

Determination of Trace Elements in a Xylene Solution of Oil By ICP-OES with Ultrasonic Nebulization and Membrane Desolvation

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

Valérie LeCourbe

Introduction

The purpose of this study was to demonstrate the accurate determination of 10 µg/kg of each of 17 elements (Mo, Ag, Ti, Sn, Ba, B, Mn, Fe, Cr, Mg, V, Ca, Cu, Pb, Ni, Cd and Al) in a xylene solution of oil by ICP-OES.

Problems that can occur during oil analysis include instability of the plasma when volatile organic compounds are introduced and deposition of carbon on the intermediate tube and on the injector tip of the torch. To avoid these problems, it is necessary to introduce oxygen with the auxiliary argon flow to convert the carbon into gaseous carbon oxides.

When we want to determine trace elements in organic samples, it can be difficult to avoid elevated background emission caused by both the organic matrix and the solvent used for diluting the sample or preparing standards. In this work an ultrasonic nebulizer was used with a membrane desolvator. The desolvator can remove much of the organic solvent before the sample enters the plasma.



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Operation of the Ultrasonic Nebulizer/Membrane Desolvator

The sample is pumped onto the transducer of the ultrasonic nebulizer where it is converted to a fine, dense aerosol. The aerosol is transported through the heated U-tube where the solvent is vaporized; the solvent vapors are then recondensed and removed by the drain pump. For further solvent removal, the sample is sent to the membrane desolvator where solvent vapor is removed through a microporous membrane while the desolvated sample goes to the plasma. The membrane desolvator preserves the high efficiency of the ultrasonic nebulizer and reduces solvent loading in ICP.

Experimental

Equipment

The Agilent Liberty 150 AX Turbo axially-viewed ICP spectrometer was used for all measurements, together with a Cetac U 6000 AT+ Ultrasonic Nebulizer and Membrane Desolvator (Cetac Technologies Inc., Omaha, Nebraska USA).

The Liberty 150 AX Turbo is equipped with a crystal controlled, 1.7 kW RF generator that operates at a frequency of 40.68 MHz. The Czerny-Turner monochromator has a 1800 grooves/mm holographic grating that can be used in up to the 4th order with a resolution of 0.006 nm (0.018 nm for the 1st order).

To introduce oxygen into the auxiliary argon gas, the AGM-1 accessory (Agilent Australia Pty Ltd, Mulgrave, Australia) was used.

Standards and samples were introduced automatically with the SPS-5 accessory (Sample Presentation System - Agilent Australia Pty Ltd, Mulgrave, Australia) .

The system was controlled with a Compaq 486/575e computer.

Instrument Parameters

General parameters for plasma, nebulizer, membrane desolvator were selected to obtain both high intensity and reduced interferences.

Power	1.5 kW
Plasma gas flow	15.0 L/min
Auxiliary gas flow	1.5 L/min
PMT	700 V
Pump speed	15.0 rpm
Background correction	Dynamic
Replicates	3
Ultrasonic nebulizer	Heating temperature = 140 °C Cooling temperature = 3 °C
Membrane desolvator	Heating temperature = 160 °C Argon flow = 1.2 L/min
AGM-1 accessory	Oxygen flow = 1.5 L/min
Sample delivery tube	Organic resistant, black/black

Emission line wavelength, order, search window, scan window and integration time were optimized for each element, and are listed in Table 1.

Table 1. Instrument Parameters for the Liberty 150 AX Turbo

Element	Wavelength nm	Order	Search window nm	Scan window nm	Integration time s
Mo	204.598	3	0.10	0.120	5.0
Ag	328.068	1	0.10	0.120	2.0
Ti	336.121	1	0.10	0.120	2.0
Sn	235.484	2	0.05	0.060	10.0
Ba	493.409	1	0.10	0.120	2.0
B	249.773	2	0.05	0.060	5.0
Mn	257.610	2	0.05	0.060	2.0
Fe	259.940	2	0.05	0.060	2.0
Cr	267.716	2	0.05	0.060	2.0
Mg	279.553	2	0.05	0.060	2.0
V	292.402	2	0.05	0.060	5.0
Ca	317.933	2	0.05	0.060	2.0
Cu	324.754	1	0.05	0.060	2.0
Pb	220.353	3	0.03	0.040	10.0
Ni	221.647	3	0.03	0.033	5.0
Cd	228.802	3	0.03	0.040	2.0
Al	396.152	2	0.05	0.060	5.0

Calibration Solutions and Sample

A 1 mg/kg standard was prepared by weighing an appropriate quantity of Conostan S21 100 mg/kg standard and dissolving in xylene. Five standards of 10, 20, 30, 40 and 50 µg/kg and the 10 µg/kg sample were then prepared by diluting the 1 mg/kg standard in xylene. The blank was prepared by diluting Conostan base oil 75 with xylene.

