



Analysis of naphtha using the Thermo Scientific iCAP PRO XP Radial ICP-OES

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Goal

This application demonstrates the analysis of trace elements in volatile organic solvents using the Thermo Scientific™ iCAP™ PRO XP Radial ICP-OES fitted with the Glass Expansion IsoMist™ Peltier cooled spray chamber. Cooling the spray chamber to -10 °C reduces the solvent loading on the plasma and allows the direct analysis of volatile organic solvents and results in stable plasma and reduces background matrix emissions.

Introduction

The analysis of trace elements in organic samples by inductively coupled plasma – optical emission spectrometry (ICP-OES) is commonplace, with a range of dedicated standard methods in use. However, when compared to aqueous analysis, there are a number of considerations that must be taken into account, which is especially true when analyzing volatile organic solvents. A volatile solvent (with respect to ICP-OES) is defined as a solvent that exhibits a vapor pressure of greater than 30 mm Hg. When a volatile solvent is introduced into an ICP, the sample transport efficiency is much greater than that with non-volatile organic solvents, which can lead to plasma instability. To successfully introduce a volatile solvent, such as naphtha, into the plasma, the volatility must first be reduced. Typically, this is achieved by using a cooled spray chamber.

The analysis of trace elements in naphtha is important in the 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).

Instrumentation

The Thermo Scientific iCAP PRO XP Radial ICP-OES fitted with a Glass Expansion IsoMist Peltier cooled spray chamber was used for the analysis. This IsoMist Peltier cooled spray chamber reduces the volatility of the sample prior to introduction into the plasma, resulting in a stable plasma. The radial system allows for the optimization of the radial viewing height, which reduces the interferences from carbon in the cooler regions of the plasma. This optimization was aided by the Plasma TV feature of the instrument, allowing direct visualization of the plasma in the torchbox. The iCAP PRO XP Radial ICP-OES has the ability to measure the entire spectrum of the sample in one analysis, increasing the speed of analysis and, therefore, reducing the consumption of argon per sample.

Sample and standard preparation

Calibration standards were prepared by diluting oil-based standards on a weight-by-weight basis. The standards used were the multi-element S21-K 100 mg·kg⁻¹ (elements contained within the standard listed in Table 3), and single element as 100 mg·kg⁻¹ and Hg 100 mg·kg⁻¹ (Conostan® from SCP SCIENCE). The solvent used for dilution was heavy naphtha (from Fisher Scientific, boiling point at 158 °C). The concentrations prepared are 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	1.02	1.01	1.01
High standard	5.02	4.97	4.95
Spike	2.54	2.51	2.50

Method development

The Glass Expansion IsoMist Peltier was set to -10 °C to reduce the volatility of the samples. 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 central 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 captured using the Plasma TV feature.

Table 2. Instrument parameters.

Parameter	Setting
Pump tubing (standard pump)	Sample Drain SolventFlex orange/white SolventFlex white/white
Pump speed	40 rpm
Nebulizer	Glass concentric
Nebulizer gas flow	0.45 L·min ⁻¹
Auxiliary gas flow	1.50 L·min ⁻¹
Coolant gas flow	12.0 L·min ⁻¹
Center tube	1.50 mm
RF power	1150 W
Radial viewing height	10 mm
Exposure time	10 s (both iFR and eUV)

Analysis

The instrument was calibrated, followed by analysis of the spiked sample. The concentrations and the subsequent analyte recoveries were calculated. A detection limit study was carried out by analyzing the calibration blank with ten replicates and multiplying the standard deviation of the calculated concentrations 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 2 shows the subarray window for Ti 334.941 nm, indicating the peak center and background points. The analyzed wavelengths can be found in Table 3.

