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# Trace Elements in Petrochemical Samples: Achieving Excellent Analytical Results



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**Executive Summary of the Thermo Scientific “How to Achieve Excellent Results for Trace Elements in Petrochemical Samples” webinar.**

## Introduction

Trace elements in petrochemicals and other organic samples are often analyzed by a standard method using inductively coupled plasma optical emission spectroscopy (ICP-OES). In this

summary we'll discuss the challenges of this type of analysis, and present several strategies for optimizing methods to meet these challenges.

Petrochemical samples typically consist of either crude oils or their distillates. Trace element analyses of these samples span the periodic table, depending on the laboratory's specific interest. Heavy metals are a major focus at refineries, as they tend to contaminate products and poison catalysts. Those examining finished products tend to focus on elements with beneficial properties, such as additives in lubricating oils, in addition to contaminant elements that may be present.

ICP-OES uses either a radial or axial argon plasma, with the former favored for analyzing organic solvents. The radial configuration will have a higher tolerance to the high matrix and allow for optimization to avoid interferences from carbon based species (which emit light in the visible region of the spectrum and cause the plasma to appear green).

### Challenge 1: Sample vapor pressure and viscosity may lead to poor plasma performance

Aqueous sample analysis is typically carried out using the default parameters for an ICP-OES system, but organic samples require different settings. These differences stem from the greater sample loading of the plasma caused by

the higher volatility of organic samples. This results in poorer performance and a reduction in the system's sensitivity to trace elements using default parameters.

The problem has several components that we need to address separately. The first consideration is the sample's volatility, which affects how it is nebulized and transported to the plasma. Second, we need to ensure that the sample is chemically compatible with the system components we've selected. As mentioned above, organic samples are typically more volatile than aqueous ones, so they're converted to aerosols more efficiently, leading to more plasma loading and correspondingly poorer sensitivity.

Use of a V-groove nebulizer and baffled spray chamber reduces the amount of the sample reaching the plasma, which helps to stabilize it. These components, plus a smaller-bore center tube combine to form an ideal sample introduction system for volatile organic samples.

We can predict a solvent's volatility from its vapor pressure at room temperature, and use this to determine what measures we need to take to reduce volatility during analysis. Samples with a vapor pressure at or below 30 mm of mercury are suitable for analysis with the V-groove nebulizer and baffled spray chamber. This includes kerosene, xylene, toluene and diesels. Samples with a vapor pressure above 30 mm of mercury at room temperature are considered to have a high volatility, and therefore requiring cooling of the spray chamber to the above to further reduce plasma loading.

Cooled spray chambers are widely available and relatively simple to use. Alternatively, the sample's volatility can be reduced by diluting it with a less volatile solvent such as xylene. This requires serial dilution followed by correction of the results afterward, ideally with internal standardization as well to correct for any signal drift or suppression.

A final strategy is to use a low-flow nebulizer at room temperature to reduce the amount of sample reaching the plasma. This reduces the system's sensitivity, leads to rela-

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tively long sample introduction and wash-out times, and also requires internal standardization.

Petrochemical samples are often oil based and may span a wide range of viscosities. As the viscosity of a sample increases, less sample reaches the plasma and sensitivity declines. In this case, it's important to ensure that all of the samples in a given set have similar viscosities, and that the nebulizer is suitable for that viscosity range. Internal standards can help counteract small differences in viscosity between samples.

## Challenge 2: Interference from carbon emission and carbon deposition in the torch.

Looking at a full spectrum capture from ICP-OES analysis of an organic solvent reveals a high level of background emissions. This comes from the different carbon species being produced during the sample's breakdown, reducing the system's sensitivity and selectivity to the trace elements. In the center of the plasma, diatomic carbon emissions are a function of the nebulizer gas flow, so higher flow rates increase these emissions. The plasma plume displays atomic carbon emissions, and in the cooler outer area of the plasma we see the formation of light-emitting organic molecules.

