



Application Notes #703038

Analysis of Selenium78 and Selenium80 in Animal Feeds Using the Bruker Aurora M90 and Nitrox 500

Selenium is necessary for growth and fertility in animals and for the prevention of a variety of diseases¹. The minimum intake requirement of Se for a given species varies with the form of Se ingested and dietary composition. The Se requirement is 0.10 ppm(mg Se/Kg) for grazing cattle and horses and 0.03 ppm(mg Se/Kg) for sheep. The maximum tolerable concentrations for cattle, sheep, and horses range from 1 to 5 ppm(mg Se/Kg). Therefore, there is a narrow gap between deficient and toxic Se levels in feed¹.

Though the ability to analyze 1 to 5 ppm($\mu\text{g Se/mL}$) in water and other “clean” samples is more routinely performed by ICP-OES, the need to digest animal feeds, and then overcome inherent matrix issues requires significantly better detection limits. Typically, a small amount of sample is digested in concentrated Nitric acid (HNO_3) followed by a significant dilution in order to remove matrix issues due to the HNO_3 . The results of dilution can bring the final concentration of Se “in solution” to sub-ppb levels.

Because the range between deficient and toxic levels of Se is so narrow, the need to “routinely” analyze samples at sub-ppb levels with increased significant figures is becoming very important.

The scope of this note is to show that sub-ppb Se analysis can be performed on the Bruker Aurora M90 ICP-MS using a Nitrox 500 gas accessory. Low-level Se recovery can be achieved routinely, with increased accuracy. Furthermore, results acquired on a second Bruker ICP-MS with only slight differences between operating parameters could be duplicated.

Instrumentation

All measurements were performed on a Bruker Aurora M90 instrument, located in Milton, Ontario Canada. The ICP-MS was equipped with a Nitrox 500 gas accessory unit. The ICP-MS was set to use a standard sample introduction system with “CRI” sampler and skimmer cones. A “reactive” gas (H_2) was delivered to the skimmer cone at a flow rate of 80-90 (mL/min) in order to reduce Ar-Ar interference. Additionally, 190-200 (mL/min) of Nitrogen (N_2) was added to the auxiliary (Argon) line supplying the torch using a Nitrox 500 gas accessory unit.

Bruker’s patented 90 degree ion mirror^{2,3} provides unsurpassed ion transfer efficiency from the interface to the mass analyzer. This enables the Aurora-MS to achieve more than 1 billion c/s per mg/L of analyte, while maintaining oxide ratios of less than 3% during analysis.

*The method is not applicable to mixtures of FAME which contain other low boiling components.

The Collision Reaction Interface (CRI) interference management System^{4,5} attenuates polyatomic ions formed in the plasma, which can interfere with the determination of elements, such as, As, Se, Cr, V, and Fe, thus improving their selectivity and detection limits.

The Nitrox 500 Gas Accessory Unit injects N₂ into the plasma in order to “constrict” the plasma around the central channel, hence increasing the plasmas ionization potential and further improving detection limits of certain elements such as Se.

Conditions

Operating parameters are summarized in Table 1. The method parameters were optimized using the Quantum software’s Automax routine, which automates setting of all CRI and plasma gas flow rates and ion optic voltages. The parameters were originally optimized on an 820CRI located at the Office of Indiana State Chemist (OISC) located on the campus of Purdue University (West Lafayette, IN.). The method worksheet was then copied to the ICP-MS in Milton, ON where gas flows for sheath gas, nebulizer flow and CRI skimmer flow were adjusted to compensate for the Nitrox 500.

Materials and Reagents

A blank solution of, 1% v/v HNO₃, was made using high purity nitric acid (67-70% as HNO₃) and 18.3 MOhm water. Four standard solutions were prepared at 0.050 µg/L, 0.100 µg/L, 0.500 µg/L and 1.000 µg/L by diluting a stock solution

of 2008 CAL-2 (Inorganic Ventures, Christiansburg, VA) with the 1% HNO₃ blank. The blanks and standards were prepared in PFA volumetric flasks and then transferred into PFA bottles. All flasks, bottles, and pipette tips were soaked in 1% HNO₃ prior to use

