



## **Application of a Desolvating Microconcentric Nebulizer with the Elan 6000 ICP-MS**

**Problem:** Conventional pneumatic nebulization systems suffer from several disadvantages. Nebulization efficiency is low and solvent loading to the plasma is high. The result is an increase in polyatomic ion interferences which can degrade the detection limit of many key elements in numerous ICP-MS applications. A system is needed that will offer the advantages of low sample consumption, increase in sensitivity and most importantly, a large reduction in spectral interferences. The system should be applicable to a wide range of applications associated with ICP-MS.

**Solution:** The Elan 6000 ICP-MS is ideally suited for membrane desolvation applications and offers seamless threading of the CETAC MCN-6000 sample introduction system via the Elan 6000 software. Combining the fundamental microvolume capabilities of a teflon microconcentric nebulizer with the high performance of CETAC's microporous membrane technology, the MCN-6000 delivers improved sensitivity and reduced polyatomic ion interferences. The result is an innovative approach to solving application problems.

**Advantages:**

- Reduction in polyatomic ion interferences
- Self-aspirating
- Completely HF resistant
- Sensitivity increased 2-3 times
- Fully automated micro-autosampler
- Microvolume sampling, 10-100  $\mu\text{L}/\text{min}$
- Nitrogen addition to further enhance signal
- Mass flow control of both argon and nitrogen
- Excellent detection limits and stability
- Direct analysis of aggressive reagents and samples

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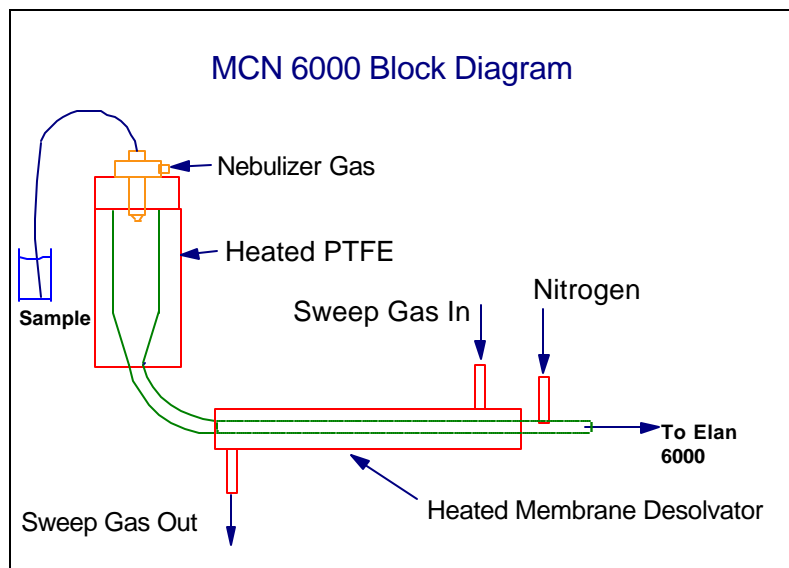
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**Introduction:** The MCN-6000 generates a fine aerosol by efficiently combining argon nebulizer gas with micro-sample flow self-aspirated through a teflon capillary. The aerosol is heated in a single pass teflon spray chamber and carried into a heated membrane desolvation system

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where the solvent is removed with a counter flow of argon, called sweep gas. The dry aerosol is then combined with nitrogen prior to entering the interface of the Elan 6000. A block diagram of the system is presented in Figure I.



**Figure I:** Schematic diagram of the MCN-6000 microconcentric nebulizer desolvation system.

The Elan 6000 ICP-MS is used in concert with the MCN-6000 system and is optimized using the computer controlled functions standard in the Elan 6000. These functions include software controlled auto-optimization and tuning using the normal tuning elements Mg, Rh and Pb; or tuning elements of choice. Oxide and polyatomic ion interference levels are easily monitored using the Realtime feature in the software. The most useful optimization data is often obtained while monitoring specific analytes in the time resolved mode.

