spex® certiprep

White Paper

ICP, ICP/ICP-MS and ICP-MS Grade Certified Reference Materials – Is There Really a Difference?

Brenda Lenkeit and Daniel Goldman • SPEX CertiPrep, Metuchen, NJ 08840
Date of study - June 2005

Introduction

A blind laboratory study was conducted to compare standards obtained from various manufacturers of certified reference materials. There are two goals for this study: first to objectively determine if a difference exists between an ICP grade standard and an ICP-MS grade standard and second to focus on the equivalency of the ICP-MS grade standard to the ICP/ICP-MS grade of standard.

The single-element standard selected for study was 1,000 ppm iron, due to its popularity and known interferences. ICP-MS standards were obtained, whenever possible, directly from the manufacturer; if this was not possible, alternate sources were used. A total of 13 single element Fe standards were analyzed. Two of these were ICP-MS grade standards, five were ICP grade standards, and six were stated for use on either an ICP or ICP-MS instrument.

The multi-element solutions were selected to be similar to the SPEX CertiPrep CLMS-2 Claritas PPT® ICP-MS standard. See Table 1 for the contents of CLMS-2. This standard was selected since it contains many elements commonly analyzed by ICP-MS. All of the multi-element solutions studied were ICP-MS grade.

Table 1. Contents of CLMS-2

Description	Components	Concentration	Matrix	Part #
ICP-MS Multi-Element Solution	Ag, Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg*, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn	10 µg/mL	5% HNO_3	**CLMS-2**

** Hg supplied as a separate solution*

Experimental

All solutions were prepared in a Class 100 clean room using glassware set aside for ICP-MS analysis. The solutions were analyzed in house on ICP and ICP-MS instrumentation.

Each standard solution was analyzed for major and minor elements. Table 2 shows a list of the trace elements analyzed. The results were compared with the concentrations listed on each corresponding certificate of analysis.

In addition, each certificate of analysis was compared to the SPEX certificate®, Certificate of Analysis provided with the PPT 1,000 ppm Fe standard (CLFE2-2Y) and multi-element ICP-MS standard (CLMS-2) analyzed in this study.

Table 2. Trace Elements Analyzed by ICP-MS

Trace Elements Analyzed by ICP-MS
Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr

Results

Each standard was evaluated for a number of factors and compared with the SPEX CertiPrep standard. Please refer to Table 3 for a summary of the results obtained from the Fe standards and Table 4 for a summary of results for the multi-element standards.

Table 3. Summary of Results for 1,000 µg/mL Fe Standards

Standard	Grade	Labeled Fe Concentration	Certified Fe Concentration	Fe Analyzed/ Verified by	Number of Trace Impurities Reported	Impurity Levels Reported by (units)	Impurities Analyzed by	Solution Analyzed for Trace Impurities	Reported Detection Limits	NIST Traceable	ISO
A SPEX Certi-Prep	ICP-MS	1,000 mg/L	998 mg/L[1]	ICP, Wet	66	ppb	ICP/ICP-MS	Final Solution	0.01-0.2 ppb	Yes	9001
B	ICP-MS	1,000 µg/mL	Labeled	ICP	44	ppm	AA/ICP	Concentrate	20 or 200 ppb	Yes	9001
C	ICP	1,000 ± 3 µg/mL	Labeled	ICP	63	ppb	ICP-MS	Final Solution	0.1 ppb for most	Yes	No
D	ICP	1,000 ± 3 µg/mL	Labeled	ICP	66	ppm	DCP/ICP	Final Solution	20-100 ppb	Yes	No
E	ICP/ICP-MS	1,000 ± 3 µg/mL	Labeled	ICP	67	ppp	ICP-MS	Final Solution	0.02 or 1 ppb for all	No	No
F	ICP/ICP-MS	1,000 ± 3 µg/mL	Labeled	ICP	67	ppp	ICP-MS	Final Solution	0.02 or 1 ppb for all	No	No
G	ICP/ICP-MS	1,000 ± 3 µg/mL	Labeled	ICP	67	ppm	ICP-MS	Final Solution	0.02 or 1 ppb for all	No	No
H	ICP	1,000 µg/mL	1002.1 µg/mL [2]	Not Given	6	ppm	Not Given	Final Solution	10 or 20 ppb	Yes	No
I	ICP/ICP-MS	1,000 µg/mL	1003 ± 2 µg/mL [3]	ICP, Wet	66	ppm	ICP/ICP-MS	Final Solution	0.1-50 ppb	Yes	9001
J	ICP/ICP-MS	1,000 µg/mL	Labeled	ICP	65	ppm	ICP	Final Solution	1-50 ppb	Yes	9002
K	ICP	1,000 ppm	Labeled	ICP	N/A	N/A	N/A	None	None Reported	Yes	No
L	ICP	1,000 µg/mL	1000.0 µg/mL [4]	ICP, Wet [5]	33	ppm	Not Given	Final Solution	10-50 ppb	Yes	9001
M	ICP/ICP-MS	1,000 µg/mL	1,000 µg/mL [6]	ICP	67	ppm	ICP, DCP	Final Solution	20-100 ppb	Yes	9002

