ₂ dosing time 2	90 s	200 s			
O ₂ dosing flow 1	50 mL/min	50 mL/min			
O ₂ dosing flow 2	50 mL/min	100 mL/min			
O ₂ cut off threshold	30 %	30 %			
Autozero delay N	15 s	15 s			
Autozero delay S	15 s	15 s			
Peak anticipation N	70 s	70 s			
Peak anticipation C	150 s	150 s			
Peak anticipation H	75 s	75 s			
Peak anticipation S	80 s	80 s			
Desorption CO ₂ (column)	240 °C	240 °C			
Desorption H ₂ O (column)	150 °C	150 °C			
Desorption SO ₂ (1) (column)	-	100 °C			
Desorption $SO_2(1)$ time	0 s	60 s			
Desorption SO ₂ (2) (column)	230 °C	230 °C			

After enough blanks were run to ensure a minimal, well-characterized background signal measurement for every element, samples were analyzed so that carryover between samples was either minimized or accounted for. Samples of SRM 143d were analyzed in order of

increasing mass. In between selected samples, blank measurements were run to determine column carryover. Two or three blanks were typically run at the end of the calibration measurements. The analytical samples were then run in a random order, beginning with a conditioning sample of the same mass to compensate for column carryover. Control samples were run immediately following the analytical samples. After running at least two blanks to minimize carryover, a second set of standard samples were run.

A preliminary analysis was performed for all elements by first fitting the calibration data to first and second order polynomials, to ensure that the calibration data was fit-for-use and to identify suspect data points. Suspect calibration points are removed because elemental analysis is prone to occasional spurious results, likely resulting from contamination or mechanical sample loss. Spurious results at the high and low ends of the detector range can also skew the calibration. Suspect results are identified through examination of residuals based on a preliminary analysis using a first or second order polynomial.

After the preliminary analysis was complete, the valid raw data from the calibrants and analytical samples for each element were exported for processing using parametric bootstrap and Monte Carlo [11] approaches. After importing the data, a best fit for the calibration data was found using an errors-in-variables model and maximum likelihood estimation. The errors-in-variables model accounts for random effects in both the *x*-axis (element mass) and *y*-axis (detector signal). The model fits a range of polynomials to the calibration data (typically an 8th order polynomial is set as the maximum for the method) and calculates the best polynomial degree as the one having the lowest value of the Bayesian information criterion [12]. In general, there is agreement between the results from the preliminary analysis and the bootstrap method.

The elemental dry mass fractions for the analytical samples and control were calculated. For C, N and S, the dry mass fraction, w_D , is

$$w_{\rm D} = m_{\rm e} / (m_0 (1 - x_{\rm w})) \tag{1}$$

where m_e is the elemental mass of the sample, m_0 is the mass of the analytical sample, and x_w is the moisture mass fraction. To account for hydrogen in water, the hydrogen dry mass fraction, w_{DH} , in samples is calculated

$$w_{\rm DH} = (m_{\rm e} - m_0 x_{\rm w} A) / (m_0 (1 - x_{\rm w}))$$
⁽²⁾

where A is the hydrogen mass fraction in water, 0.11191 g/g [13]. The components of known uncertainty, which includes the variance in the measured moisture mass fraction, are used to perturb the system and generate bootstrap data sets, using 1000 iterations of the Monte Carlo procedure.

The consensus value across bottles for the elemental mass fraction for each material in each daily run was calculated using a random effects model incorporating the test portion mass fractions. These replicates were then combined using the NIST Consensus Builder (NICOB) [14] to determine an overall consensus values, combined standard uncertainties, u, and 95 % level of confidence expanded uncertainties, U_{95} . Two sets of uncertainties are estimated, one assuming that the samples are homogenous and the other including a "dark uncertainty" [15] component of inherent inhomogeneity.

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The elemental carbon mass fraction in graphite and CHNS in the control samples were calculated in the same manner. Only two bottles with three replicates each were used to determine the mass fraction and the bootstrap distributions for the early control samples. The last two runs included more control samples (one bottle with three replicates and one bottle with six replicates) to give better uncertainty estimates. The CHN results for the SRM 2693 control were in excellent agreement with values determined in an interlaboratory study reported in the material's Certificate of Analysis (COA). While based upon only two sets of results and so associated with large uncertainty, the S value was in good agreement with the certified value.

5.1.3. Results

Measurements were performed in eight daily sessions over a period of 18 months. Table 9 lists the date of analysis, the elements analyzed, and samples evaluated.

	SRM	2693a	SRM	2693	Graphite			
Date	Set	Elements	$n_{\rm bot}{}^{\rm a}$	$n_{\rm rep}^{b}$	$n_{\rm bot}{}^{\rm a}$	$n_{\rm rep}^{b}$	$n_{\rm bot}{}^{\rm a}$	$n_{\rm rep}^{\ b}$
06/26/2019	А	C,H,N	10	3	2	3	1	4
09/11/2019	А	N,S	10	3	2	3	0	0
09/19/2019	А	C,H,N	10	3	2	3	1	4
01/14/2020	А	N,S	10	3	2	3	0	0
01/23/2020	А	C,H,N	10	3	2	3	1	4
02/06/2020	B & C	C,H,N	16	3	2	3	1	4
12/03/2020	С	C,H,N	6	3	2	3,6	1	9
01/14/2021	В	C,H,N	10	3	2	3,6	1	9

Table 9. Samples Evaluated in Each of Eight Sessions.

^a n_{bot} is the number of bottles analyzed.

^b $n_{\rm rep}$ is the number of replicate measurements made on each bottle.

5.1.3.1. Mass Loss on Drying (LOD)

The LOD for the material in each SRM 2693a and 2693 samples evaluated was determined on the same day as the elemental analyses. The LOD results for all materials (other than graphite, which was not evaluated) are displayed in Fig. 9 as a function of analysis date. Table 10 lists the summary results.





The solid circles denote the mean percent mass loss on drying, LOD, SRM 2693a results for both Sets A and B; the squares for set C, and the triangles the SRM 2693 control results. Error bars represent \pm standard deviations.

	26-Jun-2019		11-Sep	p-2019	19-Sej	19-Sep-2019		14-Jan-2020		n-2020
Bottle	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
2-4-20	0.9150	0.0250	1.0410	0.0018	1.0165	0.0122	0.9373	0.0347	0.9150	0.0250
2-8-66	0.9342	0.0252	1.0473	0.0033	1.0417	0.0028	0.9583	0.0445	0.9342	0.0252
3-3-61	0.9028	0.0664	1.0193	0.0011	0.9982	0.0077	0.9792	0.0359	0.9028	0.0664
3-7-21	0.8719	0.0071	1.1058	0.0141	1.0888	0.0109	0.9610	0.0376	0.8719	0.0071
4-5-51	0.8093	0.0171	1.0064	0.0141	0.9836	0.0122	0.7679	0.0053	0.8093	0.0171
4-8-54	0.8003	0.0197	1.0207	0.0023	0.9780	0.0016	0.7929	0.0648	0.8003	0.0197
5-3-45	0.7909	0.0346	1.0051	0.0065	0.9807	0.0111	0.7835	0.0472	0.7909	0.0346
5-8-65	0.8137	0.0001	1.0201	0.0035	0.7612	0.3388	0.8227	0.0377	0.8137	0.0001
7-1-60	0.8119	0.0351	0.9584	0.0148	0.9501	0.0040	0.8381	0.0168	0.8119	0.0351
7-3-18	0.8019	0.0626	0.9359	0.0147	0.9313	0.0248	0.7947	0.0049	0.8019	0.0626
Ctrl1	0.9439	0.0205			0.9625	0.0377	1.0496	0.0329		
Ctrl2	0.9670	0.0106			0.9474	0.0112	1.0408	0.0289		
Ctrl3			0.9601	0.0070					0.9493	0.0205
Ctrl4			0.9148	0.0333					0.9670	0.0106

Table 10. Mass Loss On Drying (LOD) Summary Results, %.

	6-Feb	-2020	_	3-Dec	2020	14-Jan-2021		
Bottle	Mean	SD		Mean	SD	Mean	SD	
2-6-38	0.9793	0.0407				0.8675	0.0095	
2-7-33	1.1367	0.0271				1.0371	0.0326	
3-3-96	1.0796	0.0447				0.8763	0.0616	
3-8-60	1.1384	0.0147				1.0211	0.0754	
4-1-2	1.1213	0.0288				1.0662	0.0305	
4-3-37	1.0506	0.0113				0.9464	0.0019	
5-1-28	0.9564	0.0075				0.8573	0.0234	
5-4-61	0.9349	0.0115				0.8601	0.0004	
7-7-52	0.9810	0.0050				0.8030	0.0491	
7-8-106	0.9975	0.0039				0.8642	0.0165	
C 1-1	1.0019	0.0285		0.8912	0.0652			
C 1-2	0.9165	0.0275		0.8546	0.0154			
C 2-1	0.7932	0.0089		0.7927	0.0385			
C 2-2	0.8974	0.0202		0.9164	0.0380			
C 3-1	0.8606	0.0134		0.7428	0.0249			
C 3-2	0.8792	0.0244		0.8125	0.0533			
Ctrl1				0.8978	0.0566			
Ctrl2				0.9105	0.0072			
Ctrl3	0.9348	0.0044				0.9081	0.1061	
Ctrl4	0.9170	0.0024				0.8839	0.0598	
5.1.3.2. Daily Results for SRM 2693a

Table 11 summarizes the daily results for the samples from the ten set A bottles; Table 12 summaries the results for the samples from the ten set B bottles; and Table 13 summarizes the results from the six set C bottles. The daily summary values for C, H, and N are displayed in Fig. 10, the values for S are displayed in Fig. 11.

	<i>w</i> _C (%)		$w_{ m H}$	(%)	WN	(%)		WN	(%)	ws ((%)	
	Bottle	Mean	SD	Mean	SD	Mean	SD		Mean	SD	Mean	SD
	2-4-20	79.716	0.139	4.4559	0.0266	1.1909	0.0023		1.1854	0.0024	0.3051	0.0059
	2-8-66	79.772	0.059	4.5254	0.0249	1.1800	0.0059		1.1856	0.0010	0.2984	0.0123
_	3-3-61	79.703	0.181	4.3843	0.0446	1.1895	0.0030	-	1.1832	0.0072	0.3063	0.0046
019	3-7-21	80.230	0.702	4.4295	0.0752	1.1932	0.0170	019	1.1884	0.0052	0.2963	0.0060
1-2(4-5-51	79.872	0.095	4.5246	0.0179	1.1887	0.0060	0-2	1.1887	0.0088	0.2948	0.0091
Jur-	4-8-54	79.800	0.087	4.4725	0.0459	1.1886	0.0021	Sel	1.1957	0.0034	0.2910	0.0080
26-	5-3-45	79.766	0.112	4.4658	0.0154	1.1866	0.0060	11-	1.1847	0.0016	0.3078	0.0175
	5-8-65	79.730	0.087	4.5186	0.0690	1.1825	0.0024		1.1872	0.0067	0.3067	0.0115
	7-1-60	79.754	0.273	4.4796	0.0944	1.1894	0.0027		1.1917	0.0040	0.3011	0.0081
	7-3-18	79.861	0.138	4.4803	0.0288	1.1822	0.0060		1.1919	0.0036	0.3014	0.0075
	2-4-20	79.979	0.589	4.4246	0.0817	1.1776	0.0073		1.1970	0.0013	0.3247	0.0178
	2-8-66	79.798	0.030	4.4101	0.0674	1.1725	0.0016		1.1968	0.0008	0.3424	0.0246
	3-3-61	79.725	0.266	4.4449	0.0553	1.1715	0.0045		1.1955	0.0024	0.3173	0.0132
019	3-7-21	79.809	0.121	4.4404	0.0413	1.1783	0.0038	020	1.1931	0.0041	0.3631	0.0366
-2	4-5-51	79.832	0.283	4.4373	0.0364	1.1636	0.0275	1-2(1.2032	0.0115	0.3529	0.0288
Sel	4-8-54	79.944	0.130	4.4618	0.0353	1.1778	0.0062	Jar	1.2065	0.0043	0.3373	0.0282
19-	5-3-45	79.684	0.060	4.4542	0.0746	1.1726	0.0047	14-	1.1961	0.0021	0.3281	0.0095
	5-8-65	79.643	0.038	4.4000	0.0663	1.1829	0.0028		1.1936	0.0017	0.3369	0.0273
	7-1-60	79.773	0.154	4.4617	0.0822	1.1663	0.0081		1.2014	0.0098	0.3263	0.0112
	7-3-18	79.791	0.075	4.4368	0.0783	1.1683	0.0081		1.2011	0.0083	0.3576	0.0308
	2-4-20	79.687	0.187	4.4766	0.0557	1.1697	0.0638					
	2-8-66	79.803	0.085	4.4299	0.0436	1.2013	0.0027					
_	3-3-61	79.939	0.212	4.4257	0.0214	1.2061	0.0070					
)2(3-7-21	79.807	0.148	4.4098	0.0399	1.2034	0.0034					
1-2(4-5-51	79.963	0.112	4.5097	0.0459	1.2062	0.0034					
Jar	4-8-54	79.876	0.100	4.4290	0.0204	1.2050	0.0054					
23-	5-3-45	79.754	0.129	4.4324	0.0199	1.2041	0.0107					
	5-8-65	79.746	0.178	4.4392	0.0181	1.2055	0.0138					
	7-1-60	79.812	0.046	4.4481	0.0432	1.2100	0.0021					
	7-3-18	79.855	0.015	4.5025	0.0369	1.2040	0.0023					

 Table 11. Mass Fraction Summary Results for Set A Bottles, %.

		w _C (%)		w_{H} (%)		$w_{\rm N}$ (%)		
	Bottle	Mean	SD	Mean	SD	Mean	SD	
	2-6-38	79.829	0.224	4.5958	0.1196	1.1833	0.0028	
	2-7-33	79.915	0.137	4.6312	0.0756	1.1839	0.0030	
	3-3-96	79.612	0.196	4.6249	0.0115	1.1769	0.0026	
20	3-8-60	79.746	0.298	4.5775	0.1134	1.1812	0.0083	
-20	4-1-2	80.244	0.910	4.6914	0.0844	1.1935	0.0133	
feb	4-3-37	79.610	0.253	4.6653	0.0117	1.1804	0.0013	
6-F	5-1-28	80.261	1.045	4.6237	0.1367	1.1920	0.0138	
	5-4-61	79.612	0.051	4.6244	0.0223	1.1757	0.0094	
	7-7-52	79.645	0.083	4.6386	0.0170	1.1772	0.0031	
	7-8-106	79.577	0.033	4.6649	0.0230	1.1762	0.0053	
	2-6-38	79.851	0.190	4.3384	0.0238	1.1757	0.0037	
	2-7-33	79.905	0.104	4.3172	0.0424	1.1682	0.0007	
	3-3-96	80.068	0.165	4.3103	0.0082	1.1715	0.0065	
020	3-8-60	79.684	0.103	4.3583	0.0236	1.1656	0.0063	
1-2(4-1-2	80.040	0.091	4.3085	0.0675	1.1698	0.0044	
Jar	4-3-37	79.921	0.250	4.3351	0.0339	1.1687	0.0060	
14-	5-1-28	79.937	0.180	4.3489	0.0078	1.1740	0.0028	
	5-4-61	79.905	0.158	4.3717	0.0181	1.1703	0.0079	
	7-7-52	80.018	0.063	4.3454	0.0055	1.1686	0.0075	
	7-8-106	79.952	0.189	4.3579	0.0283	1.1665	0.0089	

 Table 12. Mass Fraction Summary Results for Set B Bottles, %.

