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## REEs Analyses in Some Geological Standard Reference Materials utilizing LA-ICP-MS and ICP-MS Techniques

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### ABSTRACT

Rare earth elements (REEs) are examined from Standard reference materials in a liquid state (after digestion with acids) utilizing inductively coupled plasma mass spectrometry ICP-MS and in a solid form after fusion with lithium tetra borate to have transparent fused targets utilizing LA-ICP-MS. NIST 612 and NIST 614 serve as the external standards for the Laser ablation unit merged with the ICP-MS (LA-ICP-MS). This paper aims to investigate the key differences between the two approaches to data analysis. The precision of the measurements is discussed for each element that was measured. When measured by LA-ICP-MS, the relative standard deviation is typically middle 1 to 8 percent, while when measured by ICP-MS, it ranges from 1 to 3 percent. The measurements' accuracy was reported and are found, within  $\pm 10\%$  by LA-ICP-MS and  $\pm 5\%$  by ICP-MS. Techniques like the inductively coupled plasma mass spectrometer and the laser ablation that may be added to it are valuable tools for precisely measuring rare earth elements (REEs).

### INTRODUCTION

Gray was the first to introduce laser ablation merged inductively coupled plasma mass spectrometry (LA-ICP-MS) in 1984 for analysis [1]. Consequently, it has been exceedingly used as an effective analytical technique in a variety of fields [2-6] for the scrutiny of micro-solid matters. In this method, a laser beam is engrossed at the sample surface, which causes it to be ablated. The ablated material is then transported as particulates (also known as the aerosol) by the carrier gas (Ar or He) via the ICP, where it is ionized. Finally, it is brought into the mass analyzer system, where the detector detects it. When compared with liquid and fused samples for analysis by ICP-MS and LA-ICP-MS, the fused sample is faster (< 3 minutes for single-point check), has a minor background, and has rarer interferences of hydroxides and oxides [7]. In addition, the usage of LA-ICP-MS eliminates the need for the time-consuming procedure of digestion as well as the issues associated with sample digestion (such as the inability to digest some minerals completely and the instability of some aspects in weak acid solutions) [8].

The precision and accuracy of an elemental composition are impacted by some factors, including the calibration approach employed, the standards utilized, the matrix and fractionated effects, and the susceptibility drifting of the device. The instrumental settings are the most fundamental of these (i.e., the wavelength, laser pulse width, resolution, and sensitivity of ICP-MS). Standards are used for standardization and the matrix and fractionation effects. Comparing fluid assessment to LA-ICP-MS analysis can provide greater precision (>5%) and accuracy (>5%-10%) with the implementation of an appropriate calibration method and optimized equipment settings. Most rock-forming minerals get a poor absorption of Nd: YAG lasers' intrinsic infrared frequency of 1064 nm. As a result, many of the early LA-ICP-MS systems exploited this wavelength. A UV laser in LA-ICP-MS establishments led to considerable increases in the spatial resolution, enhanced material absorptivity, condensed elemental fractional process, and upgraded analytical precision [9].

Quantitative analysis of float glasses was performed using LA-ICP-MS by employing external calibration

standards. These standards included the NIST SRM 61x sequences and additional standards made accessible via the glass industry. Drift glass has near-typical matrix constituents of 72 weight percent silica oxide, 13 weight percent sodium oxide, 8 weight percent calcium oxide, and 4 weight percent magnesium oxide [10]. In comparison, the NIST SRM 610/612 glasses have a slightly different composition, specifically 72 weight percent SiO<sub>2</sub>, 14 weight percent Na<sub>2</sub>O, 12 weight percent CaO, and 2 weight percent Al<sub>2</sub>O<sub>3</sub> [11]. On the other hand, these glassy reference ingredients are utilized as exterior standardization materials most of the time. Two matrix-matched standards were developed and created to progress the precision of the quantifiable examination of float glassy performed by LA-ICP-MS [12].

LA-ICP-MS is a system that is extensively accepted for examining biological materials for elemental analysis samples like soft tissues (e.g., brain, hair, and liver) and firm tissues (e.g., teeth and bones) through development over usage last few years [13]. LA-ICP-MS has grown in popularity as efficient analytical technologies for measuring trace elements in recent years. This can be beneficial for directing exploring or mineralized drills. Completing multi-element ICP-MS experimental sets can be a powerful instrument in mineral prospecting. The exploratory community makes use of this device [14].

Using LA-ICP-MS, we measured rare earth elements and yttrium in oyster shells, as well as their provenance and the potential essential implications of those quantities [15]. An examination utilizing LA-ICP-MS was carried out on 37 blue glass drips unearthed from a tomb in the southern Faiyum district of Egypt [16]. The study's primary objective was to achieve instrumental accuracy and precision level (10% RSD) amidst various legal laboratories that are within range of the inclusive changeability of trace elements in glass. This will allow LA-ICP-MS to convert a regular performance for analyzing glass shortly.