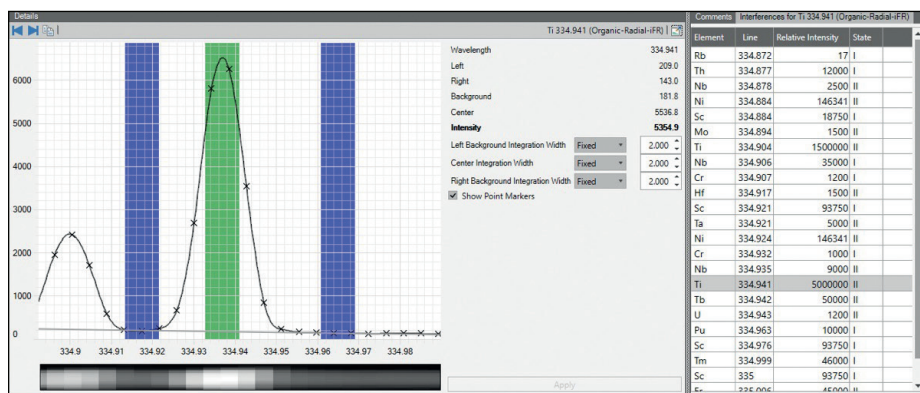


Figure 2. Subarray window for Ti 334.941 nm, indicating the peak center, right background points and possible interferences on the left side of the subarray within Qtegra ISDS Software.

Results

The results (Table 3) show that all element recoveries fall within acceptable limits of $\pm 3\%$ of the true values. The relative standard deviation (RSD) of the three replicates of the spiked blank are below 0.7% for all elements, with the exception of boron, which is known to be a problematic element when analyzed in an organic matrix. The result for boron could be further improved by the addition of a stabilizing agent. For the majority of analyzed elements, the method detection limits (MDL) are in the single digit $\mu\text{g}\cdot\text{kg}^{-1}$ range or lower. The method detection limits are depending on the grade of the solvent used.

Table 3. Results of the analysis.

Element and wavelength (nm)	Mode	Spike concentration ($\text{mg}\cdot\text{kg}^{-1}$)	Measured spike concentration ($\text{mg}\cdot\text{kg}^{-1}$)	Spike recovery (%)	Spike RSD (% , n=3)	MDL ($\mu\text{g}\cdot\text{kg}^{-1}$)
Ag 328.068	iFR	2.54	2.59	102.17%	0.24%	2.52
Al 167.079	eUV	2.54	2.55	100.57%	0.66%	0.76
As 189.042	eUV	2.51	2.50	99.64%	0.31%	17.97
B 208.959	eUV	2.54	2.58	101.71%	1.59%	53.29
Ba 233.527	eUV	2.54	2.58	101.44%	0.04%	2.24
Ca 396.847	iFR	2.54	2.64	103.78%	0.24%	0.65
Cd 228.802	eUV	2.54	2.55	100.28%	0.21%	0.51
Cr 283.563	iFR	2.54	2.60	102.21%	0.43%	1.24
Cu 324.754	iFR	2.54	2.60	102.50%	0.21%	1.28
Fe 239.562	eUV	2.54	2.56	100.98%	0.05%	0.69
Hg 184.950	eUV	2.50	2.51	100.16%	0.17%	9.42
K 766.490	iFR	2.54	2.57	101.31%	0.22%	12.13
Mg 279.553	iFR	2.54	2.58	101.76%	0.30%	0.78
Mn 257.610	iFR	2.54	2.59	102.13%	0.34%	0.73
Mo 202.030	eUV	2.54	2.54	99.84%	0.07%	1.25
Na 588.995	iFR	2.54	2.60	102.30%	0.31%	12.65
Ni 221.647	eUV	2.54	2.55	100.34%	0.13%	1.84
P 177.495	eUV	2.54	2.54	100.19%	0.50%	4.11
Pb 220.353	eUV	2.54	2.54	100.06%	0.21%	7.83
Si 251.611	iFR	2.54	2.60	102.52%	0.35%	4.04
Sn 189.989	eUV	2.54	2.56	100.62%	0.48%	5.10
Ti 334.941	iFR	2.54	2.56	100.96%	0.18%	0.63
V 309.311	iFR	2.54	2.59	101.98%	0.26%	0.70
Zn 202.548	eUV	2.54	2.56	100.93%	0.33%	0.53

Conclusion

The analysis of naphtha with the Thermo Scientific iCAP PRO XP Radial ICP-OES is simplified by the use of advanced features, such as Plasma TV, that ensure simple and fast method development. The addition of a Peltier cooled spray chamber set to -10 °C reduces the volatility of the solvent allowing the sample to be analyzed directly without comprising the detection capabilities of the iCAP PRO XP Radial ICP-OES, which are in the single figure $\mu\text{g}\cdot\text{kg}^{-1}$ range for various elements within this complex and challenging matrix.

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