Elemental Scientific LASERS
INNOVATION TO ILLUMINATE

Applications Note

Determination of REE in Fusions

Automated, rapid, accurate and precise measurement with SolidSample ICPMS

Figure 1. SolidSample ICPMS (above) and LTXS-REE-100 series reference materials (right)

SolidSample ICPMS: Robotic solid sample handling with automated barcode-reading for LA-ICPMS

Brief

Automating solid sample analysis of Li borate fusions provides a simple cost-effective approach for the determination of Rare Earth Elements (REEs) in a wide range of sample types. Robotic sample handling combined with SelfSeal™ ablation chamber delivers uninterrupted determination of 1000-2000 samples/day, without user intervention.

Introduction

Rare Earth Elements commonly occur in refractory (acid resistant) minerals such as monazite, xenotime, rutile and zircon. Four-acid digestion mixtures (HF, $HClO_4$, HNO_3 and HCl) do not fully solubilize these minerals and H_2SO_4 is required for the dissolution of phosphates (monazite and xenotime). Acid digestion times at elevated temperatures can take days and are therefore often referred to as "near-total" methods. As a result, the Industry Standard (IS) sample preparation technique for "total" REE determination requires a two-step process of a borate or peroxide fusion followed by an acid digestion. Depending on required detection limits the final digested solutions are then analyzed by either ICP or ICPMS. Here we present a new system called SolidSample ICPMS that:

1) Eliminates the acid digestion step and ICPMS exposure to acid
2) Is capable of determining the total digestion suite of elements (60+) in solid samples
3) Automates solid analysis
4) Provides superior detection limits
5) Is accurate and precise for a wide range of rock types
6) Greatly simplifies the analytical process
7) Provides tracking for chain of custody and data organization
8) Creates acid-free environment

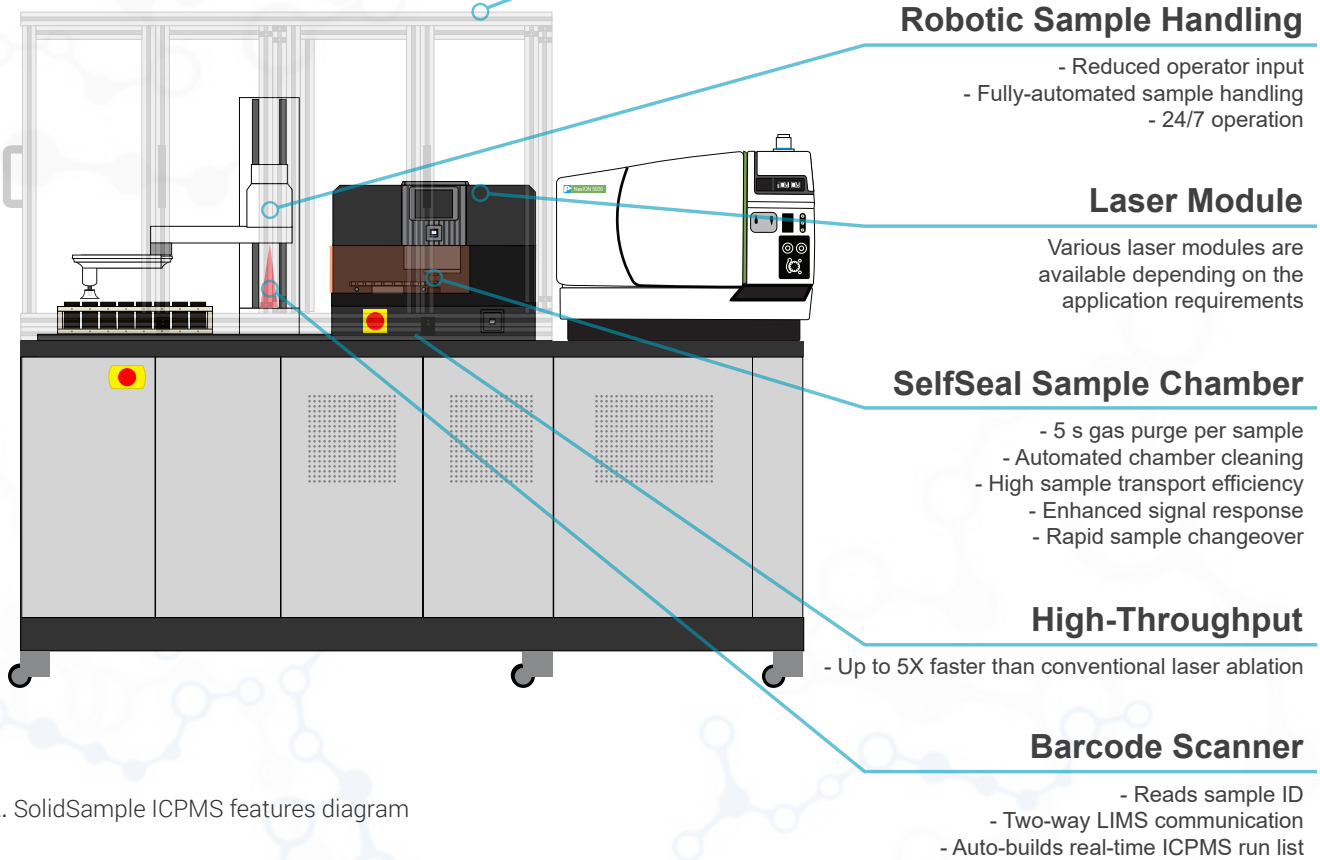


Figure 2. SolidSample ICPMS features diagram

SolidSample ICPMS

SolidSample ICPMS combines a novel automated sample handling robot with well-established LA-ICPMS techniques for the determination of a full range of metals (major and trace) in whole rock fusions. The system provides seamless sample flow by combining four main components (Figure 2):