## EXPERIMENTAL

### Instrumentation:

In order to execute the laser ablation on the materials that were being examined, a Q-switched UV wavelength Nd-YAG laser and a double-focusing ICP-MS (Thermo Electron "Element") were utilized. 99.999% pure argon was utilized as a plasma gas. To ensure optimal sensitivity and durability, the ICP-MS objective operational parameters were tuned for <sup>139</sup>La using

ablation of the reference NIST 614. This was done in order to achieve the best possible results. Table (1) shows a listing of the experimental particulars, which includes the instrument setting for the LA-ICP-MS.

### Standards and Samples

The synthetic silicate reference materials NIST 612 and 614 were obtained from the National Institute of Standards and Technology, USA. These materials were utilized for testing and exterior calibration. The LA-ICP-MS and ICP-MS techniques were utilized to analyze five geological reference materials that were provided by USGS (United States Geological Survey). The materials were BHVO-1 (basalt), GSP-1 (granodiorite), AGV-1 (andesite), and G-1 (granite).

### Sample preparation

#### a-Liquid samples:

The samples were acid-digested in a Teflon beaker that was screw-capped and contained 15 milliliters of liquid. 10 mg of each sample was heated on a hot plate at 150 °C for twenty-four hours with 0.20 ml HF, 0.15 ml HNO<sub>3</sub>, and 0.09 ml HClO<sub>4</sub>. The screw cap Teflon beakers were filled to a volume of fifteen milliliters. Following digestion, the sample solution was heated until it reached absolute dryness. The residue from the evaporation was mixed with 1.2 milliliters of 7M HNO<sub>3</sub> and then heated on a hot plate at 50 °C for one hour without a screw cover. The residue can be dissolved using concentrated HNO<sub>3</sub> (0.3 ml), which should then be diluted with water up to a volume of 10 ml.

#### b-Solid samples

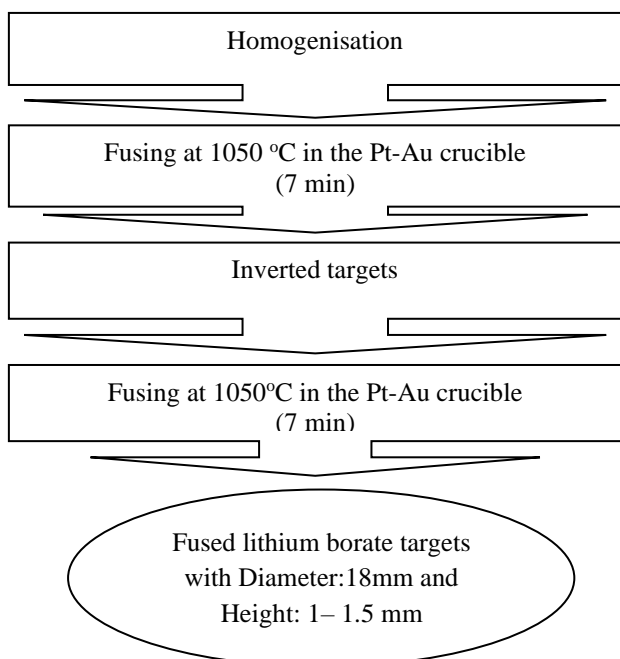
The production of the homogeneous glass targets required a unique method of melting referred to as alkali fusion, which described as follows:

The powdered material, which weighed approximately 100 mg, was homogenized after being combined through a lithium-borate combination (1: 5). To raise the laser photons quantity that the fused lithium-borate target was able to absorb at a wavelength of 266 nanometers, a UV laser light absorber (Fe<sub>2</sub>O<sub>3</sub>) was added to the lithium-borate/sample combination and then homogenized. The uniform combination was fused in a muffle kiln at 1050 °C utilizing a Pt-Au crucible twofold for seven minutes (with an overturn of the target). The entire process was additionally utilized to prepare blank samples. Secondary ion mass spectrometry (SIMS) was utilized to evaluate the generated fused targets for their level of homogeneity.