Table 13. Mass Fraction Summary Results for Set C Bottles, %.

		<i>w</i> _C (%)	$w_{ m H}$	(%)	$w_{\rm N}$ (%)		
_	Bottle	Mean	SD	Mean	SD	Mean	SD	
	C 1-1	79.583	0.209	4.6328	0.0162	1.1784	0.0065	
)20	C 1-2	79.902	0.167	4.6844	0.2656	1.1772	0.0023	
-2(C 2-1	79.598	0.064	4.6689	0.0129	1.1802	0.0036	
feb	C 2-2	79.551	0.052	4.6293	0.0915	1.1793	0.0060	
6-F	C 3-1	79.694	0.103	4.5726	0.1076	1.1797	0.0039	
	C 3-2	79.789	0.099	4.6311	0.0602	1.1828	0.0093	
(C 1-1	79.942	0.093	4.2883	0.0242	1.1775	0.0057	
)20	C 1-2	79.847	0.035	4.2775	0.0639	1.1738	0.0032	
-2(C 2-1	79.902	0.147	4.2999	0.0161	1.1754	0.0057	
Jec	C 2-2	79.895	0.078	4.2645	0.0287	1.1756	0.0063	
3-L	C 3-1	79.710	0.055	4.2915	0.0361	1.1829	0.0136	
	C 3-2	79.848	0.096	4.3009	0.0244	1.1758	0.0074	



Fig. 10. Sample and Run Mass Fraction Results for C, H, and N.

The top row displays the SRM 2693a mass fraction results expressed as percent for carbon, w_C ; the center panel for hydrogen, w_H ; and the bottom panels for nitrogen, w_N . The panel to the left in each row displays the mean result for each sample as a function of bottle identifier; the panel to right displays the mean result for each measurement run as a function of analysis date. The green circles denote results for analytical samples; the blue squares for packaged units. The error bars represent (mean \pm standard deviation). The solid horizontal lines represent the mean of the results for the analytical samples displayed within each panel; the dashed lines bound the interval (mean \pm standard deviation).



Fig. 11. Sample and Run S Mass Fraction Results.

These panels display the SRM 2693a mass fraction results expressed as percent for sulfur, w_S ;. The panel to the left displays the mean result for each sample as a function of sample identifier; the panel to right displays the mean result for each measurement run as a function of analysis date. The error bars represent (mean ± standard deviation). The solid horizontal lines represent the mean of the results displayed within each panel; the dashed lines bound the interval (mean ± standard deviation).

The daily values for C in the 23-Jan-2020 session have been corrected for a positive bias. The w_C for this session were higher than expected for the SRM 2693a set A samples, the SRM 2693 controls, and the graphite controls. While the cause is unknown, the consistency of the bias across the three materials suggests that the C measurements for this session were not well calibrated. Since the graphite carbon purity and its upper bound was known with a high degree of confidence, the daily w_C were corrected by a factor based on the WDXRF-determined w_C of the graphite (99.972 ± 0.012) % divided by the measured w_C for the graphite in the session (100.268 %).

The bias-corrected standard uncertainty for C was calculated from a combination of two factors. The first and largest factor is the difference between the WDXRF and combustion values for $w_{\rm C}$, divided by $\sqrt{3}$ to convert the rectangular difference into a standard uncertainty. The second factor is the estimated standard uncertainty of the WDXRF $w_{\rm C}$. The bias-correction uncertainty is then combined with the uncertainty generated from the parametric bootstrap method. Although the bias correction provides more realistic results for the 23-Jan-2020 session, the corrected result has a relatively large uncertainty.

5.1.3.3. Summary of Results: SRM 2693a

Carbon results show generally good agreement with CANSPEX results; however, they are slightly lower than the PGAA results. Hydrogen results are slightly higher than CANSPEX and PGAA results, but there is significant overlap in the uncertainty intervals between the determined and reported results. Both nitrogen and sulfur results show good agreement with CANSPEX and PGAA results. The results for CHN do not indicate any trend or difference between the values for the test portions taken from the three different sets (A, B, and C).

Both sets of sulfur determinations were performed on test portions taken from set A only so no comparison with sets B or C is made for sulfur.

5.1.3.4. Summary of Results: SRM 2693 Control

Compared to the CANSPEX ILS value on the certificate, the carbon, hydrogen, and nitrogen results show excellent agreement, and sulfur shows good agreement with the certified value.

5.1.3.5. Summary of Results: Graphite Control (Carbon Only)

For one run, the carbon results for graphite, candidate SRM 2693a, and SRM 2693 are all high so that a bias-corrected value can be calculated based on the known graphite purity. The consensus carbon result for five runs is slightly higher than the graphite purity; however, the uncertainty interval of those results overlaps both the reported purity value and its uncertainty interval.

5.1.3.6. Uncertainty Components

Table 14 lists the known sources of uncertainty and the range of their influence in the daily analyses.

	Variance ^a	
Component	Proportion, %	Explanation
Instrument	1.8 to 91.4	Replication uncertainty calculated based on normalizing the instrument
signal	1.0 10 74.4	signal to the test portion mass.
Calibration Y	0.3 to 95.0	Estimated from the imperfect fit of the calibration curve.
Drying correction < 0.01 to 51.9		Uncertainty of the correction to a dry mass fraction based on the loss on drying (LOD). A LOD mass fraction for each bottle sampled is drawn from a shifted and scaled Student's <i>t</i> -distribution. The shift is the mean LOD mass fraction and the scale is the standard deviation of the LOD mass fraction, taken across bottles.
Calibration X	0.1 to 3.2	Estimated from the C, H, N, and S confidence intervals in the SRM 143d COA [8] and the calibration standards' mass determination.
Test portion mass	< 0.01 to 2.2	Estimated from the mass determination of the analytical test portions.
Element mass ^b	< 0.01 to 1.7	Transformation of the Monte Carlo sampling of the calibration curve and the instrument signals to determine Monte Carlo samples of the masses of the elements measured.
Non- linearization ^b	< 0.01	Conversion from an as-is mass to a dry mass fraction of the test portion uses a non-linear transformation. This transformation can impart a very small uncertainty into the value of final mass fraction.

 Table 14. Sources of Uncertainty.

^a The range of proportions of the total variance for each element in each daily run over all runs.

^b A linear approximation of the measurement process is used to apportion variability. If the approximation is reasonable, these terms will all be small. If these terms are large, the apportionment is questionable.

The results are calculated both with and without a heterogeneity component. For carbon, nitrogen, and sulfur in candidate SRM 2693a, the results assuming no heterogeneity are

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discussed because no heterogeneity was detected for CNS in the WDXRF homogeneity assessment at estimated masses less than the test portion mass used for this ROA. For hydrogen in candidate SRM 2693a, results assuming heterogeneity are discussed because no information on heterogeneity is available. For carbon in the graphite, the results assuming no heterogeneity are discussed because the carbon fraction is nearly 100 %. For carbon, hydrogen, and nitrogen in SRM 2693, the results assuming heterogeneity are discussed because no information on heterogeneity for the test portion mass used is available. For sulfur, the results assuming heterogeneity are discussed because, according to the certificate of analysis (COA), "observed sulfur and mercury variations by isotope dilution methods were greater than expected for the analytical technique" and the use of a prediction interval for the certified value incorporates a heterogeneity component [1].

The uncertainty in these determinations has been minimized by carefully controlled sample preparation and mass determination, as well as an experimental design in which the test portions all have the same nominal mass. Minimizing the variation in the test portion masses can help decrease the uncertainty driven by sample carryover. Careful sample preparation and accurate mass determination also helps to minimize uncertainty contributions from other sources of uncertainty.

The two most important sources of uncertainty typically are the instrument signal (replication uncertainty) and calibration *Y* (imperfect fit of the calibration curve due to measurement bias and/or model choice). The absolute magnitude of the contributions from these two sources tend to decrease with increasing detector signal, since higher signal to noise ratio leads to more precise measurements and a more representative calibration curve. In general, the drying correction is a minor uncertainty source, although it is more significant for carbon compared to H, N, and S. The absolute value of the drying correction uncertainty for all the elements tends to stay within a fairly consistent range so that a lower contribution from calibration *Y* results in a higher relative contribution for the drying corrections. The low relative contributions from calibration *X* and sample mass reflect the carefully controlled sample preparation and mass determinations, as well as an experimental design in which the test portions all have the same nominal mass. Minimizing the variation in the test portion masses helps decrease measurement bias from sample carryover.

The negligible proportion attributable to the residual term is a useful indication that the linear decomposition used to apportion uncertainty contributions is fit-for-purpose.

The absolute magnitude of the of the calibration *Y* uncertainty contributions tends to decrease with increasing detector signal area, most likely as a result of the higher signal to noise ratio leading to a better fit to the calibration curve to the data. However, other factors, such as quality of the fit and the overall scatter of the data may increase the calibration *Y* uncertainty.

5.1.3.7. Daily Consensus Results

Consensus values were calculated from the results of each session. The parametric bootstrap method was used to calculate the uncertainties. The results were calculated assuming no heterogeneity and with heterogeneity. Table 15 lists the consensus values for C and H for each session; Table 16 lists the consensus values for N; and Table 17 lists the values for S.

	Carbon Mass Fraction, w _C , %					Hydrogen Mass Fraction, <i>w</i> _H , %				
Date	WC	u^{a}	$U_{95}{}^{\mathrm{a}}$	u^{b}	$U_{95}{}^{\mathrm{b}}$	W_{H}	u^{a}	$U_{95}{}^{\mathrm{a}}$	u^{b}	$U_{95}{}^{\mathrm{b}}$
06/26/2019	79.820	0.052	0.101	0.108	0.238	4.474	0.024	0.046	0.040	0.081
09/19/2019	79.798	0.047	0.087	0.099	0.212	4.437	0.035	0.067	0.038	0.075
01/23/2020	79.850	0.129	0.260	0.178	0.371	4.450	0.021	0.042	0.034	0.069
02/06/2020 ^c	79.805	0.096	0.182	0.205	0.433	4.634	0.020	0.039	0.029	0.057
02/06/2020 ^d	79.681	0.073	0.140	0.185	0.359	4.616	0.024	0.049	0.040	0.086
12/03/2020	79.857	0.037	0.069	0.085	0.156	4.287	0.012	0.025	0.016	0.034
01/14/2021	79.928	0.047	0.093	0.132	0.271	4.339	0.011	0.023	0.019	0.040

 Table 15. Carbon and Hydrogen Mass Fraction Consensus Summaries, %.

^a Uncertainties based on the assumption that the sample results are homogeneously distributed.

^b Uncertainties include a component of between-sample inhomogeneity.

^c Results for the ten set B bottles.

^d Results for the six set C bottles.

Table 16. Nitrogen Mass Fraction Consensus Summaries, %.

Date	WN	u^{a}	$U_{95}{}^{\mathrm{a}}$	u^{b}	$U_{95}{}^{\mathrm{b}}$
06/26/2019	1.1872	0.0033	0.0065	0.0040	0.0079
09/11/2019	1.1883	0.0013	0.0026	0.0028	0.0062
09/19/2019	1.1731	0.0073	0.0142	0.0084	0.0160
01/14/2020	1.1984	0.0018	0.0037	0.0044	0.0093
01/23/2020	1.2015	0.0154	0.0303	0.0171	0.0332
02/06/2020 ^c	1.1820	0.0160	0.0302	0.0167	0.0312
02/06/2020 ^d	1.1797	0.0156	0.0308	0.0157	0.0309
12/03/2020	1.1768	0.0052	0.0102	0.0058	0.113
01/14/2021	1.1699	0.0045	0.0088	0.0049	0.0095

^a Uncertainties based on the assumption that the sample results are homogeneously distributed.

^b Uncertainties include a component of between-sample inhomogeneity.

- ^c Results for the ten set B bottles.
- ^d Results for the six set C bottles.

Table 17. S	Sulfur Mass	Fraction	Consensus	Summaries,	%.
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Date	WS	u^{a}	$U_{95}{}^{\mathrm{a}}$	u^{b}	$U_{95}{}^{\mathrm{b}}$
09/11/2019	0.3009	0.0080	0.0156	0.0085	0.0166
01/14/2020	0.3387	0.0061	0.0121	0.0028	0.0209

^a Uncertainties based on the assumption that the sample results are homogeneously distributed.

^b Uncertainties include a component of between-sample inhomogeneity.

The source of the between-sample inhomogeneity component is more properly characterized as unexplained "dark" uncertainty. In addition to true between-sample differences in composition, it may include contributions from under-characterized sources of measurement bias and imprecision.

5.1.3.8. NICOB Combined Results

Consensus results obtained using the DerSimonian-Laird [16] estimator as implemented in NICOB [14] for C, H, N, and S in the 2693 control material were in excellent agreement with the values provided in its COA [1].

Table 18 summarizes the DerSimonian-Laird consensus results for CHNS in SRM 2693a. NICOB graphical summaries are displayed in Fig. 12.

	Results	homogene	ously dist	ributed	Results include inhomogeneity			
Element	W	и	$ au^{\mathrm{a}}$	U_{95}	W	u ^c	$ au^{\mathrm{a}}$	U_{95}
Carbon, <i>w</i> _C :	79.831	0.028	0.043	0.068	79.832	0.046	0	0.091
Hydrogen, w _H :	4.46	0.052	0.135	0.10	4.46	0.054	0.138	0.11
Nitrogen, w_N :	1.1842	0.0036	0.0084	0.0070	1.1838	0.0037	0.0081	0.0067
Sulfur, ws:	0.320	0.019	0.026	0.037	0.319	0.019	0.025	0.037

Table 18	NICOB	Mass F	- raction	Consensus	Estimates,	%.
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^a Dark uncertainty (unexplained variance) [15].



Fig. 12. NICOB Evaluations.

These panels display the NICOB analyses of the daily consensus estimates of the carbon, hydrogen, nitrogen, and sulfur mass fractions: $w_{\rm C}$, $w_{\rm H}$, $w_{\rm N}$, and $w_{\rm S}$. Each solid circle represents a daily result, the dark thick error bars the standard uncertainty without considering run-to-run variability (τ , dark uncertainty), the lighter error bars the standard uncertainty including the dark uncertainty component. The horizontal line represents the DerSimonian-Laird method consensus value, the yellow interval represents the estimate's standard uncertainty.

5.2. C, H, N, and S by Prompt Gamma-Ray Activation Analysis (PGAA)

Samples, standards, and controls were analyzed using both the vertical tube (VT)5 thermal neutron prompt gamma-ray activation analysis (TNPGAA) instrument and the neutron guide (NGD) cold neutron prompt gamma-ray activation analysis (CNPGAA) instruments located at the NIST Center for Neutron Research (NCNR) [17,18,19]. Although TNPGAA has ample sensitivity to measure H in these samples with good counting statistics with short irradiations, C, S, and N do not give good counting statistics at the levels to be measured without much longer irradiations.