Sample Preparation

All samples were prepared by the OISC staff on the Purdue University campus by accurately weighing 0.5 g +/- 0.01g of ground feed sample into a microwave vessel, into which 10 mL of HNO₃ was then added. Microwave digestion was conducted using a CEM Mars X, high pressure, closed-vessel microwave unit (CEM Corporation, Matthews, NC). The vessel was heated to 200°C over a 15 min period, then held at 200°C for an additional 20 min. Samples were allowed to cool to ambient temperature and brought up to 100.00 mL using ultra-pure water (>18 MΩ•cm). Prior to analysis in Milton ON, the samples were diluted ten-fold with ultrapure water (>18 MΩ•cm). The final acid concentration of both samples and standard solutions was 10% HNO₃ during the OISC analysis and 1% HNO₃ during the Milton analysis.

Sample Analysis

An internal standard solution was prepared containing 10 µg/L of ⁴⁵Sc, ⁸⁹Y, and ¹¹⁵In (in 1% HNO₃), which was added online to the sample line via a ‘T piece’. Black/Black tubing was used for both the sample and internal standard lines. In order to simplify the analysis no autosampler was used.

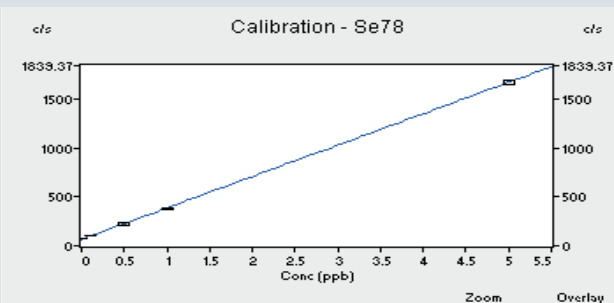
Table 1: M90 Operating Parameters

Parameter	Value	Parameter	Value
Flow Parameters (L/min)		Corner Lens	-206
Plasma Flow	18	Mirror Lens Left	27
Auxiliary Flow	1.8	Mirror Lens Right	23
Sheath Gas	0.41	Mirror Lens Bottom	32
Nebulizer Flow	1.07	Entrance Lens	3
Torch Alignment (mm)		Fringe Bias	-2.5
Sampling Depth	6.5	Entrance Plate	-35
Other		Pole Bias	0
RF Power (kW)	1.4	CRI	
Pump Rate (rpm)	6	Skimmer Gas Source	H2
Stabilization delay (s)	60	Sampler Gas Source	OFF
Ion Optics (volts)		Skimmer Flow	85
First Extraction Lens	-36	Sampler Flow	0
Second Extraction Lens	-164	Nitrox 500	
Third Extraction Lens	-234	Flow (mL/min)	200

Results and Discussion

The results of preliminary analysis of ^{78}Se and ^{80}Se are shown in Figure 1. In both calibrations the percent relative standard deviation (%RSD) of a 0.100 $\mu\text{g/L}$ std was less than 4% for both curves. Several subsequent calibrations produced similar results, suggesting the ability to "routinely" analyze samples at low ppT (ng/L) may be easily achieved. An additional calibration using a 0.050 $\mu\text{g/L}$ standard was performed in order to see if similar results could still be achieved. The results are shown in Figure 2.

Figure 1. Calibration Curve for ^{78}Se and ^{80}Se (0.100 $\mu\text{g/L}$)



Calibration (ppb), Cal Set 1, 11:54:51am 02/Feb/2012

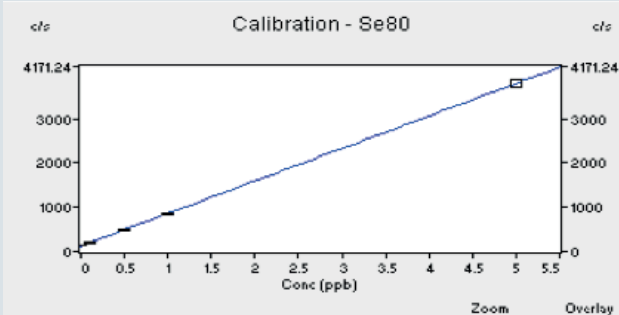
Soln Type	c/s	SD(c/s)	%RSD	Std Conc	Calc Conc	Error	%Error
Blank	71	1.9	2.61	0.0000	0.0207	0.0207	-
0.10 $\mu\text{g/L}$	102	2.5	2.41	0.1000	0.1086	0.0086	8.56
0.50 $\mu\text{g/L}$	231	9.1	3.96	0.5000	0.4942	-0.0058	-1.17
1.0 $\mu\text{g/L}$	381	6.4	1.69	1.0000	0.9702	-0.0298	-2.98
5.0 $\mu\text{g/L}$	679	23.0	1.37	5.0000	5.0064	0.0064	0.13