**Table (1): ICP–MS and LA–ICP–MS instrumentation characteristics utilized for elemental analysis**

ICP-MS	
RF power	1350 W
Auxiliary rate gas flow	1.4L/min
Cooling rate gas flow	15 L/min
Carrier rate gas flow	0.95 L/min
Skimmer cone	Ni, orifice diameter (0.9 mm)
Sampler cone	Ni, orifice diameter (1.1 mm)
Laser Ablation System	
Laser type	Nd: YAG laser (Q-switched)
Repetition frequency	20Hz
Wavelength	266 nm
Raster width	5mm x 5mm
Power density	$10^{10}$ w/cm <sup>2</sup>

Samples:	Blank:
≈ 100 mg powdered sample ≈ 50 mg Fe <sub>2</sub> O <sub>3</sub> ≈ 750 mg lithium borate combination (90% Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 10% LiBO <sub>2</sub> ) All quantity: 900 mg	≈ 50 mg Fe <sub>2</sub> O <sub>3</sub> , ≈ 750 mg lithium borate combination (90% Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 10% LiBO <sub>2</sub> ) All quantity: 800 mg

**(a) The resulting fused pellet      (b) Fused pellet after laser shot****Fig. (1): Scheme for preparation of fused pellets of silicate minerals or rocks.****RESULTS AND DISCUSSION**

LA-ICP-MS is utilized to perform analyses on a number of standard reference materials whose compositions are already well-established to appraise the precision and accuracy of the two different methods of analysis. The values that have been reported here are applicable, in general, to the analysis of solid materials in which ablation begins at the sample surface. However, they do not necessarily apply to the analysis of fluid, in which the precision and accuracy are related, among other things, to the size of the inclusions and the depth beneath the surface.

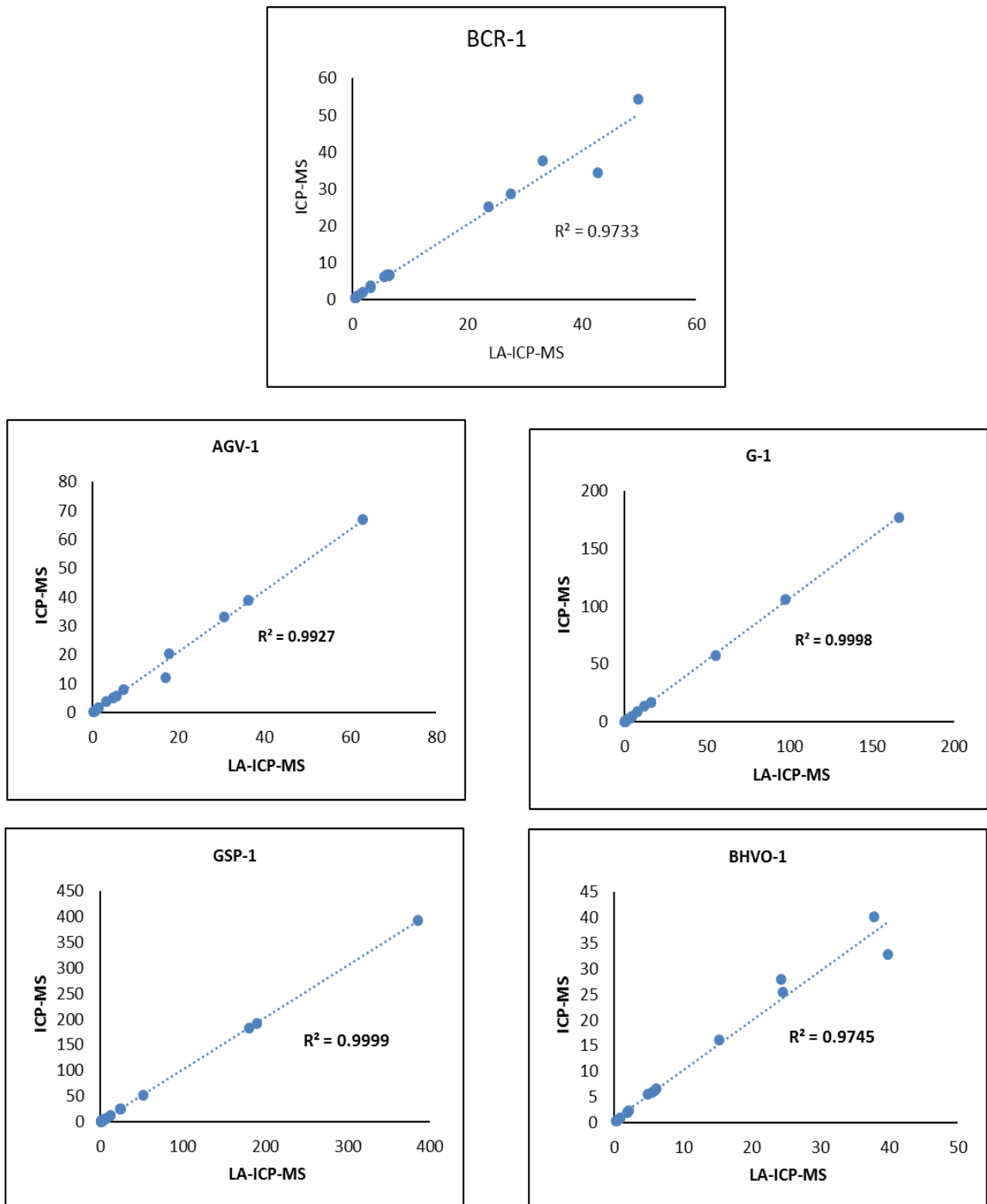
The NIST 614 glass was utilized as the reference to appraise the precision and accuracy of the analyses, and it was used as the external standard. After that, each additional standard was examined as unknown, assuming that the measured elements reflect 100% of the sample.

