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**Certification of Standard
Reference Material[®] 1270a**
Cr-Mo Low Alloy Steel A336 (F-22) (disk form)

Bruce Scruggs
John R. Sieber (Retired)
Rick Paul
Heather Chen-Mayer
Anthony F. Marlow
James H. Yen

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Abstract

The certified mass fractions delivered by Standard Reference Material (SRM) 1270a are intended primarily for use in validation of chemical and instrumental methods of analysis for element contents of iron and steel alloys. They can be used to validate value assignment of a laboratory's in-house reference materials. A unit of SRM 1270a consists of one disk approximately 32 mm in diameter and 19 mm thick.

Keywords

Compositional Analysis; Cr-Mo Steel; Low Alloy Steel; Standard Reference Material; Steel.

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1. Introduction

SRM 1270 was produced in the early '80s and was certified for 11 elements, *viz.*, C, Si, P, S, V, Cr, Mn, Co, Ni, Cu and Mo. The alloy composition from which this SRM is modeled is intended for high pressure and temperature applications. SRM 1270a is an SRM renewal with the material being produced within the same billet as the original SRM 1270 material. The goal for this renewal was to certify the original 11 certified elements, but also to explore the possibility of certifying some of the additional elements found in SRM 1270 but not certified, *viz.*, B, Al, Ti, As, Zr, Nb, Sn, Sb, Ta, W and Pb, in order to expand the use of this SRM.

This publication documents the production, analytical measurements, and data analysis leading to the certification of SRM 1270a. Analytical measurements involve measurements done in the early 1980s to characterize SRM 1270 and the material designated for SRM 1270a as well as more recent measurements targeted at expanding the number of certified elements. Past measurements utilized a number of classical chemical and electrochemical methods described in section 5 in addition to Wavelength Dispersive X-ray Fluorescence (WDXRF), Combustion analysis with infrared detection (CID), Atomic Absorption spectrophotometry (AA) and Instrumental Neutron Activation Analysis (INAA). More recent measurements are described in sections 3 and 4 using instrumental methods, *viz.*, WDXRF, CID, Spark Source Optical Emission Spectrophotometry (SS-OES) and Inert Gas Fusion (IGF). Section 6 describes the analysis of B in SRM 1270a using Prompt Gamma Activation Analysis (PGAA) at the National Institute of Standards and Technology Center for Neutron Research (NCNR).

2. Material

2.1. History and Acquisition

The planning for this SRM alloy type was coordinated through the Task Group on Temper Embrittlement, American Petroleum Institute back in the late 1970s. There was a need for an SRM to validate testing methods for alloys used in the production of pressure vessels. They also predicted a future need for this type of SRM as developments occurred in alternative fossil fuels processing technologies. In addition, this SRM alloy type was expected to serve as a supplement to the "1200 series" of iron and steel SRMs.

The material was melted and cast into a single ingot at Esco Corporation, Portland, OR, under a National Bureau of Standards (NBS)¹ contract with the Steel Founders' Society of America (SFSA).

The single ingot was fabricated at the Puget Sound Naval Shipyard, Bremerton, WA. The ingot was first forged to a slab. Portions of the slab, suspected of being inhomogeneous, were cut and discarded. The remaining slab sections were forged and swaged to rods over size 32 mm in diameter, sub-critical annealed and centerless ground to the final size of 32 mm in diameter.

¹ The National Bureau of Standards was founded in 1901. In 1988, it was reorganized and renamed the National Institute of Standards and Technology (NIST).

Extensive homogeneity testing was carried out at NBS with metallographic studies conducted by C. H. Brady; optical emission analysis conducted by J. A. Norris; and by WDXRF analysis conducted by P. A. Pella.

Composite samples for chemical analysis were prepared in the form of millings, cut from the full cross section of specimens representative of the entire lot of material.

Some data for the certification of SRM 1270a originates from a cooperative analyses for certification, carried out under the auspices of the ASTM/NBS Research Associate Program, were performed in the following analytical laboratories:

- Babcock & Wilcox Co., Alliance Research Center, Alliance, OH and Tubular Products Division, Beaver Falls, PA.
- Chicago Bridge & Iron Co., Research Division, Plainfield, IL.
- Climax Molybdenum Co. of Michigan, Ann Arbor, MI.
- Lukens Steel Co., Coatesville, PA.
- National Bureau of Standards, Inorganic Analytical Research Division, Washington, D.C.
- Phenix Steel Corp., Claymont, DE.

2.2. Form

A unit of SRM 1270a is sold in solid, disk form, nominally 32 mm in diameter and 19 mm thick.

3. Acceptance Testing of SRM 1270a

The homogeneity of SRM 1270a was evaluated by Wavelength Dispersive X-ray Fluorescence (WDXRF) as part of the process to certify the material. The following constituents were measured by WDXRF homogeneity testing: B, C, Al, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Zr, Nb, Mo, Sn, Sb, Ta, W, and Pb. Measurement results of this type are expressed in thousands of X-ray photon counts per second (kCPS) for comparative purposes. The material is in solid, cylindrical form, 19 mm in length, having been sliced from rods about 32 mm in diameter. The cylindrical form is commonly referred to as a disk on the NIST Standard Reference Materials website.

3.1. Equipment

The steel disks were surface ground on a Buehler model ECOMET 4 12" variable speed wheel and a model EcoMet 3000 8" variable speed wheel. WDXRF measurements were made on a PANalytical model Zetium Ultimate WDXRF spectrometer equipped with a 4 kW Rh-anode X-ray tube. Small spot XRF measurements were made on an Ametek EDAX model Orbis PC energy dispersive micro-XRF spectrometer equipped with a 50 W Rh-anode X-ray tube and a turret bearing collimators and a poly-capillary X-ray optic to collimate or focus the X-ray beam down to a smaller spot size.

3.2. Sampling Details

The material was sliced and stored in five storage cans and packed in layers in each can. Disk specimens for XRF measurements were obtained by selecting disks from prescribed locations in each of the five storage cans. One disk was selected at random from the first, third, fifth, and seventh layers in each can. Disks were cleaned of the protective oil applied at the time of storage. Sample identities marked on the disks consist of a layer number followed by a dash and the can number. In this report, the numbers are reversed, which is indicated in the tables. All disks were prepared by grinding the surfaces with ZIRCON paper finishing with 240 grit, a ZrO₂ based abrasive. The disks are measured twice by WDXRF while resurfacing the disks with 240 grit ZIRCON paper between measurements to remove sample material and expose a fresh surface for the second measurement. This resurfacing/measurement sequence is then repeated using 220 grit SiC paper for two further WDXRF measurements.

A single disk of the material was selected for further analysis by small spot energy dispersive XRF to assist in estimating the minimum amount of sample required to be representative of the population of material disks and to probe the material for any enriched localized phases on a 1 mm to 2 mm scale.

3.3. Summary of Analytical Methods

WDXRF measurement conditions were chosen to maximize sensitivity and minimize counting statistical error (CSE), i.e., the uncertainty in X-ray photon counting statistics. A channel mask of 29 mm inner diameter was chosen to measure the 32 mm diameter disks. For all elements, the measured line was the K-L_{2,3}, except Ta for which the line was L₃-M_{4,5}. The Rh-anode X-ray tube was operated at 3.6 kW, and the spectrometer chamber was evacuated to < 10 Pa total pressure.

As noted above, measurements were made after surface grinding with two different abrasives. Each abrasive leaves characteristic contamination on the surface and makes it impossible to obtain repeatable, unbiased measurements for certain elements. The two sets of XRF measurements were compared to identify which data was acceptable for each element. The elements Al and Zr can only be measured after grinding with SiC paper, and the element Si could only be measured after grinding with ZIRCON paper. All other elements were not affected by the composition of the paper and the datasets from both abrasive papers were combined. Hence, only two measurements are made on Si, Al and Zr for homogeneity studies while four measurements, coming from both SiC and ZIRCON papers, were made for all other elements.

Grinding of a disk to prepare a fresh surface removes small amounts of metal. When the purpose is to create a fresh surface for XRF homogeneity testing from a surface that was already prepared, the brief grinding removes roughly 80 mg to 160 mg of material across the entire diameter of a disk. When the purpose is to create a fresh surface from a disk that was previously measured by spark optical emission spectrometry or glow discharge optical emission spectrometry, about five times as much grinding is necessary, starting with a lower grit abrasive. Therefore, more than one gram of metal is removed. The conclusion is that a 120 g disk of steel used only for XRF measurements may be good for more than 500 repeated surface preparations, assuming the disk is no longer usable when its mass drops to 20 g, based

on an analyst's ability to hold the disk while grinding. For spark source optical emission methods, the same mass disk may be good for only about 100 repeated surface preparations.

Microbeam XRF measurements were performed on a single disk of SRM 1270a. Disk 2-5 (can-layer) was measured in a rectangular area using both the 2 mm beam collimator and the 1 mm beam collimator. In this case, the sample was measured in a vacuum atmosphere using a 1.6 μ s detector amplifier time constant. With the 2 mm collimator, an array of 100 locations was measured in a 10 x 10 grid pattern at 40 kV, 600 μ A and 500 s live time per location. With the 1 mm collimator, an array of 340 locations was measured in a 17 x 20 grid pattern at 45 kV, 1000 μ A and 800 s live time per location. The microbeam spectrometer measured the elements Al, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, As, Mo, and Sn.

3.4. Results of Acceptance Testing

X-ray photon count rate values, either raw count rates for major elements or background corrected count rates for minor and trace elements, were used to compare all sliced disks. For each element, the mean values for the replicate measurements of the three or four disks from each can were graphed to provide a visual representation of how the element varies across the entire population of disks. The graphs for the 22 elements are displayed in Fig. 1. The can and layer designations have no known relationship to the original bars prepared for the SRM.

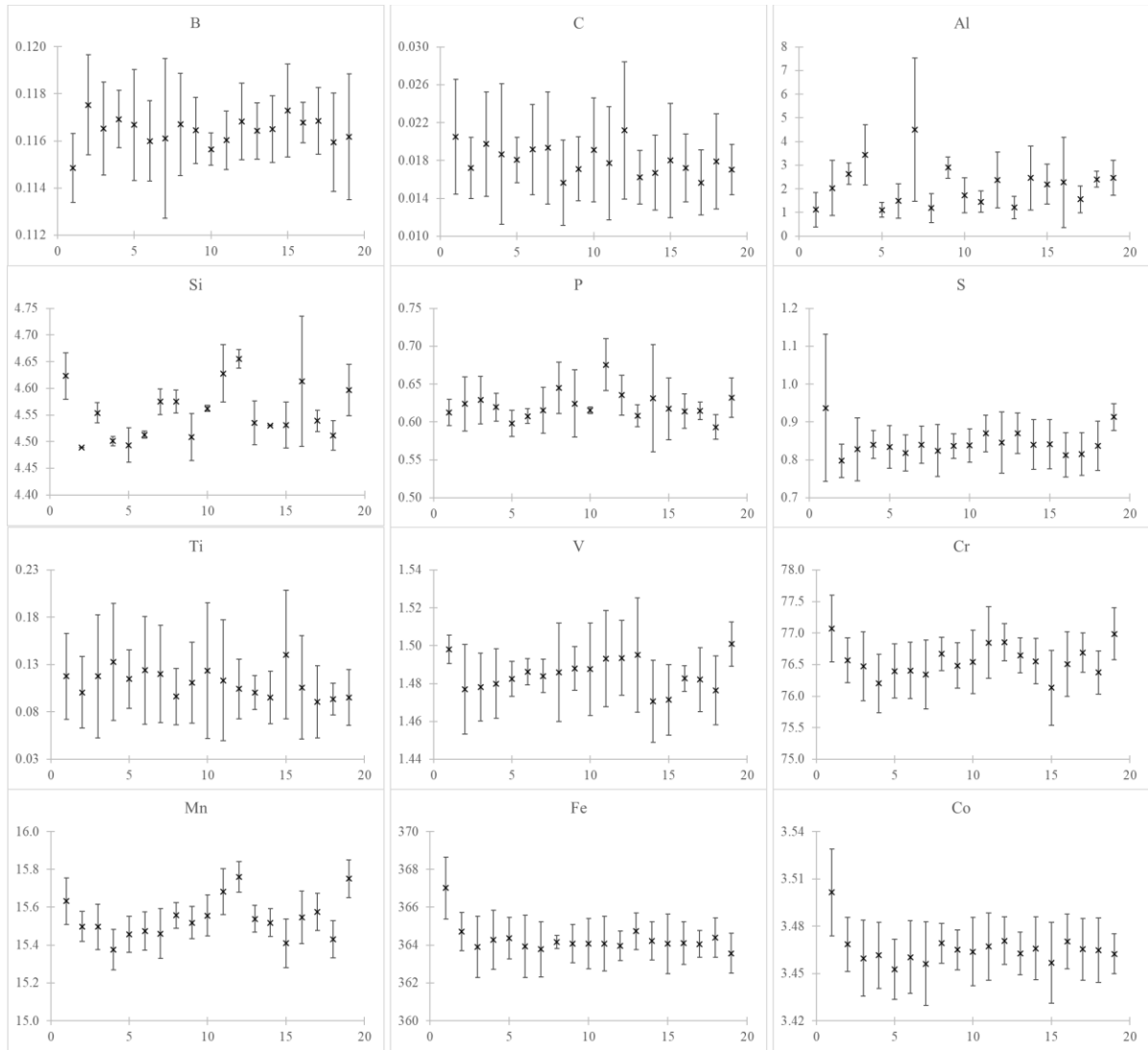


Fig. 1a. Distributions of elements among the disks of SRM 1270a Low Alloy Steel. All error bars are the standard deviation of $n = 4$ individual measurements ($n = 2$ for Al, Si, Zr) for the disk. Values on the horizontal axes are the specimen disks numbered from 1 to 19 in order from top to bottom as shown in the Analysis of Variance tables in section 3.5. Values on the vertical axes are X-ray signal intensity in thousands of counts per second (kCPS).

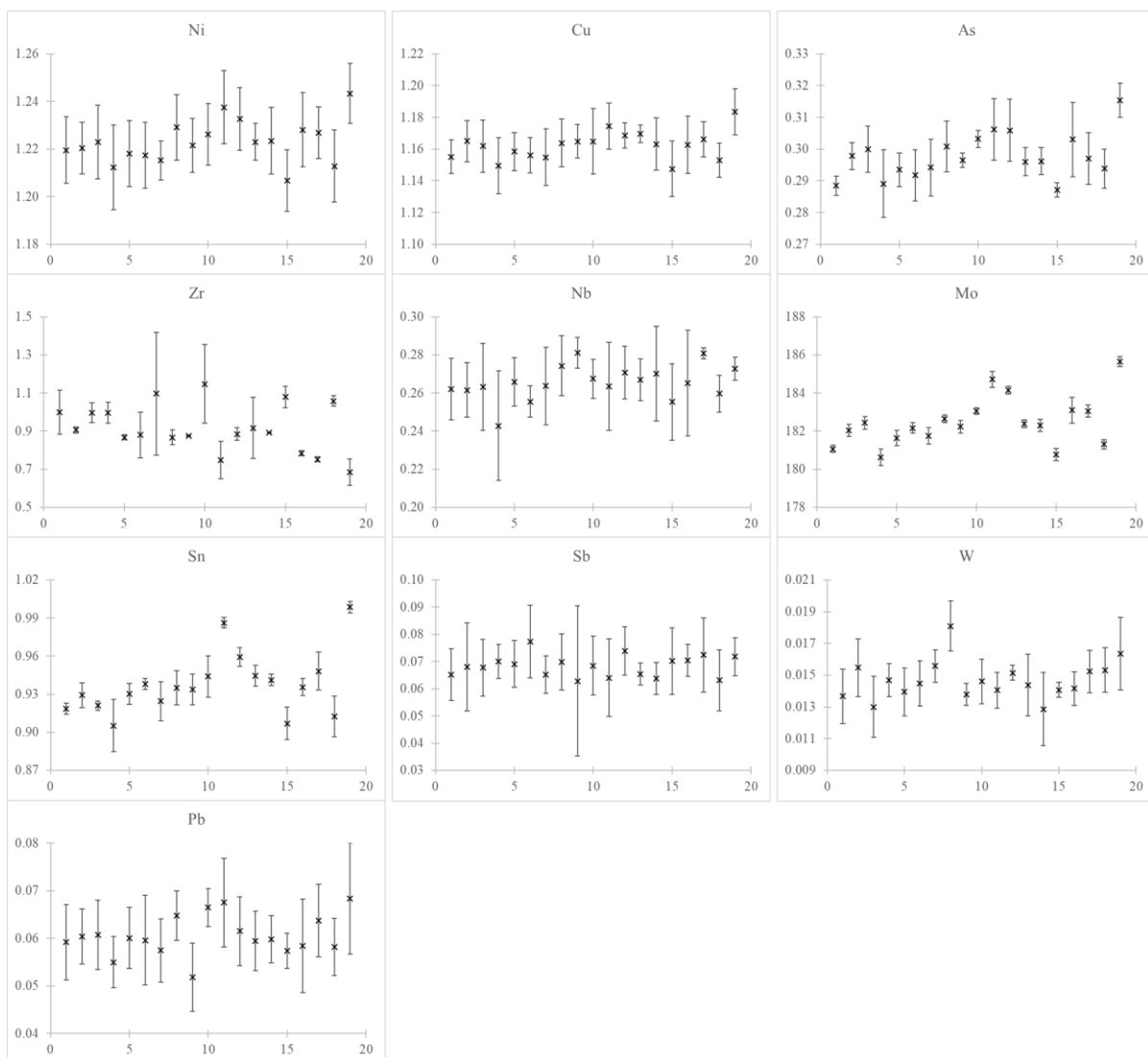


Fig. 1b. Distributions of elements among the disks of SRM 1270a Low Alloy Steel. All error bars are the standard deviation of $n = 4$ individual measurements ($n = 2$ for Al, Si, Zr) for the disk. Values on the horizontal axes are the specimen disks numbered from 1 to 19 in order from top to bottom as shown in the Analysis of Variance tables in section 3.5. Values on the vertical axes are X-ray signal intensity in thousands of counts per second (kCPS).

