Automated Multielement Analysis of Large Batches

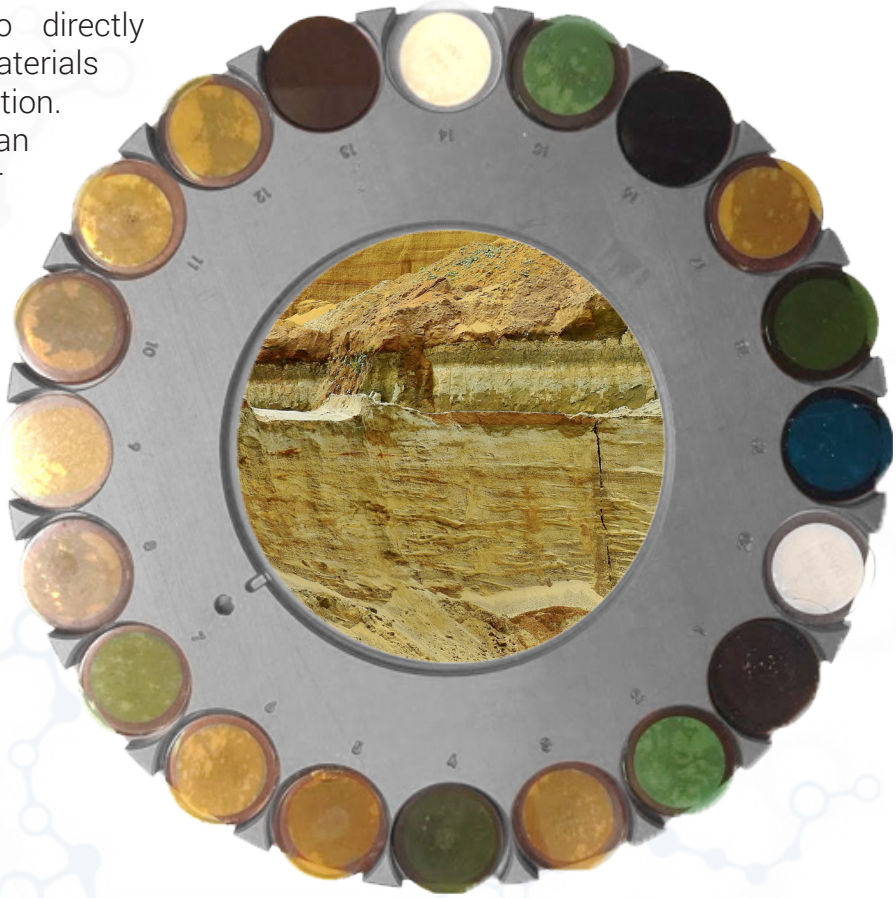
of Li-metaborate Fusion Beads Using SolidSample ICPMS

Introduction

Fusion beads are common in the analytical workflow due to their excellence for determination of major elements via X-ray fluorescence (XRF). The fusion sample preparation process creates a near-homogenous sample with almost identical matrix from one sample to the next, while eliminating effects from varying particulate size.

Unfortunately, XRF does not have the desired sensitivity or analyte range to satisfy the needs of many analytical scenarios and secondary analysis needs to be performed by another technique, most commonly solution/digestion ICPMS. Solution ICPMS necessitates one or more sample digestion protocols – including aquaregia hotblock digestion, HF microwave-assisted digestion, and fusion bead digestion – depending on which target elements are of interest to the customer.

SolidSample ICPMS from Elemental Scientific Lasers (ESL) is designed to directly determine elements in solid materials with minimal sample preparation. Li-metaborate fused beads can be analyzed with no further sample preparation steps following XRF, thereby merging the workflow of the two techniques seamlessly. Additionally, the absence of water required as a solvent and various acids (e.g. HNO_3, H_2SO_4 and HCl) typically used in solution/digestion ICPMS greatly simplifies the mass spectrum.



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SolidSample ICPMS

SolidSample ICPMS is a next-generation, single-unit instrument that fully automates the process of sample handling, laser sampling, ICPMS detection, data reduction and report generation. SolidSample ICPMS is suitable for medium throughput (>50 samples per day) up to high throughput (>1000 samples per day) solid sampling.

Some geological samples, such as quartz, can be difficult to acid digest for elemental determination. SolidSample ICPMS does not require acid digestion, and additionally, the absence of water required as a solvent, and various acids (e.g. HNO_3, H_2SO_4 and HCl) typically used in solution/digestion ICPMS greatly simplifies the mass spectrum.

SolidSample ICPMS does not require any sample preparation with acids, heat-digestion or microwave digestion as the solid sample is analyzed directly. SolidSample ICPMS is ideally suited for analyses of Li-tetraborate beads since they require zero additional sample preparation before analysis.

Method

Approximately 1000 rock core samples for mining discovery were sampled in the field in Western Australia and transported to Bureau Veritas' analytical facility in Perth, WA. Up to 2 kg of each sample was pulverized so that 90% passed a 75 µm mesh. It was then homogenized before 0.7 g was removed, mixed with 7 g of Li-tetraborate/metaborate blended flux and fused at 1100 ˚C for 10 minutes. The molten flux was poured into a platinum mold and allowed to cool for 30 minutes. The process was repeated for a number of certified reference materials and a bead blank containing no sample.

