

Technical Note: Utilizing the 193nm Analyte G2 Excimer Laser Ablation System and the Agilent 7700 ICP-MS

INTRODUCTION

The Analyte G2 is the product of more than a decade of innovative LA-ICP-MS instrumentation design and development from one of the most experienced teams in the industry. CETAC / Photon Machines excimer laser ablation systems are the #1 brand in the Americas and are now available globally.

The Analyte G2 laser ablation platform was engineered for one purpose - precision solid sampling in noble gas MS, quadrupole, high resolution, and multi-collector ICP-MS. The system incorporates the ***ultra-short sub-4ns pulse excimer laser from ATL-Lasertechnik with patented pre-ionization***, and is equipped with a number of innovations including:

- Diffractive optical laser beam homogenization for flat craters without micro-fracturing
- 100 mm travel, high accuracy, high speed XYZ stages
- High definition color CCD camera zoom video microscope
- High capacity sample cells
- Live, wide-angle (2nd) color CCD camera for instantaneous navigation throughout the sample chamber
- Fire-on-the-fly motion controlled lasing, the only means to depth profile lines and raster areas
- Flood, reflected and transmitted lighting with cross polarizers
- Auto evacuation of sample cells for rapid ICP-MS settling
- 30 different apertures interchangeable with custom selections
- Spot sizes down to <3 μm

The Analyte G2 consists of hardware, electronics and software that are field-proven and configured to provide versatile utility and seamless connectivity with the ICP-MS for greater control over the ablation process.

ANALYTICAL SET-UP

The Agilent 7700 was connected to the CETAC / Photon Machines Analyte G2 excimer laser ablation system in order to facilitate direct elemental analysis of solid samples. Laser ablation sampling provides the analyst with the ability to perform spatially resolved analysis of the solid sample with a minimum of sample preparation.

The output of the aerosol line from the laser system was connected via a 'y' connector to the injector of the torch on the ICP-MS. A make-up argon gas line was connected at this point. Triggering of the mass spectrometer was facilitated using the external trigger feature of the Analyte G2 and the remote start mechanism of the Agilent 7700.



DETECTION LIMITS

A series of ten analyses were performed on NIST 612 glass. The laser spot size was 60 microns, the fluence was 9J/cm², the repetition rate was 10Hz and the analysis time was 60 seconds. The detection limits are in parts per billion (ppb) for the given element isotope.

Li7	26.65	Nb93	0.77	Eu151	0.97
Mg25	154.40	Mo95	8.19	Gd157	4.09
Sc45	14.97	Cd111	16.82	Tb159	0.50
Ti49	59.80	Sn118	9.06	Dy163	2.14
V51	7.85	Sb121	12.52	Ho165	0.47
Cr53	101.89	Cs133	4.65	Er167	2.38
Mn55	27.87	Ba137	5.74	Tm169	0.52
Fe57	258.00	La139	0.62	Yb173	3.79
Co59	4.68	Ce140	0.56	Lu175	0.67
Ni60	16.94	Pr141	0.42	Hf177	2.23
Cu65	21.90	Nd146	3.39	Ta181	0.66
Zn66	46.58	Sm147	3.56	W182	3.02
As75	101.69	La139	0.62	Tl205	1.85
Rb85	5.95	Ce140	0.56	Pb208	3.50
Sr88	0.64	Pr141	0.42	Th232	0.82
Y89	0.67	Nd146	3.39	U238	0.83
Zr90	1.36	Sm147	3.56		