The high efficiency aerosol generation of the MCN-6000 finds immediate application in cases where sample volume is limited. For example, nuclear applications where waste must be minimized and in pharmaceutical and biochemical applications where sample volume is limited.

The MCN-6000 is constructed entirely of teflon making it resistant to many types of reagents, especially those used in the semiconductor industry; solvents, acids and proprietary photoresists.

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## **Performance Evaluation**

The MCN-6000 system, when coupled to the Elan 6000, enhances sensitivity an order of magnitude or greater under normal operating conditions. The desolvation system reduces problematic metal oxide interference species to extremely low levels. An example of the MCN-6000 performance on the Elan 6000 is given in Table 1. When both analytical systems are optimized, the Ce/CeO oxide ratio should be better than 0.03%.

**Table 1:** Performance of the MCN-6000 optimized on the Elan 6000.

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<b><u>Analyte</u></b>
Mg
Rh
Pb
Ba
Ba <sup>++</sup>
Ce
CeO
Bkgd
<b><u>Mass</u></b>
24
103
208
138
69
140
156
220
<b><u>Intensity (cps)</u></b>
239049
738221
621862
785806
0.0362
993364
0.0001
16.67

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**Std Dev**

3912  
9236  
9374  
11269  
0.00  
15384  
0.00  
2.06

**% RSD**

1.637  
1.251  
1.507  
1.434  
0.709  
1.594  
4.317  
12.293

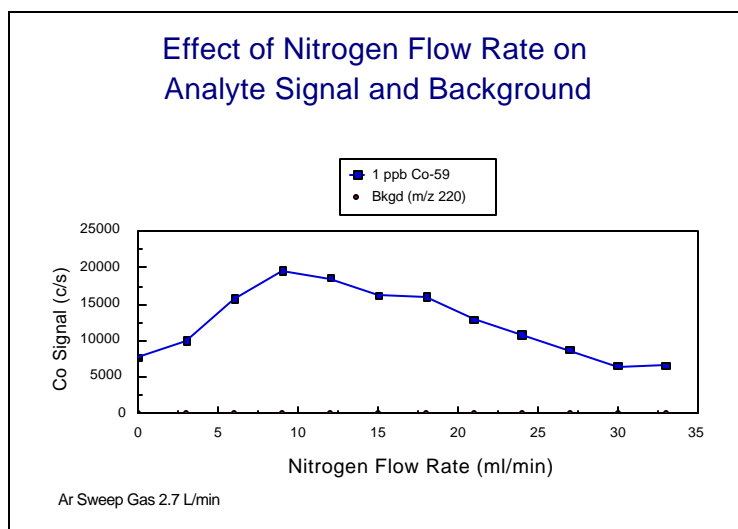
**System Operating Conditions:**

Nebulizer Gas Flow = 1.0 L/min  
Lens Voltage = 4.2 V  
RF Power = 1350 W  
Analog Stage Voltage = -2200  
Pulse Stage Voltage = 1150

Sweep Gas Flow = 3.04 L/min  
Nitrogen Addition = 13 mL./min  
Spray Chamber Temp. = 70° C  
Desolvation Temp. = 160° C

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Nitrogen addition to the sample aerosol is key to determining many problematic transition elements and in enhancing analyte signal. Nitrogen addition will increase nitrogen oxides and should be monitored depending on the application. During the optimization of the MCN-6000 and the Elan 6000, the nitrogen flow rate is adjusted to obtain the optimum signal for a particular element and matrix. The nitrogen mass flow controller is capable of operating in the range 0-100 mL/min. Advantages of mixed gas plasmas are well documented in recent literature, however, the MCN-6000 is the first commercial system that provides for mixed gas additions, using low flow nitrogen downstream of the argon carrier gas. Figure II shows the effect of nitrogen on the signal for 1 ppb Co.



