TELEDYNE CETAC TECHNOLOGIES
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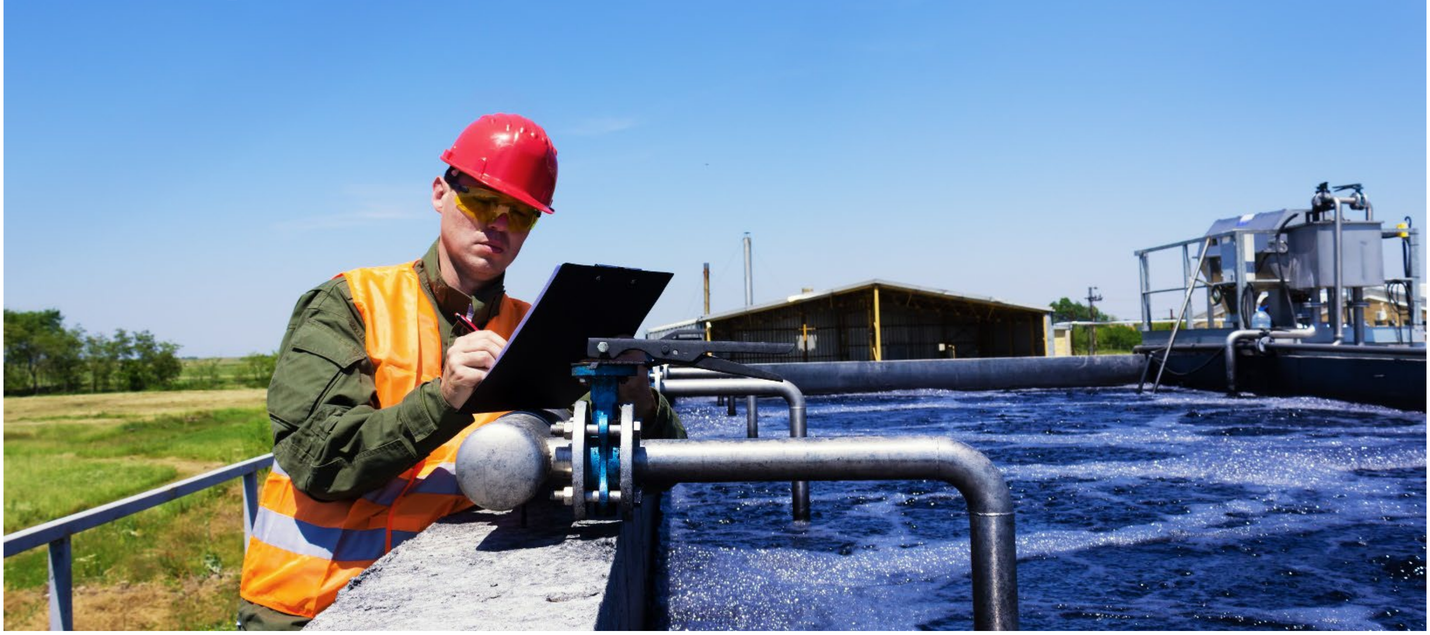
Technical Note

Lower ICP-OES Instrument Detection Limits per USEPA Method 200.7



Introduction

To safeguard human health and the environment, the United States Environmental Protection Agency (USEPA) adjusts regulations for maximum contaminant levels (MCLs) in water based on accepted scientific findings and guidelines. The current USEPA Method 200.7 revision 4.4 describes criteria for the measurement of metals and trace elements in drinking water and wastewater using inductively coupled plasma optical emission spectrometry (ICP-OES).

This technical note describes the use of an ultrasonic nebulizer (USN) as a liquid sample introduction accessory for ICP-OES. Using a piezoelectric transducer for aerosol generation, ultrasonic nebulization improves liquid sample transport efficiency versus conventional pneumatic nebulization. Trace element sensitivity is enhanced, extending the lower detection range of the host ICP-OES. The benchtop-size USN has an integrated desolvation system to ensure ICP stability and reduce solvent emission background; USN setup time is only 10 minutes with no computer control requirement.

Conventional pneumatic nebulizer and USN detection limits are measured and compared per USEPA Method 200.7 revision 4.4 criteria for 29 elements.

