

Measurement of Trace Elements in Naphtha Using Ultrasonic Nebulization / Membrane Desolvation with ICP-AES Detection

Introduction

Measurement of trace elements in volatile organic solvents with ICP-AES detection is difficult for several reasons: plasma instability and/or failure, carbon buildup on the ICP torch, and spectral interferences from carbon emission background. A specialized sample introduction accessory can reduce organic-solvent based interferences and enhance trace element detection using a combination of ultrasonic nebulization and membrane desolvation.

The Teledyne CETAC U6000AT+ Ultrasonic Nebulizer / Membrane Desolvator removes much of the sample solvent vapor during transport to the ICP-AES torch, allowing stable plasma operation. The increased aerosol production efficiency of the ultrasonic nebulizer coupled with enhanced desolvation via a membrane unit enables improved analyte signal and lower detection limits.

In this application, a naphtha sample (a mixture of C5 to C9 hydrocarbons) will be analyzed for ng/g level detection of trace elements. Naphtha-type organics are often used as a fuel source, so detection of potentially toxic levels of elements such as arsenic, cadmium, and lead is of interest.

Instrumentation

ICP-AES: PerkinElmer Avio 500

Ultrasonic Nebulizer / Membrane Desolvator: Teledyne CETAC U6000AT+

Experiment Setup

First, the standard nebulizer and spray chamber were removed from the host ICP-AES instrument. The U6000AT+ was then connected to the ICP-AES with a simple interface kit: a nebulizer gas line from the ICP-AES nebulizer gas port to the U6000AT+ Ar in port and a sample out line with a 12/5 glass socket adapter to the ICP torch. Samples were introduced using the host ICP-AES peristaltic pump and Solva PVC-based pump tubing (0.76mm ID) to the U6000AT+ transducer. No computer control is required for setup.



Figure 1. Teledyne CETAC U6000AT+ USN/Membrane Desolvator

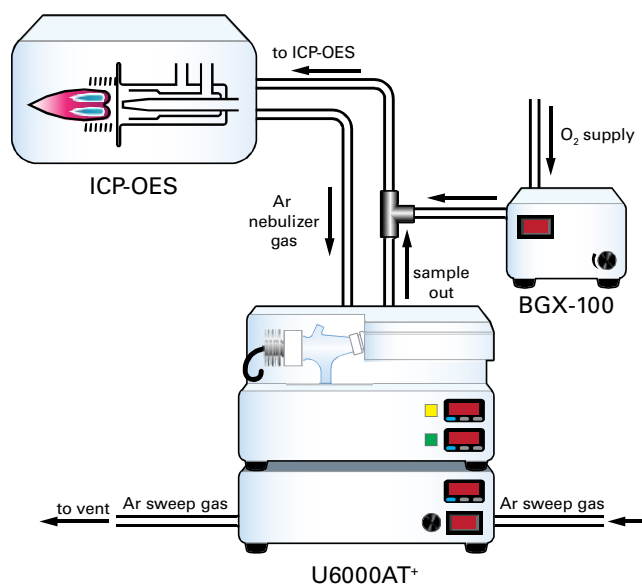


Figure 2. Schematic Diagram of U6000AT+ Setup with ICP-AES

The naphtha sample was from a commercial source and contained C5 to C9 hydrocarbons including pentane, cyclohexane, heptane, octane, and nonane.

A picture of the U6000AT+ Ultrasonic Nebulizer / Membrane Desolvator is given in Figure 1; the U6000AT+ unit can be conveniently placed on a benchtop or a laboratory cart. The ultrasonic nebulizer portion of the U6000AT+ is the top module, with the membrane module below.

A general schematic of the connections (with the optional BGX-100 Blend Gas Accessory) is given in Figure 2. The Ar sweep gas supply to the membrane desolvator may be from a separate Ar source or teed from the main Ar supply to the ICP-AES instrument.

Operating Conditions

Operating conditions of the host ICP-AES are given in are in Table 1; note that axial viewing conditions were used. Table 2 lists settings for the U6000AT+, with a lowered condenser temperature of -15 °C for the primary condenser.