Notes:

1. The certified Fe concentration is defined as the average of the values obtained by classical wet assay and ICP spectrometer analysis.

2. The certificate of analysis does not specify how this number was determined.

3. The certificate of analysis provides the formula used to determine the certified Fe concentration

4. The certified value is the concentration calculated from gravimetric, volumetric, and/or classical wet assay measurements performed during the preparation of the standard unless otherwise specified

5. The wet classical assay listed on the certificate. Method: theoretical, based on gravimetric measurements.

6. The certified Fe value is based on gravimetric procedures.

Table 4. Summary of Results for Multi-Element Standards

Standard	Grade	Number of Elements	Concentration of Each Element (ppm)	Major Elements Verified By	Measured Values	# Trace Elements Reported	Trace Levels	Impurities Analyzed By	Detection Limits for Trace Elements	Solution Analyzed for Trace Elements	ISO	NIST
MA (Spex)	ICP-MS	29	10	ICP	Yes	39	ppb	ICP-MS	0.02-7 ppb	Final	9001	Yes
MB	ICP-MS	26	10	ICP	Yes	0	N/A	N/A	N/A	N/A	9002	Yes
MC	ICP-MS	25	10	ICP	No	0	N/A	N/A	N/A	Concen-trate	9001	Yes
MD	ICP-MS	32	10	ICP	No	0	N/A	N/A	< 50 µg/g total	Starting Material	No	No
ME	ICP-MS	13	10	ICP or Wet	Yes	0	N/A	N/A	N/A	N/A	9001	Yes
MF	ICP-MS	31	10	Not Given	No	0	N/A	N/A	N/A	Starting Material	No	No
MG	ICP-MS	25	100	Not Given	No	0	N/A	N/A	N/A	N/A	No	Yes
MH	ICP-MS	32	10	ICP	No	0	N/A	N/A	< 50 g µg/g total	Starting Material	No	No
MI	ICP-MS	30	10	Not Given	No	0	N/A	N/A	N/A	N/A	No	Yes
MJ	ICP-MS	22	10	Not Given	No	0	N/A	N/A	N/A	N/A	No	Yes
MK	ICP-MS	15	10	ICP	No	0	N/A	N/A	N/A	N/A	9001	Yes

Certified Values

1,000 ppm Fe Standard

The Spex CertiPrep Claritas PPT® single-element Fe standard was analyzed by two independent methods, wet chemistry and ICP, in order to verify the Fe concentration and determine the certified value. The SPEXertificate® reports the results obtained from each of these methods as well as a certified Fe concentration. The certificate of analysis also defines the certified value as the average of the ICP and wet assay results.

Only one other standard evaluated in this study, Standard I, reported an actual measured ICP and wet assay Fe concentration. This standard also reported a certified Fe concentration on the certificate of analysis and indicated on the certificate of analysis how the certified value was determined.

The majority of the standards verified the 1,000 ppm Fe concentration by ICP, however, did not report a measured Fe concentration or an independent verification of the Fe concentration. The certified value for these (if specified) was the labeled 1,000 ppm Fe concentration with an uncertainty measurement.

Standard H provided an actual Fe value on the certificate, however, did not indicate how the number was obtained.

The Certificate of Analysis for Standard L lists “Certified Value”, “Classical Wet Assay” and “Confirmed by ICP”, however, upon further examination of the certificate, it states Certified Value is “the concentration ***calculated*** from the gravimetric, volumetric, and/or classical wet assay measurements performed during the ***preparation*** of the standard”. Note: the certified value is calculated (not measured) and based upon the preparation of the standard (not a measurement made on the final solution).

Multi-Element Standards

The Spex CertiPrep certificate of analysis for CLMS-2 provides a labeled and measured value for every element at 10 ppm. Standards MB and ME were the only other standards to include measured values for each element. All of the other standards simply reported a labeled concentration of 10 ppm or 100 ppm for each element.