The NGD cold neutron PGAA instrument has 15 to 20 times better sensitivity than the VT5 instrument, hence elemental mass fractions can be measured in a fraction of the time necessary for TNPGAA. However, elemental sensitivities are difficult to calibrate in hydrogenous targets for CNPGAA because of the energy change of cold neutrons in a room temperature target [20]. The CNPGAA element sensitivity ratios are not affected by differences in neutron scattering power and sample geometry [21]. Using a combination of CNPGAA to determine ratios of C, N, and S to H and TNPGAA to determine H enables taking advantage of the improved sensitivity of CNPGAA without having to calibrate all elemental sensitivities for H mass fraction.

Five glass bottles of SRM 2693a were received for analysis. Four bottles of SRM 2693 we received for use as a control. SRM 143d Cystine [8], SRM 912b Urea [22], SRM 920 D-Mannitol [23], and 100 mesh graphite powder (Spectrographic Services, Sussex, NJ) were used as standards.

5.2.1. Sample Preparation

Bottles were inverted and rotated to mix the material before sampling. All mass measurements were performed using an analytical balance, with calibration verified using calibrated masses.

For H by TNPGAA, two aliquots of SRM 2693a and one of SRM 2693 each having a mass of \approx 750 mg were removed from each bottle and pressed into 12.7 mm diameter pellets using a stainless-steel die and hydraulic press at 44 000 Newtons (10 000 pounds) force for (3 to 5) s. The mass of each pellet was then determined to \pm 0.01 mg using an analytical balance and sealed into a bag of fluoroethylene propylene (FEP) film.

For C/H, N/H, and S/H ratios by CNPGAA, two aliquots of SRM 2693a and one of SRM 2693, each with a nominal ≈ 1.5 g mass, were removed from each bottle, and similarly pressed. The mass of each pellet was then determined to ± 0.01 mg using an analytical balance and the pellet was wrapped in aluminum foil. Aluminum foil was used to package samples instead of the usual FEP packaging, in order to avoid correction for carbon background from neutron capture. Each foil was at least 8 cm long, with the sample wrapped approximately in the center, so that the sample pellet could be mounted in the sample holder with the FEP strings out of the neutron beam and not visible to the detector, thus avoiding carbon background from the strings.

The TNPGAA standards were prepared by transferring known masses of urea and graphite into a mixing vial and shaking them for approximately 20 minutes in a mixer mill. Previous analyses of the graphite powder by PGAA indicated a negligible amount of hydrogen, NIST SP 260-230 January 2024

therefore drying of the powder was not necessary. Because of the large neutron scattering cross section of hydrogen (80 b), sensitivities in counts per second per mg, cps/mg, of elements present in hydrogenous targets (samples, standards, controls) are dependent on both the hydrogen mass fraction and geometry of the target [24,25]. In order to match the neutron scattering power and geometry of the samples, pellets were prepared that gave roughly the same hydrogen count rate as the samples, and that were also similar in thickness. Pellets were prepared using a stainless steel die and hydraulic press and were sealed into bags of 0.025 mm (1 mil) thickness FEP for analysis.

Standards for measuring S/H sensitivity by CNPGAA were prepared from mixtures of cystine, urea, and graphite. Approximately 1 g portions were pelletized as described above and sealed into bags of FEP. Urea was used to determine the N/H sensitivity. Pellets having a mass between 700 mg and 900 mg were analyzed. Standards for measuring C/H sensitivity were prepared from a mixture of graphite and D-mannitol; pellets having a mass of 1.5 g were analyzed. These standards were wrapped in aluminum foil as described above. For comparison, two of the urea/graphite TNPGAA pellets were repacked in aluminum foil and used as C/H standards for CNPGAA. C/H ratios measured using the two sets of standards agree.

Table 19 summarizes the C/H, N/H, and S/H sensitivity ratios as determined by CNPGAA analysis of the prepared standards. The element measurements were recorded in units of counts per second per milligram (cps/mg); the ratios are in units of (cps/mg)E/(cps/mg)H where "E" represents C, N, or S.

(cps/mg) _E /(cps/mg) _H								
Standard	C/H	N/H	S/H					
1	5291	943.4	15.95					
2	5255	940.1	16.10					
3	5255	932.6	16.34					
4	5284	942.1	15.99					
5	5292	938.9	15.91					
6	5259							
Mean:	5273	939.4	16.06					
SD:	18	4.2	0.17					
RSD%:	0.34	0.45	1.08					

Table 19. Carbon, Nitrogen, and Sulfur CNPGAA Sensitivity Ratios.

5.2.2. Methods

Hydrogen was determined using TNPGAA data alone. Targets (samples, standards, controls) were irradiated by thermal neutrons from the reactor core in an aluminum sample chamber in air, with samples mounted in FEP strings strung between the prongs of an aluminum fork. The gamma-ray detection system consists of a lead-shielded high-purity germanium detector in conjunction with a digital signal processor (DSP). Prompt gamma spectra up to 10 MeV were collected on a computer workstation using software. Samples and H standards were irradiated for at least 20 minutes to obtain counting statistics of 0.3 % or better for hydrogen. A titanium foil was irradiated at regular intervals in order to monitor any variation in the

neutron fluence rate and sample positioning within the beam over the course of the investigation.

The C/H, N/H, and S/H ratios were determined using CNPGAA. Targets were irradiated by cold neutrons moderated by passage through liquid hydrogen, with targets again mounted between FEP strings in an aluminum sample chamber. The FEP strings were placed at least 8 cm apart to keep them out of the neutron beam and not visible to the detector, avoiding correction for carbon background. Samples and controls were irradiated for at least 24 hours in order to obtain good counting statistics (< 0.3 % for C and S, < 1 % for N). Irradiation times for standards ranged from 10 minutes to several hours. In order to avoid correcting the nitrogen count rates for atmospheric nitrogen (a significant correction), targets were irradiated in vacuum. The irradiation in a vacuum presented a problem for coal samples, since prolonged exposure to vacuum resulted in moisture loss (by vacuum drying) in the pellet, resulting in low H count rates. To correct this problem for each sample or control pellet, a short (5 minute) irradiation in vacuum, adequate to obtain good counting statistics for hydrogen was first performed in order to measure the H count rate before the long irradiation with vacuum drying. The short irradiation was followed by the longer 24 hour irradiation to obtain good counting statistics for the other elements. To test whether the short 5 minute irradiation would result in any significant mass loss, the masses of three SRM 2693a pellets were measured before and after a five minute period in the evacuated sample chamber. Negligible mass loss was found for each sample. The ratio of C, S, and N to hydrogen was then corrected for the change in H count rate between the short and long irradiations.

Prompt gamma-rays for CNPGAA were measured using a lead-shielded high-purity germanium detector in conjunction with a DSP. The signal was gated with a bismuth germanate Compton shield, which sits around the germanium detector, in order to reduce signal-to-baseline ratio by gating out Compton scattered gamma rays. Gamma-ray spectra up to 11 MeV were collected on a computer workstation using software for the DSP. Both Compton-suppressed and unsuppressed spectra were collected. Hydrogen, carbon, sulfur, and nitrogen gamma ray peaks were integrated using a commercial peak search program, an interactive peak fitting routine, and the SUM4 code which allows a peak region to be hand fitted [26]. Pileup corrections for all peak integrations were unnecessary because hardware pileup was used for both instruments.

For measurement of C/H and S/H ratios, C, H, and S gamma-ray peaks at (3684, 2223, and 841) keV in the Compton suppressed spectrum were analyzed because of the better signal-to-noise ratio. However, the N/H ratio was determined by integration of H and N peaks in the unsuppressed spectra because the best sensitivity for nitrogen was obtained by measuring the 10828 keV peak and its corresponding single and double escape peaks at (10318 and 9807) keV in the unsuppressed spectra using the SUM4 algorithm. At this high energy, the signal-to-noise ratio for nitrogen is not significantly improved by Compton suppression; however, Compton suppression does result in reduction of the escape peaks.

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The TNPGAA H sensitivity in cps/mg is displayed in Fig. 13 as a function of pellet thickness, estimated using the carbon/urea standards. The data were modeled as both linear and logarithmic functions of thickness . Although the logarithmic function gives a somewhat better fit, H sensitivities determined from about 4.6 mm to 4.8 mm thickness agree to within 0.1 % of those determined from the linear plot. The linear fit was used in the determination of the sensitivities.



Fig. 13. Hydrogen Sensitivity as a Function of Pellet Thickness.

The symbols represent results of (pellet thickness, hydrogen sensitivity) measurements. The solid and dashed curves represent linear and logarithmic fits to the data, respectively. The vertical dotted lines bound the approximate range of sample and control pellet thicknesses.

Elemental mass fractions for SRM 2693a samples and SRM 2693 controls were calculated on a dry mass basis. Dry mass was determined by oven drying of ≈ 1 g samples from each bottle for 1 h at 108 °C. Calculation of sample moisture was made by assuming that the entire mass lost on drying was due to H₂O. Table 20 lists the estimated water mass fraction, x_w , expressed as a percent

$$x_{\rm w} = 100(m_{\rm wet} - m_{\rm dry})/m_{\rm wet} = 100(1 - m_{\rm dry}/m_{\rm wet})$$
(3)

and the wet-mass to dry-mass correction factor (drying correction factor)

$$D_{\rm c} = m_{\rm dry}/m_{\rm wet} = 1 - x_{\rm w}/100 \tag{4}$$

where m_{wet} is the as-is sample mass and m_{dry} is the sample mass after drying and 100 is a factor to convert the mass fraction to a percent.

	SRM	2693a		SRM 2693			
Bottle	<i>x</i> _w , %	Dc	Bottle	<i>x</i> _w , %	Dc		
2-1-90	0.972	0.99028	1	0.876	0.99124		
3-2-104	0.978	0.99022	2	0.824	0.99176		
4-7-34	0.938	0.99062	3	0.966	0.99034		
5-2-78	0.814	0.99186	4	0.927	0.99073		
7-1-25	0.827	0.99173	Mean:	0.898	0.99102		
Mean:	0.906	0.99094	SD:	0.061	0.00061		
SD:	0.080	0.00080					

 Table 20. Water Mass Fraction and Drying Correction Factors.

The hydrogen mass fraction, expressed as a percentage, $w_{\rm H}$, determined by TNPGAA, was evaluated using

$$w_{\rm H} = 100 \frac{(C_{\rm H}/S_{\rm Hcal})(\phi_{\rm corr})}{(m_{\rm sa})(D_{\rm c})}$$
(5)

where $C_{\rm H}$ is the count rate in cps for hydrogen in the sample or control, $S_{\rm Hcal}$ is the calibrated hydrogen sensitivity in cps/mg determined from the standards plot, $\phi_{\rm corr}$ is the dimensionless correction for difference in neutron flux between the sample and standards, and $m_{\rm sa}$ is the as-received sample mass in mg, and $D_{\rm c}$ is the drying correction factor.

The mass fraction of each other element in the samples was evaluated by combining the hydrogen mass fraction (uncorrected for H₂O lost on drying) with CNPGAA data

$$w_{\rm E} = w_{\rm H} (C'_{\rm E} / C'_{\rm H}) (S'_{\rm E} / S'_{\rm H})$$
(6)

where w_E is the mass fraction of the other element, w_H is the hydrogen mass fraction, C'_E and C'_H are the count rates of element E and H in the sample or control, and S'_E/S'_H is the sensitivity ratio of the hydrogen to element E, determined from standards.

Since hydrogen was calculated on a dry mass basis, it was necessary to further correct the hydrogen mass fraction to account for hydrogen lost as H₂O upon drying. This "dry" hydrogen mass fraction, expressed as a percentage is calculated

$$w_{\rm Hdry} = 100 \frac{(C_{\rm H}/S_{\rm Hcal})(\phi_{\rm corr}) - (m_{\rm sa})(x_{\rm w}/100)(0.1119)}{(m_{\rm sa})(D_{\rm c})}$$
(7)

where m_{sa} is the wet mass of the sample in mg and 0.1119 is the H mass fraction in water.

During the initial measurements of samples, controls, and standards by CNPGAA, a resolution problem was encountered with the germanium detector due to loss of vacuum in the cryostat, which resulted in a \approx 30 % broadening of the gamma-ray peaks. Thus, resolution of C and S peaks from interference peaks from other elements was less reliable using commercial software in the sample, as was comparison with count rates of C and S in standards since these interferences were absent. The peak broadening was less of a problem for integration of the H peak, which was significantly larger than other peaks in the spectra, and hence had no significant interference peaks. Likewise, integration of the high energy nitrogen peaks was also not a problem in the peak broadened spectra since there are no other

elements that emit gamma rays in this energy region. Hence, adequate results for nitrogen were attained by using N/H ratios obtained from these initial spectra.

To assess the quality of the C/H and S/H ratios measured from the distorted spectra, additional CNPGAA measurements of C, S, and H were performed on sample and control pellets. These measurements were performed after the germanium detector was pumped out to restore vacuum, returning the resolution to its original factory specification. Because of limits on beam time, however, only five samples of SRM 2693a (one sample from each bottle) and 3 pellets of SRM 2693 (one from each of 3 bottles) were measured with the restored resolution.

Both the wet-mass and dry-mass H mass fraction for the SRM 2693 control agree with the consensus result determined in an interlaboratory study reported in the material's COA, as does the nitrogen mass faction. The C and S mass fractions determined using the spectra with good resolution also agree well, but the result for C using the poorly-resolved spectra does not. In all samples, the C and S results using poor resolution CNPGAA spectra are low compared to those obtained using the well-resolved spectra.

5.2.3. Results

Table 21 lists the H mass fraction results, expressed as percent of sample composition, and summary statistics for the SRM 2693a samples. Results are provided for the TNPGAA wet mass measurements and as corrected to the dry mass basis. Table 22 lists the uncertainty components for $w_{\rm H}$, expressed in relative form, and the derived combined and expanded uncertainties. Uncertainties in the determinations discussed in this section are propagated using the Guide to the Expression of Uncertainty in Measurement (GUM) [27] and NIST [28] guidelines for the propagation of uncertainty. The derived uncertainties are expressed in their relative and absolute forms.

Bottle	Wet Mass	Dry Mass
2-1-90 a	4.493	4.392
2-1-90 b	4.541	4.439
3-2-104 a	4.495	4.393
3-2-104 b	4.502	4.400
4-7-34 a	4.461	4.359
4-7-34 b	4.462	4.361
5-2-78 a	4.479	4.377
5-2-78 b	4.429	4.328
7-1-25 a	4.495	4.393
7-1-25 b	4.483	4.381
Mean:	4.484	4.382
SD:	0.030	0.029
RSD%:	0.66	0.67

Table 21. Wet- and Dry-Mass Hydrogen Mass Fractions, *w*_H, %.

	Wet M	lass	Dry N	A ass
Uncertainty Source	$u_{\rm rel}{}^{\rm a}$	v^{b}	$u_{\rm rel}{}^{\rm a}$	v^{b}
H sensitivity calibration	0.3	9	0.3	9
Neutron fluence rate & Sample positioning	0.25	24	0.25	24
Replication	0.22	9	0.21	9
H from moisture correction	0.2	4	0.2	4
Peak integration	0.2	60	0.2	60
Purity of standards	0.05	60	0.05	60
Dry mass determination			0.003	4
Standard uncertainty, u_{rel}^{a} :	0.53	45	0.53	45
Coverage factor:	2.014		2.014	
Expanded uncertainty, U_{95rel}^{a} :	1.07		1.06	
Standard uncertainty, u ^c :	0.024		0.023	
Expanded uncertainty, U_{05}^{c} :	0.048		0.047	

^a Relative uncertainty.

