

Exploration with LA-ICP-MS

Know Your Dirt

Current Situation

Following receipt of the sample by the laboratory a portion of the sample is typically fused with Li-metaborate into a glass bead with subsequent XRF analysis to determine the major elemental composition of the sample.

Simultaneous to the above process, a second portion of the sample is subject to time consuming and hazardous sample preparation, to enable presentation to the ICP-MS instrument for trace elemental determination. For instance, samples are often digested in hazardous acids for periods in excess of 12 hours. To exacerbate this, multiple digestions with different acid recipes are often required in order to determine a complete elemental suite. Such processes greatly inhibit time to result and ultimately throughput.

In this way, XRF and ICP-MS analysis are often considered to be “complimentary techniques” for elemental analysis in the mineral exploration industry. However, the acid digestion step can be considered an Achilles heel if quick time to result and high sample throughput is the goal. Further, the financial, safety and environmental implications that arise from the use of acids in such process are a real concern for the mineral exploration industry.

Solution

Elemental Scientific’s laser ablation instrumentation can be easily integrated with the ICP-MS instrument and employed to enable direct sampling of the XRF bead. In this way, the requirement to perform lengthy acid digestions is completely removed, with LA-ICP-MS providing the complete elemental suite in a single analysis. Figures of merit are comparable or better than the traditional ICP-MS approach since a larger volume of the sample can be utilized, significantly improving sampling statistics. By removing the acid digestion step, time to result is dramatically reduced. When combined with Elemental Scientific’s unique automation solution, sample throughput can be as high as 1000 samples per day.



Introduction

Mining operations rely on fast turnaround of precise and accurate analysis of rock and soil sampled from the field. A large mine can supply up to 10,000 samples to the analytical services per month, each requiring extensive sample preparation for analysis by XRF (for composition analysis) and solution/digestion ICP-MS (for trace elements). The latter is typically performed by various wet chemical digestion techniques, which have significant time, cost, disposal, environmental and health-and-safety considerations.

Elemental Scientific has pioneered methodology and instrumentation for analysis of XRF discs by laser ablation ICP-MS in order to eliminate solution-digestion sample preparation and its associated costs and risks from the current workflow. Furthermore, XRF discs are highly stable long term and can be recalled for repeat analysis without the need for specialist storage.

The LA-ICP-MS methodology represents improvement in cost, manpower, throughput and risk when compared to solution ICP-MS analysis.

Methods

LA-ICP-MS was used to directly analyze Li-metaborate XRF discs to determine the concentration of trace elements in samples from the mining industry. The discs have already been produced for pre-analysis by XRF and provide a homogeneous solid matrix that can be easily and reproducibly ablated. The work flow shown in Figure 1 shows the simplified process, relative to solution ICP-MS.

17 fused discs were provided by Bureau Veritas Minerals. The samples were already characterized by solution ICP-MS methodology and represented a range of concentrations of all elements. 7 discs were selected as standards while the remaining 10 samples were treated as “unknowns.” All 17 discs were placed into the ablation chamber of a NWR213 laser ablation system which was connected to a quadrupole ICP-MS instrument running in standard mode. Three replicate line scans were placed on each sample with a scan time of 90 seconds per replicate. Key instrumental parameters are shown in Table 1. The data was acquired for 25 m/z, plus ⁶Li for internal standardization against the Li-metaborate matrix.

LA System	NWR213
Ablation Cell	TwoVol
Fluence	10 J/cm ²
Spot size	100µm
Scan speed	100µm/s
Scan length	8 mm
Repetition rate	20 Hz
Replicates	3
He gas flow rate	0.9 L/min
ICP-MS	Quadrupole ICP-MS
Forward Power	1400 W
Ar gas flow rate	0.95 L/min
Dwell time/m/z	0.01-0.1 s

Table 1. Instrumental settings for LA-ICP-MS analysis of Li-metaborate XRF discs.