Table 1. ICP-OES Operating Conditions

ICP-AES Parameter	Setting
RF Power	1500 W
Plasma Gas Flow	15 L/min
Auxiliary Gas Flow	1.5 L/min
Nebulizer Gas Flow	0.35 L/min
Uptake Rate	1 mL/min
Peri Pump Tubing	Solva PVC-based, 0.76 mm i.d.
Torch Position	-2
Viewing	axial
Injector	0.8 mm ceramic
Integration time	10 s
Replicates	3

Table 2. U6000AT+ Ultrasonic Nebulizer/Membrane Desolvator Operating Conditions

U6000AT+ USN/Membrane Desolvator Parameter	Setting
Heater Temperature	120 °C
Cooler Temperature	-15 °C
Membrane Desolvator Temperature	160 °C
Membrane Desolvator Ar Sweep Gas	2.00 L/min

Calibration

The ICP-AES was calibrated with the U6000AT+ using oil-based standards diluted in the naphtha sample. Four standards were prepared by weight in 50-mL polypropylene vials: 20, 50, 100, and 200 ng/g. Magnesium was calibrated from 20-100 ng/g. Calibration coefficients had to be greater than 0.995 to be considered valid for analysis. Correlation coefficients for several elements of interest are listed in Table 3.

Table 3: Correlation Coefficients for As, Cd, and Pb Calibration

Element (wavelength)	Correlation Coefficient
Arsenic (188.979 nm)	0.9990
Cadmium (226.502 nm)	0.9995
Lead (220.353 nm)	0.9995

The actual calibration curves for As, Cd, and Pb are shown in Figures 3a-3c.