Operation is simplified through an intuitive SolidSample ICPMS User Interface (UI). Once samples are loaded into the system the user simply defines the number of samples and the frequency of blanks, standards and QCs. A sequence is then generated and started:

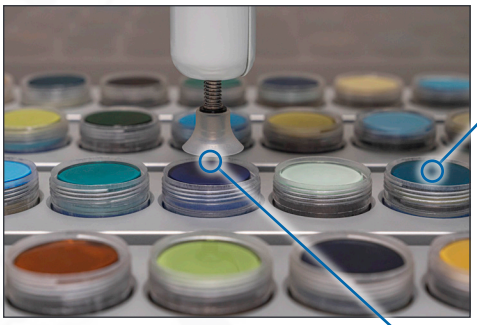
1) The sample is picked up by the robotic arm
2) The sample is scanned for barcode ID (unbarcoded samples can also be analyzed)
3) The sample is loaded onto the carousel using a robotic arm with a pneumatic suction cup
4) The carousel rotates the next bead in the sequence to the analytical location
5) The sample is coupled with the SelfSeal™ chamber using a pneumatic piston
6) A 5 second purge and 2 second settling time is used to flush the system of atmosphere
7) The laser fires to ablate the sample (Line scan: 100 µm, 20 Hz, 100 µm/s, 7 J/cm2, Table 1)
8) SolidSample ICPMS triggers the ICPMS to acquire data
9) The raw data file is imported by SolidSample ICPMS
10) The SolidSample ICPMS software performs all calculations, associates final concentrations with barcodes (if sample has barcode)
11) The system provides finalized data for LIMS. (See Figure 3 for SolidSample ICPMS sample and data flow path)

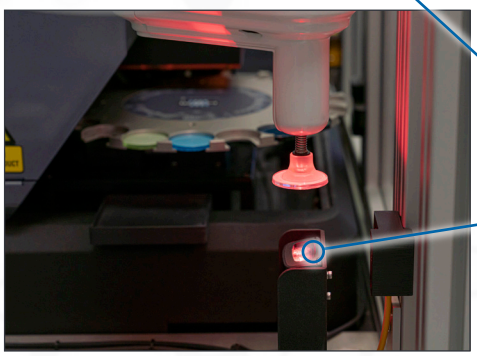
Table 1. SolidSample ICPMS and ICPMS Parameters

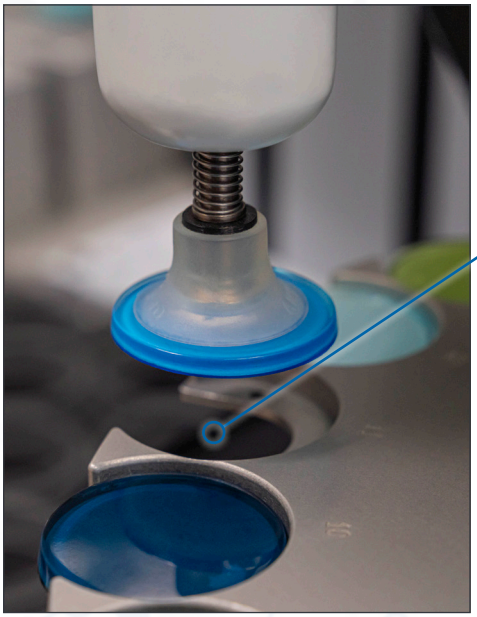
Parameters	
SolidSample ICPMS	Standard
Fluence	7 J/cm^2
Spot Size	100 µm
Repetition Rate	20 Hz
Scan Speed	100 µm/sec
Line Length	3 mm
He Flow Rate	800 mL/min
ICPMS	
Dwell time / isotope	10 ms (1 ms for ^{6}Li)
Number of Isotopes	20
RF Power	1300 W
Nebulizer Ar Flow Rate	840 mL/min
Acquisition / sample	40 seconds

