Application Note: 40987

Petrochemical Series - Simplified analysis of trace elements in gasoline with the Thermo Scientific iCAP 6000 Series ICP

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Key Words

- IsoMist
- Gasoline
- Organics
- EMT Torch
- Volatile organics

Key Benefits

- Dedicated volatile organics sample handling kit makes selecting the right sample introduction approach easy
- EMT torch effortlessly copes with high volatility organic samples without carbon deposition, offering exceptional long-term stability
- High resolution optics reduce the impact of spectral complexity, leading to greater confidence in analytical results
- iTEVA software subarray view facilitates method development and helps provide better quality data

Introduction

Background

The presence of trace elements in gasoline can lead to a number of detrimental effects both on the automobile engine using the fuel as well as the environment. The analysis of trace elements is therefore essential to ensure the performance of the engine is not affected by the fuel and that environmental damage does not occur when trace elements are transported from the engine to the environment via emissions. A common example is lead, which will not only affect the performance of an engine by poisoning the catalytic converter but will also be transported to the environment via exhaust emissions. Once in the environment, lead can enter the food chain of many animals via different pathways (soils, water, plants etc.) and bio-accumulate, causing adverse effects or even death, due to its toxicity.

The presence of particular elements such as silicon will dramatically decrease the performance of the engine. This was highlighted in the spring of 2007 when a fuel depot in southern England supplied a large proportion of the country's automobile filling stations with gasoline contaminated with silicon. This resulted in the oxygen sensor within some engines to fail causing automobiles to misfire and experience a dramatic loss of power. The source of the contamination is likely to have been from one of two sources: either an octane-enhancing agent blended with the fuel or from a storage or transportation tank which previously stored diesel which contains an anti-foaming agent based on a silicon compound.

For the reasons discussed above, the concentrations of trace elements in gasoline are controlled by fuel specifications which vary from country to country and are influenced by engine performance and environmental factors.

Methodological Considerations

The presence of trace elements in gasoline can be determined by ICP. However, a number of challenges are presented since gasoline has a high volatility (and therefore vapor pressure) and if aspirated into the plasma at room temperature, may extinguish the plasma. There are a number of approaches to overcome this problem as follows:

- Reduce the temperature of the sample – this will reduce the vapor pressure exhibited by the sample and allow the sample to be introduced directly into the plasma. This can be achieved by cooling the spray chamber to a suitable temperature, which for gasoline this is around -40 °C.
- Dilute the sample with a miscible solvent which has a lower vapor pressure e.g. kerosene. A large dilution factor of approximately 20 is required to reduce the vapor pressure sufficiently for room temperature analysis. Unfortunately, such large dilution factors degrade the method detection limits significantly.
- Use a low flow nebulizer with a flow rate of 75 µL/min or less. By introducing a small amount of solvent into the plasma per unit time, the vapor pressure exerted on the plasma from the sample is minimal and the plasma stability is not affected. The downsides of this approach are that the sensitivity will be reduced slightly and, due to the low flow rate, the analysis time will be increased.

For ease of use, one approach is to use a combination of cooled spray chamber and dilution of the sample with a less volatile solvent. Furthermore, if the samples are diluted with a lower volatility solvent, they will evaporate at a much slower rate making them easier to handle. This dilution also means that the temperature of the spray chamber can be increased from -40 °C to perhaps -15 °C. It will therefore reach a stable temperature in shorter period of time and the higher temperature is easier to achieve with typical equipment.

Another challenge for this analysis is that different gasoline samples are blended to have different volatilities. For example, in warmer climates, gasoline is less volatile to reduce vaporization in the fuel lines of an engine which can cause vapor-lock preventing the fuel pump from working correctly. The result of this is that when samples with different volatilities pass through the nebulizer, the system will experience different transport efficiencies of the sample aerosol into the plasma. In the case of a gasoline sample of higher volatility than that of the calibration matrix, more sample aerosol will be transported to the plasma per unit time than in the case of the standard. This will cause a positively biased result. To overcome this problem an internal standard should be employed. The use of an internal standard will also correct for any loss of volume of the gasoline sample due to evaporation of highly volatile organic compounds (which is likely to occur at a low rate during sample analysis).

Instrumentation

The Thermo Scientific iCAP 6000 Series Radial ICP was used for this analysis. The radial view instrument was chosen as the radial viewing height can be optimized to minimize interferences from matrix elements such as carbon (see Figure 1 below). The IsoMist temperature controlled spray chamber (Figure 2) was used to reduce the temperature of the spray chamber to -15°C for the analysis and was used in conjunction with a glass concentric nebulizer.

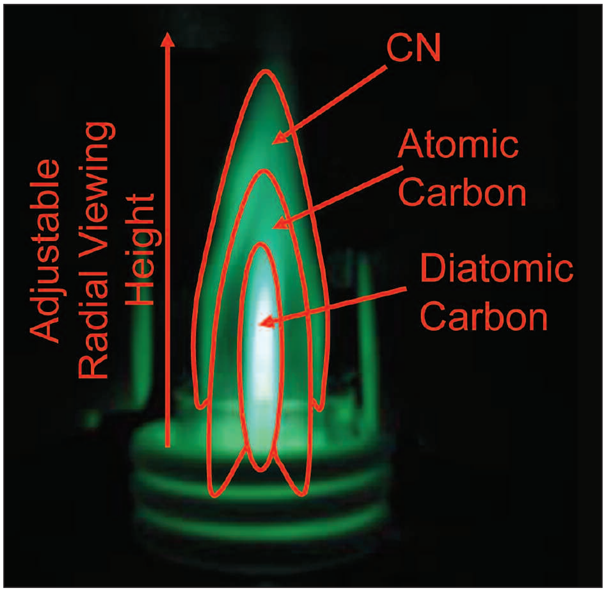


Figure 1: An image of a plasma with an organic solvent being introduced into it. The regions of different carbon-based emissions are highlighted. By optimizing the radial viewing height, background emission bands can be avoided.

