

Detection of Trace Elements in High-Purity Sulfuric Acid Using Ultrasonic Nebulization with ICP-AES Detection

INTRODUCTION

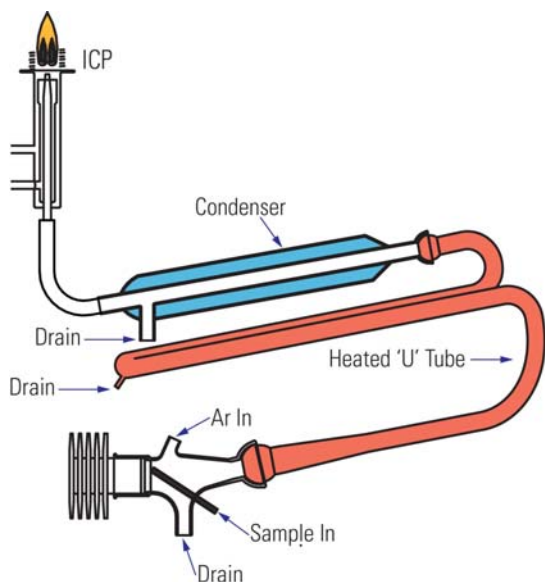
Water quality is a critical issue in boiler water reactor (BWR) nuclear power plants. Plant water for steam generation is analyzed after passage through sampling filters to check for indications of corrosion. Corrosion particulate matter can cause numerous problems, including reduced water flow rates, increased pump head pressures, and loss of heat exchange efficiency due to solids buildup on metal surfaces. These problems can all lead to expensive component repairs and/or replacements.

The filters in the water filter packs are periodically removed and digested in a sulfuric acid solution to check for indications of corrosion. This application note will examine the use of an efficient ultrasonic nebulizer (USN) with ICP-AES to improve trace element detection in a 7.5% high-purity sulfuric acid matrix. Elements of interest include Al, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Ti, W, Zn, and Zr. A particular goal is to lower instrument detection limits (IDLs) below 0.1 $\mu\text{g/L}$ for K and Na in the sulfuric acid matrix. Figures of merit using the USN for introduction of diluted sulfuric acid include instrument detection limits (IDLs), calibration, and analyte recoveries.

INSTRUMENTATION

ICP-AES: **Thermo Fisher Scientific iCAP 6500**

Ultrasonic Nebulizer (USN): **CETAC U5000AT⁺**



CETAC U5000AT⁺ Schematic: The U5000AT⁺ consists of a piezoelectric transducer, a heated u-tube, and an electrothermally cooled condenser.

CETAC U5000AT⁺ Ultrasonic Nebulizer with Thermo Fisher iCAP 6500 ICP-AES

Operating Conditions – 1. Standard Nebulizer

ICP-AES:	Thermo Fisher Scientific iCAP 6500
RF Power:	1200 W
Coolant Gas:	12 L/min
Auxiliary Gas:	0.5 L/min
Nebulizer Gas:	0.60 L/min
Viewing:	Axial
Solution Uptake:	3.0 mL/min (pumped)
Pump Tubing:	PVC
Nebulizer:	Glass Concentric
Spray Chamber:	Glass Cyclonic
Torch Injector:	2 mm diameter
Integration Time:	30 seconds
Replicates:	5

Operating Conditions – 2. Ultrasonic Nebulizer

Nebulizer System:	CETAC U5000AT ⁺
ICP RF Power:	1300 W
Coolant Gas:	12 L/min
Auxiliary Gas:	0.5 L/min
Nebulizer Gas:	0.50 L/min
Viewing:	Axial
Heater Temp:	140°C
Cooler Temp:	3°C
Solution Uptake:	3.0 mL/min (pumped)
Pump Tubing:	PVC
Dwell time:	30 seconds
Replicates:	5

Experimental Parameters – I**Reagents:**

- Sulfuric Acid, Ultrex-II Ultrapure Reagent, J.T. Baker, Phillipsburg N.J. USA
- Various Single-Element Standards, SCP Science, Baie D'Urfe, Quebec Canada

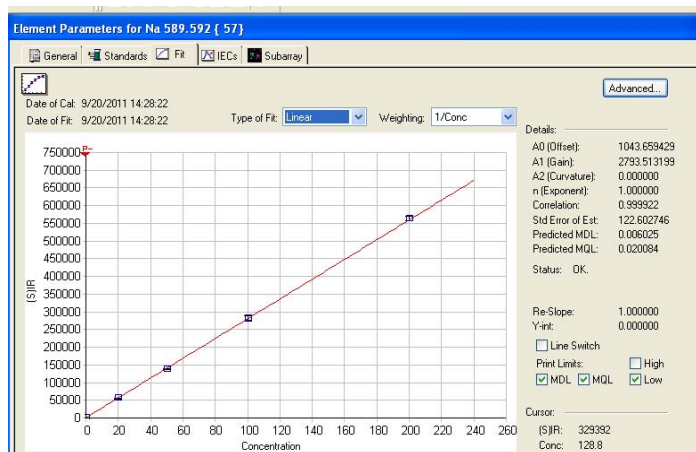
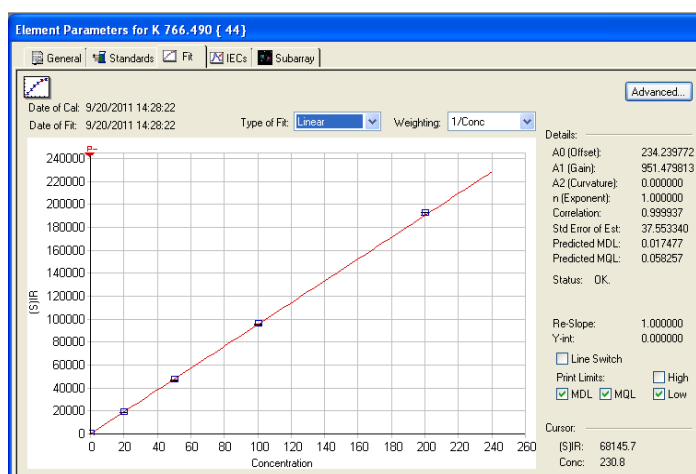
Blank and Standards Preparation:

Reagent blank and calibration standards were prepared by volume in glass volumetric flasks in 7.5% (v/v) sulfuric acid. Standard concentrations were 20, 50, 100, and 200 µg/L.

Experimental Parameters – II**Calibration, Detection Limits, and Recoveries:**

The reagent blank and the four calibration standards were introduced to the ICP-AES with the standard glass concentric nebulizer and cyclonic spray chamber and then the ultrasonic nebulizer. Switching between the standard nebulizer and the ultrasonic nebulizer takes only 5 minutes. Instrument detection limits (IDLs) are calculated as 3 times the standard deviation of the blank concentration; the 100 µg/L standard was run as a check for analyte recoveries.

Calibration curves for K and Na with the ultrasonic nebulizer are given below:



SENSITIVITY COMPARISON

Net analyte intensities are compared between the standard concentric pneumatic nebulizer and the U5000AT+ ultrasonic nebulizer. Intensities listed are for a 100 µg/L multi-element spike in 7.5% (v/v) high-purity sulfuric acid, and analyte signals are markedly improved by a range of 6.8 to 17.6 times (average factor of 9.9 times) versus the standard nebulizer.

Element	Wavelength (nm)	Std. Neb. Intensity	USN Intensity	Factor
Al	167.079	318	3901	12.2
Co	228.616	822	7213	8.7
Cr	267.716	1428	13461	9.4
Cu	324.754	2922	20149	6.9
Fe	259.940	1321	11736	8.9
K	766.490	6130	95482	15.5
Mg	279.553	54437	443040	8.1
Mn	257.610	9615	72267	7.5
Na	589.592	15945	281440	17.6
Ni	221.647	720	6748	9.3
Ti	323.452	8053	55035	6.8
W	207.911	142	1331	9.3
Zn	202.548	1901	20662	10.8
Zr	339.198	4710	40066	8.5

DETECTION LIMIT COMPARISON

The U5000AT+ Ultrasonic Nebulizer lowers detection limits for 13 of the 14 measured elements below 0.1 µg/L (tungsten is 0.24 µg/L), for an average improvement of 5.7 times the standard nebulizer.

Element	Wavelength (nm)	Std. Neb. IDLs (µg/L)	USN IDLs (µg/L)	Factor
Al	167.079	0.19	0.02	9.5
Co	228.616	0.21	0.05	4.2
Cr	267.716	0.35	0.06	5.8
Cu	324.754	0.23	0.05	4.6
Fe	259.940	0.23	0.09	2.5
K	766.490	0.38	0.05	7.6
Mg	279.553	0.02	0.002	10
Mn	257.610	0.10	0.03	3.3
Na	589.592	0.20	0.03	6.7
Ni	221.647	0.25	0.06	4.2
Ti	323.452	0.14	0.03	4.7
W	207.911	0.83	0.24	3.4
Zn	202.548	0.08	0.01	8.0
Zr	339.198	0.21	0.04	5.2

ANALYTE RECOVERIES

Analyte recoveries for the 100 µg/L standard in 7.5% v/v high-purity sulfuric acid using both the standard concentric pneumatic nebulizer and the U5000AT+ Ultrasonic Nebulizer are in a narrow range within ± 5% of 100%.

Element	Wavelength (nm)	Std. Neb. % Recovery	USN % Recovery
Al	167.079	100.8	102.3
Co	228.616	100.6	101.8
Cr	267.716	98.5	101.7
Cu	324.754	99.2	102.9
Fe	259.940	100.1	101.8
K	766.940	97.3	102.1
Mg	279.553	98.7	103.2
Mn	257.610	97.1	101.8
Na	589.592	100.6	97.8
Ni	221.647	100.1	101.7
Ti	323.452	99.3	101.8
W	207.911	98.6	102.6
Zn	202.548	101.1	100.8
Zr	339.198	97.5	101.6

SUMMARY:

1. The U5000AT+ Ultrasonic Nebulizer (USN) significantly improves analyte instrument detection limits (IDLs) in diluted (7.5% v/v) high-purity sulfuric acid due to the higher nebulization efficiency of the USN transducer. IDLs are lowered from a factor of 2.5 to 10 for 14 different elements.
2. IDLs for K and Na are below 0.1 µg/L with the USN: 0.03 µg/L and 0.05 µg/L, respectively. Note that these results were obtained under non-cleanroom conditions.
3. Switching from the standard nebulizer to the USN is easy and fast, taking approximately 5 minutes. The only significant modifications in operating parameters were a change in the nebulizer gas flow rate from 0.60 L/min (standard nebulizer) to 0.50 L/min (USN), and an increase in RF power from 1200 W (standard nebulizer) to 1300 W (USN).