

Introduction

The lithium-ion (Li-ion) battery (LIB) industry is thriving due to demand for portable electronic devices and a surge in the use of battery electric vehicles (EVs). The four main components in a LIB are the anode, cathode, separator, and electrolyte. Electrolyte composition is a key factor in the overall performance of the battery. The common salts used in LIB electrolytes include lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), and lithium perchlorate (LiClO₄). Imide-based Li salts such as lithium bis(fluorosulfonyl)imide (LiFSI) are also used as additives to increase battery lifetime at high temperatures (1).

Electrolyte performance is strongly affected by the presence of elemental impurities, which must be monitored in the lithium salts to ensure consistency and quality of the electrolyte and the final battery product (2). ICP-OES is often used to determine contaminant elements in battery electrolyte salts and other raw materials. But many labs are interested in quantifying trace elements at sub-µg/kg (ppb) levels in the solid Li salts, and ICP-OES may not achieve the low detection limits required (3). ICP-MS is the preferred technique for trace element analysis across multiple industries and applications, because of its high speed, low detection limits, wide elemental coverage, and good selectivity. These characteristics make ICP-MS the ideal technique to meet the increasingly stringent requirements for trace elements in the components used in LIBs.

In this study, a standard addition calibration method was developed to quantify 68 elements in the lithium salts, LiPF₆, LiBF₄, LiClO₄, and LiFSI using single quadrupole ICP-MS. The analytes included the 12 metals (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pd, and Zn) listed in the draft ICP-OES method ISO/WD 10655 for the analysis of LiPF₆ (4), plus a further 56 elements.

The analysis was performed using an Agilent 7900 ICP-MS with an HF resistant PFA sample introduction system. Method performance, in terms of linearity, method detection limit (MDL), spike recovery, and robustness, was evaluated for all target elements in the four lithium salts.

Experimental

Reagents and standards

Ultrapure water and high purity nitric acid (HNO₃, ≥99.999% trace metal basis) were used for sample and standard preparation. Agilent multi-element and single element calibration standards were used to prepare an intermediate standard mix containing 67 analytes (excluding sulfur) at a concentration of 50 µg/L for Hg and 1,000 µg/L for other elements. The mixed multi-element intermediate standard was used as the standard addition spiking solution. For sulfur, no intermediate standard was used due to the higher calibration levels; the 1000 ppm stock standard was spiked directly into the standard addition calibration solutions.

Table 1. Agilent multi-element and single element standards used to prepare standard addition calibration spikes

Standard Description	Analyte	Concentration µg/mL	Agilent Part Number
Multi-element calibration standard-1	Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb	10	8500-6944
Multi-element calibration standard-2A	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Ti, U, V, Zn	10	8500-6940
Multi-element calibration standard-3	Sb, Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn	10	8500-6948
Multi-element calibration standard-4	B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr	10	8500-6942
Single element standard	Mercury (Hg)	10	5190-8575
Single element standard	Indium (In)	10	8500-6946
Single element standard	Bismuth (Bi)	10	8500-6936
Single element standard	Sulfur (S)	1000	5190-8529

Sample preparation and spiking

Four commercially available battery grade (≥ 99.9% purity on a trace metals basis) lithium salts – LiPF₆, LiBF₄, LiClO₄, and LiFSI – were analyzed in this study.

To prepare the solid Li salts for analysis, 5 g ± 0.01 g of each salt was weighed into a 50 mL PFA bottle. Ultrapure water was then added to give a final sample weight of 50 g ± 0.01 g (10x dilution). The bottles were tightly capped and placed in an ultrasonic bath for 5 mins to aid dissolution.

For each Li salt matrix, 2.5 g ± 0.001 g of the concentrated Li salt solution was transferred to each of nine 15 mL polypropylene (PP) sample tubes. These solutions were spiked with an appropriate volume of the mixed intermediate standard and sulfur stock solution to give the standard addition calibration levels, as shown in Figure 1. The solutions were made up to 5.0 g ± 0.01 g with 2% HNO₃ giving an additional 2x dilution (20x total dilution; 5% TDS).