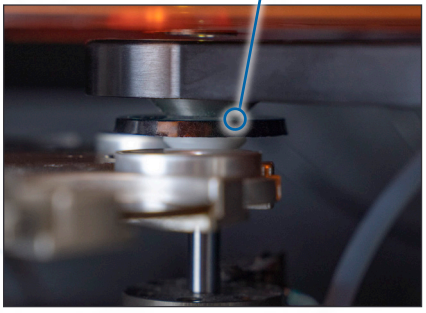
SolidSample ICPMS

Robotic Sample Handling









Analytical Cycle

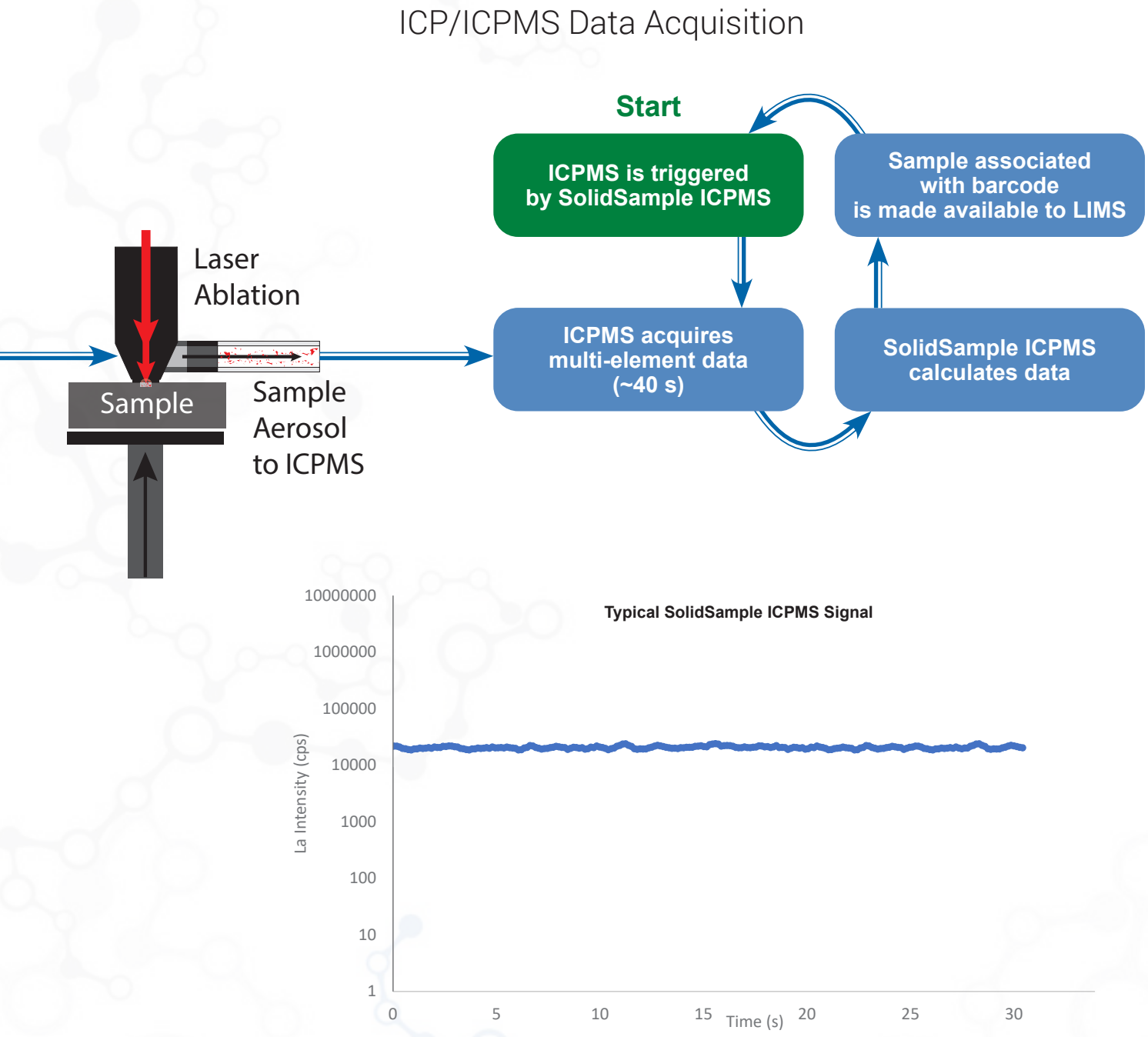


Figure 3. SolidSample ICPMS sample to sample time is defined by the analytical conditions. In this example the system is purged (5 s), REE and other elements are measured (<40 s), cell is cleaned with N_2 purge and next sample is sealed (10 s) for a total analytical time of <60 s. During the analytical cycle the robot unloads a previously analyzed sample, picks up next sample, scans barcode and loads next sample onto carousel. Higher throughput can be achieved if shorter analytical times are used.

Sample and standard preparation

Unknown samples and Certified Reference Materials (CRMs) were prepared by thoroughly mixing 1.25 g of sample milled to 200 mesh (<74 µm particle size) with 2.5 g of $NaNO_3$ oxidizing agent, 10 g of flux (49.75% Li Metaborate; 49.75% Li Tetraborate; 0.5% LiBr) and 1 mL of 1000 ppm In solution in a Pt crucible. The samples were then oxidized in a fusion furnace at 450 °C for 10 minutes before fusing at 1000 °C for 20 minutes. The molten mixtures were poured into a preheated 40 mm Pt mold and cooled to room temperature.