Overall, the graphs in **Fig. 1a** and **Fig. 1b** show that all 19 disks show no trends other than high levels of overlap of the vertical error bars for all 19 disks for most elements. Because the error bars are at the level of $1s$, this indicates very good homogeneity among disks. The elements Mo and Sn show very small values of $1s$, which is evidence the variance among disks is greater than variance within disks. However, that does not indicate a problem at the $1s$ comparison level. If the error bars were expanded to $2s$, the problem would be less evident. Overall, the material was found acceptable. More detailed evidence is discussed below in the ANOVA of WDXRF measurements.

3.5. Results of Homogeneity Testing

The analysis of variance (ANOVA) results for all measured elements in SRM 1270a are given in **Table 1** through **Table 22**, one element per table. Each table shows the storage can and layer number for each disk, the average count rate and variance of the measurements of the disk, the overall average of disk averages, the standard deviation of the disk averages, and the relative standard deviation (RSD) of the set of disk average values.

Table 1. Analysis of Variance for Boron in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.11485	0.0000021			
1 - 3	4	0.11753	0.0000045			
1 - 5	4	0.11653	0.0000039			
1 - 7	4	0.11693	0.0000015			
2 - 1	4	0.11668	0.0000056			
2 - 3	4	0.11600	0.0000029			
2 - 5	4	0.11610	0.0000115	X		
2 - 7	4	0.11670	0.0000047			
3 - 1	4	0.11645	0.0000020			
3 - 3	4	0.11565	0.0000005			
3 - 5	4	0.11603	0.0000015			
3 - 7	4	0.11683	0.0000026			
4 - 1	4	0.11643	0.0000014			
4 - 3	4	0.11650	0.0000020			
4 - 5	4	0.11730	0.0000039			
4 - 7	4	0.11678	0.0000007			
5 - 1	4	0.11685	0.0000020			
5 - 3	4	0.11595	0.0000044			
5 - 5	4	0.11618	0.0000071			
<i>Average</i>		0.11643				
<i>Standard Deviation</i>		0.00061	0.52%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.000027	18	0.0000015	0.433	0.974	1.788
<i>Within Samples</i>	0.000195	57	0.0000034			
<i>Total</i>	0.000221	75				

Table 2. Analysis of Variance for Carbon in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	0.0205	0.000037			
1 - 3	4	0.0172	0.000011			
1 - 5	4	0.0197	0.000031			
1 - 7	4	0.0187	0.000055			
2 - 1	4	0.0181	0.000006			
2 - 3	4	0.0192	0.000023			
2 - 5	4	0.0193	0.000035			
2 - 7	4	0.0157	0.000020			
3 - 1	4	0.0171	0.000011			
3 - 3	4	0.0191	0.000030			
3 - 5	4	0.0177	0.000036			
3 - 7	4	0.0212	0.000053			
4 - 1	4	0.0162	0.000008			
4 - 3	4	0.0167	0.000016			
4 - 5	4	0.0180	0.000037			
4 - 7	4	0.0172	0.000013			
5 - 1	4	0.0157	0.000012			
5 - 3	4	0.0179	0.000025			
5 - 5	4	0.0171	0.000007			
<i>Average</i>		0.0180				
<i>Standard Deviation</i>		0.0015	8.6%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.00017	18	0.0000096	0.393	0.984	1.788
<i>Within Samples</i>	0.00139	57	0.0000244			
<i>Total</i>	0.00157	75				

Table 3. Analysis of Variance for Aluminum in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	2	0.197	0.0273			
1 - 3	2	0.069	0.0003			
1 - 5	2	0.119	0.0045			
1 - 7	2	0.102	0.0012			
2 - 1	2	0.084	0.0004			
2 - 3	2	0.181	0.0255			
2 - 5	2	0.374	0.1372	X	X	
2 - 7	2	0.081	0.0005			
3 - 1	2	0.066	0.0000			
3 - 3	2	0.339	0.0521	X	X	
3 - 5	2	0.169	0.0142			
3 - 7	2	0.076	0.0004			
4 - 1	2	0.122	0.0049			
4 - 3	2	0.073	0.0007			
4 - 5	2	0.168	0.0073			
4 - 7	2	0.077	0.0000			
5 - 1	2	0.069	0.0001			
5 - 3	2	0.102	0.0024			
5 - 5	2	0.139	0.0068			
<i>Average</i>		0.137				
<i>Standard Deviation</i>		0.088	64%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.28	18	0.015	1.027	0.476	2.182
<i>Within Samples</i>	0.29	19	0.015			
<i>Total</i>	0.56	37				

Table 4. Analysis of Variance for Silicon in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	2	4.572	0.0022			
1 - 3	2	4.544	0.0007			
1 - 5	2	4.541	0.0000			
1 - 7	2	4.557	0.0001			
2 - 1	2	4.549	0.0001			
2 - 3	2	4.530	0.0005			
2 - 5	2	4.492	0.0000			
2 - 7	2	4.616	0.0013			
3 - 1	2	4.590	0.0011			
3 - 3	2	4.577	0.0064	X		
3 - 5	2	4.592	0.0067	X		
3 - 7	2	4.722	0.0012			X
4 - 1	2	4.604	0.0012			
4 - 3	2	4.546	0.0013			
4 - 5	2	4.516	0.0001			
4 - 7	2	4.538	0.0006			
5 - 1	2	4.557	0.0001			
5 - 3	2	4.504	0.0017			
5 - 5	2	4.604	0.0035			
<i>Average</i>		4.566				
<i>Standard Deviation</i>		0.051	1.1%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.094	18	0.0052	3.453	0.0051	2.182
<i>Within Samples</i>	0.029	19	0.0015			
<i>Total</i>	0.123	37				

Table 5. Analysis of Variance for Phosphorus in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.613	0.0003			
1 - 3	4	0.624	0.0013			
1 - 5	4	0.629	0.0010			
1 - 7	4	0.620	0.0003			
2 - 1	4	0.598	0.0003			
2 - 3	4	0.608	0.0001			
2 - 5	4	0.615	0.0009			
2 - 7	4	0.645	0.0012			
3 - 1	4	0.624	0.0020			
3 - 3	4	0.616	0.0000			
3 - 5	4	0.676	0.0012			X
3 - 7	4	0.635	0.0007			
4 - 1	4	0.608	0.0002			
4 - 3	4	0.632	0.0050	X		
4 - 5	4	0.617	0.0016			
4 - 7	4	0.614	0.0005			
5 - 1	4	0.615	0.0001			
5 - 3	4	0.593	0.0003			
5 - 5	4	0.632	0.0007			
<i>Average</i>		0.622				
<i>Standard Deviation</i>		0.018	2.9%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.024	18	0.00133	1.429	0.154	1.788
<i>Within Samples</i>	0.053	57	0.00093			
<i>Total</i>	0.077	75				

Table 6. Analysis of Variance for Sulfur in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.937	0.0378	X	X	
1 - 3	4	0.798	0.0020			
1 - 5	4	0.828	0.0069			
1 - 7	4	0.840	0.0013			
2 - 1	4	0.834	0.0031			
2 - 3	4	0.818	0.0023			
2 - 5	4	0.840	0.0024			
2 - 7	4	0.825	0.0046			
3 - 1	4	0.837	0.0010			
3 - 3	4	0.838	0.0020			
3 - 5	4	0.870	0.0023			
3 - 7	4	0.846	0.0065			
4 - 1	4	0.870	0.0029			
4 - 3	4	0.841	0.0043			
4 - 5	4	0.841	0.0042			
4 - 7	4	0.813	0.0034			
5 - 1	4	0.816	0.0032			
5 - 3	4	0.837	0.0043			
5 - 5	4	0.913	0.0013			
<i>Average</i>		0.844				
<i>Standard Deviation</i>		0.034	4.0%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.081	18	0.0045	0.895	0.586	1.788
<i>Within Samples</i>	0.288	57	0.0050			
<i>Total</i>	0.369	75				

Table 7. Analysis of Variance for Titanium in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	0.118	0.0020			
1 - 3	4	0.101	0.0014			
1 - 5	4	0.118	0.0042			
1 - 7	4	0.133	0.0038			
2 - 1	4	0.115	0.0009			
2 - 3	4	0.124	0.0032			
2 - 5	4	0.120	0.0026			
2 - 7	4	0.096	0.0009			
3 - 1	4	0.111	0.0018			
3 - 3	4	0.124	0.0051			
3 - 5	4	0.113	0.0041			
3 - 7	4	0.104	0.0010			
4 - 1	4	0.100	0.0003			
4 - 3	4	0.095	0.0008			
4 - 5	4	0.141	0.0046			
4 - 7	4	0.106	0.0030			
5 - 1	4	0.091	0.0015			
5 - 3	4	0.093	0.0003			
5 - 5	4	0.095	0.0009			
<i>Average</i>		0.110				
<i>Standard Deviation</i>		0.014	13%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.014	18	0.00080	0.356	0.991	1.788
<i>Within Samples</i>	0.128	57	0.00224			
<i>Total</i>	0.142	75				

Table 8. Analysis of Variance for Vanadium in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	1.4981	0.00006			
1 - 3	4	1.4770	0.00056			
1 - 5	4	1.4783	0.00032			
1 - 7	4	1.4800	0.00033			
2 - 1	4	1.4824	0.00009			
2 - 3	4	1.4862	0.00005			
2 - 5	4	1.4840	0.00008			
2 - 7	4	1.4859	0.00068			
3 - 1	4	1.4881	0.00013			
3 - 3	4	1.4875	0.00060			
3 - 5	4	1.4932	0.00064			
3 - 7	4	1.4936	0.00039			
4 - 1	4	1.4951	0.00092			
4 - 3	4	1.4707	0.00047			
4 - 5	4	1.4715	0.00035			
4 - 7	4	1.4827	0.00004			
5 - 1	4	1.4821	0.00028			
5 - 3	4	1.4764	0.00033			
5 - 5	4	1.5008	0.00014			
<i>Average</i>		1.4849				
<i>Standard Deviation</i>		0.0085	0.57%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0052	18	0.00029	0.850	0.636	1.788
<i>Within Samples</i>	0.0194	57	0.00034			
<i>Total</i>	0.0246	75				

Table 9. Analysis of Variance for Chromium in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	77.07	0.282			
1 - 3	4	76.57	0.127			
1 - 5	4	76.47	0.295			
1 - 7	4	76.20	0.213			
2 - 1	4	76.40	0.183			
2 - 3	4	76.41	0.197			
2 - 5	4	76.34	0.298			
2 - 7	4	76.67	0.071			
3 - 1	4	76.48	0.128			
3 - 3	4	76.54	0.255			
3 - 5	4	76.85	0.327			
3 - 7	4	76.86	0.087			
4 - 1	4	76.64	0.078			
4 - 3	4	76.56	0.131			
4 - 5	4	76.13	0.349			
4 - 7	4	76.51	0.263			
5 - 1	4	76.69	0.099			
5 - 3	4	76.38	0.118			
5 - 5	4	76.99	0.171			
<i>Average</i>		76.57				
<i>Standard Deviation</i>		0.25	0.32%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	4.4	18	0.25	1.280	0.236	1.788
<i>Within Samples</i>	11.0	57	0.19			
<i>Total</i>	15.5	75				

Table 10. Analysis of Variance for Manganese in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	15.63	0.015			
1 - 3	4	15.50	0.006			
1 - 5	4	15.50	0.014			
1 - 7	4	15.38	0.011			
2 - 1	4	15.46	0.009			
2 - 3	4	15.47	0.010			
2 - 5	4	15.46	0.018			
2 - 7	4	15.56	0.005			
3 - 1	4	15.52	0.007			
3 - 3	4	15.56	0.012			
3 - 5	4	15.68	0.015			
3 - 7	4	15.76	0.007			
4 - 1	4	15.54	0.005			
4 - 3	4	15.52	0.005			
4 - 5	4	15.41	0.017			
4 - 7	4	15.55	0.019			
5 - 1	4	15.58	0.010			
5 - 3	4	15.43	0.010			
5 - 5	4	15.75	0.010			
<i>Average</i>		15.54				
<i>Standard Deviation</i>		0.11	0.68%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.81	18	0.045	4.175	0.00002	1.788
<i>Within Samples</i>	0.61	57	0.011			
<i>Total</i>	1.42	75				

Table 11. Analysis of Variance for Iron in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	367.02	2.67			
1 - 3	4	364.71	1.03			
1 - 5	4	363.89	2.62			
1 - 7	4	364.28	2.42			
2 - 1	4	364.37	1.23			
2 - 3	4	363.93	2.73			
2 - 5	4	363.78	2.16			
2 - 7	4	364.15	0.12			
3 - 1	4	364.08	1.04			
3 - 3	4	364.07	1.76			
3 - 5	4	364.07	2.07			
3 - 7	4	363.96	0.60			
4 - 1	4	364.74	0.93			
4 - 3	4	364.22	1.04			
4 - 5	4	364.06	2.50			
4 - 7	4	364.10	1.29			
5 - 1	4	364.06	0.51			
5 - 3	4	364.39	1.08			
5 - 5	4	363.56	1.11			
<i>Average</i>		364.29				
<i>Standard Deviation</i>		0.72	0.20%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	37	18	2.1	1.364	0.186	1.788
<i>Within Samples</i>	87	57	1.5			
<i>Total</i>	124	75				

Table 12. Analysis of Variance for Cobalt in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	3.501	0.00076			
1 - 3	4	3.468	0.00030			
1 - 5	4	3.460	0.00058			
1 - 7	4	3.461	0.00044			
2 - 1	4	3.453	0.00036			
2 - 3	4	3.460	0.00053			
2 - 5	4	3.456	0.00071			
2 - 7	4	3.469	0.00016			
3 - 1	4	3.465	0.00016			
3 - 3	4	3.464	0.00047			
3 - 5	4	3.467	0.00046			
3 - 7	4	3.471	0.00023			
4 - 1	4	3.463	0.00018			
4 - 3	4	3.466	0.00040			
4 - 5	4	3.457	0.00066			
4 - 7	4	3.470	0.00030			
5 - 1	4	3.465	0.00038			
5 - 3	4	3.465	0.00042			
5 - 5	4	3.462	0.00016			
<i>Average</i>		3.466				
<i>Standard Deviation</i>		0.010	0.29%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0072	18	0.00040	0.987	0.487	1.788
<i>Within Samples</i>	0.0230	57	0.00040			
<i>Total</i>	0.0302	75				

Table 13. Analysis of Variance for Nickel in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	1.2195	0.00020			
1 - 3	4	1.2203	0.00012			
1 - 5	4	1.2229	0.00024			
1 - 7	4	1.2124	0.00032			
2 - 1	4	1.2180	0.00019			
2 - 3	4	1.2174	0.00019			
2 - 5	4	1.2152	0.00007			
2 - 7	4	1.2291	0.00019			
3 - 1	4	1.2216	0.00013			
3 - 3	4	1.2262	0.00017			
3 - 5	4	1.2376	0.00024			
3 - 7	4	1.2327	0.00017			
4 - 1	4	1.2230	0.00006			
4 - 3	4	1.2235	0.00019			
4 - 5	4	1.2067	0.00017			
4 - 7	4	1.2281	0.00024			
5 - 1	4	1.2268	0.00012			
5 - 3	4	1.2128	0.00023			
5 - 5	4	1.2434	0.00016			
<i>Average</i>		1.2230				
<i>Standard Deviation</i>		0.0089	0.73%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0057	18	0.00032	1.780	0.051	1.788
<i>Within Samples</i>	0.0102	57	0.00018			
<i>Total</i>	0.0159	75				

Table 14. Analysis of Variance for Copper in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	1.1552	0.00011			
1 - 3	4	1.1650	0.00017			
1 - 5	4	1.1618	0.00027			
1 - 7	4	1.1495	0.00032			
2 - 1	4	1.1584	0.00014			
2 - 3	4	1.1562	0.00012			
2 - 5	4	1.1548	0.00032			
2 - 7	4	1.1638	0.00023			
3 - 1	4	1.1649	0.00011			
3 - 3	4	1.1649	0.00042			
3 - 5	4	1.1745	0.00021			
3 - 7	4	1.1687	0.00006			
4 - 1	4	1.1695	0.00003			
4 - 3	4	1.1632	0.00027			
4 - 5	4	1.1476	0.00031			
4 - 7	4	1.1627	0.00033			
5 - 1	4	1.1661	0.00012			
5 - 3	4	1.1530	0.00012			
5 - 5	4	1.1835	0.00021			
<i>Average</i>		1.1623				
<i>Standard Deviation</i>		0.0087	0.75%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0054	18	0.00030	1.470	0.136	1.788
<i>Within Samples</i>	0.0117	57	0.00020			
<i>Total</i>	0.0171	75				

Table 15. Analysis of Variance for Arsenic in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.2884	0.000010			
1 - 3	4	0.2978	0.000018			
1 - 5	4	0.2999	0.000054			
1 - 7	4	0.2891	0.000113			
2 - 1	4	0.2935	0.000028			
2 - 3	4	0.2917	0.000065			
2 - 5	4	0.2942	0.000080			
2 - 7	4	0.3009	0.000063			
3 - 1	4	0.2964	0.000005			
3 - 3	4	0.3032	0.000007			
3 - 5	4	0.3062	0.000093			
3 - 7	4	0.3059	0.000095			
4 - 1	4	0.2960	0.000020			
4 - 3	4	0.2962	0.000018			
4 - 5	4	0.2871	0.000005			
4 - 7	4	0.3030	0.000137			
5 - 1	4	0.2970	0.000067			
5 - 3	4	0.2938	0.000038			
5 - 5	4	0.3154	0.000029			
<i>Average</i>		0.2977				
<i>Standard Deviation</i>		0.0070	2.4%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0035	18	0.000197	3.957	0.00004	1.788
<i>Within Samples</i>	0.0028	57	0.000050			
<i>Total</i>	0.0064	75				

