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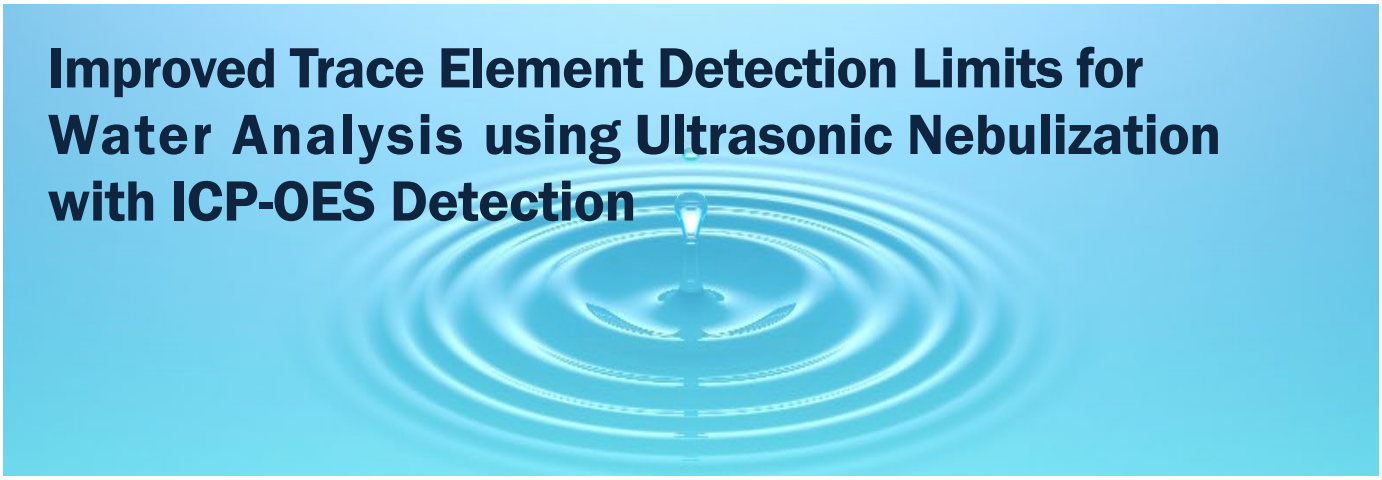
Application Note

# Improved Trace Element Detection Limits for Water Analysis using Ultrasonic Nebulization with ICP-OES Detection

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## Introduction

This application note examines the use of a Teledyne CETAC U5000AT+ Ultrasonic Nebulizer (USN) with ICP-OES detection for enhanced measurement of trace elements in a well water sample. Ultrasonic nebulization improves element transport efficiency to the ICP over conventional pneumatic nebulizers, thereby extending the lower detection range of the ICP-OES.

This application will show significant improvements in signal enhancement, calibration, and detection limits which is especially important for the more difficult, regulated elements such as As, Cd, Pb, Sb, Se, and Tl. Data is presented for an untreated well water sample (no water softening or chlorination).

## Experimental

### *Sample selection and preparation*

A well water sample (not part of a public water supply) was collected from a source in the northwestern region of the US (Wisconsin). The sample was not turbid and qualified for direct analysis per USEPA Method 200.7. The sample was acidified to 2% (v/v) with double-distilled nitric acid ($HNO_3$) prior to analysis. Approximately 400-mL of the water sample was evaporated in a borosilicate beaker, leaving the residue shown in Figure 1.

### *Instrumental Conditions*

Analyses were performed using a Teledyne CETAC U5000AT+ USN coupled with a PerkinElmer Avio® 500 ICP-OES. The standard setup uses a glass concentric-type (Meinhard K) nebulizer. The U5000AT+ USN setup requires approximately 5 to 10 minutes after removal of the standard nebulizer kit; no computer control of the USN is needed. A comparison of operating conditions is given in Table 1 and a picture of the USN can be seen in Figure 2.