Results

For all 17 elements, the calibration with five standards of 10, 20, 30, 40 and 50 µg/kg was successful. All the correlation coefficients are better than 0.99. Calibration results, signal intensities and %RSD for the 50 µg/kg standard are presented in Table 2.

Table 2. Calibration Results for 17 Elements in Oil

Element	Standard intensity	50 µg/kg %RSD	Correlation coefficient
Mo	12090	3.56	0.9919
Ag	60340	2.68	0.9995
Ti	379300	3.64	0.9930
Sn	2331	1.85	0.9991
Ba	1862000	3.21	0.9984
B	6180	1.65	0.9998
Mn	529600	1.63	0.9981
Fe	97220	0.645	0.9967
Cr	70020	0.637	0.9959
Mg	1712000	2.21	0.9992
V	19720	1.56	0.9992
Ca	54830	0.631	0.9988
Cu	42330	1.54	0.9992
Pb	6563	3.51	0.9995
Ni	35720	2.06	0.9972
Cd	60990	1.19	0.9993
Al	30510	2.81	0.9982

The 10 µg/kg sample was then analyzed, and each reported concentration was compared to the known concentration. Recoveries varied from 89-107%. Results are presented in Table 3.

Table 3. Analysis of 10 µg/kg Solution in Oil

Elements	Sample 10 µg/kg		
	Intensity	Concentration	% Recovered
Mo	3478	10.36	103.6
Ag	11410	9.799	97.99
Ti	90540	10.09	100.9
Sn	465.3	10.86	108.6
Ba	422700	10.49	104.9
B	1721	9.135	91.35
Mn	97600	9.776	97.76
Fe	17680	8.944	89.44
Cr	14020	10.12	101.2
Mg	376000	10.50	105
V	4254	10.16	101.6
Ca	13920	11.69	116.9
Cu	7913	9.276	92.76
Pb	1930	9.210	92.1
Ni	8310	10.74	107.4
Cd	12870	10.17	101.7
Al	10720	10.17	101.7

Calibration graphs, and signals obtained for 10 µg/kg of cadmium, lead, vanadium and chromium, are presented in Figures 1–4.

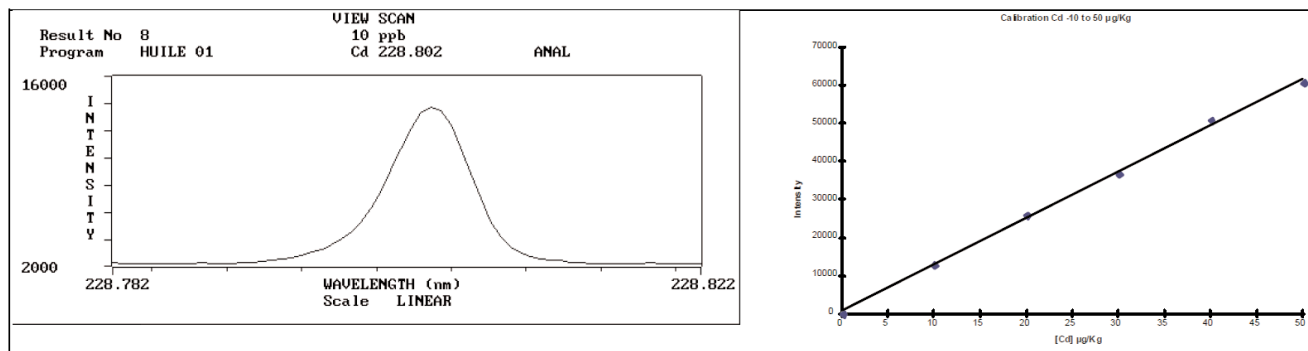


Figure 1. Calibration graph and signal for 10 µg/kg of Cadmium in oil.