Table 16. Analysis of Variance for Zirconium in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	2	1.00	0.0134			
1 - 3	2	0.91	0.0003			
1 - 5	2	1.00	0.0027			
1 - 7	2	1.00	0.0031			
2 - 1	2	0.87	0.0002			
2 - 3	2	0.88	0.0144			
2 - 5	2	1.10	0.1039	X		
2 - 7	2	0.87	0.0016			
3 - 1	2	0.87	0.0000			
3 - 3	2	1.15	0.0422	X		
3 - 5	2	0.75	0.0095			
3 - 7	2	0.88	0.0012			
4 - 1	2	0.92	0.0254			
4 - 3	2	0.89	0.0000			
4 - 5	2	1.08	0.0033			
4 - 7	2	0.78	0.0002			
5 - 1	2	0.75	0.0001			
5 - 3	2	1.06	0.0008			
5 - 5	2	0.68	0.0049			
<i>Average</i>		0.92				
<i>Standard Deviation</i>		0.13	14%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.58	18	0.032	2.684	0.019	2.182
<i>Within Samples</i>	0.23	19	0.012			
<i>Total</i>	0.80	37				

Table 17. Analysis of Variance for Niobium in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	0.2621	0.00026			
1 - 3	4	0.2616	0.00020			
1 - 5	4	0.2632	0.00052			
1 - 7	4	0.2428	0.00083	X		
2 - 1	4	0.2659	0.00016			
2 - 3	4	0.2555	0.00007			
2 - 5	4	0.2637	0.00041			
2 - 7	4	0.2744	0.00025			
3 - 1	4	0.2812	0.00007			
3 - 3	4	0.2675	0.00011			
3 - 5	4	0.2635	0.00053			
3 - 7	4	0.2708	0.00019			
4 - 1	4	0.2670	0.00012			
4 - 3	4	0.2702	0.00061			
4 - 5	4	0.2554	0.00040			
4 - 7	4	0.2653	0.00077			
5 - 1	4	0.2809	0.00001			
5 - 3	4	0.2597	0.00010			
5 - 5	4	0.2728	0.00004			
<i>Average</i>		0.2654				
<i>Standard Deviation</i>		0.0090	3.4%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0058	18	0.00032	1.092	0.383	1.788
<i>Within Samples</i>	0.0169	57	0.00030			
<i>Total</i>	0.0228	75				

Table 18. Analysis of Variance for Molybdenum in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	181.1	0.036			
1 - 3	4	182.0	0.093			
1 - 5	4	182.4	0.109			
1 - 7	4	180.6	0.182			
2 - 1	4	181.6	0.173			
2 - 3	4	182.2	0.076			
2 - 5	4	181.7	0.187			
2 - 7	4	182.7	0.037			
3 - 1	4	182.2	0.116			
3 - 3	4	183.0	0.032			
3 - 5	4	184.7	0.178			
3 - 7	4	184.2	0.039			
4 - 1	4	182.4	0.039			
4 - 3	4	182.3	0.107			
4 - 5	4	180.8	0.097			
4 - 7	4	183.1	0.444	X		
5 - 1	4	183.1	0.096			
5 - 3	4	181.3	0.063			
5 - 5	4	185.6	0.068			X
<i>Average</i>		182.5				
<i>Standard Deviation</i>		1.3	0.71%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	121.0	18	6.72	58.780	< 0.00001	1.788
<i>Within Samples</i>	6.5	57	0.11			
<i>Total</i>	127.5	75				

Table 19. Analysis of Variance for Tin in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	0.918	0.00002			
1 - 3	4	0.929	0.00010			
1 - 5	4	0.921	0.00001			
1 - 7	4	0.905	0.00043	X		
2 - 1	4	0.930	0.00007			
2 - 3	4	0.938	0.00002			
2 - 5	4	0.924	0.00024			
2 - 7	4	0.935	0.00018			
3 - 1	4	0.934	0.00015			
3 - 3	4	0.944	0.00026			
3 - 5	4	0.986	0.00002			
3 - 7	4	0.959	0.00006			
4 - 1	4	0.945	0.00007			
4 - 3	4	0.941	0.00002			
4 - 5	4	0.907	0.00016			
4 - 7	4	0.936	0.00005			
5 - 1	4	0.948	0.00022			
5 - 3	4	0.913	0.00026			
5 - 5	4	0.999	0.00002			
<i>Average</i>		0.938				
<i>Standard Deviation</i>		0.024	2.6%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0414	18	0.00230	18.567	< 0.00001	1.788
<i>Within Samples</i>	0.0071	57	0.00012			
<i>Total</i>	0.0485	75				

Table 20. Analysis of Variance for Antimony in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.0652	0.00009			
1 - 3	4	0.0681	0.00026			
1 - 5	4	0.0678	0.00011			
1 - 7	4	0.0701	0.00004			
2 - 1	4	0.0691	0.00007			
2 - 3	4	0.0773	0.00018			
2 - 5	4	0.0652	0.00005			
2 - 7	4	0.0698	0.00011			
3 - 1	4	0.0628	0.00076	X		
3 - 3	4	0.0685	0.00012			
3 - 5	4	0.0641	0.00020			
3 - 7	4	0.0739	0.00008			
4 - 1	4	0.0654	0.00002			
4 - 3	4	0.0637	0.00003			
4 - 5	4	0.0702	0.00015			
4 - 7	4	0.0705	0.00003			
5 - 1	4	0.0724	0.00019			
5 - 3	4	0.0631	0.00013			
5 - 5	4	0.0718	0.00005			
<i>Average</i>		0.0684				
<i>Standard Deviation</i>		0.0040	5.8%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0011	18	0.000063	0.446	0.970	1.788
<i>Within Samples</i>	0.0080	57	0.000140			
<i>Total</i>	0.0091	75				

Table 21. Analysis of Variance for Tungsten in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between</i>	<i>from set of</i>	
				<i>replicates</i>	<i>samples</i>	
1 - 1	4	0.0137	0.0000030			
1 - 3	4	0.0155	0.0000033			
1 - 5	4	0.0130	0.0000037			
1 - 7	4	0.0147	0.0000011			
2 - 1	4	0.0140	0.0000023			
2 - 3	4	0.0145	0.0000020			
2 - 5	4	0.0156	0.0000011			
2 - 7	4	0.0181	0.0000025			
3 - 1	4	0.0138	0.0000005			
3 - 3	4	0.0146	0.0000020			
3 - 5	4	0.0141	0.0000013			
3 - 7	4	0.0152	0.0000002			
4 - 1	4	0.0144	0.0000037			
4 - 3	4	0.0129	0.0000053			
4 - 5	4	0.0141	0.0000002			
4 - 7	4	0.0142	0.0000011			
5 - 1	4	0.0152	0.0000018			
5 - 3	4	0.0153	0.0000020			
5 - 5	4	0.0164	0.0000053			
<i>Average</i>		0.0147				
<i>Standard Deviation</i>		0.0012	8.3%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.00011	18	0.0000059	2.650	0.0027	1.788
<i>Within Samples</i>	0.00013	57	0.0000022			
<i>Total</i>	0.00023	75				

Table 22. Analysis of Variance for Lead in SRM 1270a

<i>Identity</i>	<i>Count</i>	<i>Average</i>	<i>Variance</i>	<i>Significant Difference</i>		
<i>Can - Layer</i>		<i>kcps</i>		<i>between replicates</i>	<i>from set of samples</i>	
1 - 1	4	0.0592	0.00006			
1 - 3	4	0.0604	0.00003			
1 - 5	4	0.0607	0.00005			
1 - 7	4	0.0550	0.00003			
2 - 1	4	0.0600	0.00004			
2 - 3	4	0.0596	0.00009			
2 - 5	4	0.0574	0.00004			
2 - 7	4	0.0647	0.00003			
3 - 1	4	0.0518	0.00005			
3 - 3	4	0.0664	0.00002			
3 - 5	4	0.0675	0.00009			
3 - 7	4	0.0615	0.00005			
4 - 1	4	0.0594	0.00004			
4 - 3	4	0.0598	0.00002			
4 - 5	4	0.0574	0.00001			
4 - 7	4	0.0584	0.00010			
5 - 1	4	0.0638	0.00006			
5 - 3	4	0.0582	0.00004			
5 - 5	4	0.0683	0.00014			
<i>Average</i>		0.0605				
<i>Standard Deviation</i>		0.0042	6.9%			
ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
<i>Between Samples</i>	0.0013	18	0.000070	1.340	0.199	1.788
<i>Within Samples</i>	0.0030	57	0.000052			
<i>Total</i>	0.0042	75				

The ANOVA was calculated on the basis of individual disks measured either two times or four times at different depths from the original surface on one side of each disk. The columns with the X flags mark the disks that are outside the 95 % confidence interval based on control chart limits [1] for variance of replicates (*between replicates*) and for individual disks from the average (*from set of samples*). The *F*-test is used to compare within-disk variance to among-disk variance. The *p*-value is the probability of the *F*-test statistic being at least as extreme as the one observed while the null hypothesis is true. A small *p*-value is an indication

that the null hypothesis is false [2]. The p -value is considered “small” when it is less than the significance level, α . In this case, $\alpha < 0.05$. These statistical tests are based solely on the measured data for samples grouped by disk. Their significance must be judged on the basis of the intended use of the material, the quantity of material sampled, and the data quality goals of the certification project.

The findings for within-disk heterogeneity indicate that, at the 95 % confidence level, zero to as many as two disks for each element exhibited a statistically significant difference among replicate measurements. In a population of 19 samples, it is reasonable to expect one or two disks to be flagged at the 95 % confidence level. Therefore, there were no statistically anomalous variances observed within disks for any element.

The findings for among-disk heterogeneity indicate that, at the 95 % confidence level, zero or one disk exhibited a statistically significant difference from the rest of the population of disks. In a population of 19 samples, it is reasonable to expect one or two disks to be flagged at the 95 % confidence level. Therefore, there were no statistically anomalous variances observed among disks for any elements. The only element to have two disks flagged is Al, which may be attributable to carryover off the ZrO₂ based abrasive, after grinding with SiC. However, the Al data is not quantitative with an RSD exceeding 10 %. Note in **Table 2** that the C measurements include all four measurements from SiC and ZIRCON abrasive papers when the measurements from surfaces prepared with the SiC abrasive paper could potentially be contaminated by the abrasive. The ANOVA analysis for C was not redone as the C XRF measurements were not considered quantitative as discussed in Section 4.5.

Table 23 provides a summary tabulation of relevant statistical parameters to allow easier comparisons of elements. The RSD of the measured data for each element is based on the individual measurements. The RSD values for Al, Ti, and Zr indicate the measurements are not precise enough for quantitative analysis. In fact, Al, along with Ta, are less than the detection limits. In comparison, the RSD values listed in Tables 1 through 22 are the precision of the disk mean values. In **Table 23**, the estimate of the relative counting statistical error (CSE%) comes from Poisson counting statistics expressed at the level of 1s.

Table 23. Summary of Results for Homogeneity Testing of SRM 1270a

Element	$F^{(a)}$	Passed	p -value	RSD ^(b)	CSE% ^(c)	Sampling Depth (μm)	Mass of Alloy (mg)
B	0.433	X	0.97	1.5	1.2	0.1	0.7
C	0.393	X	0.98	25	3.5	0.3	1.3
Al	1.027	X	0.48	90	1.2	0.7	3.6
Si	3.453		0.0051	1.3	0.14	1.0	5.5
P	1.429	X	0.15	5.1	0.47	1.4	8.0
S	0.895	X	0.90	8.3	0.50	2.2	12
Ti	0.356	X	0.99	39	7.9	14	71
V	0.850	X	0.64	1.2	0.66	18	91
Cr	1.280	X	0.24	0.59	0.032	22	120
Mn	4.175		0.00002	0.89	0.082	28	150
Fe	1.364	X	0.19	0.35	0.074	35	180
Co	0.987	X	0.49	0.58	0.20	44	230
Ni	1.780	X	0.051	1.2	0.34	6.7	35
Cu	1.470	X	0.14	1.3	0.40	8.0	42
As	3.957		0.00004	3.1	2.3	16	84
Zr	2.684		0.019	16	0.74	49	260
Nb	1.092	X	0.38	6.6	6.7	21	300
Mo	58.78		< 0.00001	0.71	0.038	24	340
Sn	18.57		< 0.00001	2.7	1.1	70	970
Sb	0.446	X	0.97	16	14.4	79	1100
Ta				Not evaluated ^(d)			
W	2.650		0.0027	12	11.8	8.3	43
Pb	1.340	X	0.20	12	11.1	16	84

^aCritical F value: $F_{\text{crit}} = 1.788$, except for Al, Si, and Zr for which $F_{\text{crit}} = 2.182$.

^bRSD is the relative standard deviation of individual measurements.

^cCSE% is the relative counting statistical error from Poisson statistics [3].

^dTa was not detected and could not be statistically evaluated.

As shown in **Table 23**, the material passed the F -test for all elements, except Si, Mn, As, Zr, Mo, Sn, and W. These numbers are consistent with the qualitative pictures shown in **Fig. 1**. For these same elements that failed the F -test, the p -value is also less than 0.05 confirming that the compared variances are different. For the elements that passed, variability within any single disk is the more important source of composition variance than the disk-to-disk variability. Except for Zr, the elements that failed the F -test have repeatability of individual measurements of 3.1 % or better. That means the apparent heterogeneity among disks is of no practical significance for all tested elements that can be quantified. XRF measurements for W were not used and the W mass fraction was not certified. The Zr mass fraction was certified but the larger variability observed was incorporated into the uncertainty of the certified value.

Microbeam XRF (μ XRF) measurements were performed on disk 2-5 of SRM 1270a, which came from layer 5 in can number 2. The maps of count rates were evaluated for apparent trends of element concentrations by location within the disk, such as radial segregation. No trends were observed, and all distributions of count rates appear to be relatively normal, giving no evidence for localized segregation of an element. See **Fig. 2** for the distributions of count rates from the 1 mm diameter X-ray beam measurements. The y-axis in **Fig. 2** indicates the number of occurrences of a particular intensity while the x-axis represents the normalized XRF intensity. The XRF intensities of a particular analyte are normalized to achieve varying values for the line shape centroid while maintaining line shape in order to simplify the visualization of the all the various analyte intensity distributions. These distributions represent normal (Gaussian) or near normal distributions of data with no significant skewing or kurtosis [4]. Therefore, the physical distributions of these elements within the alloy matrix are uniform across the measured surface region with no identifiable, localized phases rich in or depleted of one or more elements. Except for Al and Ca, the repeatability standard deviations were ≤ 10 % relative, indicating quantifiable amounts present. Calcium was not measured by WDXRF.

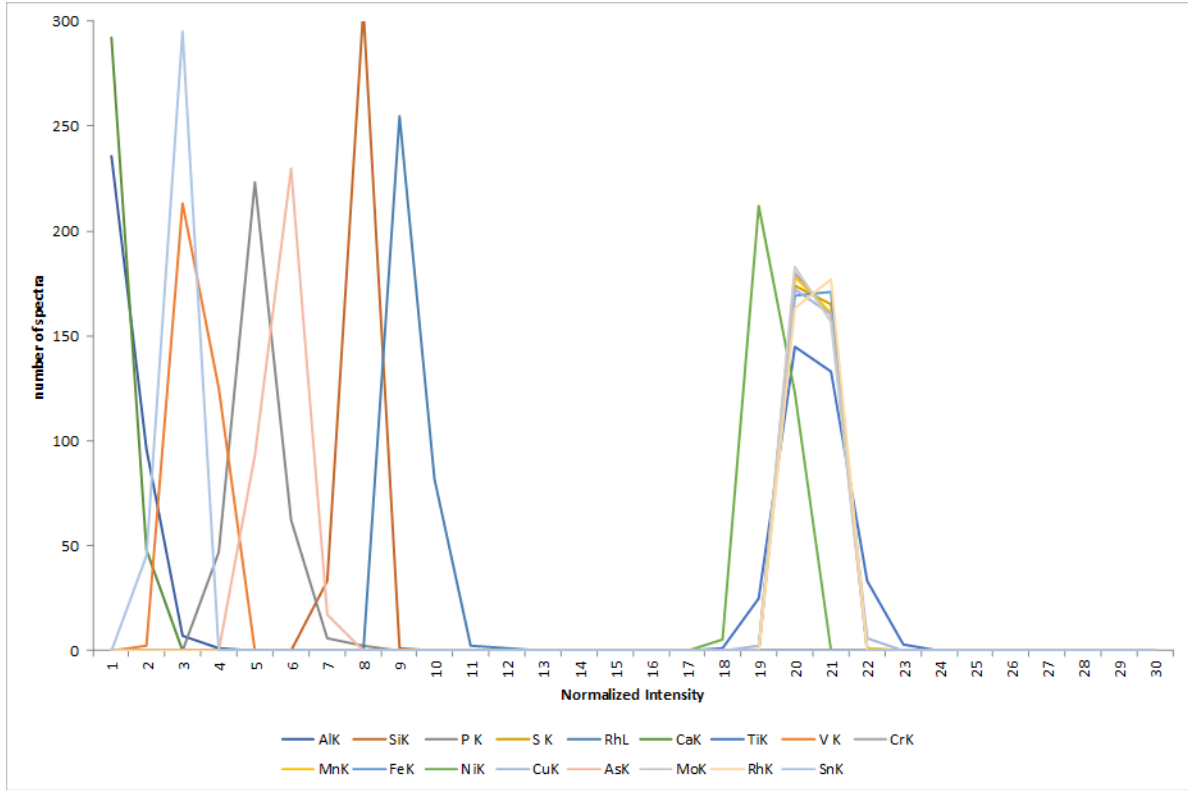


Fig. 2. Distributions of measured count rates across a single disk of SRM 1270a with measurements made using a 1 mm diameter X-ray beam and measured locations spaced 1 mm apart in a 17 x 20 grid. Measured lines RhL and RhK are characteristic lines from the Rh X-ray tube anode scattered from the steel sample surface. Rhodium is not present in the steel sample.