**Figure II:** Effect of nitrogen flow rate on signal intensity.

During optimization of the MCN-6000 and Elan 6000 stability of the systems should be monitored. Shown in Figure III is the short-term stability of the MCN-6000 using 10  $\mu\text{g/L}$  tuning solution. The stability of the teflon microconcentric nebulizer is excellent. Short-term stability was performed under typical sample analysis conditions.

Typically, long term stability is  $<4.0\%$  RSD over four hours.

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**Replicate**

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25

**Time (sec)**

0.23  
2.35  
4.47  
6.59  
8.71  
10.83  
12.95  
15.07  
17.19  
19.31  
21.43  
23.55  
25.67  
27.79  
29.91  
32.03  
34.15  
36.27  
38.39  
40.51  
42.63  
44.75  
46.87  
48.99  
51.11

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**Element**

Mg  
Rh  
Pb  
Bkgd

**Mg 24**

122457.18  
119904.46  
120350.83  
119559.56  
117316.01  
119788.82  
121044.77  
119192.36  
122339.47  
123583.63  
122926.01  
119780.70  
122197.41  
121389.74  
121513.52  
120492.86  
123683.09  
119472.32  
121316.68  
119257.28  
123086.35  
121951.85  
122402.39  
123465.90  
121748.92

**Average**  
**Intensity**

121208.88  
957870.23  
745143.53  
45.68

**Rh 103**

961398.73  
954751.71  
964540.58  
955654.98  
953110.85  
952697.34  
951215.53  
948228.11  
955603.55  
970390.91  
965820.92  
952936.50  
954966.34  
958376.53

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956019.44  
956833.39  
970890.37  
954432.01  
952733.10  
956372.74  
962137.10  
956339.20  
961671.69  
959635.84  
959998.23

**Standard  
Deviation**

1650.09  
5677.14  
6803.09  
10.21

**Pb 208**

750826.32  
741070.34  
746325.73  
735338.43  
744025.02  
751365.85  
735759.25  
750088.07  
751252.26  
747795.10  
737209.39  
737643.39  
757232.92  
742833.42  
746485.10  
745561.67  
743682.36  
746216.57  
735011.38  
737277.00  
761964.41  
741890.74  
747028.73  
744175.61  
750529.27

