

**Abstract:** Groundwaters from certain regions (ex. southern England, southern Germany) can be very hard, as evidenced by Ca, Fe, K, Mg, and Na concentrations above 200 mg/L. This work will examine the use of two different enhanced nebulizer systems for the detection of regulated elements in a very hard water matrix with ICP-AES detection. Nebulizer systems include an ultrasonic nebulizer and a temperature controlled (heated spray chamber) system. Elements of interest include regulated elements such as As, Be, Cd, Cr, Cu, Pb, Sb, Se, Ti. Uranium will also be investigated due to its relatively higher detection limit range (typically 1 to 10 µg/L) by conventional pneumatic nebulization with ICP-AES. Figures of merit for the enhanced nebulizer systems will be compared to conventional pneumatic nebulization. These figures will include nebulizer system operating conditions, calibration settings (background and interelement corrections), instrument detection limits (IDLs), limits of quantitation (LOQs), and analyte recoveries.

## Instrumentation

### ICP-AES:

PerkinElmer Optima 5300DV

### Enhanced Nebulizer Systems:

CETAC U5000AT+ Ultrasonic Nebulizer

CETAC Marin-5 Nebulizer System

## Operating Conditions - II

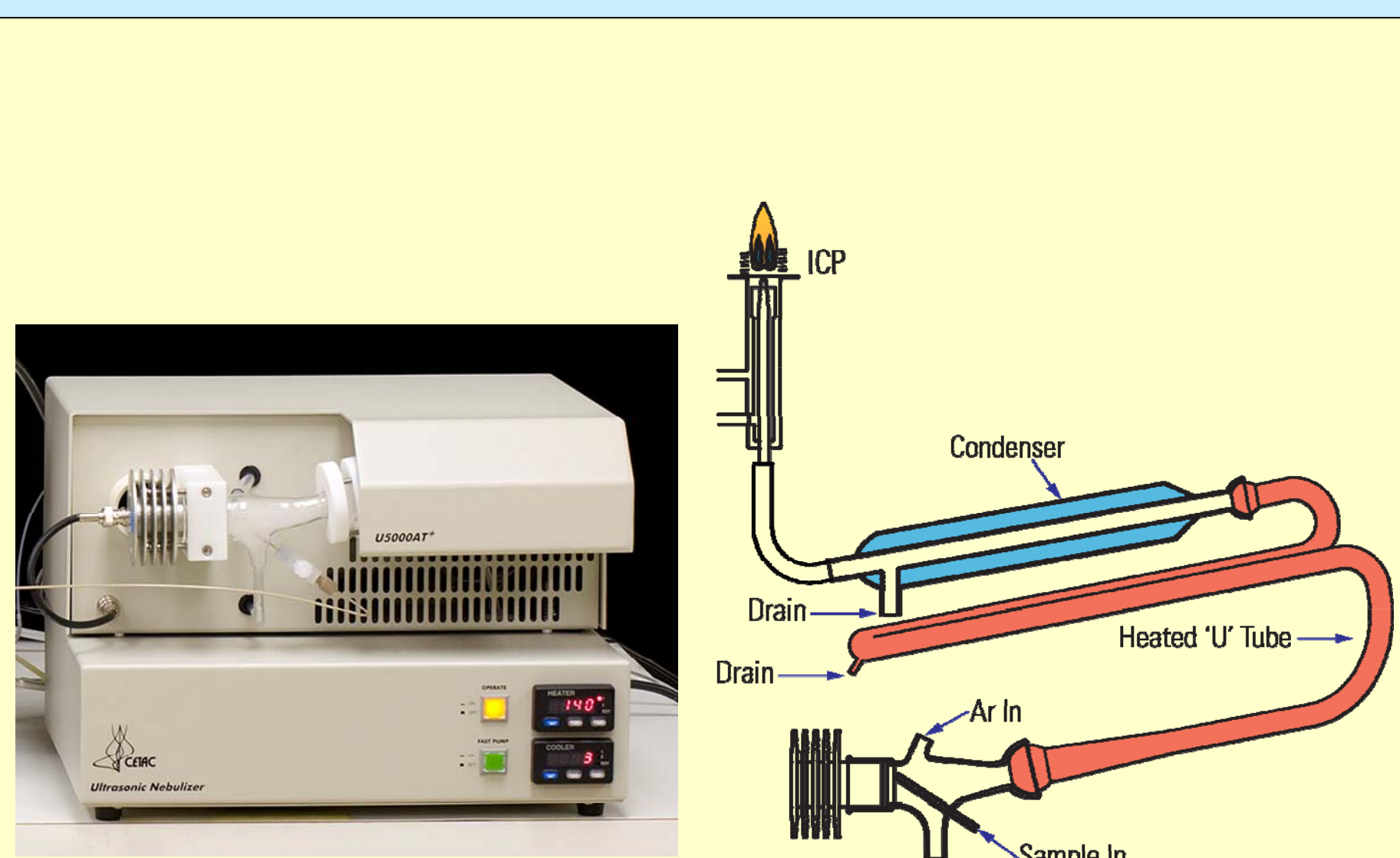
**Nebulizer System:** CETAC Marin-5  
**Heater Temp:** 125°C  
**Cooler Temp:** 3°C  
**Torch Position:** -4