The samples AGV-1 (andesite), GSP-1 (granodiorite), BHVO-1 (basalt), BCR-1 (basalt), and G-1 (granite) from the USGS standard collection were examined. The precision of the measurements is provided as the percent relative standard deviation (RSD%) for each element. This value is obtained by dividing the standard deviation by the average concentration, and it is used to report the precision of the measurements. In other words, the RSD% provides an estimate of how consistent the measurements of the same standard are, which is often referred to as the reproducibility of the measurement.

Rare earth elements (REEs) can be measured using liquid or solid standards. Tables (2 to 6) display the obtained results for both liquid and solid samples, with the reference values included for each standard. The precision and accuracy of the measured standards were assessed for each standard individually. The accuracy of the measurements is presented for each constituent. It is determined by taking the average of the disparities between each analysis's results and the standard's known concentration. An approximation of the degree of dissimilarity between the calculated and known concentrations can be derived from the average percent error value. The accuracy of the analyses was reported as an average percent error by LA-ICP-MS of better than 10% for the rare earth elements in BCR-1, GSP-1, AGV-1, BHVO-1, G-1, and NIST 612; for liquids, the error was determined to be within 1-5%. In standards BCR-1 and BHVO-1, the R<sup>2</sup> (Fig.2) was found to be 0.933 and 0.9745, respectively. While R<sup>2</sup> is

better in the other standards (0.999, 0.995, and 0.9945) for Standards AGV-1, G-1, and GSP-1, respectively, this may refer to the matrix composition for each

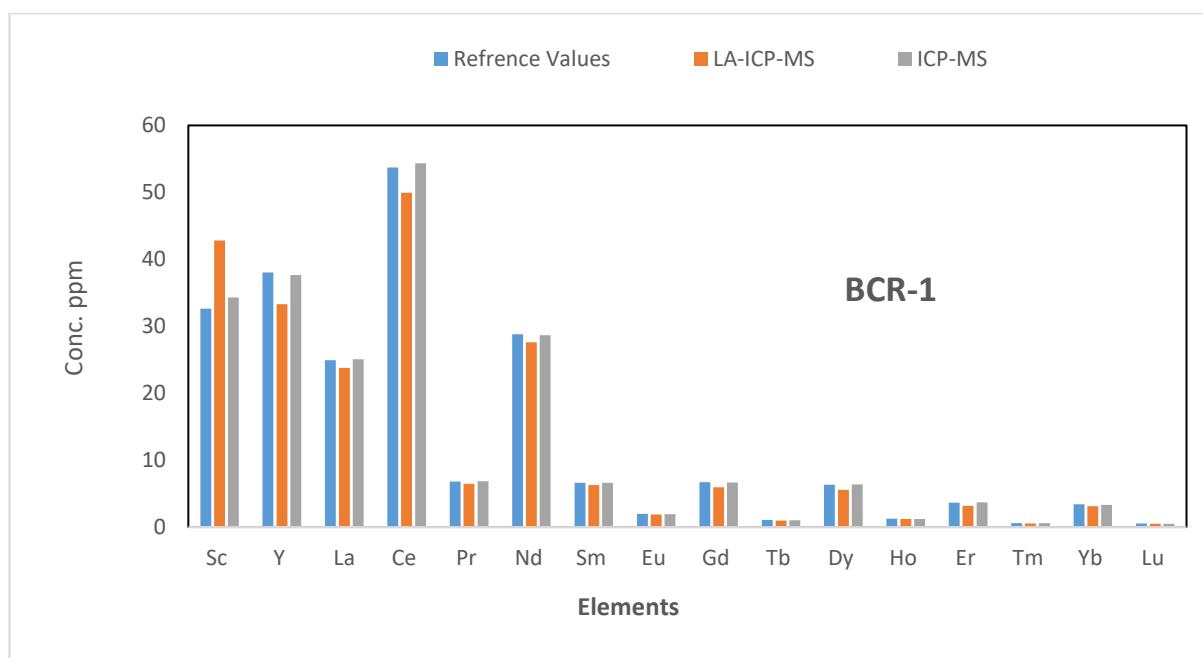
standard. Comparison of the results from LA-ICP-MS and ICP-MS with reference amounts are summarized in Fig.3 to Fig.7.



**Fig. (2):** Correlation between LA-ICP-MS and ICP-MS in BCR-1, AGV-1, G-1, GSP-1 and BHVO-1 (using Ce as an accuracy correlation check element).