Measured concentrations using the standard nebulizer setup for major dissolved elements in the well water are listed in Table 2.

*Table 1 – Operating Conditions of Avio 500 ICP-OES and U5000AT+ USN*

| Parameter | Standard Setup | U5000AT+ USN |
|---|---|---|
| ICP Power | 1500 W | 1500 W |
| Plasma Gas | 8.0 L/min | 8.0 L/min |
| Auxiliary Gas | 0.2 L/min | 0.2 L/min |
| Nebulizer Gas | 0.70 L/min | 0.62 L/min |
| Torch Injector | 2 mm | 2 mm |
| Uptake Rate | 1.5 mL/min | 1.0 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 |
| Integration Time | 10s | 10s |
| Peak area | 3 pts/peak | 3 pts/peak |
| Replicates | 3 | 3 |

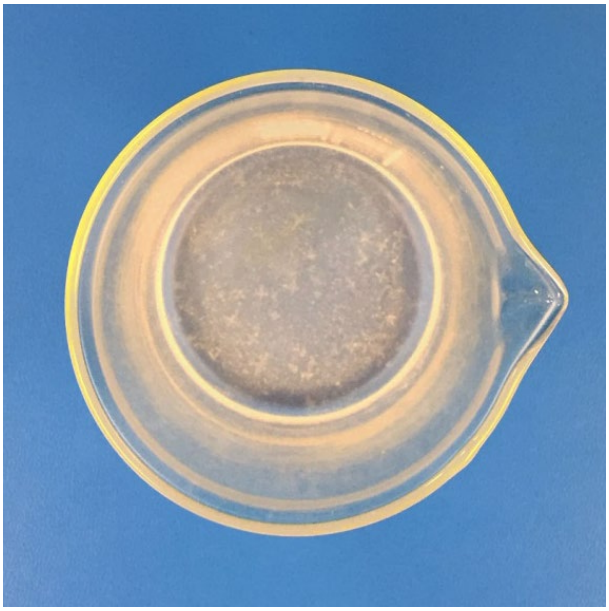

*Figure 1 – Evaporated Well-Water Sample (400 mL)*


*Figure 2 – Teledyne CETAC Technologies U5000AT+ Ultrasonic Nebulizer (USN)*

*Table 2 – Major Dissolved Elements in Well Water Sample*

| Element | Wavelength (nm) | Concentration |
|---|---|---|
| Ca | 317.933 | 52.0 ± 0.6 mg/L |
| Na | 589.592 | 24.4 ± 0.5 mg/L |
| Mg | 285.213 | 16.4 ± 0.1 mg/L |
| K | 766.490 | 1.45 ± 0.03 mg/L |
| Ba | 493.408 | 90.2 ± 2.5 µg/L |
| Sr | 421.552 | 73.7 ± 1.8 µg/L |
| Zn | 206.200 | 9.56 ± 0.45 µg/L |

Uncertainties in reported concentrations are based on 2s (95% confidence interval).

### *Blank and Standards Preparation*

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. An internal standard solution of yttrium (Y) at 50 µg/L was added to all samples and standards using a mixing tee. All samples and standards introduced to the USN had 40 µL of 30% hydrogen peroxide ($H_2O_2$) per 10 mL added prior to analysis. The $H_2O_2$ oxidizes $As^{3+}$ to $As^{5+}$ for uniform transport efficiency through the ultrasonic nebulizer.

## Results

### Calibration

The correlation coefficient of the element calibration curves must be 0.995 or better to be considered valid for analysis. Coefficients for selected elements are shown in Table 3; use of the U5000AT+ USN enables 0.9999 coefficients for all examples except Tl (0.9997). As an example, the full calibration curve for As using the USN is given in Figure 3.

