

## Application Note # CA-270689

## Typical Detection Limits for the Bruker 810-MS in Normal Sensitivity Mode

### Introduction

The Bruker ICP-MS is the world's first ICP-MS system with tunable gigahertz sensitivity (over  $10^9$  cps per mg/L) without compromising oxide and/or doubly charged interference performance, thanks to the patented 90-degree ion mirror [1, 2]. This tunable sensitivity provides the flexibility to choose a suitable sensitivity mode for different sample types or applications, and hence, to achieve the lowest detection limits for a selected application. In this application note, typical instrument detection limits for most elements commonly monitored in environmental analyses are determined using the Bruker 810-MS under normal sensitivity mode.

### Basic principles

#### Limit of detection

According to the recommendation given by the International Union of Pure and Applied Chemistry (IUPAC) [3], the limit of detection expressed as the concentration  $c_L$  or the quantity  $q_L$  is derived from the smallest measure  $X_L$  that can be detected with reasonable certainty for a given analytical procedure. The value of  $X_L$  is given by the equation,

$$(1) X_L = X_{bl} + k s_{bl}$$

where  $X_{bl}$  is the mean of the blank measures,  $s_{bl}$  is the standard deviation of the blank measures, and  $k$  is a numerical factor chosen according to the confidence level desired. IUPAC has also recommended a value of 3 for  $k$ , which gives a confidence level of about 98%. In ICP-MS, the  $X_{bl}$  is the mean cps of the blank measurements, and a typical ICP-MS calibration plot can be expressed by the following equation,

$$(2) X_A = X_{bl} + m C_A$$

where  $X_A$  is the cps measured at an analyte concentration of  $C_A$ , and  $m$  is the sensitivity (i.e. slope of the calibration plot).

Hence in ICP-MS, the value of  $X_L$  can also be given as,

$$(3) X_L = X_{bl} + m C_L$$

From equations (1) and (3), the concentration  $C_L$  can be calculated by the following equation,

$$(4) C_L = 3 s_{bl} / m$$

#### Background Equivalent Concentration

In the Bruker ICP-MS Expert software, the background equivalent concentration (BEC) is calculated by the following equation,

$$(5) BEC = X_{bl} / m$$

Hence, the concentration  $C_L$  can be calculated alternatively from the BEC and the % relative standard deviation (RSD) of the blank, that is,

$$(6) C_L = 3 RSD_{blank} BEC / 100$$

$$\text{where } RSD_{blank} = 100 s_{bl} / X_{bl}$$

### Experimental

#### Instrument

Typical instrument detection limits were measured using two 810-MS instruments, one located in Australia and the other in Japan. Both instruments were installed in non-clean room environment.

#### Reagents and Samples

A blank solution, 1% v/v  $\text{HNO}_3$ , was made using high-purity nitric acid (Ultrapur®, 60%, Merck) and pure deionized water (18MΩ cm, Millipore Milli-Q, Bedford, USA). Two standards, at 1μg/L and 10μg/L levels, were prepared by diluting ICP-MS multi-element stocks with the blank. Prior to use, all labwares were thoroughly cleaned (i.e. acid washing and deionized water rinsing), and then the clean containers were left filled with 1% v/v  $\text{HNO}_3$  until use.

## Results and discussion

### Sensitivity Mode

The 810/820-MS can be operated in a number of sensitivity modes (eg. normal, high, etc.) without any hardware changes. In general, the “high” sensitivity mode is used for applications requiring highest sensitivity, such as laser ablation and analysis of semiconductor materials; while the “normal” sensitivity mode is used for general chemical analyses, including environmental, agriculture and clinical research applications. Hence the “normal” mode is recommended for most ICP-MS analyses. Typical method parameters used for tuning the instrument to a “normal” sensitivity mode are shown in Table 1.

Table 1: Typical method parameters for a Bruker 810-MS tuned to “normal” mode.