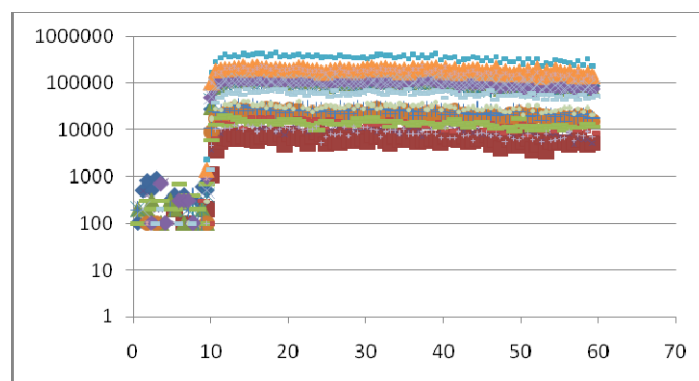
These detection limits are excellent for a 60 micron spot and demonstrate the detection power of the Analyte G2 and Agilent 7700 combination. The Analyte G2 is unique in that its ablation cell options have been optimized to efficiently entrain ablated material. Washouts as fast as 1s to 0.1% of the original signal have been noted with the HelEx two volume cell! This ability to efficiently sweep out the material provides the best possible detection limits while ensuring there is no chance of sample to sample contamination. The active cup technology in the HelEx two volume cell is unique to CETAC / Photon Machines.

ANALYSIS

The U.S. Geological Survey notes that in the geo sciences, reference materials are very important because they help us develop a better understanding of the processes that have shaped and continue to shape the world around us. The USGS has and no doubt will continue to develop a series of reliable reference materials.

This work includes data from the analysis of three of these materials, all of which are basaltic glass standard reference materials. The Analyte G2 / Agilent 7700 system was calibrated using NIST612 as the calibration standard. Each analysis was approximately 60 seconds in length and included an in-run time period for the gas blank. The data was exported from the Agilent 7700 into 'Glitter' laser ablation data processing software and a single point calibration was set up using the NIST612 with Calcium as the internal standard. BIR1G, BCR2G, and BHVO2G were then all subjected to analysis.

A series of ten analyses was performed for each sample. The laser spot size was 60 microns, the fluence was 9J/cm², the repetition rate was 10Hz and the analysis time was 60 seconds. Graph 1 shows the time resolved data for elements during the 60 seconds analysis. The data is presented in Tables 1, 2, and 3.



Graph 1. Time resolved data plot for sixty second laser ablation analysis. This sample is the first NIST612 calibration standard.

Table 1. Data for BIR1G

All data is expressed as parts per million (ppm). The preferred and the compiled range data come from the GeoReM database which can be found at georem.mpch-mainz.gwdg.de.

BIR1G	GeoReM	GeoReM	GeoReM	G2/7700	G2/7700
Element	Preferred	Range (from)	Range (to)	MEAN	STD DEV
Sc45	43	40.200	46.100	43.670	0.595
V51	326	294.000	370.000	346.983	3.165
Cr53	392	364.000	507.000	410.174	5.717
Co59	52	47.700	63.000	57.214	0.792
Ni60	178	151.000	211.000	191.103	2.817
Cu65	119	109.000	132.000	130.356	2.090
Zn66	78	59.200	98.000	86.599	0.983
Rb85	0.197	0.000	0.260	0.221	0.018
Sr88	109	87.000	118.000	109.640	0.931
Y89	14.3	11.000	15.900	13.477	0.196
Zr90	14	11.960	17.800	13.074	0.258
Nb93	0.52	0.460	0.650	0.522	0.016
Mo95	0.075	0.075	0.096	0.072	0.019
Cd111	0.14	0.114	0.220	0.107	0.041
Sb121	0.56	0.470	0.630	0.616	0.020
Cs133	0.007	0.005	0.013	0.008	0.004
Ba137	6.5	5.660	7.010	6.591	0.187
La139	0.609	0.539	0.910	0.585	0.022
Ce140	1.89	1.660	2.200	1.934	0.047
Pr141	0.37	0.330	0.450	0.359	0.015
Nd146	2.37	2.100	2.600	2.327	0.074
Sm147	1.09	0.980	1.260	1.082	0.041
Eu151	0.517	0.459	0.570	0.494	0.021
Gd157	1.85	1.200	1.970	1.703	0.084
Tb159	0.35	0.290	0.414	0.318	0.010
Dy163	2.55	2.000	2.730	2.410	0.075
Ho165	0.56	0.470	0.599	0.518	0.016
Er167	1.7	1.300	1.790	1.630	0.057
Tm169	0.24	0.190	0.260	0.232	0.009
Yb173	1.64	1.300	1.790	1.586	0.071
Lu175	0.248	0.200	0.270	0.225	0.015
Hf177	0.57	0.449	0.640	0.550	0.026
Ta181	0.036	0.026	0.087	0.037	0.004
Pb208	3.7	2.980	4.250	3.712	0.091
Th232	0.03	0.027	0.041	0.029	0.004
U238	0.023	0.013	0.075	0.021	0.004