ESL fusions blanks, oxide check standards and calibration standards were used to accurately quantify unknown samples and certified reference materials (Table 2). Blanks are used to subtract any contribution of REEs from the sample preparation procedure and calculate Limits of Detection (LODs), whereas, oxide interference check standards are spiked with Low mass (LREE) and Medium mass (MREE) rare earths to correct any oxide interference on the MREE and High mass HREE, respectively. Calibration standards are ESL customized fusion standards based on the typical range of relative abundance of REEs in differentiated crustal rocks and REE ore samples and the wide range of concentrations in target samples encompassing typical crustal abundances to highly enriched REE ores (e.g. Ce= 50-27,000 ppm Ho= 0.4-8 ppm Lu= 0.1 to 1.0 ppm). This customized suite of standards encompasses the full range of potential REE concentrations and is preferable to single concentration REE standard as it ensure all REEs in all samples fall within an appropriate calibration range that minimizes error propagation.

Table 2. Table of ESL solid laser ablation standards for REE

Standards Table			
Elements	La, Ce, Pr, Nd, Sm Conc. (ppm)	Eu, Gd, Tb, Dy Conc. (ppm)	Ho, Er, Tm, Yb, Lu Conc. (ppm)
S0 LTXS-REE-100	0	0	0
S1 LTXS-REE-101	17.5	1.75	0.5
S2 LTXS-REE-102	32.5	3.25	0.8
S3 LTXS-REE-103	6.8	6.75	1.75
S4 LTXS-REE-104	200	20	5
S5 LTXS-REE-105	400	40	10
S6 LTXS-REE-106	800	80	20
S7 LTXS-REE-107	1600	160	40
S8 LTXS-REE-108	3750	375	90
S9 LTXS-REE-109	7500	750	180
S10 LTXS-REE-110	30000	3000	700
LREE Oxide Check LTXS-REE-111	200	0	0
MREE Oxide Check LTXS-REE-112	0	200	0

Results

Data Calculation

SolidSample ICPMS automatically imports raw time-resolved data files from the ICPMS as each sample is completed and displays calculated final concentrations in real time. The automation combines flexibility with simplicity allowing the user to specify:

1) Gas blank integration window
2) Sample integration window
3) Internal standard(s)
4) Calibration fit

The number of standards, standard concentrations, blanks, QCs, QC concentrations, and sample ID information can all be imported with barcode IDs eliminating user error associated with sample ordering or transcription. Together these features ensure the correct answer is associated with the corresponding sample every time.

Calibration curves for the ESL standard suite are very linear having correlation coefficients better than >0.999 R^2 for all REEs (Figure 4). Stability is demonstrated with very reproducible laser energy (Fluence RSD <0.40%, Cell pressure RSD <0.01%, IS RSD < 3.0%) and sample sealing (Cell Pressure, RSD) resulting a stable laser aerosol stream delivered to the plasma (Figure 5). Analytical results confirm the stability of the system as illustrated by IS recovery (Figure 5) SolidSample ICPMS stability combined with customized calibration result in sample intensities that fall within a highly linear calibration curves (Figure 6) providing the fundamental requirements for high quality data. All data for CRMs presented below cover a wide range of natural and ore grade REEs concentration illustrating the broad application of the method to provide precise and accurate data.