Curve Fit: Linear, Weighted Fit: No, Thru Blank: No

Correlation Coefficient: 0.999958

Blank Equivalent Concentration: 0.2221 ppb

Calibration Equation: $c/s = (71.3 - 6.662 + 321.1 \cdot \text{conc}) \cdot [I/S \text{ Ratio}]$



Calibration (ppb), Cal Set 1, 11:54:51am 02/Feb/2012

Soln Type	c/s	SD(c/s)	%RSD	Std Conc	Calc Conc	Error	%Error
Blank	133	1.8	1.39	0.0000	0.0111	0.0111	-
0.10 $\mu\text{g/L}$	210	7.3	3.48	0.1000	0.1098	0.0098	9.75
0.50 $\mu\text{g/L}$	497	12.6	2.54	0.5000	0.4860	-0.0140	-2.81
1.0 $\mu\text{g/L}$	862	21.2	2.46	1.0000	0.9900	-0.0100	-1.00
5.0 $\mu\text{g/L}$	3808	91.4	2.40	5.0000	5.0032	0.0032	0.06

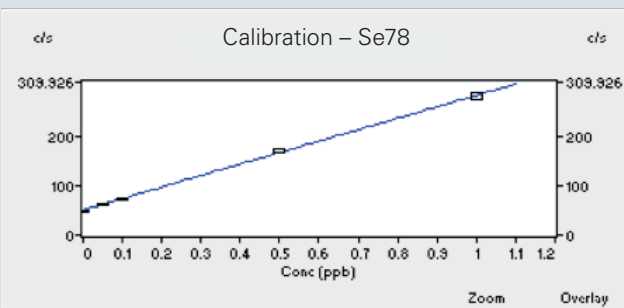
Curve Fit: Linear, Weighted Fit: No, Thru Blank: No

Correlation Coefficient: 0.999985

Blank Equivalent Concentration: 0.1808 ppb

Calibration Equation: $c/s = (132.5 - 8.140 + 733.1 \cdot \text{conc}) \cdot [I/S \text{ Ratio}]$

Figure 2: Calibration Curve for ^{78}Se and ^{80}Se (0.050 $\mu\text{g/L}$)



Calibration (ppb), Cal Set 1, 02:30:10pm 02/Feb/2012

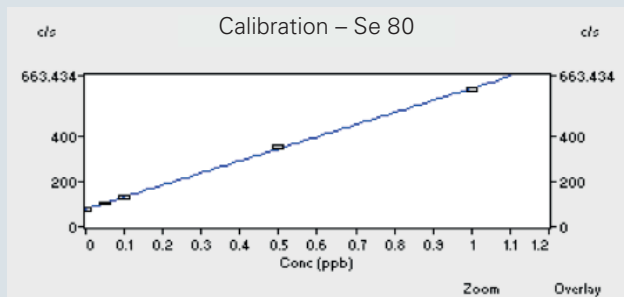
Soln Type	c/s	SD(c/s)	%RSD	Std Conc	Calc Conc	Error	%Error
Blank	49	2.1	4.29	0.0000	-0.0085	-0.0085	-
0.05 $\mu\text{g/L}$	64	2.5	3.99	0.0500	0.0483	-0.0017	-3.46
0.10 $\mu\text{g/L}$	74	2.2	3.03	0.1000	0.1005	0.0005	0.52
0.50 $\mu\text{g/L}$	168	2.8	1.66	0.5000	0.5193	0.0193	3.86
1.0 $\mu\text{g/L}$	274	8.0	2.93	1.0000	0.9904	-0.0096	-0.96

