

# The benefits of the XSeries<sup>II</sup> ICP-MS for the analysis of geological samples prepared using the lithium metaborate fusion method.

*XSeries<sup>II</sup> ICP-MS with 3<sup>rd</sup> Generation CCT<sup>ED</sup>*

## Key Words

- CCT - Kinetic Energy Discrimination (KED)
- Geochemistry
- Lithium metaborate fusion
- Multi-element analysis
- Xs- mode

## Introduction

Geochemists were amongst the first analysts to adopt ICP-MS as a routine technique due to its high sensitivity and low backgrounds for elements such as the rare earth elements. Since the beginning, geochemists have sought to improve the technique further and have adopted new technologies that lowered detection limits and broadened the range of elements that can be measured. Many geological materials are difficult to prepare into a solution and traditionally the lithium metaborate fusion technique has been used for many materials. This sample preparation technique has often presented problems for ICP-MS as the dissolved solids level is raised due to the need for ratios of 3:1-5:1 of fusion flux to sample. The fusion material can deposit on cones and lenses and cause drift in signal so high dilution factors are used which then lead to detection limit concerns for ultra-trace elements. As the flux material purity is the limiting factor for blanks the precision of measurement and therefore detection limits are influenced mainly by the sensitivity of the ICP-MS. However, the accuracy of many elements in these geological materials can be severely compromised by interferences which have traditionally been corrected using mathematical equations. This work will take the routine analytical work performed on an X7 ICP-MS at the University of Greenwich (UK) and compare the same 15 hour sample set on Thermo Electron Corporation's new XSeries<sup>II</sup> ICP-MS running in both high sensitivity mode (Xs-) and collision cell mode with energy discrimination (CCT KED).

## Methods

Samples were prepared as 0.2500 g +/- 0.0005 g sample mixed with 1.2500 g LiBO<sub>2</sub> flux, placed in a carbon crucible and fused in a muffle furnace for 20 mins at 1,000 °C. The melt was poured into 150 ml of 3.5 % Aristar grade HNO<sub>3</sub>, filtered and made to a final volume of 250 ml (1,000 fold dilution). 0.5 ml of this solution was diluted 20 fold with 2 % HNO<sub>3</sub> to give the working solution at 20,000 fold dilution in very slightly over 2 % HNO<sub>3</sub>. Common geological reference materials were prepared in the same manner as the samples. Calibration blanks and standards were prepared from stock solution using blank fusion flux at the same level as the samples for matrix matching. A calibration block was used every ten samples and throughout a run of 226 solutions the reference materials were analyzed six times. A series of separate blanks were also analyzed to determine the detection limits.

## Results

Table 1 shows the detection limit capability of the three instrument configurations. The values shown are dilution corrected back to detection limits in the solid sample. The differences in the detection limits are mainly due to the changes in sensitivity (Xs->HPI>KED) however many elements in the transition metal region are significantly better on the XSeries<sup>II</sup> due to the new ion optics design that reduces the Blank Equivalent Concentrations achievable in real world samples.