Comparative workflows for solution ICP-MS analysis of mining samples and laser ablation ICP-MS

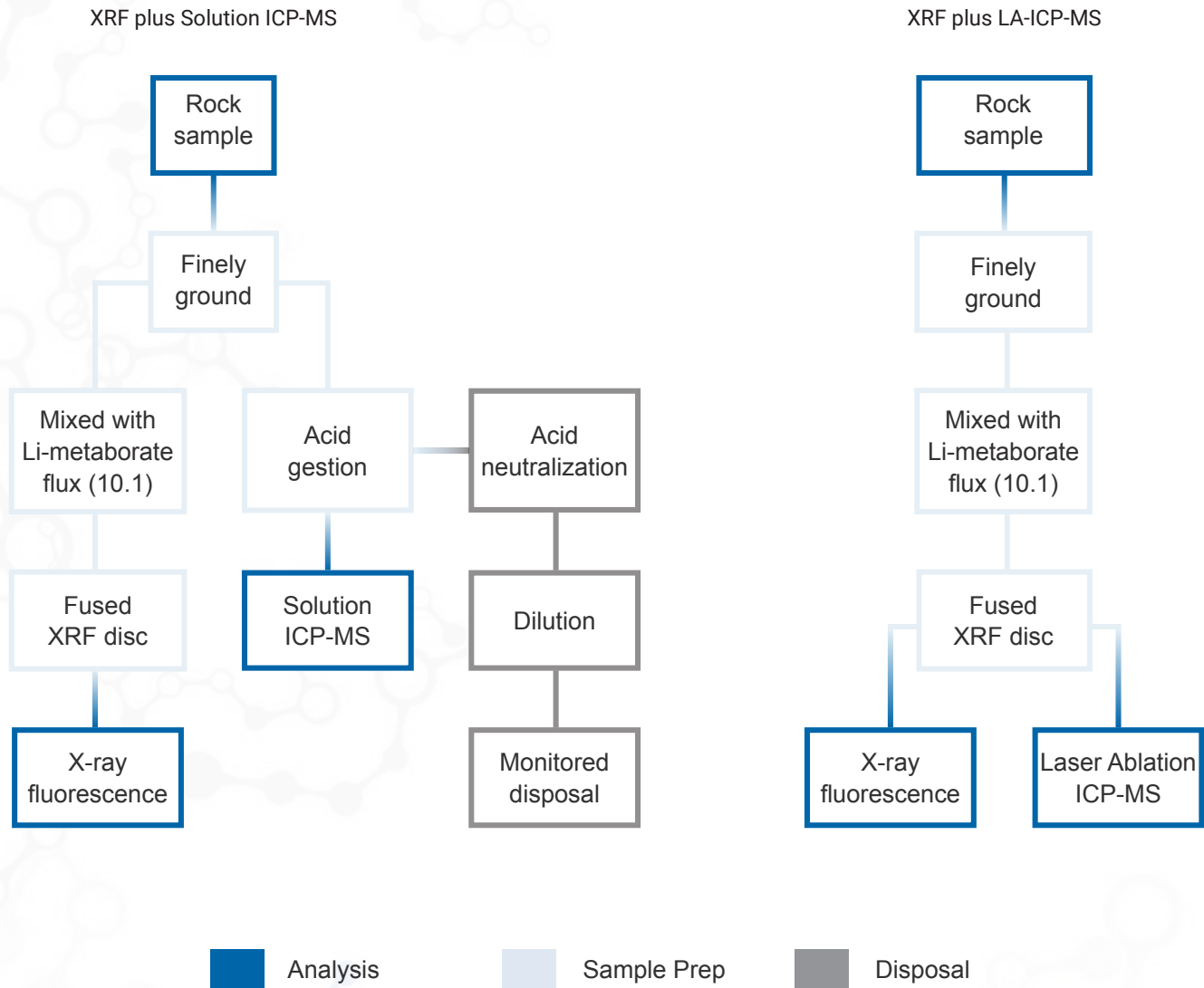
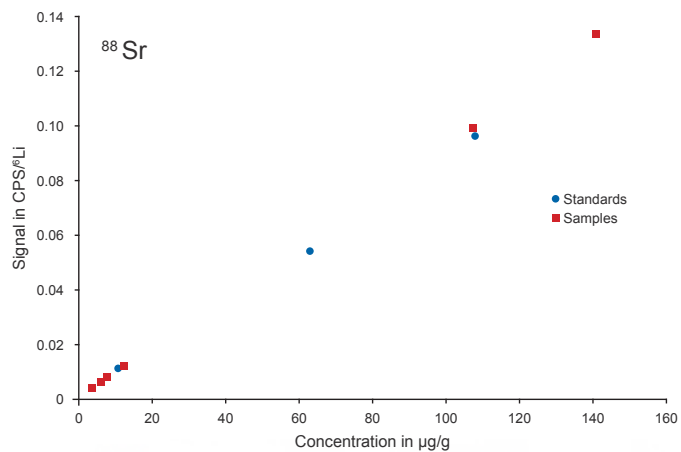