**Nebulizer:** Glass concentric  
**Neb. type:** K-Micro (Precision Glass)  
**Nebulizer Gas:** 0.88 L/min  
**Neb. Port Adapter:** 15° angle  
**Solution uptake:** 0.65 mL/min (pumped)

## Standard Concentric Nebulizer

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Ag	328.068	0.3	1.0	99.7
Al	396.153	1.0	3.3	97.2
As	188.979	2.6	8.6	99.6
Ba	455.403	0.03	0.1	100.2
Be	313.107	0.04	0.13	100.1
Bi	223.061	4.3	14.1	100.1
Cd	228.802	0.3	1.0	99.7
Co	228.616	0.7	2.3	99.7
Cr	267.716	0.2	0.7	99.5
Cu	327.393	0.4	1.3	99.6
Mn	257.610	0.08	0.26	99.6

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Mo	202.031	0.7	2.3	99.5
Ni	221.648	0.6	1.9	99.5
Pb	220.353	1.6	5.3	99.1
Sb	206.836	3.5	11.6	99.1
Se	196.026	4.7	15.5	94.0
Sr	407.771	0.1	0.33	100.0
Ti	334.940	0.1	0.33	99.9
Tl	190.801	4.1	13.5	97.7
U	424.167	8.7	28.7	99.2
V	290.880	0.4	1.3	100.4
Zn	213.857	0.3	1.0	99.2



CETAC U5000AT+ Ultrasonic Nebulizer: Front View and Schematic

## Operating Conditions - III

**Nebulizer System:** CETAC U5000AT+  
**Heater Temp:** 140°C  
**Cooler Temp:** 3°C  
**Torch position:** -4

**Nebulizer Gas:** 0.52 L/min  
**Solution Uptake:** 2.0 mL/min (pumped)

## Marin-5 Enhanced Nebulizer System

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Ag	328.068	0.09	0.3	97.3
Al	396.153	0.5	1.7	96.2
As	188.979	2.2	7.3	97.8
Ba	455.403	0.008	0.02	97.4
Be	313.107	0.009	0.03	97.6
Bi	223.061	2.3	7.6	97.9
Cd	228.802	0.2	0.7	97.6
Co	228.616	0.2	0.7	97.6
Cr	267.716	0.1	0.3	97.3
Cu	327.393	0.1	0.3	97.0
Mn	257.610	0.05	0.16	97.2

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Mo	202.031	0.4	1.3	97.2
Ni	221.648	0.3	1.0	97.6
Pb	220.353	1.2	3.9	96.9
Sb	206.836	1.2	3.9	97.1
Se	196.026	3.4	11.2	98.4
Sr	407.771	0.1	0.3	97.9
Ti	334.940	0.04	0.13	97.1
Tl	190.801	1.8	5.9	98.4
U	424.167	2.0	6.6	98.8
V	290.880	0.1	0.3	97.1
Zn	213.857	0.2	0.7	97.6