**DETECTION LIMITS BASED ON 20,000:1 DILUTION**

ANALYTE		X7 HPI	Xs- STD	Xs- KED
9Be	ug/g	0.0604	0.0213	
51V	ug/g	0.6205	0.0903	1.0180
52Cr	ug/g	0.9888	0.7049	0.5707
59Co	ug/g	0.2928	0.0130	0.2020
60Ni	ug/g	37.1432	0.9343	1.0741
65Cu	ug/g	9.2454	0.1193	0.4280
66Zn	ug/g	33.0333	0.0234	1.2076
71Ga	ug/g	0.1695	0.0068	0.0752
85Rb	ug/g	0.1086	0.0156	0.2214
88Sr	ug/g	0.6617	0.0055	1.6054
89Y	ug/g	0.2402	0.0023	0.1160
90Zr	ug/g	0.1853	0.0034	0.3547
93Nb	ug/g	0.0942	0.0071	0.0436
95Mo	ug/g	0.0944	0.0305	0.1277
118Sn	ug/g	8.5475	0.0100	0.3751
133Cs	ug/g	0.0443	0.0007	0.0194
137Ba	ug/g	0.4518	0.0089	2.1713
139La	ug/g	0.0382	0.0003	0.1658
140Ce	ug/g	0.0600	0.0007	0.1852
141Pr	ug/g	0.0068	0.0002	0.0211
146Nd	ug/g	0.0194	0.0004	0.0538
147Sm	ug/g	0.0117	0.0005	0.0284
151Eu	ug/g	0.0039	0.0003	0.0036
157Gd	ug/g	0.0147	0.0008	0.0452
159Tb	ug/g	0.0032	0.0002	0.0035
163Dy	ug/g	0.0068	0.0003	0.0089
165Ho	ug/g	0.0016	0.0002	0.0044
166Er	ug/g	0.0061	0.0002	0.0087
169Tm	ug/g	0.0005	0.0001	0.0024
172Yb	ug/g	0.0028	0.0003	0.0073
175Lu	ug/g	0.0006	0.0001	0.0017
178Hf	ug/g	0.0055	0.0003	0.0121
181Ta	ug/g	0.0025	0.0002	0.0034
205Tl	ug/g	0.0041	0.0002	0.0029
208Pb	ug/g	0.1719	0.0007	0.0964
209Bi	ug/g	0.0019	0.0003	0.2100
232Th	ug/g	0.0094	0.0002	0.0338
238U	ug/g	0.0104	0.0002	0.0958

Table 1: Detection limits for the three instrument configurations.

