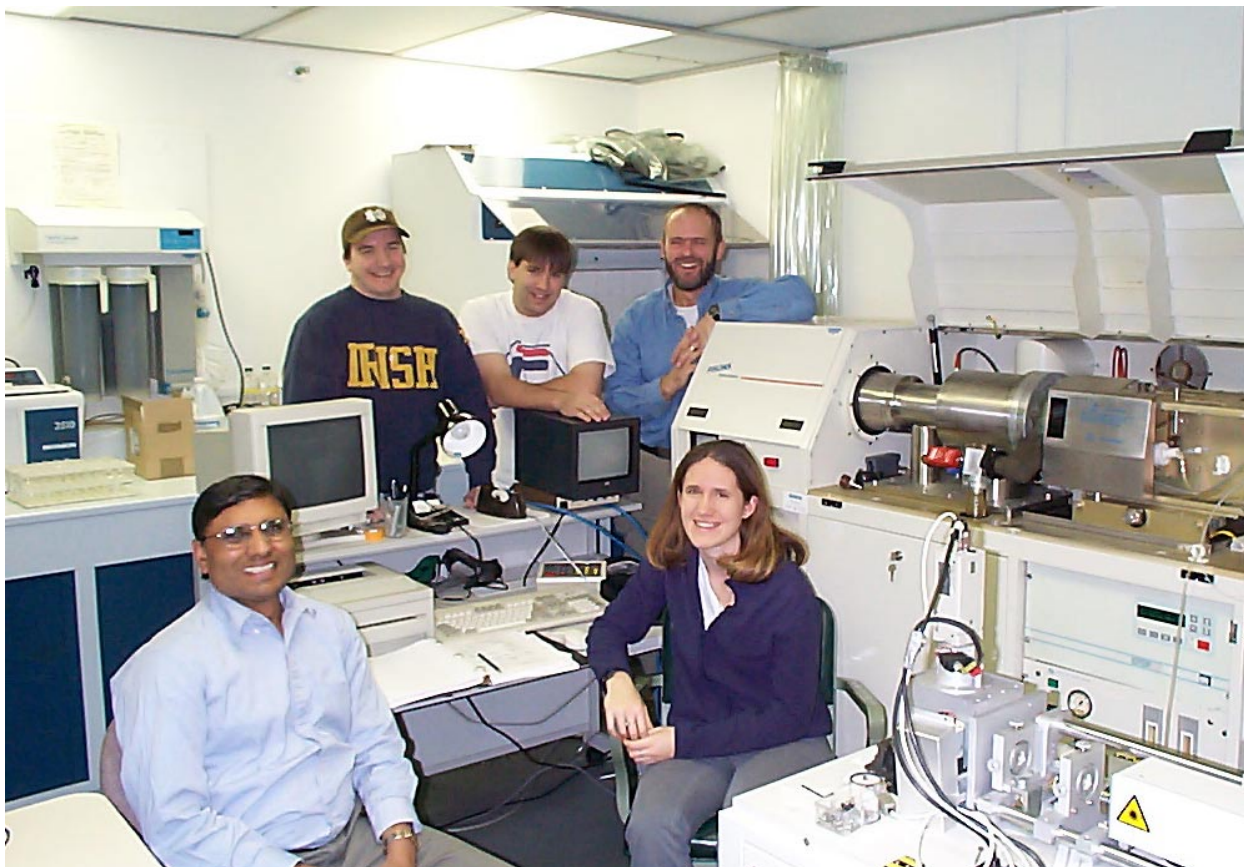


# THE NOTRE DAME INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICP-MS) FACILITY: INTO THE NEW MILLENIUM



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**COVER:** The Notre Dame ICP-MS Facility and personnel. Clockwise from left: Dr. Jinesh C. Jain (Manager), Dr. James C. Ely (Postdoctoral Fellow), Mr. William J. Chazey, III (Ph.D. Candidate), Dr. Clive R. Neal (Director), Ms. Colleen Pepper (Undergraduate Student).  
Not present: Dr. Amy Birkhold (Graduated Ph.D. Student), Dr. Cathleen McMahon (Graduated Ph.D. Student), Mr. James Seidler (Undergraduate Student), Ms. Rebecca Glatz (Undergraduate Student), Ms. Jennifer Ryan (Undergraduate Student).



## INTRODUCTION

The University of Notre Dame ICP-MS facility (Fig. 1 and cover) is operated through the Department of Civil Engineering & Geological Sciences (CE-GEOS) and collaborates with the Center for Environmental Science and Technology (CEST). Strong ties between these two entities have allowed the facility to grow since its inception in 1993 through diverse research and the analysis of samples from within the Notre Dame community, as well as from other universities, industry, and governmental organizations. Scientific links have been forged with many researchers nationally and internationally. Since 1993, the Notre Dame ICP-MS Facility has gained an international reputation through the generation of high quality data and collaborative research.



**FIGURE 1:** View of the ICP-MS Laboratory showing the PQII STE ICP-MS, Electrothermal Vaporization, and Laser Ablation units

The report supercedes that published in 1996 (Jain and Neal, 1996), which detailed the equipment in and documented the activities of the Notre Dame ICP-MS facility up to 1995. Only a brief summary of the facility will be given here and the activities reported here include those just initiated at the time of writing the previous report.



**FIGURE 2:** Damage that resulted from the 1997 fire in the ICP-MS sample preparation laboratory, 112F Cushing Hall.

The ICP-MS Facility was purchased using a combination of money from the National Science Foundation with matching funds furnished by the University of Notre Dame. It is housed in 106 Cushing Hall and is inside a modular, Class 1000 clean laboratory built by Clean Air Technologies, Inc., of Michigan. Currently, the ICP-MS Facility comprises a FISIONS (now VG

Elemental or TJA Solutions) PlasmaQuad II STE, LaserProbe (tuned to 266 nm, but with 532 nm and 1046 nm capabilities), CETAC Ultrasonic Nebulization Unit, Electrothermal Vaporization Unit (Mark IIIa), Hydride Generator, Gilson Autosampler, and a Flow Injector. An ultrapure water system is available within the clean lab (Fig. 1). Sample preparation continues to be conducted in a Class 1000 clean laboratory in 112F Cushing Hall and all acids are double-distilled in-house. A fire in 1997 (Fig. 2 a-d) caused extensive damage to the sample preparation lab and resulted in a 3 month hiatus and extensive damage. The repairs resulted in a more efficient air handling system being installed and the quality of data produced has remained high.

### **LABORATORY OPERATION & MANAGEMENT**

The University of Notre Dame ICP-MS facility operates under the direction of Dr. Clive R. Neal with Dr. Jinesh C. Jain, the ICP-MS Lab manager, coordinating the day-to-day running and maintenance of the facility. Dr. Jain was hired as the ICP-MS Laboratory Manager on May 1, 1995. His previous experience helped in enhancing the productivity of the lab soon after his joining and familiarizing himself with the PlasmaQuad. There are regular meetings of the principal users to discuss progress, problems of the laboratory, new directions, priorities, and improve the efficiency of the lab. The ICP-MS facility is available on a priority basis to University of Notre Dame researchers and students. Non-university research and industrial work is accepted to help defer the maintenance costs of the facility, developmental research work, and research of both graduate and undergraduate students.

#### **Activities of the Laboratory Manager**

Dr. Jain's duties are to co-ordinate users of the facility, train new users, assist in sample preparation and data reduction, and develop new analytical techniques. He is teaching a graduate level course (GEOS 562) to provide basic knowledge and hands on experience of ICP techniques to the students. Dr. Jain's efforts are successful in publicizing the facility to potential users within and outside Notre Dame. In addition to participating in a number of departmental research projects (with Drs. Neal, Fein, and Burns) he has used his expertise in biochemistry to initiate the following collaborations that have allowed the Notre Dame ICP-MS facility to expand into a new realm of environmental applications and projects.