*Table 3 – Correlation Coefficients of Selected Elements*

| Element | Wavelength (nm) | Corr. Coeff. Std. Neb. | Corr. Coeff. U5000AT+ USN |
|---|---|---|---|
| As | 188.979 | 0.9999 | 0.9999 |
| Cd | 228.802 | 0.9997 | 0.9999 |
| Pb | 220.353 | 0.9997 | 0.9999 |
| Sb | 206.836 | 0.9997 | 0.9999 |
| Se | 196.026 | 0.9988 | 0.9999 |
| Tl | 190.801 | 0.9983 | 0.9997 |

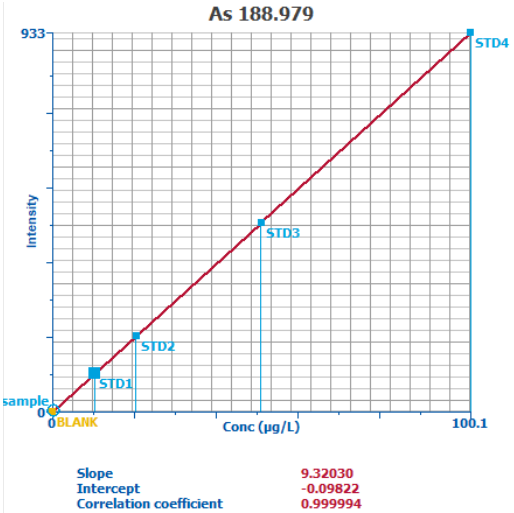


*Figure 3 – As calibration curve at 188.979 nm using U5000AT+ USN*

### Instrument Detection Limits

The standard deviation of 10 blank solution (2% $HNO_3$) measurements multiplied by 3 was used to calculate instrument detection limits (IDLs). In this example, IDLs obtained with the USN are 2.5x to 38.5x lower with an average improvement of 9.5x. Variation in observed detection limits can be caused by numerous factors, including background spectra complexity, elevated blanks, and integration times; results are listed in Table 4.

*Table 4 – Instrument Detection Limits: Standard Nebulizer vs U5000AT+ USN*

| Element | Wavelength (nm) | Std Neb IDL (µg/L) | USN IDL (µg/L) | Factor |
|---|---|---|---|---|
| Ag | 328.068 | 0.54 | 0.076 | 7.2 |
| Al | 394.401 | 7.01 | 0.29 | 24.1 |
| As | 188.979 | 3.47 | 0.56 | 6.2 |
| Ba | 493.408 | 0.065 | 0.019 | 3.4 |
| Be | 313.107 | 0.054 | 0.0067 | 8.1 |
| Cd | 228.802 | 0.95 | 0.11 | 8.5 |
| Co | 228.616 | 0.65 | 0.087 | 7.5 |
| Cr | 267.716 | 0.31 | 0.056 | 5.6 |
| Cu | 324.752 | 0.53 | 0.042 | 12.8 |
| Fe | 238.204 | 0.31 | 0.046 | 6.8 |
| Mn | 257.610 | 0.025 | 0.010 | 2.5 |
| Mo | 202.031 | 1.55 | 0.052 | 30.1 |
| Ni | 231.604 | 0.74 | 0.26 | 2.8 |
| P | 178.221 | 4.08 | 1.63 | 2.5 |
| Pb | 220.353 | 1.09 | 0.32 | 3.5 |
| Sb | 206.836 | 3.21 | 0.46 | 6.9 |
| Se | 196.026 | 3.3 | 0.86 | 3.9 |
| Sn | 189.927 | 1.2 | 0.36 | 3.3 |
| Sr | 421.552 | 0.038 | 0.0018 | 21.2 |
| Ti | 334.940 | 0.28 | 0.051 | 7.5 |
| Tl | 190.801 | 2.72 | 0.88 | 3.1 |
| V | 292.402 | 0.75 | 0.020 | 38.5 |
| Zn | 206.200 | 0.31 | 0.092 | 3.3 |

Figure 4 shows a spectral comparison of 100 µg/L Sb standard introduced to the ICP-OES using the standard pneumatic nebulizer and then the U5000AT+ USN. The top peak intensity is with the U5000AT+ USN while the lower peak intensity is with the standard nebulizer. In this example, the USN offers an intensity enhancement (after background correction) of approximately 7x.