Each sample and standard bead was first analyzed by EDXRF before being dispatched to Elemental Scientific (Omaha, NE, USA). In addition, QC standard beads were produced by mixing reference standards and fusing them to produce multiple replicate beads to determine long-term performance. All samples and standards were given a unique reference number and barcode that was labelled onto the underside of the sample.

The unknown samples were placed into the Class 1 laser safe and interlocked loading area of a SolidSample ICPMS system (Figure 1). This consists of a robotized sample handling arm that can deliver samples from the staging area to the carousel, and from the carousel to the disposal area; a barcode reader; a 193 nm laser ablation system; a sample carousel; a SelfSeal sample chamber; and a quadrupole ICPMS detector.

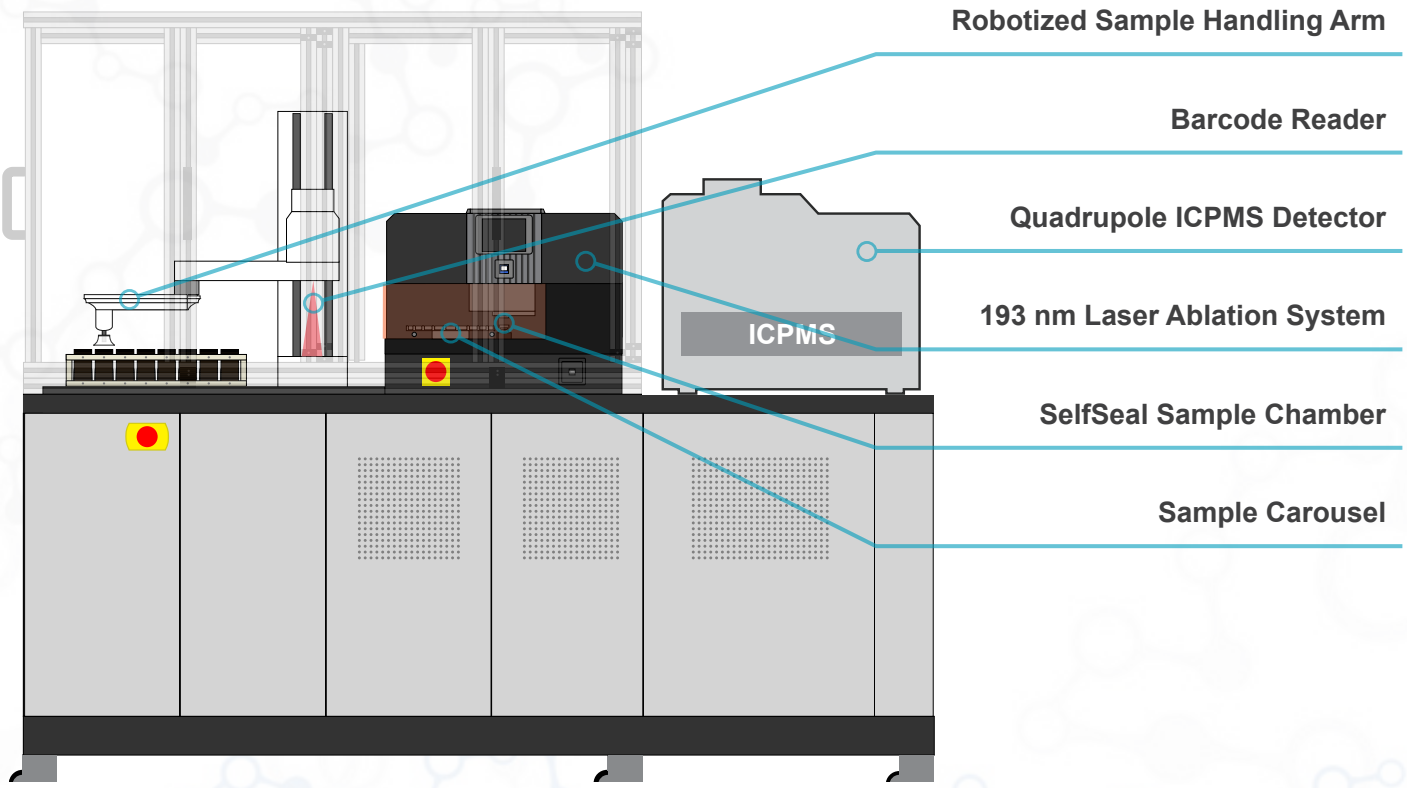


Figure 1. Diagram of a SolidSample ICPMS system consisting of a: robotized sample handling arm; barcode reader; 193 nm laser ablation system; sample carousel; SelfSeal sample chamber; and quadrupole ICPMS detector.

The standards and QC beads were placed on the carousel (Figure 2), and the unknowns were loaded into tubes of 25 beads which were stacked in the loading area (Figure 3). A run queue was created in the order [blank] → [calibration standards] → [QC bead] → [50 unknown samples] that was run until all the unknown samples had been analyzed once. The queue was concluded with a final analysis of the calibration standards.