^b Degrees of freedom.

^c Absolute uncertainty, the product of the mean value and the relative uncertainty, divided by 100.

Table 23 lists the C, N, and S mass fraction results, expressed as percent of sample composition, and summary statistics. Since spectral interferences were not a problem for nitrogen or hydrogen, nitrogen was evaluated using the poorly resolved gamma-ray spectra. The C and S mass fractions are provided as determined from both the initial poorly-resolved and the subsequent subset of well-resolved spectra. Both the C and S results from the poorly-resolved spectra are on average ≈ 2 % smaller than those from the well-resolved spectra. These smaller values may result from incompletely resolved interference peaks.

	WC	, %	w _N , %	ws,	%
Bottle	Poor ^a	Good ^b	Poor ^a	Poor ^a	Good ^b
2-1-90 a	78.09		1.170	0.3295	
2-1-90 b	80.35	81.46	1.187	0.3304	0.3394
3-2-104 a	80.85		1.175	0.3297	
3-2-104 b	80.22	82.56	1.168	0.3261	0.3346
4-7-34 a	80.74	81.18	1.167	0.3298	0.3316
4-7-34 b	80.77		1.185	0.3268	
5-2-78 a	78.71	81.29	1.179	0.3299	0.3338
5-2-78 b	80.29		1.159	0.3216	
7-1-25 a	78.15		1.169	0.3305	
7-1-25 b	81.19	81.18	1.189	0.3273	0.3329
Mean:	79.9	81.53	1.175	0.3282	0.3345
SD:	1.2	0.59	0.010	0.0028	0.0030
RSD%:	1.46	0.72	0.84	0.85	0.89

Table 23. Carbon, Nitrogen, and Sulfur Mass Fractions.

^a Results derived from poorly-resolved spectra.

^b Results derived from well-resolved spectra.

Table 24 lists the uncertainty components for *w*_C, *w*_N, and *w*_S, expressed in relative form, and the derived combined and expanded uncertainties. The derived uncertainties are expressed in their relative and absolute forms.

		wc, %			<i>w</i> _N , %		<i>w</i> _S , %				
	Poo	Poor ^a		Good ^b P		Poor ^a		Poor ^a		Good ^b	
Uncertainty Source	$u_{\rm rel}^{\ c}$	v^{d}	$u_{\rm rel}^{\ c}$	v^{d}	$u_{\rm rel}^{\ c}$	v^{d}	$u_{\rm rel}^{\rm c}$	v^{d}	$u_{\rm rel}^{\ c}$	v^{d}	
Replication	0.462	9	0.322	4	0.264	9	0.269	9	0.398	4	
Sensitivity ratio determination	0.341	5	0.341	5	0.20	4	0.478	4	0.478	4	
Normalization to $w_{\rm H}$	0.53	46	0.53	46	0.53	46	0.53	46	0.53	46	
Purity of standards	0.1	60	0.1	60	0.2	60	0.2	60	0.2	60	
Peak integration	0.1	60	0.1	60	0.1	60	0.1	60	0.1	60	
Standard uncertainty, $u_{\rm rel}^{\rm c}$:	0.794	41	0.722	42	0.664	72	0.795	25	0.847	24	
Coverage factor:	2.020		2.024		1.993		2.060		2.064		
Expanded uncertainty, U_{95rel}^{c} :	1.60		1.46		1.32		1.64		1.75		
Standard uncertainty, <i>u</i> ^e :	0.63		0.59		0.0078		0.0026		0.0028		
Expanded uncertainty, U_{95}^{e} :			1.19		0.016		0.0054		0.0058		

^a Results derived from poorly-resolved spectra.

^b Results derived from well-resolved spectra.

^c Relative uncertainty

^d Degrees of freedom

^e Absolute uncertainty, the product of the mean value and the relative uncertainty, divided by 100.

Table 25 provides a brief explanation of the uncertainty components in the TNPGAA determination of w_H and the combined TNPGAA and CNPGAA determinations of w_C , w_N , and w_S .

Uncertainty Source	Explanation
H sensitivity calibration (S_{Hcal})	Determined by comparison of H sensitivities determined using the calibration curve using freshly prepared graphite/SRM 912b pellets with those determined from a previously prepared set of five graphite/urea standards. Sensitivities determined using the two sets differed by about 1 %; the standard relative uncertainty was estimated the difference divided by $\sqrt{12}$.
Neutron fluence rate & Sample positioning (ϕ_{corr})	RSD%/ \sqrt{n} of repeated measurements of titanium foil. ^a
Replication	RSD%/ \sqrt{n} of repeated measurements of samples. ^a
H from moisture correction (x_w)	RSD%/ \sqrt{n} values from mass loss on drying (LOD) measurements. ^a
Peak integration	Estimated from results of peak integration by two methods.
Purity of standards	Estimated as standard uncertainties from material purity specifications. For SRMs, the standard uncertainties are estimated as one-half of the expanded uncertainty.
Dry mass determination (D_c)	RSD%/ \sqrt{n} values from mass loss on drying (LOD) measurements. ^a
Sensitivity ratio determination $(S'_{\rm E}/S'_{\rm H})$	RSD%/ \sqrt{n} from replicate measurements of each sensitivity ratio. ^a
Normalization to <i>w</i> _H	Standard relative uncertainty, $u_{\rm rel}$, of $w_{\rm H}$ measurements.

Table 25. Explanation of PGAA Uncertainty Components.

^a n is the number of measurements.

5.3. AI, Br, Ca, CI, Dy, Mn, Na, Ti, and V by Instrumental Neutron Activation Analysis (INAA)

Instrumental Neutron Activation Analysis (INAA) was used to determine the mass fractions of Al, Br, Ca, Cl, Dy, Mn, Na, Ti, and V in SRM 2693a. The comparator INAA method used for these elements is designed for nuclides with relatively short half-lives.

While F and Mg were requested analytes, the 11 s half-life of ²⁰F is too short for current sample loading/unloading procedures and Mg was not detectable because of a high background signal.

Bromine is a challenging element to measure as it has a meta-stable state that feeds into its detectable isotope, which results in the requirement to measure the standards and samples after the exact same amount of decay. The relatively high Al mass fraction of SRM 2693a causes an increase in the background near the ^{80m}Br peak. Typically, three detectors are used so that one can be dedicated to measuring the Ti flux monitors, but because of electrical issues only two detectors were operable. Without a dedicated Ti detector, it was not possible to measure the standards and samples after the exact same decay time to correct for any ^{80m}Br decaying to ⁸⁰Br. A separate irradiation, two months after the initial irradiation, was carried out on the previously irradiated samples for Br measurement. The two-month delay ensured that all ⁸²Br activated in the initial irradiation had decayed and would not interfere in the measurement.

Established irradiation and counting procedures were used for samples, controls, and standards.

5.3.1. Sample Preparation

Two bottles from each of the five sublots of SRM 2693a were analyzed. Samples were prepared in nominally 250 mg aliquots. Controls consisted of two aliquots from three containers each of SRM 1632e Trace Elements in Coal (Bituminous) [29] and SRM 2682c Subbituminous Coal (Nominal Mass Fraction 0.5 % Sulfur) [30].

SRM 2693a and control samples were placed in high density polyethylene vials and sealed with snap-caps. While prior SRM analyses used a die and press to create pellets, vials have the advantage in that they do not break during irradiation and keep their geometry throughout the experiment. Additionally, standards and samples have the exact same irradiation and counting geometries which reduces the corrections required and their resulting uncertainties.

Four standard solutions were used, previously prepared from high-purity SRM compounds and solutions:

- "S318", a combination of SRMs 3101a Aluminum (Al) [31], 3114 Copper (Cu) [32], 3132 Manganese (Mn) [33], and 3165 Vanadium (V) [34]. The Cu component was not relevant to the present analysis.
- "Ca/Mg/Dy 19", a combination of SRMs 3109a, Calcium (Ca) [35], 3115a Dysprosium (Dy) [36], and 3131a Magnesium (Mg) [37].
- "NaCl19", prepared from SRM 919b Sodium Chloride (NaCl) [38]
- "Br19", prepared from SRM 3184 Bromide Anion (Br) [39]

These solutions were dispensed by mass into polyethylene vials filled with cellulose of the same geometry as the samples and allowed to air-dry in a fume hood overnight. After the vial contents had dried, the vials were closed with their snap-caps and were ready for irradiation.

SRM 1632e is certified for Ti mass fraction and was used as the Ti standard for the SRM 2693a measurements. High-purity Ti foils irradiated during these measurements were not used as Ti standards because of the difference in geometries between the thin foil (disk form of 0.03 mm thick, 3 mm diameter) versus the larger polyethylene vial containing the coal powder.

High-purity Ti foil standards were used as neutron-flux monitors during the first irradiations. High-purity Fe foil standards of the same dimension were used for the second irradiations. A disk was included in each irradiation between the standard and sample vial.

Calibrated analytical balances were used to measure sample and/or standard masses. Balance calibration was verified prior to use.

5.3.2. Method

A dry-mass correction factor for SRM 2693a was determined by LOD of nominal 1 g test portions taken after the first INAA aliquot and immediately before the second. Table 26 lists the measured water mass fraction expressed as percent of sample mass (x_w , Eq. (3) and the drying correction factor (D_c , Eq. 4) for the samples from the ten bottles.

Bottle	n^{a}	<i>x</i> _w , %	Dc
2-1-90	3	0.927	0.99073
2-8-6	1	1.046	0.98954
3-1-102	1	1.129	0.98871
3-2-104	1	1.098	0.98902
4-1-49	2	1.165	0.98835
4-7-34	1	1.010	0.98990
5-2-78	2	1.042	0.98958
5-5-40	1	0.995	0.99005
7-1-25	1	0.998	0.99002
7-7-87	2	1.046	0.98954
Ν	lean:	1.046	0.98954
	SD:	0.070	0.00070

 Table 26. Water Mass Fraction and Drying Correction Factor.

^a Number of 1 g test portions evaluated.

The first irradiations were carried out for 60 s in the RT-2 pneumatic facility of the NIST Research Reactor. Each analytical and control sample was irradiated with a Ti foil disk between the standard and sample vials. The set of material to be irradiated was positioned at the middle of the cylindrical irradiation vessel with the vials oriented perpendicular to the longitudinal axis of the vessel. The linear neutron flux gradient in irradiations were determined using two additional Ti foils on the ends of the sample packet.

The second irradiation, two months after the first, was carried out on the previously irradiated samples for Br measurement. The vials were arranged into six columns of approximately nine vials each and high-purity Fe foil disks were placed between each vial to serve as a flux monitor. The columns were loaded into 3 rabbits with each rabbit containing 2 columns. The rabbits were irradiated for 30 min, flipped, and another 30 min. The flip was to correct for a known neutron gradient present in the rabbit tubes.

Table 27 lists the relevant nuclear and experimental parameters for the INAA assay of Al, Br, Ca, Cl, Dy, Mg, Mn, Na, Ti, and V [40].

Element,	Half	Gamma Energy	Count,	Detector	Number
Nuclide	Life	KeV	Decay	Geometry	Standards
Al, ²⁸ Al	134 s	1778.97	10 min, 5 min	Astrid, 20 cm	4
V, ⁵² V	225 s	1343.07	10 min, 5 min	Astrid, 20 cm	4
Ti, ⁵¹ Ti	345.6 s	320	10 min, 5 min	Astrid, 20 cm	6
Ca, ⁴⁹ Ca	523 s	3084	10 min, 5 min	Astrid, 20 cm	6
Mg, ²⁷ Mg	568.48	1014.42	10 min, 5 min	Astrid, 20 cm	6
Cl, ³⁸ Cl	37 m	1642.59	15 min, 10 min	Elias, 10 cm	5
Dy, ¹⁶⁵ Dy	2.3 h	362	15 min, 10 min	Elias, 10 cm	6
Mn, ⁵⁶ Mn	2.6 h	1810.77	15 min, 10 min	Elias, 10 cm	4
Na, ²⁴ Na	15 h	1368.6	15 min, 10 min	Elias, 10 cm	5
Br, ⁸² Br	35 h	776	2 h, 2 days	Alena, 0 cm	6

I ADIE ZI . INUCIENI ANU EXDEMINENTAL FALAMETERS	Table 27	Nuclear and	d Experimental	Parameters.
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The Elias and Astrid detectors were controlled by DSPs. These detectors were employed for the assay of short-lived nuclides in samples with high overall count rates and were therefore operated in loss-free counting mode. This mode is designed to accurately account for dead-time drops during data acquisition when measuring multiple radionuclides with variable half-lives.

The shaping times of the Elias and Astrid detector were set at 6 μ s and 3 μ s, respectively, and the gamma-energy range for both was 13 keV to 3000 keV. The detectors had their loss-free counting modules optimized by determining the peak area of a low activity ¹⁵²Eu source by itself and with a pulse generator, with and without the presence of a high-activity source (irradiated Mo foils). The loss-free counting module was adjusted until the 1408 keV ¹⁵²Eu peak had the same area when counted for 5 minutes by itself and with the high-activity source. The high-activity source created count rates > 80 000 cps, approximately equal to the highest count rate encountered in the samples analyzed.

The Alena detector was also controlled by a DSP. A sample changer was used to analyze and load the samples. The samples and Fe foils were counted on-contact with the detector head and had dead-times below 20 % which did not require any pulse-pileup corrections.

Gamma-ray spectrum evaluation was conducted using a neutron-activation analysis software package [41]. Peak identifications and area calculations for each spectrum were done with the program ND-PEAK V16.9. Peak area calculations were checked with an interactive peak-fitting utility. All gamma-ray count rates for samples and standards were corrected for radioactive decay between the end of irradiation and the start of count and for radioactive

decay during data acquisition. Gamma lines were chosen so there would be no interferences from potential fission products.

Command files were used to direct the quantitative evaluation by first calculating massic count rates for each element based on the irradiated standards. Massic count-rate values and statistical uncertainties for multiple standards were combined and propagated to yield one value and associated uncertainty for each of one or more gamma-ray lines in each element being assayed. Uncertainties in the determinations discussed in this section are propagated using the GUM [27] and NIST [28] guidelines for the propagation of uncertainty. Count rates of the elements in the samples were compared to those of the standards for the calculation of elemental mass fractions. The resulting elemental mass fraction values were exported to a spreadsheet for the final statistical evaluation.

Manual peak-fitting was required for Cl, Ca, and Mn because of poor peak intensity and resolution. The Br data itself required some manual peak-fitting to account for adjacent peaks that the software did not correctly identify. Uncertainty was calculated by the peak fitting program and input into the uncertainty propagation manually.