The calibration concentrations ranged from 0.05 to 5 µg/kg (ppb) for Hg, 0.5 to 10 µg/g (ppm) for sulfur, and 1 to 500 µg/kg for all other elements. The unspiked solution (Cal 1) was used as the sample blank (SB) for each salt.

With ICP-MS MassHunter, standard addition calibrations can be automatically converted to external calibrations during the run, and the other (matrix-matched) samples can then be quantified by external calibration.

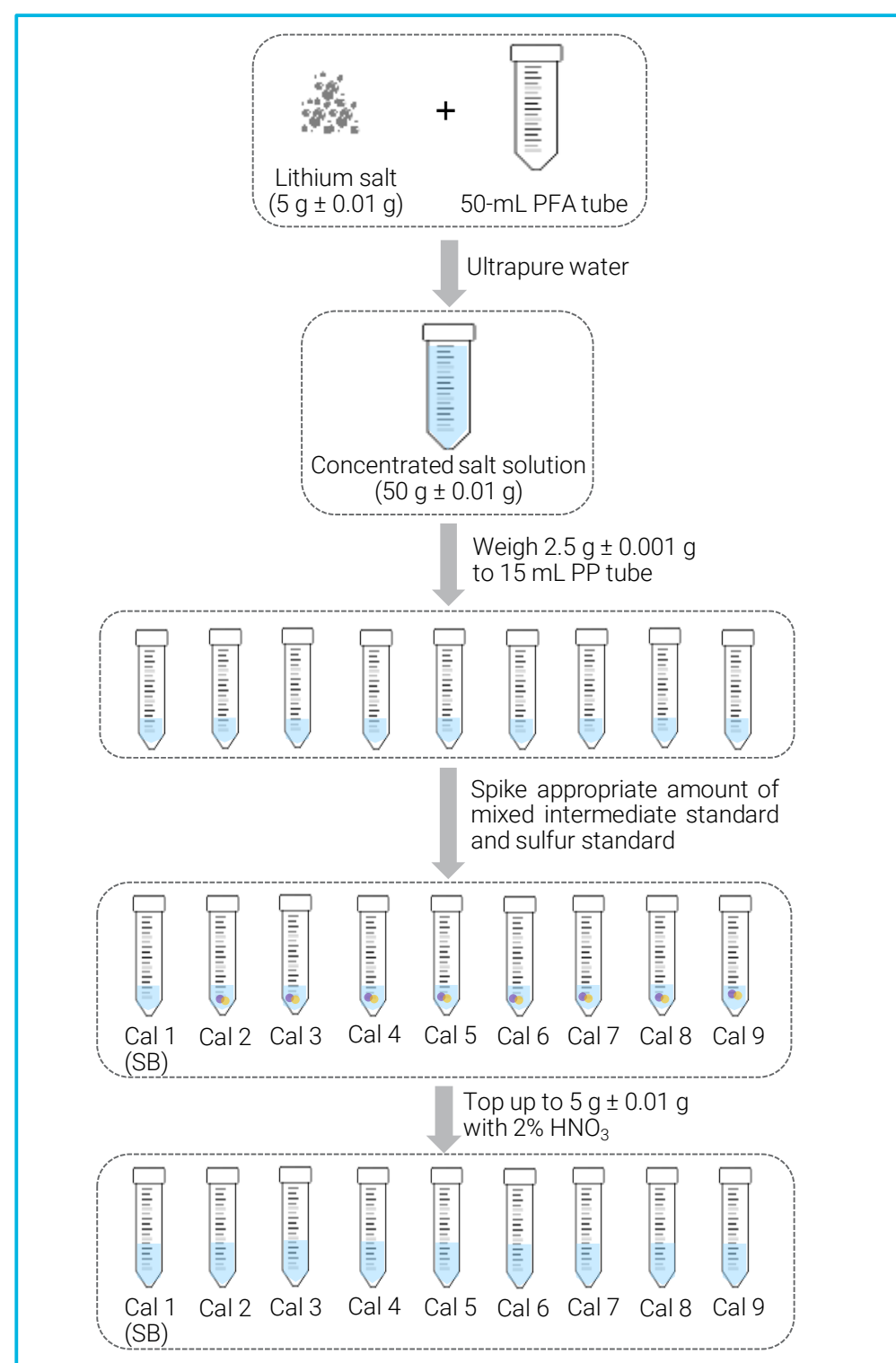


Figure 1. Sample preparation & standard addition procedure.

