Application Note: 40899

The Analysis of Trace Elements in Naphtha using the Thermo Scientific iCAP 6000 Series ICP

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Key Words

- ICP
- iCAP Radial
- Trace elements
- Volatile solvents
- Organics
- Cooled spray chamber
- IsoMist

Benefits in Brief

- Adjustable radial viewing height and automated optimize source function for ultimate radial sensitivity
- Peltier temperature controlled spray chamber to allow the introduction of volatile organics

Introduction

The analysis of organic solvents by ICP is often seen as problematic, even more so when the solvents are volatile. A volatile solvent (with respect to ICP) is defined as a solvent which exhibits a vapor pressure of greater than 30 mm Hg. When a volatile solvent such as naphtha is introduced in to an ICP, the sample transport efficiency is much greater than that with aqueous samples and this can lead to undesirable effects such as plasma instability.

To introduce a solvent such as naphtha into a plasma the volatility must first be reduced. This can be done in two ways; either by dilution with another solvent such as kerosene, or by cooling the solvent prior to introduction into the plasma which is typically done using a cooled spray chamber. The second of these two options is preferable as this first will degrade the sensitivity of the analysis.

The analysis of trace metals in naphtha is important in petrochemical industry, especially in the cracking of hydrocarbons. The presence of trace metals can severely hamper this process as well as poisoning the catalysts used, which are often expensive.

One such example is arsenic (in the form of arsine) which can poison catalysts at trace concentrations (as low as 50 µg/kg). In addition, arsenic can cause problems with high temperature naphtha cracking tubes due to the formation of coke build-up. This build-up can result in the eventual failure of the tubes and subsequently reduce the production capabilities.

Arsenic free naphtha is also the preferred feedstock for a number of down stream processes such as catalytic reforming, gasoline blending, and C_5 and C_6 isomerization - using platinum and palladium catalysts where the presence of arsenic would course serious problems.

Instrumentation

The Thermo Scientific iCAP 6500 Radial ICP (Figure 1) was used for this analysis. The radial was chosen because the interferences from carbon based emissions can be reduced by optimizing the radial viewing height. The IsoMist (below in Figure 1, Radial IsoMist – Part Number 8423 120 51651) is a Peltier cooled spray chamber which was used in conjunction with a glass concentric nebulizer for this analysis.

Figure 1: The iCAP 6500 Radial ICP with the GE IsoMist peltier cooled spray.

Method

Standards were prepared by diluting Conostan S21 300 mg/kg and Spex CertiPrep As 1000 mg/kg oil-based standards in naphtha (Fisher Scientific) to give working standard solutions of 1.1 and 4.8 mg/kg and a blank was also prepared from the naphtha. A further blank naphtha sample was also spiked to 2.4 mg/kg using the Conostan S21 and Spex CertiPrep as standards.

Method development

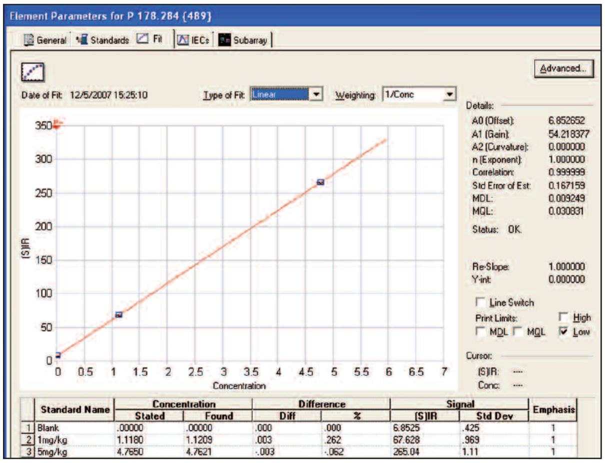
The IsoMist was set to -5 °C. Naphtha was then aspirated into the IsoMist and the plasma was observed, the auxiliary gas flow was adjusted until the base of the plasma was half way between the top of the auxiliary tube and the base of the load coil. The nebulizer gas flow was adjusted until the green sample channel was just below the top of the torch (Figure 2). The radial viewing height was adjusted using the Optimize Source function of the Thermo Scientific iTEVA software package to give the best signal-to-background ratio for all of the elements to be analyzed. Associated plasma gas settings for sample introduction are shown in Table 1.

Figure 2: The plasma aspirating naphtha after the auxiliary and nebulizer gas flows have been optimized.

The instrument was then calibrated and the spiked sample analyzed. A detection limit study was carried out by analyzing ten replicates of the calibration blank and multiplying the standard deviation of this analysis by 3. The subarray plots for each of the wavelengths were examined to ensure freedom from interference and to confirm that the background correction points were set appropriately.

Parameter	Setting
Tubing	Sample orange white solvent flex Drain white white solvent flex
RF Power	1150 W
Pump Speed	40 rpm
Nebulizer Gas Flow	0.4 L/min
Auxiliary Gas Flow	1.5 L/min
Coolant Gas Flow	12 L/min
Radial Viewing Height	8 mm
Nebulizer	Glass concentric
Spray Chamber	IsoMist
Spray Chamber Temperature	- 5°C

Table 1: Instrument conditions.