Table 2. Data for BCR2G

BCR2G	GeoReM	GeoReM	GeoReM	G2/7700	G2/7700
Element	Recommended	Range		Mean	SD
Sc45	33.00	29.79	37.10	35.37	0.39
V51	425.00	374.00	457.00	444.75	5.94
Cr53	17.00	13.00	20.40	15.49	0.52
Co59	38.00	35.00	48.75	39.74	0.67
Ni60	13.00	10.10	51.00	12.72	0.34
Cu65	21.00	15.50	66.00	18.87	0.45
Zn66	125.00	120.30	210.00	161.62	2.75
Rb85	47.00	38.00	63.85	51.19	1.37
Sr88	342.00	282.00	373.00	342.73	7.59
Y89	35.00	27.67	39.40	33.13	0.71
Zr90	184.00	143.58	209.00	180.66	3.61
Nb93	12.50	10.22	30.40	12.56	0.24
Mo95	270.00	230.00	300.00	272.01	6.21
Cd111	0.20	0.00	0.51	0.20	0.06
Sb121	0.35	0.30	0.51	0.36	0.02
Cs133	1.16	1.00	1.54	1.24	0.04
Ba137	683.00	571.00	780.00	696.62	14.49
La139	24.70	22.40	27.00	24.86	0.43
Ce140	53.30	41.60	57.03	53.52	0.84
Pr141	6.70	5.90	7.60	6.57	0.12
Nd146	28.90	24.50	32.00	28.92	0.44
Sm147	6.59	5.87	7.35	6.65	0.14
Eu151	1.97	1.60	2.27	1.90	0.04
Gd157	6.71	5.50	8.10	6.47	0.12
Tb159	1.02	0.90	1.20	0.97	0.02
Dy163	6.44	5.30	7.00	6.36	0.08
Ho165	1.27	1.10	1.40	1.27	0.02
Er167	3.70	3.10	4.02	3.63	0.06
Tm169	0.51	0.40	0.59	0.52	0.01
Yb173	3.39	2.60	3.72	3.39	0.09
Lu175	0.50	0.40	0.56	0.50	0.01
Hf177	4.84	3.88	5.43	4.67	0.08
Ta181	0.78	0.57	0.89	0.80	0.02
W182	0.50	0.40	0.70	0.55	0.04
Ti205	0.30	0.22	0.40	0.28	0.01
Pb208	11.00	9.60	14.80	11.24	0.19
Th232	5.90	4.30	6.50	5.96	0.12
U238	1.69	1.10	2.07	1.72	0.03