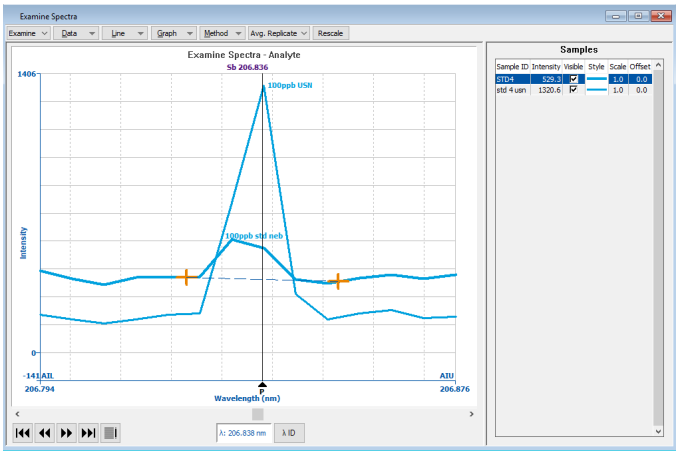


*Figure 4 – Comparison of signal intensities for 100 µg/L Sb using standard nebulizer and U5000AT+ USN*

### Spiked Well-Water Sample

A reagent blank and well-water sample were spiked with 19 elements at 5 µg/L. Spike recoveries for the laboratory control sample (LCS) are within the range of 85-115% which is specified by USEPA Method 200.7. The spiked well-water sample recovery passes the 70-130% criteria also specified in this method. Co and Ni results are passing but low, most likely due to a sample matrix effect (Table 5).

Figure 5 is a comparison of the spiked well-water sample spectra generated by the standard nebulizer and the U5000AT+ USN for As at 188.979 nm. The blue line represents the standard nebulizer while the red line is the USN result. For As, the USN lowered the background and enhanced the signal such that a peak is detected at the low spike concentration of 5 µg/L.

### Reliability and % Recovery

To demonstrate the reliability of the method, an NIST 1643f – Trace Elements in Water standard was run as a sample using the U5000AT+ USN. The recoveries (Table 6) are within 85-115% for all except Ag (82%). Since the Ag value in the NIST standard is quite low compared to the ICP-OES calibration with the USN, the slightly lower % recovery may be due to a lower signal intensity.

*Table 5 – Laboratory Control Sample and Well-Water Matrix Spike Recoveries*

| Element | LCS (µg/L) | % Recovery | Spike (µg/L) | % Recovery |
|---|---|---|---|---|
| Ag | 4.85 | 97 | 4.25 | 85 |
| Al | 5.12 | 102 | 5.60 | 112 |
| As | 5.03 | 101 | 5.62 | 113 |
| Be | 4.66 | 93 | 4.59 | 92 |
| Cd | 5.07 | 101 | 4.77 | 95 |
| Co | 5.08 | 102 | 3.79 | 76 |
| Cr | 4.97 | 99 | 4.49 | 90 |
| Cu | 5.19 | 104 | 5.11 | 102 |
| Fe | 5.58 | 112 | 4.46 | 89 |
| Mn | 4.98 | 100 | 5.00 | 100 |
| Mo | 5.06 | 101 | 4.73 | 97 |
| Ni | 5.14 | 103 | 3.87 | 77 |
| Pb | 5.23 | 105 | 4.31 | 86 |
| Sb | 4.88 | 98 | 5.04 | 101 |
| Se | 4.56 | 94 | 5.35 | 107 |
| Sn | 4.84 | 97 | 4.88 | 98 |
| Ti | 4.93 | 99 | 5.19 | 104 |
| Tl | 5.16 | 103 | 5.33 | 107 |
| V | 4.94 | 99 | 4.45 | 89 |