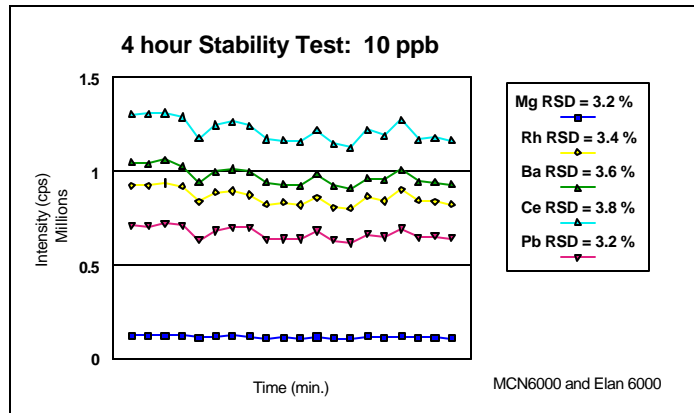
**% RSD**

1.4  
0.6  
0.9  
22.3

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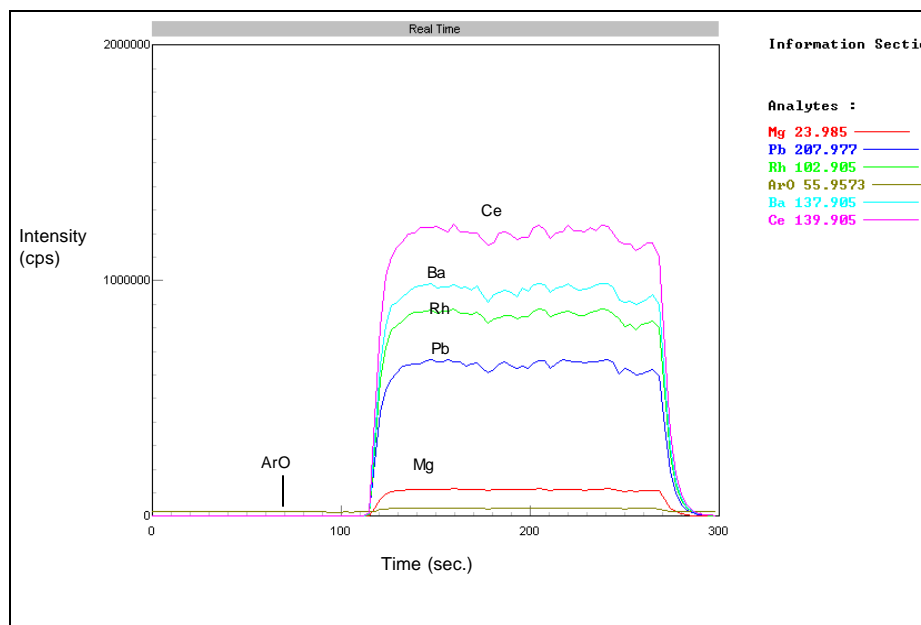
**m/z 220**

48  
46  
50  
40  
48  
56  
28  
60  
50  
62  
26  
42  
36  
26  
44  
44  
46  
34  
60  
60  
50  
40  
52  
48  
46



**Figure III:** Long term stability of the MCN-6000 and Elan 6000.

The ICP-MS signal profile and sample dynamics are very important in monitoring uptake and rinse out times. Figure IV shows a typical signal profile for the tune elements.



**Figure IV:** Signal profile (10 ppb), MCN-6000 and Elan 6000.

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# Application

## Semiconductor

The high efficiency MCN-6000 finds immediate application in cases where sample volume is limited. For example, in semiconductor reagent analysis the system is ideal for the determination of vapor phase deposition samples in a single analytical run under hot plasma conditions.

Experimental conditions of the Elan 6000 and the MCN-6000 are given in Table 2.

**Table 2:** Experimental conditions for the analysis of VPD samples.

Nebulizer Gas Flow	0.8 L/min
Lens Voltage (auto)	3.9 V
RF Power	1350 W
Sweep Gas Flow Rate	2.7 L/min
Nitrogen Addition	15 L/min
Spray Chamber Temperature	80° C
Desolvation Temperature	160° C

Background count rates are critical in determining trace elements under hot plasma conditions. Table 3 shows the dramatic reduction in polyatomic interference while giving adequate signal for the analysis of VPD samples without changing plasma conditions when analyzing cool plasma elements.

**Table 3:** Background count rates under hot plasma conditions.

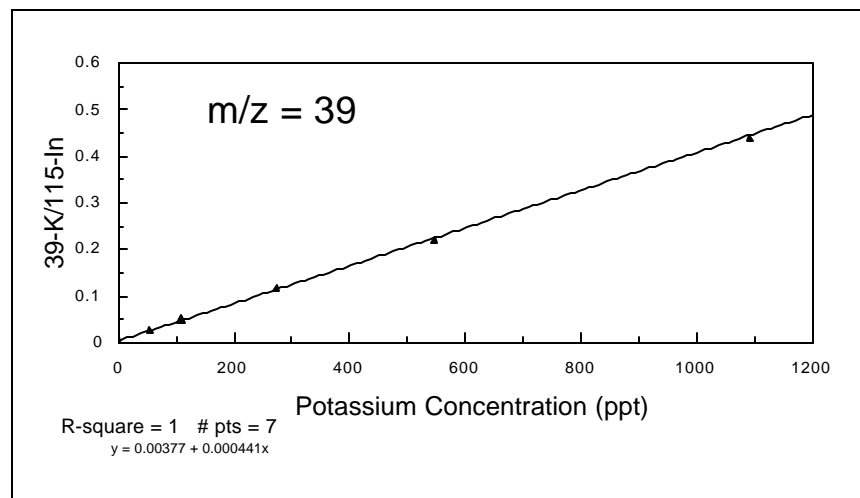
**Main Interferent**

**Analyte**

**m/z**  
**Intensity**  
**(cps)**

ArH  
K  
39  
148  
CO<sub>2</sub> , N<sub>2</sub>O  
Ca  
44  
270  
ArO  
Fe  
56  
441  
-  
Co  
59  
15,900 (1 ppb)

The calibration curve for K under hot plasma conditions is shown in Figure V.