Estimating Measured Mass: The nature of X radiation is such that the mean-free-path of an X-ray in a particular specimen depends strongly on the X-ray energy, the elemental composition of the matrix, and the preparation of the specimen. Path lengths range from a fraction of a micrometer in metals to centimeters in liquids and low atomic number solids. The characteristic X-rays of some elements will originate from a few micrometers deep in a specimen while others may come from the entire thickness of a specimen with low X-ray absorptivity. Therefore, it is necessary to estimate the path lengths of the measured X-rays in the material, and from that information, estimate the mass of material sampled by measuring X-rays for each element.

The composition of SRM 1270a is > 95 % Fe with small amounts of alloying elements. X-ray path lengths can be estimated using the database of “*X-Ray Interactions with Matter*” of Lawrence Berkeley Laboratories [5]. Path lengths are used along with the density of Fe and the diameter of the measured area to calculate an estimate of the mass of material from which 99 % of X-rays of a given energy originate and escape to be detected. Converting depth estimates to estimates of mass sampled gives the values shown in the last column of Table 23. All values are rough estimates involving assumptions in modeling the material by fundamental parameters calculations. The estimated uncertainty of a given mass value is approximately 20 % relative. The steel disks are infinitely thick for all measured X-rays.

With limited data and a wide range of X-ray attenuation lengths across the range of measured elements, it is difficult to provide a recommended minimum sample mass. Based on experience with more heterogeneous steel alloys, the recommended minimum measured area of a disk is 13 mm². A conservative estimate of the mass of material sampled in that area by X-ray, arc-spark or glow discharge excitation is 20 mg. This estimate was obtained from the WDXRF measurements, using the 29 mm diameter measured area in the Zetium spectrometer. μ XRF data for SRM 1270a support this conclusion and indicate that most measured elements performed better, allowing smaller quantities to be measured and still be representative of the overall, bulk composition.

3.6. Conclusion

WDXRF measurements were used to evaluate the population of bars of SRM 1270a. The only significant source of variance of composition is within individual disks. That means the repeatability of individual determinations covers the material heterogeneity in the uncertainty budget for calculation of certified values. Only those elements present at low milligram per kilogram mass fractions will have significant repeatability variance.

Based on XRF measurements and the understanding that SRM 1270a will be used primarily (but not exclusively) with XRF and arc-spark optical emission spectrometry, the recommended minimum mass per sample is 20 mg. For direct measurement techniques, the minimum recommended measurement is a total area of 13 mm² covered by one or more measurements.

4. Quantitative Analyses of SRM 1270a by WDXRF, SSOES, IGF, CID

Material for SRM 1270a is available in disk form and is known from work during the SRM 1270 development project to be nearly identical in composition to the original SRM 1270. The objectives of the analyses reported hereafter are to provide quantitative results by WDXRF from NIST and Spark Source Optical Emission Spectrometry (SSOES), Inert Gas Fusion (IGF), and Combustion with Infrared Detection (CID) results from a collaborating laboratory for SRM 1270a. Quantitative results for 24 elements are summarized here. The test results will be used for assigning values to SRM 1270a.

4.1. Collaborating Laboratory

NSL Analytical Services, Inc. of Cleveland, OH performed SSOES, CID for carbon mass fraction and IGF for nitrogen mass fraction. The collaborating laboratory is accredited by the ANSI National Accreditation Board (ANAB), to fulfill the requirements of ISO 17025:2017 for elemental analysis test methods in compliance to ASTM International Standard Test Methods. Their work was performed per instructions from the NIST Technical Project Leader and with a quality assurance material, one disk of SRM 1762, from NIST.

4.2. Equipment

The steel disk samples were surface ground on a Buehler model ECOMET 4 12" variable speed wheel and a model EcoMet 3000 8" variable speed wheel. WDXRF measurements were made on a PANalytical model Zetium Ultimate WDXRF spectrometer equipped with a 4 kW

Rh-anode X-ray tube. SSOES measurements were conducted at the collaborating laboratory using two different models of equipment, a SpectroLab LAC M12 and a SpectroLab M, both made by Spectro Analytical Instruments. IGF measurements for N were measured on a LECO model TC-436DR Oxygen-Nitrogen Analyzer and CID measurements for C and S were done on a LECO model CS-844 Combustion Analyzer.

4.3. Sampling Details

Disk specimens for quantitative WDXRF measurements were prepared as described in section 3.2. Calibration validation materials, SRM 1762 and SRM 1270, were also prepared in the same fashion alongside the SRM 1270a material.

The collaborating laboratory was provided with one disk of SRM 1762 and six disks of SRM 1270a. For SSOES measurements, they measured each disk by preparing the surface and making four spark measurements. SSOES leaves a “burn” mark at each point of analysis. When the disk surface has been fully consumed with SSOES burn marks, the surface must be refinished by removing a substantial amount of material. See section 3.3. Four subsequent SSOES measurements were made after refinishing the disk surface. Each reported SSOES result was the mean of results from each set of four burns. The collaborating laboratory also determined N by IGF and C and S by CID, after cutting specimens of appropriate sizes from the disks.

4.4. Summary of Analytical Methods

All NIST and collaborator quantitative results were obtained using the test methods summarized below. NIST WDXRF: WDXRF measurements were performed using the Zetium wavelength dispersive spectrometer. Measurement conditions were chosen to maximize sensitivity and to minimize counting statistical uncertainty. A channel mask of 29 mm inner diameter was chosen to measure the 32 mm diameter disks. For all elements, the measured line was the K-L_{2,3}, except As, for which the line was K-M, Ta for which the line was L₃-M_{4,5} and Pb for which the line was L₂-M₄. X-ray measurements were conducted with up to 4 kW tube power and the spectrometer chamber was evacuated to < 10 Pa total pressure. Calibration standards in disk form included SRMs 1261, 1262, 1263, 1264, 1265, 1270, 1271, 1761, 1762, 1763, 1764, 1765, 1766, 1767, and 1768. Also used were reference materials Euro-CRM 097-1, Spectroscopic Standard 452 Mild Steel, and Spectroscopic Standard 454 Mild Steel from Bureau of Analyzed Samples. Calibration measurements were handled in a similar way to specimens of SRM 1270a and SRM 1762 with two measurements per sample – one with each grinding paper. The SRM 1270a data used for quantification is the same data reported for acceptance and homogeneity testing in section 3. Calibration standards measurements were interspersed among the SRM 1270a material measurements.

As noted above, measurements were made after surface grinding with two different abrasives. Each abrasive leaves characteristic contamination of the surface and makes it impossible to obtain repeatable, unbiased measurements for certain elements. The two sets of WDXRF measurements were compared to identify which data was acceptable for each element. The elements Al and Zr can only be measured after grinding with SiC paper, and the elements C and Si can only be measured after grinding with ZIRCON paper. The element Ti was affected

by contamination from the zircon abrasive in a few specimens. All other elements are not affected by the composition of the abrasive paper.

Collaborator SSOES: The collaborating laboratory performed SSOES determinations in compliance with ASTM Standard Test Method E415 using two SSOES spectrometers [6]. Due to the collaborator's concerns about biases in Mn calibration for one SSOES spectrometer (*viz.*, SpectroLab LAC M12), a second SSOES system (*viz.*, SpectroLab Model M) was used to measure and report Mn only. Calibration standards were based on Analytical Reference Materials International CRM IARM-31A for 4340 steel, Brammer Standard Co. BS 46E Steel – Low Alloy, and Brammer Standard Co. BS 14b Steel – Low Alloy.

Collaborator C, N and S: Inert gas fusion (IGF) determinations of total nitrogen and combustion with infrared detection (CID) determinations of carbon and sulfur were performed in accordance with ASTM Standard Test Methods in E1019 [7]. The nitrogen calibration was based on reference materials from Alpha Resources, AR657 Oxygen & Nitrogen Steel Pin CRM LOT# 420T ($N = 0.101\%$, $s = 0.0002\%$, $n = 55$) and AR1653 Oxygen & Nitrogen Steel Pin CRM LOT# 819D ($N = 0.0030\%$, $s = 0.0005\%$, $n = 76$), both with certified mass fractions traceable to primary reference materials from NIST, the German Federal Institute for Materials Research and Testing (BAM), the Ukrainian National Science Centre Institute of Metrology (NSC) and the Japan Iron and Steel Federation (JISF).

4.5. Results of Quantitative Analyses

Test results for 23 elements by NIST WDXRF, *viz.*, Al, As, B, C, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, S, Sb, Si, Sn, Ta, Ti, V, W and Zr and 20 elements from collaborator test methods, *viz.*, Al, As, B, C, Co, Cr, Cu, Mn, Mo, N, Nb, Ni, P, S, Si, Sn, Ta, Ti, V, and Zr are presented and discussed below.

NIST WDXRF Results: The NIST WDXRF results for SRM 1270a are shown in **Table 24**, **Table 25** and **Table 26**. NIST WDXRF results for SRM 1270 are listed in **Table 27** and **Table 27b**. Components of uncertainty are itemized and explained in **Table 28**. Gray highlighted cells in **Table 27** and **Table 27b** are results that include contamination from the grinding paper and were not used in the summary calculations. **Table 26** provides the summaries of values and uncertainty components for candidate SRM 1270a. To check the data for anomalous results, histograms were created by plotting the number of occurrences of the mass fractions found in the data for binned mass fractions with the bins covering the entire range of the mass fraction data, like those shown in **Fig. 3** for C, Ni, P, and Ti. The illustrated distributions for C, P and Ti are clearly skewed from normal. The distribution for Ni is bimodal with the distributions for B, Cr, Fe, Nb, and Pb (not shown) looking very similar. The distributions of the remaining elements are nearly normal in the expert opinion of the analysts. NIST analysts have found B and C to be difficult elements to quantify using XRF at these levels in these materials and XRF results were not used for certification. Hence, B and C plots are not relevant. The reasons that P and Ti plots show high end tailing are not clear. It may be possible that the results are due to mild contamination due to grinding or possibly inhomogeneity. The high results were reviewed as outliers (see gray highlighting in **Table 24** and **Table 25**) but it was eventually decided to keep all measurements for certification because there was no obvious reason for discarding them. All measurements for Ni, Cr, Fe, Nb and Pb were also

used for certification. The effects of skewing and dispersion in these plots are captured in the estimate of combined uncertainty.

Table 26. Summary of SRM 1270a Results and Uncertainty Components for NIST WDXRF Analysis

	Al	As	B	C	Co	Cr	Cu	Fe	Mn	Mo	Nb	
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	
Mean	< 0.02	0.01815	0.00782	0.179	0.03541	2.3038	0.1146	92.22	0.6272	0.9385	0.00112	
<i>s</i>	0.0067	0.00056	0.00082	0.070	0.00047	0.015	0.0016	0.15	0.0055	0.0067	0.00010	
RSD (%)	310	3.1	11	39	1.3	0.63	1.4	0.16	0.88	0.71	9.1	
<i>n</i>	38	76	76	35	76	76	76	76	76	76	76	
<i>K</i> factor		0.000094	0.000045	0.0046	0.00013	0.000065	0.000060	0.053	0.00010	0.000068	0.000062	
<i>C</i> ₀		0.01	0	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
<i>u</i> _K		0.00002	0.000004	0.0019	0.00003	0.00010	0.00002	0.51	0.00008	0.00007	0.00001	
<i>u</i> _c		0.00006	0.00009	0.012	0.00006	0.0017	0.00018	0.30	0.00064	0.00077	0.00001	
<i>U</i> _{k=2}		0.00013	0.00019	0.024	0.00011	0.0033	0.00036	0.59	0.0013	0.0015	0.00002	
	Ni	P	Pb	S	Sb	Si	Sn	Ta	Ti	V	W	Zr
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Mean	0.17246	0.00419	0.00212	0.01065	0.00047	0.2244	0.01641	0.00133	0.00143	0.01221	0.00278	0.0053
<i>s</i>	0.0020	0.00050	0.00022	0.00072	0.00025	0.0032	0.00044	0.00035	0.00058	0.00016	0.00038	0.0010
RSD (%)	1.2	12	11	6.7	52	1.4	2.7	27	41	1.3	14	19
<i>n</i>	76	76	76	75	76	38	76	38	76	76	76	38
<i>K</i> factor	0.000086	0.000081	0.00019	0.00024	0.000060	0.00014	0.00013	0.000070	0.00011	0.000063	0.000063	0.000063
<i>C</i> ₀	0.01	0.01	0.01	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
<i>u</i> _K	0.00004	0.00001	0.00002	0.00003	0.00001	0.00007	0.00002	0.00001	0.00001	0.00001	0.00001	0.00001
<i>u</i> _c	0.00023	0.00006	0.00003	0.00008	0.00003	0.00052	0.00005	0.00006	0.00007	0.00002	0.00004	0.00017
<i>U</i> _{k=2}	0.00047	0.00012	0.00006	0.00017	0.00006	0.0010	0.00010	0.00012	0.00013	0.00004	0.00009	0.00033

Table 27a. Quantitative Results for SRM 1270 Based on Low Alloy Steel Calibration

Disk	Paper	Al (%)	As (%)	B (%)	C (%)	Co (%)	Cr (%)	Cu (%)	Fe (%)	Mn (%)	Mo (%)	Nb (%)
SRM	Zircon		0.01761	0.00764	0.206	0.03497	2.287	0.1128	92.10	0.6212	0.9319	0.00102
"	"		0.01772	0.00713	0.197	0.03464	2.285	0.1123	92.05	0.6213	0.9327	0.00113
"	SiC	0.0162	0.01748	0.00810		0.03542	2.310	0.1143	92.32	0.6281	0.9346	0.00119
"	"	0.0039	0.01763	0.00866		0.03578	2.310	0.1150	92.25	0.6284	0.9344	0.00111
C1	Zircon		0.01695	0.00802	0.370	0.03442	2.277	0.1116	92.09	0.6171	0.9272	0.00119
"	"		0.01814	0.00719	0.188	0.03483	2.284	0.1125	92.12	0.6184	0.9270	0.00105
"	SiC	0.0055	0.01744	0.00953		0.03532	2.304	0.1139	92.33	0.6244	0.9286	0.00099
"	"	0.0004	0.01790	0.00847		0.03513	2.306	0.1141	92.42	0.6257	0.9294	0.00110
D1	Zircon		0.01804	0.00672	0.260	0.03512	2.292	0.1133	92.07	0.6231	0.9358	0.00129
"	"		0.01865	0.00665	0.119	0.03507	2.297	0.1130	92.13	0.6251	0.9370	0.00113
"	SiC	0.0019	0.01812	0.00928		0.03572	2.318	0.1160	92.32	0.6297	0.9398	0.00118
"	"	-0.0020	0.01861	0.00838		0.03569	2.316	0.1159	92.29	0.6291	0.9389	0.00129
D3	Zircon		0.01750	0.00726	0.222	0.03496	2.287	0.1121	92.27	0.6153	0.9255	0.00108
"	"		0.01723	0.00767	0.106	0.03453	2.282	0.1118	92.18	0.6170	0.9251	0.00103
"	SiC	0.0072	0.01751	0.00874		0.03561	2.302	0.1138	92.33	0.6225	0.9283	0.00101
"	"	-0.0007	0.01747	0.00835		0.03573	2.305	0.1150	92.29	0.6230	0.9283	0.00105
	Mean	< 0.02	0.01775	0.00799	< 0.25	0.03518	2.2975	0.11359	92.22	0.6231	0.9315	0.00111
	<i>s</i>	0.0058	0.00047	0.00086	0.083	0.00045	0.013	0.0014	0.12	0.0045	0.0048	0.000092
	RSD (%)	145	2.6	11	40	1.3	0.56	1.2	0.12	0.73	0.51	8.3
	<i>n</i>	8	16	16	8	16	16	16	16	16	16	16
	<i>K</i> factor	0.00042	0.00014	0.00004	0.0041	0.00015	0.00011	0.00008	0.052	0.00010	0.00007	0.00005
	<i>C</i> ₀	0.01	0.001	0.1	0	0.001	0.01	0.01	0.1	0.01	0.01	0.01
	<i>u</i> _K		0.00002	0.00001		0.00003	0.00017	0.00003	0.50	0.00008	0.00007	0.000005
	<i>u</i> _c		0.00012	0.00022		0.00011	0.0032	0.00035	0.29	0.0011	0.0012	0.00002
	<i>U</i> _{k=2}		0.00023	0.00043		0.00023	0.0065	0.00070	0.58	0.0023	0.0024	0.00005
1270 Certificate		0.005	0.02	0.0033	0.077	0.038	2.34	0.114	95.30	0.626	0.956	0.008
	2 <i>u</i>				0.004	0.004	0.04	0.004	by diff.	0.050	0.012	
Bias Detected	No	No	Yes		No	No	No	No		No	Yes	
% Difference			11	-142		7.4	1.8	0.36		0.46	2.6	86

Table 27b. Quantitative Results for SRM 1270 Based on Low Alloy Steel Calibration