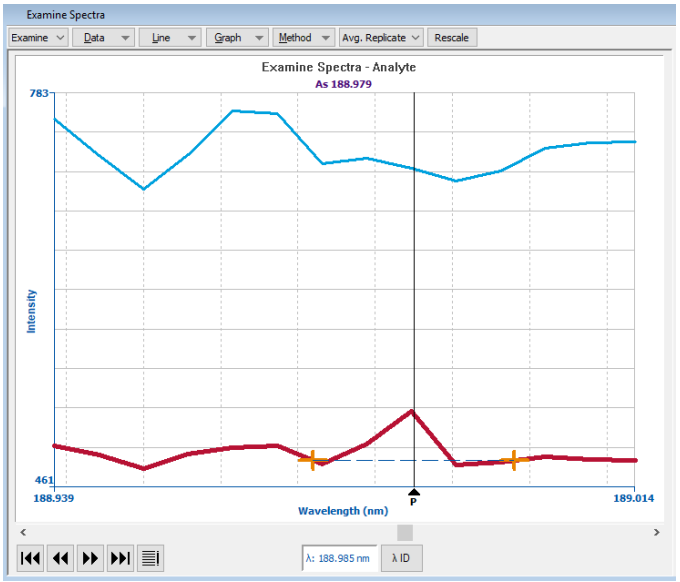


*Figure 5 – Well water spectra with 5 µg/L As spike, standard nebulizer vs. U5000AT+ USN*

*Table 6 – % Recovery NIST 1643f Trace Elements in Water:*

| Element | Measured (µg/L) | Certified (µg/L) | % Recovery |
|---|---|---|---|
| Ag | 0.793 ± 0.110 | 0.9703 ± 0.0055 | 82 |
| Al | 148.9 ± 1.1 | 133.8 ± 1.2 | 111 |
| As | 63.00 ± 1.92 | 57.42 ± 0.38 | 110 |
| Ba | 451.4 ± 16.6 | 518.2 ± 7.3 | 87 |
| Be | 13.91 ± 0.02 | 13.67 ± 0.12 | 102 |
| Cd | 6.63 ± 0.22 | 5.89 ± 0.13 | 113 |
| Co | 22.15 ± 0.31 | 25.30 ± 0.17 | 87 |
| Cr | 17.55 ± 0.26 | 18.50 ± 0.10 | 95 |
| Fe | 91.04 ± 0.55 | 93.44 ± 0.78 | 97 |
| Mn | 35.46 ± 0.17 | 37.14 ± 0.60 | 95 |
| Mo | 120.6 ± 0.6 | 115.3 ± 1.7 | 105 |
| Ni | 52.7 ± 0.5 | 59.8 ± 1.4 | 88 |
| Pb | 17.483 ± 1.721 | 18.488 ± 0.084 | 95 |
| Sb | 57.88 ± 1.65 | 55.45 ± 0.40 | 104 |
| Se | 11.218 ± 1.997 | 11.700 ± 0.081 | 96 |
| Sr | 289 ± 6 | 314 ± 19 | 92 |
| Tl | 7.252 ± 1.026 | 6.892 ± 0.035 | 105 |
| V | 35.78 ± 0.11 | 36.07 ± 0.28 | 99 |
| Zn | 82.4 ± 1.0 | 74.4 ± 1.7 | 111 |

## Summary

An ultrasonic nebulizer, such as the U5000AT⁺used in conjunction with an ICP-OES offers significantly increased analyte signal and subsequent lower instrument detection limits for important regulated elements such as As, Cd, Pb, Sb, Se, and Tl in a spiked well water sample. Setting up the ultrasonic nebulizer is straightforward via a dedicated nebulizer gas inlet line and a sample out line; installation takes approximately 5 to 10 minutes. The USN requires no computer control and the host ICP-OES peristaltic pump can be used to introduce samples and can easily be automated using an autosampler.

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