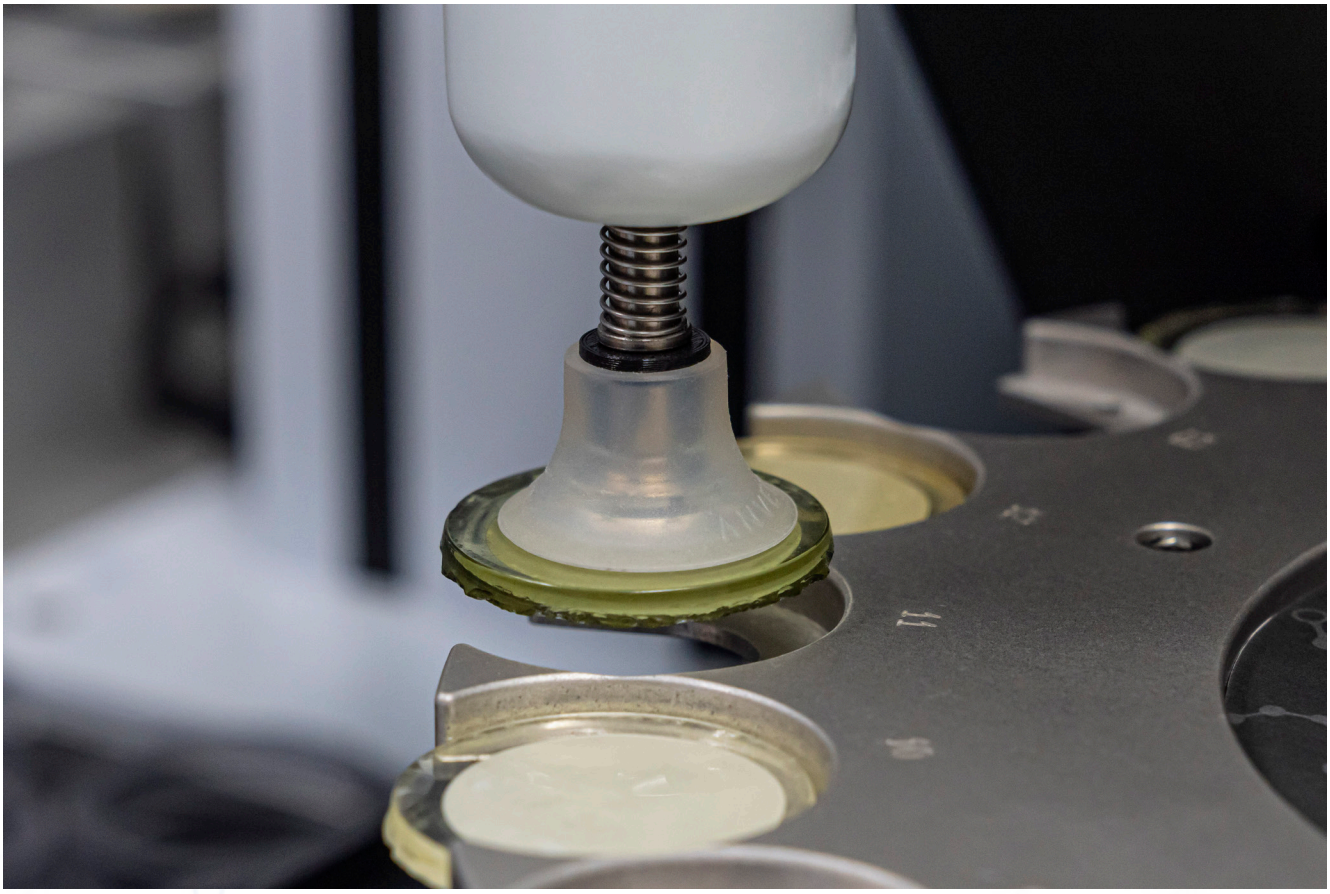


Figure 2. Samples in the carousel ready for analysis, and a sample being delivered from the loading area with the robot arm.