Table 3. Data for BHVO2G

BHVO2G	GeoReM	GeoReM	GeoReM	G2/7700	G2/7700
Element	Preferred	Range		Mean	SD
Sc45	33.00	27.40	36.40	31.39	0.26
V51	308.00	286.00	329.00	340.23	4.24
Cr53	293.00	280.88	307.00	302.28	5.36
Co59	44.00	43.00	51.00	45.94	0.48
Ni60	116.00	112.00	139.00	123.05	2.12
Cu65	127.00	112.00	163.00	122.64	3.75
Zn66	102.00	93.00	154.00	121.65	2.29
Rb85	9.20	8.21	11.00	9.79	0.16
Sr88	396.00	355.00	414.00	404.65	6.01
Y89	26.00	21.51	29.20	22.08	0.31
Zr90	170.00	151.43	180.00	152.37	1.76
Nb93	18.30	15.50	20.00	17.94	0.25
Mo95	3.80	3.64	4.21	4.25	0.08
Cd111	0.10	0.09	0.20	0.08	0.02
Sb121	0.30	0.12	0.39	0.20	0.07
Cs133	0.10	0.09	0.14	0.10	0.01
Ba137	131.00	111.00	139.00	135.59	1.31
La139	15.20	14.60	18.00	14.56	0.17
Ce140	37.60	33.10	45.00	38.07	0.44
Pr141	5.35	4.90	5.77	5.05	0.06
Nd146	24.50	22.70	26.60	23.81	0.41
Sm147	6.10	5.60	6.56	5.80	0.06
Eu151	2.07	1.94	2.22	1.97	0.04
Gd157	6.16	5.62	6.43	5.59	0.12
Tb159	0.92	0.80	0.96	0.80	0.02
Dy163	5.28	4.59	5.55	4.78	0.13
Ho165	0.98	0.86	1.03	0.87	0.03
Er167	2.56	2.12	2.61	2.27	0.05
Tm169	0.34	0.29	0.36	0.30	0.01
Yb173	2.01	1.80	2.69	1.84	0.03
Lu175	0.28	0.25	0.34	0.25	0.01
Hf177	4.32	3.83	4.60	3.82	0.09
Ta181	1.15	0.91	1.30	1.12	0.03
W182	0.23	0.21	0.24	0.25	0.01
Pb208	1.70	1.40	2.64	1.96	0.08
Th232	1.22	1.10	1.50	1.12	0.04
U238	0.40	0.38	0.60	0.45	0.01

CONCLUSIONS

The combination of the CETAC / Photon Machines Analyte G2 and the Agilent 7700 provides the user with a very sensitive, precise, and accurate tool for analysis of solid materials. We see excellent agreement between preferred values, the range of compiled values, and the Analyte G2 and Agilent 7700 combination data for the three basaltic rock glasses. NIST612 is not a matrix match for these basaltic glasses and yet the agreement is very good.

The Analyte G2 is compatible with a full complement of matrices.

The 4ns pulse length and 193nm wavelength lead to exceptional coupling efficiency resulting in sub-micron particles that ionize readily with less fractionation.

This short pulse length delivers 4 GW/cm² of irradiance, 25% more than the 3 GW/cm² of a large, 15 ns pulse length excimer lasers. Irradiance, not fluence, and wavelength (shorter is better) determines the capability of a laser ablation system to tackle all materials.

Using proprietary beam shaping and homogenization technology, the Analyte G2 ablates clean, flat, craters of repeatable shape and size on a wide variety of opaque and transparent materials - from powders, to quartz, to carbonate.

High demagnification delivers energy densities capable of ablating all materials.

30 spot selections ranging from <3 to >250 μm make the Analyte G2 the most versatile instrument of its kind with unique capabilities, ideal for both micro-feature and bulk analysis.

The CCD cameras, video microscope, and laser beam delivery optics, deliver co-linear viewing and lasing perpendicular to the sample. There are no off-axis components that distort the image or require correction.

The Analyte G2 has 100 X 100mm travel X,Y,Z stages and a long working distance (distance between the output of the laser and the sample) that accepts large format and specialized sample chambers. 150 mm X 150 mm stages are optional.

The reliability and affordability of the Analyte G2 in combination with its deep UV 193nm wavelength, ultra-short pulse length, flat beam profile, and surplus energy make it the preferred choice for laser ablation. The Analyte G2 provides the best value (price-performance) of any excimer based system.

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