## U5000AT+ Ultrasonic Nebulizer

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Ag	328.068	0.03	0.1	99.6
Al	396.153	0.2	0.7	99.7
As	188.979	0.8	2.4	98.5
Ba	455.403	0.005	0.017	99.7
Be	313.107	0.004	0.013	99.1
Bi	223.061	0.8	2.4	99.3
Cd	228.802	0.06	0.2	99.2
Co	228.616	0.08	0.3	98.7
Cr	267.716	0.1	0.3	99.0
Cu	327.393	0.07	0.2	99.2
Mn	257.610	0.05	0.17	99.3

Element	λ (nm)	IDL (µg/L)	LOQ (µg/L)	% Recovery
Mo	202.031	0.2	0.7	99.0
Ni	221.648	0.2	0.7	98.8
Pb	220.353	0.7	2.3	98.5
Sb	206.836	0.4	1.3	98.8
Se	196.026	2.7	8.9	97.4
Sr	407.771	0.2	0.7	99.2
Ti	334.940	0.07	0.2	99.4
Tl	190.801	1.6	5.3	98.4
U	424.167	1.1	3.6	99.6
V	290.880	0.2	0.7	99.1
Zn	213.857	0.2	0.7	98.9

The Marin-5 and the U5000AT+ both provide LOQs for uranium below 10 µg/L in a very hard water matrix at 424.167 nm.

## Experimental Setup - I

1. A matrix blank and four calibration standards were prepared using the 10,000 mg/L single element standards, preserved in 1% high-purity nitric acid.
2. Four calibration standards were prepared by volume: 20, 50, 100 and 200 µg/L.
3. The matrix blank and matrix-matched standards were introduced to the standard concentric nebulizer, the Marin-5, and the U5000AT+ using the on-board peristaltic pump provided with the host ICP-AES instrument.
4. Instrument detection limits (IDLs) are 3x the standard deviation of the matrix blank concentration, limits of quantitation (LOQs) are 10x the standard deviation of the matrix blank concentration.

## Experimental Setup - II

1. The high standard (200 µg/L) was first introduced to the Marin-5 and U5000AT+ to optimize various instrument parameters for highest analyte sensitivity.

Mn (λ = 257.610 nm) was monitored for optimal Marin-5 heater and cooler temperatures, ICP-AES viewing position, and nebulizer gas flow.

2. Analyte wavelengths and background correction points were then selected for highest sensitivity and/or least sample matrix interference.
3. The wavelength of 424.167 nm was chosen for measurement of uranium due to least matrix interference from Ca and Fe.

## Sample Information

### Very hard water matrix composition:

200 mg/L Fe, K, Mg, Na; 500 mg/L Ca in 1% nitric acid

10,000 mg/L single element standards (Inorganic Ventures, Christiansburg, VA USA) were used to prepare the very hard water matrix, preserved in 1% high-purity nitric acid (GFS Chemicals Veritas™ Grade, Columbus, OH USA).

USEPA MCLs in Drinking Water (µg/L): As (10), Ba (2000), Be (4), Cd (5), Cr (100), Cu (1300), Pb (15), Sb (6), Se (50), Tl (2), U (30)

## Operating Conditions - I

**ICP-AES:** PerkinElmer Optima 5300DV  
**ICP RF Power:** 1350 W  
**Plasma Gas:** 15 L/min  
**Auxiliary Gas:** 0.2 L/min  
**Nebulizer Gas:** 0.62 L/min  
**Viewing:** Axial  
**Torch Injector:** Alumina, 2.0 mm i.d.  
**Torch Position:** -2  
**Nebulizer:** Glass concentric  
**Spray Chamber:** Glass cyclonic  
**Resolution:** Normal  
**Points/peak:** 3  
**Integration time:** 20 sec, 3 replicates

## Notes and Observations

**Marin-5 Heater Temperature:** Manganese signal increases most through the range of 90°C to 110°C and then begins to level off above 115°C. Heater temperature was set at 125°C.

**Cooler Temperatures:** The cooler temperature was set at 3°C for both the Marin-5 and U5000AT+ to reduce water loading to the ICP but above 0°C to prevent ice formation in the condenser.

**ICP Torch Injector:** The normal aqueous alumina torch injector (2.0 mm diameter) was used for highest analyte sensitivity.

**Other ICP Operating Conditions:** ICP power, plasma and auxiliary gas flows, viewing, resolution, points per peak, and integration times were constant between the three experiments (standard nebulizer, Marin-5 and U5000AT+). All data taken under non-cleanroom conditions.