Experimental

Instrumentation

An Agilent 7900 ICP-MS equipped with a PFA inert sample introduction kit (p/n G4912-68000) and nebulizer (p/n G3285-80000) was used for this work. A platinum (Pt) tipped copper sampling cone (p/n G3280-67036) and Pt-tipped Ni skimmer cone (p/n G8400-67202) were used. The 7900 ICP-MS features a fourth-generation collision/reaction cell (CRC), the ORS⁴, which supports helium (He) collision mode using either standard gas flow and KED settings, or enhanced (high flow, high collision energy, HE) conditions. H₂ cell gas mode was also used to give the most effective removal of plasma-based spectral overlaps on ²⁸Si (main overlap from N₂), ⁴⁰Ca (Ar), ⁵⁶Fe (ArO), and ⁷⁸Se (Ar₂) (6).

Table 2. Agilent 7900 ICP-MS operating conditions.

Cell Mode	No Gas	He	HE He	H ₂
RF Power (W)			1550	
Sampling Depth (mm)		10		
Nebulizer Gas Flow (L/min)		1.09		
EXT 1 (V)		0		
EXT 2 (V)	-250	-245	-250	
Omega Bias (V)	-100		-120	
Omega Lens (V)	11.3	10.4	12.3	10.3
ORS Gas (mL/min)	-	4.3	9	5
Energy Discrimination (V)		5	7	3

Optimization

The 7900 ICP-MS operating conditions given in Table 2 were optimized automatically for all tune modes, using the Agilent ICP-MS MassHunter autotune function. To ensure that the best performance was achieved for the wide variety of analytes, several cell gas modes were used – switched automatically during the acquisition – as shown in Figure 2.

Helium mode, which gives universal reduction or removal of polyatomic ion overlaps, was used as the default mode for most elements, as usual for Agilent single quadrupole (SQ) ICP-MS systems. Beryllium (Be) was measured in no gas mode.

High energy (HE) He mode was used for P and S, as this mode provides better control of the interfering polyatomic ions, while also increasing the sensitivity for ³¹P and ³⁴S. P and S have traditionally been considered difficult to determine by SQ ICP-MS due to interference from intense polyatomic ions, such as NO⁺, NOH⁺, O₂⁺, O₂H⁺, and O₂H₂⁺, formed from the surrounding air and aqueous solvent (5).

Finally, H₂ mode was used for ²⁸Si, ⁴⁰Ca, ⁵⁶Fe, and ⁷⁸Se.

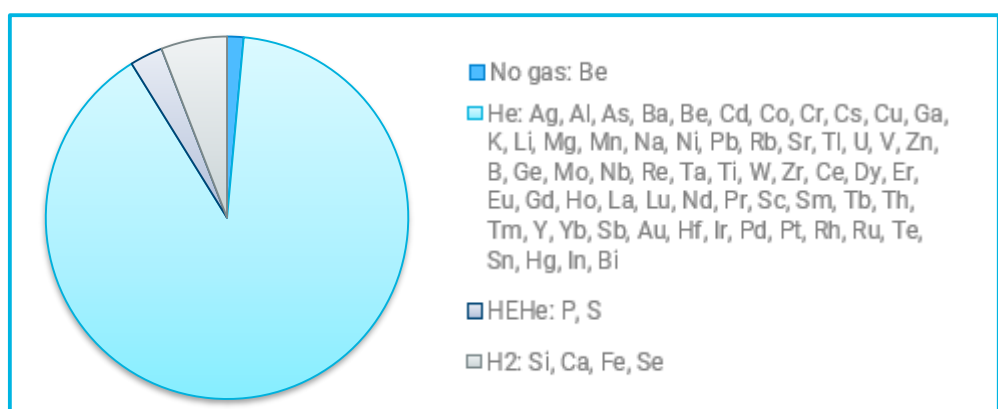


Figure 2. Cell mode used for each analyte in this study.