MODE	GRANITE AC-E				BASALT BE-N				GRANITE GS-N				MARINE SEDIMENT MAG-1				CODY SHALE SCO-1			
	Refn.	X7 HPI	Xs- STD	Xs- KED	Refn.	X7 HPI	Xs- STD	Xs- KED	Refn.	X7 HPI	Xs- STD	Xs- KED	Refn.	X7 HPI	Xs- STD	Xs- KED	Refn.	X7 HPI	Xs- STD	Xs- KED
98e ug/g	12	98.5%	105.0%		1.9	97.5%	99.6%		5.4	101.9%	102.5%		3.2	99.5%	104.1%		1.8	96.1%	96.6%	
51V ug/g	3	94.3%	189.5%	214.0%	235	100.7%	112.5%	111.9%	65	117.7%	107.4%	120.0%	140	99.4%	141.3%	140.5%	130	100.3%	96.0%	100.7%
52Cr ug/g	3.4	65.9%	60.4%	68.5%	360	97.2%	103.1%	102.2%	55	101.2%	95.5%	103.9%	97	99.3%	102.6%	105.1%	68	93.9%	89.2%	96.5%
59Co ug/g	0.2	104.9%	65.0%	113.1%	60	95.8%	98.0%	99.0%	65	100.4%	101.0%	100.8%	20	108.1%	117.7%	117.3%	11	97.4%	96.0%	97.4%
60Ni ug/g	1.5	1235.4%	52.9%	69.3%	267	100.3%	103.9%	100.9%	34	151.8%	115.7%	111.6%	53	107.4%	131.6%	127.0%	27	117.7%	94.8%	91.4%
65Cu ug/g	4	66.6%	78.2%	77.0%	72	96.7%	109.4%	96.9%	20	101.1%	115.7%	103.6%	30	99.5%	135.8%	125.4%	29	95.1%	100.9%	93.7%
66Zn ug/g	224	101.8%	94.8%	94.7%	120	120.6%	106.4%	95.9%	48	147.1%	97.5%	90.8%	130	125.6%	95.9%	90.7%	100	149.4%	95.3%	96.3%
71Ga ug/g	39	101.7%	110.4%	109.2%	17	104.8%	110.2%	156.5%	22	95.1%	98.1%	115.9%	20	112.1%	116.7%	112.0%	15	104.1%	106.7%	99.1%
85Rb ug/g	152	91.1%	98.7%	96.2%	47	98.7%	90.5%	100.3%	185	99.2%	99.8%	97.4%	150	93.1%	92.7%	90.2%	110	95.1%	93.3%	96.2%
88Sr ug/g	3	113.3%	74.8%	116.5%	1370	99.9%	101.0%	101.4%	570	96.4%	102.1%	101.3%	150	88.5%	99.1%	100.3%	170	90.1%	95.2%	94.3%
89Y ug/g	184	86.3%	93.2%	92.2%	30	91.0%	81.2%	94.7%	16	103.0%	88.8%	102.8%	28	93.4%	85.1%	97.2%	26	84.6%	75.6%	87.2%
90Zr ug/g	780	88.0%	88.1%	88.1%	260	88.8%	80.8%	80.0%	235	92.8%	87.1%	87.4%	130	89.7%	76.9%	84.9%	160	97.2%	89.4%	91.4%
93Nb ug/g	110	80.2%	84.4%	89.1%	105	89.7%	83.0%	90.0%	21	99.5%	86.1%	102.4%	12	116.6%	100.2%	119.1%	11	88.9%	73.3%	87.4%
95Mo ug/g	2.5	104.7%	97.4%	94.6%	2.8	102.6%	123.9%	124.3%	1.2	134.1%	110.5%	108.7%	1.6	96.9%	120.0%	119.2%	1.4	120.9%	102.7%	103.6%
118Sn ug/g	13	103.3%	89.1%	92.5%	2	57.7%	22.3%	33.5%	3	84.2%	55.5%	61.0%	3.6	68.8%	35.1%	41.1%	3.7	69.2%	38.0%	46.4%
133Cs ug/g	3	88.4%	88.2%	88.0%	0.8	93.6%	83.7%	89.0%	5.4	100.2%	94.8%	94.5%	8.6	77.8%	69.2%	68.0%	7.8	88.9%	88.4%	88.2%
137Ba ug/g	55	110.3%	70.8%	92.3%	1025	97.0%	97.4%	97.6%	1400	99.0%	98.8%	98.4%	480	99.9%	98.8%	104.7%	570	96.6%	97.8%	98.2%
139La ug/g	59	100.8%	98.1%	103.8%	82	103.2%	101.0%	100.0%	75	106.2%	102.4%	101.6%	43	106.7%	114.2%	121.5%	30	105.6%	93.5%	106.3%
140Ce ug/g	154	95.8%	104.4%	103.1%	152	99.8%	102.7%	101.8%	135	103.5%	104.7%	104.4%	88	99.9%	106.8%	105.8%	62	89.5%	90.1%	92.9%
141Pr ug/g	22.2	93.6%	88.5%	99.6%	17.5	99.9%	88.0%	100.8%	14.5	105.5%	92.1%	104.6%					6.6	104.7%	93.8%	106.8%
146Nd ug/g	92	94.4%	99.3%	100.1%	67	98.8%	97.2%	99.1%	49	104.4%	101.8%	103.4%	38	102.7%	105.0%	106.1%	25.9	98.8%	99.1%	100.0%
147Sm ug/g	24.2	95.5%	103.2%	102.7%	12.2	98.7%	100.9%	100.2%	7.5	101.8%	102.0%	101.5%	7.5	98.9%	103.2%	103.7%	5.3	93.0%	95.3%	94.7%
151Eu ug/g	2	95.3%	102.7%	102.7%	3.6	106.1%	108.8%	108.5%	1.7	101.6%	101.1%	100.5%	1.6	97.2%	100.0%	98.9%	1.19	94.6%	96.9%	95.2%
157Gd ug/g	26	90.2%	89.7%	98.8%	9.7	102.9%	100.0%	103.0%	5.2	106.4%	105.5%	102.8%	5.8	109.2%	113.2%	117.4%	4.6	96.4%	94.1%	100.0%
159Tb ug/g	4.8	91.0%	97.6%	96.3%	1.3	98.0%	102.8%	98.3%	0.6	109.4%	110.8%	106.0%	0.96	95.6%	101.1%	97.9%	0.7	94.7%	97.1%	95.5%
163Dy ug/g	29	97.6%	104.4%	102.7%	6.4	99.0%	102.7%	101.6%	3.1	107.6%	106.3%	106.0%	5.2	102.0%	105.0%	103.8%	4.2	93.7%	96.4%	96.6%
165Ho ug/g	6.5	89.1%	95.3%	94.7%	1.1	97.4%	100.7%	100.7%	0.6	100.9%	98.8%	99.6%	1	103.1%	104.3%	104.0%	0.97	83.0%	83.6%	83.6%
166Er ug/g	17.7	95.4%	100.9%	100.4%	2.5	103.0%	108.1%	104.6%	1.5	110.9%	111.0%	108.2%	3	95.9%	97.9%	96.5%	2.5	93.1%	94.8%	93.9%
169Tm ug/g	2.6	96.6%	102.9%	102.4%	0.34	92.5%	96.9%	96.5%	0.22	104.6%	104.8%	106.2%	0.43	95.8%	96.0%	95.5%	0.42	81.7%	82.1%	83.6%
172Yb ug/g	17.4	93.4%	99.1%	98.1%	1.8	101.0%	104.4%	102.3%	1.4	108.3%	107.7%	107.6%	2.6	101.9%	103.7%	102.2%	2.27	99.9%	102.2%	103.1%
175Lu ug/g	2.45	92.6%	98.6%	97.6%	0.24	102.9%	110.8%	110.2%	0.22	103.6%	103.0%	103.1%	0.4	97.9%	99.7%	98.1%	0.338	100.7%	103.3%	103.4%
178Hf ug/g	27.9	74.4%	76.3%	76.3%	5.6	77.6%	72.4%	71.5%	6.2	88.2%	83.2%	83.6%	3.7	83.3%	79.2%	79.5%	4.6	81.7%	78.7%	78.7%
181Ta ug/g	6.4	89.5%	92.5%	91.7%	5.7	90.1%	92.9%	92.6%	2.6	93.9%	86.7%	86.6%	1.1	98.6%	97.9%	97.8%	0.92	82.6%	76.9%	76.9%
205Tl ug/g	0.9	23.2%	30.9%	31.1%	0.04	38.0%	100.1%	99.1%									0.72	28.1%	28.7%	28.9%
208Pb ug/g	39	56.7%	37.7%	39.0%	4	118.0%	50.9%	55.8%	53	62.1%	42.1%	43.9%	24	47.8%	12.8%	13.6%	31	68.7%	45.0%	46.7%
209Bi ug/g	0.4	6.8%	-3.4%	6.7%					0.18	17.4%	14.0%	28.5%	0.34	4.4%	-5.7%	1.8%	0.37	24.4%	4.3%	9.4%
232Th ug/g	18.5	90.3%	87.1%	94.2%	10.4	98.7%	90.2%	98.8%	41	100.5%	92.2%	99.5%	12	100.0%	94.4%	102.4%	9.7	90.9%	85.6%	93.0%
238U ug/g	4.6	91.5%	94.0%	94.0%	2.4	103.2%	98.6%	98.2%	7.5	106.2%	109.9%	106.7%	2.7	107.0%	109.8%	107.6%				