	Parameters	Settings*
Gas flow (L/min)	Plasma Flow	16.5
	Auxiliary Flow	1.65 (1.60)
	Nebulizer Flow	0.95 (1.00)
	Sheath Flow	0.28 (0.45)
RF	RF Power (kW)	1.30 (0.70)
Sample Introduction	Sampling Depth (mm)	5.0 (5.5)
	Pump Rate (rpm)	3 (20)
	Stabilization Time (s)	30
	Spray chamber (°C)	3
Ion Optics (volts)	1 <sup>st</sup> Extraction Lens	-1
	2 <sup>nd</sup> Extraction Lens	-140 (-20)
	3 <sup>rd</sup> Extraction Lens	-200 (-190)
	Corner Lens	-180 (-110)
	Mirror Lens Left	75 (105)
	Mirror Lens Right	5 (15)
	Mirror Lens Bottom	50 (20)
	Entrance Lens	1
	Entrance Plate	-37 (-50)
Quadrupole Scan	Fringe Bias	-5
	Pole Bias	0
	Scan mode	Peak Hopping
	Dwell Time (ms)	100
	Points per Peak	1
	Scans/Replicate	30
	Replicates/Sample	10

\* Settings in parentheses are used for “Cool Plasma” conditions.

Settings used for typical “cool” plasma are also listed in Table 1. The “cool” plasma technique is used to minimize polyatomic interferences associated with the plasma gas, such as  $\text{ArO}^+$  and  $\text{Ar}^+$ . This technique can improve the detection limits for elements affected by such interferences, including Fe, Ca, Na, K and Mg. More discussions on the use of cool plasma and more detection limit values under cool plasma conditions can be found in other Bruker’s Application Notes (from Bruker’s web site [www.bruker.com](http://www.bruker.com) under the ICP-MS Application Note section).

### Better detection limits

It should be noted that tuning an ICP-MS to its highest sensitivity does not necessarily provide the lowest detection limit. To achieve the lowest possible detection limits and accurate analytical results, strict precautions must be taken to eliminate or minimize any potential contamination. Where possible, glassware including volumetric pipettes and flasks should be avoided when preparing and/or storing any solutions (with exception of Hg solutions), because some metals may be leached out from the glass or adsorbed onto the glass surface, which could result in sample contamination or loss of analyte. Prior to use, all the labwares, new or used, should be thoroughly cleaned. A typical cleaning procedure includes acid washing the labwares for at least 24 hours to remove elemental contamination, thoroughly rinsing them with high-purity deionized water, and then leaving clean containers filled with 1% v/v  $\text{HNO}_3$  until use.

It is clear from the equations (4) and (6), the lower the standard deviation (or RSD) of the blank, the better the detection limits. A lower RSD can often be obtained by using a relative longer replicate reading and stabilization time. The replicate reading time is dependent on the dwell time and the number of scans per replicate. Typical stabilization and scan settings used in this work are listed in Table 1. Also, the lower the BEC, the better the detection limits. To keep BEC low, high-purity reagents and deionized water should be used in all the samples and standards preparations, and ideally the solutions should be prepared and measured in a class 100 clean room, or at least the sample preparation area should be air-conditioned and dust free. When running the Bruker 810-MS under normal sensitivity mode, the counts for a blank solution should not exceed a few thousand cps per isotope for most isotopes. A higher blank count is often an indication of blank contamination. The lower the contamination (blank counts) the better the detection limits.

### Typical detection limits

Table 2 shows the typical detection limits (DLs) for the elements commonly measured in environmental samples. All DLs were calculated using equation (3), i.e. three times the standard deviation of 10 replicates of the blank (i.e. 1% v/v HNO<sub>3</sub>). The instrument was tuned to “normal” sensitivity mode under either “hot” or “cold” plasma conditions. All the measurements, however, were made under routine analytical laboratory, not clean-room, conditions. This work indicates typical DL values that can be routinely achieved outside a clean-room in a clean laboratory.

