Application Note

Detection Limits in Water Using Assorted Sample Introduction Systems

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1 Introduction

A variety of sample introduction systems exist to achieve improvements in detection limits. The standard system used for HORIBA Scientific on ICP spectrometers is typically the concentric pneumatic nebulizer combined with a cyclonic spray chamber. This system is referred to as pneumatic nebulization and provides the results shown in Table 4 (pneumatic nebulization).

The Ultrasonic Neublization system, shown in Figure 1 to the right, offers improved sensitivity due to the high efficiency of small droplet production using a transducer and desolvation system. An improvement of 5 to 20 times can be seen in detection limits, depending on the element and the matrix. In addition, the quantity of aerosol injected into the plasma is very high with up to 30% compared to less than 2% with other nebulizers. For difficult organic solutions such as naptha and gasoline where extra desolvation is necessary, a membrane desolvator is available.

To improve detection limits for elements such as Hg, As, Sb, Se Bi, Ge, Te and Sn, one can use hydride generation. This is particularly useful for environmental analysis, where the concentration ranges are close to the µg/L level. One of the main drawbacks of this technique, until recently, has been the requirement of performing the analysis twice: once for the normal elements and the other for the hydride species. Additionally, it was necessary to replace the standard spray chamber system with a hydride generator device. With the unique Concomitant Metals Analyzer (CMA) from HORIBA Scientific shown in Figure 2 to the right, it is possible to run one analysis with detection limits improved for the hydrides by a factor of 5 to 50 times with little difference in detection limits for the other normal elements. See Application Note 13: *Comparison of Classical Hydride Generator and Concomitant Metals Analyzer* for a detailed comparison of standard hydride generation with the CMA system.

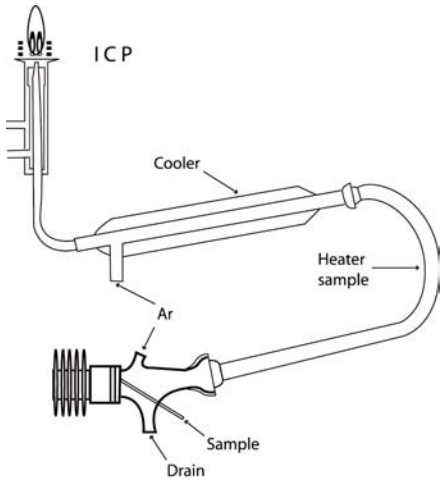

Figure 1: Diagram of an ultrasonic nebulizer (Courtesy of Cetac Technologies, Omaha, Nebraska, USA)

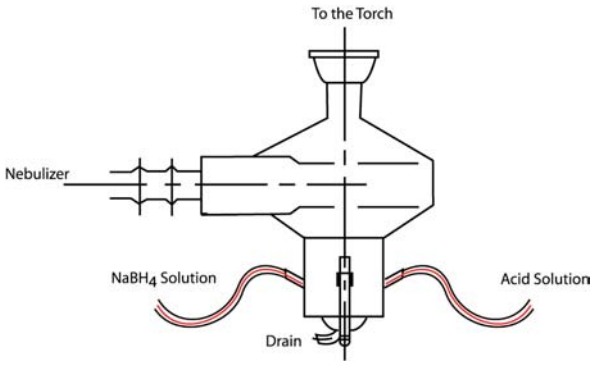

Figure 2: Concomitant Metals Analyzer (CMA)

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2 Instrument specification

The work presented in this note was done on a ULTIMA 2 configured with the appropriate sample introduction system. The specifications of this instrument are listed in Table 1 and 2.

Table 1: Specification of spectrometer

Parameter	Condition
Mounting	Czerny Turner
Focal length	1 m
Optic thermoregulation	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
1st order resolution	0.010 nm
2nd order resolution	0.005 nm
Order	2^{nd}order(120-330 nm)

Table 2: Specification of RF Generator

Parameter	Condition
Type of generator	Solid state
Observation	Radial view
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

3 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1000 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.1 L/min
Nebulizer gas flowrate	1 L/min
Nebulizer flowrate	3.4 bars (51 psi)
Sample uptake	1 mL/min
Type of nebulizer	Glass concentric
Type of spray chamber	Glass cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm

4 Detection Limits

The limits of detection at 3 sigma are calculated using the following formula:

$$LOD = 3 \times BEC \times RSD_B$$

With:
LOD = limit of detection,
BEC = background equivalent concentration,
RSD_B = relative standard deviation of the blank on 10 replicates.