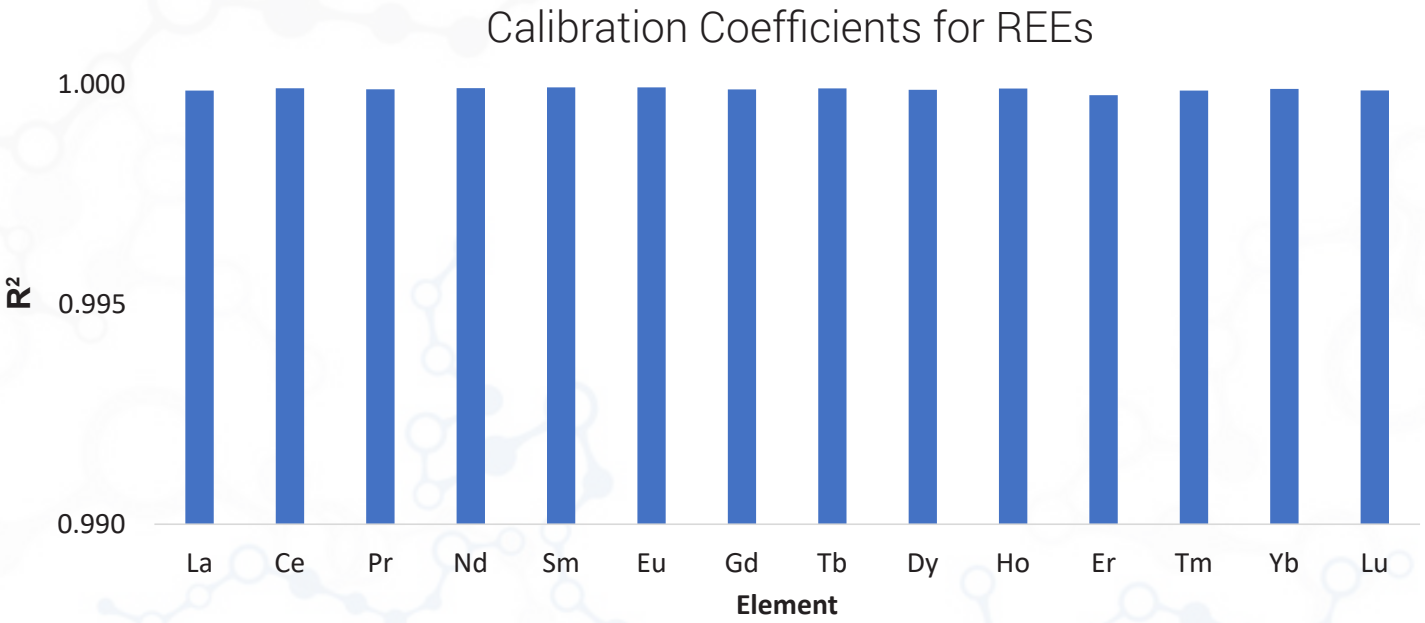


Figure 4. Calibration coefficients are plotted for all for REEs

SolidSample ICPMS Stability

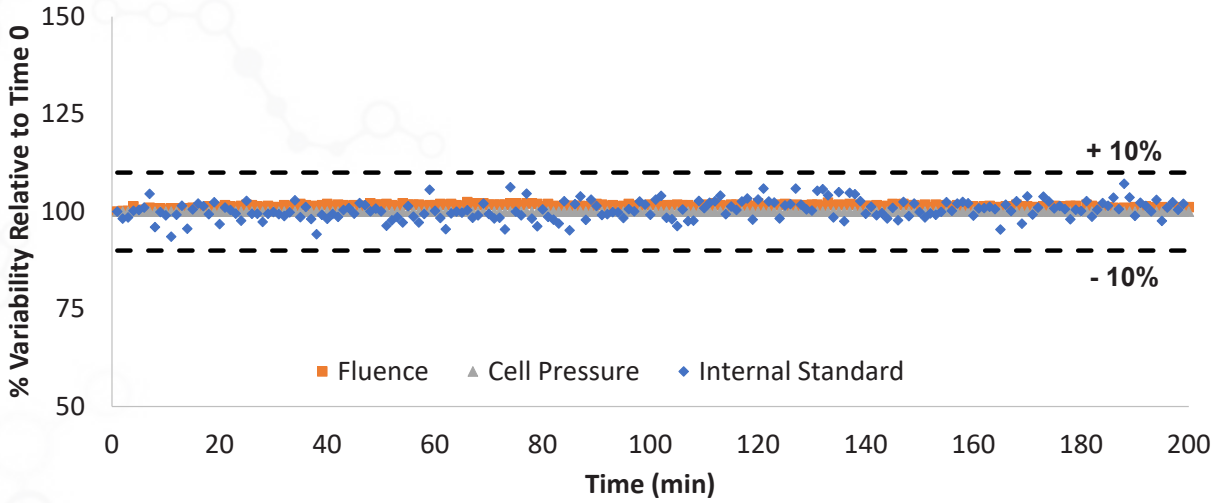


Figure 5. Cell pressure, fluence and internal standard are normalized to time 0 and plotted a relative drift