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Type of Fit: Linear

Weighting: 1/Conc

Details:

A0 (Offset): 6.852652

A1 (Gain): 54.218377

A2 (Curvature): 0.000000

n (Exponent): 1.000000

Correlation: 0.999999

Std Error of Est: 0.167159

MDL: 0.009249

MQL: 0.030831

Status: OK.

Re-Slope: 1.000000

Y-int: 0.000000

☐ Line Switch

Print Limits: ☐ High ☐ MDL ☐ MQL ☑ Low

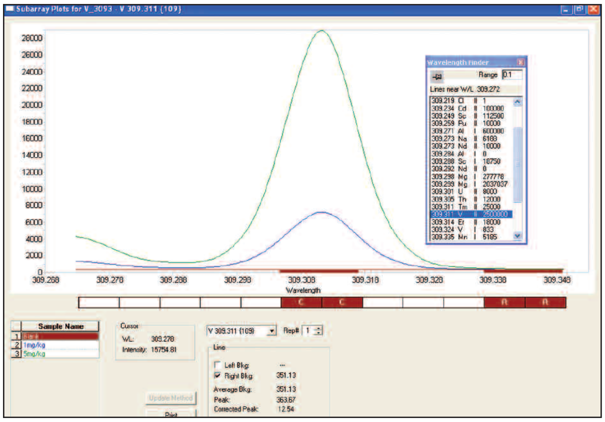
Cursor:

(S)IR: ----

Conc: ----

	Standard Name	Concentration		Difference		Signal		Emphasis
		Stated	Found	Diff	%	(S)IR	Std Dev	
1	Blank	.00000	.00000	.000	.000	6.8525	.425	1
2	1mg/kg	1.1180	1.1209	.003	.262	67.628	.969	1
3	5mg/kg	4.7650	4.7621	-.003	-.062	265.04	1.11	1

Figure 3: The calibration plot of P 178.284 nm.



Range: 0.1

Lines near W/L 309.272

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309.219 Cl  II 1
309.234 Cd  II 100000
309.249 Sc  II 112500
309.259 Pu  II 10000
309.271 Al  I  600000
309.273 Na  II 6183
309.273 Nd  II 10000
309.284 Al  I  0
309.288 Sc  I  18750
309.292 Nd  II 0
309.298 Mg  I  277778
309.299 Mg  I  2037037
309.301 U   II 8000
309.305 Th  II 12000
309.311 Tm  II 25000
309.311 V   II 2500000
309.314 Er  II 18000
309.324 V   I  833
309.335 Mn  I  5185
```

Sample Name
1 Blank
2 1mg/kg
3 5mg/kg

Cursor

WL: 309.278

Intensity: 15754.81

V 309.311 (109) Rep# 1

Line

☐ Left Bkg: ---

☑ Right Bkg: 351.13

Average Bkg: 351.13

Peak: 363.67

Corrected Peak: 12.54

Figure 4: The sub-array plot of V 309.311 nm showing the calibration blank and standards.

Results

	Naphtha spike at 2.4mg/kg	RSD on three replicates of the spike	Instrument Detection Limit
	mg/kg	%	µg/kg
Ag 338.389 nm	2.39	0.558	0.8
Al 308.215 nm	2.37	0.188	2.6
As 189.042 nm	2.44	0.302	15
B 208.595 nm	2.17	1.207	14
Ba 223.527 nm	2.35	0.637	1.3
Ca 184.006 nm	2.35	1.426	8.1
Cd 214.438 nm	2.38	0.970	1
Cr 267.716 nm	2.37	0.246	0.8
Cu 324.754 nm	2.41	0.207	0.4
Fe 238.204 nm	2.39	0.546	1.8
Mg 279.553 nm	2.40	0.087	0.08
Mn 293.930 nm	2.38	0.227	0.8
Mo 281.615 nm	2.38	0.233	2.2
Na 589.592 nm	2.41	0.546	13
Ni 231.604 nm	2.37	0.751	5.0
P 178.284 nm	2.40	0.442	15
Pb 220.353 nm	2.35	0.391	16
Si 212.412 nm	2.40	0.467	10.5
Sn 283.999 nm	2.37	0.456	20
Ti 334.941 nm	2.37	0.153	0.4
V 309.311 nm	2.37	0.387	0.9
Zn 213.856 nm	2.39	0.235	0.8

Table 2: Results of the analysis of the spiked sample with RSD% of the three replicate measurement and the detection limit.

The results for the spiked naphtha are all within acceptable limits of the spiked value (± 5 %) with the exception of boron which is within 10 % of the spiked value. A stabilizer is often added to organic solvents when analyzing for boron. However, in this case a stabilizer was not used and this could explain the slightly low recovery and the instability of this element, which is also reflected in the high %RSD. All of the %RSDs are below 2 % with the vast majority below 0.5 %. Figure 3 gives a calibration plot for phosphorus, indicating excellent precision and linearity at relatively low concentrations. Figure 4 shows the subarray window for vanadium at 309.311 nm, indicating the peak center and background points. This window makes method development extremely simple.

Conclusion

The analysis of naphtha on the iCAP 6500 Radial ICP is made simple by the addition of a Peltier cooled sprayed chamber set to -5 °C. This reduces the volatility of the solvent, which in turn lowers the plasma loading when the solvent is aspirated. The iCAP 6000 Series is capable of detecting single figure sub ppb concentrations of various elements within this complex and challenging matrix.

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AN40899_E 01/10C