- Cadmium uptake in durum wheat (with the University of Saskatchewan, Canada): Use of artificial fertilizers promotes cadmium accumulation in soils that results in uptake by crops and has a potentially severe environmental impact. This project identifies the durum wheat line for genetic manipulation to produce cadmium-free durum wheat.
- Quality control in Paint and Coatings (with Sherwin Williams Company, Chicago): ICP-MS is being utilized for characterizing trace metals in raw materials to improve the quality of the finished product; such research identifies any components that would have an adverse effect on environment.
- Alzheimer s Disease (with Washington University School of Medicine): The aim of the project is to identify metalloproteins as markers in Alzheimer s patients. The brain tissues obtained from Alzheimer s patients and healthy humans are being screened for metal ions and the build up of certain metals in Alzheimer s patients is being related to environmental influences.
- Phytoremediation (with the University of Western Kentucky): Genetically modified plants are being assessed for heavy metal uptake to decontaminate soils. The plants that show promise at the laboratory scale will be assessed for adaptability in contaminated soils for environmental cleanup.
- New York Angler Cohort Study (with University of Buffalo): Blood samples collected from fish consumers are being analyzed for toxic metals to assess a correlation between environmentally important trace elements and various diseases.
- Heart Disease (with the Henry Ford Hospital, Detroit): The trace element concentrations of heart tissues obtained from normal and diseased hearts from dogs are being determined to investigate any correlation between metal ions and heart disease. The research was ignored in the past due to unavailability of ultra sensitive techniques. ICP-MS is an ideal technique for this purpose.

#### **TECHNIQUES DEVELOPED AND IN USE**

- Trace element analyses of paint samples (Jain et al., 2001a);
- Trace element analysis of blood;

- Trace element analysis of brain tissue (Jain et al., 2001b);
- Analyses of platinum group elements in geological and biological samples (Ely et al., 1999);
- High field strength element determinations in geological materials, free from memory effects (McGinnis et al., 1997);
- Trace element analyses of zircons and zircon-bearing rocks (Jain et al., 2001c);
- HF/HNO<sub>3</sub> digestion procedure for trace element analysis in rock powders (see Procedure 5 in the Appendix);
- Sodium peroxide fusion procedure for determination of rare earth elements, Zr, Hf, Nb, Ta, and Th in refractory minerals;
- Determination of trace elements in superconductors and ceramics;
- HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> digestion procedure for multi-element analysis in plant and resin samples;
- Laser Ablation ICP-MS for trace element analysis of solid materials (e.g., Hanchar et al., 2001).

#### **DATA QUALITY**

The quality of the data produced is demonstrated by the reproducibility of reference materials. Since 1995, we have compiled over 130 analyses of the USGS basalt reference material BHVO-1, and compare them with reference values from Govindaraju (1989) (Table 1). All but four of the 40 elements quantified have been consistently reproduced to generally <10% of the reference value over the last five years. However, the abundances of Rb, Y, and Pb (*italics* in Table 1) are consistently lower than the reference values, whereas those for Th are consistently higher. Values for Rb, Th, and Pb have been determined by isotope dilution at the University of Hawaii (Mahoney et al., *Journal of Petrology*, 39, 1285-1306, 1999; J. Mahoney, pers. Comm., 2000) and demonstrate values consistent with those produced by the Notre Dame ICP-MS Facility (2.051 ppm, 1.233 ppm, and 9.4 ppm, respectively). We fused a portion of the BHVO-1 powder and analyzed it via laser ablation ICP-MS in our lab using the NIST 612 glass as the calibration standard and Ca as the internal standard. Average values on the basis of 6 analyses are: Rb = 9.6 – 0.7 ppm; Y = 22.8 – 0.7 ppm; Pb = 2.3 – 0.6 ppm; Th = 1.2 – 0.1 ppm (see Table 8). Splits of our BHVO-1 powder have been sent for spark source mass spectrometric analysis at the Max-Planck Institut für Chemie, Germany to obtain an independent determination of Y. Investigation of these discrepancies forms the basis of the Masters thesis for graduate student William J. Chazey, III.

**Table 1:** Average and standard deviation of 138 analyses of BHVO-1 conducted by the Notre Dame ICP-MS Facility since 1995. Reference values from Govindaraju (1989, Geostandards Newsletter 13, 1-113). Values highlighted in bold face represent elements that have been quantified to better than 10% precision.

ELEMENT	REFERENCE VALUE (PPM)	NOTRE DAME AVERAGE (PPM)	STD DEV (PPM)
Li	4.6	4.6	0.3
Be	1.1	1.0	0.1
Sc	<b>31.8</b>	32.0	1.6
V	<b>317</b>	320.2	18.1
Cr	<b>289</b>	292.8	20.6
Co	<b>45</b>	47.6	2.1
Ni	<b>121</b>	123.5	5.0
Cu	<b>136</b>	145.7	7.5
Zn	<b>105</b>	115.2	7.7
Ga	21	21.9	0.9
<b>Rb</b>	<b>11</b>	<b>9.2</b>	<b>0.5</b>
Sr	403	404.9	19.7
<b>Y</b>	<b>27.6</b>	<b>23.9</b>	<b>1.2</b>
Zr	179	170.4	7.2
Nb	19	19.0	1.3
Mo	1.02	1.03	0.11
Sn	2.1	2.2	0.2
Sb	0.16	0.16	0.04
Cs	0.13	0.11	0.03
Ba	139	133.8	3.6
La	15.8	15.5	0.5
Ce	39	39.5	1.9
Pr	5.7	5.5	0.3
Nd	25.2	24.7	0.7
Sm	<b>6.2</b>	6.2	0.2
Eu	<b>2.06</b>	2.11	0.09
Gd	6.4	6.4	0.5
Tb	0.96	0.95	0.07
Dy	5.2	5.4	0.2
Ho	0.99	0.97	0.07
Er	2.4	2.5	0.1
Tm	0.33	0.32	0.06
Yb	2.02	2.07	0.10
Lu	0.29	0.27	0.03
Hf	4.38	4.50	0.18
Ta	1.23	1.21	0.10
W	0.27	0.22	0.07
<b>Pb</b>	<b>2.6</b>	<b>2.12</b>	<b>0.23</b>
<b>Th</b>	<b>1.08</b>	<b>1.17</b>	<b>0.10</b>
U	0.42	0.41	0.05

Samples analyzed using Meinhardt nebulization and complete dissolution using double distilled hydrofluoric and nitric acids. See Procedure 5 of the Appendix for full details.



The quality of platinum-group element data produced by the Notre Dame ICP-MS facility can be seen in Table 2. The reference material used is UMT-1, a low level PGE material obtained from the Canadian Centre for Mineral and Energy Technology (CANMET) made from Canadian nickel mine tailings.

**Table 2:** Average and standard deviation for 76 analyses of the CANMET PGE reference material UMT-1 conducted by the Notre Dame ICP-MS Facility since 1995. All concentrations are in ppb (ng/g).

<b>Isotope</b>	<b>Reference Value</b>	<b>Standard Deviation</b>	<b>ND Average Value</b>	<b>Standard Deviation</b>	<b>ND Acid Blank</b>	<b>ND Proc. Blank</b>
<sup>99</sup> Ru	10.9	0.8	10.6	1.1	<5x10 <sup>-5</sup>	<8x10 <sup>-5</sup>
<sup>102</sup> Ru	10.9	0.8	11.1	1.6	<1x10 <sup>-5</sup>	<2x10 <sup>-5</sup>
<sup>103</sup> Rh	9.8	1.5	9.7	1.4	<2x10 <sup>-4</sup>	<7x10 <sup>-4</sup>
<sup>104</sup> Pd	104.2	2.9	101.3	8.4	<9x10 <sup>-5</sup>	<3x10 <sup>-4</sup>
<sup>105</sup> Pd	104.2	2.9	102.3	8.3	<2x10 <sup>-4</sup>	<3x10 <sup>-5</sup>
<sup>191</sup> Ir	8.8	0.3	7.9	1.2	<6x10 <sup>-5</sup>	<7x10 <sup>-5</sup>
<sup>193</sup> Ir	8.8	0.3	8.4	1.3	<2x10 <sup>-5</sup>	<1x10 <sup>-4</sup>
<sup>194</sup> Pt	128.3	4.9	121.3	30.5	<5x10 <sup>-5</sup>	<2x10 <sup>-4</sup>
<sup>195</sup> Pt	128.3	4.9	119.5	28.7	<2x10 <sup>-5</sup>	<1x10 <sup>-4</sup>
<sup>196</sup> Pt	128.3	4.9	118.7	31.0	<1x10 <sup>-4</sup>	<2x10 <sup>-4</sup>
<sup>198</sup> Pt	128.3	4.9	120.4	33.2	<1x10 <sup>-4</sup>	<2x10 <sup>-4</sup>

See Ely et al. (1999) for details regarding sample preparation and analysis.