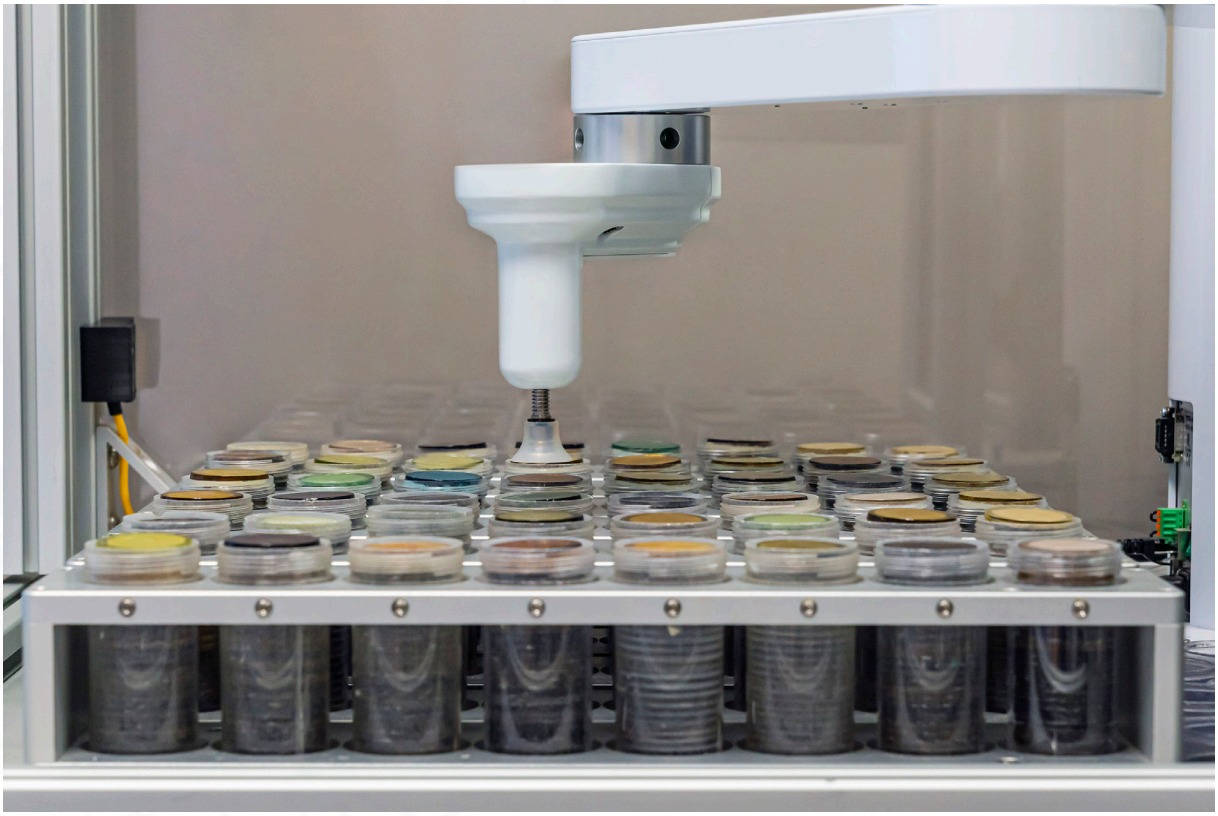


Figure 3. Unknown sample beads in the loading area ready for analysis. The robot arm collects samples and transports them to the carousel for analysis.

Each sample was analyzed using a scanning pulsed laser source across the sample surface in a pattern that is replicated on every standard, QC and sample bead. The ablated material is analyzed by the ICPMS detector. There is no requirement to refocus the ablation since the SelfSeal chamber ensures the sample is at the same Z position each time.

The ICPMS acquired 51 element isotopes from ^{6}Li to ^{238}U with a typical integration time of 10 ms per mass. A period of 20 seconds was integrated to obtain data. Key experimental parameters are shown in Table 1.

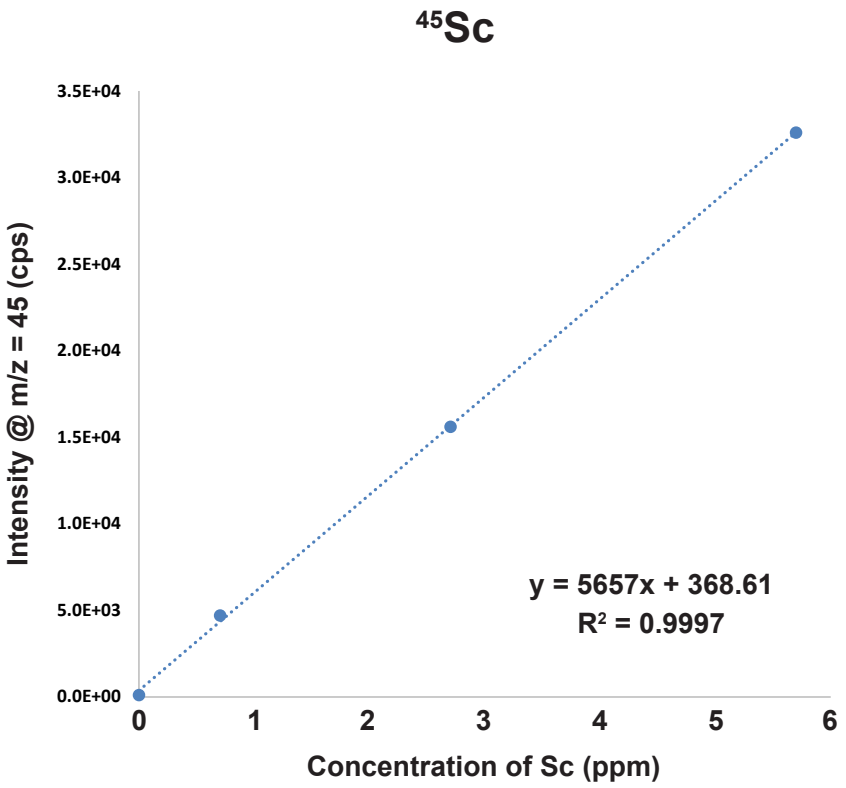
Parameter	Setting
Laser Ablation System	SolidSample ICPMS
Laser Repetition Rate	20 Hz
Laser Scan Speed	50 µm/s
Laser Spot Size	100 µm
Laser Scan Length	2 mm
Fluence	8 J/cm^2
He flow rate	1.0 L/min
Ar flow rate	0.8 L/min
ICPMS System	Quadrupole (standard mode)
RF Power	1300 W