Results and Discussion

Standard addition calibration

In ICP-MS analysis, a sample matrix that contains a high concentration of an easily ionized element, such as Li, will cause ionization suppression of other, less easily ionized analytes (6). Optimizing for robust plasma (low CeO/Ce) conditions reduces ionization suppression (6, 7), but external calibration using simple, synthetic calibration standards is still unlikely to give accurate results in high salt samples.

One possible solution is to apply very high dilution factors to the high salt sample matrix to reduce the effect of ionization suppression. But this approach makes it more difficult to meet the required detection limits and increases the potential for errors due to contamination from the diluent.

Ionization suppression effects can be reduced by matrix-matching the standards, for example by preparing external calibration standards in a pure lithium salt matrix. An even better matrix match is obtained by using a standard addition calibration, where standards are spiked into each sample matrix. In this study, standard addition was applied for the quantitative analysis of 68 elements in four lithium salts.

Representative standard addition calibration curves for Si, Ca, Fe (all in H₂ cell gas mode), Cr, Ni, and Cu (all in He mode) in LiFSI are shown in Figure 3. These plots illustrate the low and sub-µg/kg levels measured for several critical elements in Li salt samples. Good linearity with calibration coefficients ≥ 0.999 (minimum 3 points) was achieved for all target analytes as described in detail in reference (8).