Calibration Curves

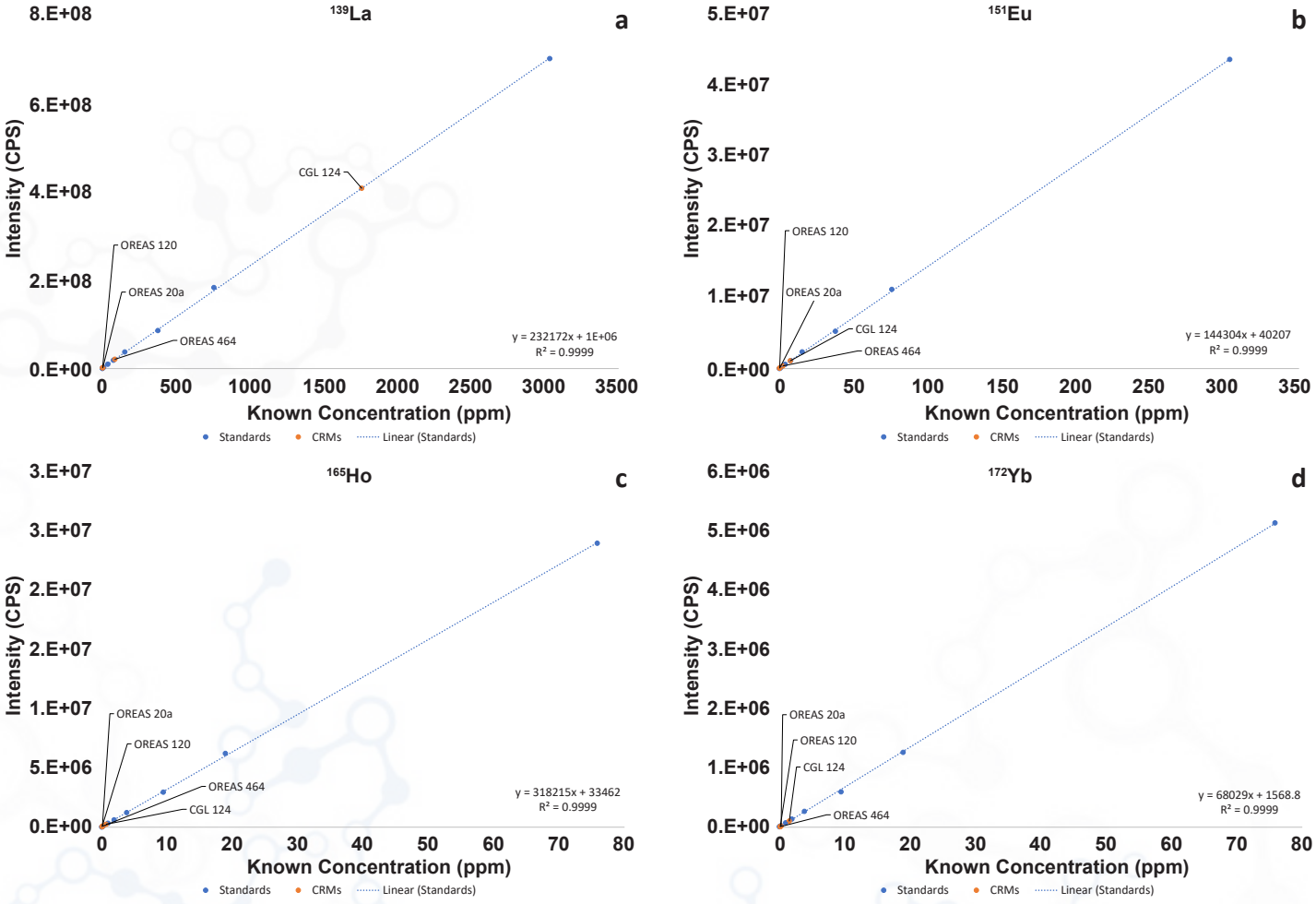


Figure 6. Calibration curves are plotted for ESL REE standards with CRM determined values for selected REEs in CRMs OREAS 20a, OREAS 120, OREAS 464 and CGL 124

Blanks and LODs

In laser applications it is common practice to determine blanks and LODs while flowing carrier through the cell into the plasma without firing the laser (Gas Blanks, GB). However, with fusions samples it is important to take into consideration the full procedural blank associated with processing the sample and contributions from fusion reagents (Procedural Blank, PB). Therefore, procedural blanks are dependent on quality of fusion reagents and care taken during sample preparation. Procedural blanks determined for this method are more than sufficient to measure REEs in at natural abundances (typically above 0.1 ppm) in average differentiated lithospheric rocks (Table 3). Furthermore, the blanks and LODs are comparable to lower than most other common methods.

Table 3. SolidSample ICPMS limits of detection compared typical industry standard methods

	Limits of Detection	
Element	Quartz Fusion Blank Purity (ppm)	Fusion + Disolution ICPMS (ppm)
La	0.01	1
Ce	0.02	1
Pr	0.01	0.01
Nd	0.03	0.1
Sm	0.02	0.01
Eu	0.01	0.01
Gd	0.03	0.01
Tb	0.04	0.01
Dy	0.04	0.01
Ho	0.01	0.01
Er	0.01	0.01
Tm	0.01	0.01
Yb	0.01	0.01
Lu	0.01	0.01

Accuracy and Precision

Accuracy and precision of the method is determined from replicate analysis of well-established commercial CRMs. For this application four CRMs were chosen to encompass the expected range of REEs (Oreas 20a Granodiorite, Oreas120 Uranium, Ore 464 Lateritic REE Ore, and CGL 124 xenotime REE Ore). The analytical results of the CRMs demonstrate the methods power to accurately quantifying REEs over the full range of expected concentrations from background differentiated crustal values (Granodiorite) to highly enriched ores (Xenotime), and the full range of expected relative LREE/HREE enrichments (La/Lu 40-2500). One to one plots for certified vs determined concentrations for all the REEs for the four CRMs are illustrated in (Figure 7). High linearity (> 0.999) and slope near 1.00 (0.990-1.00) represents <+ 10% agreement of determined values with certified values for the full suite of REEs. Furthermore, SolidSample ICPMS stability allows determination of high quality data with demonstrated recovery between 90% and 110% at a precision of <4% (for the QC sample) over a 12-hour run (Figure 8).

