

Analysis of Trace Elements in Naphtha Using the Thermo Scientific iCAP 7000 Series ICP-OES

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Key Words

Cooled spray chamber, IsoMist, Naphtha, Volatile organic solvents

Goal

This application demonstrates how volatile organic solvents can be easily analyzed with the Thermo Scientific iCAP 7000 Series ICP-OES fitted with a cooled spray chamber to reduce volatility of the solvent. Cooling down the spray chamber to as low as -10 °C reduces the solvent load on the plasma and allows straight forward analysis of organic solvents with a more stable plasma and reduced background emission.

Introduction

The analysis of organic solvents by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) is often seen as problematic, especially when the solvents are volatile. Typically, a volatile solvent (with respect to ICP-OES) 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 into 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 the plasma, the volatility must first be reduced. This can be done in two ways; either by dilution with a less volatile solvent such as kerosene, or by cooling the solvent prior to introduction into the plasma which is typically done using a cooled spray chamber. As the first option will degrade the sensitivity of the analysis, the second of these two options is preferable. The analysis of trace elements in naphtha is important in petrochemical industry, especially in the cracking of hydrocarbons. The presence of trace elements can severely hamper this process as well as poison the catalysts used, which are often expensive. One example is arsenic (in the form of arsine), which can poison catalysts at trace concentrations (as low as 50 µg kg⁻¹). 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 downstream processes such as catalytic reforming, gasoline blending, and C₅ and C₆ isomerization. These processes are using platinum and palladium catalysts where the presence of arsenic would cause serious problems, poisoning the catalysts.

Instrumentation

The Thermo Scientific™ iCAP™ 7600 ICP-OES Radial was used for this analysis. The radial system was chosen because the interferences from carbon based emissions can be reduced by optimizing the radial viewing height. The GE IsoMist™ is a Peltier cooled spray chamber which was used in conjunction with a glass concentric nebulizer for this analysis.

Sample and Standard Preparation

Calibration standards were prepared by diluting oil based standards S21-K 100 mg kg⁻¹ (elements contained within the standard listed in Table 3), As 100 mg kg⁻¹ and Hg 100 mg kg⁻¹ (Conostan, from SCP SCIENCE) on weight basis in naphtha (from Fisher Scientific™) to concentrations shown in Table 1. A calibration blank was prepared from naphtha and a further blank was spiked (Table 1) using the same standards as for the calibration.

Table 1: Concentrations of calibration solutions and spiked blank.

Solution	Concentration (mg kg ⁻¹)		
	S-21+K	As	Hg
Low Standard	0.96	0.95	0.97
High Standard	4.88	4.90	4.89
Spike	2.34	2.37	2.36

Method Development

The GE IsoMist was set to -10 °C to reduce the volatility of the samples to be within the range of the plasma load that the instrument can handle. Naphtha was then aspirated into the IsoMist and the plasma position in relation to the coil 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 1). The radial viewing height was adjusted to the height that gave 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 2.



Figure 1: Plasma aspirating naphtha after auxiliary and nebulizer gas flows have been optimized.

Table 2: Instrument parameters.

Parameter	Setting
Pump Tubing	Sample solvent flex orange/white Drain solvent flex white/white
Pump Speed	40 rpm
Nebulizer	Glass concentric
Nebulizer Gas Flow	0.45 L min ⁻¹
Auxiliary Gas Flow	1.5 L min ⁻¹
Coolant Gas Flow	12 L min ⁻¹
Center Tube	1.5 mm
RF Power	1150 W
Radial Viewing Height	8 mm
Exposure Time	UV 15 s, Vis 5 s

Analysis

The instrument was calibrated and the spiked blank was analyzed and the recovery calculated. A detection limit study was carried out by analyzing the calibration blank with ten replicates and multiplying the standard deviation of this analysis by three. For each element, wavelengths were selected using the intuitive wavelength selection tool of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. To ensure freedom from interferences, the subarray plots were examined and background correction points were set appropriately. Figure 3 shows the subarray window for Ti 334.941 nm, indicating the peak center and background points. The analyzed lines can be found in Table 3.