Curve Fit: Linear, Weighted Fit: No, Thru Blank: No

Correlation Coefficient: 0.999624

Blank Equivalent Concentration: 0.2116 ppb

Calibration Equation: $c/s = (49.1 + 1.965 + 231.9 \cdot \text{conc}) \cdot [I/S \text{ Ratio}]$



Calibration (ppb), Cal Set 1, 02:30:10pm 02/Feb/2012

Soln Type	c/s	SD(c/s)	%RSD	Std Conc	Calc Conc	Error	%Error
Blank	75	6.4	8.51	0.0000	-0.0038	-0.0038	-
0.05 $\mu\text{g/L}$	105	4.0	3.80	0.0500	0.0482	-0.0018	-3.65
0.10 $\mu\text{g/L}$	128	6.2	4.80	0.1000	0.0974	-0.0026	-2.58
0.50 $\mu\text{g/L}$	342	5.5	1.61	0.5000	0.5157	0.0157	3.15
1.0 $\mu\text{g/L}$	588	8.3	1.41	1.0000	0.9925	-0.0075	-0.75

Curve Fit: Linear, Weighted Fit: No, Thru Blank: No

Correlation Coefficient: 0.999771

Blank Equivalent Concentration: 0.1418 ppb

Calibration Equation: $c/s = (75.1 + 2.019 + 529.7 \cdot \text{conc}) \cdot [I/S \text{ Ratio}]$

After creating the calibration curves (Figures 1 and 2), seven replicate measurements were taken of the lowest standard. By multiplying the standard deviation of the results by 3, a reasonable estimate of the MDL is calculated to be between 0.01 and 0.02 $\mu\text{g/L}$. The data is found in Table 2.

Table 2: Table 2 MDL Study from calibrations using 0.100 µg/L and 0.050 µg/L as lowest standards.

	⁷⁸ Se ppb	⁸⁰ Se ppb	⁴⁵ Sc ratio	⁸⁹ Y ratio	¹¹⁵ In ratio
Blank	0	0	1	1	1
0.10 ng/mL	0.1	0.1	1.03	1.026	0.997
0.50 ng/mL	0.5	0.5	1.057	1.034	1.006
1.0 ng/L	1	1	1.039	1.014	1.008
5.0 ng/L	5	5	1.021	1.004	1.012
ICB-0	0.0063	-0.0048	1.04	1.011	1.037
ICB-1	0.0088	0.0008	1.01	0.974	0.931
0.1 ng/mL	0.0948	0.0843	1.041	1.015	0.994
0.1 ng/mL	0.0946	0.1042	1.016	0.976	0.961
0.1 ng/mL	0.096	0.0942	1.006	0.981	0.955
0.1 ng/mL	0.1032	0.0996	1.011	0.975	0.965
0.1 ng/mL	0.0968	0.0975	0.993	0.959	0.984
0.1 ng/mL	0.1011	0.0977	0.985	0.954	0.957
0.1 ng/mL	0.0939	0.0881	0.996	0.959	0.954
CCV 1.0	0.9477	0.9689	1.053	1.075	1.041
Average	0.0972	0.09509			
Std Dev	0.00356	0.00686			
MDL	0.01069	0.02057			

	⁷⁸ Se ppb	⁸⁰ Se ppb	⁴⁵ Sc ratio	⁸⁹ Y ratio	¹¹⁵ In ratio
Blank	0	0	1	1	1
0.05 ng/mL	0.05	0.05	1.013	1.021	0.967
0.10 ng/mL	0.1	0.1	1.023	0.996	1.011
0.5 ng/L	0.5	0.5	0.988	0.977	0.978
1.0 ng/L	1	1	0.975	0.975	1.017
ICB-0	0.0086	-0.0058	0.963	0.955	0.947
ICB-1	0.0109	0.0064	0.971	0.952	0.952
0.05 ng/mL	0.0567	0.0444	0.966	0.939	0.941
0.05 ng/mL	0.0655	0.0532	0.954	0.922	0.95
0.05 ng/mL	0.0545	0.046	0.956	0.922	0.95
0.05 ng/mL	0.0539	0.0457	0.953	0.921	0.905
0.05 ng/mL	0.056	0.041	0.967	0.938	0.929
0.05 ng/mL	0.0594	0.0414	0.966	0.927	0.962
0.05 ng/mL	0.0642	0.0451	0.95	0.924	0.929
ICV-1.0	0.9773	0.993	0.971	0.934	0.94