Table 2: Recoveries of 5 geological reference materials for the 3 X Series ICP-MS configurations

Table 2 shows the recoveries for five different reference materials using the three different instrument configurations; X7 HPI as used at the University of Greenwich, the XSeries<sup>II</sup> with high sensitivity Xs- mode and XSeries<sup>III</sup> with Xs- and energy discrimination CCT. The data shows that for most elements the recovery in these materials is good with all three analysis methods, although improvements can still be seen with the XSeries<sup>III</sup> for elements like nickel and zinc.

On first examination of the reference materials, it appears that the collision cell produced little benefit over analysis without the cell. A classic interference in geological samples is the problem of BaO causing inaccuracy on the analysis of <sup>151</sup>Eu. This is typically corrected mathematically and Table 3 shows the results for the reference material with the highest Ba content. The agreement between measuring with or without a correction equation and with the CCT is within the error of the measurements, although this can mask the true situation where the barium content of geological samples can be much higher. From the other measurements during this 15 hour run, the data from

samples with barium concentrations of more than 6,000 ug/g were extracted to check for inconsistencies. For uncorrected data, as the barium concentration increases the apparent <sup>151</sup>Eu concentration should also increase meaning that a plot of [Ba] vs. [uncorrected <sup>151</sup>Eu]/[corrected Eu] should be linear with the slope being proportional to the level of the interference of BaO. By comparing the plots for mathematical correction and CCT KED correction, if the correction factor is accurate the slopes should be the same. The correlation coefficients for the two regression lines will show the precision of the correction; the better the correlation coefficient, the more robust is the correction mechanism. Figure 1 shows the plots for mathematical and CCT correction. It should be noted that the mathematical correction was applied to the same data as used for the uncorrected data points, whereas the CCT data was from a different analysis so the higher correlation coefficient for the CCT correction is further proof that interference removal is preferable to interference correction.