In addition to the analysis of geochemical samples, the Notre Dame ICP-MS facility has also analyzed a variety of plant (biological) and medical materials. For these samples, we have analyzed a number of different reference materials (obtained from the National Institute of Standards and Technology), the analyses of which are reproduced in Tables 3 & 4 along with the reference values.

**Table 3:** Elemental composition of NIST durum wheat reference material SRM 8436.

ELEMENTS	SRM 8436 (mg/kg or ppm)	
	ANALYZED	REFERENCE
Mg	1109	1070
Al	12.3	11.7
P	2723	2900
Ca	287	278
Ti	4.21	5
V	0.027	0.021
Cr	0.058	0.023
Mn	14.93	16
Fe	43.3	41.5
Co	0.009	0.008
Ni	0.192	0.17
Cu	4.31	4.3
Zn	20.4	22.2
As	0.023	0.03
Se	1.28	1.23
Rb	1.84	2
Sr	1.17	1.19
Mo	0.739	0.7
Cd	0.108	0.11
Sn	0.051	---
Sb	0.015	---
Ba	2.07	2.11
Tl	0.001	---
Pb	0.029	0.023
Bi	0.002	---
Th	0.007	---
U	0.002	---

Sample digestion was conducted using a HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> protocol. ICP-MS analysis was completed using an external calibration/internal standardization procedure.

The Notre Dame ICP-MS facility was involved in developing a new EPA method for the analysis of water. During this project, we analyzed two different reference materials, SRM

1643d (from NIST) and SLRS-3 (from the National Research Council of Canada). Our analyses and reference values are given in Table 5.

**Table 4:** Elemental Composition of Mussel (SRM8414) and Liver (SRM 1577b) NIST standard reference materials analyzed by the Notre Dame ICP-MS. Data are in ppm ( g/g).

Element	SRM 8414		SRM 1577b	
	ANALYZED	REFERENCE	ANALYZED	REFERENCE
B	0.66	0.6	0.90	-
Na	2268	2100	2562	2420
Mg	937	960	597	601
Al	1.78	1.7	1.44	3
P	8582	8360	11934	11000
Ca	152	145	113.8	116
V	0.0045	0.005	0.09	0.123
Cr	0.092	0.071	0.11	-
Mn	0.392	0.37	9.83	10.5
Fe	73.62	71.2	170.3	184
Ni	0.049	0.05	0.31	-
Cu	2.67	2.84	158.4	160
Zn	133.7	142	115.4	127
As	0.013	0.009	0.047	0.05
Se	0.079	0.076	0.76	0.73
Rb	25.02	28.7	11.54	13.7
Mo	0.067	0.08	3.22	3.5
Ag	0.0046	-	0.044	0.039
Cd	0.013	0.013	0.49	0.50
Sb	0.025	0.01	0.029	0.003
Cs	0.03	0.05	0.01	-
Ba	0.03	0.05	0.044	-
Pb	0.49	0.38	0.119	0.129

Sample digestion was conducted using a HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> protocol. ICP-MS analysis was completed using an external calibration/internal standardization procedure.

**Table 5:** Analyses of water reference materials SRM 1643d (NIST: filtered and acidified fresh water) and SLRS-3 (NRC Canada: Riverine Water). Data are in ppb ( g/l).

Element	SRM 1643d		SLRS-3	
	ANALYZED	REFERENCE	ANALYZED	REFERENCE
V	-	35.1	0.31	0.30
Cr	-	18.53	0.33	0.30
Ni	57.2	58.1	0.85	0.83
Cu	20.2	20.5	1.43	1.35
Zn	70.69	72.48	1.03	1.04
As	-	56.02	0.71	0.72
Se	11.35	11.43	-	-
Mo	-	112.9	0.21	0.19
Ag	1.32	1.27	-	-
Cd	6.41	6.47	0.014	0.013
Sb	53.79	54.1	0.13	0.12
Tl	7.56	7.28	-	-
Pb	18.82	18.15	0.09	0.068

Analyses were conducted using an external calibration/internal standardization procedure.

We have also analyzed sediments for a suite of toxic heavy metals and in this study, SRM 2704 Buffalo River Sediment was used as the reference material (Table 6). The low As values are being investigated; they are probably a result of As loss during sample preparation. Another study required the analysis of bullet lead for a trial in St. Joseph County, Indiana. Here, NIST standard C2416 was analyzed for quality control (Table 7).

The laser ablation system is producing data on mineral and fused whole-rock samples. We have analyzed fused whole-rock reference materials in order to evaluate the accuracy of the system. The software used to reduce the time-resolved data is LAMTRACE written by Simon Jackson. Averages of 6 laser ablation analyses are given for the fused reference materials in Table 8. For these analyses, NIST 612 glass was used as the external standard. Most elements analyzed

are reproducible, although Zr is coming out a little low compared to our solution analyses of the reference materials and the reference values.

**Table 6:** Elemental composition of NIST standard SRM 2704 Buffalo River Sediment .

ELEMENTS	SRM 2704 (mg/kg or ppm)	
	ANALYZED	REFERENCE
V	94.2	95
Cr	132.6	135
Co	14.2	14
Ni	45.9	44.1
Cu	96.8	98.6
Zn	431.9	438.0
As*	14.2	23.4
Mo	3.53	--
Cd	3.56	3.45
Sb	3.92	3.79
Tl	1.11	1.06
Pb	162.4	161
Th	9.49	9.20
U	3.35	3.13

\* Arsenic lost during sample preparation.

Sample digestion was conducted using HF/HNO<sub>3</sub> followed by H<sub>2</sub>O<sub>2</sub> treatment to decompose any organic material. ICP-MS analysis was conducted using an external calibration/internal standardization procedure.

**Table 7:** Average elemental composition of the National Bureau of Standards reference material C2416 Bullet Lead (4 analyses). Data are in ppm ( g/g).

ELEMENT	ANALYZED	REFERENCE
Cu	687	650
As	522	560
Ag	43	44
Sb	6784	7900
Bi	930	1000

Samples were digested at 100°C on a hotplate in HNO<sub>3</sub>. ICP-MS analysis was conducted using an external calibration/internal standardization procedure.

## UPGRADES

Major upgrades since 1995 include a new STE controller unit, an expansion chamber S-option, and a new transducer plate for the ultrasonic nebulizer. The laser ablation system was finally made operational 4 years after it was shipped for upgrading to UV radiation. This delay was due to the loss of controller boards that disappeared during the upgrade and a faulty lead from the controller to the laser unit. The laser data are reduced using the LAMTRACE program written by Dr. Simon Jackson of MacQuarie University, Sydney, Australia. The first paper using laser ablation data from the Notre Dame ICP-MS facility is currently under review (Jain et al., 2001c).