Disk	Paper	Ni (%)	P (%)	Pb (%)	S (%)	Sb (%)	Si (%)	Sn (%)	Ta (%)	Ti (%)	V (%)	W (%)	Zr (%)
SRM	Zircon	0.1698	0.00389	0.00242	0.01060	0.00033	0.2240	0.01617		0.00165	0.01228	0.00310	
"	"	0.1706	0.00376	0.00224	0.01068	0.00049	0.2220	0.01597		0.00212	0.01217	0.00290	
"	SiC	0.1717	0.00433	0.00166	0.01057	0.00050		0.01628	0.00043	0.00112	0.01216	0.00252	0.0100
"	"	0.1732	0.00471	0.00193	0.00960	0.00072		0.01607	0.00150	0.00116	0.01196	0.00295	0.0085
C1	Zircon	0.1692	0.00395	0.00208	0.01125	0.00077	0.2222	0.01576		0.00205	0.01221	0.00260	
"	"	0.1686	0.00410	0.00230	0.01108	0.00053	0.2259	0.01559		0.00193	0.01214	0.00244	
"	SiC	0.1731	0.00435	0.00191	0.00995	0.00066		0.01608	0.00154	0.00107	0.01216	0.00297	0.0071
"	"	0.1737	0.00414	0.00198	0.00945	0.00020		0.01597	0.00150	0.00102	0.01199	0.00266	0.0065
D1	Zircon	0.1698	0.00376	0.00210	0.01159	0.00055	0.2206	0.01639		0.00158	0.01232	0.00298	
"	"	0.1700	0.00369	0.00198	0.01057	0.00051	0.2261	0.01623		0.00150	0.01225	0.00280	
"	SiC	0.1749	0.00483	0.00240	0.00971	0.00017		0.01596	0.00123	0.00083	0.01215	0.00311	0.0051
"	"	0.1743	0.00522	0.00201	0.00955	0.00040		0.01647	0.00101	0.00076	0.01171	0.00273	0.0046
D3	Zircon	0.1679	0.00347	0.00224	0.01024	0.00046	0.2188	0.01589		0.00197	0.01228	0.00318	
"	"	0.1685	0.00359	0.00214	0.01033	0.00070	0.2209	0.01550		0.00157	0.01230	0.00307	
"	SiC	0.1716	0.00442	0.00192	0.00942	0.00006		0.01596	0.00139	0.00111	0.01211	0.00258	0.0059
"	"	0.1726	0.00607	0.00201	0.00913	0.00080		0.01574	0.00144	0.00097	0.01199	0.00265	0.0052
	Mean	0.1712	0.00427	0.00208	0.01023	<0.001	0.2226	0.01600	0.00125	0.00140	0.01214	0.00283	0.0066
	<i>s</i>	0.0022	0.00068	0.00020	0.00073	0.00022	0.0026	0.00027	0.00038	0.00045	0.00016	0.00023	0.0019
	RSD (%)	1.3	16	9.6	7.1	45	1.2	1.7	30	32	1.3	8.3	28
	<i>n</i>	16	16	16	16	16	8	16	8	16	16	16	8
	<i>K</i> factor	0.00008	0.00010	0.00005	0.00014	0.00003	0.00057	0.00009	0.00012	0.00013	0.00007	0.00009	0.00006
	<i>C</i> ₀	0.01	0.01	0.01	0	0.01	0.01	0.01	0.001	0.01	0.01	0.001	0.01
	<i>u</i> _K	0.00004	0.00001	0.000005	0.00001		0.00027	0.00001	0.00001	0.00001	0.00001	0.00001	0.00001
	<i>u</i> _c	0.00056	0.00017	0.00005	0.00018		0.00092	0.00007	0.00013	0.00011	0.00004	0.00006	0.00066
	<i>U</i> _{k=2}	0.0011	0.00034	0.00010	0.00036		0.0018	0.00014	0.00027	0.00023	0.00008	0.00012	0.0013
1270 Certificate		0.174	0.0065	0.0016	0.0065	0.02	0.247	0.02	0.005	0.003	0.013	0.003	0.010
	2 <i>u</i>	0.004	0.0040		0.0020		0.008				0.002		
Bias Detected		No	No		Yes		Yes				No		
% Difference		1.6	34	-30	-57		9.9	20	75	53	6.7	5.7	34

Table 28. Components of Uncertainty of NIST WDXRF Results

Uncertainty	Basis	Type	DF
Repeatability standard deviation, s	The estimate of the standard deviation of the results for individual samples. The variable n is the number of specimens. For Al and C, this estimate was calculated after removal of contaminated results.	A	$n - 1$
Weighted residual error from calibration standards, K	$K = \sqrt{\frac{1}{m-k} \sum \frac{(C_{Chem} - C_{Calc})^2}{C_{Chem} + C_0}}$ The K factor is a weighted residual error and a measure of the differences between the calculated mass fraction, C_{Calc} , and the known mass fraction, C_{Chem} , for the calibration standards. The variable C_0 is a constant chosen by the analyst to adjust the sensitivity of the calibration regression to better represent lower mass fraction standards. The variable m is the number of standards. The variable k is the number of parameters in the calibration model: slope intercept, line overlap, and matrix corrections.	B	∞
Uncertainty in the calibration model, u_K	$u_K = K \sqrt{C_{routine} + C_0}$ Standard uncertainty associated with the fit of the calibration model to the known mass fractions and measured count rates of the calibration standards. $C_{routine}$ is the mass fraction calculated for a routine sample analyzed using the method and its calibration. In this work, $C_{routine}$ is the mean of n results.	B	∞
Combined Uncertainty, u_c	The individual uncertainty components are added in quadrature: $u_c = \sqrt{\frac{s^2}{n} + \frac{u_K^2}{3}}$ The factor of 3 is due to the assumption of a uniform uncertainty distribution.		

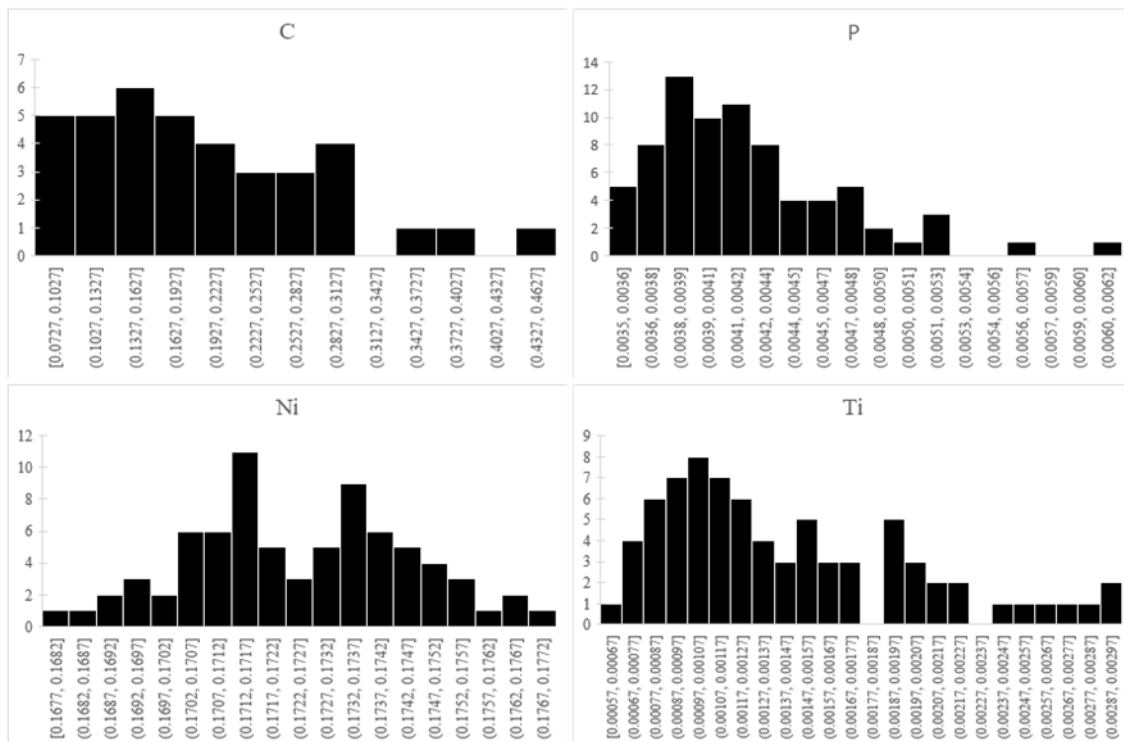


Fig. 3. Histograms of measured results by WDXRF for elements in SRM 1270a showing skewed distributions for C, P, and Ti and a bimodal distribution for Ni. Values on the horizontal axes are mass fractions in percent (%). Values on the vertical axes are the counts of results in each bin of the histogram.

The RSD shown in **Table 26** can be used as an indicator of whether the measured results exceed the limit of quantification (LOQ) or not when contributions to the RSD are based primarily on XRF counting statistics². When the measurement result's RSD is dominated by XRF counting statistics, the measurement result would approach the measurement method's LOQ when the RSD exceeds 10%. The measurement method LOQ for a given analyte can be estimated by calculating the sensitivity (S) and counting statistical error (CSE) of the background, where the CSE is an estimate of the standard deviation of the background, using steel calibrants with trace levels of the analyte. The estimated LOQ is then shown in Eq. 1:

$$LOQ \sim 10 \times \frac{CSE}{S} \quad (1)$$

where the sensitivity, S, is in units of signal intensity per mg/kg [8]. The RSD may be influenced by other factors such as sample contamination or sample homogeneity. Inspection of **Table 26** shows several elements with RSDs near or exceeding 10%, *viz.*, Al, B, C, Nb, P, Pb, Sb, T, Ti, W and Zr. A review of the estimated analyte LOQs is as follows for these analytes:

- Al: The LOQ for Al is estimated to be around 200 mg/kg. Trace Al in steels is difficult to quantify by XRF as this requires characterization of the background Al signal

² There are many references describing XRF counting statistics. A good discussion on XRF counting statistics can be found in de Vries and Vrebos [2].

fluoresced from instrumentation components by the strong Fe signal from the steel specimens.

- B and C: The results for these elements are not quantitative as previously discussed.
- Nb: The LOQ for Nb is estimated at around 7.0 mg/kg to 7.5 mg/kg using measurements on SRMs 1761 and 1764. Hence, the Nb mass fraction measured by XRF here is approaching the LOQ as indicated by the RSD.
- P: The LOQ for P is estimated to be around 2 mg/kg using measurements on SRMs 1761, 1764, 1765 and 1766. As the P LOQ is about 20 times lower than the measured P mass fraction, the higher RSD may be the result of grinding contamination or inhomogeneity.
- Pb: The estimated LOQ for Pb is 14.0 mg/kg to 14.5 mg/kg using SRMs 1764 and 1764a. Hence, the Pb mass fraction measured by XRF here is approaching the LOQ as indicated by the RSD.
- Sb: The estimated LOQ for Sb is about 16 mg/kg using SRMs 1264a and 1763. The LOQ exceeds the measured mass fraction indicating the result is not quantitative.
- Ta and W: Ta and W are nearest neighbors by atomic mass and exhibit similar behavior in XRF. The estimated Ta and W LOQs are about 30 mg/kg and 35 mg/kg respectively estimated using SRMs 1167, 1264a and 1764. The Ta and W results are not quantitative.
- Ti: The estimated LOQ for Ti is 9 mg/kg to 10 mg/kg using measurements on SRMs 1764 and 1765. The measured Ti mass fraction is approaching the quantitative limit. The high RSD may be due to a combination of statistical measurement limits, grinding contamination and/or material inhomogeneity. It may be difficult to use the measured results to certify Ti due to the high RSD.
- Zr: The estimated LOQ for Zr is about 3.5 mg/kg using measurements on SRMs 1761 and 1762. Zr measurement time was about 3 times longer than that for Nb. The Zr LOQ is significantly lower than the measured mass fraction; hence, the higher RSD may be the result of grinding contamination and/or material inhomogeneity.

In summary, the XRF measurements from B, C, Al, Sb, Ta and W will not be used for certification as the results were not quantitative.

For SRM 1270, the certified values and combined standard uncertainty estimates, u_c , from the certificate of analysis are given in **Table 27** and **Table 27b** for comparison to the found results. Results for SRM 1270 agree with the certified and information values within the $2u_c$ intervals, except for C, Si, S and Mo. When the poor repeatability of WDXRF carbon results is considered, there is no detectable bias. However, the carbon results are known to be biased, because some measurements are contaminated by C from the SiC grinding paper that was not completely removed by zircon grinding. The lowest two C results of 0.119 % and 0.106 % are still significantly greater than the certified value. Sulfur is often a difficult element to quantify in alloys using WDXRF. The analysts within the NIST WDXRF laboratory have previously encountered low alloy steel and iron compositions which have crystalline phases that appear to bias the S measurements by XRF. Another possible factor may be differences in microscale distributions of S atoms between surface and bulk portions of a specimen. This sulfur bias

phenomenon has not been adequately characterized to enable the problem to be corrected and the XRF measurements for S were not used for certification. Low results for Mo and Si also cannot be adequately explained; however, these results were included for certification along with historical and recent collaborator measurements as there were no significant technical or statistical reasons to omit the results. The overall impact of differences will be captured in the combined uncertainty estimate. It is worth noting that the recent 1270a Mo XRF result is consistent with historical measurements discussed in section 5.

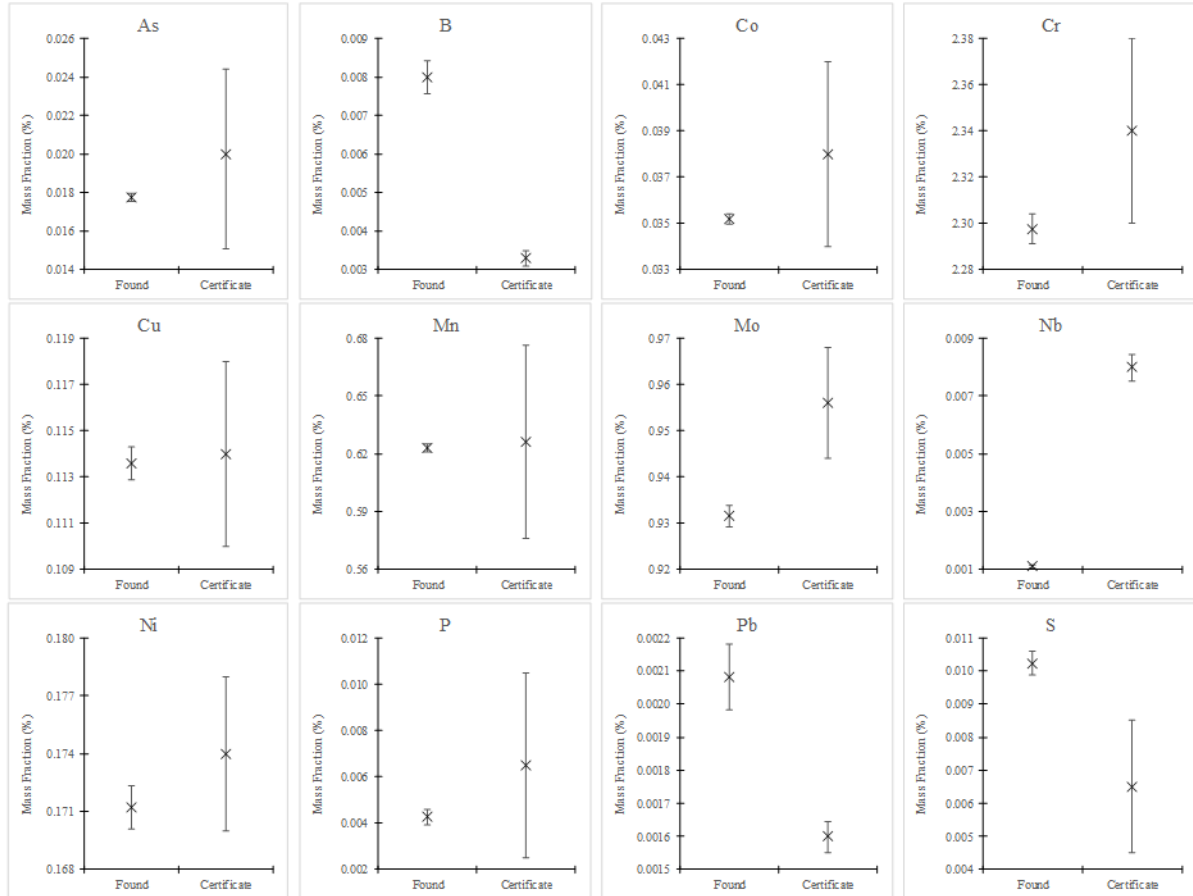


Fig. 4. Graphical comparisons of found results for SRM 1270 from NIST WDXRF to certificate values for SRM 1270. Error bars for found results are expanded uncertainty estimates, $U_{k=2}$, from both a and b portions of **Table 27**. Error bars for certified elements Co, Cr, Cu, Mn, Mo, Ni, P, and S are $2u$ again from **Table 27**, where u is the standard uncertainty estimate from the certificate. Error bars for information values for elements As, B, Nb, and Pb assume the values were rounded from more precise results.

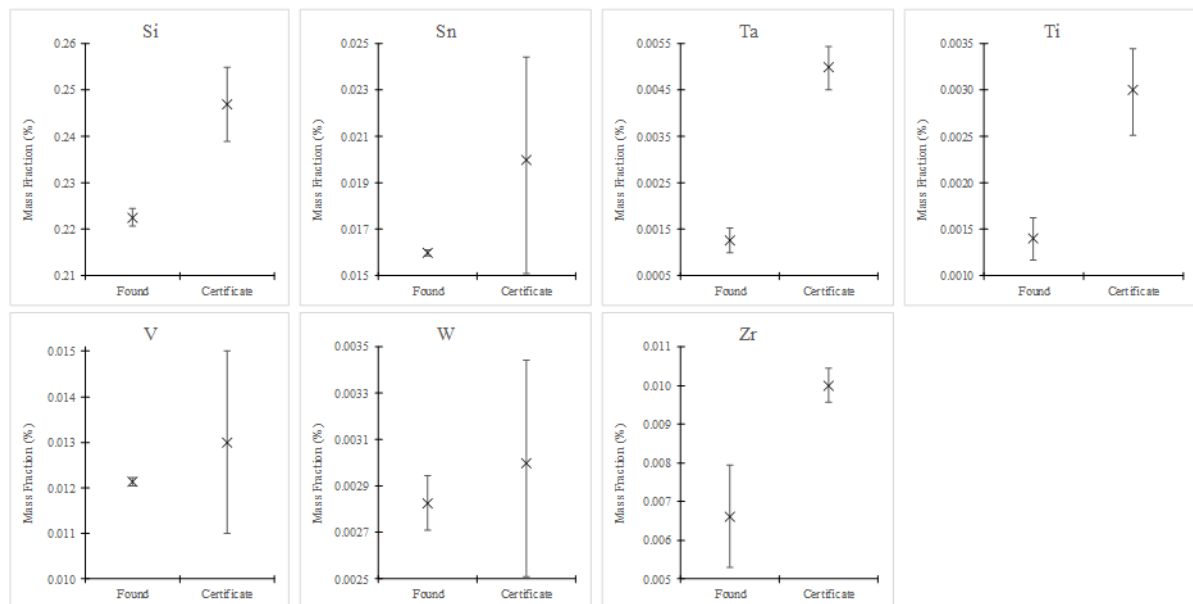


Fig. 5. Graphical comparisons of found results for SRM 1270 from NIST WDXRF to certificate values for SRM 1270. Error bars for found results are the expanded uncertainty estimates, $U_{k=2}$, from **Table 27a** and **b**. Error bars for certified elements Si and V are $2u$ from **Table 27b**, where u is the standard uncertainty estimate from the certificate. Error bars for information values for Sn, Ta, Ti, W, and Zr assume the values were rounded from more precise results.