**Figure V:** Calibration curve for K in VPD application.

The major advantage of using the MCN-6000 with the Elan 6000 for VPD analysis is that all elements can be determined in a single analytical run. Normally, the ICP-MS is optimized under cool plasma conditions and cool plasma elements are determined. The MCN-6000 is optimized under hot plasma conditions and an entire suite of analytes can then be determined.

The matrix for this work is approximately 1% HF and the sample has been preconcentrated. Many laboratories use different sample preparation techniques and it is often proprietary in nature. Detection limits for this application are given in Table 4.

**Table 4:** 3s detection limits under hot plasma conditions, units are ppt.

Isotope	Detection Limit	Isotope	Detection Limit
7 Li	0.6	56 Fe	5
23 Na	3	58 Ni	0.2
27 Al	10	59 Co	0.8
39 K	2	63 Cu	1
44 Ca	20	64 Zn	4
53 Cr	10	98 Mo	0.4
55 Mn	8	208 Pb	3

Accuracy of the technique is shown in Table 5. A 100 ppt matrix spike was evaluated and recoveries for cool plasma elements and Pb are given.

**Table 5:** 100 ppt spike recoveries in 1% HF, Elan 6000 and MCN-6000.

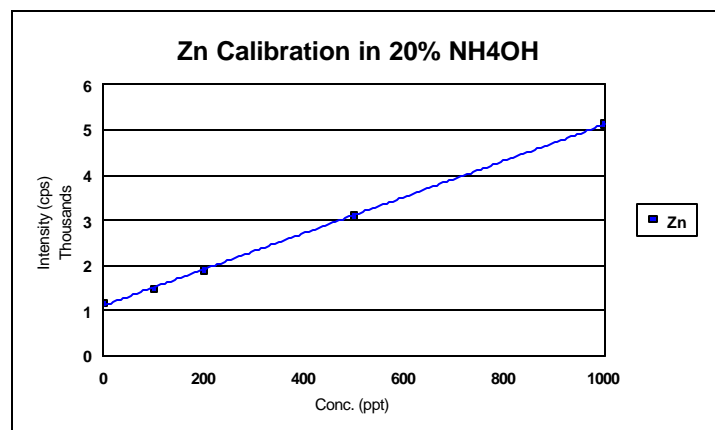
#	Inten. (c/s)	Al	Ca	Cu	Fe	K	Pb
1	53912	97.4	91.2	98	96.3	101.6	97.6
2	54940	96.6	89.8	97.2	95	111.4	97.9
3	53374	99.1	84.9	97.4	99.1	101.4	99
4	56206	96.8	78.8	98	99.3	101.4	96.9
5	57364	97.6	88.3	99.3	98.4	107.4	97.6
6	54468	101	82.9	99.3	100.3	103	97.4

The analysis of aggressive reagents at trace levels is a primary concern among semiconductor laboratories. The MCN-6000 is constructed of entirely inert materials and allows the determination of trace elements

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in concentrated acids and aggressive reagents such as ammonium hydroxide. Figure VI shows the calibration of Zn-66 in 20% NH<sub>4</sub>OH. The desolvation step, now considered mandatory in many semiconductor applications, dramatically reduces solvent based polyatomic ions allowing un-interfered determination of elements such as Fe, K, V and As in strong acid matrices

One major hurdle in performing analyses in these reagents is the viscosity of the sample. Since the system is usually operated in self-aspiration mode to obtain the low flow rates (60µL/min), special consideration must be given to sample viscosity. Alternatively, the sample can be delivered by the peristaltic pump, although tubing contamination and compatibility must also be addressed, as are the higher sample flow rates.



