

DIRECT ANALYSIS OF TERRESTRIAL AND METEORITE SAMPLES USING LASER-ABLATION INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY. M.R. Smith, D.W. Koppenaal, D.C. Gosselin and J.C. Laul, Battelle Pacific Northwest Laboratories, Richland, WA 99352.

Mass spectrometric methods have long been used to determine isotopic trace element ratios as well as trace to ultratrace elements in various matrices. The ICP/MS technique employs the popular ICP emission source as an ion source for mass spectrometric determination of elemental isotope ratios and/or concentrations. Unlike thermal ionization-high resolution mass spectrometry, the low resolution and detection method characteristics of quadrupole mass spectrometer preclude present ICP/MS systems from obtaining ultra-precise isotopic ratio determinations. However, the advantage of this analytical tool is its versatility for accepting virtually any sample form (liquids, solids, gasses). Conventional ICP/MS involves sample introduction as solutions; however, the ICP can serve as an ionization source for any sample form provided the sample is introduced as sub-micron sized particles. Besides introducing nebulized liquids (aqueous and organic) and gasses (halides and hydrides), we have been experimenting with solids introduction by ablation using a Nd:YAG laser. The use of lasers to ablate or vaporize solid samples for direct injection into an ICP provides an attractive alternative to solution sampling, especially for clasts, chondrules, glasses or mineral grains which require microanalytical, spatially resolved compositional information.

The laser ablation (LA) sampling capability involves the use of a 0.5-1 Joule Nd:YAG laser operated in either a Q-switched or normal pulse mode. Depending on the sensitivities required, the laser power and pulse rate can be adjusted (100-1000 mJ and 1-15 pulses per second). Typically, about 2 minute acquisition times covering 240 amu and a 5 Hz pulse rate have provided ng/g detection limits for most elements (Table 1). Sampling heterogeneities were minimized by rastering the laser shots over a prespecified area. For the powdered geologic standards, approximately 3 mm² areas were ablated, consuming about 3 mg of sample.

The laser focusing capability (10-100 μm) allows analysis of individual minerals or clasts without physical separation of their respective rock matrix. Although the laser used in this work has a focusing limit of approximately 10 μm , it is possible, through frequency doubling, to obtain <1 μm spot sizes.

RESULTS and CONCLUSIONS: The results shown in Table 1 indicate that this method may be used to detect >60 elements (45 reported) simultaneously in solid samples. The data was quantified using BHVO (in noted cases, BCR) for standardization. A major factor influencing the accuracy of this method is a change in mass sensitivity between sample and standard determinations due to differences in transport efficiencies and the unavoidable accumulation of molten sample on the sampling interface. These sensitivity changes were calculated for each of the standards based on reported concentrations [1, 2, 3]. Using elements with well known concentrations and relatively low volatilities, curves were generated which were found to be essentially parallel and provided a normalization factor to account for differences in ablation and transport efficiencies. Volatile element sensitivity (e.g., Sb, Cd, Tl, Bi, etc.) was enhanced; however, good agreement between our LA data and literature results (Table 1) indicates that this enhancement is reproducible. Determination of the normalization factors for the unknown samples were obtained by assuming a composition for the REEs in the sample, usually chondrite abundances. Although this may not be completely appropriate, this approach does yield reasonable results (see below). Some of the major elements were

excluded from Table 1 because their high concentrations resulted in detector saturation.

Based on triplicate analyses (not shown) a precision of 10% is achievable. Relative to literature values, this preliminary study suggests accuracies of 10-30% for most elements with >5 ng/g concentrations.

One of the most important potential applications for this analytical tool is its ability to determine in situ trace element concentrations of minerals, chondrules, glass beads, etc. To assess this capability, a white clast (~0.2 mm²) within the Allende matrix, an area assumed to represent the Dhajala matrix (~1 mm²), and a chondrule (~0.1 mm²) from Dhajala were ablated and analyzed. The assumption of chondritic REE abundances for these samples, especially the Allende clast, appears to be justified in that the use of significantly different values results in unreasonable major element concentrations. Our analysis of the Dhajala matrix shows distinctly lower Fe, Ni, Co compared to those reported by [4], suggesting that the Dhajala matrix sampled (0.6 mg) is dominated by silicates. The Dhajala chondrule is distinctly lower in Co and Ni relative to the matrix suggesting a further reduction in the metal component. High Mg concentrations in the Dhajala chondrule and presumably in its matrix, where Mg concentrations resulted in detector saturation, indicates a predominance of enstatite.

REFERENCES [1] Flanagan F.G. (1972) U.S.G.S. Prof. Paper 840, 192p. [2] Lau J.C. (1979) Atomic Energy Review, 173, 603-695. [3] Jarosewich E., Clark Jr., R.S. and Barrows J.N., (1987) Smithsonian Contrib. Earth Sciences, 27, 49p. [4] Sears D.W. and Weeks K.S. (1986) GCA 50, 2818.