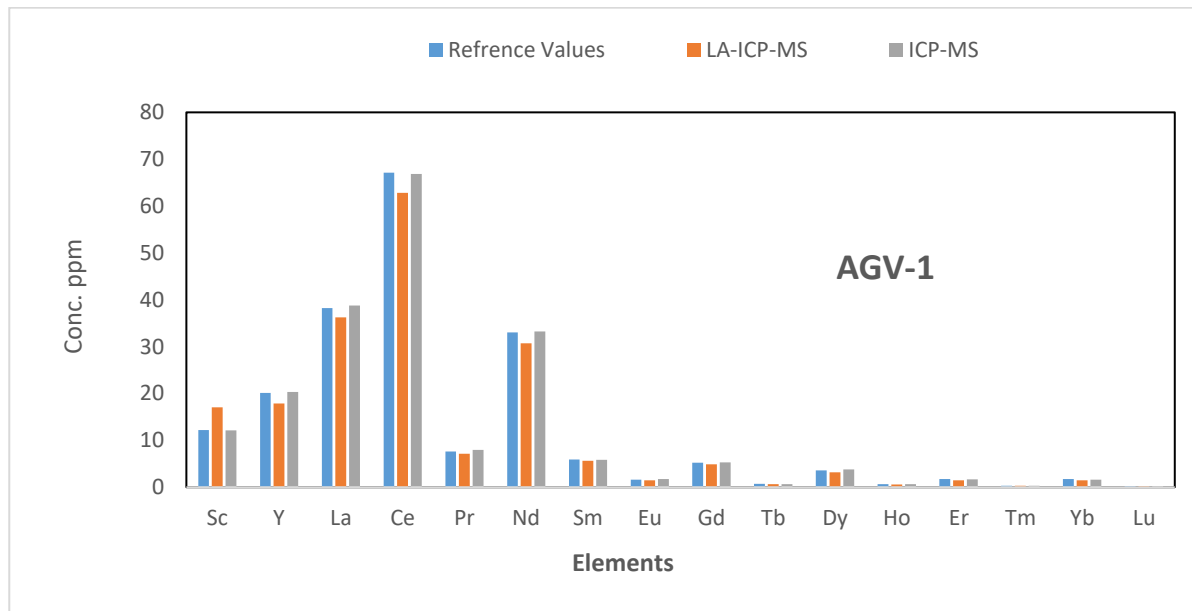
**Table (2): REEs analysis with Precision and accuracy of BCR-1 utilizing LA-ICP-MS and ICP-MS Compared to reference values.**

Element	BCR-1						
	Reference value (ppm)	Measured value (ppm)		RSD%		Accuracy	
		LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Sc	32.60	42.80	34.32	0.57	0.44	31.29	5.28
Y	38.01	33.29	37.65	3.58	1.54	12.39	0.92
La	24.9	23.77	25.08	2.41	0.52	4.54	0.71
Ce	53.7	49.95	54.34	3.46	0.69	6.98	1.18
Pr	6.81	6.44	6.85	2.38	0.67	5.29	0.78
Nd	28.80	27.62	28.66	3.01	0.62	4.17	0.48
Sm	6.59	6.29	6.61	5.34	0.59	4.55	0.29
Eu	1.95	1.86	1.93	5.27	0.57	4.62	0.97
Gd	6.68	5.94	6.66	4.81	0.56	11.08	0.37
Tb	1.05	0.95	1.02	4.31	0.81	9.24	5.24
Dy	6.34	5.54	6.36	2.83	0.71	12.62	0.35
Ho	1.26	1.19	1.21	3.29	0.32	5.95	3.73
Er	3.63	3.15	3.68	5.33	0.76	13.22	1.32
Tm	0.56	0.54	0.59	3.35	0.18	4.107	1.96
Yb	3.38	3.12	3.29	3.46	0.73	7.69	2.63
Lu	0.51	0.48	0.49	8.13	1.23	5.88	4.12