Optimizing the nebulizer gas flow can reduce diatomic carbon emissions, bringing the total background emissions down. Lowering the gas flow too far prevents the sample from being properly aspirated into the plasma, while setting it too high produces excessive background emissions. With the gas flow set properly on a radial plasma system, the plasma's sample channel will be about halfway between the top of the load coil and the top of the outer tube of the torch.

An axial plasma system, in contrast, has its optics aligned along the axis of the plasma, looking directly into the zone where diatomic carbon forms.

In this case, it's impossible to reduce the emissions by adjusting the gas flow. Instead, we can add oxygen to the plasma to convert the diatomic carbon to CO and CO<sub>2</sub>, shifting the background signal away from the wavelengths where we're detecting our trace elements.

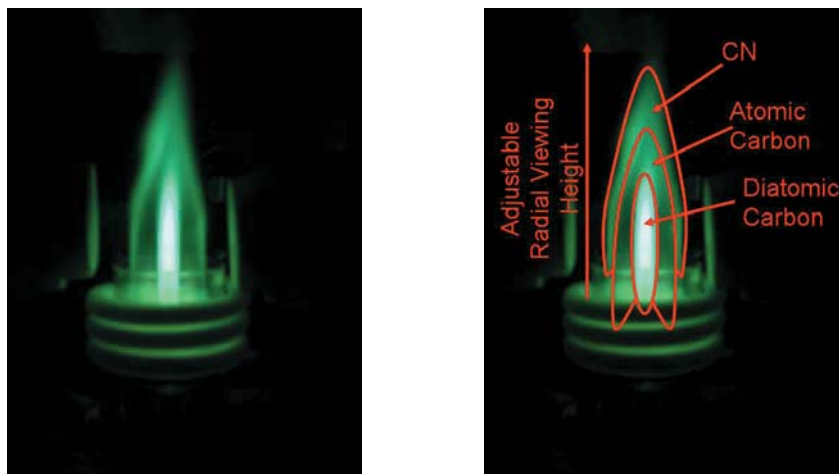
As an example of how this works in practice, we can look at the analysis of sodium in kerosene on an axial plasma system. Comparing the emission spectrum of pure kerosene with that of a kerosene sample with 10 ppm of sodium reveals very little difference, demonstrating that the background emissions of the kerosene are largely masking the analyte. If we add oxygen to the plasma, we can easily distinguish the sodium peak from the background. In this case, the addition of oxygen increases

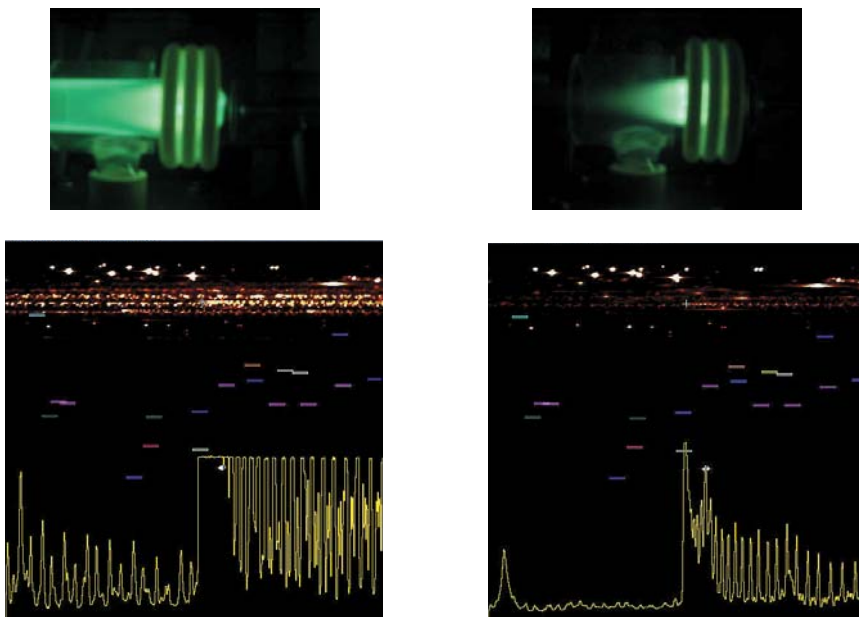
**Figure 1:** What do volatile solvents do to a plasma?