The following is the general-use equation for propagating uncertainties for mass fraction determination using INAA [42]. There are uncertainty sources included in the equation that are relevant to this analysis.

$$w_{\rm E(unk)} = \frac{w_{\rm E(std)} m_{\rm std}}{m_{\rm unk}} \left(\frac{A_{0({\rm unk})}}{A_{0({\rm std})}}\right) R_{\theta} R_{\varphi} R_{\sigma} R_{\varepsilon} \left(1 - \frac{m_{\rm E(blank)}}{m_{\rm E({\rm unk})}}\right)$$
(8)

where:	WE(unk)	mass fraction of element E in the unknown sample (mg/kg).
	WE(std)	mass fraction of element E in the comparator standard (mg/kg).
	<i>M</i> std	total mass of the comparator standard (mg).
	<i>M</i> unk	total mass of the unknown sample (mg).
	$A_{0(unk)}$	decay corrected count rate of the unknown sample (cps). This uncertainty is
		accounted for in the sample measurement replication.
	$A_{0(std)}$	decay corrected count rate of the comparator standard (cps). This
		uncertainty is accounted for in the standard measurement replication.
	Rø	ratio of isotopic abundances for the unknown and standard. This ratio is
		typically not mentioned because the isotopic abundances for most elements
		are identical, thus the uncertainty contribution is significantly less than
		other sources.
	R_{arphi}	ratio of neutron fluences. This uncertainty includes contributions from
		neutron self-shielding and irradiation geometries.
	R_{σ}	ratio of effective cross sections between comparator and sample. This ratio
		is usually never an issue unless neutron shielding in a sample causes the
		neutron energy spectrum to change between the samples and comparators;
	_	which would be a rare event.
	R_{ε}	ratio of counting efficiencies between the standard and sample. <i>This</i>
	maalla	uncertainty is accounted for in counting geometry and photon attenuation.
	$\frac{m_{\rm E}({\rm blank})}{m_{\rm E}({\rm unk})}$	mass of element E in the blank divided by the mass of E in the unknown.
	···•E(uiik)	This is a relative correction factor for the contribution of the blank on the
		total mass fraction (mg/mg). This uncertainty is typically not reported

unless a blank correction is performed. Blanks only become an issue when the samples and standards are packaged differently and elements which are known to exist in blank materials are being reported. A correction factor for the blank contribution was required for Al, Br, and Cl.

The results for the SRM 1632e and SRM 2682c control samples results agree with their certified and reference values, within the limits of the measurement uncertainties. However, because SRM 1632e was used as the Ti standard and the SRM 2682c certificate does not list a Ti mass fraction, there is no bias assessment for the Ti SRM 2693a measurements.

5.3.3. Results

Table 28 lists the mass fraction values for each element quantitatively determined by the INAA procedure. Magnesium had a high detection limit of 600 mg/kg that was driven by the background from the relatively high Al mass fraction and no Magnesium was detected above that detection limit.

The Cl value for sample 2-1-90a is 30 % higher than the other Cl values. An investigation showed no difference in peak shape relative to the other samples except for its 30 % increased peak area. The Na value for this sample is consistent with the other SRM 2693a samples, implying that this is not an increase in NaCl. The higher Cl value might have come from contamination by a fragment of KCl during the sample preparation or from the foam inside the rabbit post-irradiation. The Cl value for 2-1-90 1a was not included for the mean calculation for Cl in candidate SRM 2693a.

A blank correction was required for both Al and Cl. Al was present in the polyethylene vial at approximately 45 mg/kg, which had to be subtracted out from the standards and samples. However, the intensity of Al in the samples and standards were such that the correction did not impart a significant increase to the overall uncertainty. The contribution for Cl was at approximately 17 mg/kg, much closer to the mass fraction measured, so the uncertainty of the Cl mass fraction was notably increased.

The Br data was corrected for flux-gradient influences by using the sandwiching Fe foils. The cellulose used for the matrix material in the standard vials had a small (8.67 ± 0.08) mg/kg amount of bromine, which, if not corrected, caused a bias of approximately +6.8 % in the total amount of Br in the standards. An iterative process of correcting for the Br contaminant was carried out a total of four times until the resulting standard constant changed by less than 0.03 %. A blank correction uncertainty component was applied to the final measurement.

Table 29 lists the uncertainty components for *w*Al, *w*Br, *w*Ca, *w*Cl, *w*Dy, *w*Mn *w*Na, *w*Ti, and *w*V, expressed in relative form, and the derived combined and expanded uncertainties. The derived uncertainties are expressed in their relative and absolute forms. Table 30 describes the sources of INAA measurement uncertainty relevant to this study.

	WAI	WBr	WCa		WC	1	WE)y	WN	ĺn	WN	la	WT	i	W	/
Sample	$x_i^{a} u_i^{b}$	x_i^{a} u_i^{b}	x_i^{a} ι	l_i^{b}	x_i^{a}	u_i^{b}	x_i^{a}	u_i^{b}	x_i^{a}	u_i^{b}	x_i^{a}	u_i^{b}	x_i^{a}	u_i^{b}	x_i^{a}	u_i^{b}
2-1-90a	15175 46	0.456 0.037	945 ´	73	98.7°	<i>4.9</i> ^c	1.67	0.13	23.94	0.24	36.71	3.28	1199	27	53.14	0.50
2-1-90b	15068 46	0.422 0.022	944 '	74	60.57	4.02	1.80	0.12	25.80	0.19	35.79	2.28	1141	27	51.92	0.48
2-8-6a	15332 43	0.404 0.023	998	30	59.90	3.90	1.52	0.10	24.44	0.18	34.15	2.34	1221	26	51.79	0.49
2-8-6b	15102 44	0.402 0.024	1039 (55	58.93	3.26	1.43	0.09	25.79	0.18	36.61	1.63	1204	25	51.49	0.51
3-1-102a	15050 41	0.446 0.024	996 (57	59.51	2.99	1.55	0.08	23.06	0.17	32.43	1.62	1180	25	52.55	0.42
3-1-102b	15157 45	0.381 0.025	869 [~]	2	61.92	8.01	1.56	0.10	24.57	0.18	34.22	2.10	1196	27	51.10	0.46
3-2-104a	15182 52	0.442 0.023	941 [′]	0	59.04	2.89	1.56	0.07	29.14	0.20	33.24	1.53	1201	26	52.87	0.54
3-2-104b	15113 46	0.415 0.029	868 ´	2	60.69	6.54	1.79	0.22	26.19	0.19	31.91	3.44	1128	28	52.67	0.50
4-1-49a	15031 43	0.437 0.028	926 ~	79	63.37	2.98	1.56	0.09	22.69	0.17	33.21	1.83	1182	25	53.08	0.46
4-1-49b	15005 41	0.380 0.020	1072 ~	73	58.17	3.73	1.40	0.10	26.23	0.19	35.31	2.02	1162	26	52.00	0.45
4-7-34a	15149 50	0.446 0.022	954 (58	58.90	3.42	1.55	0.10	24.64	0.18	35.64	3.07	1194	30	51.92	0.49
4-7-34b	15020 43	0.449 0.023	1031	33	59.41	3.67	1.38	0.09	23.92	0.18	35.75	2.28	1210	25	52.47	0.46
5-2-78a	15165 45	0.383 0.021	970 (66	53.67	4.40	1.75	0.10	24.82	0.18	35.12	1.92	1207	26	51.98	0.47
5-2-78b	14927 42	0.374 0.025	1095 [°]	71	59.02	3.98	1.36	0.09	22.91	0.17	35.27	1.94	1151	26	52.15	0.46
5-5-40a	14934 42	0.441 0.027	954 0	52	61.27	3.42	1.56	0.10	23.17	0.17	33.94	2.05	1197	26	52.29	0.47
5-5-40b	15077 43	0.395 0.025	984 (57	60.59	3.05	1.43	0.08	22.31	0.16	31.40	1.66	1211	25	52.15	0.47
7-1-25a	15109 45	0.424 0.025	987 (55	60.15	3.65	1.58	0.20	25.36	0.18	33.32	4.43	1134	31	51.70	0.48
7-1-25b	15078 43	0.461 0.026	876 <i>°</i>	2	58.94	3.47	1.48	0.10	22.62	0.17	36.64	2.07	1180	26	52.27	0.51
7-7-87a	15063 42	0.428 0.029	956	96	59.70	3.71	1.61	0.11	23.00	0.18	34.53	3.23	1216	27	52.34	0.53
7-7-87b	14874 43	0.381 0.024	1215 7	73	55.64	3.61	1.46	0.09	21.94	0.16	33.12	1.77	1204	24	52.32	0.48
<i>N</i> :	20	20	20		19		20		20		20		20		20	
Mean, pSD ^d :	15081 44	0.418 0.025	981 [′]	73	59.44	4.12	1.55	0.11	24.33	0.18	34.42	2.44	1186	26	52.21	0.48
SD:	103	0.029	82		2.11		0.13		1.75		1.58		28		0.51	
RSD%:	0.69	6.9	8.4		3.6		8.2		7.2		4.6		2.4		0.98	

^a x_i is the measurement result for the *i*th sample. ^b u_i is the intrinsic measurement uncertainty associated with x_i . ^c Result identified as a possible technical outlier. ^d pSD is the pooled standard deviation: $pSD = \sqrt{\sum u_i^2/N}$.

Component	WAI	WBr	WCa	WCl	w_{Dy}	w_{Mn}	W_{Na}	w_{Ti}	$w_{ m V}$
Sample replication, u_{rel}^{a} :	0.15	1.54	1.87	0.82	1.84	1.61	1.03	0.53	0.22
Standard replication, u_{rel}^a :	0.18	0.13	0.47	0.15	0.23	0.2	0.16	0.6	0.17
Blank Correction, u_{rel}^a :	0.01	0.01	n/a	0.46	n/a	n/a	n/a	n/a	n/a
Drying correction, u_{rel}^{a} :	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Sample mass, u_{rel}^{a} :	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Neutron self-shielding, u_{rel}^{a} :	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Photon attenuation, u_{rel}^{a} :	0.06	0.09	0.04	0.06	0.12	0.06	0.07	0.13	0.07
Irradiation geometry, u_{rel}^{a} :	0.11	0.09	0.11	0.11	0	0.11	0.11	0.11	0.11
Standard uncertainty, u_{rel}^{a} :	0.27	1.55	1.93	0.96	1.86	1.63	1.05	0.82	0.31
Degrees of freedom, $v_{\rm eff}$:	18	21	23	21	21	21	22	18	28
Coverage factor:	2.10	2.08	2.07	2.08	2.08	2.08	2.07	2.10	2.05
Expanded uncertainty, U_{95rel}^{a} :	0.57	3.23	4.00	1.99	3.87	3.39	2.18	1.72	0.63
Standard uncertainty, <i>u</i> ^b :	41	0.006	19	0.57	0.03	0.40	0.36	10	0.16
Expanded uncertainty, U_{95}^{b} :	85	0.013	39	1.18	0.06	0.82	0.75	20	0.33

 Table 29. Uncertainty Components for INAA Measurements.

a

Relative uncertainty expressed as percent. Absolute uncertainty in mg/kg, the product of the mean value and the relative uncertainty, divided by 100. b

Component	Explanation
Samula Dauliantian	SD/\sqrt{n} where SD is the standard deviation of the results for the samples and
Sample Replication	<i>n</i> is the number of samples analyzed
	SD/\sqrt{n} where SD is the standard deviation of the results for the standards
Standard Replication	and n is the number of standards analyzed. This uncertainty includes the
-	inherent uncertainty of the mass fraction of the standard solutions.
	Determined by measuring empty vials and vials with just cellulose to
Blank Correction	determine matrix elements. Five blanks of each were measured; corrections
	were required for Al, Br, and Cl measurements.
Drying Correction	The samples drying correction uncertainty contribution was calculated
Drying Conection	from repeated samplings of four SRM 2693a bottles.
Sample Mass	Uncertainty from the mass measurement on the balance using a rectangular
Sample Mass	distribution.
	The correction factor for neutron self-shielding is reliant on the elemental
Neutron Self-shielding	abundances of the samples. The uncertainty was calculated based on a
	triangular distribution.
	The correction factor for neutron self-shielding is reliant on the elemental
Photon Attenuation	abundances of the samples. The uncertainty was calculated based a
	triangular distribution.
	The correction factor for irradiation geometry is reliant on the
Irradiation Geometry	reproducibility of the flux gradient measurements. It is estimated as 10 %
	of the correction factor, typically 1.112 for this analysis.

Table 30. Explanation of the INAA Uncertainty Components.

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The largest uncertainty for most elements was sample measurement replication, which ranged from as low as 0.15 % in the case of Al, to 1.87 % for Ca. For a fixed number of measurements, replication uncertainty is primarily due to counting statistics. Increasing the count rate by taking a larger test portion mass or moving the sample closer would increase the number of counts collected during the counting window, but the increase in activity causes the dead time to also increase. Higher dead-times are more difficult to accurately correct and would result in a higher uncertainty contribution. Counting longer would improve the uncertainty for some of the elements, but only if their count rate is higher than the background rate, especially if the isotope has a shorter half-life than the isotope that is contributing the most to the background. For example, Mn and Na have half-lives in the hours versus Cl at 30 min; thus, while the background uncertainty would decrease for Na and Mn, it would increase for Cl.

The relatively large RSD% for the Ca measurements is most likely due to the low peak intensity of the Ca 3084 keV peak. A longer count time was impractical because of the risk of increasing the uncertainty for the shorter-lived isotopes while not gaining much improvement for Ca.

The INAA results for the nine quantitatively determined elements are displayed in Fig. 14 as functions of the bottle identifier. The results for all elements are displayed at a uniform resolution of ± 25 % of the mean value to enable direct comparison of the relative variability. The results for Al and V are displayed in Fig. 15 at a resolution of ± 3 % of their mean values to better evaluate possible systematic trends.



Fig. 14. INAA Measurement Results as Functions of Bottle Identifier.

The symbols represent the mean mass fraction in mg/kg of measurement results for two aliquots from each of ten bottles, plotted as functions of sample identifier. The error bars represent the standard uncertainty of the measurements, combining the within-aliquot measurement uncertainty with the between-aliquot standard deviation. The solid horizontal line represents the mean of the measurements. The vertical mass fraction axis of each panel is scaled to span a symmetrical interval about the mean equal to 25 % of the mean.



Fig. 15. Higher-Resolution INAA Measurement Results for AI and V.

The same format as (above), but with the vertical mass fraction axis of both panels scaled to span a symmetrical interval about the mean equal to 3 % of the mean.

With the exception of a potential decline in the Al and Mn mass fraction with increasing bottling sequence, the measurement uncertainties mask any between-bottle trends that may exist.

5.4. Hg by Direct Combustion Atomic Absorption Spectrometry (AAS)

The original intent was to determine the mercury mass fraction of SRM 2693a using isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) [43]. However, an initial screening study using direct combustion atomic absorption spectrometry (AAS) revealed considerable within-bottle Hg heterogeneity. It was then decided to use the more expedient AAS to characterize the Hg mass fraction of SRM 2693a because Hg would be a non-certified value.

5.4.1. Materials

Six bottles of SRM 2693a (2-6-98, 2-5-61, 3-4-92, 4-2-39, 5-8-96, and 7-4-73) were analyzed. Two bottles each of SRMs 2684c Bituminous Coal (Nominal Mass Fraction 3 % Sulfur) [44] and 2693 [1] were used as controls. One unit of SRM 3133 Mercury (Hg) Standard Solution (Lot No. 160921) [45] was used to make the calibration solutions. Empty nickel weigh boats were used as procedural blanks.