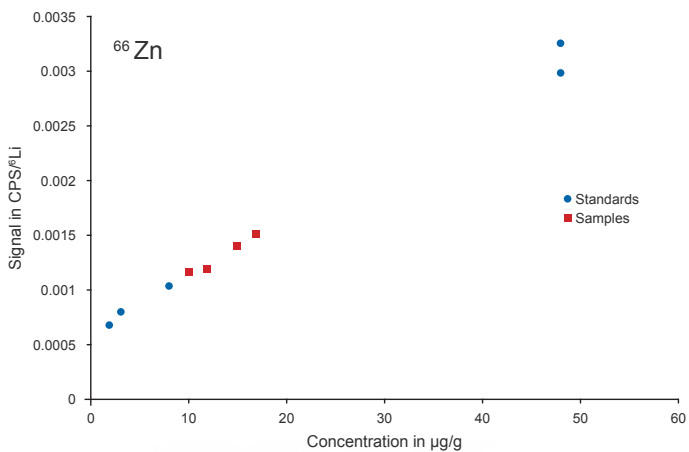
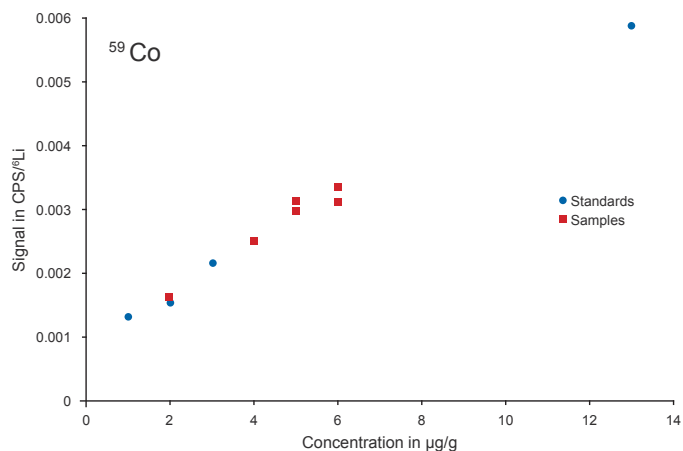
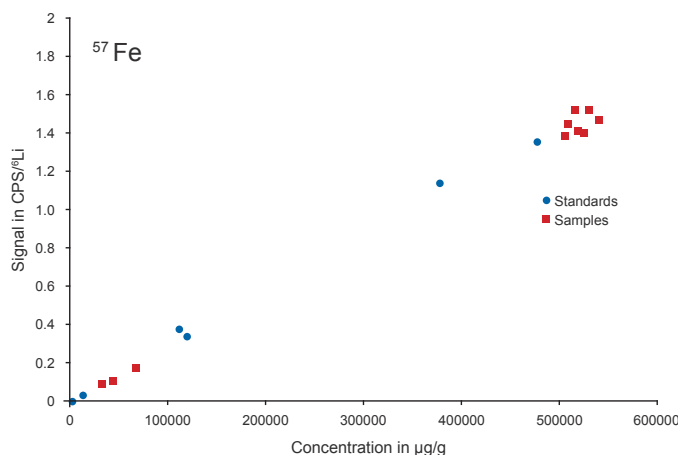
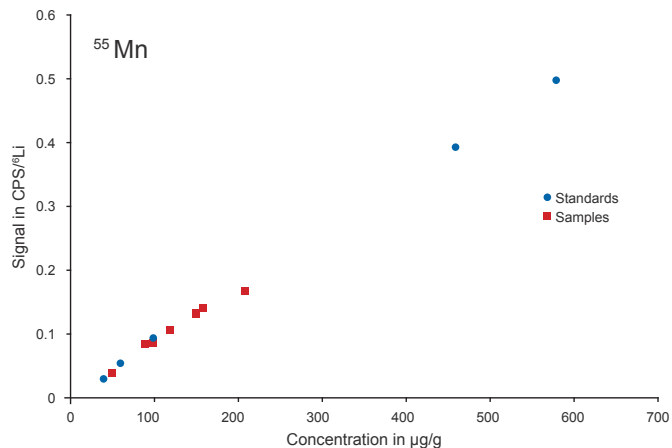
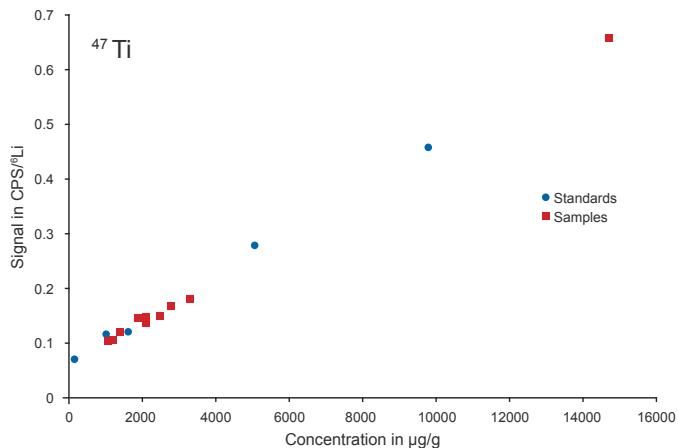