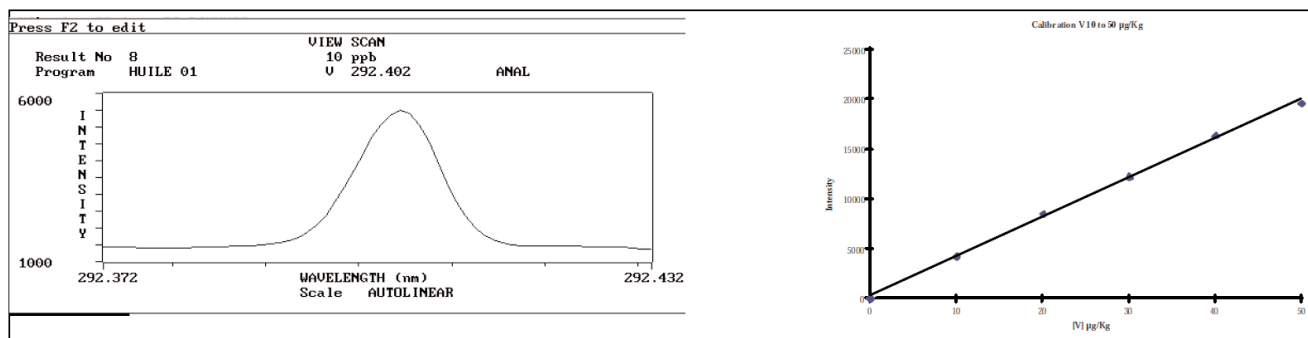


Figure 2. Calibration graph and signal for 10 µg/kg of Vanadium in oil.

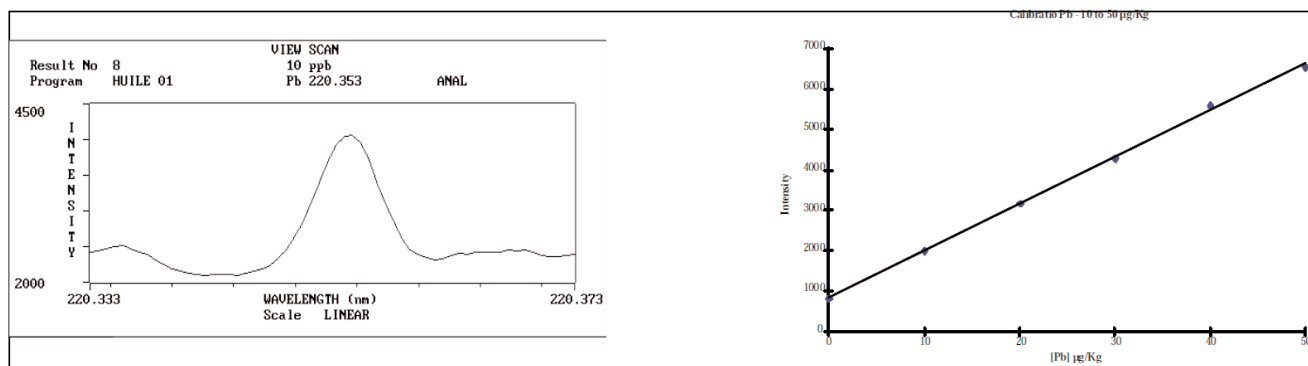


Figure 3. Calibration graph and signal for 10 µg/kg of lead in oil.

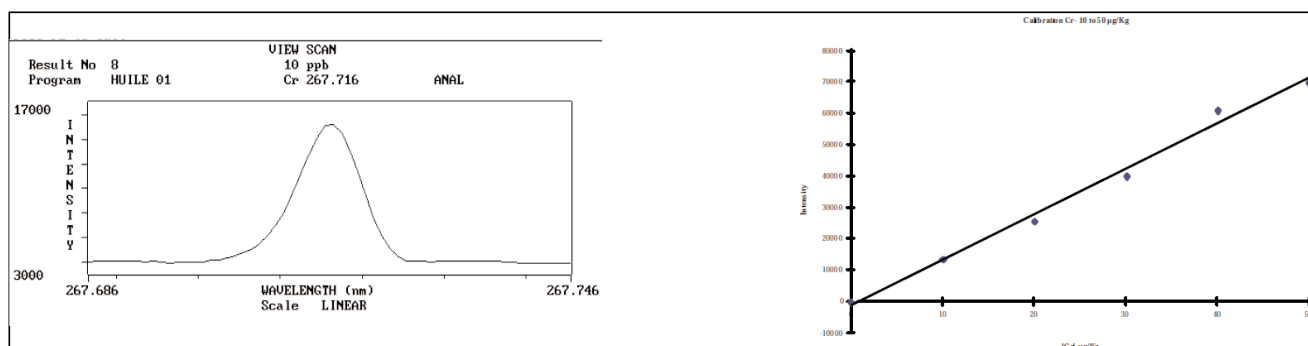


Figure 4. Calibration graph and signal for 10 µg/kg of chromium in oil.

Conclusion

The axially-viewed ICP-OES is an appropriate instrument for analyzing trace elements in oils because it offers both accurate and rapid results without a long sample preparation. The precision of measurements of a 10 µg/kg solution of 17 elements ranged from 1 to 3.7 %RSD.

This method can be used routinely to determine trace elements in oil automatically with the SPS-5.

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