Experimental

Instrument Conditions

Measurements were performed using a Teledyne CETAC U5000AT$^+$ Ultrasonic Nebulizer (USN) coupled with a PerkinElmer Avio® 500 ICP-OES instrument. The standard liquid sample introduction kit of the ICP-OES comprises a glass concentric type pneumatic nebulizer (Meinhard K type) and a glass cyclonic spray chamber with internal baffle. Detection limits were measured with both nebulizer types.

An interface kit consisting of a gas supply line and a sample out line with torch adapter was used to connect the USN to the ICP-OES. The host ICP-OES peristaltic pump was used to supply blank and standard solutions to the USN, and the ICP-OES nebulizer gas was used as the Ar carrier gas supply to the USN. A PerkinElmer S23 Autosampler was used to automate the introduction of blank and standard solutions to both nebulizers.

A comparison of operating conditions is given in Table 1; a front view of the U5000AT$^+$ USN is given in Figure 1.

Figure 1. Teledyne CETAC Technologies U5000AT$^+$ Ultrasonic Nebulizer (USN)

Instrument Calibration

The ICP-OES instrument was calibrated using standards prepared in double distilled 2% HNO_3 at concentrations of 10, 20, 50 and 100 µg/L; the calibration blank consists of the 2% HNO_3 diluent used to prepare the standard solutions. Note that no internal standard was used for calibration. Following calibration, the calibration blank was measured 10 times against the calibration curves per USEPA Method 200.7 Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma - Atomic Emission Spectrometry.

Table 1. Operating Conditions of the Avio® 500 ICP-OES and the U5000AT$^+$ USN

Parameter	Standard Nebulizer	U5000AT$^+$ USN
ICP Power	1500 W	1500 W
Plasma Gas	8.0 L/min	10.0 L/min
Auxiliary Gas	0.2 L/min	0.2 L/min
Nebulizer Gas	0.65 L/min	0.50 L/min
Torch Injector	2 mm	2 mm
Uptake Rate	1.0 mL/min	1.25 mL/min
Cassette Position	-3.0	-5.0
Resolution	Normal	Normal
Nebulizer Type	Meinhard K	Piezoelectric
Spray Chamber	Baffled cyclonic	Conical
Heater Temp	N/A	140°C
Cooler Temp	N/A	3°C
Viewing	Axial	Axial; Ba, Ca, Li Radial
Integration Times	0.01 s min / 0.2 s max	0.01 s min / 3 s max
Peak Area	3 pts / peak	3 pts / peak
Replicates	4	4

Results

Calibration Coefficients

The correlation coefficients of the element calibration curves must be 0.995 or better to be considered valid for analysis. For the 29 elements measured, the correlation coefficients range from 0.9950 to 0.9999 with the standard nebulizer and from 0.9993 to 0.9999 for the USN.

The correlation coefficients obtained are listed by element and wavelength for both nebulizers in Table 2.

Table 2. Correlation Coefficients with Standard Pneumatic Nebulizer and the U5000AT+ USN

Element	Wavelength (nm)	Std. Neb. Corr. Coeff.	U5000AT+ Corr. Coeff.
Ag	328.068	0.9999	0.9999
Al	394.401	0.9999	0.9993
As	188.979	0.9999	0.9997
Ba	493.408	0.9999	0.9999
Be	313.107	0.9999	0.9996
Ca	315.887	0.9950	0.9999
Cd	214.440	0.9998	0.9998
Co	228.616	0.9999	0.9999
Cr	267.716	0.9999	0.9998
Cu	324.752	0.9999	0.9996
Fe	238.204	0.9999	0.9998
K	766.490	0.9998	0.9996
Li	670.784	0.9997	0.9994
Mg	285.213	0.9999	0.9999
Mn	257.610	0.9999	0.9999
Mo	203.845	0.9999	0.9998
Na	589.592	0.9999	0.9999
Ni	231.604	0.9999	0.9999
P	178.221	0.9999	0.9996
Pb	220.353	0.9995	0.9999
Sb	206.836	0.9999	0.9999
Se	196.026	0.9999	0.9999
Si	251.611	0.9999	0.9991
Sn	189.927	0.9996	0.9998
Sr	421.552	0.9999	0.9999
Ti	334.940	0.9999	0.9998
Tl	190.801	0.9999	0.9999
V	292.402	0.9999	0.9998
Zn	206.200	0.9999	0.9999

Element Signal Enhancement and Reduced Background Emission

The increased sample transport efficiency of the U5000AT+ USN enhances ICP-OES signal for all 29 measured elements including important and more difficult to detect elements such as As, Pb, Sb and Se. In addition, the integrated desolvation system of the U5000AT+ USN reduces excess solvent (i.e. water) loading to the plasma, providing stable plasma operation and lower solvent-induced background signal. This reduced background emission can contribute to lower detection limits.