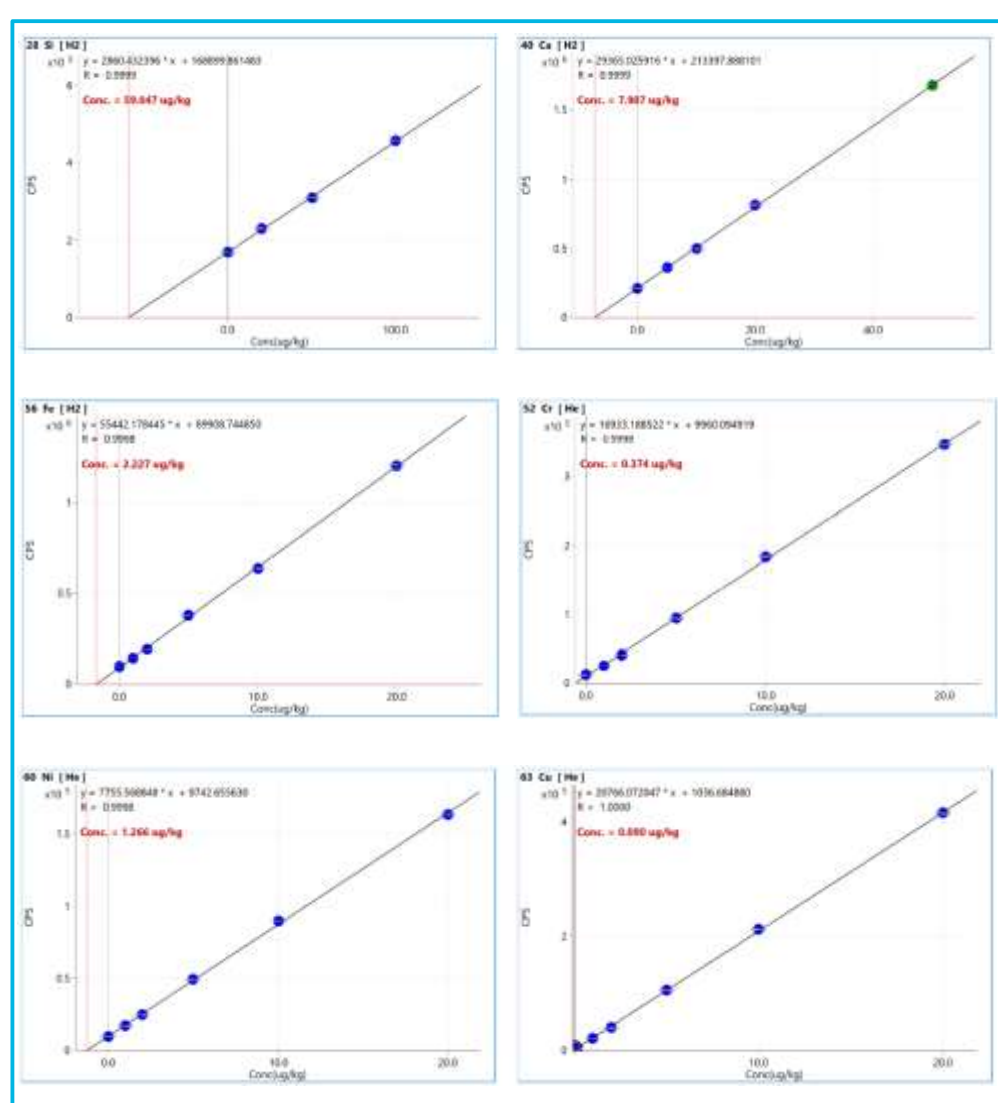


Figure 3. Representative calibration curves for Si, Ca, Fe, Cr, Ni, and Cu in LiFSI salt matrix.

Method detection limits

Method detection limits (MDLs) were determined for all analytes from 3 x the standard deviation (SD) of 11 replicate measurements of the SB for each Li salt matrix. The MDLs calculated for the diluted electrolyte solutions were multiplied by the dilution factor of 20 to give MDLs in the original solid Li salt. MDLs for all target analytes in all four lithium salts are reported in reference (8).

Sub-µg/kg detection limits were achieved for most of the trace elements, demonstrating the excellent selectivity and sensitivity of the 7900 ICP-MS for the determination of multiple elements in the high Li salt matrices. The relatively high level of some analytes in the matrix blanks increased the standard deviation, which resulted in higher MDLs for some elements.

Results and Discussion

Sample analysis and spike recovery results

The quantitative results for all 68 analytes, calibrated using standard addition and dilution corrected to give the concentrations in the original solid Li salts, are summarized in Table 3. For each Li salt, three separate aliquots were prepared and spiked to evaluate the method accuracy and precision. Full results, including spike recovery precision, are provided in reference (8).

Spike recoveries between 80 to 120% with precision (%RSD of recovery) <12% (n=3) were obtained for all analytes except B, Si, P, and S. These elements were not determined, either because they were a main component of the salt matrix (P in LiPF₆, for example), or because the native concentration in the salt matrix was too high relative to the spike levels.

Table 3. Measured concentrations and spike recoveries for 68 elements in four lithium salts.