Trace Impurities

For an accurate trace metals analysis at low levels, trace impurities present in the certified reference material must be identified. Laboratories using ICP-MS instruments are typically analyzing at ppb and ppt levels. At these low levels, trace impurities present in the reference material can contribute towards increased interferences. For an accurate ICP-MS analysis, the certified reference material must list the concentrations of all the impurities present at ppb and ppt levels. If impurities are not identified they can contribute towards increased interferences and may result in an inaccurate analysis.

1,000 ppm Fe Standards

The number of trace metallic impurities reported on the certificate of analysis.

The number of trace impurities reported on the certificates of analysis ranged of 0 to 69. Standard K did not have any trace metallic impurities listed while many of the standards reported more than sixty trace elements. SPEX CertiPrep reported sixty-seven trace element impurities in the 1,000 ppm Fe standard.

In general, the ICP-MS and ICP/ICP-MS grade standards reported a greater number of elements than did the ICP-MS standards. However, Standard C, an ICP grade standard, reported sixty-three trace elements while Standard B, an ICP-MS grade standard, reported only forty-four. Standard B had sixty-eight elements listed on the certificate, however, twenty-four of those elements were not analyzed in the Fe solution. Five other standards had elements listed on the certificate which were not analyzed. Standard C did not report values for Al, Ge, Mn, or Si due to interference from the major element.

Table 3 shows the number of trace metallic impurities reported for each standard.

The levels of the impurities reported on the certificate of analysis.

The SPEX CertiPrep 1,000 ppm Fe standard reported trace metallic impurities at ppb levels. Only four others other standards, Standards C, E, F, and G, included trace impurities at ppb levels. The other eight standards, including one ICP-MS and three ICP/ICP-MS grade standards, reported trace impurities at ppm levels. See Table 3 for the levels reported from each certificate of analysis.

The instrument used to analyze for the trace impurities.

SPEX CertiPrep analyzed for trace impurities by using our in-house ICP and ICP-MS instruments in order to report ppb and ppt levels. Five of the other standards also reported that the trace metallic impurities were analyzed by ICP-MS. The certificates for two of the standards did not report how the trace impurities were analyzed. The remaining standards were analyzed by AA, ICP or DCP. Standard B, an ICP-MS grade standard, reported AA and ICP analyzed the trace impurities.

The solution analyzed to report the trace impurities.

The trace metallic impurities in the SPEX CertiPrep Fe standard were analyzed in the final 1,000 ppm Fe solution. 10 of the other standards report the trace metallic impurity information was obtained by analyzing the final solution. Standard B reported the trace impurities were measured in the concentrate instead of the final solution.

Detection limits reported on the certificate of analysis.

The detection limits for the trace elements analyzed in the SPEX CertiPrep Fe standard ranged from 0.01-0.2 ppb. The detection limits reported varied by the element. Table 3 shows the range of detection limits reported for each standard for the majority of the elements. Detection limits ranged from < 0.01 ppb for some standards to < 50 ppb for others. The lower the detection limit reported for an ICP-MS analysis, the more useful the trace impurities information.

Trace impurities analyzed in this study were found to be higher than the concentration reported on the certificate of analysis.

The concentration of each trace element analyzed in this study was compared with the concentration reported on the certificate of analysis. Table 5 shows the reported and measured values for Al, Ca, Co, Cu, K, Mn, Na, and Ni for each of the 1,000 ppm Fe standards.

- Standard C: Higher concentration of Co (Al and Mn were not reported due to an interference with the major element)
- Standard D: Higher concentration of Ca
- Standards E, F and G: Higher concentrations of Ca, Co, Cu, K, Mn, and Ni
- Standard H: Higher concentrations of Co, Mn and Ni (Al, Ca, K, and Na were not analyzed in this standard)
- Standard I: Higher concentrations of Ca, K and Na
- Standard J: Higher concentrations of Co, Cu, Mn, and Ni
- Standard K: Did not report any trace metallic impurities
- Standard M: Higher concentration of Ca

Table 5. Trace Metallic Impurities in 1,000 Fe Standards.