Addition of the S-option has resulted in a five-fold increase in sensitivity at Indium using Meinhardt nebulization (from 250,000 to 1,400,000 counts per second using a 10 ppb stock solution). Using laser ablation, the sensitivity at Cerium in NIST 612 glass (38.5 ppm) was increased from 20,000 to 100,000 counts per second. It is now possible to analyze samples with low levels of incompatible trace elements with this upgrade (e.g., ultramafic rocks). However, the sensitivity is still not sufficient for the accurate and precise determination of incompatible trace elements in minerals from depleted mantle materials. Analysis of such materials by laser ablation will require a new, high sensitivity/high resolution ICP-MS. Finally, a Microwave Digestion unit (MDS 2100) was purchased from CEM Corporation in 1007. The cost for this facility was \$12,000.

**Table 8:** Laser ablation ICP-MS analyses of fused whole-rock reference materials. Data are in ppm (g/g). Values highlighted in bold face represent elements that have been quantified in the reference materials to better than 10% precision. Ca was used as the internal standard.

Element	BHVO-1	AVERAGE	BIR	AVERAGE	G2	AVERAGE
CaO	<b>11.4</b>	11.4	<b>13.24</b>	13.24	<b>1.97</b>	1.97
TiO <sub>2</sub>	<b>2.71</b>	3.03	0.96	1.06	0.492	0.50
Be	1.1	1.3	0.58	0.84	2.4	2.62
Sc	<b>31.8</b>	31.9	44	50.1	3.5	5.1
V	<b>317</b>	349	313	321	36	37.8
Cr	<b>289</b>	319	382	361	9	8.7
Co	<b>45</b>	45.2	51.4	53.8	<b>4.6</b>	2.6
Rb	11	9.6	0.27	0.26	<b>170</b>	195
Sr	403	403	108	100	<b>478</b>	478
Y	27.6	22.8	16	13.3	11.4	8.3
Zr	179	151	22	11.8	<b>300</b>	318
Nb	19	19.1	2	0.46	13	13.8
Cs	0.13	0.12	0.45	0.12	<b>1.33</b>	1.36
Ba	139	132	7.7	7.6	<b>1880</b>	1826
La	15.8	14.8	0.88	0.53	<b>86</b>	79.3
Ce	39	38.6	2.5	1.9	<b>159</b>	159
Pr	5.7	5.1	0.5	0.34	<b>19</b>	14.5
Nd	25.2	24.1	2.5	2.3	53	48.1
Sm	<b>6.2</b>	5.2	1.08	1.21	<b>7.2</b>	6.4
Eu	<b>2.06</b>	2.06	0.54	0.48	1.41	1.20
Gd	6.4	5.9	1.9	1.8	4.1	4.2
Tb	0.96	0.89	0.41	0.33	0.48	0.38
Dy	5.2	5.1	2.4	2.5	2.5	2.1
Ho	0.99	0.90	0.5	0.56	<b>0.37</b>	0.32
Er	2.4	2.3	1.8	1.7	1.2	0.74
Tm	0.33	0.32	0.27	0.27	0.17	0.10
Yb	2.02	1.91	1.7	1.6	0.78	0.73
Lu	0.291	0.28	0.26	0.26	0.113	0.11
Hf	4.38	3.83	0.58	0.53	<b>7.9</b>	7.9
Ta	1.23	1.17	0.062	0.05	0.88	0.84
Pb	2.6	2.3	3.2	58.0	31	39.2
Th	1.08	1.13	0.031	0.05	<b>24.6</b>	22.3
U	0.42	0.47	0.01	0.03	<b>2.04</b>	2.01

**Table 8:** Continued.

<b>Element</b>	<b>RGM</b>	<b>AVERAGE</b>	<b>SY-2</b>	<b>AVERAGE</b>	<b>MRG</b>	<b>AVERAGE</b>
CaO	1.15	1.15	<b>7.96</b>	7.96	<b>14.7</b>	14.7
TiO <sub>2</sub>	0.267	0.27	0.15	0.13	3.77	3.60
Be	2.37	2.50	22	23.2	0.61	0.88
Sc	4.4	4.4	7	13.6	55	56.7
V	13	14.1	50	61	526	590
Cr	3.7	4.1	9.5	6.8	<b>430</b>	539
Co	2	3	8.6	9.6	87	101
Rb	149	179	217	322	8.5	7.8
Sr	108	96.5	271	303	<b>266</b>	274
Y	25	20	128	124	14	10.7
Zr	219	202	280	183	108	84
Nb	8.9	10.7	29	38.7	20	18.4
Cs	9.6	12.5	2.4	3.7	0.57	0.65
Ba	807	807	460	529	61	49.2
La	<b>24</b>	22.8	75	78	<b>9.8</b>	8.6
Ce	47	46.5	175	198	26	27.4
Pr	4.7	4.9	18.8	22.2	3.4	3.6
Nd	19	18.8	73	86.5	19.2	17.4
Sm	4.3	3.7	16.1	17.4	4.5	3.9
Eu	0.66	0.56	2.42	2.64	<b>1.39</b>	1.41
Gd	3.7	3.9	17	17.5	4	3.8
Tb	0.66	0.56	2.5	3.0	0.51	0.50
Dy	<b>4.08</b>	3.74	18	21.7	2.76	2.82
Ho	0.95	0.78	3.8	4.95	0.49	0.49
Er	2.6	2.5	12.4	15.9	1.12	1.10
Tm	0.37	0.35	2.1	2.6	0.11	0.15
Yb	2.6	2.8	17	20.5	0.6	0.8
Lu	0.41	0.39	2.7	3.2	0.13	0.09
Hf	6.2	6.2	7.7	6.6	3.76	3.20
Ta	0.95	1.17	2.01	2.4	0.8	0.74
Pb	24	38.3	85	98	10	3.9
Th	15.1	15.3	379	393	0.93	0.74
U	5.8	7.4	287	386	0.24	0.32



## **REPAIRS**

- Replaced breaker to Mains Distribution Unit (MDU)
- Replaced MDU
- Replaced 2 circuit boards in the STE controller and STE circuit box
- Replaced one turbo and one roughing pump
- Replaced RF coil
- Modified the torch box grounding strip

As the machine was still under our negotiated extended warranty (until 1998), all but the last two items were corrected by the manufacturer. A letter was written to Fisons to seek a compensation for the loss of time resulting from the breakdown and they responded positively by extending the warranty on the instrument for one more year (monetary value \$39,000). The extended warranty has now expired, so we have looked for cheaper maintenance alternatives. We now use VHG Labs out of Massachusetts. VHG Labs fixed a problem with the failure of the mass flow control unit. They also installed the S-option upgrade. The total cost for repairs in the past three years (after the warranty expired) was \$29,000, considerably cheaper than the \$39,000 *per year* for a full service contract from the manufacturer.

## **ANALYTICAL FEES**

Analytical fees (Table 9) are calculated using lab expenses and number of analyses over a given time period (usually one year). The calculation is not simple, however, as the complexity of the sample matrix, number of elements required to be quantified, and whether the research is collaborative or not, all need to be considered. The bottom line is that as the ICP-MS facility is a recharge center, we cannot make a profit. Therefore, if a deficit/profit occurs at the end of a given year, rates are adjusted accordingly to theoretically produce a zero balance at the end of the next year. This scenario is, however, also complicated by the fact that we cannot predict major machine malfunctions. Discounts are given depending upon the number of samples to be analyzed and whether the customer is willing to be involved in the sample preparation. Approx-

imately seventy five percent of the machine time was used for research purposes and remaining was utilized for contract work.

The income from users of the Notre Dame ICP-MS facility has allowed the lab to be self sufficient and has kept student training costs low, while expanding our educational and research efforts. Specifically, it has allowed:

- the completion of an unfunded Master s thesis on the analyses of the platinum group elements and gold (PGEs + Au) in geological samples;
- the development of a technique to analyze high-field strength elements in geological samples;
- the hiring of a post-doctoral fellow to initiate a project on environmental impact of platinum, a product of automobile discharge;
- three undergraduate students to work in the lab;
- four undergraduate research projects to be completed.