**Figure VI:** Zn calibration curve in 20% NH<sub>4</sub>OH,  $r^2 = 1.0$ .

Experimental conditions for the analytical systems are given below:

**Elan 6000**

Nebulizer Gas Flow = 1.0 L/min  
Lens Voltage = 3.9 V  
RF Power = 1400 W  
Analog Stage Voltage = -2200  
Pulse Stage Voltage = 1150  
Discriminator Threshold = 70  
AC Rod Offset = -8.0

**MCN-6000**

Sweep Gas = 3.58 L/min  
Nitrogen Addition = 14 ml/min  
Spray Chamber Temp = 70°C  
Desolvation Temp = 160°C

Application: Trace Analysis of 20% NH<sub>4</sub>OH using the MCN-6000 and Elan 6000.

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Precision for the analysis of 20% NH<sub>4</sub>OH is good. The physical and chemical properties of the matrix do not appear to cause problems during self-aspiration. However, more dilute solutions of NH<sub>4</sub>OH showed some adverse effects on signal stability. This is most likely due to a sporadic leaching effect in the membrane system. Again, the sample can be delivered using a peristaltic pump provided contamination and compatibility are not an issue.

Detection limits over the mass range in this application are given in Table 6.

**Table 6:** 3s detection limits and stability for selected analytes in 20% NH<sub>4</sub>OH.

<u>Element</u>	<u>% RSD</u> <u>(200 ppt)</u>	<u>3s DL (ppt)</u>
Mg 23	1.6	12
Zn 64	1.5	7.1
Zn 66	0.8	8.5
Rh 103	1.2	12
Ba 138	1.4	1.1
Ce 140	1.2	2.2
Pb 208	1.3	27.1

## Organic Solvent Analysis

Trace analysis of organic solvents is easily accomplished using the MCN-6000. Unlike most conventional sample introduction systems, the MCN-6000 spray chamber and membrane desolvator are both heated. The temperature of the membrane is adjusted above the boiling point of the sample matrix. The membrane efficiently carries the solvent to waste venting and drastically reduces solvent loading to the plasma.

The upper temperature of the membrane is 160° C. This allows the user to adjust to the temperatures that suit a particular solvent application. For example, the real time optimization software is used to monitor particular tune elements at different membrane temperatures. It is important to note that nebulization efficiencies vary greatly between solvents.

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Table 7 shows the Elan 6000 optimization report in isopropylalcohol (IPA).

**Table 7:** Performance of the MCN-6000 optimized on the Elan 6000 in Isopropylalcohol..

<u>Analyte</u>
Mg
Rh
Pb
Ba
Ba++
Ce
CeO
Bkgd
<u>Mass</u>
24
103
208
138
69
140
156
220
<u>Intensity (cps)</u>
11611
180105
149002
98888
0.0438
163212
0.0002
18.8