Figure 1. Compares the work flows for the solution-digestion method and the new LA-ICP-MS method. The method completely removes an entire sample preparation stream, thereby saving consumables, reducing man hours per sample and improving environmental credentials for the analysis.

Typical calibration plots showing standards (blue) and samples (red) for selected elements



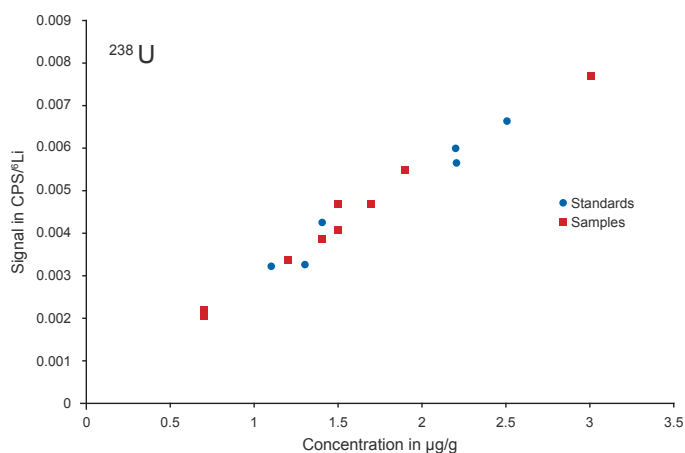
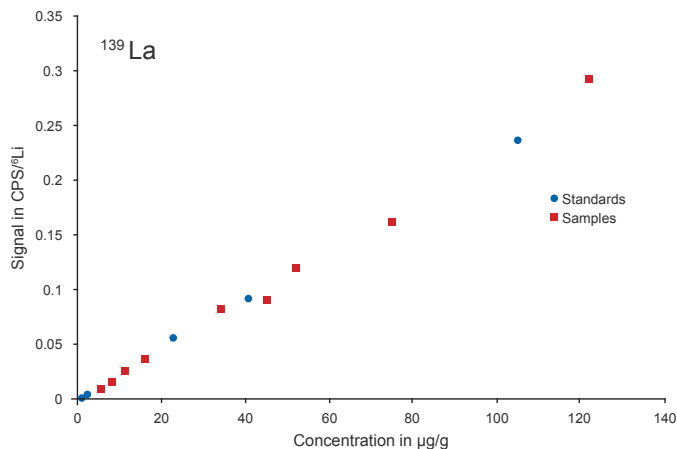
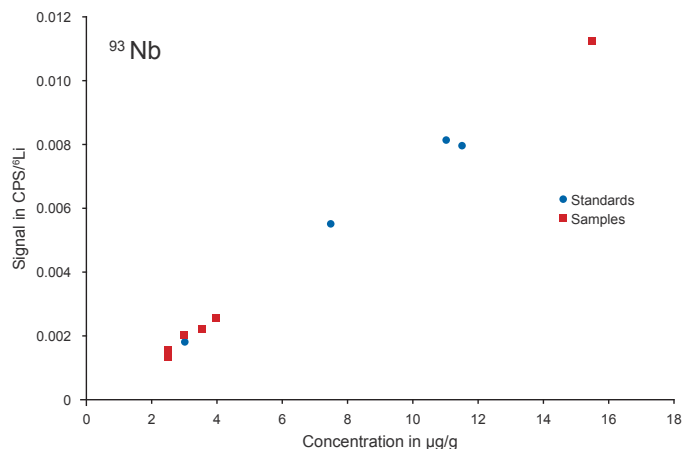