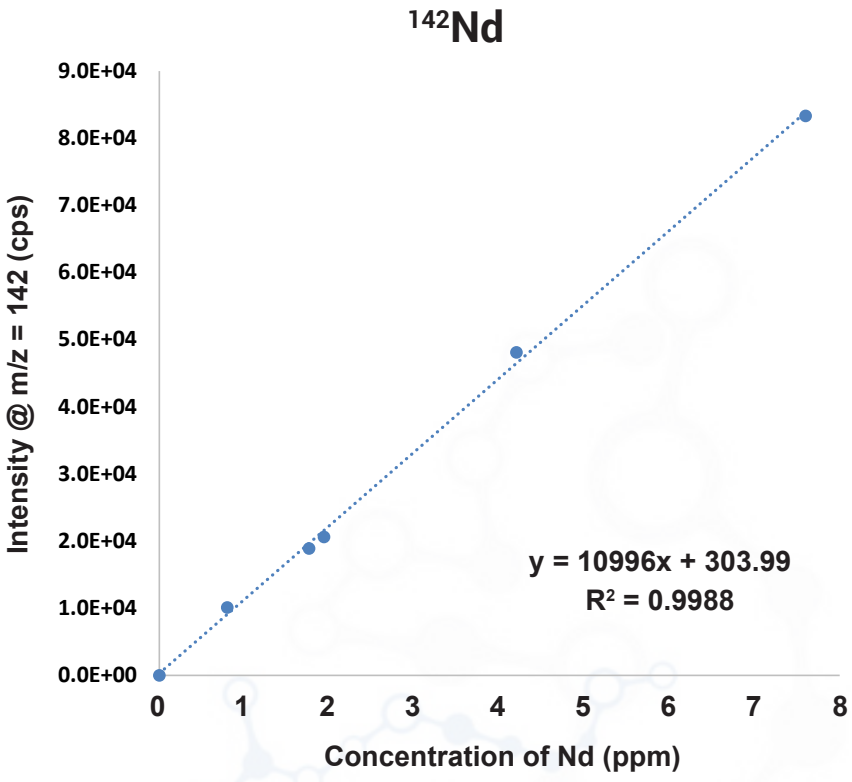
Table 1. System parameters.

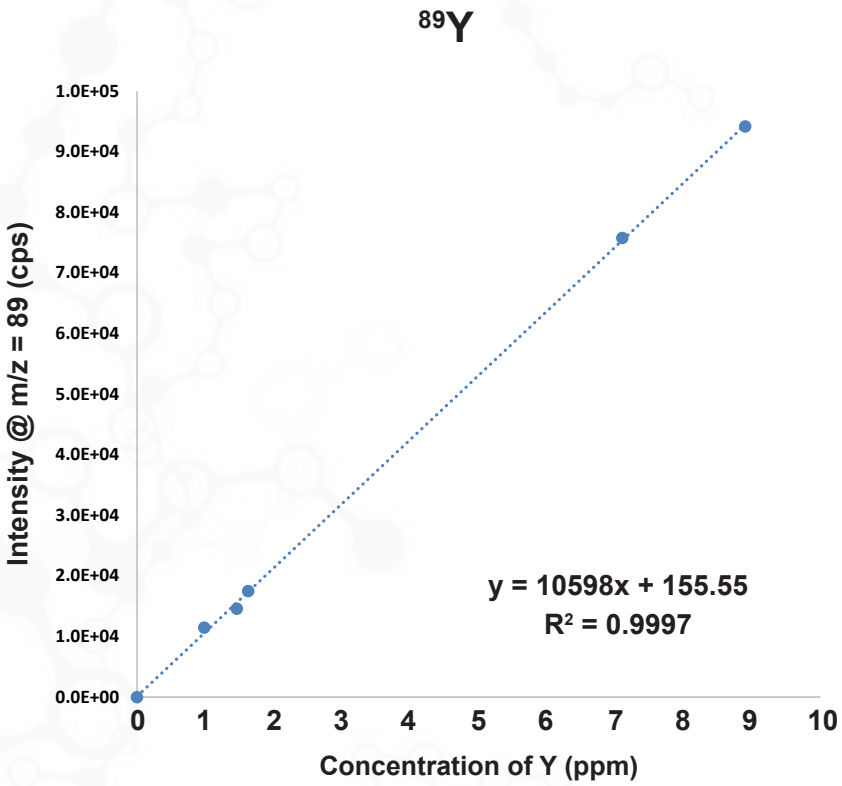
Results

Calibration

The selection of standards meant that each trace element calibration was based on a minimum of three data points, and each major element was based on a minimum of two data points (most elements calibrated with ≥4 data points). A selection of typical trace element calibrations is shown in Figure 4. Correlation coefficients in excess of 0.99 are typical.