Emission spectra in Figures 2a – 2d depict the improved analyte signal and decreased background emission using the U5000AT+ USN versus the standard nebulizer kit. The 100 µg/L standard was used for comparison spectra of As, Pb, Sb, and Se; the solid line represents the U5000AT+ USN signal and the dashed line the standard nebulizer signal.

Net USN signal enhancement for these four selected elements are given in Table 3; the enhancement range is 6.0x to 8.4x versus the standard nebulizer.

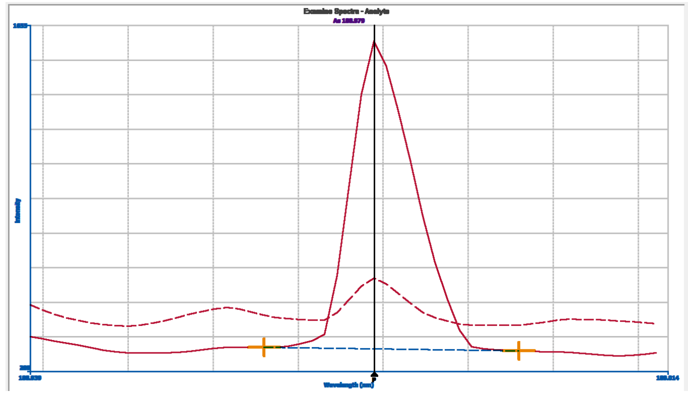


Figure 2a. Overlay of As (188.979 nm) signal

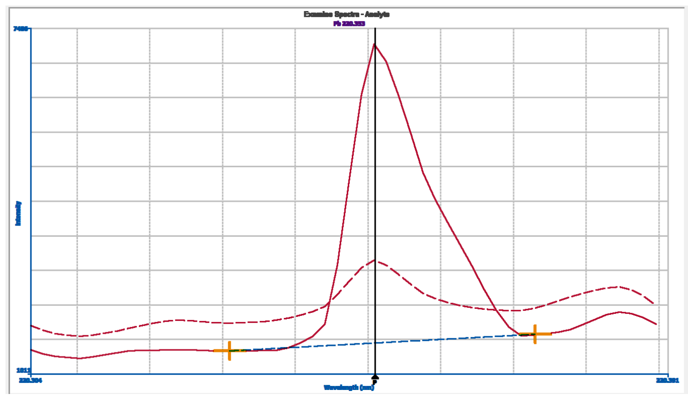


Figure 2b. Overlay of Pb (220.353 nm) signal

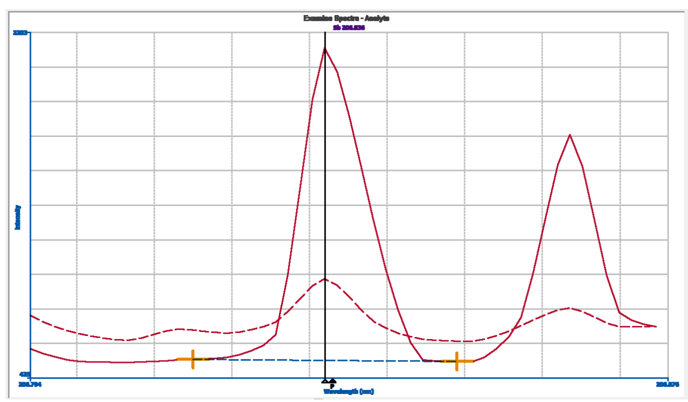


Figure 2c. Overlay of Sb (206.836 nm) signal

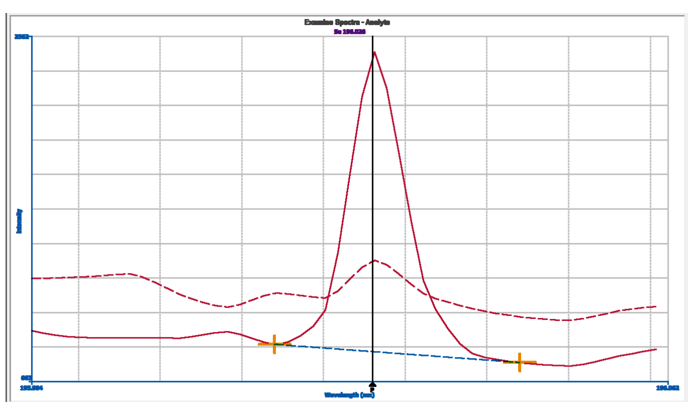


Figure 2d. Overlay of Se (196.026 nm) signal

Instrument Detection Limits

Instrument detection limits (IDLs) were obtained for the 29 selected elements using both the standard nebulizer kit and the U5000AT+ USN with the host ICP-OES. Instrument detection limits were calculated per EPA Method 200.7.

After ICP-OES calibration, the reagent blank was measured 10 times as a sample; the individual IDLs defined as 3x the standard deviation of the reagent blank concentration. The mean of the 10 individual blank runs for each element was calculated as the final IDL per Method 200.7 criteria; a summary is given in Table 4. The average reduction in IDLs across the 29 measured elements is 14.3x the standard nebulizer, with a range of 1.5x to 63.3x. The lower 1.5x to 2.7x factors may be due to reagent blank contamination.

Summary