MATERIAL	GRANITE GS-N (ug/g)				
ELEMENT	BARIUM		EUROPIUM		
INSTRUMENT	X SERIES	X SERIES	X SERIES	X SERIESII	X SERIESII
CORRECTION	NONE	EQUATION	NONE	EQUATION	ENERGY DISCRIM. CCT
Analysis 1	1426	1.851	1.875	1.742	1.695
Analysis 2	1386	1.716	1.738	1.745	1.684
Analysis 3	1355	1.643	1.665	1.7	1.725
Analysis 4	1373	1.719	1.741	1.658	1.744
Analysis 5	1378	1.73	1.752	1.731	1.672
Analysis 6	1401	1.703	1.726	1.735	1.733
Reference	1400	1.7	1.7	1.7	1.7
Mean	1386.5	1.727	1.750	1.719	1.709
%RSD	1.77%	3.94%	3.93%	1.96%	1.71%

Table 3: Comparison of correction techniques for the BaO interference on <sup>151</sup>Eu

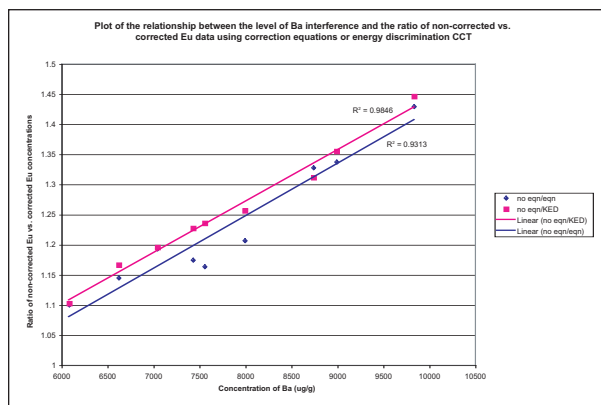


Figure 1: Graph showing the improved correlation of data corrected by CCT compared to mathematical correction.

The issue of instrument drift whilst running lithium metaborate samples was also examined and Figure 2 shows the response of the <sup>103</sup>Rh internal standard in each sample over the 15 hour run for the X7 at the University of Greenwich and both modes of the XSeries<sup>II</sup>. No drift in the signal was seen and the variability of the recovery was <10 % from sample to blank.

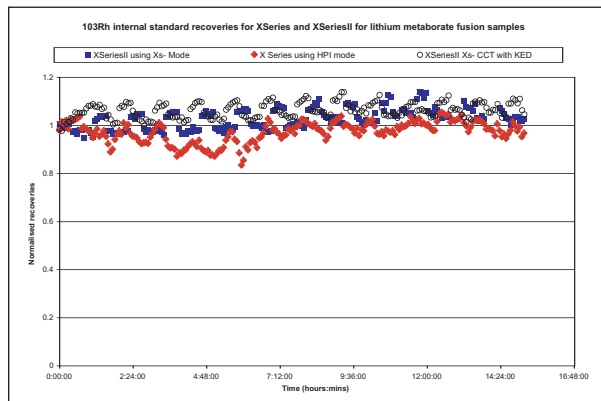
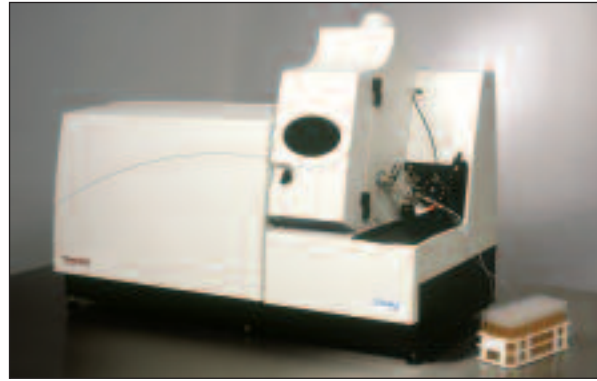


Figure 2: Internal standard drift over 15 hours for the 3 X Series ICP-MS configurations.

## Conclusion

This work has shown that the XSeries<sup>II</sup> is an excellent instrument for routine analysis of lithium metaborate fusion samples, exhibiting better detection limits with the same high stability of the X7 that is used throughout the geochemistry community. This study has also shown the benefits of energy discrimination CCT as a more robust interference correction technique compared to mathematical equations.



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