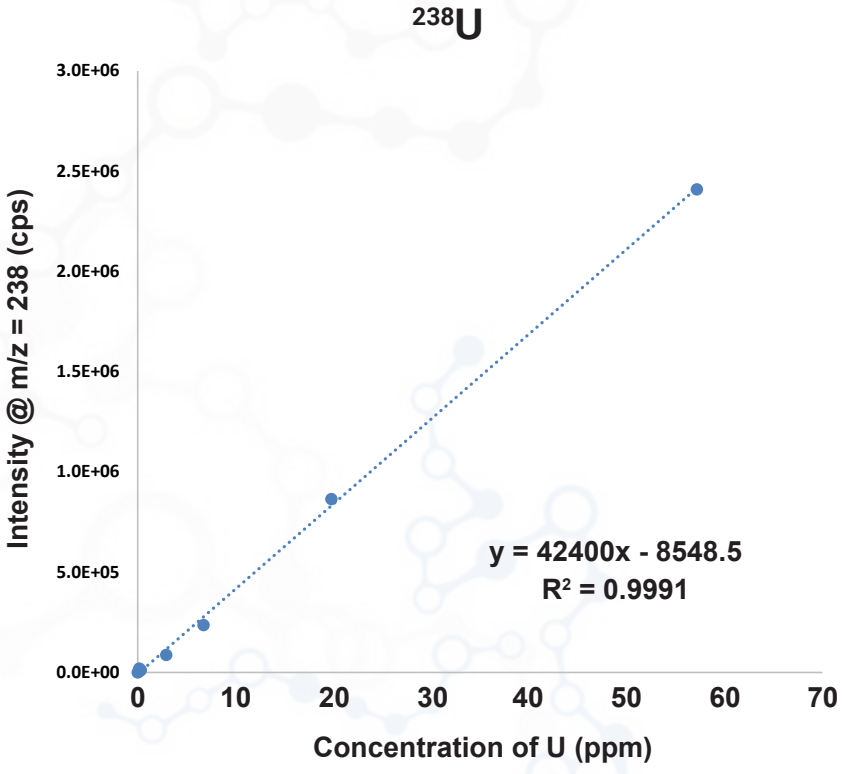


Figure 4. Typical calibration curve examples (Sc, Y, Nd and U) from the 51 element SolidSample ICPMS fused disc method. The SolidSample ICPMS method can be setup to include a few elements of interest up to all of the elements on the periodic table that can be measured by ICPMS.

Assessment of Accuracy

In order to determine general accuracy of the technique quantitative data obtained by XRF and solution-digestion ICPMS were compared with quantitative data obtained by SolidSample ICPMS by plotting the recovered values for each element against one another. Two samples – OREAS 20a and OREAS 100a – were selected due to the larger range of elemental data available. SolidSample ICPMS and XRF are compared in Figure 5, where a total of 36 data points covering 23 elements were available from the XRF dataset.

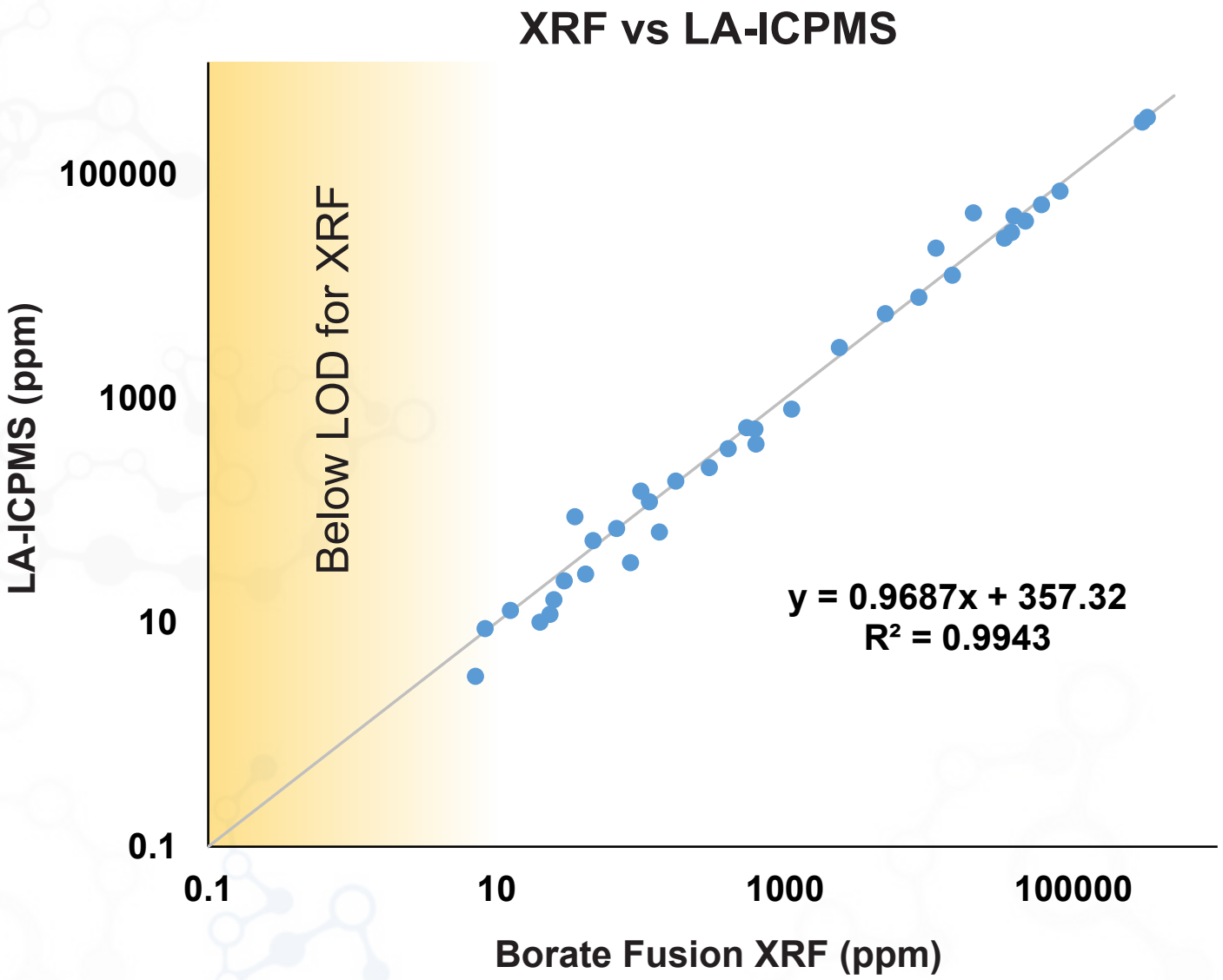


Figure 5. Plot of quantitative data for 23 elements for two different reference materials (36 data points) as assessed by XRF and SolidSample ICPMS.