5.4.2. Methods

Moisture was determined by measuring the mass loss on drying (LOD) from duplicate and triplicate sub-samples, under the assumption that all of the lost mass is water. Moisture was determined during the initial screening and subsequent value assignment studies. A mass of approximately 1 g of each sample was transferred into glass weighing bottles, oven-dried for 1 h at 107 °C, stored in a glass desiccator over calcium sulfate desiccant for 2 h at ambient temperature, and the mass was redetermined again. Mercury mass fraction for each analytical

sample was corrected to dry-mass fraction on a sample-by-sample basis using the mean correction factor for each bottle.

The total Hg mass fraction, *w*Hg, was determined using a direct Hg analyzer (DMA) by external calibrations. Calibrants were constructed by gravimetrically aliquoting different masses (between 0.0182 g and 0.8991 g) of aqueous dilutions of SRM 3133 into quartz sample boats. Mercury was measured in candidate SRM 2693a and control material samples by transferring a known mass of approximately 120 mg of material into pre-cleaned nickel weigh boats and placing them into the instrument auto-sampler rotor. Control material samples amples and procedural blanks were bracketed between blocks of candidate SRM 2693a samples to verify instrument calibration and monitor instrumental drift. Table 31 lists the instrumental parameters used for the aqueous solution calibrants and the test, control, and procedural blank samples.

	Method				
Parameter	Calibrants	Samples			
Ramp 1	90 s to 200 °C	30 s to 200 °C			
Hold 1	30 s	60 s			
Ramp 2	90 s to 650 °C	90 s to 650 °C			
Hold 2	180 s	240 s			

Two external calibration curves were prepared, the first for the screening study and the second for the value assignment study. A second order fit was applied to account for non-ideal Beer-Lambert Law behavior. The calibration curves with their polynomial equations are displayed in Fig. 16.



Fig. 16. Atomic Absorption Spectrometry Calibration Curves.

The symbols represent measured Hg peak areas as a function of the mass of calibrant Hg. The curve represents the best-fit second-order polynomial. The panel to the left is the calibration curve for the screening study; the panel to the right is the curve for the value-assignment study.

The following functional relationship was used to calculate the Hg mass fraction results:

$$w_{\rm Hg} = \left(\frac{-b \pm \sqrt{b^2 - 4a(c-A)}}{2a} - B\right) / (m_{\rm s} D_{\rm c})$$
 (9)

where: w_{Hg} is the mercury dry mass fraction in the sample in ng/g (µg/kg),

a, *b*, *c* are the quadratic, linear, and constant coefficients of the calibration function. The result from the quadratic equation has units of ng.

A is the peak area of the AAS absorbance (arbitrary units),

 $m_{\rm s}$ is the mass of the sample aliquot (g),

B is the mean measured blank (ng), and

 $D_{\rm c}$ is the wet-mass to dry-mass correction factor.

5.4.3. Results

5.4.3.1. Mass Loss on Drying (LOD)

Table 32 lists the mean water mass fraction, *w*_{H2O}, in the as-is SRM 2693a material at the time of the study and dying correction factor for each bottle.

Bottle	n^{a}	WH2O, %	Dc
2-6-98 ^b	3	0.9564	0.99044
2-6-98 ^c	3	1.1344	0.98866
2-5-61 ^c	2	1.1808	0.98819
3-4-92 ^c	2	1.1679	0.98832
4-2-39 ^c	2	1.1832	0.98817
5-8-96 ^c	2	1.0017	0.98998
7-4-73 ^c	2	1.0299	0.98970
М	ean ^d :	1.116	0.98884
	SD ^d :	0.080	0.00080

 Table 32.
 Water Mass Fraction and Drying Correction Factor.

^a Number of 1 g test portions evaluated.

^b Determined during the screening study.

^c Determined during the value assignment study.

^d Summary of the six evaluations determined during the value assignment study.

The difference in w_{H2O} determined for the screen and value assignment studies may be attributable to the difference in ambient humidity in Charleston, SC, between May and July.

5.4.3.2. Screening Study

In preparation for total Hg value assignment, SRM 2693a bottle 2-6-98 was screened for Hg by AAS along with the SRM 2684c and SRM 2693 controls. The mass fraction result for SRM 2693 agreed well with its certified value; the result for SRM 2684c was slightly below the expanded uncertainty of its certified value; and the mass fractions of Hg in procedural blanks were very small. None of the measured values were technically compromised.

Table 33 lists the determined values for six replicates of the material in bottle 2-6-98 of SRM 2693a along with the summary mean and standard deviation (SD). The between-replicate relative standard deviation (RSD%) was nearly 25 %, suggesting that there is considerable Hg heterogeneity with 120 mg samples.

	$w_{ m Hg}$
Replicate	µg/kg
1	53.0269
2	72.1670
3	62.6540
4	52.2775
5	55.7858
6	93.6813
N:	6
Mean:	64.9
SD:	15.9
RSD%:	24.5

 Table 33. Mercury Mass Fraction in Bottle 2-6-98 from Screening Study.

5.4.3.3. Value Assignment Study

The Hg mass fraction of SRM 2693a was further studied using 120 mg samples from the other five bottles. As in the screening study, the mass fraction result for the SRM 2693 control material agreed well with its certified value; the result for the SRM 2684c control material was slightly below the expanded uncertainty of its certified value; and the procedural blanks were very small, as shown in Table 34.

Bottle	Peak Area	Hg (pg)
1	0.0032	87.0
2	0.0020	72.3
3	0.0041	98.1
4	0.0032	87.0
	Mean:	86.1
	SD:	10.6

 Table 34. Total Hg in Value Assignment Procedural Blanks.

Table 35 lists the SRM 2693a w_{Hg} measurements, expressed in $\mu g/kg$ on a dry-mass basis.

						With Outliers		Without	Outliers
Bottle	Rep ₁	Rep ₂	Rep ₃	Rep ₄	Rep ₅	Mean	SD	Mean	SD
2-5-61	51.257	52.844	57.673			53.92	3.34	53.92	3.34
3-4-92	53.889	57.354	53.209			54.82	2.22	54.82	2.22
4-2-39	56.881	71.533ª	54.030	58.404		60.21	7.76	56.44	2.22
5-8-96	58.047	148.234 ^a	56.785	52.991	54.089	74.03	41.53	55.48	2.34
7-4-73	58.741	56.995	51.189			55.64	3.95	55.64	3.95
N:	18	16 ^b				5		5	
Mean:	61.3	55.3 ^b				59.7		55.3	
SD:	22.2	2.6^{b}				8.4		0.9	
RSD%:	36.1	4.7 ^b				14.0		1.7	

Table 35. Mercury Mass Fraction, *w*_{Hg}, µg/kg.

^a Identified as a statistical outlier.

^b Excluding the identified statistical outliers.

Three replicates from each of the five bottle of candidate were initially evaluated. Additional replicates were measured for bottles 4-2-39 and 5-8-96 because the Hg mass fraction in one of the three initial replicates was much larger than the other two. There was no reason to consider any of the values as technically invalid; however, two values are identified as statistical outliers using Iglewicz and Hoaglin's outlier test (modified *Z* score threshold value ≥ 3.5) [46].

Table 36 lists the uncertainty components, calculated using GUM [27] and NIST [28] guidelines, for the SRM 2693a Hg mass fraction assessment.

Component	и
Sample replication:	5.22
Blank correction:	0.04
Drying correction:	0.0004
Mass measurement:	0.061
Calibrant:	0.112
Quadratic calibration:	0.006
Combined standard uncertainty, <i>u</i> _c :	5.22
Degrees of freedom, v _{eff} :	17
Coverage factor:	2.11
Expanded uncertainty, U_{95} :	11.02

Table 36. Uncertainty Components for AAS Measurements, μ g/kg.

Table 37 describes the components. The sample replication component is the only significant contributor.

Component	Explanation
Sample Replication	Relative standard deviation (RSD) of the samples analyzed.
Diant Composition	Standard deviation (SD) of repeated measurements of procedural blanks as
Blank Correction	a percentage of the mean sample Hg.
During Connection	Pooled SD of drying correction factor repeatability as a percentage of the
Drying Correction	mean sample Hg.
Maga Magaunamant	Balance calibration, temporal and electrostatic drift and their relative
Mass Measurement	impact on mass measurement. Estimated at 0.1 %.
Calibrant	Stated 95 % expanded uncertainty of Hg in SRM 3133 divided by the
Canorant	coverage factor.
Quadratic calibration	Best fit line estimated uncertainty based on explained variance (R^2) .

 Table 37. Explanation of the AAS Uncertainty Components.

5.4.3.4. Summary

The results of the value assignment measurements are consistent with the result from the screening study. The mass fraction results are displayed in Fig. 17 for all six SRM 2693a bottles evaluated.



Fig. 17. Mercury Mass Fraction, *w*_{Hg}, in SRM 2693a.

The symbols represent the mean mercury mass fraction in each of the six SRM 2693a bottles evaluated. The open circle to the left denotes the material evaluated in the initial screening study. The solid circles to the right denote the estimates for the five bottles in the value assignment study after outlier rejection. The solid triangles are the values for the complete 4-2-39 and 5-8-96 results. The error bars represent standard deviations of the mean values. The horizontal line marks the grand average of the value assignment measurements after outlier rejection.

Mercury in coal has been associated with pyrite, sulfides, selenides, organic compounds, and organometallic compounds along with being present in several forms [47]. Not all of the forms will homogenously bind across components of bituminous coal. The distribution of values suggests that Hg is heterogeneously scattered as small particles on top of a fairly uniform $\approx 55 \ \mu g/kg$ Hg background.

6. CANSPEX Interlaboratory Study

In early 2018, the quality assurance CANSPEX program run by Quality Associates International (QAI), Ltd. distributed bottles of SRM 2693a in their interlaboratory study CANSPEX 2018-1. Measurands included in CANSPEX 2018-1 included C, H, N, S, Cl, Hg, F, Se, water, ash, volatiles and calorific. QAI ceased business upon retirement of its president shortly after completing this study.

QAI was provided with 134 bottles of SRM 2693a, sufficient to provide one bottle of SRM 2693a to each participating laboratory. Roughly equal numbers of bottles from the five sublots were provided to QAI. All of these bottles were marked with a number (1 to 134) and each number was matched to the sublot, run within that sublot, and bottle within that run. The bottle identity information was not shared with QAI. QAI noted which bottle number was sent to each laboratory so that the sublot information could be matched to each laboratory.

Participants were asked to determine each measurand on two test portions from their one bottle of SRM 2693a and to document the analytical method used. Four results for each measurand were to be reported, two results for day 1 and two results for day 2. Day 1 and day 2 runs were not to be more than five days apart. 119 of the 134 laboratories returned results for at least one measurand. The number of results per participant ranged from 1 to 12. The number of result means per measurand ranged from 16 (Se) to 116 (moisture).

6.1. Homogeneity Assessment With C, H, N, S, CI, and Hg

The way the bottles were identified and the information provided by QAI enable using the CANSPEX-2018-1 results to help evaluate SRM 2693a homogeneity. To limit the influence of technically suspect results on this assessment, some of the results for C, H, N, S, Cl, and Hg have been excluded from the homogeneity analyses. The suspect results were identified based upon internal evidence that the participant did not follow the study protocol, their measurement process was not in adequate control, or that their process was not well calibrated. The most common reason for exclusion was that on both days the within-day values were identical, indicating that the results did not reflect measurement of independent aliquots.

The Cl measurements from the CANSPEX laboratories were not considered in the certificate value assignment because of the general imprecision of the entirety of the Cl CANSPEX measurements, which may have been caused by the existence of heterogeneity or by the challenges in measuring Cl at the low nominal 50 mg/kg level using the methods employed by the laboratories.

Table 38 to Table 43 list summary mean and standard deviations for all reported C, H, N, S, Cl, and Hg results. The values are presented in order of increasing value. These summary results are displayed in Fig. 18 to Fig. 23 as functions of rank-order. The values excluded from the homogeneity evaluation are identified in both tables and figures using red font.

The distributions of the homogeneity results for C, H, N, S, Cl, and Hg are displayed in Fig. 24 with regard to sublot.

Code	Mean	SD	Code	Mean	SD	Code	Mean	SD
56 ^a	76.378	0.109	33	79.612	0.546	239	80.098	0.144
240 ^a	78.174	0.945	148	79.630	0.177	133	80.114	0.054
74	78.586	0.141	203	79.649	0.080	179	80.208	0.014
235	78.734	0.068	124	79.654	0.010	195	80.211	0.215
127	78.983	0.061	119	79.660	0.227	284	80.229	0.088
204	79.095	0.035	181	79.663	0.166	73	80.299	0.301
45	79.099	0.140	196 ^a	79.700	0.141	283	80.320	0.059
116	79.120	0.075	192	79.702	0.162	194	80.377	0.067
176	79.159	0.683	177	79.707	0.005	228	80.448	0.078
206	79.267	0.101	4	79.730	0.089	252	80.459	0.032
114	79.316	0.465	243	79.741	0.028	270	80.497	0.491
175	79.320	0.004	47	79.757	0.103	248	80.505	0.095
287	79.371	0.010	574 ^a	79.776	0.003	104	80.963	0.274
1	79.376	0.005	256	79.778	0.227	125	81.075	0.194
38	79.383	0.145	146	79.781	0.114	202	81.212	0.250
226	79.391	0.007	247	79.793	0.086	27	81.510	0.060
51	79.442	0.308	162	79.796	0.135	123	81.963	0.103
28	79.480	0.079	174	79.825	0.000	274	82.232	0.007
268	79.481	0.046	160	79.863	0.124	75	82.507	0.583
266 ^a	79.517	0	59	79.940	0.006	197	82.941	1.051
267	79.574	0.067	164	79.946	0.181	244	83.450	0.875
90	79.587	0.457	257	79.968	0.034			
126	79.592	0.348	141	80.033	0.442			

Table 38. CANSPEX Carbon Mass Fraction, %, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 18. CANSPEX Carbon Mass Fraction, %, Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.

Code	Mean	SD	Code	Mean	SD	Code	Mean	SD
75	4.171	0.026	1	4.339	0.012	257	4.381	0.012
133	4.176	0.005	177	4.345	0.016	206	4.381	0.030
4	4.182	0.001	252	4.346	0.007	119	4.388	0.076
204	4.195	0.007	179	4.348	0.011	176	4.398	0.074
38	4.197	0.004	124	4.349	0.006	126	4.412	0.059
266 ^a	4.212	0	267	4.349	0.035	274	4.422	0.010
123 ^a	4.236	0.028	181	4.351	0.035	239	4.424	0.014
51	4.268	0.062	125	4.351	0.002	59	4.442	0.045
248	4.271	0.024	127	4.358	0.025	160	4.450	0.007
228	4.272	0.052	195	4.362	0.004	283	4.458	0.034
287	4.284	0.006	116 ^a	4.364	0.058	27	4.470	0.025
146	4.290	0.052	192	4.366	0.004	45	4.531	0.008
268	4.293	0.021	162	4.372	0.037	175	4.542	0.036
226	4.301	0.008	73	4.374	0.055	74	4.565	0.021
202 ^a	4.307	0.023	47	4.375	0.013	270	4.576	0.086
196	4.310	0.014	114	4.375	0.021	247	4.585	0.005
33	4.311	0.002	235	4.375	0.003	90	4.586	0.021
164	4.312	0.012	28	4.376	0.002	284	4.648	0.028
240	4.312	0.044	194	4.379	0.012	203	4.714	0.005
243	4.335	0.004	174	4.379	0.022	56 ^a	4.731	0.103

 Table 39. CANSPEX Hydrogen Mass Fraction, %, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 19. CANSPEX Hydrogen Mass Fraction, %, Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.