Table 2: Typical IDLs for Varian ICP-MS.

Element	Isotope (m/Z)	Measured in		Back-ground species
		Hot plasma (ng/L)	Cold plasma (ng/L)	
Li	7	1	0.01	
Be	9	3		
B	11	30		
Na	23	200	0.5	
Mg	24	2	0.2	
	25	5	0.08	
Al	27	2	0.2	
Si	28	1000		Co <sup>+</sup> , N <sub>2</sub> <sup>+</sup>
P	31	700		NOH <sup>+</sup>
S	34	20000		(OH) <sub>2</sub> <sup>+</sup>
K	39	500	0.5	ArH <sup>+</sup>
Ca	40	500	1	Ar <sup>+</sup> , CO <sub>2</sub> <sup>+</sup>
	44			
Sc	45	0.8		CO <sub>2</sub> H <sup>+</sup> , N <sub>2</sub> OH <sup>+</sup>
Ti	47	3		
V	51	3		ArNH <sup>+</sup> , ClO <sup>+</sup>
Cr	52	8		ArO <sup>+</sup> , ArC <sup>+</sup>
	53	3		
Mn	55	2		ArNH <sup>+</sup>
Fe	56	4000	0.3	ArO <sup>+</sup>
	57	300	0.9	ArOH <sup>+</sup>

### Conclusions

Detection limits are influenced by a number of factors, including the sensitivity of a given isotope, and the presence of background interferences or contamination. It is vitally important to control contamination in the laboratory to achieve the lowest possible detection limits.

Element	Isotope (m/Z)	Measured in		Back-ground species
		Hot plasma (ng/L)	Cold plasma (ng/L)	
Co	59	0.2		ArOH <sup>+</sup>
Ni	60	2		
Cu	63	0.3		
	65	2		
Zn	66	5		
	68	20		
Ga	69	0.3		
	71	0.2		
Ge	72	4		
As	75	20		
Se	77	30		
	78	400		
	82	300		
Rb	85	1		KrH <sup>+</sup>
Sr	88	0.7		
Y	89	0.2		
Zr	90	0.4		
Nb	93	0.8		
Mo	98	0.4		
Ru	101	0.4		
Rh	103	0.1		
Pd	108	0.3		
Ag	107	0.6		

Table 2 (cont.): Typical IDLs for Varian ICP-MS.

Element	Isotope (m/Z)	Measured in		Back-ground species
		Hot plasma (ng/L)	Cold plasma (ng/L)	
Cd	111	0.2		
In	115	0.1		
Sn	118	7		
Sb	121	0.1		
Te	125	4		
Cs	133	0.4		
Ba	138	0.2		
La	139	0.4		
Ce	140	0.06		
Pr	141	0.06		
Nd	146	0.3		
Sm	147	0.2		
Eu	153	0.1		
Gd	157	0.2		
Tb	159	0.09		
Dy	163	0.2		
Ho	165	0.06		
Er	166	0.18		

Element	Isotope (m/Z)	Measured in		Back-ground species
		Hot plasma (ng/L)	Cold plasma (ng/L)	
Tm	169	0.08		
Yb	172	0.3		
Lu	175	0.05		
Hf	178	2		
Ta	181	0.2		
W	182	1.3		
Re	185	0.2		
Ir	193	0.2		
Pt	195	0.3		
Au	197	0.3		
Hg	202	1		
Tl	205	1		
Pb	206+	0.3		
Bi	209	0.3		
Th	232	0.04		
U	238	0.06		

## References

- [1] I. Kalinitchenko, Ion Optical System for a Mass Spectrometer, US Patent 6,614,021 B1, 2 September 2003
- [2] S. Elliott, M. Knowles and I. Kalinitchenko, "A New Direction in ICP-MS", Spectroscopy, 19(1), 30 (2004).
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### Keywords

Sensitivity  
Detection Limit  
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### Instrumentation & Software

Bruker 810-MS  
ICP-MS Expert Software

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