Collaborator Results: The collaborator's SSOES results for candidate SRM 1270a are given in **Table 29** and **Table 30**. **Table 29** is results for all elements obtained using the SpectroLab LAC M12 spectrometer. **Table 30** is results for Mn only, using the SpectroLab M spectrometer and different set of calibration parameters. The collaborator provided two sets of Mn results, because they are not highly confident in the Mn calibration for the newer LAC M12 SSOES spectrometer. Results from SSOES for SRM 1762 are given in **Table 31** for the newer spectrometer and in **Table 32** for just Mn from the SpectroLab M spectrometer. Collaborator CID results for C and S are provided in **Table 33** for candidate SRM 1270a and in **Table 34** for SRM 1762. Nitrogen results from IGF are shown in **Table 35** for candidate SRM 1270a and in **Table 36** for SRM 1762.

Table 29. Elements in SRM 1270a by Spark Source OES at Collaborator Lab

(All result values shown in number of decimal places reported from spectrometer.)

Sample ID			Al	As	B	C	Co	Cr	Cu	Mn	Mo	Nb
Can	Layer	Run	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
2	1	A	< 0.005	0.0165	0.0040	0.0804	0.0355	2.339	0.1161	0.6200	0.9312	0.0042
2	1	B	< 0.005	0.0160	0.0040	0.0750	0.0351	2.322	0.1127	0.6094	0.9116	0.0030
5	1	A	< 0.005	0.0182	0.0047	0.0847	0.0357	2.329	0.1142	0.6190	0.9386	0.0029
5	1	B	< 0.005	0.0166	0.0049	0.0867	0.0364	2.325	0.1137	0.6166	0.9529	< 0.01
2	3	A	< 0.005	0.0164	0.0046	0.0848	0.0357	2.331	0.1135	0.6192	0.9527	0.0031
2	3	B	< 0.005	0.0172	0.0046	0.0881	0.0362	2.329	0.1133	0.6177	0.9451	0.0030
4	3	A	< 0.005	0.0158	0.0041	0.0837	0.0359	2.322	0.1134	0.6116	0.9402	0.0031
4	3	B	< 0.005	0.0156	0.0046	0.0862	0.0358	2.333	0.1131	0.6202	0.9493	0.0023
4	5	A	< 0.005	0.0166	0.0046	0.0862	0.0359	2.331	0.1143	0.6260	0.9540	0.0021
4	5	B	< 0.005	0.0163	0.0043	0.0829	0.0357	2.318	0.1134	0.6129	0.9424	0.0027
4	7	A	< 0.005	0.0167	0.0042	0.0821	0.0355	2.319	0.1131	0.6142	0.9407	0.0034
4	7	B	< 0.005	0.0178	0.0041	0.0831	0.0359	2.329	0.1135	0.6209	0.9519	0.0023
		Mean	< 0.005	0.01664	0.00439	0.0837	0.03578	2.3273	0.11369	0.6173	0.943	0.00292
		s		0.00077	0.00031	0.0035	0.00034	0.0062	0.00088	0.0046	0.012	0.00059
		n		12	12	12	12	12	12	12	12	11

Sample ID			Ni	P	S	Si	Sn	Ta	Ti	V	Zr
Can	Layer	Run	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
2	1	A	0.1818	0.0035	0.0054	0.2354	0.0170	< 0.005	0.0016	0.0129	0.0062
2	1	B	0.1782	0.0035	0.0047	0.2317	0.0158	< 0.005	0.0022	0.0129	0.0083
5	1	A	0.1829	0.0040	0.0055	0.2411	0.0171	< 0.005	0.0020	0.0130	0.0071
5	1	B	0.1842	0.0036	0.0057	0.2391	0.0172	< 0.005	0.0019	0.0130	0.0065
2	3	A	0.1825	0.0037	0.0056	0.2392	0.0171	< 0.005	0.0017	0.0129	0.0100
2	3	B	0.1829	0.0037	0.0056	0.2381	0.0170	< 0.005	0.0016	0.0123	0.0096
4	3	A	0.1821	0.0036	0.0055	0.2347	0.0167	< 0.005	0.0017	0.0129	0.0070
4	3	B	0.1837	0.0040	0.0055	0.2383	0.0171	< 0.005	0.0018	0.0126	0.0058
4	5	A	0.1845	0.0042	0.0061	0.2405	0.0174	< 0.005	0.0014	0.0126	0.0107
4	5	B	0.1817	0.0041	0.0053	0.2381	0.0165	< 0.005	0.0016	0.0131	0.0065
4	7	A	0.1812	0.0036	0.0053	0.2368	0.0165	< 0.005	0.0016	0.0129	0.0073
4	7	B	0.1826	0.0043	0.0053	0.2404	0.0171	< 0.005	0.0017	0.0129	0.0064
		Mean	0.1824	0.00382	0.00546	0.2378	0.01688	< 0.005	0.00173	0.01283	0.0076
		s	0.0016	0.00029	0.00033	0.0027	0.00044		0.00021	0.00022	0.0016
		n	12	12	12	12	12	12	12	12	12

Table 30. Manganese in SRM 1270a by Spark Source OES at Collaborator Lab

(Result values shown in number of decimal places reported by spectrometer.)

Sample ID			Mn
Can	Layer	Run ^(a)	(%)
2	1	A	0.63
2	1	B	0.63
5	1	A	0.63
5	1	B	0.63
2	3	A	0.63
2	3	B	0.63
4	3	A	0.63
4	3	B	0.65
4	5	A	0.64
4	5	B	0.64
4	7	A	0.63
4	7	B	0.64
		Mean	0.6342
		<i>s</i>	0.0067
		<i>n</i>	12

^(a) Runs performed using SPECTROLAB M spectrometer

Table 31. Elements in SRM 1762 by Spark Source OES at Collaborator Lab

(All result values shown in number of decimal places reported from spectrometer.)

	Al	As	B	C	Co	Cr	Cu	Mn	Mo	Nb
Run	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
A	0.0705	0.0189	0.0041	0.356	0.0620	0.9387	0.121	2.01	0.343	0.0693
B	0.0743	0.0169	0.0041	0.355	0.0625	0.9379	0.120	2.02	0.344	0.0740
C	0.0708	0.0194	0.0041	0.355	0.0619	0.9394	0.119	1.99	0.342	0.0723
D	0.0753	0.0182	0.0045	0.359	0.0625	0.9399	0.120	2.01	0.340	0.0701
Mean	0.0727	0.0184	0.00420	0.3560	0.06223	0.93898	0.11993	2.0053	0.3422	0.0714
<i>s</i>	0.0024	0.0011	0.00020	0.0020	0.00032	0.00087	0.00056	0.0091	0.0018	0.0021
<i>n</i>	4	4	4	4	4	4	4	4	4	4
Certificate	0.069	0.018	0.0049	0.337	0.062	0.92	0.120	2.00	0.35	0.070
<i>2u</i>	0.004	0.004	0.0004	0.008	0.010	0.02	0.008	0.04	0.02	0.004

	Ni	P	S	Si	Sn	Ta	Ti	V	Zr
Run	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
A	1.1870	0.0384	0.0348	0.344	0.0475	0.0217	0.0911	0.199	0.0272
B	1.1860	0.0383	0.0353	0.347	0.0476	0.0197	0.0978	0.199	0.0284
C	1.1870	0.0385	0.0368	0.347	0.0473	0.0208	0.0939	0.197	0.0271
D	1.1840	0.0392	0.0373	0.347	0.0480	0.0186	0.0927	0.197	0.0288
Mean	1.1860	0.03860	0.0361	0.3463	0.04760	0.0202	0.0939	0.1979	0.02788
<i>s</i>	0.0014	0.00041	0.0012	0.0013	0.00029	0.0013	0.0029	0.0010	0.00085
<i>n</i>	4	4	4	4	4	4	4	4	4
Certificate	1.15	0.033	0.030	0.35	0.046	0.021	0.095	0.200	0.029
<i>2u</i>	0.04	0.002	0.004	0.02	0.006	0.002	0.010	0.010	0.004

Table 32. Manganese in SRM 1762 by Spark Source OES at Collaborator Lab

(Result values shown in number of decimal places reported by spectrometer.)

Run ^(a)	Mn (%)
A	2.09
B	2.10
C	2.09
D	2.11
Mean	2.0975
<i>s</i>	0.0096
<i>n</i>	4
Certified	2.00
<i>2u</i>	0.04

^(a) Runs performed using SPECTROLAB M spectrometer

Table 33. Carbon and Sulfur in SRM 1270a by Combustion with IR Detection at Collaborator Lab

Sample ID			C (%)	S (%)
Can	Layer	Run	(%)	(%)
2	1	A	0.0721	0.0059
2	1	B	0.0723	0.0059
5	1	A	0.0791	0.0067
5	1	B	0.0809	0.0068
2	3	A	0.0792	0.0066
2	3	B	0.0802	0.0064
4	3	A	0.0818	0.0067
4	3	B	0.0838	0.0068
4	5	A	0.0794	0.0066
4	5	B	0.0784	0.0068
4	7	A	0.0806	0.0069
4	7	B	0.0764	0.0063
		Mean	0.0787	0.00653
		<i>s</i>	0.0035	0.00034
		<i>n</i>	12	12

Table 34. Carbon and Sulfur in SRM 1762 by Combustion with IR Detection at Collaborator Lab

Run	C (%)	S (%)
A	0.3371	0.0296
B	0.3382	0.0301
C	0.3362	0.0293
D	0.3402	0.0300
Mean	0.3379	0.02975
<i>s</i>	0.0017	0.00037
<i>n</i>	4	4
Certified	0.337	0.030
<i>2u</i>	0.008	0.004

Table 35. Nitrogen in SRM 1270a by Inert Gas Fusion at Collaborator Lab

Can	Layer	Sample ID Run	(%)
2	1	A	0.0096
2	1	B	0.0096
5	1	A	0.0102
5	1	B	0.0096
2	3	A	0.0105
2	3	B	0.0094
4	3	A	0.0102
4	3	B	0.0098
4	5	A	0.0099
4	5	B	0.0097
4	7	A	0.0103
4	7	B	0.0094
		Mean	0.00985
		<i>s</i>	0.00037
		<i>n</i>	12

Table 36. Nitrogen in SRM 1762 by Inert Gas Fusion at Collaborator Lab

	(%)
Run	
A	0.0023
B	0.0026
C	0.0024
D	0.0024
Mean	0.00243
<i>s</i>	0.00013
<i>n</i>	4
Certified	0.0022
<i>2u</i>	0.0006

Comparisons between collaborator SSOES results for SRM 1762 and the certificate values for SRM 1762 are provided in graphical form in **Fig. 6**, which is split into two parts, a and b, for better viewing. The graphs show good agreement between found and certified values for all elements, except C and P. For those two elements, the error bars for found and certified values do not overlap. That does not necessarily indicate a bias, because the error bars for the found results are just $2s$ based on repeatability with no other components of uncertainty included. For carbon, the SSOES mean result is higher than both the certified value and the results from CID.

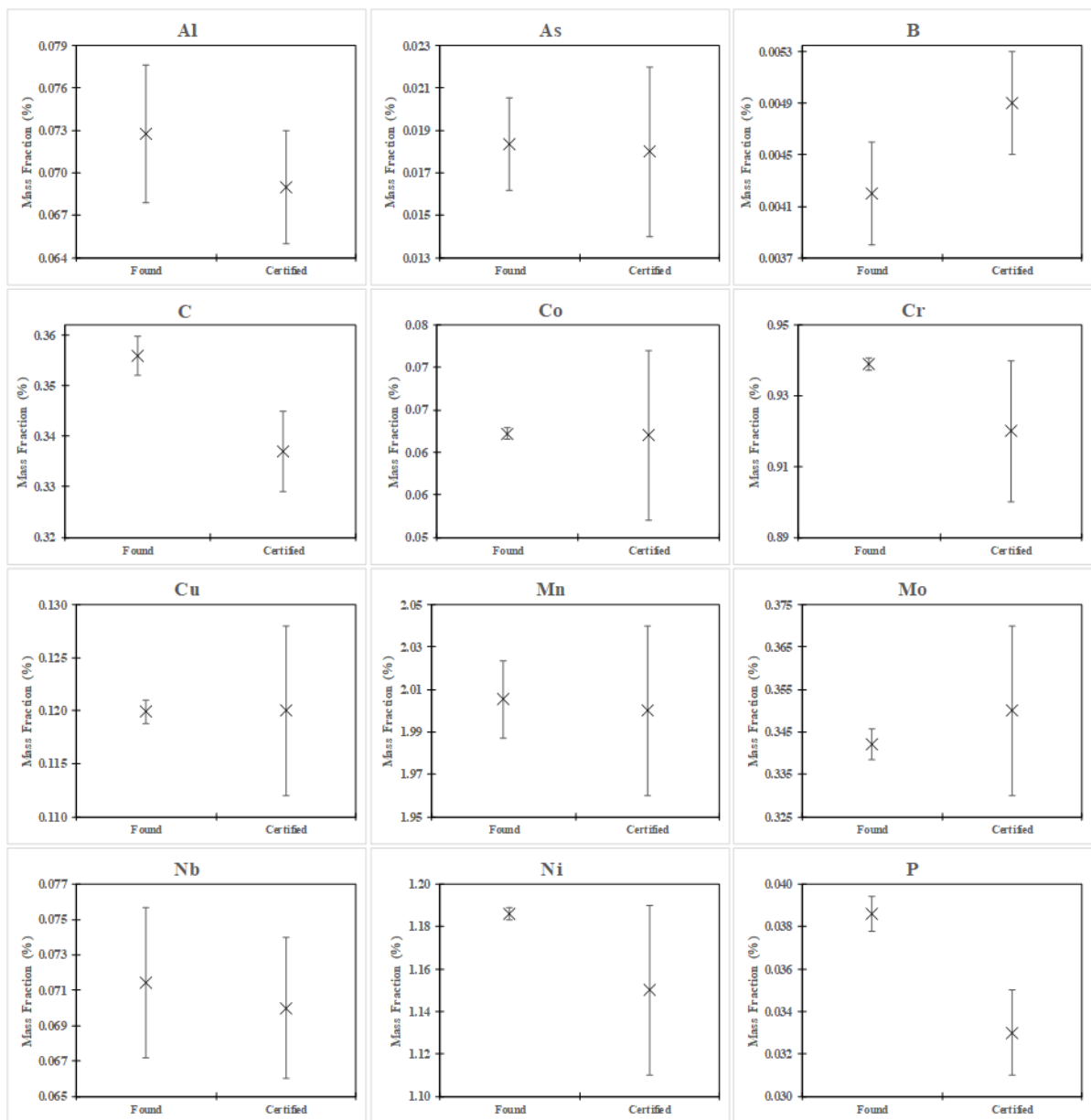


Fig. 6a. Comparisons of collaborator found results for SRM 1762. Error bars for found results are two times the repeatability standard deviation, $2s$. Error bars for certified values are two times the combined standard uncertainty estimate, $2u$.