As the university has created a position for the ICP-MS facility manager, Dr. Jain s salary does not have to be recovered from laboratory operations. This allows the lab to be self supporting.

### **MAIN USERS OF THE NOTRE DAME ICP-MS FACILITY**

#### University of Notre Dame:

1. Dr. C. Neal, Civil Engineering & Geological Sciences
2. Dr. S. Silliman, Civil Engineering & Geological Sciences
3. Dr. J.K. Rigby, Civil Engineering & Geological Sciences
4. Dr. P. Morris, Civil Engineering and Geological Sciences
5. Dr. J.B. Fein, Civil Engineering & Geological Sciences
6. Dr. J.C. Jain, Civil Engineering & Geological Sciences
7. Dr. P. Burns, Civil Engineering & Geological Sciences
8. Dr. Slavi Sevov, Chemistry and Biochemistry
9. Dr. P. McGinn, Chemical Engineering
10. Dr. D. McAbee, Biological Sciences
11. Dr C.F. Kulpa, Director CEST
12. Dr. Mark Schneegurt, Biological Sciences
13. 3 Post-doctoral Fellows, 8 graduate Students, 7 undergraduate students

Outside Users/Collaborators:

1. Dr. B. Ensley, Phytotech, New Jersey
2. Dr. N. Jain, Sherwin Williams paint Company, Chicago
3. Dr. S. Wilson, USGS
4. Dr. P. Jauhar, USDA, Fargo, North Dakota
5. Dr. S.J. Barnes, University of Quebec, Canada
6. Dr. S. Jana, University of Saskatchewan, Canada
7. Dr. A.R. Mermut, University of Saskatchewan, Canada
8. Dr. J. Mahoney, University of Hawaii
9. Dr. J. Brannon, Washington University, St Louis
10. Dr. F.A. Podosek, Washington University, St Louis
11. Dr. K. Johnson, University of New Orleans
12. Dr. L.A. Taylor, University of Tennessee
13. Dr. G.A. Snyder, University of Tennessee
14. Dr. John Vena, University of New York, Buffalo
15. Dr. Bruce Cristal, Burke Medical Research Institute, NY
16. Dr. Gregory Bydlinsky, Delmar Chemicals, Montreal , Canada
17. Dr. Bill Brand, Huntsman Polyurethanes, NJ
18. Dr. Poonam. Singh, AKZONOBEL, St Louis
19. Dr. R.A.K. Srivastava, Washington University, St Louis
20. Dr. J. M. Hanchar, George Washington University, D.C.
21. Mr. Walt Kolbe, Industrial Services Group, Pacifica, CA
22. Dr. Richard Gomer, Rice University, Houston
23. State of Nevada
24. Dr Doug McAbee, California State University, Long Beach
25. Dr S. Sahi, Western Kentucky University, Bowling Green
26. Mr. Robert Kirkland, University of Kentucky, Lexington
27. Ms. Sherry Lutz, US EPA, Washington, D.C.
28. Ms. Nina Whiddon, TRW, Redondo Beach, CA
29. Dr. Robert Sherrell, Rutgers University, NJ
30. Dr. Ken Kemner, Argonne National Laboratory, Argonne
31. Mr. Phil Skodinski, St Joseph County, South Bend
32. Dr. Laura Pyrak-Nolte, Purdue University, IN
33. Dr. Merritt Birky, NTSB, Washington D.C.
34. Dr. Ali Polat, MaxPlank Institute, Mainz, Gemany
35. Dr. Rob Wilson, Univ of Pennsylvania, PA
36. Mr. Fred Green, Eureka Technology, KS



## EDUCATION IN THE NOTRE DAME ICP-MS FACILITY

The following Undergraduate Research projects have been completed or are in progress:

*Volcanism on the Moon* - Jennifer Ryan, 1999

*Crustal Xenoliths from the Ontong Java Plateau* - Jennifer Ryan, 2000

*Petrogenesis of Mantle Xenoliths from the SW Pacific* - Bernadette Lipari, 1999

*Magma Chamber Processes in a Large Igneous Province* – Rebecca Glatz, 2001

The following Masters projects have been completed or are in progress:

*Development of an ICP-MS Analytical Technique for the Quantification of the Platinum Group Elements (PGEs) and Gold in Geological Samples using Cation Exchange Pretreatment* - James A. O Neill, Jr, 1996.

*Characterization of memory effects and development of an effective wash protocol for the measurement of petrogenetically critical trace elements in geological samples by ICP-MS* - Cathleen McGinnis, 1997.

*Verification of Y, Rb, Pb, and Th values for reference material BHVO-1.* —William J. Chazey, III, 2001 (expected)

The following Ph.D. projects have been completed or are currently in progress:

*The Nature of the Sub-Continental Lithospheric Mantle Beneath Northern Venezuela: Implications for Plate Collision and Magmagenesis* - Cathleen McGinnis, 2000.

*A Geochemical Investigation of the Ontong Java Plateau* - Amy Birkhold-VanDyke, 2000.

*Analysis of Platinum-Group Elements (PGEs) and Au in Geological Materials at Ultra-Trace Levels: Technique Development and Applications* - James C. Ely, 1999.

*A Comparison of LIP Magmatism: Examples from the Earth and the Moon* - William J. Chazey, III. Expected, 2002

### **SIGNIFICANT ACTIVITIES:**

1. The only ICP-MS laboratory in the USA funded by NASA to undertake analyses of lunar and Martian samples.
2. Participated in validation studies of United States EPA programs.
3. Forensic work for St Joseph County's Prosecutors' Office
4. Consulted on analysis of TWA Flight 800 wreckage by the NTSB.
5. Participated in national and international Standard Reference material programs.

## **PUBLICATIONS & CONFERENCE ABSTRACTS REPORTING DATA FROM THE NOTRE DAME ICP-MS FACILITY**

### **1) PAPERS.**

#### **IN PREPARATION**

- Birkhold A.L., Neal C.R., Mahoney J.J., Duncan R.A., and Petterson M.G. (2001) Periodic growth of the Ontong Java Plateau: Evidence from Makira (San Cristobal), Solomon Islands. *Earth & Planetary Science Letters* (in prep).
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- Hanchar J.M., Neal C.R., and Jain J.C. (2001) Detailed geochemistry of a gem-quality zircon: Implications of redox conditions. *Geochimica et Cosmochimica. Acta* (in prep.).
- Jain J.C., and Neal C.R. (2001) Problems associated with ICP-MS analysis of niobium and tantalum in tungsten-carbide-milled rock powders. *Canadian Journal of Applied Spectroscopy* (in prep.).
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- Jain J.C., Neal C.R., and Srivastava R.A.K. (2001b) Evaluating the role of metal ions in different regions of brain from alzheimer s patients. *Journal of Cell Physiology* (in prep.).
- Neal C.R., Ely J.C., and Jain J.C. (2001) The siderophile element contents of mare basalts: Implications for the differentiation of the Moon. *Geochimica et Cosmochimica. Acta* (in prep.)
- Prinya P., Taylor L.A., Neal C.R., and Kurosawa M. (2001) Trace-element characteristics of the spinel peridotite xenoliths from Thailand: Melting and metasomatism of the mantle beneath a suture zone. *International Geology Review* (in prep.).

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- Ely J.C., Neal C.R., and O Neill, J.A. Jr. (2001) Method of data reduction and precision analysis for platinum-group element (PGE) data using inductively coupled plasma - mass spectrometry (ICP-MS). *Geostandards Newsletter* (submitted).