Figure 2. Shows the linear calibrations that can be achieved using the LA-ICP-MS technique. The blue markers represent the calibration standards, while the red markers are unknown samples where the determined concentration has been plotted against the predetermined value from solution ICP-MS. Where a predetermined value was not provided the data has not been plotted. The majority of calibration plots have coefficients of correlation >0.95.

Results

Results for all elements in the 10 unknown samples are summarized in Tables 2 and 3, and include absolute concentration in the original mineral, percentage recovery and limits of detection and quantization. Limits of detection typically range from <10 ng/g to 2 μg/g for non-matrix elements, and percentage recoveries are typically ±10%.

Table 2. Full results for multi-element determination of unknown samples. Concentrations are presented as in the original rock samples, not the XRF discs. Actual analytical sensitivity is approximately 10-fold greater due to dilution in Li-metaborate flux. Elements where no true value was supplied have been marked “-”.

Unknown Sample Concentration µg/g

Sample ID	⁹ Be	²³ Na	²⁴ Mg	²⁹ Si	³⁹ K	⁴³ Ca	⁴⁵ Sc	⁴⁷ Ti	⁵¹ V	⁵⁵ Mn	⁵⁷ Fe
20	<LLOQ	884	49259	275171	3169	65445	7.12	2557	57.6	95.3	29794
25	<LLOQ	953	43834	237666	2672	78582	7.31	2820	61.3	-	36682
218	2.70	251	1067	26363	168	<LLOQ	6.92	1757	72.2	94.2	475104
221	2.30	343	1334	39522	168	<LLOQ	7.21	1986	68.4	153.0	521595
224	1.69	251	1059	34876	124	<LLOQ	6.04	896	75.5	92.9	481436
232	1.48	223	1544	51003	105	<LLOQ	<LLOQ	1379	39.8	121	496378
236	1.88	152	1352	36118	107	<LLOQ	12.70	1010	48.7	160	483114
257	1.10	375	1361	39011	204	<LLOQ	<LLOQ	2055	41.6	149	521167
347	5.30	128	1288	50644	178	<LLOQ	<LLOQ	2091	68.0	193	503731
359	1.66	182	6594	329831	358	<LLOQ	10.50	14577	56.9	41.7	58217
LOD µg/g	1.28	17.60	2.96	2024	22.90	1547	1.49	50.6	1.13	1.92	887
LLoQ µg/g	4.26	58.70	9.85	6746	76.30	5156	4.98	169	3.77	6.41	2955