SolidSample ICPMS is compared to solution-digestion analysis methods where a total of 71 data points covering 50 elements were available from the ICPMS dataset.

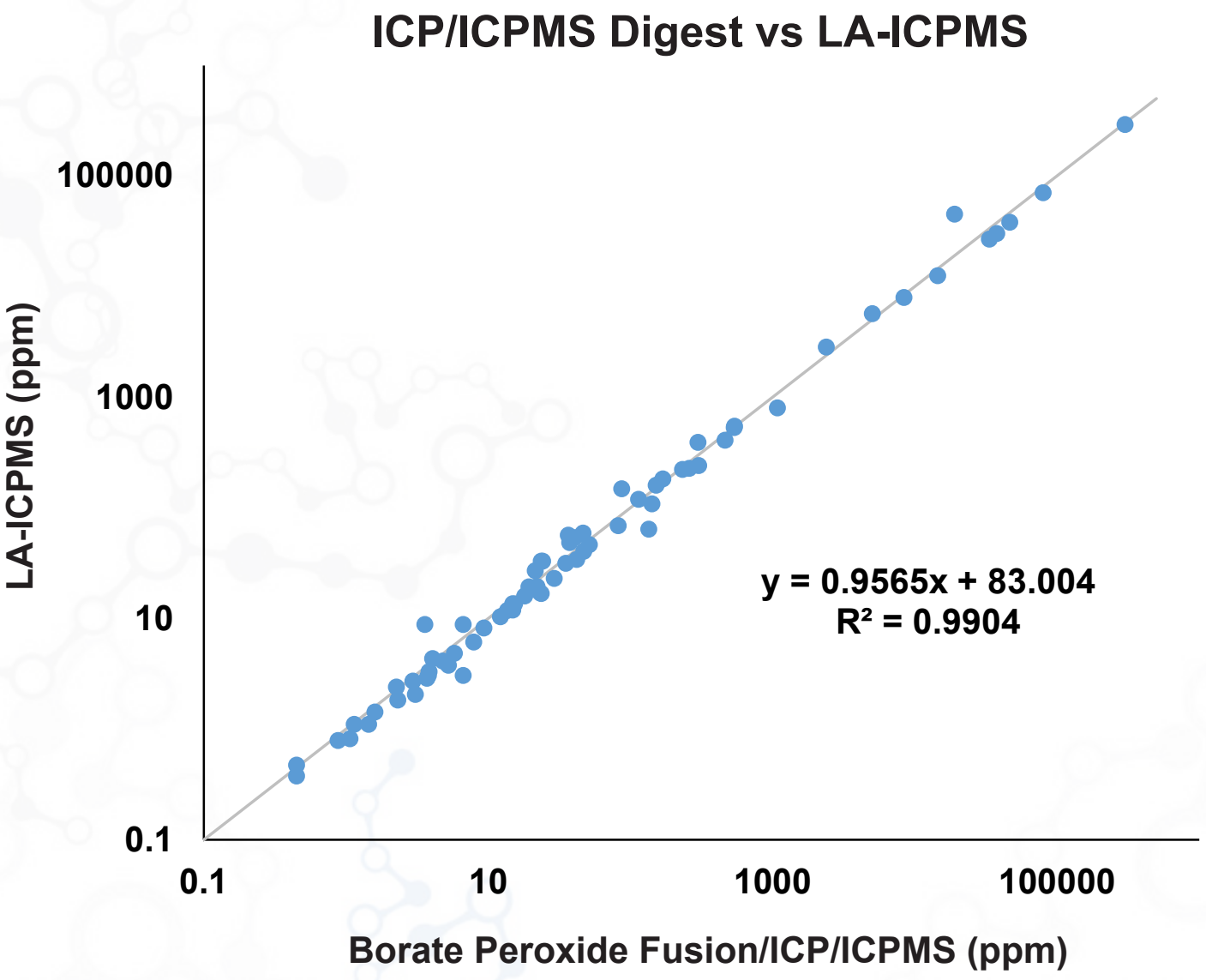


Figure 6. A plot of quantitative data for 50 elements for two different reference materials (71 data points) as assessed by solution-digestion and SolidSample ICPMS.

Detection Limits

Detection limits for all elements were determined using 3σ of the blank signal. Detection limits for trace metals ranged from 5 ppb to 5 ppm, with most elements in the 10-20 ppb range. An improvement in detection limit of 2 to 3 orders of magnitude compared to XRF is typical. The full list of limits of detection for SolidSample ICPMS and comparable values for XRF are shown in Table 2.