	BCR [1,2]			ALLENDE [3]			AGV [1,2]			DHAJALA	
	RUN 2	RUN 3	PUBL	RUN 3	PUBL	CLAST	RUN 3	PUBL	MATRIX	CHONDR	
(%)											
Mg	1.80	1.81	2.10	8.82	14.83	17.7	1.00	0.80		25.83	
Fe	8.80	8.80	8.80	22.88	22.87	8.22	8.30	4.80	17.70	18.83	
Ca	4.38	4.31	4.84	1.83	1.84	2.08	3.01	3.70	1.88	2.08	
Ti	1.34	1.38	1.32	0.88	0.88	0.73	0.78	0.83	0.87	0.88	
(ppm)											
Be	1.81	1.38	1.70	0.10	0.03	0.18	2.83	3.00	0.08	0.17	
B	1.84	1.75	2.00	0.85	1.00	2.33	4.38	8.00	4.48	1.88	
Cr	13	13	18	3884	3848	8621	17	13	8128	8172	
Mn	1381	1411	1380	1478	1472	1391	848	750	3343	3872	
Co	33 (std)	38	884	800	422	18	18	188	37	37	
Ni	18	12	10	14218	14200	8889	20	11	4487	289	
Cu	18	18	18	100	118	60	81	80	88	30	
Zn	141	138	130	111	110	118	123	88	71	88	
Ga	23	20	22	7	8	8	20	21	8	7	
Ge	1.4	1.2	1.8	7.8	18.0	8.7	0.7	1.3	4.8	2.1	
As	0.80 (std)	0.70	3.1	2.0	3.4	0.40	0.80	8.7	2.8		
Sr	80.0 (std)	88.8	3.8	1.2	4.1	87.0	87.0	3.8	8.0		
Rb	334	312	330	18	12	18	87.8	88.7	11	8.4	
Y	42.8	41.8	37.1	2.8	3.1	4.8	22.3	21.3	2.1	2.8	
Zr	188	181	188	8	8	8	238	208	8	8.80	
Nb	13.8	13.4	13.8	0.8	0.8	0.8	17.1	18.0	8.48	8.83	
Mo	1.3	1.4	1.1	1.0			2.1	2.3	8.38	8.20	
Cd	0.18	0.17	0.14	0.32	0.80	0.18	0.88	0.88	0.82	0.88	
Sb	2.18	2.23	2.80	0.82	0.30	1.10	4.88	4.20	3.80	3.32	
Sn	0.88 (std)	0.70	0.23			0.084	4.88	4.80	0.882	0.882	
CS	0.88 (std)	0.88	0.74	0.10	0.17		1.0	1.2	0.21	0.28	
Ba	848	847	878	8	4	11	828	1240	3	4	
La	28.8	30.1	28.0	0.81	0.82	0.83	38.7	37.1	8.47	8.48	
Ce	88.1	88.4	83.8	8.2	1.3	2.0	72.8	70.3	8.80	1.18	
Pr	7.4	7.5	7.8	0.23	0.21	0.27	7.7	8.8	0.13	0.22	
Nd	32.0	31.8	28.0	1.0	1.0	1.2	28.8	32.8	0.84	0.78	
Sm	7.00	7.33	8.80	0.41	0.34	0.22	8.38	8.80	0.23	0.80	
Eu	1.88	1.88	2.00	0.11	0.11	0.11	1.33	1.81	0.888	0.882	
Gd	8.08	8.23	8.70	0.38	0.42	0.88	4.07	8.40	0.21	0.32	
Tb	1.28	1.28	1.04	0.078	0.081	0.082	0.88	0.83	0.048	0.082	
Dy	8.78	8.23	8.30	0.37	0.42	0.88	2.88	3.70	0.28	0.40	
Ho	1.28	1.27	1.28	0.88	0.18	0.13	0.88	0.80	0.880	0.873	
Er	3.18	3.14	3.80	0.23	0.28	0.44	1.37	1.28	0.18	0.18	
Tm	0.48	0.80	0.88	0.083	0.088	0.078	0.28	0.28	0.038	0.037	
Yb	3.42	3.88	3.38	0.28	0.30	0.37	1.44	1.70	0.20	0.28	
Lu	0.88	0.81	0.88	0.048	0.052	0.084	0.28	0.24	0.033	0.044	
Hf	4.4 (std)	4.7	0.18	0.21	0.22		3.8	8.1	0.13	0.28	
Ta	0.73 (std)	0.80	0.84		0.047		0.78	0.81	0.017	0.082	
Pb	18 (std)	18	3.8	1.4	0.88		38	38	18	48	
Bi	0.031	0.038	0.048	0.084	0.028	0.031	0.038	0.087	0.007	0.007	
Th	8.7 (std)	8.8	0.128		0.017		8.8	8.4	0.038	0.038	
U	1.7 (std)	1.8	0.028	0.018	0.048		1.8	1.8	0.014	0.038	

Table 1