Sample ID	⁵⁹ Co	⁶³ Cu	⁶⁶ Zn	⁶⁹ Ga	⁸⁸ Sr	⁹⁰ Zr	⁹³ Nb	¹³⁸ Ba	¹³⁹ La	¹⁴⁰ Ce	¹⁴¹ Pr
20	5.12	-	15.2	11.50	152	54.6	3.20	171	4.77	8.88	1.06
25	5.60	21.10	17.4	10.60	113	69.7	3.87	197	7.14	14.1	1.80
218	4.00	13.50	11.1	4.95	3.48	57.1	3.36	8.22	11.4	14.7	1.88
221	5.77	11.70	10.7	4.49	4.29	66.4	3.21	12.2	16.3	19.2	2.14
224	6.27	10.30	<LLOQ	3.35	7.65	52.9	2.15	11.8	71.4	69.6	6.64
232	5.48	7.09	<LLOQ	<LLOQ	12.7	65.8	2.53	8.06	128.9	120	10.5
236	5.74	9.68	<LLOQ	2.51	7.03	82.9	2.28	<LLOQ	52.7	52.0	4.64
257	4.09	-	<LLOQ	<LLOQ	6.23	80.1	3.19	7.54	36.2	31.0	2.81
347	-	<LLOQ	<LLOQ	<LLOQ	5.98	50.2	3.09	22.3	10.3	22.1	3.49
359	<LLOQ	10.30	<LLOQ	19.80	13.1	198	15.5	27.9	40.1	71.0	7.26
LOD µg/g	0.64	1.56	2.27	1.47	0.39	0.27	0.16	0.26	0.02	0.14	0.02
LLoQ µg/g	2.12	5.19	7.55	4.90	1.31	0.89	0.54	0.85	0.08	0.48	0.07

Sample ID	¹⁴² Nd	¹⁵² Sm	¹⁵³ Eu	¹⁵⁸ Gd	¹⁵⁹ Tb	¹⁶⁴ Dy	¹⁶⁵ Ho	¹⁶⁶ Er	¹⁷⁴ Yb	¹⁷⁵ Lu	²⁰⁸ Pb	²³² Th	²³⁸ U
20	3.42	0.81	0.18	0.79	0.09	0.72	0.15	0.46	0.53	0.08	8.69	3.60	2.95
25	5.15	1.34	0.28	1.17	0.16	0.99	0.21	0.61	0.65	0.10	6.84	4.89	1.73
218	5.47	2.14	0.66	2.24	0.43	2.56	0.51	1.62	1.63	0.25	4.77	5.28	2.06
221	6.25	2.09	0.62	2.28	0.39	2.44	0.50	1.53	1.55	0.26	4.58	5.35	1.72
224	15.6	2.06	0.61	2.15	0.33	2.04	0.40	1.24	1.25	0.19	10.80	5.54	1.39
232	24.1	2.80	0.78	2.68	0.40	2.33	0.50	1.54	1.36	0.24	19.50	9.50	0.66
236	12.2	2.46	0.76	2.58	0.42	2.59	0.55	1.56	1.57	0.28	9.17	8.39	1.19
257	8.34	2.25	0.73	2.63	0.40	2.46	0.50	1.49	1.41	0.24	3.62	12.40	0.71
347	8.68	2.53	0.83	3.17	0.51	3.43	0.74	2.13	1.77	0.30	11.80	2.97	1.48
359	18.4	3.10	1.00	2.99	0.49	3.12	0.75	-	-	-	14.70	13.00	-
LOD µg/g	0.02	0.04	0.01	0.04	0.02	0.02	0.01	0.03	0.02	0.01	0.43	0.01	0.01
LLoQ µg/g	0.07	0.13	0.05	0.14	0.05	0.05	0.03	0.11	0.07	0.01	1.44	0.01	0.02

Table 3. Percentage recovery of unknown samples.

Achieved Recovery %

Sample ID	⁹ Be	²³ Na	²⁴ Mg	²⁹ Si	³⁹ K	⁴³ Ca	⁴⁵ Sc	⁴⁷ Ti	⁵¹ V	⁵⁵ Mn	⁵⁷ Fe
20	<LLOQ	103%	16%	99%	91%	98%	89%	93%	78%	95%	88%
25	<LLOQ	108%	111%	91%	88%	95%	91%	85%	75%	-	82%
218	104%	119%	89%	82%	211%	<LLOQ	87%	84%	93%	105%	94%
221	100%	122%	95%	94%	168%	<LLOQ	90%	106%	107%	102%	101%
224	85%	104%	81%	85%	124%	<LLOQ	76%	86%	92%	103%	92%
232	123%	80%	97%	96%	17%	<LLOQ	<LLOQ	99%	110%	101%	98%
236	134%	69%	90%	80%	119%	<LLOQ	127%	83%	94%	100%	93%
257	100%	125%	91%	91%	204%	<LLOQ	<LLOQ	99%	104%	99%	98%
347	93%	116%	92%	86%	162%	<LLOQ	<LLOQ	84%	95%	92%	93%
359	127%	53%	103%	104%	75%	<LLOQ	132%	99%	105%	83%	85%