Code	Mean	SD	Code	Mean	SD	Code	Mean	SD
27 ^a	0.830	0.007	243	1.147	0.003	51	1.193	0.021
90	0.991	0.021	195 ^a	1.149	0.007	146	1.196	0.016
56 ^a	1.017	0.074	124	1.157	0.001	133	1.203	0.040
74	1.068	0.026	125 ^a	1.160	0.036	268	1.206	0.001
181	1.084	0.024	119	1.161	0.005	123	1.210	0.001
175	1.090	0.015	105	1.163	0.009	247	1.211	0.004
45	1.094	0.044	283 ^a	1.163	0.014	179	1.213	0.011
196	1.108	0.018	79	1.165	0.015	203	1.219	0.001
160	1.110	0.014	252	1.165	0.022	28	1.220	0.007
127	1.118	0.025	267	1.167	0.014	287	1.224	0.026
4	1.118	0.004	202 ^a	1.168	0.022	59	1.231	0.001
239	1.121	0.032	240	1.171	0.010	235	1.241	0.002
226	1.130	0.003	174	1.172	0	206	1.260	0.010
194 ^a	1.130	0.007	248	1.175	0.007	270	1.264	0.007
116	1.134	0.025	33	1.176	0.016	75	1.269	0.004
204	1.138	0.011	38	1.177	0.032	192	1.277	0.010
284	1.139	0.008	266 ^a	1.178	0.004	164	1.282	0.004
73	1.140	0.022	114	1.182	0.004	228	1.286	0.001
47	1.143	0.004	126	1.188	0.003	162	1.300	0.018
176	1.143	0.035	177	1.189	0.025			
274	1.145	0.012	1 ^a	1.193	0			

 Table 40. CANSPEX Nitrogen Mass Fraction, %, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 20. CANSPEX Nitrogen Mass Fraction Nitrogen, %, Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.
0.1	3.6	CD	0.1	3.6	CD	0.1	14	CD	0.1	3.6	CD
Code	Mean	SD									
235 ^a	0.1491	0.0034	277	0.3224	0.0008	279	0.3338	0.0101	125	0.3469	0.0106
56 ^a	0.2668	0.0020	197	0.3226	0.0022	267	0.3341	0.0011	51	0.3471	0.0051
133	0.2811	0.0037	257	0.3228	0.0013	179	0.3342	0.0071	126	0.3472	0.0062
248	0.2832	0.0076	227	0.3240	0.0043	228 ^a	0.3343	0.0002	164	0.3473	0.0011
105	0.2898	0.0006	221	0.3240	0.0019	124 ^a	0.3345	0.0002	74	0.3480	0.0008
250	0.2925	0.0052	211	0.3242	0.0117	284	0.3354	0.0021	60	0.3483	0.0011
146	0.2970	0.0001	47	0.3245	0.0028	57	0.3356	0.0024	286	0.3484	0.0058
59	0.3021	0.0028	220	0.3248	0.0004	104	0.3361	0.0052	176	0.3489	0.0003
181	0.3024	0.0033	243	0.3252	0.0011	90	0.3369	0.0046	195	0.3494	0.0000
247	0.3072	0.0037	162	0.3268	0.0035	189	0.3374	0.0019	238	0.3495	0.0001
193	0.3104	0.0034	275	0.3271	0.0036	259	0.3375	0.0035	285 ^a	0.3500	0
215	0.3113	0.0103	212	0.3275	0.0035	249	0.3384	0.0005	239	0.3504	0.0027
114 ^a	0.3139	0	175	0.3280	0.0014	223	0.3386	0.0144	202	0.3510	0.0022
123 ^a	0.3140	0.0002	203	0.3287	0.0003	38	0.3394	0.0072	118	0.3511	0.0002
209 ^a	0.3140	0.0144	234 ^a	0.3293	0.0141	15	0.3400	0.0071	14 ^a	0.3550	0.0071
217	0.3145	0.0007	204	0.3300	0.0000	137 ^a	0.3400	0	55	0.3551	0.0001
196	0.3150	0.0071	213	0.3302	0.0018	258 ^a	0.3400	0	27	0.3570	0.0036
45	0.3151	0.0120	287	0.3303	0.0060	73	0.3404	0.0016	20	0.3578	0.0025
117	0.3156	0.0024	19	0.3303	0.0037	79	0.3408	0.0044	127	0.3581	0.0002
198	0.3158	0.0056	266 ^a	0.3305	0	174	0.3409	0.0043	252	0.3598	0.0145
148 ^a	0.3200	0.0141	270	0.3313	0.0036	6	0.3411	0.0035	177	0.3635	0.0070
271	0.3200	0.0212	160	0.3315	0.0064	278	0.3413	0.0024	206	0.3904	0.0002
280	0.3200	0.0011	28	0.3316	0.0036	226	0.3414	0.0147	116	0.3916	0.0035
216	0.3202	0.0034	33	0.3319	0.0011	274	0.3417	0.0040	75 ^a	0.4383	0.0179
256	0.3216	0.0002	106	0.3321	0.0001	119	0.3435	0.0007	192 ^a	0.6019	0.3644
4	0.3217	0.0016	141	0.3321	0.0044	1 ^a	0.3437	0.0001	200 ^a	0.6634	0.0199
268	0.3219	0.0003	165	0.3321	0.0129	240 ^a	0.3440	0.0001			
42	0.3222	0.0064	276	0.3323	0.0005	194	0.3447	0.0002			
159	0.3223	0.0052	283 ^a	0.3338	0.0002	282	0.3465	0.0105			

Table 41. CANSPEX Sulfur Mass Fraction, %, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 21. CANSPEX Sulfur Mass Fraction, %, Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.

Code	Mean	SD	Code	Mean	SD	Code	Mean	SD
265 ^a	-100.00	0	270	50.57	3.58	125	68.88	7.12
287 ^a	23.50	2.12	195	51.15	1.43	194	71.97	1.48
127 ^a	26.36	0.73	1	52.25	1.77	123	75.20	2.56
282	30.85	0.74	176	52.33	2.55	226 ^a	76.94	22.58
75	33.95	2.15	192	52.87	1.04	164	77.25	1.77
105	34.46	0.73	275	53.00	1.08	119 ^a	93.73	1.44
126	37.99	0.01	240	53.11	0.70	133 ^a	101.30	0.04
117ª	41.44	1.42	228	54.19	4.27	266 ^a	111.38	0
203	41.47	0.76	146 ^a	55.60	14.25	90 ^a	114.80	1.65
206	41.58	6.43	45	56.49	0.31	239 ^a	127.75	5.75
137	43.33	0.39	73 ^a	56.73	10.73	27 ^a	146.33	2.14
174ª	43.50	0.71	284 ^a	59.78	0.01	79 ^a	201.40	0.13
162	44.58	1.45	54 ^a	60.50	4.24	258 ^a	202.75	2.47
33	45.80	2.49	252 ^a	60.99	12.46	59 ^a	211.50	32.53
267	46.17	5.02	274	61.79	3.45	160 ^a	298.00	12.02
38	46.36	2.50	181 ^a	64.15	11.42	116 ^a	585.67	22.26
256	49.64	2.12	179	67.60	2.50			

Table 42. CANSPEX Chlorine Mass Fraction, mg/kg, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 22. CANSPEX Chlorine Mass Fraction, mg/kg Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.

Code	Mean	SD	Code	Mean	SD	Code	Mean	SD
196 ^a	28.25	2.47	267	53.50	5.66	206	60.25	1.77
56	45.95	2.12	481 ^a	53.75	3.89	45	60.75	1.06
275	46.50	0.00	277	54.25	1.91	274	60.75	4.60
181	47.00	0.71	38	54.50	0.71	137 ^a	61.00	0
127	48.75	2.47	243	54.75	1.77	59	62.68	0.25
240	48.75	2.47	159	55.03	2.46	177	64.00	1.41
28	49.25	1.06	116	55.13	4.10	223	65.15	2.83
270 ^a	50.00	0	123	55.45	2.76	114	65.83	0.46
4	50.75	1.06	117	55.50	1.41	164	65.95	0.64
176	51.25	5.30	248	55.50	0.71	239	70.25	6.72
90	51.57	1.50	162	56.25	1.06	287	72.00	0.71
244 ^a	51.81	2.07	105	56.50	1.41	284	72.50	3.54
1	52.00	1.41	174	57.75	1.77	160	74.50	4.24
55	52.50	6.36	203	57.75	2.47	216 ^a	77.73	5.41
119	53.10	0.92	125	58.37	0.75	252	82.00	4.95
265	53.25	1.77	247	60.00	3.54			

Table 43. CANSPEX Mercury Mass Fraction, µg/kg, Dry Basis.

^a Result identified as unsuited for use in homogeneity assessment.



Fig. 23. CANSPEX Mercury Mass Fraction, µg/kg, Dry Basis.

The symbols represent the mean \pm SD mass fraction reported by the participants in the CANSPEX study. Open circles denote values identified as unsuited for use in homogeneity assessment. The solid horizontal line represents the median result, the dashed lines bound the central 50 % of the results.



Fig. 24. CANSPEX Homogeneity Evaluation: Sublot.

Boxplot representations of the distribution of suitable results are displayed grouped by sublot. The width of each box is proportional to the number of results for the element. The central line of each box represents the median of the distribution, the top and bottom lines enclose the central 50 % of the distribution, and the whiskers span the central 95 % of the distribution.

6.2. Summary Results

Table 44 summarizes the results for the CANSPEX measurands. No (non-negative) value has been excluded on the basis of its magnitude; however, the summary estimates are based upon the non-repeated results reported by each participant: when the same value is reported for all replicates, only one value is included in the summary analysis. Given the presence of highly atypical measurement results for several of the elements, the robust median is used to estimate the central value and the statistically efficient robust Q_n estimator[48,49] is used to estimate the standard deviation.

Measurand	Units	Labs ^a	Data ^b	Median ^c	$Q_{\mathrm{n}}{}^{\mathrm{d}}$	%RSD ^e
С	(%)	67	262	79.77	0.68	0.86
Н	(%)	60	236	4.362	0.102	2.3
Ν	(%)	61	229	1.172	0.063	5.4
S	(%)	113	417	0.334	0.018	5.5
Cl	mg/kg	50	182	54	22	41
Hg	µg/kg	47	182	56	8.7	16

 Table 44. Summary of CANSPEX Results.

^a Number of participants reporting at least one result for the given measurand.

^b Number of non-repeated results reported by all participants.

^c The median is a robust estimator for the central location of a distribution.

^d Q_n is an efficient and robust estimator of standard deviation.

^e Robust estimate of the relative standard deviation: $%RSD = 100Q_n$ /Median.

7. Statistical Analysis

The uncertainty evaluations reported in the previous sections used techniques from the GUM [27] and NIST [28] guidelines and, for C, H, and N, used a parametric bootstrap algorithm and Monte Carlo uncertainty propagation [11] approaches and the Bayesian information criteria [12]. The uncertainty analyses in this section augment the uncertainty analyses of the previous sections by combining results from multiple methods into a single value and statement of uncertainty. Bayesian data analysis techniques and Monte Carlo uncertainty propagation methods are leveraged to accomplish those goals [50].

7.1. C

Three sets of measurements are available for C: first, measurements from 62 CANSPEX laboratories, each using quadruplicates on a single bottle, second, measurements from PGAA using single measurements on each of five bottles (Table 23 "Good Spectra" values), and third, measurements from combustion with thermal conductivity detection over seven different daily runs. A statistical model is used to reduce the three sets of measurements and their uncertainties into a consensus value. The part of the model associated with the CANSPEX measurements considers three nested sources of variability. At the lowest level of the hierarchy, the quadruplicate measurements within a laboratory (and bottle) inform a within-laboratory (or bottle) source of variability. The differences between laboratory averages inform a between-laboratory component of variability. Laboratory-to-laboratory differences may also be interpreted as bottle-to-bottle differences since a laboratory receives only a single bottle. At the highest level in the hierarchy, differences between sublot averages inform a between sublot component of variability. This component of variability may also be interpreted as a component of uncertainty attributable to material heterogeneity.

For the PGAA measurements the model considers only variability between the five measurements. This variability is due to between-bottle differences, within-bottle differences, and measurement errors specific to PGAA.

For the combustion measurements, the model considers two nested sources of variability. At the highest level there exist differences between the daily runs. Within a run there are other sources of variability and uncertainty like differences between bottles, differences within a bottle, and calibration uncertainty. These sources are combined externally to the current statistical model and are represented by a standard deviation. Heterogeneity is another component of uncertainty accounted for within each daily run. Results are provided for both the with and without heterogeneity combustion measurements.

Inference proceeds by the Bayesian paradigm, with flat or weakly informative priors to reflect a lack of knowledge a priori. The three sets of measurements each provide a posterior distribution for the mean measurement from that method. Those posterior distributions are combined using the opinion pool with equal weights [51] to arrive at a posterior distribution for the consensus value. Certificate values and uncertainties are derived from that distribution; the value is the mean, the standard uncertainty is the standard deviation, and the 95 % coverage interval is the range between the 2.5th percentile and the 97.5th percentile.

The appropriateness of the statistical model can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 25 shows the

observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle (PGAA) sent to random lab (CANSPEX) or for a new run (combustion). In all cases, approximately 95 % of the points fall within the intervals, and the statistical model is deemed appropriate.



Fig. 25. Summary of Available Results for C.

Upper left: Solid circles represent replicate results reported by CANSPEX participants, sorted by increasing participant mean value. Horizontal lines depict a 95 % prediction interval. Upper right: solid circles represent PGAA results ordered by the sample bottle subplot-run-fill order. Lower right: solid circles represent results from combustion analysis that do not include a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainties. Lower right: solid circles represent results from combustion analysis including a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence.

Fig. 26 compares the observed measurements to values and coverage intervals for the certificate. Note that the CANSPEX, PGAA, and combustion values and intervals appear next to the measurements. The with heterogeneity intervals are on the left.



Fig. 26. Statistical Reductions for C.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circle with error bars but without neighboring measurement results represents the consensus reduction of the three sets of measurements.

7.2. H

Three sets of measurements are available for H: first, measurements from 57 CANSPEX laboratories, each using quadruplicates on a single bottle; second, measurements from PGAA using duplicate measurements on each of five bottles; and third, measurements from combustion with thermal conductivity detection over seven different daily runs. the statistical model used to reduce the three sets of measurements into a value and uncertainty is essentially the same as for C, except that, since duplicate measurements are made by PGAA, the part of the statistical model that corresponds to the PGAA measurements accounts for two nested sources of variability, differences between the bottle averages and within bottle differences.

As with C, the appropriateness of the statistical model can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 27 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle (PGAA) sent to random lab (CANSPEX) or for a new run (combustion). In all cases, approximately 95 % of the points fall within the intervals, and the statistical model for H is deemed appropriate.



Fig. 27. Summary of Available Results for H.

Upper left: Solid circles represent replicate results reported by CANSPEX participants, sorted by increasing participant mean value. Horizontal lines depict a 95 % prediction interval. Upper right: solid circles represent PGAA results ordered by the sample bottle subplot-run-fill order. Lower right: solid circles represent results from combustion analysis that do not include a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainties. Lower right: solid circles represent results from combustion analysis including a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence.