Standard	Al		Ca		Co		Cu	
	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)
A - Spex CertiPrep	6	6	6	6	1	1	1	1
B	< 20	6	< 20	5	N/A	0.07	< 20	< 0.6
C	INT	1	15	3	12	20	6.4	0.9
D	< 40	4	< 2	4	< 20	< 0.04	40	30
E	2.0	1	< 1	2	0.5	18	0.02	1
F	2.0	1	< 1	2	0.5	17	0.02	30
G	2.0	< 1	< 1	2	0.5	17	0.02	30
H	N/A	20	N/A	65	< 10	20	< 10	10
I	< 2.7	< 1	< 0.34	9	< 0.66	< 0.4	< 25	< 0.6
J	< 13	< 1	28	21	7	19	< 0.3	2
K	N/A	7	N/A	18	N/A	0.5	N/A	3
L	< 50	7	< 10	2	< 40	< 0.4	< 30	< 0.6
M	< 40	3	< 2	4	< 20	< 0.4	40	40

Standard	Mn		K		Na		Ni	
	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)	Reported (ppb)	Measured (ppb)
A	5	5	20	20	4	4	1	1
B	< 20	7	N/A	9	< 20	9	N/A	< 1
C	INT	20	< 70	6	8	4	9.3	7
D	< 20	6	< 500	8	< 100	5	< 20	< 1
E	7	20	< 1	12	< 1	0.7	0.5	7
F	7	20	< 1	12	< 1	0.7	0.5	7
G	7	20	< 1	12	< 1	0.8	0.5	7
H	< 10	40	N/A	36	N/A	40	< 10	16
I	< 20	6	< 1.7	7	< 1.2	7	< 50	< 1
J	< 0.2	20	< 93	8	11	3	< 6	10
K	N/A	10	N/A	12	N/A	50	N/A	< 1
L	< 30	6	< 70	10	< 30	0.7	< 80	< 1
M	< 20	6	< 500	19	< 100	0.7	< 20	< 1

N/A = Not analyzed

INT = Interference from major element

Exact same trace metallic impurities reported for two different lots of a standard.

Two different lots of 1,000 ppm were analyzed from one of the suppliers. The certificate of analysis had the *exact* same trace metallic impurities listed for both lots.

Multi-Element Standards

SPEX CertiPrep reported thirty-nine trace metallic impurities in the final solution of CLMS-2 at ppb and ppt levels by ICP-MS. The certificates for two of the other standards, standards MD and MH, stated "< 50 µg/g total impurities in the standard" however, the certificate did not report concentrations for individual elements.

Standard MF states the starting materials were analyzed by ICP-MS for trace impurities. However, the certificate does not report any trace impurities and there is no indication any ICP-MS analysis was performed on the final solution. Standard MC says ICP or AA analyzed all trace elements and impurities on the concentration (not the final solution). Again, no data is reported for the trace metals.

Standard ME had a section heading for trace metallic impurities on the certificate, however, it said "N/A" for this section. No impurities were reported.

While many manufacturers reported trace impurities for the 1,000 ppm Fe standard, SPEX CertiPrep was the only manufacturer in this study to provide measured trace metallic impurities in the multi-element standard.

Density

1,000 ppm Fe Standards

The SPEX CertiPrep certificate of analysis for the 1,000 ppm Fe standard provided the density of the standard as an uncertified property. Standards C, E, F, G, J, L, and I also provided the density. Standard M reports a certified weight-to-weight concentration. Standards B, D, H, and K provided no information on the density of the solution.

Multi-Element Standards

None of the multi-element ICP-MS standards reported density.

Uncertainty

1,000 ppm Fe Standards

The SPEX CertiPrep 1,000 ppm Fe standard is certified to be 998 ± 3 mg/L. This is the uncertainty in the reported certified concentration. The stability of the solution is guaranteed stable to ± 0.5% of the certified concentration inclusive of uncertainty measurements and other effects, such as transportation losses, for a period of one year from the date of certification.

Standards B and J do not provide any uncertainty associated with the certified or labeled Fe concentration, however, both reported they guarantee the accuracy of the standard ± 0.5% until the expiration date.

Standard C reports the uncertainty as 1,000 ± 3 µg/mL, however, it is not explained. The accuracy and stability of this standard was also reported as 0.3%. Standards D, E, F, G, and H listed the Fe concentration as 1,000 ± 3 µg/mL with no information on how the uncertainty was determined. Standard I reported the certified Fe concentration as 1,003 ± 2 µg/mL and provided a detailed explanation of how the certified value and uncertainty were determined. Standard K reported the theoretical value for the standard as 1,000 ppm Fe (995-1,005 ppm). Standard L reported the uncertainty was 1,000 µg/mL ± 0.2% relative. Standard M reported the uncertainty was 1,000 µg/mL ± 0.3% relative with a detailed explanation. However, standards C, D, E, F, G, H, I, K, and M did not include a statement on the solutions stability on the certificate of analysis.