- As the vapour pressure increases
  - More solvent is aspirated
  - The sample channel is extended
  - The base of the plasma moves up
- The plasma becomes unstable



**Figure 2:** Carbon based emissions.



**Figure 3:** Oxygen addition.

the signal to background of the system by more than an order of magnitude.

Carbon can also cause another problem. An orange glow at the base of the plasma indicates that incorrect plasma conditions are causing carbon deposits to accumulate there. If allowed to continue, this will ultimately destabilize the plasma and extinguish it. We will then have to remove the plasma torch and clean it either by heating it in a furnace or by bathing it in chromic acid.

The easiest way to prevent these carbon crystals from forming is to optimize the nebulizer gas flow as described above, then adjust the auxiliary gas flow. The auxiliary gas controls the position of the plasma within the torch; higher flows place the plasma higher in the torch and further from the center tube. For organic samples, a flow of 1.5-2 liters per minute is ideal, putting the plasma about halfway between the auxiliary tube and the base of the load coil.

In summary, to overcome the problems caused by carbon emission and deposition, we need to consider the volatility and chemical properties of the sample, use cooled spray chambers for more volatile organic solvents, ensure that the plasma conditions are set properly by optimizing the nebulizer and gas flow, and for axial view plasmas, use oxygen to minimize background emissions.

### Challenge 3: Making the right choice of hardware and core technologies to speed up analysis and achieve excellent results

Thermo Scientific offers several models and configurations of ICP-OES systems ideally suited for different types of

petrochemical analysis. The Thermo Scientific iCAP 7000 Plus Series ICP-OES comes in three different models: the Thermo Scientific iCAP 7200 ICP-OES entry-level instrument, and the Thermo Scientific iCAP 7400 ICP-OES and Thermo Scientific iCAP 7600 ICP-OES systems for more sophisticated analyses and higher sample throughput.

The iCAP 7200 ICP-OES is ideal for laboratories stepping up from flame atomic absorption spectroscopy to ICP-OES. Researchers who have been analyzing single elements but want to move to multi-element analysis will find this a convenient entry into the iCAP 7000 Plus Series.

In the middle of the range, the iCAP 7400 ICP-OES is a

good choice for routine petrochemical analysis. Petrochemical companies or those manufacturing synthetic compounds typically have moderate sample throughput needs, and are most often analyzing up to about 20 elements. The iCAP 7400 ICP-OES, which offers more flexible gas flow control than the iCAP 7200 Plus, is perfect for those laboratories.

Investigators who process hundreds of samples per day, such as facilities carrying out wear metal analysis on lubrication oils, may need higher throughput than the iCAP 7400 ICP-OES can offer. For them, we recommend the iCAP 7600 ICP-OES. This instrument includes an integrated sample valve that accelerates analyses considerably.

In the iCAP 7600 ICP-OES, a vacuum system pulls the sample into the sampling loop while the valve directs a carrier solution, pumped via the instrument's peristaltic pump, through the nebulizer and spray chamber to clean them. The valve then switches and the sample is directed into the nebulizer. After a few seconds the sample stream stabilizes in the plasma and we can read the data. When the reading is complete, the valve switches back and the cycle starts again. This configuration reduces the total sample uptake time from typically more than 30 seconds to around 10 seconds. The iCAP 7600 ICP-OES can handle 1,000-1,500 samples a day, depending on the specific analyses being performed.