Fig. 28 compares the observed measurements to the certificate values and coverage intervals. Note that the CANSPEX, PGAA, and combustion values and intervals appear next to the measurements. The with heterogeneity intervals are on the left. For combustion, we see the unintuitive situation where the with heterogeneity interval is narrower than the without heterogeneity interval. This happens because, for each daily run, the with heterogeneity standard uncertainties are larger than the without heterogeneity standard uncertainties, which leads to more consistent daily runs, which then leads to a decrease in uncertainty in the estimated combustion value. The behavior is not observed for C because the increase in the standard uncertainties for the daily runs due to heterogeneity overwhelms differences between daily runs.



Fig. 28. Statistical Reductions for H.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circles with error bars but without neighboring measurement results represent consensus reductions of the three sets of measurements.

7.3. N

Three sets of measurements are available for N: first, measurements from 52 CANSPEX laboratories, each using quadruplicates on a single bottle; second, measurements from PGAA using duplicate measurements on each of five bottles; and third, measurements from combustion with thermal conductivity detection over nine different daily runs. The notation and statistical reduction for N is the same as for H.

The appropriateness of the statistical model can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 29 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle (PGAA) sent to a random lab (CANSPEX) or for a new run (combustion). In all cases, approximately 95 % of the points fall within the intervals, and the statistical model for N is deemed appropriate.



Fig. 29. Summary of Available Results for N.

Upper left: Solid circles represent replicate results reported by CANSPEX participants, sorted by increasing participant mean value. Horizontal lines depict a 95 % prediction interval. Upper right: solid circles represent PGAA results ordered by the sample bottle subplot-run-fill order. Lower right: solid circles represent results from combustion analysis that do not include a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainties. Lower right: solid circles represent results from combustion analysis including a heterogeneity uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence. The error bars represent standard uncertainty component; they are ordered by run sequence.

Fig. 30 compares the observed measurements to potential certificate values and intervals. Note that the CANSPEX, PGAA, and combustion values and intervals appear next to the measurements. The with heterogeneity intervals are on the left. We again see the situation for combustion where the without heterogeneity interval is wider than the with heterogeneity interval. The situation occurs for the same reason as for H.



Fig. 30. Statistical Reductions for N.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circles with error bars but without neighboring measurement results represent consensus reductions of the three sets of measurements.

7.4. C, H, and N

The certificate values and uncertainties are provided without accounting for heterogeneity because, for all three of these elements, there does not exist strong evidence of heterogeneity. The expanded uncertainties for these elements are provided as 95 % coverage intervals because the uncertainty is asymmetric about the value. The 95 % coverage intervals are associated with the mean of all bottles of SRM 2693a because the underlying mass fraction is assumed to be the same for each bottle. Table 45 lists the value, standard uncertainty, and 95 % coverage interval lower (U_{95-LL}) and upper U_{95-UL}) limits for the combined mass fractions of w_{C} , w_{H} , and w_{N} .

Measurand	W	<i>u</i> _c	$U_{95 ext{-LL}}$	$U_{ m 95-UL}$
С	80.0	0.87	79.8	82.5
Н	4.39	0.056	4.33	4.54
Ν	1.179	0.010	1.155	1.193

Table 45. N	Aass Fractions	of C,	Н,	and	N,%.
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7.4.1. Use of Asymmetric Intervals When Comparing Results or Performing Calibrations

The use of the asymmetric intervals provided for values on the SRM 2693a certificate will depend on the context, and instructions for two common uses follow.

1. Direct comparison to a result of a user determination: For this case, directly compare a coverage interval calculated by the user for their result to the appropriate coverage interval provided in the certificate.

2. Propagation of uncertainty when using SRM 2693a as a calibration standard: When a value provided in the certificate is used to calibrate a measurement process, the uncertainty associated with that value should be appropriately propagated into the user's uncertainty using the value of u_c provided in the certificate.

7.5. S

Two sets of measurements are available for S: first, measurements from 93 CANSPEX laboratories, each using quadruplicates on a single bottle, and second, measurements from PGAA using single measurements on each of five bottles (Table 23 "Good Spectra" values). The statistical model used to reduce the two sets of measurements into a consensus value is similar to the CANSPEX and PGAA parts of the model used to reduce the measurements of C. The combustion part of the statistical model is omitted because there are no measurements of S by combustion. As with the previous constituents, the appropriateness of the statistical model in Eq. 11 may be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 31 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle measured by a random CANSPEX lab (on left) and for a new random bottle measured by PGAA. In all cases, approximately 95 % of the points fall within the intervals, and the statistical model for S is deemed appropriate.



Fig. 31. Summary of Available Results for S.

Left: Solid circles represent replicate results reported by CANSPEX participants, sorted by increasing participant mean value. Horizontal lines depict a 95 % prediction interval. Right: solid circles represent PGAA results ordered by the sample bottle subplot-run-fill order.

Fig. 32 compares the observed measurements to potential values and intervals for the certificate. Note that the CANSPEX and PGAA values and intervals appear next to the measurements. The with heterogeneity intervals are on the left.



Fig. 32. Statistical Reductions for S.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circle with error bars but without neighboring measurement results represents the consensus reduction of the two sets of measurements.

Table 46 lists the mean, standard uncertainty, coverage factor, expanded uncertainty, and relative expanded uncertainty for the combined mass fraction of w_S . The uncertainty does not include a between-bottle heterogeneity component. The 95 % coverage interval is associated with the mean of all bottles of SRM 2693a because each bottle is assumed to contain the same mass fraction of S on average.

Table 46. Mass	Fraction of S, %.
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Measurand	W	<i>U</i> _c	k	U	$U_{ m rel},\%$
S	0.3334	0.0036	2.19	0.0078	2.4

7.6. AI, Br, Ca, Dy, Mn, Na, and V

These elements were determined in duplicate on each of ten bottles by INAA. The statistical model used to reduce the measurements into a consensus value accounts for two nested sources of variability, differences between the bottle averages and within bottle differences.

As with the previous constituents, the appropriateness of the statistical model in Eq. 12 can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 33 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle measured by INAA. In all cases,

approximately 95 % of the points fall within the intervals, and the statistical model for Al, Br, Ca, Dy, Mn, Na, and V is deemed appropriate.



Fig. 33. Summary of Available Results for Al, Br, Ca, Dy, Mn, Na, and V.

Solid circles represent INAA results ordered by the sample bottle subplot-run-fill order. Horizontal lines depict a 95 % prediction interval.

Fig. 34 compares the observed measurements to potential values and intervals for the certificate.



Fig. 34. Statistical Reductions for Al, Br, Ca, Dy, Mn, Na, and V.

Solid circles without error bars represent the measurement results. Solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals.

Table 47 lists the mean, standard uncertainty, coverage factor, expanded uncertainty, and relative expanded uncertainty for the combined mass fractions of w_{Al} , w_{Br} , w_{Ca} , w_{Dy} , w_{Mn} , w_{Na} , and w_V , without including between-bottle heterogeneity, except for Mn and Na, because, for these two elements, there is weak evidence of heterogeneity. For Al, Br, Ca, Dy, and V, the 95 % coverage intervals are associated with the mean of all bottles of SRM 2693a because the underlying mass fraction is assumed to be the same for each bottle. For Mn and Na, the 95 % coverage interval is associated with the mean of a single randomly chosen bottle of SRM 2693a. For elements that were determined to have values of the coverage factor, k, where $1.96 \le k \le 2.04$, k = 2.

Measurand	W	<i>u</i> _c	k	U	$U_{\rm rel},$ %
Al	15080	55	2	110	0.7
Br	0.418	0.0078	2	0.016	3.7
Ca	981	22.3	2	45	4.5
Dy	1.550	0.036	2	0.072	4.7
Mn	24.3	1.1	2.18	2.4	9.9
Na	34.4	1.0	2.11	2.1	6.2
V	52.22	0.22	1.85	0.41	0.8

7.7. CI

Two sets of measurements are available for Cl: first, measurements from 27 CANSPEX laboratories, each using quadruplicates on a single bottle, and second, measurements from INAA using duplicate measurements on each of ten bottles, denoted y_{lm} where *l* indexes bottle, and *m* indexes replicate within. As discussed stated in section 6.1, the Cl measurements are not used in the value assignment for the certificate. The Cl value and uncertainty for the certificate are calculated only using the INAA measurements. Further, a component of uncertainty accounting for heterogeneity is included because heterogeneity may be indicated by some extreme values in the CANSPEX measurements and by the existence of one measured INAA value that is clearly extreme compared to the others. The statistical model used to reduce the measurements into a consensus value is the same as for Al, Br, Ca, Dy, Mn, Na, and V, with one exception. For the aforementioned constituents, the within-bottle variability was assumed to follow a Gaussian distribution; however for Cl, that Gaussian distribution is replaced by a Student's *t*-distribution with 3 degrees of freedom to mitigate the effect of the extreme value on the results.

As with the previous constituents, the appropriateness of the statistical model can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 35 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle measured by INAA. Approximately 95 % of the points fall within the intervals, and the statistical model for Cl is deemed appropriate.



Fig. 35. Summary of Available Results for Cl.

Solid circles represent INAA results ordered by the sample bottle subplot-run-fill order. Horizontal lines depict a 95 % prediction interval.

Fig. 36 compares the observed measurements of Cl to potential values and intervals for the certificate. The CANSPEX measurements, values, and intervals, and the combined values and intervals are included for completeness.



Fig. 36. Statistical Reductions for Cl.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circles with error bars but without neighboring measurement results represent consensus reductions of the two sets of measurements.

Table 48 lists the mean, standard uncertainty, coverage factor, expanded uncertainty, and relative expanded uncertainty for the combined mass fraction of w_{Cl} including between-bottle heterogeneity. The 95 % coverage interval is associated with the mean of a single randomly chosen bottle of SRM 2693a.

Table 48. Mas	s Fraction o	of CI,	mg/kg.
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Measurand	W	$u_{\rm c}$	k	U	$U_{ m rel}$, %
Cl	59.7	0.86	2.08	1.8	3.0

7.8. Hg

Two sets of measurements are available for Hg: first, measurements from 42 CANSPEX laboratories, each using quadruplicates on a single bottle, and second, measurements with a DMA using AAS from each of five bottles, using between three and five replicates from each bottle. The statistical model used to reduce the measurements into a consensus value and corresponding uncertainty is a combination of the models used for the CANSPEX measurements for C, H, N, and S, and the model used for the INAA measurements of Cl, the latter corresponding to the DMA measurements of Hg. Note that there are also extreme measurements of Hg by DMA, so the Student's-*t* distribution used for the INAA measurements are calculated accounting for heterogeneity because heterogeneity may be indicated by the existence of some extreme values in the CANSPEX measurements, extreme values measured in preliminary DMA determinations, and by one DMA measured value that is clearly extreme compared to the others.

As with the previous constituents, the appropriateness of the statistical model in Eq. 13 can be assessed by comparing the observed measurements to the appropriate posterior predictive distributions. Fig. 37 shows the observed measurements (blue points) and 95 % prediction intervals (orange lines) for a new random bottle measured by a random CANSPEX lab (on left) and for a new random bottle measured by DMA (on right). Approximately 95 % of the points fall within the intervals, and the statistical model for Hg is deemed appropriate.



Fig. 37. Summary of Available Results for Hg.

Left: Solid circles represent replicate results reported by CANSPEX participants, sorted by increasing participant mean value. Horizontal lines depict a 95 % prediction interval. Right: solid circles represent PGAA results ordered by the sample bottle subplot-run-fill order.

Fig. 38 compares the observed measurements of Hg to potential values and intervals for the certificate.



Fig. 38. Statistical Reductions for Hg.

Solid circles without error bars represent the measurement results. Neighboring solid circles with error bars represent the statistical reduction of those results. Error bars depict 95 % confidence intervals. The solid circles with error bars but without neighboring measurement results represent consensus reductions of the two sets of measurements.

Table 49 lists the mean, standard uncertainty, coverage factor, expanded uncertainty, and relative expanded uncertainty for the combined mass fraction of w_{Hg} including between-bottle heterogeneity. The 95 % coverage interval is associated with the mean of a single randomly chosen bottle of SRM 2693a.

Measurand	W	<i>u</i> _c	k	U	$U_{ m rel},$ %
Hg	56.3	2.8	2.22	6.2	11

Table 49. Mass Fraction of Hg, µg/kg.

7.9. Proposed Certified and Non-Certified Values for SRM 2693a

Table 50 (symmetric uncertainty interval) and Table 51 (asymmetric uncertainty interval) list the values proposed as certified values. Table 52 (symmetric uncertainty interval) and Table 53 (asymmetric uncertainty interval) list the values proposed as non-certified values.

Table 50. Proposed Certified Mass Fraction Values for S.

Measurand	Units	W	k	U
S	%	0.3334	2.19	0.0078

 Table 51. Proposed Certified Mass Fractions Values for H and N.

Measurand	Units	W	$u_{ m c}$	$U_{ m 95-LL}$	$U_{ m 95-UL}$
Н	%	4.39	0.056	4.33	4.54
Ν	%	1.179	0.010	1.155	1.193

Table 52. Proposed Non-Certified Mass Fraction Values with Symmetric Uncertainty Interval.

Measurand	Units	W	k	U
Al	mg/kg	15 080	2	110
Br	mg/kg	0.418	2	0.016
Ca	mg/kg	981	2	45
Cl	mg/kg	59.7	2.08	1.8
Dy	mg/kg	1.550	2	0.072
Hg	µg/kg	56.3	2.22	6.2
Mn	mg/kg	24.3	2.18	2.4
Na	mg/kg	34.4	2.11	2.1
V	mg/kg	52.22	1.85	0.41

Table 53. Proposed Non-Certified Mass Fraction Values for C with Symmetric Uncertainty Intervals.

Measurand	Units	W	$u_{\rm c}$	$U_{ m 95-LL}$	$U_{ m 95-UL}$
С	%	80.0	0.87	79.8	82.5

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Appendix A. List of Acronyms

AAS	atomic absorption spectrometry
CANSPEX	Coal and Ash Sampling Proficiency Exchange
CHN	carbon, hydrogen, and nitrogen
CHNS	carbon, hydrogen, nitrogen, and sulfur
CNPGAA	cold neutron prompt gamma-ray activation analysis
COA	Certificate of Analysis
cps	counts per second
DSP	digital signal processor
FEP	fluoroethylene propylene
GCV	gross calorific value
GUM	Guide to the Expression of Uncertainty in Measurement
INAA	instrumental neutron activation analysis
kcps	thousands of counts per second
LOD	mass loss on drying
NCNR	NIST Center for Neutron Research
NGD	neutron guide
NICOB	NIST Consensus Builder
NIST	National Institute of Standards and Technology
PGAA	prompt gamma-ray activation analysis
PSA	particle size analysis
PSD	particle size distribution
RSD%	relative standard deviation expressed as percent
SOP	standard operating procedures
SD	standard deviation
SI	International System of Units
SRM	Standard Reference Material®
TCD	thermal conductivity detector
TNPGAA	thermal neutron prompt gamma-ray activation analysis
WDXRF	wavelength dispersive X-ray fluorescence