- Jain J.C., Neal C.R. and Hanchar J.M. (2001c) Identification and removal of fluoride interferences in determination of rare-earth elements in zircon by ICP-MS. *Geostandards Newsletter* (submitted).
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- Neal C.R. (2001) The interior of the Moon: The presence of garnet in the primitive, deep lunar mantle. *Journal of Geophysical Research* (submitted).
- Schneegurt M.A., Jain, J.C., Menicucci J.A., Brown S., Garofalo D.F., Quallick M.R., Neal C.R., and Kulpa C.F. Jr. (2001) Use of biomass by-products for the remediation of wastewaters contaminated with toxic metals. *Environmental Science and Technology* (submitted).
- Snyder G.A., Sano Y., Taylor L.A., Terada K., and Neal C.R. (2001) Lunar meteorite EET 96008: Geochemistry and petrogenesis. *Meteoritics & Planetary Science* (submitted).
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# APPENDIX A

## PROTOCOLS

### 1) ICP-MS LAB PROTOCOLS

- 1) CLEAN CONES IN THE EMP LAB;
- 2) ALWAYS WIPE DOWN BENCH TOPS, TOPS OF THE MACHINERY, DESKS, ETC., WITH 18 MEGAOHM WATER WHEN YOU ARE ABOUT TO HAND OVER TO ANOTHER USER;
- 3) MEET WITH THE NEXT USER BEFORE HANDING THE MACHINE OVER TO DISCUSS PERFORMANCE, PROBLEMS, ETC.;
- 4) MAKE SURE CLEAN CONES AND GLASSWARE ARE INSTALLED AFTER YOU HAVE RUN YOUR LAST SAMPLE AND BEFORE HANDING OVER TO THE NEXT MACHINE (YOU WILL HAVE TO OBTAIN THE NEXT USERS CONES);
- 5) DO NOT STORE SAMPLES IN THE AUTOSAMPLER RACKS. ALL SAMPLES LEFT IN THESE RACKS AFTER USER CHANGE OVER WILL BE DISCARDED;
- 6) ALL SAMPLES LEFT OUTSIDE A USERS DESIGNATED CUPBOARDS SPACE AFTER THAT USER HAS HANDED THE MACHINE OVER WILL BE THROWN OUT;
- 7) THE USER OPERATING ON THE FIRST OF EACH MONTH HAS TO CLEAN THE TACKY MAT;
- 8) MAKE SURE THE ARGON AND CHILLER ARE TURNED OFF AFTER LEAVING FOR THE DAY - FOLLOW THE PROCEDURE ATTACHED TO THE AR TANK FOR TURNING THE ARGON OFF;
- 9) WHEN USING THE ETV, MAKE SURE THE VALVE IN THE AR LINE IS OPEN TO ALLOW AR TO FLOW TO THE ETV. **MAKE SURE YOU CLOSE IT AGAIN AFTERWARDS - IF NOT, A LOT OF AR IS LOST.**
- 10) INFORM CLIVE/JINESH WHEN NEW ARGON IS NEEDED AT LEAST TWO DAYS PRIOR TO IT RUNNING OUT (IF YOU CAN EASILY TILT THE TANK, IT'S TIME FOR NEW ARGON!);
- 11) **ALL BREAKAGES AND/OR MISHAPS TO BE REPORTED IMMEDIATELY!!!!**

### 2) SAMPLE PREPARATION CLEAN-LAB PROTOCOLS

- Always wear a lab coat and overshoes in the lab;
- When handling acids, wear safety goggles and plastic gloves;
- NO OPEN BEAKERS OUTSIDE THE FUME HOOD;
- Before handling hydrofluoric acid (HF), make sure you know where the antidote cream is;
- IF YOU SPILL HF ON YOURSELF, PUT THE ANTIDOTE CREAM ON THE AFFECTED AREA AFTER QUICKLY RINSING THE AREA WITH WATER. CONTACT SECURITY IMMEDIATELY FOR TRANSPORT TO THE INFIRMARY OR EMERGENCY ROOM.
- When handling HF, always wear a full face mask and always keep open containers of HF well inside the fume hood;
- When using the pipettes, always use a new pipette tip for each new solution.

- When using the balance, remove static from Teflon containers using the anti-Static gun provided;
- Always use container that have been cleaned following the Cleaning Protocol .

### **3) WHOLE-ROCK SAMPLE PREPARATION (POWDERING) PROTOCOL**

This protocol is designed to minimize the contamination of the whole-rock powder during the preparation procedure. Potential contaminants are weathered surfaces, coolant oil from the rock saw, and in the case of the platinum group elements, the rock saw, hammer, splitter, jaw crushers, and personal jewelry.

By following this procedure, the resultant powder will be able to be analyzed for any element or isotope in the knowledge that the powder is free of contamination and it is the fresh whole-rock that is being analyzed.

#### **1) REMOVE ALL JEWELRY FROM HANDS AND WRISTS and WASH HANDS**

#### **2) SAWING AND GRINDING**

- Use the water-cooled rock saw to trim off the weathered surfaces of the larger samples.
- Use the 75 disk (diamond impregnated) to grind off the sawn surfaces; to ensure that the surface is ground far enough, grind until the striations from the disk are parallel on the surface, then turn the sample 90° and repeat until the original striations have been removed. This disk may also be used to remove weathered surface remaining on the sawn large samples and from samples too small to saw.
- Make sure that all surfaces have been ground using the 75 disk such that fresh surfaces are now exposed.
- After each sample has been ground, remove the disk from the grinding wheel and rinse thoroughly under the tap in order to avoid cross contamination between samples. Replace for the next sample.
- Wash the ground sample under the tap and dry.

#### **3) SPLITTING THE SAMPLE**

- Place the sawn/ground sample in a heavy duty freezer bag and then put this inside a second. Place on a sturdy flat surface (NOT a bench or desk top).
- The sample will be split into peanut-sized chips (or smaller) by using a hammer, but in order to eliminate contact with metal, the metal hammer is covered with cloth duct tape. A new layer is added for each sample in order to avoid cross contamination between samples.

- (c) As the sample has flat surfaces, hitting the sample with the duct tape-covered hammer should not split the bags unduly.
- (d) Gather the peanut-sized chips (or smaller) and place in a Pyrex beaker and cover with 18 megaohm (ultra-pure) water and ultrasonic for 30 minutes.
- (e) Air dry the sample and pick out any chip with a weathered surface.

#### **4) POWDERING THE SAMPLE**

- (a) Put the chips in the agate mill so that they fill the gap between ball and the chamber so that it is **HALF FULL. DO NOT OVERLOAD OR PUT LARGE CHIPS IN THE MILL.**
- (b) Put in the mill and start - check after 5-10 minutes the consistency of the powder by putting on a clean pair of plastic gloves (a new pair for each sample) and feeling the consistency. It should feel like talcum powder when the grinding is complete. If it still feels gritty, grind some more.
- (c) Tip the milled powder onto a clean piece of paper then pour into a clean, new ziplock plastic bag and label accordingly.
- (d) Wash the mill under the tap using a kitchen scouring pad to remove all powder. Rinse thoroughly water and then with acetone. Use the compressed air unit to dry the mill. Before adding the bulk of the chips of the next sample, add a small amount (to cover the bottom of the mill) and grind to ensure the mill is cleaned out of the previous sample. Remove and discard this powder, wash as before and dry. Then add the bulk of the sample chips to the mill.

#### **REMEMBER TO:**

- (A) CLEAN EQUIPMENT/UTENSILS THOROUGHLY BETWEEN SAMPLES IN ORDER TO AVOID CROSS CONTAMINATION;
- (B) AVOID CONTACT OF THE SAMPLE WITH METAL TO AVOID ANY POTENTIAL PGE CONTAMINATION.