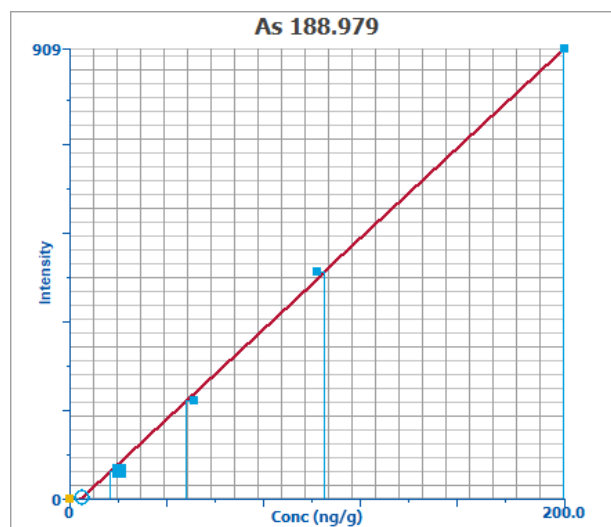


Figure 3a. Calibration curve for As spiked into naphtha

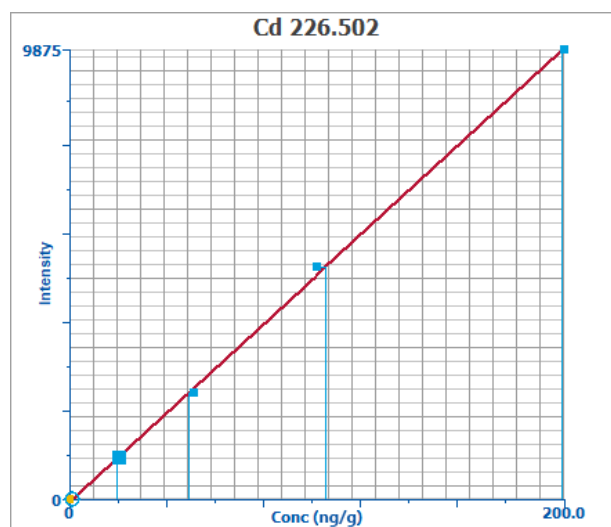


Figure 3b. Calibration curve for Cd spiked into naphtha

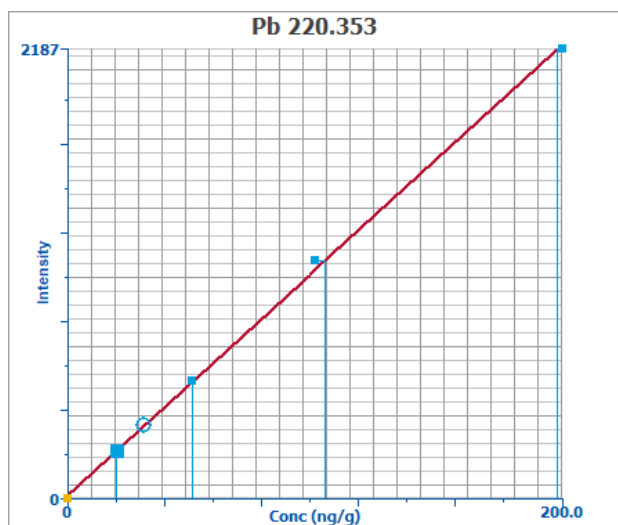


Figure 3c. Calibration curve for Pb spiked into naphtha

Instrument Detection Limits

An unspiked naphtha sample was analyzed 10 times against the calibration curves for calculation of instrument detection limits (IDLs). The IDL is defined as 3x the standard deviation of the analyte concentration measured in the unspiked sample replicates. Limits of quantitation (LOQs) are defined as 10x the standard deviation of the analyte concentrations in the unspiked sample replicates. Results in ng/g are in Table 4 for 22 elements.

Table 4: Instrument Detection Limits and Limits of Quantitation

Element	Wavelength (nm)	IDL (ng/g)	LOQ (ng/g)
Aluminum	394.401	0.16	0.53
Antimony	206.836	1.1	3.7
Arsenic	188.979	1.1	3.7
Barium	455.403	0.054	0.18
Beryllium	313.107	0.038	0.13
Bismuth	223.061	0.56	1.9
Calcium	393.366	0.10	0.33
Cadmium	226.502	0.19	0.63
Chromium	267.716	0.20	0.66
Cobalt	238.892	0.15	0.50
Copper	324.752	0.079	0.26
Iron	238.204	1.5	5.0
Lead	220.353	0.56	1.9
Magnesium	285.213	0.13	0.43
Manganese	257.610	0.14	0.47
Molybdenum	202.031	0.28	0.93
Nickel	221.648	0.28	0.93
Potassium	766.490	1.4	4.6
Silver	328.068	0.083	0.28
Thallium	190.801	2.0	6.7
Titanium	334.940	0.020	0.067
Vanadium	292.402	0.067	0.22

Spike Results

The naphtha sample was then spiked at 5 ng/g and 20 ng/g to demonstrate the accuracy of the method at low element concentrations. As the 5 ng/g spike is 4x lower than the first calibration standard, recoveries of 70-120% are considered acceptable. Results for the 20 ng/g spike validate the low standard of the curve with recoveries of 90-120%. Results are in Table 5.

Table 5. Spike % Recoveries in Naphtha Sample Matrix

Element	Wavelength (nm)	5 ng/g % Recovery	20 ng/g % Recovery
Aluminum	394.401	120	109
Antimony	206.836	95	114
Arsenic	188.979	120	109
Barium	455.403	88	111
Beryllium	313.107	112	110
Bismuth	223.061	84	115
Calcium	393.366	77	112
Cadmium	226.502	119	110
Chromium	267.716	82	112
Cobalt	238.892	103	110
Copper	324.752	82	110
Iron	238.204	80	118
Lead	220.353	92	112
Magnesium	285.213	111	117
Manganese	257.610	75	108
Molybdenum	202.031	93	110
Nickel	221.648	99	111
Potassium	766.490	*	111
Silver	328.068	78	114
Thallium	190.801	105	90
Titanium	334.940	73	110
Vanadium	292.402	80	108

*no peak was detected at 5 ng/g

The ability to detect multiple elements at 5 ng/g is attributable to the effect of the ultrasonic nebulizer / membrane desolvator combination. The As emission spectra from an ultrasonic nebulizer only (top) and the ultrasonic nebulizer/membrane desolvator combination (below) are shown in Figure 4. For the ultrasonic nebulizer test, a sample of 1% isopropyl alcohol (IPA) in deionized water was introduced to maintain plasma stability.