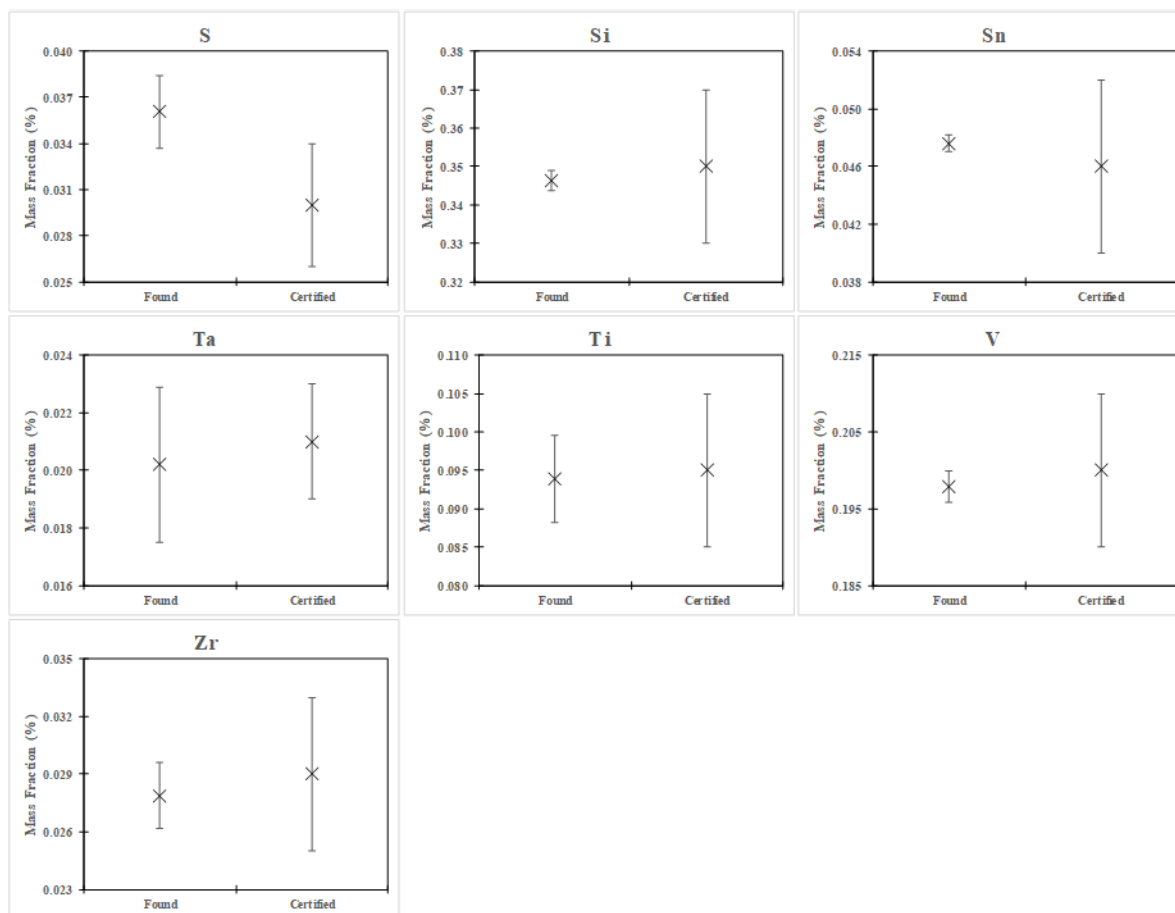


Fig. 6b. Comparisons of collaborator found results for SRM 1762. Error bars for found results are two times the repeatability standard deviation, $2s$. Error bars for certified values are two times the combined standard uncertainty estimate, $2u$.

Collaborator total carbon and sulfur results for SRM 1762 from the CID method are shown in **Fig. 7**, which shows there is no detectable bias for either element. Therefore, the CID carbon and sulfur results for candidate SRM 1270a are expected to be unbiased.

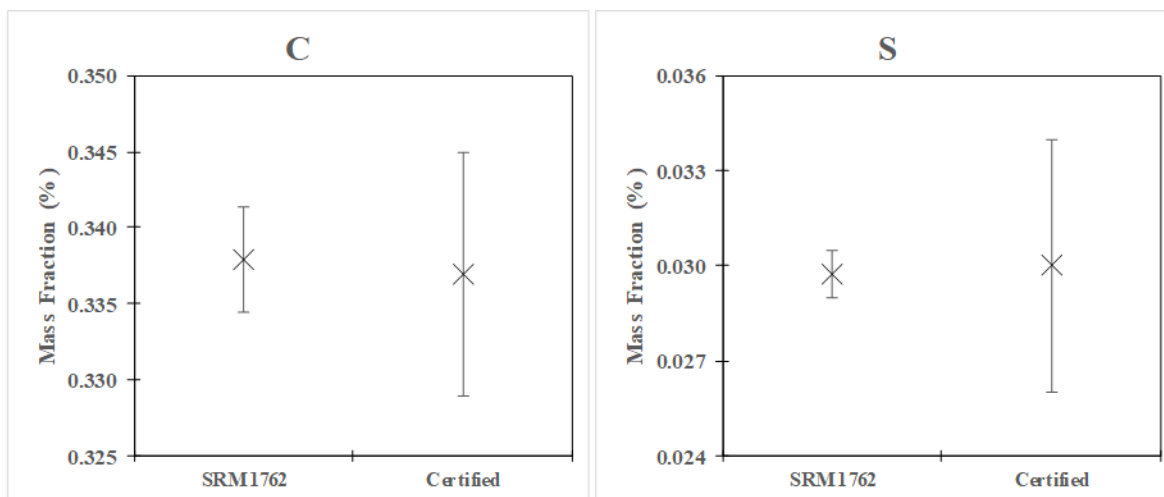


Fig. 7. Graphical comparison of collaborator CID results for total carbon and sulfur in SRM 1762 to the certified values for SRM 1762. Error bars for test results are two times the repeatability standard deviation for the measured results. For the certified values, they are two times the combined standard uncertainty of the certified value.

Collaborator total nitrogen results from the IGF method for SRM 1762 are shown in **Fig. 8**, which indicates no detectable bias. Therefore, the IGF nitrogen results for candidate SRM 1270a are expected to be unbiased.

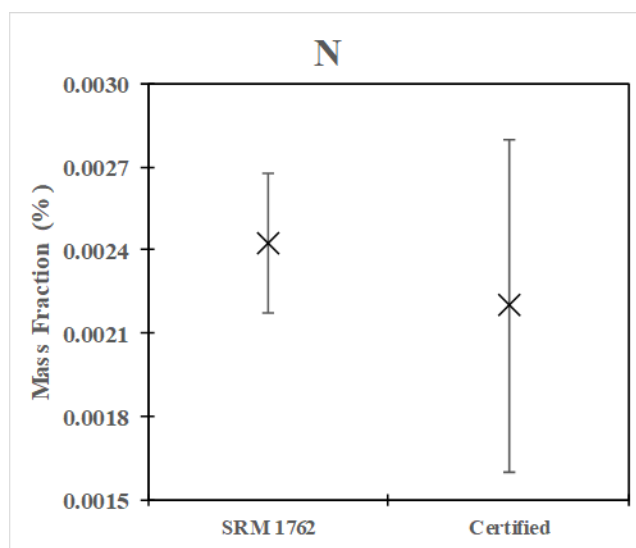


Fig. 8. Graphical comparison of collaborator IGF results for total nitrogen in SRM 1762 to the certified value for SRM 1762. Error bars for test results are two times the repeatability standard deviation for the measured results. For the certified value, they are two times the combined standard uncertainty of the certified value.

4.6. Conclusion

NIST WDXRF and collaborator SSOES results and combustion C and S results are in good agreement for all 19 elements in common. The only notable differences are for carbon with the problem quantifying C by WDXRF due to surface contamination and poor repeatability

and the collaborator's SSOES result potentially being biased high. With the exception of nitrogen, these results can be used in certification value assignments of candidate SRM 1270a. Nitrogen results can be provided as a non-certified value with uncertainty estimate.

NIST WDXRF results will be used for certification of Si, P, Ti, V, Cr, Mn, Co, Ni, Cu, As, Zr, Mo, Nb, Sn and Pb. WDXRF results were below limits of quantification for Al, Sb, Ta, and W. C WDXRF results seemed to suffer from contamination and were not quantitative while B has not been used for quantification due to the sensitivity to surface preparation.

The collaborating laboratory's SSOES results will be used for certification of B, C, Si, P, S, Ti, V, Cr, Mn, Co, Ni, Cu, As, Zr, Mo, Nb, Sn. Ta and Al were below limits of quantification. Combustion analysis will be used for C and S certification. Inert Gas Fusion was the only method to analyze N which will be published as a non-certified value.

5. Quantitative Analyses of SRM 1270a using SRM 1270 Development Data

Candidate material for SRM 1270a and SRM 1270 were produced from a single heat. At the time that certification measurements were made on SRM 1270, measurements were also made on SRM 1270a and set aside for later consideration.

The work reported herein was performed from 1980 through 1982 predating the current NIST Quality System. The work was performed in accordance with procedures employed by the National Bureau of Standards Office of Standard Reference Materials that produced numerous SRMs for a wide range of steel alloys. Many of those SRMs are still in use at this time. The fundamental precepts of the certification practices of that time are part of the foundations of today's certification processes, especially the concept of using multiple, independent test methods.

5.1. Methods

Methods used at this time involved a variety of classical methods as well as instrumental methods. **Table 37** provides the method and the elements measured by that method.

Table 37. Measurements Methods for SRM 1270a Historical Data

Method	Analyte
Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF)	Si, V, Cr, Mn, Co, Ni, Cu, As, Mo, Sn
Combustion with Infrared Detection (CID)	C, S
Zeeman Graphite Furnace Atomic Absorption Spectrophotometry (Z-GFAA)	Al, Co, Pb
Instrumental Neutron Activation Analysis (INAA)	V, Mn, Cu
Persulfate-Arsenite Titration	Mn
Ag Diethyldithiocarbamate Spectrophotometry	As
Isotope Dilution Thermal Ionization Mass Spectrometry (ID-TIMS)	Mo
Benzoine Oxime Gravimetric analysis	Mo
Brilliant Green Spectrophotometry	Sb
Polarography	Pb

5.2. Equipment

The following equipment was used for the first four instrumental methods listed in Table 1.

- INAA Spectrometer: Nuclear Data ND6600 with proprietary software and an 82 cc Ge(Li) detector.
- Combustion with Infrared Detection: LECO model CS-46 carbon and sulfur analyzer.
- WDXRF Spectrometer: Philips model AXS wavelength dispersive X-ray fluorescence spectrometer.
- Z-GFAA: Hitachi Zeeman graphite furnace atomic absorption spectrometer, circa 1980.

5.3. Sampling Details

Specimens for analyses were provide in two forms. Chipped material was made into a composite representing the material identified as 1270a³, blended and sampled for the test methods that used digested material put into solution. Disk form samples were taken from across the lot of material for WDXRF analyses.

5.4. Results of Quantitative Analyses

Test results for 15 elements by the various methods are presented and discussed below.

³ In internal NBS documentation, the material for SRM 1270a, which was taken from the same production heat as the material for SRM 1270, was sometimes designated as 1270II.

Carbon: The carbon test results by CID were reported as a mean, x , and standard deviation, s , of five replicate determinations from the 1270a composite material.

$$C: x_C = 0.076 \%, s = 0.002 \%, n = 5$$

Aluminum: The aluminum test results by Z-GFAA were reported as a mean, x , and standard deviation, s , of six replicate determinations from the 1270a composite material.

$$Al: x_{Al} = 0.0079 \%, s = 0.0005 \%, n = 6$$

Silicon: The silicon test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Si:

0.2513, 0.2424, 0.2484, 0.2515, 0.2511, 0.2467, 0.2565, 0.2456, 0.2504, 0.2491, 0.2482,
0.2502, 0.2453, 0.2509, 0.2453, 0.2449, 0.2412

$$Si: x_{Si} = 0.2488 \%, s = 0.0034 \%, n = 17$$

Sulfur: The sulfur test results by CID were reported as a mean, x , and standard deviation, s , of five replicate determinations from the 1270a composite material.

$$S: x_S = 0.0071 \%, s = 0.0005 \%, n = 5$$

Vanadium: The vanadium test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % V:

0.0133, 0.0135, 0.0134, 0.0134, 0.0135, 0.0134, 0.0136, 0.0134, 0.0135, 0.0135, 0.0135,
0.0133, 0.0134, 0.0136, 0.0133, 0.0134, 0.0136

$$V: x_V = 0.01344 \%, s = 0.00010 \%, n = 17$$

The vanadium test results by INAA were reported as three replicate results from the 1270a composite material. Individual results in % V:

0.01394, 0.01319, 0.01327

$$V: x_V = 0.01347 \%, s = 0.00041 \%, n = 3$$

Chromium: The chromium test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Cr:

2.3217, 2.3188, 2.3263, 2.3247, 2.3182, 2.3188, 2.3290, 2.3110, 2.3252, 2.3228, 2.3273,
2.3163, 2.3168, 2.3282, 2.3120, 2.3105, 2.3335

$$Cr: x_{Cr} = 2.3212 \%, s = 0.0067 \%, n = 17$$

Manganese: The manganese test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Mn:

0.6317, 0.6326, 0.6365, 0.6339, 0.6275, 0.6292, 0.6393, 0.6271, 0.6355, 0.6358, 0.6327,
0.6332, 0.6267, 0.6466, 0.6287, 0.6167, 0.6396

$$Mn: x_{Mn} = 0.6325 \%, s = 0.0066 \%, n = 17$$

The manganese test results by INAA were reported as three replicate results from the 1270a composite material. Individual results in % Mn:

0.6433, 0.6583, 0.6501

Mn: $x_{\text{Mn}} = 0.6506 \%$, $s = 0.0075 \%$, $n = 3$

The manganese test results by persulfate-arsenite titration were reported as three replicate results from the 1270a composite material. Individual results in % Mn:

0.654, 0.654, 0.653

Mn: $x_{\text{Mn}} = 0.6537 \%$, $s = 0.0006 \%$, $n = 3$

Cobalt: The cobalt test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Co:

0.0436, 0.0437, 0.0440, 0.0442, 0.0437, 0.0438, 0.0438, 0.0449, 0.0444, 0.0439, 0.0446,
0.0442, 0.0442, 0.0448, 0.0447, 0.0438, 0.0446

Co: $x_{\text{Co}} = 0.04417 \%$, $s = 0.00043 \%$, $n = 17$

The cobalt test results by Z-GFAA were reported as a mean, x , and standard deviation, s , of six replicate determinations from the 1270a composite material.

Co: $x_{\text{Co}} = 0.045 \%$, $s = 0.004 \%$, $n = 6$

Nickel: The nickel test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Ni:

0.1770, 0.1767, 0.1772, 0.1765, 0.1764, 0.1759, 0.1790, 0.1748, 0.1784, 0.1768, 0.1783,
0.1753, 0.1760, 0.1785, 0.1736, 0.1742, 0.1791

Ni: $x_{\text{Ni}} = 0.1767 \%$, $s = 0.0016 \%$, $n = 17$

Copper: The copper test results by WDXRF were reported as 17 individual results from homogeneity testing of disks of SRM 1270a. Individual results in % Cu:

0.1187, 0.1190, 0.1174, 0.1186, 0.1172, 0.1181, 0.1186, 0.1176, 0.1183, 0.1186, 0.1199,
0.1177, 0.1173, 0.1184, 0.1158, 0.1148, 0.1181

Cu: $x_{\text{Cu}} = 0.1179 \%$, $s = 0.0012 \%$, $n = 17$

The copper test results by INAA were reported as three replicate results from the 1270a composite material. Individual results in % Cu:

0.1208, 0.1218, 0.1200

Cu: $x_{\text{Cu}} = 0.12087 \%$, $s = 0.00090 \%$, $n = 3$

Arsenic: The arsenic test results by WDXRF were reported as 17 replicate results from homogeneity testing of disks of SRM 1270a. Individual results in % As:

0.0185, 0.0186, 0.0190, 0.0188, 0.0182, 0.0185, 0.0198, 0.0178, 0.0196, 0.0187, 0.0192,
0.0183, 0.0188, 0.0193, 0.0177, 0.0174, 0.0199

As: $x_{\text{As}} = 0.01871 \%$, $s = 0.00071 \%$, $n = 17$

The arsenic test results by Ag diethyldithiocarbamate spectrophotometry were reported as two replicate results. Individual results in % As:

0.0153, 0.0154

As: $x_{\text{As}} = 0.01535 \%$, $s = 0.00007 \%$, $n = 2$

Molybdenum: The molybdenum test results by WDXRF were reported as 17 replicate results from homogeneity testing of disks of SRM 1270a. Individual results in % Mo:

0.9378, 0.9365, 0.9450, 0.9401, 0.9338, 0.9375, 0.9479, 0.9263, 0.9445, 0.9405, 0.9438,
0.9305, 0.9376, 0.9476, 0.9285, 0.9220, 0.9538

Mo: $x_{\text{Mo}} = 0.9385 \%$, $s = 0.0084 \%$, $n = 17$

The molybdenum test results by ID-TIMS were reported as four replicate results from the 1270a composite material. Individual results in % Mo:

0.9573, 0.9551, 0.9603, 0.9523

Mo: $x_{\text{Mo}} = 0.9563 \%$, $s = 0.0034 \%$, $n = 4$

The molybdenum test results by the benzoine oxime gravimetric analysis were reported as three replicate results from the 1270a composite material. Individual results in % Mo:

0.924, 0.930, 0.944

Mo: $x_{\text{Mo}} = 0.9327 \%$, $s = 0.0103 \%$, $n = 3$

Tin: The tin test results by WDXRF were reported as 17 replicate results from homogeneity testing of disks of SRM 1270a. Individual results in % Sn:

0.0149, 0.0148, 0.0152, 0.0151, 0.0147, 0.0148, 0.0156, 0.0143, 0.0154, 0.0152, 0.0154,
0.0145, 0.0149, 0.0157, 0.0142, 0.0141, 0.0159

Sn: $x_{\text{Sn}} = 0.01498 \%$, $s = 0.00053 \%$, $n = 17$

Antimony: The brilliant green spectrophotometry method for Sb gave very high results for the replicate specimens from the 1270a composite. The two values of 0.0197 % and 0.0195 % are completely unrealistic given results for SRM 1270 (1270I composite) that are two orders of magnitude lower and are confirmed by new NIST WDXRF results (see Section 4, **Table 26**). Both candidate materials came from a single heat of low alloy steel. Such heterogeneity for Sb has never been observed to the knowledge of the authors and, therefore, the results of this method have been set aside. The inconsistency may be due to the limited sensitivity of the brilliant green spectrophotometry method, known inconsistencies among and within batches of the reagent [9], and the very low Sb mass fraction in candidate SRM 1270a.

Lead: The lead test results by Z-GFAA were reported as a mean, x , and standard deviation, s , of six replicate determinations from the 1270a composite material.

Pb: $x_{\text{Pb}} = 0.0022 \%$, $s = 0.0001 \%$, $n = 6$

The lead test results by the polarography method were reported as two replicate results from the 1270a composite material. Individual results in % Pb:

0.0017, 0.0014

Pb: $x_{\text{Pb}} = 0.00155 \%$, $s = 0.00021 \%$, $n = 2$

5.5. Conclusions

For 14 reported elements, the test results from 1980 through 1982 are in good agreement with the test results leading to certification of SRM 1270, bearing in mind that the material for SRM

1270 and 1270a were pulled from a single heat. A review of more recent results in Section 4 indicates good agreement and consistent precision of replicates. Antimony is the only element for which the test results from the original 1270 certification project are inconsistent with other available results. The test results for these 14 elements, not including antimony, will be used for the certification value assignment of SRM 1270a.