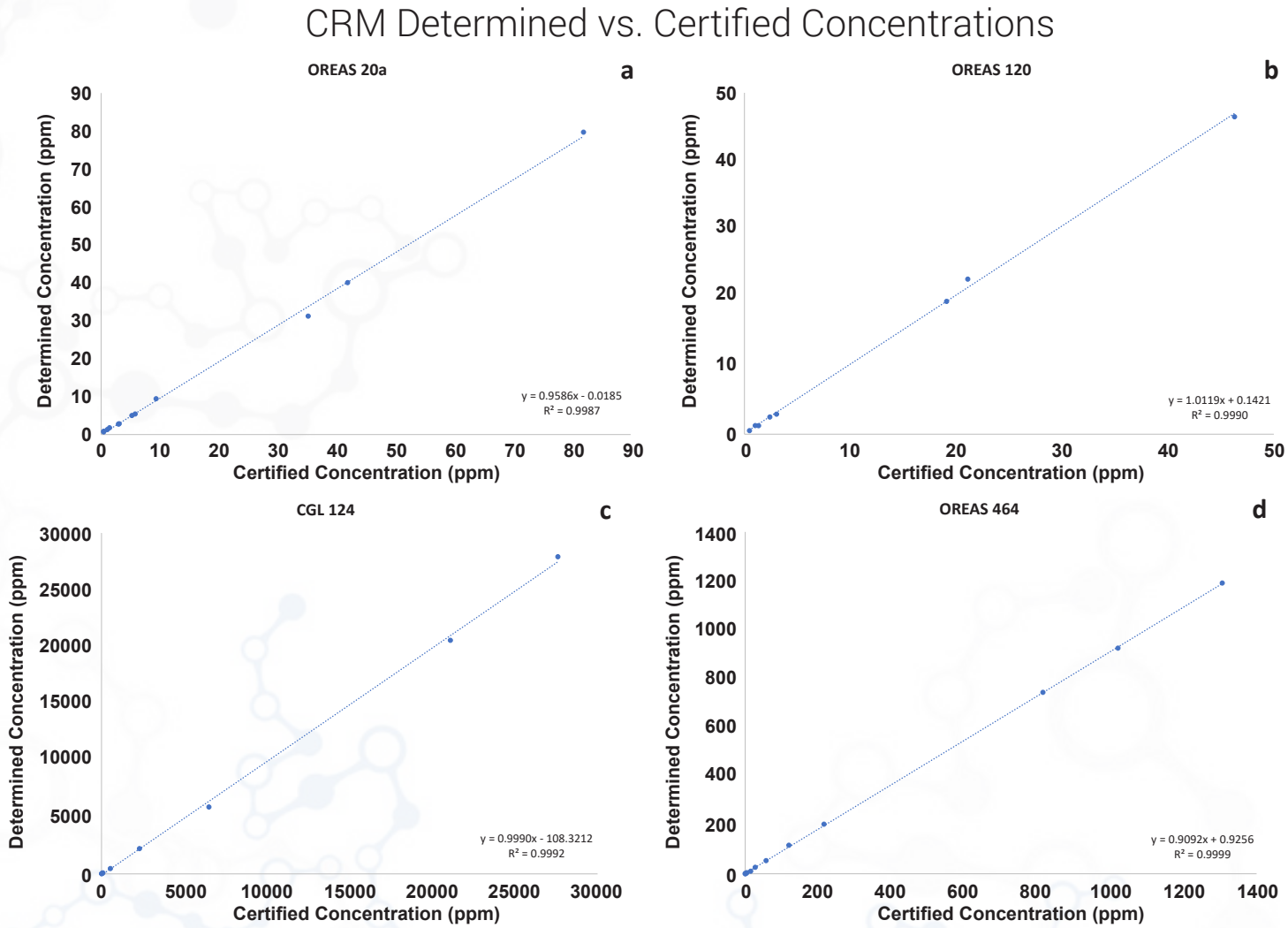


Figure 7. Certified values plotted against determined values for selected REEs in CRMs OREAS 20a, OREAS 120, OREAS 464 and CGL 124 – autocalibration range and high linearity are demonstrated

One final consideration in evaluating accuracy of REE is oxide interference correction and requires monitoring for LREE (eg $^{140}Ce^{16}O$ on ^{156}Gd) interferences on MREE and MREEs ($^{159}Tb^{16}O$ on ^{175}Lu) interferences on HREEs. The effect of these interferences is well established and varies greatly depending on rock type and degree of relative REE enrichment. An additional advantage of solid sampling over solution analysis is that no water is introduced into the plasma greatly reducing the formation of oxide interference (>10x). To ensure the robustness of the data calculations we monitor Oxide interferences using the ESL check standards and found no significant interference corrections are needed in the sample suite we tested. If required, interferences could be corrected using the check oxide check standards or REEs could be mass shifted away from interferences using O_2 reaction gas in the triple quad.