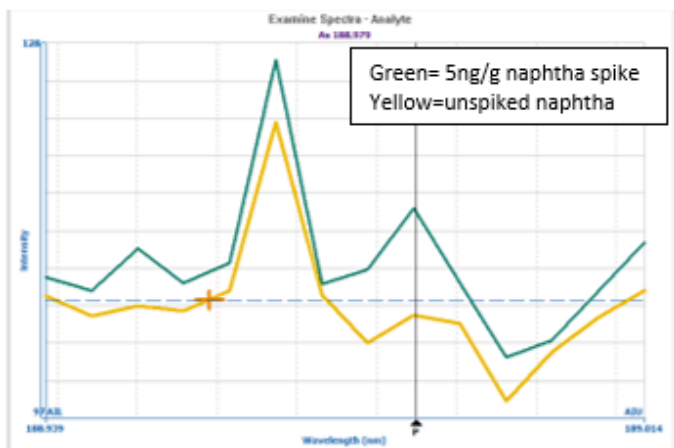
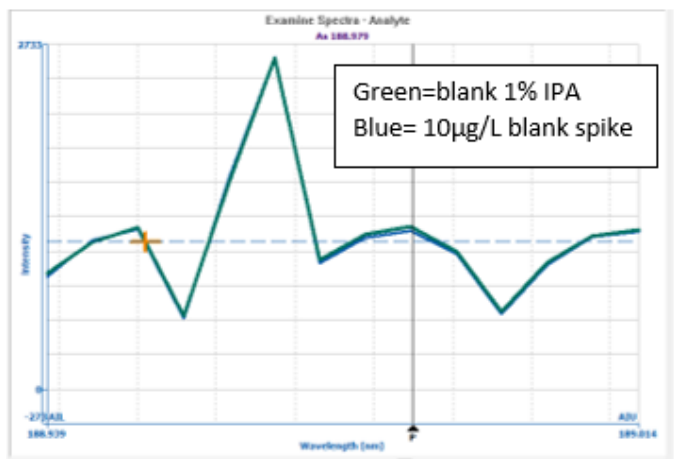


Figure 4. Comparison of organic solvent background emission for As 188.979 nm line

Using only the ultrasonic nebulizer (the U5000AT+), there is no discernible peak for 10 µg/L As in the presence of 1% isopropyl alcohol. With an ultrasonic nebulizer / membrane desolvator (the U6000AT+ combination), much of the 100% naphtha-based emission is removed so a 5 ng/g As spike can be detected and an acceptable As spike recovery of 120 % is achieved.

Standard Reference Material Results

NIST® 1085a Wear-Metals in Lubricating Oil was diluted in the naphtha sample by a factor of 10,000 to give an approximate analyte concentration of 30 ng/g. Measured concentrations (after correcting for dilution) are in Table 6. Despite analyzing the standard at only 10 ng/g above the low standard of the calibration curves, recoveries are still within 20% of the certified value. This result validates the accuracy of the method for this sample type diluted in naphtha.

Table 6: Per Cent Recoveries of Spiked Elements in Naphtha-Diluted NIST® 1085a Wear-Metals in Lubricating Oil

Element	NIST reported (µg/g)	Measured (µg/g)	% Recovery
Chromium	296.3	321.6	108
Copper	295.1	305.4	103
Iron	296.8	319.0	107
Lead	297.4	308.0	104
Magnesium	296.0	353.1	119
Molybdenum	302.9	311.4	103
Nickel	302.9	331.2	109
Silver	305.7	298.8	98
Titanium	305.1	308.6	101
Vanadium	292.4	300.1	103

Conclusions

The U6000AT+ Ultrasonic Nebulizer / Membrane Desolvator combination with ICP-AES detection reduces naphtha-matrix emission background enabling single digit and sub ng/g element detection limits and acceptable % recoveries of a low 5 ng/g spike. Adding the membrane desolvator to the base ultrasonic nebulizer (the U5000AT+) only requires an Ar gas supply and connecting tubing; the membrane desolvator module can be placed directly beneath, saving valuable bench space. In addition, the enhanced removal of organic solvent improves the working lifespan of sample introduction components such as the ICP torch and injector tube.

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