#### **4) TUNE-UP PROTOCOLS**

- Always wear overshoes or socked feet in the ICP-MS Lab;
  - Always do a Fine Mass Calibration before starting;
  - Always do a short term stability test and ensure RSD † 2% for all elements before starting;
  - Always fill out the log book each time you use the machine;
- 1) Check coolant level in main chiller;
  - 2) Make sure main chiller and gas are turned on;
  - 3) Check that the rotary switch on the side of the machine is set to Normal ;
  - 4) Check that the sampler and skimmer cones, glassware, and tubes are clean and undamaged;
  - 5) Check the initial Expansion Pressure (E3), Intermediate Pressure (E-4) and Analyzer Pressure (E-8) - enter values into log book;



- 6) Turn on mini-chiller to spray chamber;
- 7) Start the peripump after extracting the nebulizer and manually start the gas flows - check that the spray is constant (let spray hit a tissue). If it is not (i.e., it is pulsing), adjust tension in pipes at peripump. If that does not fix it, seek help. Switch pump off after this procedure;
- 8) Go from Pumping mode to Stand-By mode (computer) and ensure that the cool gas flow rate is  $\sim 14 \text{ l sec}^{-1}$ ;
- 9) Let machine purge for about 15 seconds more than the minimum indicated by the computer;
- 10) Light the plasma;
- 11) After stabilization, switch to Operate mode;
- 12) The running pressures should be approximately: Expansion Pressure (E0), Intermediate Pressure (E-4), Analyzer Pressure (E-6) - enter values in log book;
- 13) Start the peripump;
- 14) Have the machine set at mass 115 (Indium) - can be set using the computer;
- 15) Let the machine stabilize for  $\sim 1$  hour;
- 16) Then check that the torch is centered - adjust horizontal and vertical settings checking cps read out on screen at the left of the machine;
- 17) To begin with, the lenses should be set to their default settings (i.e., Extraction = 2.0; Collector = 7.8; L1 = 7.7; L2 = 5.4; L3 = 5.0; L4 = 3.8). RF power should be 1350 Watts.
- 18) Gas Flows: Nebulizer  $\sim 0.85 \text{ l min}^{-1}$ ; Cool Gas  $\sim 14 \text{ l min}^{-1}$ ; Auxiliary  $\sim 1.5 \text{ l min}^{-1}$ . Gas flows may be adjusted slightly during the tuning procedure, but do this under supervision. Do not touch any other knob on the front panel.
- 19) Run a quick 30 second scan to check the resolution;
- 20) Then start tuning on mass 115 in the following order of lens stack controls: Extraction, Collector, L1, L3, L2, L4. Need to maximize counts at best stability.
- 21) Once the tuning procedure has been conducted once, adjust Auxiliary and Nebulizer flows to maximize counts at best stability;
- 22) Repeat steps 20) & 21);
- 23) Set the machine at mass 156 = Cerium Oxide - adjust gas flows (Auxiliary & Nebulizer) to minimize oxides;
- 24) Re-set to mass 115 and repeat step 20);
- 25) Set machine to mass 9 (Beryllium) and repeat step 20);
- 26) Set machine to mass 238 (Uranium) and repeat step 20);
- 27) Once the tuning procedure is complete, enter lens settings and gas flows in the log book;

- 28) Run short term stability test - only acceptable if elements are  $\pm$  2% standard deviation and oxides < 10% of element (preferably < 5%);
- 29) If stability test is OK, you are ready to run samples. If not, repeat tuning procedure.

### **5) SAMPLE PREPARATION AND MACHINE SET-UP USING FULL TRACE ELEMENT ANALYSIS PROTOCOL**

This procedure allows data to be reduced using both a modified standard addition protocol as well as using external calibration. It allows an independent check of the data, if it is questioned, or if the spike may have been made up incorrectly.

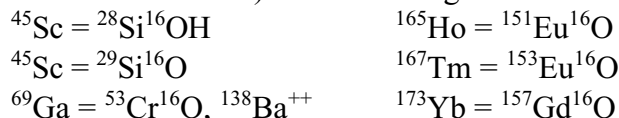
- 1) Dissolution of sample. After HF/HNO<sub>3</sub> treatment, dissolve 50mg of rock in 100 ml of 5% HNO<sub>3</sub> - gives 0.05% of rock in solution.
- 2) Make up a stock solution of As, Rh, In, Re, & Tl at 40 ppb in 5% HNO<sub>3</sub>. These will act as Internal Standards.
- 3) Prepare stock solutions of Matrix Standards A & B in DOUBLE the concentrations (ppb) shown in the table. Each Matrix Standard is prepared by adding 3 g of a stock solution to a test tube followed by 3 g of the Internal Standard stock. The Matrix Standard concentration for each element in the final solution should be close to those given in the table. Internal Standards are again at 20 ppb.
- 4) Prepare a stock solution of the Spike shown in the table (concentrations are again in ppb). In this stock solution should be the Internal Standards at 40 ppb concentration. 3g of this solution is added to 3 g of sample or concentration standards, such that the concentrations are half those in the table and the Internal Standards are again at 20 ppb.
- 5) **SAMPLE PREPARATION:** Prepare two sets of tubes for each concentration standard, each standard reference material, and each unknown sample:
  - (a) Prepare Concentration Standards of 1, 5, 10, 50, 100 ppb - prepare two test tubes each containing 3 g of Concentration Standard solution of double the concentration required (i.e., 2, 10, 20, 100, or 200 ppb) to one add 3 g of the Internal Standard stock solution, to the other add 3g of the spike stock solution containing the internal standards at 40 ppb. This will give you Concentration Standards of 1, 5, 10, 50, & 100 ppb, the former unspiked (except for the internal standards) and the latter spiked with all elements listed in the table (plus the internal standards). Throughout this and the next two steps, the former is the unspiked aliquot and the latter the spiked aliquot;
  - (b) Add 3 g of each Procedural Blank to each tube; to one tube then add 3 g the Internal Standard stock solution, to the other add 3 g of the Spike containing the internal standards;
  - (c) Add 3 g of the standard reference material/unknown sample (0.05% concentration) to each sample; to one tube then add 3 g of the Internal Standard stock solution, to the other add 3 g of the spike containing the internal standards. The former is the unspiked aliquot and the latter the spiked aliquot.
  - (d) For each acid blank, add 3 g of 5% HNO<sub>3</sub> to 3g of the Internal Standard stock solution.
- 6) **ANALYSIS:** Set up the Matrix Standard, Concentration Standards, Standard Reference Materials, Acid Blanks, and Unknown Samples as follows:

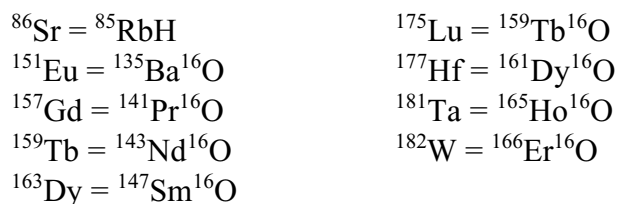
1)	Matrix Std A	21)	Procedural Blank Unspiked
2)	Matrix Std B	22)	Procedural Blank Spiked
3)	5% HNO <sub>3</sub> Acid Blank	23)	5% HNO <sub>3</sub> Acid Blank
4)	1ppb Concentration Std Unspiked	24)	Matrix Std A
5)	1ppb Concentration Std Spiked	25)	Matrix Std B
6)	5% HNO <sub>3</sub> Acid Blank	26)	5% HNO <sub>3</sub> Acid Blank
7)	5ppb Concentration Std Unspiked	27)	Std Ref. Material Unspiked
8)	5ppb Concentration Std Spiked	28)	Std Ref. Material Spiked
9)	5% HNO <sub>3</sub> Acid Blank	29)	5% HNO <sub>3</sub> Acid Blank
10)	10ppb Concentration Std Unspiked	30)	Unknown Sample 1 Unspiked
11)	10ppb Concentration Std Spiked	31)	Unknown Sample 1 Spiked
12)	5% HNO <sub>3</sub> Acid Blank	32)	5% HNO <sub>3</sub> Acid Blank
13)	Matrix Std A	33)	Unknown Sample 2 Unspiked
14)	Matrix Std B	34)	Unknown Sample 2 Spiked
15)	50ppb Concentration Std Unspiked	35)	5% HNO <sub>3</sub> Acid Blank
16)	50ppb Concentration Std Spiked	36)	Matrix Std A
17)	5% HNO <sub>3</sub> Acid Blank	37)	Matrix Std B
18)	100ppb Concentration Std Unspiked	38)	5% HNO <sub>3</sub> Acid Blank
19)	100ppb Concentration Std Spiked		ETC., ETC.!
20)	5% HNO <sub>3</sub> Acid Blank		

- 7) Between each test tube, a 3 stage wash sequence is run: (a) 10% HNO<sub>3</sub> + 1 drop of HF per 150 ml of nitric; 2) 10% HNO<sub>3</sub>; 3) 5% HNO<sub>3</sub> (depending on which is used as the matrix for your standards and samples). Each wash is run for 90 seconds.
- 8) Run a Standard Reference Material (unspiked and spiked) at the beginning, middle, and end of your run.
- 9) At the end of your run, end up with Matrix Std A, Matrix Std B, then the concentration standards of 1, 10, 100 ppb (unspiked and spiked). Again, run the wash sequence between each test tube.
- 10) Do not run more than 12 unknown samples in one run.