**Fig. (3): REEs Concentration analysis utilizing LA-ICP-MS and ICP-MS compared to reference values for BCR-1 SRM.**

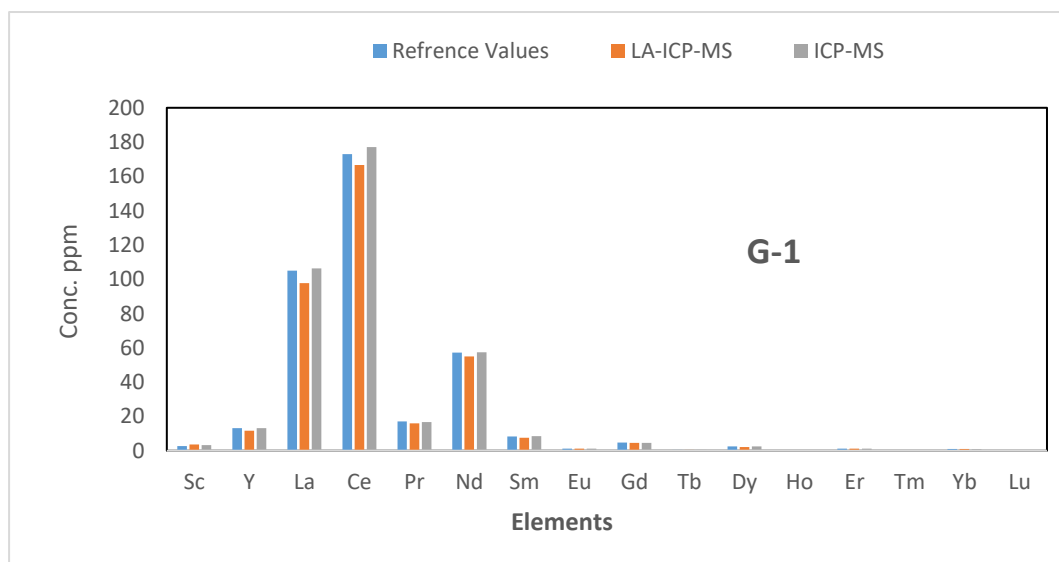
**Table (3): REEs analysis with Precision and accuracy of AGV-1 utilizing LA-ICP-MS and ICP-MS Compared to reference values.**

Element	Reference value (ppm)	AGV-1					
		Measured value (ppm)		RSD%		Accuracy	
		LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Sc	12.21	17.06	12.11	0.64	0.437	39.84	0.75
Y	20.11	17.86	20.32	2.01	1.414	10.715	1.48
La	38.21	36.25	38.77	0.91	0.35	4.61	2.02
Ce	67.13	62.85	66.82	1.218	0.54	6.19	0.32
Pr	7.62	7.15	7.97	2.392	0.87	5.97	4.842
Nd	33.01	30.72	33.25	3.086	0.75	6.92	0.75
Sm	5.91	5.61	5.85	5.687	0.62	4.93	0.81
Eu	1.64	1.45	1.75	2.626	1.89	11.77	6.65
Gd	5.21	4.88	5.29	7.935	4.82	2.46	5.71
Tb	0.71	0.64	0.66	7.244	0.61	9.29	5.285
Dy	3.6	3.21	3.81	4.43	2.61	10.97	5.64
Ho	0.67	0.56	0.68	3.191	0.73	15.82	2.09
Er	1.72	1.49	1.68	6.894	2.74	12.12	1.35
Tm	0.34	0.31	0.33	4.966	1.21	11.18	2.06
Yb	1.72	1.48	1.63	7.718	1.16	14.13	5.12
Lu	0.27	0.23	0.27	15.38	2.93	13.33	1.11

**Fig. (4): REEs concentration analysis utilizing LA-ICP-MS and ICP-MS compared to reference values for AGV-1 SRM.**

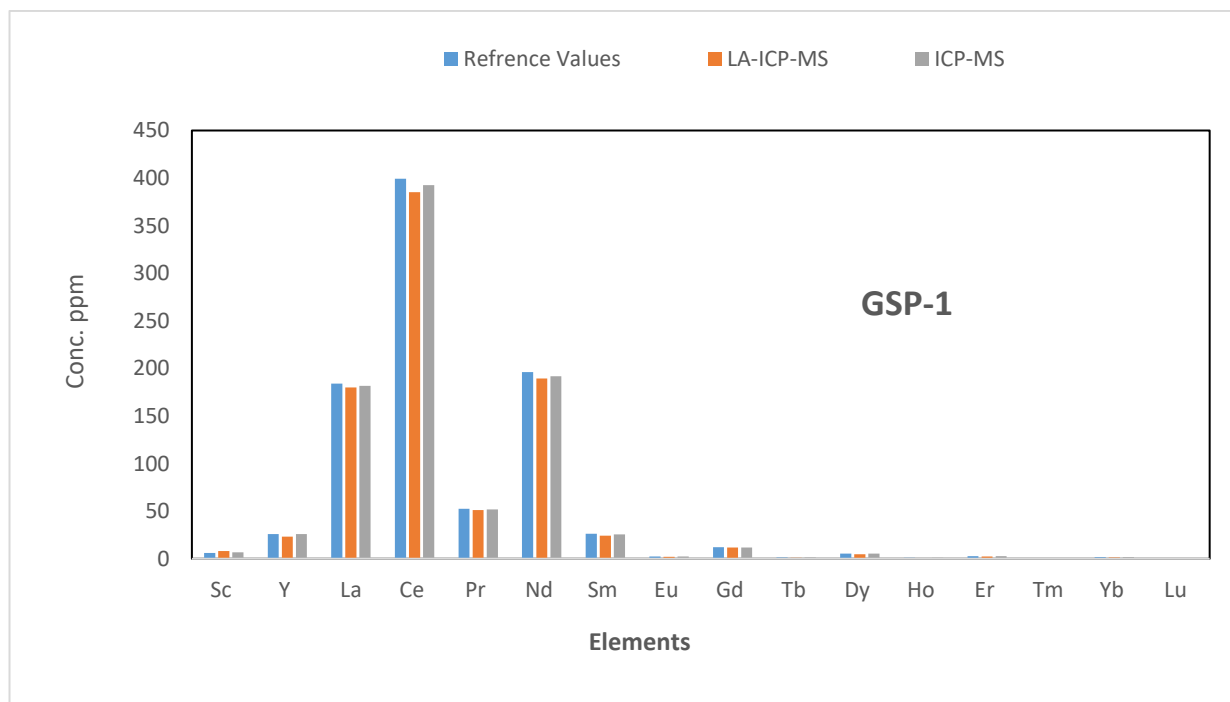
**Table (4): REEs analysis with precision and accuracy of G-1 utilizing LA-ICP-MS and ICP MS compared to reference amounts.**