Multi-Element Standards

The SPEX CertiPrep CLMS-2 is guaranteed stable and accurate ± 0.5% on the average of all of the certified concentrations with no single analyses exceeding ± 2%. This includes the uncertainty of the measurements and other effects, such as transportation losses. This guarantee is valid for one year from the date of certification.

Standard MB was guaranteed to be stable and accurate to within ± 1% of the actual concentrations up to the expiration date.

The uncertainty is 0.5% relative for standards MC, MD, MF, MG, MH, and MK. Standard MI states the tolerances for labeled values are ± 0.3%.

Standard ME provides an uncertainty for each of the certified values and explains how the certified value and the uncertainty were determined. There is an explanation of shelf life and expiration date, however, no mention is made about the stability of the standard.

Standard MJ provides no information of the uncertainty of the concentrations of the major elements or the stability of the solution.

ISO 9001

1,000 ppm Fe Standards

The SPEX CertiPrep Claritas PPT® 1,000 ppm Fe standard was manufactured under an ISO 9001 Quality System. This is documented on the SPEXertificate®, Certificate of Reference Material. Standards B, L and I, on the certificate of analysis, indicated that they are also ISO 9001 certified. Standards J and M indicate ISO 9002 certification on their certificate of analysis. The remaining seven standards do not indicate they are manufactured under an ISO quality system.

Multi-Element Standards

The SPEX CertiPrep multi-element standard was also manufactured under an ISO 9001 Quality System. Standards MC, ME and MK are also ISO 9001 certified. The certificate for standard MB indicates the company is ISO 9002 registered. The remaining six multi-element solutions do not indicate they are manufactured under an ISO quality system.

NIST Traceable

Many laboratories require the use of NIST traceable certified reference materials.

1,000 ppm Fe Standards

The SPEX CertiPrep Claritas PPT® 1,000 ppm Fe standard reported on the certificate of analysis that it is directly traceable to NIST and provides the NIST SRM number.

Ten of the single-element Fe standards analyzed were NIST traceable. All of these also listed the NIST SRM on the certificate of analysis. Only three of the standards, standards E, F and G, were not directly compared to NIST standards. The certificates of analysis for these indicated the standard was "*certified by spectrometric analysis against an independent source which is directly traceable to the National Institute of Standards and Technology*". This is not directly NIST traceable.

Multi-Element Standards

The SPEX CertiPrep CLMS-2 ICP-MS multi-element standard is also NIST traceable with the NIST SRMs listed for each element.

Seven of the other ICP-MS multi-element solutions were also NIST traceable with the SRMs documented on the certificate of analysis. However, three of the multi-element solutions, standards MD, MF and MH, were certified against an independent source, which is not directly traceable to NIST. This is not NIST traceable.

Conclusion

At first glance, the certified reference materials appeared similar. However, upon further examination of the standards evaluated in this study, it became apparent that there were many differences between them.

In particular, there were many differences found in the number and level of trace metallic impurities reported on the certificates of analysis between the ICP, ICP/ICP-MS and ICP-MS standards. It is particularly important to know what trace metallic impurities are present in the final solution for an accurate ICP-MS analysis. If trace metallic impurities are present, but not identified in the certified reference material, they can contribute towards increased interferences that may result in an inaccurate analysis.

Differences were also found between the ICP-MS grade standards evaluated in this study. The SPEX CertiPrep single-element Fe certificate of analysis reported sixty-seven trace metallic impurities at ppb levels by ICP-MS.

Another single-element Fe ICP-MS grade standard reported forty-four trace metallic impurities at ppm levels analyzed by AA and ICP. SPEX CertiPrep reported detection limits of < 0.01-0.2 ppb on the certificate. The other ICP-MS standard reported detection limits of < 20 or <200 ppb. The difference was even greater for the multi-element solutions. Of the eleven multi-element ICP-MS standards evaluated, only the SPEX CertiPrep Claritas PPT® ICP-MS standard reported measured trace metallic impurities in the actual solution.

The difference in the trace impurities was just one of many factors that were found to be different between the standards. When selecting a standard for low-level analysis, such as for ICP-MS, it is important to look beyond the label, evaluate the certificate of analysis, and select the appropriate certified reference material.

spex.com

Phone: +1.732.549.7144 • +1.800.LAB.SPEX
Fax: +1.732.603.9647
spexsales@antylia.com

Connect with us