The use of the U5000AT+ USN offers a significant increase in analyte signal and subsequent lower IDLs (up to an average of 14x) for a wide range of elements using ICP-OES detection and USEPA Method 200.7 criteria. IDLs in the 2% HNO_3 matrix for more difficult-to-detect elements such as As, Pb, Sb, Se, and Tl are measured below 1 µg/L using the USN accessory.

Setup of the compact U5000AT+ is fast (10 minutes) and easy with a supplied interface kit. No computer control of the U5000AT+ is required and introduction of samples can be done efficiently with an autosampler and the host ICP-OES peristaltic pump.

Table 3. Selected Element Signal Intensity Comparison

Element	Wavelength (nm)	Intensity Std Neb 100 µg/L	Intensity U5000AT+ 100 µg/L	Enhancement Factor
As	188.979	254	1838	7.2
Pb	220.353	1499	9025	6.0
Sb	206.836	284	2395	8.4
Se	196.026	289	2272	7.8

Table 4. Summary of Instrument Detection Limits per USEPA Method 200.7

Element	Wavelength (nm)	IDL Std Neb (µg/L)	IDL U5000AT+ (µg/L)	Factor
Ag	328.068	0.09	0.008	11.2
Al	394.401	0.17	0.018	9.4
As	188.979	1.1	0.15	7.3
Ba	493.408	0.03	0.02	1.5
Be	313.107	0.02	0.01	2.0
Ca	315.887	0.09	0.04	2.3
Cd	214.440	0.57	0.009	63.3
Co	228.616	0.46	0.02	23.0
Cr	267.716	0.15	0.01	15.0
Cu	324.752	0.28	0.012	23.3
Fe	238.204	0.24	0.02	12.0
K	766.490	0.33	0.014	23.5
Li	670.784	0.08	0.03	2.7
Mg	285.213	0.03	0.004	7.5
Mn	257.610	0.01	0.002	5.0
Mo	203.845	1.3	0.04	32.5
Na	589.592	0.37	0.04	9.3
Ni	231.604	0.43	0.02	21.5
P	178.221	5.4	0.28	19.2
Pb	220.353	1.4	0.06	23.3
Sb	206.836	2.2	0.12	18.3
Se	196.026	2.0	0.15	13.3
Si	251.611	1.1	0.51	2.1
Sn	189.927	0.98	0.07	14.0
Sr	421.552	0.08	0.01	8.0
Ti	334.940	0.05	0.004	12.5
Tl	190.801	1.4	0.19	7.3
V	292.402	0.07	0.004	17.5
Zn	206.200	0.19	0.02	9.5

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