All of the iCAP 7000 Plus Series ICP-OES instruments use a simple clip-in sample introduction system, making it easy to switch between different types of samples or remove the torch for cleaning, this is especially important during the method development process, when the torch may accumulate carbon deposits from operating with less-than-ideal parameters. We

also offer a choice of quartz or ceramic torches with the same geometry. Investigators can use the transparent quartz torch during method development, as it allows them to see the plasma, and then switch to the more robust and longer-lasting ceramic torch for production analysis.

The iCAP 7000 Plus Series ICP-OES employs a simple optical design to ensure maximum light transmission and sensitivity. Each instrument also includes a non-blooming detector with a high dynamic range, allowing us to analyze very high and very low concentrations of trace elements. The Thermo Scientific Qtegra Intelligent Scientific Data Solution (ISDS) software controls the entire system. Qtegra ISDS also runs our other ICP based analytical instruments, such as our quadrupole ICP-MS, the Thermo Scientific iCAP RQ, reducing training requirements and providing an easy transition between different types of analyses.

### Example methods: oil and naphtha analyses

A couple of examples will illustrate how to use these systems for typical petrochemical analyses. One common type of procedure is the ASTM D4951 or D5185 standard analytical methods for testing crude or lubrication oils. These simple methods entail diluting the sample tenfold in a suitable solvent. To keep the volatility low, xylene is used for the dilution. Diluting the samples also helps normalize their viscosities, which can vary significantly across oil samples. Including an internal standard further helps to ensure consistent results.

In lubrication oil, we can look for organometallic additives and wear metals. The former will show how much of the oil's original additive package remains, and the latter will reveal whether components of

the engine are failing or wearing out. We can also look for silicon from dust, which can enter the engine through faulty air filters, and sodium, a marker for water contamination in the oil. Altogether, a typical analysis might include ten to twenty elements.

Because the samples in this example are relatively non-volatile, we can use the standard organic sample introduction

**Figure 4:** EMT torch for ease of use for routine maintenance.



### TORCH ORIENTATION LOCK

- Auto alignment of the torch in the torch box
- Automatically establishes robust plasma gas connections

### SCREW-THREADED CENTRE TUBE HOLDER

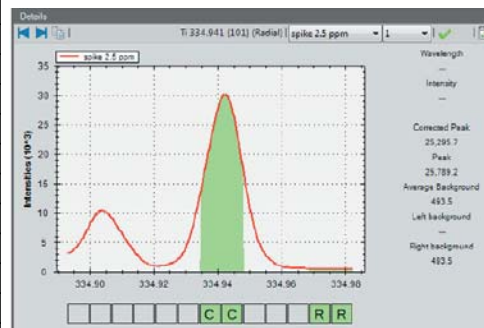
- Simple routine maintenance operations with the plasma on!