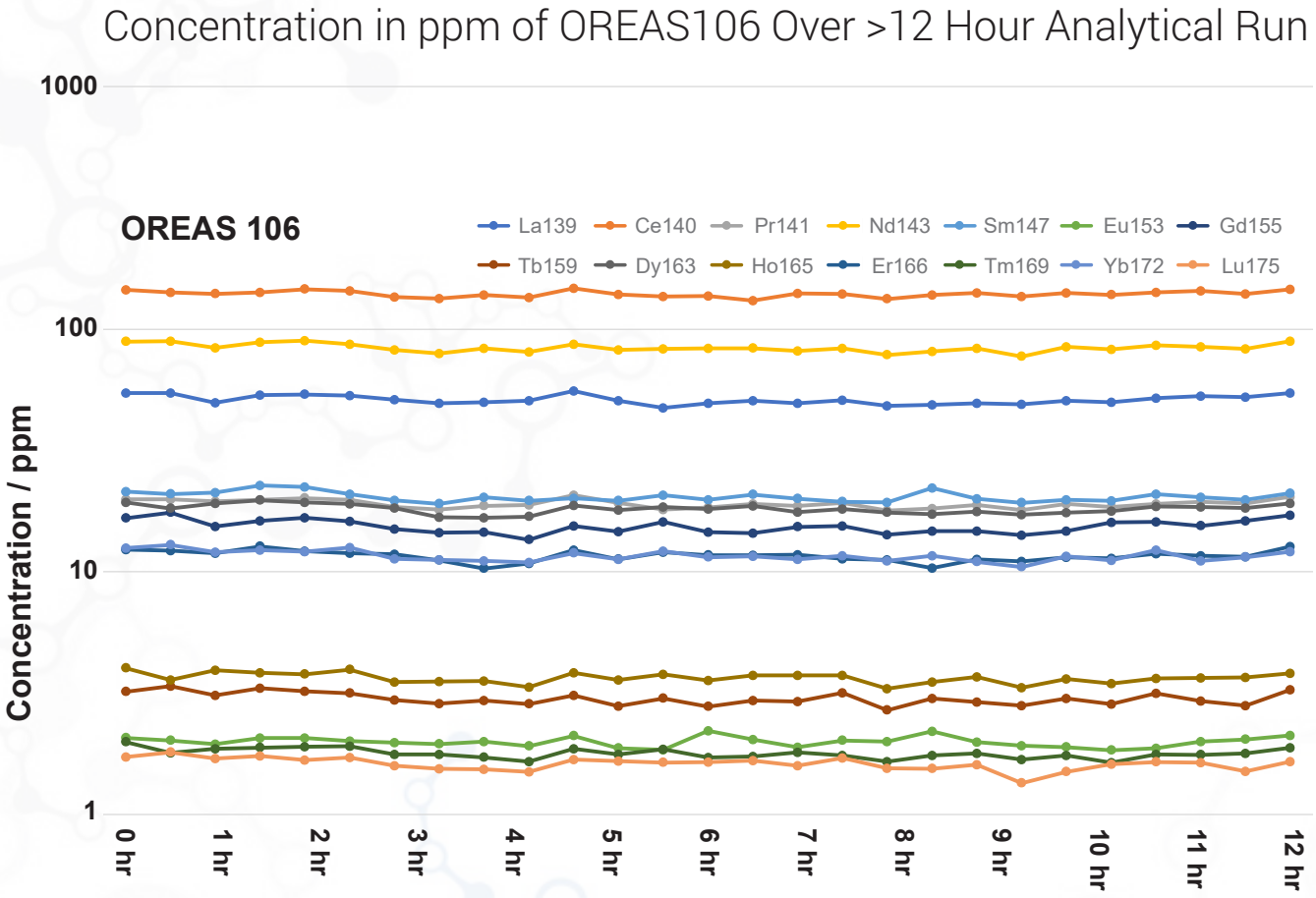


Figure 8. Long-term stability of recovered concentrations from the OREAS106 reference standard; 96% of value have recovery within +/- 10%, and 100% are within +/- 20%; Precision of recovered values ranges from 1.8% (Nd) to 4% (Lu) over a 12 hour period

Conclusions

This application note demonstrates a streamline solution that eliminates acid digestion and provides high quality REE data that meets or exceeds current Industry Standards.

SolidSample ICPMS:

- Combines automation with LA-ICPMS to achieve a solid sample throughput of greater than 1000 samples per 24 hrs
- Provides high quality data with demonstrated recovery between 90% and 110% at a precision of <4% (for the QC sample) over a 12-hour period
- Exhibits a high degree of linearity (>0.995 R^2) over a concentration range that incorporates sample ranging from low background (<ppm) to highly concentrated ores (Wt%)
- Delivers industry leading LOD's compared to other solid and solution-based techniques
- Incorporates barcode reading that can be used to track samples, manage data and import relevant sample or standard information
- Minimizes operator intervention
- Enables the quantitative analysis of "total" REEs in fused beads without requiring a subsequent digestion of the fusion
- Negates the use of HF, $HClO_4$, HNO_3 and HCl acids that constitute the basis of the mixture typically used for "near-total" or 4-acid digestions or H_2SO_4 used for phosphate REE ores
- Eliminates safety concerns associated with using hydrofluoric acid (toxic by skin absorption), and perchloric acid (can produce explosive salts)
- Greatly reduces operation costs associated with acid
    1) Purchase
    2) Handling
    3) Fume extraction
    4) Disposal
- Is a powerful tool for the high-throughput determination of REEs in geological samples