6. Determination of Boron in SRM 1228 and Candidate SRM 1270a Low Alloy Steels

The boron mass fractions in SRM 1228 and candidate material for SRM 1270a were determined by cold-neutron Prompt Gamma Activation Analysis (CN-PGAA). PGAA has an excellent limit of detection for boron in steels in the range of parts per billion. For these measurements, SRM 1763b low alloy steel and SRM 2168 electrolytic iron were used as controls.

6.1. Preparation of Samples, Standards, and Controls

Both materials were received in the form of small metal chips. Six bottles each of SRM 1270a and SRM 1228 were sampled. For SRM 1270a, one portion of metal chips weighing between 100 mg and 150 mg was removed from each of six bottles, for a total of six samples. Similarly, for SRM 1228, one metal portion weighing between 130 mg and 360 mg was removed from each of six bottles. Preliminary analyses revealed that SRM 1270a contained approximately 45 mg/kg of boron, while the boron content of SRM 1228 was < 1 mg/kg. Therefore, to cover the range of materials analyzed, two control materials were chosen for this investigation: SRM 1763b Low Alloy Steel, with a certified B mass fraction of (53.5 ± 3.2) mg/kg of boron, and SRM 2168 Electrolytic Iron, with a reference value of (0.064 ± 0.026) mg/kg. Measurements were carried out on four portions of SRM 1763b. Due to beam time constraints, only two portions of SRM 2168 were analyzed. Samples and controls for analysis were prepared by sealing each portion of steel or iron chips into a bag of FEP Teflon. Sample mass was determined to ± 0.01 mg using an analytical balance. All masses were determined using a Mettler Toledo Model# XP205DR analytical balance. **Table 38** gives masses of samples and controls used in the analysis.

Table 38. Masses of samples and controls measured by PGAA

Bottle/sample #	Mass (mg)
Samples	
SRM 1270a	
1_1	124.48
1_4	130.07
3_3	118.55
3_5	122.83
5_5	116.97
7_2	115.28
SRM 1228	
13_3	353.42
5_2	313.21
8_1	131.94
2_1	366.18
9_2	138.48
6_3	335.84
Controls	
SRM 1763b	
1	368.26
2	368.35
3	382.31
4	307.47
SRM 2168	
3	303.95
4	330.01

Six standards for measurement of boron were prepared by pressing graphite doped with a boron standard solution prepared as follows. SRM 3107 Boron Standard Solution, Lot #110830 (certified boron mass fraction = 5.014 mg/g \pm 0.010 mg/g) was gravimetrically diluted to yield a solution with a boron mass fraction of (0.2626 \pm 0.0005) mg/kg. Approximately 1.3 g of graphite (100 mesh, Lot #110892, Spectrographic Services, Sussex, NJ) were weighed into each of two mixing vials with the vials being weighed before and after addition to determine the mass of graphite. Four to five drops of the dilute boron standard solution were added to the graphite in each vial using a disposable plastic pipette, with the pipette weighed before and after dispensing to determine the mass of solution added. The graphite in each vial was allowed to dry for two days, after which two mixing balls were added, and each graphite mixture shaken for 20 minutes using a ball mixer mill. Three nominally 0.25 g portions of graphite were removed from each vial and pressed into pellets using a 13 mm die and hydraulic press. Each pellet contained nominally 8 μ g boron. **Table 39** summarizes the standards measured.

Table 39. Summary of standards measured by PGAA^a

Standard	Mass of element in pressed pellet	cps/ μ g B	cps/g Fe / cps/ μ g B
B standards (SRM 3107 Boron Standard Solution on graphite mixtures)			
B pellet 4a	8.407 μ g B	12.79	31.22
B pellet 4b	8.632 μ g B	12.41	31.77
B pellet 4c	7.886 μ g B	13.18	30.79
B pellet 5a	9.231 μ g B	12.37	30.47
B pellet 5b	8.445 μ g B	12.99	31.15
B pellet 5c	8.775 μ g B	12.49	30.87
Average			
Average		12.70	31.05
Standard deviation		0.34	0.45
Relative standard deviation (%)		2.64	1.44

^aEach B standard was irradiated alone, and sandwiched between two iron foils of total mass 0.218 g.

6.2. Analysis of samples

Samples, standards, and controls were analyzed using the cold neutron PGAA facility located at neutron guide D (NGD) at the NIST Center for Neutron Research (NCNR) [10]. Boron standards, SRM 1270a samples and SRM 1763b controls were irradiated for < 30 minutes each. Portions of SRMs 1228 and 2168 with low boron were irradiated for 12 h to 24 h each to obtain counting statistics of < 5 % for the boron peak at 478 keV. Gamma-ray measurements were made using a high purity Ortec germanium detector (designated as Willie), with signal processing performed using a Mirion/Canberra Lynx analyzer. Gamma-ray spectra up to 11 MeV were collected on a computer workstation. An empty Teflon bag was also irradiated overnight to serve as a background. A 14.05 mg titanium foil was measured at regular intervals to monitor the neutron flux.

The 477 keV boron peak was integrated by hand fitting the energy region between \approx 468.5 keV to 486.5 keV using Mirion/Canberra Genie 2000 software. Due to the Doppler broadening of the peak, standard peak fitting programs that fit peaks with a Gaussian shape are not useful for integration of this peak. The boron count rate in samples and controls was corrected for background by subtracting the boron background count rate measured from the empty Teflon bag. Pulse pileup corrections were unnecessary because pileup rejection circuitry was used. No corrections for neutron self-shielding or gamma-ray attenuation were performed but an uncertainty was calculated to account for potential differences in geometry and composition between samples and standards.

Because small differences in target positioning at the NGD PGAA instrument can result in significant differences in neutron flux exposure, the boron mass fraction was measured both relative to the measured mass of the sample, and to the iron content of the sample. For measurement of boron by sample mass, each boron standard pellet was irradiated by itself in

the neutron beam. For ratio measurements, each boron standard was measured sandwiched between two 0.1 mm thick iron foils, with a combined iron mass of 0.218 g. The iron doublet at 7630 keV and 7645 keV was integrated using PeakEasy software.

For calculation of boron mass fractions in the samples and controls, w_B , in mg/kg, based on the measured mass of the sample, the following equation was used:

$$w_B = ((C_B - C_{\text{bkg}}) / S_B) / m_{\text{sa}} \quad (2)$$

where C_B is the count rate of B ($\text{counts} \cdot \text{s}^{-1}$) measured in the sample or control; C_{bkg} is the B count rate from the empty Teflon bag; S_B is the average sensitivity ($\text{counts} \cdot \text{s}^{-1} \cdot \mu\text{g}^{-1}$ of boron) determined from the standards, and m_{sa} is the mass of the sample or control in grams.

For calculation of boron mass fraction using a ratio method, $w_{B'}$, with iron as comparator element, the following equation was used:

$$w_{B'} = ((C_B - C_{\text{bkg}}) / C_{\text{Fe}}) * S_{\text{Fe}} / S_B * w_{\text{Fe}} \quad (3)$$

where C_{Fe} is the count rate of iron ($\text{counts} \cdot \text{s}^{-1}$) given by the sum of the 7630 keV and 7645 keV peaks; S_{Fe}/S_B is the Fe/B sensitivity ratio ($\text{counts} \cdot \text{s}^{-1} \cdot \text{g}^{-1} \text{Fe} / \text{counts} \cdot \text{s}^{-1} \cdot \mu\text{g}^{-1} \text{B}$) measured from the iron and boron stacked standards; and w_{Fe} is the iron mass fraction of the SRM taken either directly from the certificate or calculated indirectly as the balance of the material, i.e., (100 % minus the sum of all measured components). The following values were used for w_{Fe} :

- SRM 1270a: 0.954 (by balance from components in certificate of SRM 1270, assuming the same composition);
- SRM 1763b: 0.950 (information value from certificate);
- SRM 1228: 0.995 (by balance from certificate);
- SRM 2168: 1.000 (as this iron SRM has only impurities at mg/kg levels and below).

For the uncertainty budget for SRM 1270a and SRM 1763b, an Fe mass fraction uncertainty of 0.5 % was included. This assumes $2s$ uncertainty of approximately 1 % for iron (i.e., iron mass fraction = 0.95 ± 0.01), which is likely larger than the actual uncertainty in the iron content. For SRMs 1228 and 2168, it was assumed that the uncertainty in the Fe composition was not significant compared to the total uncertainty.

6.3. Results

Boron mass fractions measured in SRM 1270a and SRM 1228 are given in **Table 40** and **Table 41**. The relative values for each source of uncertainty are also listed together with degrees of freedom and combined standard and expanded uncertainties calculated according to the guidelines in NIST Technical Note 1297 [11]. **Table 42** details components of uncertainty. Use of the B/Fe ratio method for SRM 1270a boron measurements and also for measurement of the SRM 1763b control results in the next section yield a significant reduction in the overall measurement uncertainty. In these measurements, the overall uncertainty is dominated by sample and standard replication, and may be significantly affected by small differences in target position in the beam when direct measurement of the B signal intensity is used. For SRM 1228, where a large fraction of measurement uncertainty comes from peak

fitting and subtraction of B background, the use of the ratio method does not result in a significant difference in overall measurement uncertainty.

Table 40. Boron mass fraction determined in SRM 1270a.

Bottle	B (mg/kg)			
	Determined relative to measured sample mass		Determined using ratio of boron to iron	
1_1	44.78		43.77	
1_4	44.15		44.64	
3_3	47.13		44.72	
3_5	46.29		44.48	
5_5	49.25		44.39	
7_2	43.99		44.71	
Avg.	45.93		44.45	
Std. Dev.	2.04		0.36	
% Std. Dev.	4.45		0.80	
% Counting Statistics	0.5		0.5	
Relative Uncertainties (%):				
Sample meas. replication (s/√n)	<i>u</i>	DF	<i>U</i>	DF
	1.81	5	0.33	5
Standard replication	1.08	5	0.59	5
Standard mass (purity)	0.1	∞	0.1	∞
Peak integration	0.25	∞	0.25	∞
Background subtraction	0.03	∞	0.03	∞
Gamma-ray and neutron self shielding	0.25	∞	0.25	∞
Normalization to Fe			0.5	∞
Relative combined u	2.14		0.92	
DF	8.67		26.7	
Coverage factor	2.31		2.06	
Relative expanded uncertainty (%) <i>U</i>	4.93		1.89	
Value with Expanded Uncertainty (<i>U</i>)	45.93 (2.27)		44.45 (0.84)	
Recommended Value (<i>U</i>)	45.2 (1.6)			

Table 41. Boron mass fraction determined in SRM 1228.

Bottle	B (mg/kg)			
	Determined relative to measured sample mass		Determined using ratio of boron to iron	
13_3	0.294		0.288	
5_2	0.291		0.296	
8_1	0.352		0.339	
2_1	0.282		0.283	
9_2	0.297		0.243	
6_3	0.295		0.297	
Avg.	0.302		0.290	
Std. Dev.	0.030		0.031	
% Std. Dev.	8.33		10.94	
% Counting Statistics	2		2	
Relative Uncertainties (%):				
Sample meas. replication (s/√n)	<i>u</i>	DF	<i>u</i>	DF
	3.4	5	4.3	5
Standard replication	1.08	5	0.59	5
Standard mass (purity)	0.1	∞	0.1	∞
Peak integration	3	∞	3	∞
Background subtraction	2.8	∞	2.8	∞
Gamma-ray and neutron self shielding	0.25	∞	0.25	∞
Normalization to Fe			0.5	∞
Relative combined u	5.44		5.98	
DF	37.9		18.7	
Coverage factor	2.03		2.10	
Relative expanded uncertainty (%) <i>U</i>	11.1		12.6	
Value with Expanded Uncertainty (<i>U</i>)	0.302 (0.033)		0.290 (0.036)	
Recommended Value (<i>U</i>)	0.30 (0.04)			

Table 42. Explanation of Components of Uncertainty.

Sample measurement replication	s/\sqrt{n} , where s is standard deviation of the sample data, and n is the number of samples analyzed.
Standard measurement replication	s/\sqrt{n} , where s is standard deviation, and n is the number of measurements made, or uncertainty from counting statistics when the uncertainty was determined from a single measurement.
Background correction	Determined as uncertainty from counting statistics in background correction/total counts in the uncorrected boron peak.
Neutron/gamma-ray self shielding	Estimated as 10 % of the correction made using empirical equations.
Standard mass (purity)	Half the uncertainty given on the certificate for SRM 3107, assuming a coverage factor of 2.
Peak fitting	Estimated from results of peak integration by 2 different methods, as $(\text{method 1 cps} - \text{method 2 cps}) / (2 * \sqrt{3})$.
Iron mass fraction (for ratio method)	Estimated as 0.5 %, assuming a 2s uncertainty of 1 % for iron from the certificate.
Relative Combined Uncertainty, u .	All uncertainty components as described above were added in quadrature without weighting.

For the purpose of reporting a value for the B mass fraction, both measurement methods, direct and ratio, provide equally valid results. Hence, measured values and uncertainties for both methods will be averaged to formulate a recommended value and expanded uncertainty.

6.4. Quality Assurance Measurements

Boron results for control materials SRM 1763b and 2168 are shown in **Table 43** and **Table 44**, together with the total expanded uncertainties as defined in NIST Technical Note 1297 [11]. Again, the measured values and uncertainties for both measurement methodologies, direct and B/Fe ratio, are documented. The average measurement value and average expanded uncertainty of both methodologies will be used for determination of whether the measurement is in control or not. For SRM 1763b, the average PGAA measured value of $(55.59 \pm 1.37 \text{ mg/kg})$ is in agreement with the certified value of $(53.5 \pm 3.2) \text{ mg/kg}$. For SRM 2168, the average PGAA measured value of $(0.065 \pm 0.014 \text{ mg/kg})$ is in agreement with the reference value on the certificate, $(0.064 \pm 0.026 \text{ mg/kg})$, which was originally measured by cold neutron PGAA.

Table 43. B mass fraction results for control SRM 1763b.

	B (mg/kg)	
	Determined relative to measured sample mass	Determined from ratio of boron to iron
1	54.78	55.14
2	56.34	55.48
3	55.69	55.17
4	56.60	55.52
u_c	0.76	0.49
DF	9.47	25.8
k	2.26	2.06
Mean Value (U)	55.85 (1.72)	55.32 (1.02)
Certified Value (U)	53.5 (3.2)	

Table 44. B mass fraction results for control SRM 2168.

	B (mg/kg)	
	Determined relative to measured sample mass	Determined from ratio of boron to iron
3	0.0677	0.0660
4	0.0619	0.0643
u_c	0.0071	0.0066
DF	8.29	3157
k	2.03	1.97
Mean Value (U)	0.065 (0.015)	0.065 (0.013)
Reference Value (U)	0.064 (0.026)	

6.5. Conclusions

Measured values for the controls, SRM 1763b and SRM 2168, were in good agreement with the certified and reference values. The B/Fe ratio method provides higher uncertainty values as is typical of ratio type methods. Hence, it is safe to conclude that the B mass fraction calibrations are under control. Recommended values for B mass fraction of SRM 1270a and SRM 1228 to be used for certification are given in **Table 40** and **Table 41**, respectively.

7. Summary

SRM 1270a is an SRM renewal with the candidate material being pulled from the same billet as the original SRM 1270 material. The goal in this renewal certification was to certify the original 11 analyte mass fractions certified in SRM 1270, *viz.*, C, Si, P, S, V, Cr, Mn, Co, Ni, Cu and Mo, and to certify as many of the additional uncertified elements, *viz.*, B, Al, Ti, As,

Zr, Nb, Sn, Sb, Ta, W and Pb, found in SRM 1270 during the original certification project circa 1980 as possible. The goal in certifying a broader range of elements is to expand the utility of the SRM alloy without having to justify and invest in new candidate material production.

For each analyte, lists measurement methods used to assign the value type to the analyte. All 11 of the original analyte mass fractions were certified along with certification of six additional elements.

Table 45. Measurements Methods for SRM 1270a Historical Data.

Analyte	Measurement Methods^(a)	Value Type^(b)
B	PGAA; SS-OES	C
C	CID (NBS, Collaborator); SS-OES	C
N	IGF	NC
Al	Z-GFAA; WDXRF; SS-OES	NC
Si	WDXRF (NBS, NIST); SS-OES	C
P	WDXRF; SS-OES	C
S	CID (NBS, Collaborator); SS-OES	C
Ti	WDXRF; SS-OES	C
V	WDXRF (NBS, NIST); INAA; SS-OES	C
Cr	WDXRF (NBS, NIST); SS-OES	C
Mn	WDXRF (NBS, NIST); INAA; SS-OES; Persulfate-Arsenite Titration	C
Co	WDXRF (NBS, NIST); Z-GFAA; SS-OES	C
Ni	WDXRF (NBS, NIST); SS-OES	C
Cu	WDXRF (NBS, NIST); INAA; SS-OES	C
As	WDXRF (NBS, NIST); SS-OES; Ag diethyldithiocarbamate spectrophotometry	C
Zr	WDXRF; SS-OES	C
Mo	WDXRF (NBS, NIST); ID-TIMS; SS-OES; Benzoine Oxime Gravimetric analysis	C
Nb	WDXRF; SS-OES	OI
Sn	WDXRF (NBS, NIST); SS-OES	C
Sb	WDXRF; Brilliant Green Spectrophotometry	LOQ
Ta	WDXRF; SS-OES	LOQ
W	WDXRF	LOQ
Pb	WDXRF; Z-GFAA; Polarography	C

^aWDXRF was typically performed at NBS in 1981 and NIST in 2020

^bThere are four types of values reported:

C = certified value

NC = non-certified value

OI = other information value reported without uncertainty

LOQ = other information reported as a limit of quantification

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