Element	Reference value (ppm)	G-1					
		Measured value (ppm)		RSD%		Accuracy	
		LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Sc	2.8	3.65	3.208	0.71	0.59	30.21	14.57
Y	13.11	11.73	13.19	1.55	0.95	9.79	1.476
La	105.02	97.73	106.32	3.39	1.11	6.92	1.24
Ce	173.03	166.59	177.02	2.14	0.65	3.71	2.33
Pr	17.11	16.04	16.81	0.42	0.31	5.68	1.18
Nd	57.22	55.08	57.43	5.24	0.49	3.38	0.75
Sm	8.32	7.54	8.46	11.62	0.58	9.18	1.98
Eu	1.22	1.18	1.31	3.32	2.31	3.61	6.64
Gd	4.83	4.67	4.67	1.65	1.18	2.77	2.63
Tb	0.58	0.53	0.57	3.04	1.05	9.31	1.91
Dy	2.45	2.17	2.45	4.88	0.73	9.42	2.17
Ho	0.39	0.33	0.39	2.74	0.76	15.91	1.03
Er	1.32	1.21	1.28	1.99	0.94	7.08	1.307
Tm	0.15	0.13	0.14	3.01	0.69	11.33	4.01
Yb	1.01	0.96	0.95	5.85	2.74	4.31	5.11
Lu	0.156	0.18	0.16	6.74	3.18	14.11	0.64

**Fig. (5): REEs concentration analysis utilizing LA-ICP-MS and ICP-MS compared to reference amounts for G-1 SRM.**

**Table (5): REEs analysis with Precision and accuracy of GSP-1 utilizing LA-ICP-MS and ICP-MS compared to reference amounts.**