Limits of Detection (ppm)								
Analyte	SolidSample ICPMS	XRF	Analyte	SolidSample ICPMS	XRF	Analyte	SolidSample ICPMS	XRF
Ag	0.1		Ge	0.05		Sb	0.1	
Al	2	100	Hf	0.01		Sc	0.1	
As	0.2		Ho	0.01		Se	5	
Au	0.005		In	0.05		Sm	0.1	
Ba	0.5	10	K	1	100	Sn	0.2	
Be	0.2		La	0.01		Sr	0.1	
Bi	0.02		Lu	0.01		Ta	0.01	
Br	10		Mg	3	100	Tb	0.01	
Ca	10	100	Mn	1	10	Te	0.2	
Cd	0.1		Mo	0.2		Th	0.01	
Ce	0.02		Na	2	100	Ti	0.05	100
Co	0.02		Nb	0.01		Tl	0.2	
Cr	0.1	10	Nd	0.01		Tm	0.01	
Cs	0.01		Ni	0.1	10	U	0.01	10
Cu	0.7	10	P	5	10	V	0.1	
Dy	0.01		Pb	0.4	10	W	0.05	10
Er	0.01		Pr	0.01		Y	0.02	10
Eu	0.01		P	0.005		Yb	0.01	
Fe	2	100	Rb	0.05		Zn	5	10
Ga	0.1		Re	0.01		Zr	0.5	10
Gd	0.01		S	120	10			

Table 2. Detection limits of elements in fused beads of mining discovery samples based on analysis by SolidSample ICPMS and XRF.

Long-term Performance

A QC bead was run every 50 unknown samples during analytical runs over the course of one month (over 5000 separate anlayses) and the recovered values for all elements plotted against time (Figure 6). The rolling mean recovered value for each element throughout the month was unchanged, and the %RSD was typically below 10% for elements above the low ppm range.

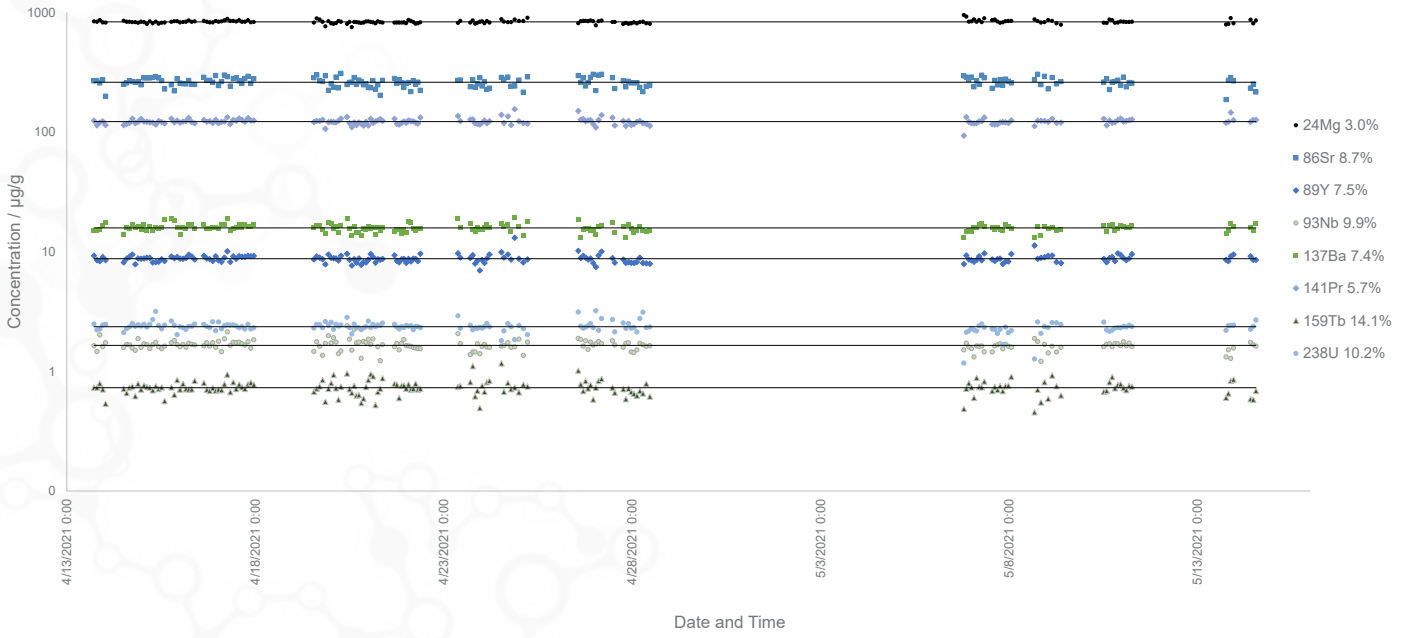


Figure 7. A plot of recovered values for analysis of the QC bead using SolidSample ICPMS over a one month period. Gaps in the data are where the SolidSample ICPMS system was being used for other projects.

Conclusions

A workflow for analysis of large batches of mining discovery samples that includes solution-digestion ICPMS has to accommodate large volumes of reagents, considerable energy usage and environmental and safety concerns. SolidSample ICPMS avoids all of these issues by using exactly the same fusion bead sample that is already produced for XRF analysis. SolidSample ICPMS has been designed to be operated with minimal operator input, and can run indefinitely as long as new samples are added periodically.

Throughput with SolidSample ICPMS is considerably higher and with considerably less operator input required than conventional LA-ICPMS, and with comparable analytical performance. Batches of up to 1400 samples can be analyzed in a single day.

SolidSample ICPMS produces accurate, precise and reproducible data for large batches of samples over prolonged periods of time, while offering considerable cost savings.

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