## DATA REDUCTION

- 1) **BLANK CORRECTION:** *Sample Counts - Acid Blank Counts* (nearest acid blank to where sample was analyzed in the sequence).
- 2) **INTERFERENCE CORRECTION:** *Blank-Corrected Sample Counts - % of Interference Counts* (calculated from Matrix Standards A & B directly above and below the sample in the analysis sequence outlined above). The following interferences are corrected for:





3) **CALCULATION OF MATRIX FACTORS**: These corrections are required to account for fluctuations in sensitivity (counts per ppb) due to signal suppression/enhancement. This can be conducted in two ways:

- (a) Signal fluctuation in the regularly spaced Matrix Standards: Look at the counts on each element in these standards. Not only can you calculate the % of interferences on certain elements, but you can see the change in signal intensity on all elements. The assumption is that the change is linear between each set of Matrix Standards, and the counts on the samples/standards in between can be corrected on the basis of position in the analytical sequence.
- (b) Signal fluctuation on each element in the spike: Using the spiked samples/standards, the change in counts per ppb for each element in the spike can be monitored and corrected for:

$$\text{[(Spiked Sample or Std Counts - Unspiked Sample or Std Counts)/ppb in spike]*Dilution Factors}$$

Dilution Factors are those incurred by the dilution of the spike by the sample.

- (c) The Matrix Factor applied to the analysis is basically (b)/(a). As matrix factors are consistent over a range of masses, the correction applied to unspiked elements is that of the closest element, or can be calculated assuming linear change between matrix factors of elements bracketing these unspiked elements.

4) **MACHINE DRIFT CORRECTION**: This corrects for changes in machine response across the mass range during the time of analysis. It is related to 3), but is used to look at drift between spiked and unspiked samples. This allows a better (more precise) determination of the counts per ppb of elements in you spike because we use elements that are NOT included in the spike. Therefore, ASSUMING THAT EXACTLY THE SAME AMOUNT OF SAMPLE/STANDARD HAS BEEN ADDED TO EACH TEST TUBE (or you know the EXACT amount of sample in each tube), we should have the same number of counts from each test tube. Elements to be used: Li, Rb, Ce, Bi - these are not in the spike.

5) **FINAL CALCULATION**:

$$\text{(Corrected Unknown Counts/Corrected Std Counts per ppb)* Drift Factor*Matrix Factor*Dilution Factor}$$

Elements	Standard A	Standard B	Spike
<sup>7</sup> Li	40	–	–
<sup>9</sup> Be	40	–	40
<sup>45</sup> Sc	40	–	80
<sup>51</sup> V	40	–	80
<sup>53</sup> Cr	–	100	–
<sup>59</sup> Co	40	–	80
<sup>60</sup> Ni	40	–	80
<sup>65</sup> Cu	40	–	80
<sup>66</sup> Zn	40	–	80
<sup>69</sup> Ga	–	40	80
<sup>85</sup> Rb	40	40	–
<sup>86</sup> Sr	100	–	200
<sup>89</sup> Y	20	–	20
<sup>90</sup> Zr	40	–	80
<sup>93</sup> Nb	20	–	20
<sup>95</sup> Mo	20	–	20
<sup>118</sup> Sn	20	–	20
<sup>121</sup> Sb	20	–	20
<sup>133</sup> Cs	20	20	20
<sup>137</sup> Ba	200	–	400
<sup>139</sup> La	20	–	40
<sup>140</sup> Ce	20	20	–
<sup>141</sup> Pr	20	–	40
<sup>145</sup> Nd	–	40	80
<sup>147</sup> Sm	–	40	80
<sup>151</sup> Eu	–	40	20
<sup>157</sup> Gd	–	40	40
<sup>159</sup> Tb	40	–	20
<sup>163</sup> Dy	20	–	40
<sup>165</sup> Ho	20	–	20
<sup>167</sup> Er	40	–	80
<sup>169</sup> Tm	20	–	40
<sup>173</sup> Yb	20	–	20
<sup>175</sup> Lu	–	40	20
<sup>177</sup> Hf	–	20	40
<sup>181</sup> Ta	–	20	20
<sup>182</sup> W	–	20	20
<sup>206</sup> Pb	40	–	40
<sup>207</sup> Pb	40	–	40
<sup>208</sup> Pb	40	–	40
<sup>209</sup> Bi	20	–	–
<sup>232</sup> Th	20	20	20
<sup>238</sup> U	20	–	20

**Concentrations in ppb**

**6) WASHING OF TEFLON AND GLASSWARE (REFERRED TO AS *ITEM*)**

- rinse used *item* in 18 MΩ H<sub>2</sub>O
- Place rinsed *item* in 50% HCl on hot plate (medium) in rear of laminar flow fume hood for 5 days
  - place date on glass beaker with tape and marker
- remove *item* using Teflon tongs and rinse in 18 MΩ H<sub>2</sub>O

- Place rinsed *item* in 50% HNO<sub>3</sub> on hot plate in rear of laminar flow fume hood for 5 days  
-place date on glass beaker with tape and marker
  - remove *item* from 50% HNO<sub>3</sub> using Teflon tongs
  - rinse used *item* in 18 MΩ H<sub>2</sub>O
  - place *item* in 18 MΩ H<sub>2</sub>O bath on hot plate in rear of laminar flow fume hood for 3 days
  - discard 18 MΩ H<sub>2</sub>O and rinse *item*
  - air dry *item* under laminar flow fume hood
  - After *item* is dry:
    - cap screw top Teflon beakers with correct cover
    - cover glassware with parafilm
  - place clean *item* in appropriate cabinet
- Discard used 50% HNO<sub>3</sub> & HCl after 3-5 uses (depending upon batch sizes)

## 7) PGE (+ Au) ION EXCHANGE COLUMN PROTOCOLS

### CLEANING

- place column in 10% HNO<sub>3</sub> bath for 24 hours (room temperature)
- rinse column in 18 MΩ H<sub>2</sub>O
- place column in 10% HCl bath for 24 hours (room temperature)
- rinse column in 18 MΩ H<sub>2</sub>O
- air dry

### PACKING RESIN

- fill columns with 18 MΩ H<sub>2</sub>O
- spatula desired amount of resin into column reservoir
- allow to settle
- adjust resin depth if needed

### CLEANING COLUMN/RESIN AFTER USE

- fill reservoir (~20 ml) with 6M (50%) HCl
- collect and discard effluent
- repeat
- fill 50 ml Teflon beaker with 5% HCl
- place column in Teflon beaker containing 5% HCl
- fill column (not reservoir) with 5% HCl
- using 5 ml pipette, draw resin up column and into pipette
- decant resin into reservoir and allow to settle
- add 10 ml of 5% HCl to re-equilibrate column

### STORING COLUMNS

- clean columns using cleaning protocol
- add 10ml 5% HCl to reservoir
- seal with parafilm
- place column in 4 L beaker containing ~ 1 L of 5% HCl
- Cover beaker with Saranwrap
- Place under fume hood