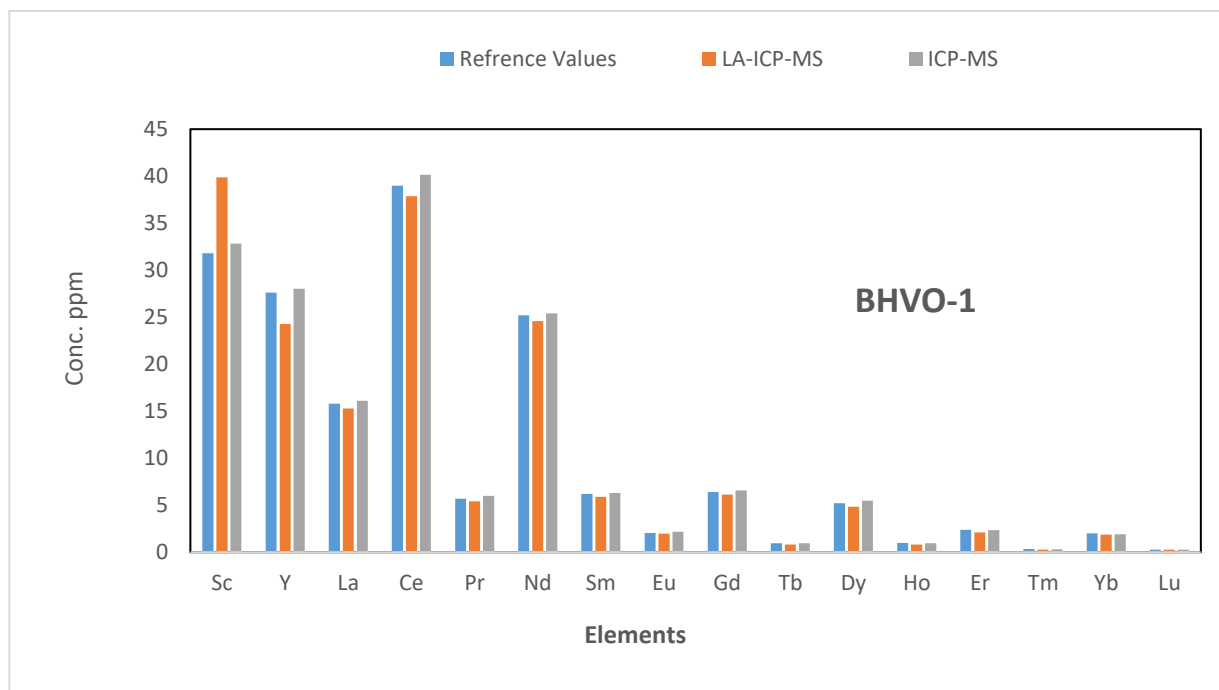
Element	Reference value (ppm)	GSP-1					
		Measured value (ppm)		RSD%		Accuracy	
		LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Sc	6.2	8.15	6.94	0.80	0.22	31.39	11.85
Y	26.12	23.30	25.81	0.20	0.15	10.58	0.73
La	184.17	179.90	181.85	2.90	1.61	2.23	1.17
Ce	399.33	385.30	392.64	0.73	0.55	3.43	1.61
Pr	52.45	51.36	51.82	4.11	3.03	1.23	0.34
Nd	196.22	189.60	191.76	3.30	2.51	3.27	2.17
Sm	26.33	24.14	25.48	2.25	0.85	8.21	3.13
Eu	2.33	2.25	2.30	1.69	1.31	3.43	1.51
Gd	12.14	11.70	11.91	6.84	1.66	3.28	1.55
Tb	1.34	1.13	1.29	4.80	1.24	15.97	3.66
Dy	5.51	4.89	5.45	2.35	1.39	11.09	0.89
Ho	1.01	0.85	0.98	1.88	0.82	15.74	3.37
Er	2.72	2.38	2.81	2.57	1.24	12.01	4.15
Tm	0.38	0.34	0.36	3.25	0.83	11.05	5.12
Yb	1.73	1.53	1.66	6.61	1.08	10.10	2.41
Lu	0.21	0.20	0.20	3.03	1.97	7.476	5.14

**Fig. (6): REEs concentration analysis utilizing LA-ICP-MS and ICP-MS compared to reference amounts for GSP-1 SRM.**



**Table (6): REEs analysis with Precision and accuracy of BHVO-1 utilizing LA-ICP-MS and ICP-MS compared to reference amounts.**

Element	Reference value (ppm)	BHVO-1					
		Measured value (ppm)		RSD%		Accuracy	
		LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS	LA-ICP-MS	ICP-MS
Sc	31.80	39.86	32.84	1.48	0.66	25.33	3.28
Y	27.60	24.29	28.01	0.97	0.52	11.99	1.48
La	15.80	15.28	16.10	0.89	0.73	3.29	1.91
Ce	39.00	37.86	40.14	0.46	0.39	2.93	2.92
Pr	5.70	5.42	5.98	1.493	0.95	4.86	4.84
Nd	25.20	24.58	25.39	2.26	0.87	2.45	0.75
Sm	6.20	5.89	6.32	2.07	0.46	5.08	1.97
Eu	2.06	1.98	2.20	0.96	0.68	3.88	6.65
Gd	6.40	6.13	6.56	5.07	3.28	4.23	2.56
Tb	0.96	0.81	0.95	9.79	1.27	15.94	1.25
Dy	5.20	4.83	5.49	2.45	2.06	7.19	5.63
Ho	0.99	0.83	0.96	4.20	1.15	15.86	3.33
Er	2.40	2.10	2.37	1.76	0.76	12.50	1.33
Tm	0.33	0.29	0.32	5.46	0.63	11.21	3.94
Yb	2.02	1.88	1.92	5.85	1.62	6.98	5.10
Lu	0.29	0.26	0.29	3.86	3.74	10.99	1.03

**Fig. (7): REEs concentration analysis utilizing LA-ICP-MS and ICP-MS compared to reference amounts for BHVO-1 SRM.**

## CONCLUSION

The sample preparation used for obtaining homogenous targets for LA-ICP-MS from heterogeneous geological (or procedural) acceptable powdered samples (100 mg) via lithium-borate fusion is uncomplicated, quick, inexpensive, and simple to work. It may be utilized in every normal laboratory. While the fusion of geological samples (50–100 mg), which calls for a specialized apparatus operating at substantially higher temperatures, is impossible without prior preparation. The results of LA-ICP-MS performed on fused geological targets with lithium-borate showed acceptable agreement with the results of the analysis performed on direct fused glass targets. Measurements using a secondary ion mass spectrometer (SIMS) showed that fused geological targets with lithium-borate and melted glassy targets had an element distribution consistent throughout.

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