Using the calibrations shown in Figure 1, the samples from the OISC lab were analyzed. The results are shown in Table 3. Although the samples were diluted tenfold, it can be seen that the Aurora in Milton was still able to reproduce the same numbers that were determined on the Purdue campus. The diluted samples had Se concentration in solution between 0.500 µg/L and 1.000 µg/L, suggesting a hundredfold dilution (hence further reducing background due to HNO₃) would still be possible.

Authors: Martin Bennett (Bruker), Natalie Newlon (OISC), James Bartos (OISC)

References

- [1] J.G. Davis, T.J. Steffens, T.E. Engle, K.L. Mallow, S.E. Cotton, Diagnosing Selenium Toxicity [2] I. Kalinitchenko, Ion Optical System for a Mass Spectrometer, US Patent 6614021 B1, 2 December, 2003 [3] Elliott, S., Knowles, M. and Kalinitchenko, I. 2004. A New Direction in ICP-MS. Spectroscopy, 19 (1): 30 [4] I. Kalinitchenko, Mass spectrometry apparatus and method, US Patent 7,329,863 B2, 12 February 2008 [5] X. Wang and I. Kalinitchenko, Principles and performance of the Collision Reaction Interface for the 820-MS, Bruker Technical Note # CA-270111

Table 3: Comparison of Samples

OISC Data				
Sample Label	Se78 ppm	Se80 ppm	Mean 78,80	Std Dev
1571	4.7719	4.806	4.7890	0.0241
1594	2.4492	2.4604	2.4548	0.0079
1865	2.8991	2.8283	2.8637	0.0501
2179	3.3522	3.2812	3.3167	0.0502
2765	3.374	3.3016	3.3378	0.0512
1571-2	5.5906	5.434	5.5123	0.1107
1594-2	2.3065	2.2708	2.2887	0.0252
1865-2	3.0685	2.9061	2.9873	0.1148
2179-2	3.0453	3.0225	3.0339	0.0161
2765-2	3.2927	3.4182	3.3555	0.0887
1571-3	5.7432	5.4311	5.5872	0.2207
1594-3	3.1622	2.9804	3.0713	0.1286
1865-3	3.675	3.3651	3.5201	0.2191
2179-3	4.053	3.8941	3.9736	0.1124
2765-3	4.1844	4.1913	4.1879	0.0049

Milton Data (tenfold dilution)				
Sample Label	Se78 ppm	Se80 ppm		
1571	4.973237	4.98064	4.9769	0.0052
1594	2.434714	2.51824	2.4765	0.0591
1865	3.244652	3.2364	3.2405	0.0058
2179	3.427456	3.40272	3.4151	0.0175
2765	3.541841	3.58018	3.5610	0.0271

Conclusion

By using a Nitrox 500 it is possible to decrease the detection limits of the Aurora M90 by at least one to two orders of magnitude. By injecting Nitrogen into the plasma, the biggest gain comes from a significant reduction of background noise, especially that which results from oxide formation. This allows for an increase in the amount of aerosol used during analysis which should result in better detection limits for several elements in addition to Se. By lowering the overall background noise, another benefit will be the ability to run higher total dissolved solids.

It was observed that using the Nitrox 500 resulted in a very stable analysis of Se that could be reproduced on several occasions. The lower detection limits coupled with increased analytical stability resulted in both better precision and accuracy when performing Se analysis. This will be useful when more significant figures become necessary to distinguish the narrow range between deficient and toxic levels of Se in animal feeds.



Bruker Daltonics Inc.

Billerica, MA · USA
Phone +1 (978) 663-3660
Fax +1 (978) 667-5993
ms-sales@bdal.com

www.bruker.com

Fremont, CA · USA
Phone +1 (510) 683-4300
Fax +1 (510) 490-6586
ms-sales@bdal.com

Bruker Daltonik GmbH

Bremen · Germany
Phone +49 (0)421-2205-0
Fax +49 (0)421-2205-103
sales@bdal.de