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**Std Dev**

283.245  
1132.155  
1091.093  
970.415  
0.008  
2530.573  
0.000  
3.293

**% RSD**

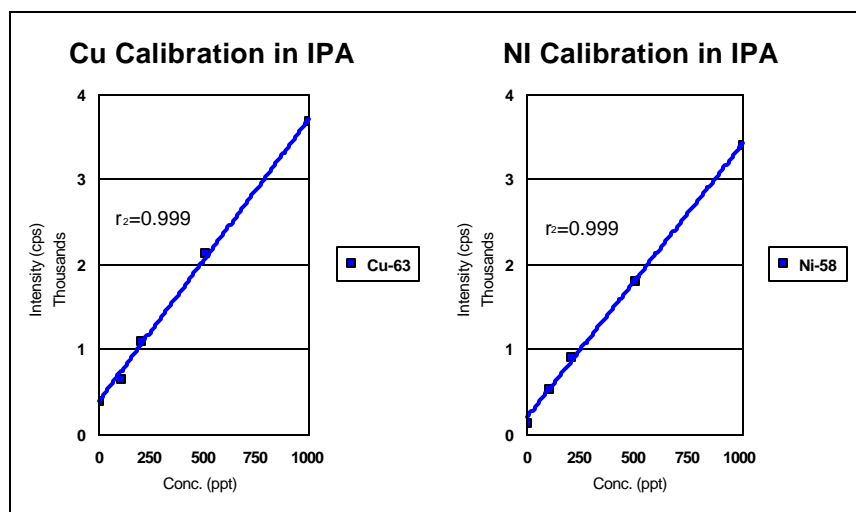
2.439  
0.629  
0.732  
0.931  
18.878  
1.55  
10.926  
17.516

**System Operating Conditions:**

Nebulizer Gas Flow = 0.8 L/min  
Lens Voltage = 5.5 V  
RF Power = 1350 W  
Analog Stage Voltage = -2300  
Pulse Stage Voltage = 1100

Sweep Gas Flow = 1.57 L/min  
Nitrogen Addition = 16 mL./min  
Spray Chamber Temp. = 70° C  
Desolvation Temp. = 160° C

Calibration curves for Cu and Ni are presented in Figure VII. Detection limits are typically in the ppt range in solvents that have boiling points less than 170° C. Detection limits will be higher when performing mixed gas additions with oxygen or some other gas.



**Figure VII:** Trace element calibration in isopropylalcohol.

Non-oxygenated organic solvents such as toluene, hexane and other hydrocarbons often require the addition of low flow oxygen (5-20 mL/min.) to achieve a stable plasma with little carbon formation on the torch and cones. For example, the addition of oxygen results in the formation of volatile species such as  $\text{CO}_2$  and  $\text{CO}$ . Mixed gas addition is most often done with a mixing tee in the sample stream after the desolvation step. The tee is fitted with an accurate flow meter or other suitable device for precision control of oxygen flow.

## Application Summary

The MCN-6000 desolvating microconcentric nebulizer combines a number of application-oriented innovations. It is a powerful sample introduction system that is well suited to many matrix and detection limit oriented applications. The coupling with the Elan 6000 offers many advantages: seamless threading of software control, improved sensitivity and reduction in polyatomic ion interferences. The optimization procedures given in this application report are simple to perform using the software controlled auto-optimization functions. The solutions identified in this report are common in ICP-MS applications and can be easily overcome using analytical systems that are focused on better ways to introduce sample into the plasma.

## **Instrumentation**

### **Perkin-Elmer/SCIEX Elan 6000 Quadrupole ICP-MS**

### **CETAC Technologies MCN-6000 System**

#### **Specifications**

Nebulizer \_\_\_\_\_ Teflon, Microconcentric

Microporous Desolvating Membrane

Sweep Gas: 0-5.0 L/min.  
Nitrogen Gas: 0-100 ml/min.  
Membrane Temperature: 0-160°C

Voltage: \_\_\_\_\_ 120 VAC +/- 10% 50/60

Hz 6 A

220 VAC +/- 10% 50/60

Hz 3 A

Spray Chamber \_\_\_\_\_

Construction: Teflon  
Temperature: 0-110°C

ASX-100 Autosampler (Fully compatible with Elan 6000)

Sample Tray: Positions 1-5, 20 ml  
capacity for

rinse and optimization

solutions.

Positions 6-14, 5 ml

capacity for

standards and reagents.

Optional Sample Racks:

24 x 1 mL

24 x 4 mL

48 x 0.5 mL

96 x 1 mL

Computer Interfaces: RS-232 and IEEE-488  
Voltage: 100-240 VAC +/- 10% 50/60  
Hz. , 2 A

System Dimensions: 36.8 cm W x 29.5 cm H x 21.6 cm D

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