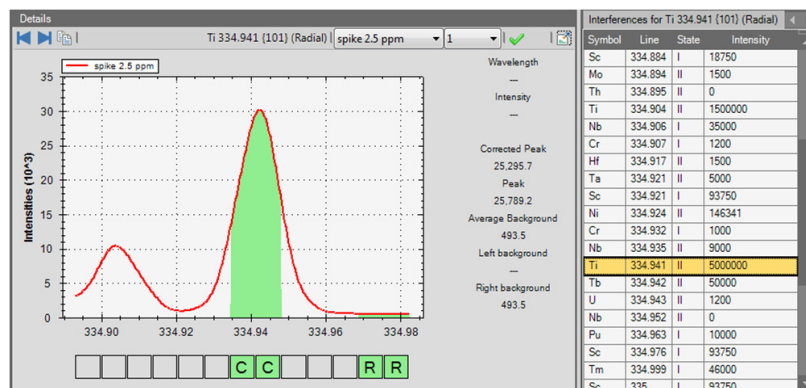


Figure 3: Subarray window for Ti 334.941 nm, indicating the peak center, right background points and possible interferences on the left side of the subarray.

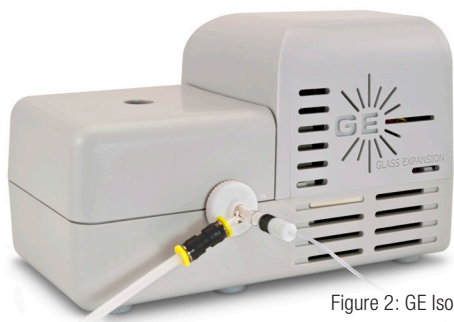


Figure 2: GE IsoMist with nebulizer.

Table 3: Results of the analysis.

Element and Wavelength (nm)	Spike Concentration mg kg ⁻¹	Measured Spike Concentration mg kg ⁻¹	Spike Recovery %	RSD on Three Replicates of the Spike %	MDL µg kg ⁻¹
Ag 328.068	2.34	2.44	104	1.36	3.4
Al 396.152	2.34	2.46	105	1.20	7.9
As 189.042	2.37	2.39	101	0.25	7.4
B 208.893	2.34	2.44	104	0.58	13
Ba 455.403	2.34	2.40	103	0.86	0.2
Ca 393.366	2.34	2.44	104	0.33	0.1
Cd 228.802	2.34	2.37	101	0.28	0.6
Cr 267.716	2.34	2.34	100	0.57	1.0
Cu 324.754	2.34	2.44	104	1.15	1.3
Fe 259.940	2.34	2.34	100	0.35	1.9
Hg 184.950	2.36	2.38	101	0.44	2.7
Mg 279.553	2.34	2.39	102	0.22	0.04
Mn 257.610	2.34	2.34	100	0.38	0.3
Mo 202.030	2.34	2.35	100	0.19	2.7
Na 589.592	2.34	2.43	104	1.43	10
Ni 221.647	2.34	2.30	98	0.32	1.6
P 178.284	2.34	2.36	101	0.19	11
Pb 220.353	2.34	2.27	97	0.12	7.6
Si 212.412	2.34	2.39	102	0.46	8.0
Sn 189.989	2.34	2.27	97	0.92	8.1
Ti 334.941	2.34	2.37	101	0.40	0.4
V 309.311	2.34	2.37	101	0.39	1.0
Zn 213.856	2.34	2.35	100	0.01	0.4

Results

The results (Table 3) show that all element recoveries fall within acceptable limits of $\pm 5\%$ of the true values. The relative standard deviation (RSD) of the three replicates of the spiked blank are below 1.5% for all elements, with the vast majority being below 0.5%. For the majority of analyzed elements, the method detection limits (MDL) are in the single digit $\mu\text{g kg}^{-1}$ range or lower.

Conclusion

The analysis of naphtha with the Thermo Scientific iCAP 7600 ICP-OES Radial is simplified by the addition of a Peltier cooled spray chamber set to $-10\text{ }^{\circ}\text{C}$. This reduces the volatility of the solvent, which lowers the plasma loading, when the solvent is aspirated. The iCAP 7600 ICP-OES Radial can also detect sub single figure ppb concentrations of various elements within this complex and challenging matrix.

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