5 Results

Detection limit results obtained are shown in Table 4. Elements shown were analyzed at the same time in one run under identical conditions as shown in Tables 1,2 and 3.

Table 4: Typical Detection Limits in µg/L at 3 sigma

Element	Pneumatic Nebulization	Ultrasonic Nebulization	Hydride (CMA) 200.7	US EPA Method 200.8	US EPA Method (LOD-wavelength in nm)	EN ISO 11885:1996
Ag	0.60	0.09		7.0	0.1	20-328/338
Al	0.20	0.03		45	1.0	40-167 100-308/396
As	1.5	0.12	0.2	53	1.4	80-189 100-193/197
Au	0.60					
B	0.30	0.05		5.7		5-208 6-249 10-247
Ba	0.04	0.01		2.3	0.8	4-233 2-455 3-493
Be	0.04	0.006		0.27	0.3	2-313.042 5-234
Bi	2.6					40-223 80-306
Br	100					
Ca	0.03			30		100-315 10-317 2-393
Cd	0.19	0.015		3.4	0.5	10-214/226/228
Cl	200					
Co	0.2	0.06		7	0.09	10-228
Cr	0.2	0.06		6.1		10-205/267 10-283/284
Cu	0.2	0.05		5.4	0.5	10-324/327
Fe	0.20	0.05		6.2		20-259
Hg	0.4		0.03	2.5		
I	0					
K	1.5	0.3		700		200-769
Li	0.50	0.1		3.7		900-460 2-670
Mg	0.03			30		30-279.0 0.5-279.5 1-285
Mn	0.05	0.01		1.4	0.1	2-257 20-293
Mo	0.20	0.09		12	0.3	30-202 50-204
Na	0.60	0.15		29		100-589 20-588/330
Ni	0.30	0.06		15		0.5-231
P	1.5	0.3		76		500-178/177 100-213/214
Pb	1.5	0.2		42	0.6	200-220 70-283
S	3.0					500-182/180

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Element	Pneumatic Nebulization	Ultrasonic Nebulization	Hydride (CMA)	US EPA Method 200.7	US EPA Method 200.8	EN ISO 11885:1996 (LOD-wavelength in nm)
Sb	1.5	0.15	0.2	32	0.4	100-206/217
Sc	0.09					
Se	1.5	0.2	0.2	75	7.9	100-196/203
Si	1.5			26 (SiO_2)		20-251/212 30-288
Sn	1.3		0.2	25		100-235/189
Sr	0.03			0.77		0.5-407 10-421 100-460
Ti	0.15	0.03		3.8		5-334 10-336/337/368
Tl	1.0	0.2		40	0.3	
V	0.20	0.05		7.5	2.5	10-290/292 10-310/311
W	2.0					30-207 60-209/239 60-222/202
Y	0.20					
Zn	0.15	0.025		1.8	1.8	10-206 5-213
Zr	0.30					10-343 50-354

6 Conclusion

The race for lower detection limits is continuous. The ICP spectrometer system offered by HORIBA Scientfic configures a rugged, flexible sample introduction system with a high-resolution spectrometer to provide trace and ultra-trace detection limits on a routine basis.

This capability of providing trace detection limits with a radial view plasma and the standard sample introduction system is enhanced to the ultra-trace level with the addition of either the ultrasonic nebulization system or a hydride generation system. This performance is made possible by the combination of several factors including a robust plasma, radial plasma viewing, large injector bore, and the unique sheath gas system. For more details on the features of HORIBA Scientific ICP spectrometers, read Technical Note 7: *Unique Features of HORIBA Scintific ICP spectrometers.*

In December 2001, the Official Journal of French Republique issued decree number 2001-1220 (December 20th, 2001), for waters for human consumption (natural mineral water not included). Water should respect values less or equal to limits of quality defined as: Sb 5ppb, As 10ppb, Ba 0.7ppm, Cd 5ppb, Cr 50ppb, Cu 2ppm, Hg 1ppb, Ni 20ppb, Pb 10ppb, and Se 10ppb.

The sensitivity provided by the ULTIMA 2 configured with a variety of sample introduction systems is sufficient to perform environmental analysis in compliance with the detection limits of US EPA Method 200.7 for water and wastewater effortlessly. Even detection limit requirements for US EPA Method 200.8 (ICP-MS) are well within reach with the USN and/or CMA accessories. For more details on environmental analysis please read Application Note 36: *Environmental Analysis using a High Throughput ICP AES*.

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