Sample ID	⁵⁹ Co	⁶³ Cu	⁶⁶ Zn	⁶⁹ Ga	⁸⁸ Sr	⁹⁰ Zr	⁹³ Nb	¹³⁸ Ba	¹³⁹ La	¹⁴⁰ Ce	¹⁴¹ Pr
20	102%	-	101%	156%	108%	152%	107%	111%	87%	99%	97%
25	93%	117%	102%	133%	105%	188%	97%	104%	87%	99%	88%
218	100%	112%	9%	60%	99%	92%	96%	91%	99%	100%	100%
221	115%	117%	107%	75%	107%	105%	107%	110%	101%	106%	106%
224	105%	86%	<LLOQ	58%	96%	80%	86%	107%	95%	95%	92%
232	110%	118%	<LLOQ	<LLOQ	106%	89%	101%	101%	106%	103%	103%
236	115%	81%	<LLOQ	50%	94%	87%	91%	<LLOQ	101%	98%	96%
257	102%	-	<LLOQ	<LLOQ	104%	97%	106%	84%	106%	104%	104%
347	-	<LLOQ	<LLOQ	<LLOQ	100%	111%	103%	101%	95%	97%	99%
359	<LLOQ	129%	<LLOQ	117%	101%	114%	100%	93%	88%	93%	87%

Sample ID	¹⁴² Nd	¹⁵² Sm	¹⁵³ Eu	¹⁵⁸ Gd	¹⁵⁹ Tb	¹⁶⁴ Dy	¹⁶⁵ Ho	¹⁶⁶ Er	¹⁷⁴ Yb	¹⁷⁵ Lu	²⁰⁸ Pb	²³² Th	²³⁸ U
20	90%	90%	117%	98%	77%	103%	108%	91%	118%	104%	87%	100%	98%
25	70%	92%	80%	84%	78%	95%	106%	101%	108%	99%	98%	106%	102%
218	74%	95%	102%	93%	102%	75%	92%	92%	96%	90%	159%	112%	8%
221	88%	102%	103%	114%	102%	99%	96%	99%	100%	101%	153%	119%	115%
224	94%	86%	87%	90%	88%	83%	80%	86%	83%	89%	108%	101%	99%
232	115%	95%	91%	96%	95%	91%	96%	99%	88%	92%	115%	112%	94%
236	95%	88%	90%	86%	84%	82%	86%	84%	85%	99%	102%	110%	99%
257	98%	94%	104%	101%	96%	91%	89%	93%	97%	100%	91%	109%	102%
347	62%	92%	104%	99%	111%	111%	106%	104%	101%	107%	118%	110%	99%
359	69%	84%	100%	115%	137%	152%	107%	-	-	-	98%	97%	-

Conclusions

Laser ablation ICP-MS has been demonstrated to be a viable alternative to solution-digestion methodology, having both the sensitivity and accuracy required to give fit for purpose data to clients in the mining industry.

The direct analysis of Li-metaborate XRF discs significantly reduces sample preparation time and provides a matrix which is 90% consistent from sample to sample, thereby reducing matrix-related variation in results, and also gives a useful internal standard in ${}^6\text{Li}$, which can be used to correct for variations in volumetric ablation. The XRF discs are highly stable long term, thereby facilitating repeat analysis without the need to perform a new sample digestion.

The laser ablation methodology offers cost, health and safety, time and environmental benefits and can result in all analysis being performed in a dry-only laboratory, thereby saving thousands of liters of acid, water and neutralization agents as well as reducing regulatory red tape associated with disposal.

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