Analyte	LiPF ₆		LiBF ₄		LiClO ₄		LiFSI	
	Measured conc. (µg/kg)	Spike recovery	Measured conc. (µg/kg)	Spike recovery	Measured conc. (µg/kg)	Spike recovery	Measured conc. (µg/kg)	Spike recovery
B	<MDL	ND ^a	<MDL	Major	<MDL	103%	<MDL	115%
Be	<MDL	ND	<MDL	Major	<MDL	103%	<MDL	115%
Bi	2247.32	103%	4267.21	90%	556.01	113%	300.77	108%
Ba	185.14	93%	293.43	99%	3894.96	114%	1519.33	107%
Bk	94.92	104%	269.32	101%	38.63	106%	47.82	107%
Br	<MDL	ND	5810.56	109%	636.93	109%	1171.70	107%
Bu	Major	Major	1812.42	103%	229.22	83%	441.95	83%
Bz	5033.49	117%	5990.05	101%	10079.49	101%	Major	Major
Ca	1764.23	82%	993.26	98%	1375.92	82%	1023.11	112%
Ca	177.41	104%	290.54	86%	228.05	114%	147.55	107%
Ca	1.23	105%	3.50	102%	0.03	102%	0.24	112%
Cl	478.35	83%	16.36	103%	5.43	103%	3.81	106%
Cl	0.43	105%	2.73	104%	2.28	99%	0.62	103%
Cl	43.19	103%	301.49	103%	252.52	103%	18.69	122%
Co	5.34	106%	33.27	103%	3.98	104%	1.75	107%
Co	113.61	115%	1583.58	84%	93.78	114%	37.18	114%
Co	0.37	102%	3.40	97%	0.20	102%	0.79	108%
Co	25.90	103%	139.66	108%	13.48	102%	25.01	108%
Cr	3.14	101%	12.71	107%	21.87	101%	2.48	109%
Cr	22.65	107%	18.14	112%	14.19	102%	32.22	108%
Cr	0.24	105%	<MDL	110%	0.18	104%	0.06	108%
Cr	<MDL	105%	<MDL	109%	<MDL	104%	<MDL	109%
Fe	2.18	103%	55.61	105%	0.23	104%	2.47	107%
Fe	<MDL	108%	<MDL	105%	<MDL	91%	0.18	110%
Fe	0.10	102%	<MDL	104%	0.13	104%	0.12	107%
Fe	0.67	103%	1.16	107%	1.54	104%	0.71	108%
Fe	0.06	100%	0.03	108%	2.79	103%	0.03	108%
Fe	1.30	100%	3.60	107%	0.07	102%	0.05	107%
Fe	6.13	100%	0.15	93%	<MDL	103%	<MDL	107%
Fe	2.44	101%	24.98	112%	1.46	103%	0.99	110%
Fe	0.21	104%	<MDL	111%	<MDL	104%	<MDL	111%
Fe	1.03	107%	0.88	112%	0.76	106%	0.24	114%
Fe	<MDL	101%	<MDL	104%	<MDL	102%	<MDL	108%
Fe	<MDL	105%	<MDL	106%	<MDL	101%	<MDL	107%
Fe	<MDL	105%	<MDL	108%	0.03	104%	<MDL	112%
Fe	1.30	102%	0.01	103%	4.74	106%	<MDL	112%
Fe	9.47	105%	1.15	111%	2.16	105%	2.24	112%
Fe	16.31	106%	0.35	99%	<MDL	106%	0.03	113%
Fe	0.19	102%	<MDL	106%	0.25	105%	<MDL	111%
Fe	0.61	98%	<MDL	102%	63.68	113%	0.02	111%
Fe	2.42	103%	162.34	105%	23.14	102%	<MDL	112%
Fe	0.02	102%	0.02	97%	0.36	105%	0.06	113%
Fe	0.03	104%	0.09	101%	3.17	106%	<MDL	115%
Fe	<MDL	103%	<MDL	100%	0.01	105%	<MDL	113%
Fe	<MDL	111%	<MDL	114%	<MDL	114%	<MDL	114%
Fe	<MDL	105%	<MDL	109%	<MDL	114%	<MDL	114%
Fe	0.62	103%	<MDL	99%	25.90	114%	<MDL	110%
Fe	0.20	108%	<MDL	108%	0.15	115%	<MDL	111%
Fe	<MDL	109%	<MDL	108%	0.12	115%	<MDL	112%
Fe	<MDL	108%	<MDL	107%	<MDL	115%	<MDL	114%
Fe	<MDL	111%	<MDL	101%	<MDL	115%	<MDL	112%
Fe	<MDL	106%	<MDL	93%	<MDL	114%	<MDL	112%
Fe	<MDL	109%	<MDL	94%	<MDL	114%	<MDL	114%
Fe	<MDL	109%	<MDL	95%	0.06	115%	<MDL	109%
Fe	<MDL	104%	<MDL	108%	0.03	115%	<MDL	114%
Fe	0.23	110%	0.11	98%	0.05	115%	<MDL	108%
Fe	1.00	115%	0.18	94%	0.12	114%	<MDL	111%
Fe	0.32	111%	0.39	101%	0.23	114%	<MDL	108%
Fe	<MDL	108%	<MDL	105%	<MDL	113%	<MDL	103%
Fe	<MDL	108%	<MDL	111%	0.04	114%	<MDL	99%
Fe	0.88	113%	20.63	109%	0.07	114%	0.34	113%
Fe	<MDL	85%	<MDL	106%	<MDL	97%	<MDL	82%
Fe	<MDL	111%	<MDL	99%	<MDL	87%	<MDL	96%
Fe	1.00	115%	0.18	94%	0.12	114%	<MDL	111%
Fe	1.13	111%	0.67	103%	0.73	113%	0.17	108%
Fe	0.04	109%	<MDL	101%	0.10	114%	<MDL	106%
Fe	0.01	110%	0.04	100%	<MDL	109%	<MDL	113%
Fe	<MDL	111%	<MDL	101%	<MDL	113%	<MDL	105%