**Figure 5:** Results for the analysis of oils.

|               | New oil (mg/kg) | Intermediate oil (mg/kg) | Old oil (mg/kg) | Nist 1084a found (mg/kg) | NIST 1084a cert (mg/kg) |
|---------------|-----------------|--------------------------|-----------------|--------------------------|-------------------------|
| Ag 338.389 nm | 0.76            | 0.87                     | 0.94            | 99.2                     | 99.2                    |
| Al 308.215 nm | 0.09            | 0.05                     | 0.05            | 100.6                    | 101.7                   |
| B 208.959 nm  | 2.14            | 1.63                     | 2.46            |                          |                         |
| Ba 223.527 nm | ND              | 0.46                     | 0.82            |                          |                         |
| Ca 184.006 nm | 1103            | 2293                     | 3014            |                          |                         |
| Cd 214.438 nm | 0.15            | 0.17                     | 0.27            |                          |                         |
| Cr 267.716 nm | 0.12            | 1.15                     | 2.54            | 97.5                     | 99.6                    |
| Cu 324.754 nm | 0.58            | 2.03                     | 3.49            | 101.0                    | 100.3                   |
| Fe 238.204 nm | 2.76            | 23.2                     | 30.8            | 101.3                    | 101.5                   |
| Mg 279.553 nm | 870.8           | 631.2                    | 323.4           | 108.9                    | 101.3                   |
| Mn 293.930 nm | 0.21            | 0.63                     | 0.89            |                          |                         |
| Mo 281.615 nm | ND              | 0.16                     | 0.38            | 99.5                     | 99.4                    |
| Na 589.592 nm | 5.71            | 5.20                     | 3.71            |                          |                         |
| Ni 231.604 nm | 0.73            | 0.59                     | 0.48            | 98.1                     | 100.4                   |
| P 178.284 nm  | 972.4           | 1045                     | 984.1           |                          |                         |
| Pb 220.353 nm | 16.0            | 12.1                     | 8.0             | 97.1                     | 100.8                   |
| S 180.731 nm  | 5731            | 5776                     | 5134            |                          |                         |
| Si 212.412 nm | 7.15            | 10.3                     | 10.8            | 100.9                    | 100.7                   |
| Sn 283.999 nm | 7.70            | 4.58                     | 2.53            | 98.8                     | 99.2                    |
| Ti 334.941 nm | 0.40            | 0.48                     | 0.51            | 100.1                    | 102.4                   |
| V 309.311 nm  | 2.20            | 1.46                     | 0.70            | 99.2                     | 101.8                   |
| Zn 213.856 nm | 1038            | 1143                     | 1106            |                          |                         |

**Figure 6:** Results for the analysis of naphtha.

|               | Naphtha spike at<br>2.4mg/kg | RSD on three replicates<br>of the spike | Instrument Detection<br>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                           |
| 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                           |



kit without cooling. We use an RF power level of 1,150 watts and an auxiliary gas flow of 1.5 liters per minute, parameters that ensure good sensitivity and plasma stability.

Looking at three oil samples of different ages in this setup clearly reveals the lubricant's life cycle. New oil contains high levels of additives and little or no wear metal, while additives decline and wear metals rise in progressively older samples. All of the quality control samples show good sensitivity and consistency, indicating that the plasma remains stable throughout the analysis.

To show how to analyze a more volatile sample, we can use naphtha as an example. Naphtha has a relatively high vapor pressure at room temperature, well above the critical 30 mm of mercury threshold. We can address that with a cooled sample introduction system and a narrower bore center tube, as described above. In this example, we've chosen the IsoMist cooled spray chamber, a programmable system from Glass Expansion. We set the temperature of the spray chamber to minus five degrees to bring the vapor pressure of the naphtha sample down to a workable range.

The volatile sample will still create a lot of aerosol, which will then be sent to the plasma chamber where it may generate excessive diatomic carbon emissions. To combat that, we reduce the nebulizer gas flow to 0.45 liters per minute and keep the auxiliary gas flow at 1.5 liters per minute. With the parameters adjusted, we can detect a variety of elements

with good sensitivity and consistency. This type of volatile sample analysis is typical in the petroleum industry, where investigators need to monitor levels of contaminating elements in gasoline production.

## Summary

ICP-OES is an ideal technique for many types of trace element analysis in petrochemicals, provided we take the time to optimize our methods. The volatility and chemical compatibility of the sample dictate the type of spray chamber and the plasma conditions we'll need to use. Samples with a vapor pressure under 30 mm of mercury at room temperature are relatively non-volatile, requiring little more than optimizing the nebulizer gas flow and auxiliary gas flow to ensure a stable plasma. More volatile samples require specific measures to prevent them from destabilizing the plasma, such as a chilled sample introduction system, narrower bore center tube and reduced nebulizer gas flow.

The carbon matrix of organic samples can also cause interference by generating background emissions, and by carbon deposition on the torch that can destabilize the plasma. Adjusting the nebulizer and auxiliary gas flows can generally resolve these problems, and an easily removable plasma torch eases the cleaning often required during method development. The Thermo Scientific iCAP 7000 Plus Series ICP-OES includes a range of instruments ideally suited to all of these analyses.