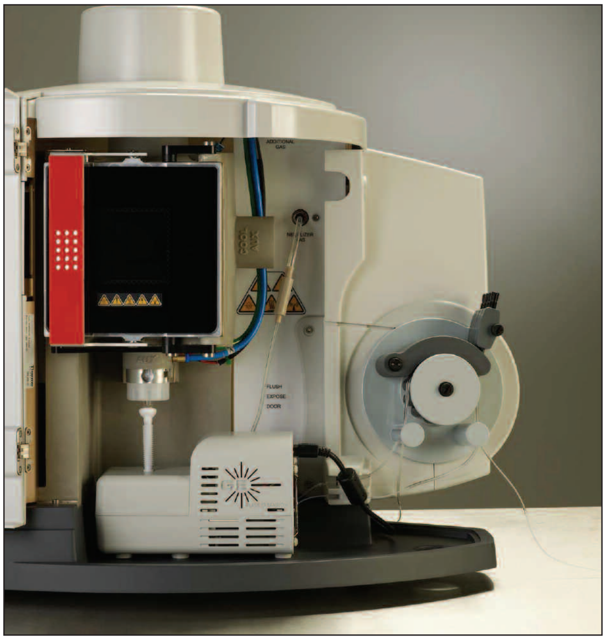


Figure 2: The iCAP 6000 Series Radial with the IsoMist temperature controlled spraychamber

Method

Standards were prepared by diluting Conostan S21, 300 mg/kg, oil-based standard (Conostan, Baie D'urfe) in petroleum ether (40-60 °C boiling range) (Fisher Scientific), 15 g. 15 g of kerosene containing 1 mg/kg of yttrium (diluted from Conostan 5000 mg/kg oil-based yttrium standard) was then added to the solution, giving a total mass of 30 g. Yttrium was used as an internal standard for the analysis to correct for differences in volatility between standards and samples and losses due to evaporation. Calibration standards were prepared at the concentrations shown in Table 1 below.

Standard	Concentration
Blank	0 mg/kg
Calibration Standard 1	0.07 mg/kg
Calibration standard 2	0.257 mg/kg
Calibration Standard 3	0.649 mg/kg
Calibration Standard 4	1.184 mg/kg

Table 1: The concentration of standards used for the analysis. A full list of the S21 elements can be seen in Table 3.

Gasoline samples were prepared by weighing the sample and then adding the same mass of kerosene containing 1 mg/kg yttrium. Spikes of the sample were also prepared in the same manner as the standards but using the gasoline sample instead of the petroleum ether for the initial dilution.

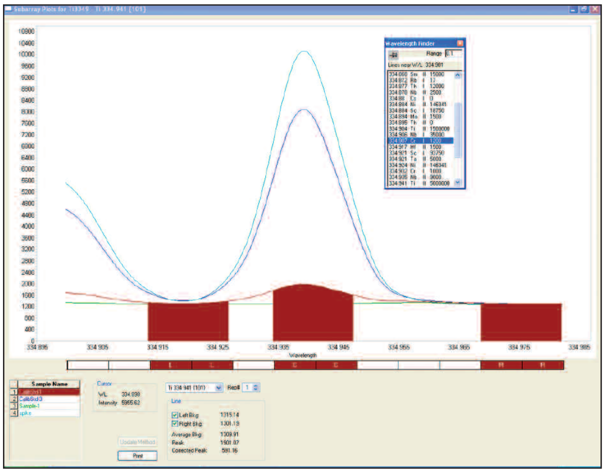
Method development

The IsoMist was set to a temperature of -15 °C. A solution of 1:1 petroleum ether (40-60 °C) and kerosene was aspirated into the plasma (by natural aspiration) and the nebulizer and auxiliary gas flows were adjusted until the base of the plasma was half-way between the top of the auxiliary tube and the bottom of the load coil and the sample channel was just below the top of the outer tube. The plasma parameters and sample introduction configuration used for the analysis are shown in Table 2 below.

Parameters	Setting
RF Power	1600 W
Nebulizer Gas Flow	0.2 L/min
Auxiliary Gas Flow	1 L/min
Coolant Gas Flow	14 L/min
Radial Viewing Height	12 mm
Pump Speed	50 rpm
Pump Tubing (drain only)	White/White solvent flex
Nebulizer	Glass Concentric
Spray Chamber	IsoMist
Spray Chamber Temperature	-15 °C
Centre tube	1 mm
Torch	EMT

Table 2: Plasma parameters and sample introduction kit used

The subarray plots for each of the wavelengths was examined to ensure freedom from interference. Where a peak at a neighboring wavelength was identified using the Wavelength Finder function of iTEVA, the affected background point was moved to ensure that false negative results were not obtained. Figure 3 below, shows a titanium wavelength has a neighboring peak from a chromium wavelength that may interfere with the background subtraction measurement. If the background correction point is located on the chromium peak, too much background will be taken away from the titanium (sample analyte peak) and the result obtained will be significantly lower than it should be. By simply moving the background point in the sub-array display, this issue is easily resolved.



334.866	Sm	II	15000
334.872	Rb	I	17
334.877	Th	I	12000
334.878	Nb	II	2500
334.88	Cs	I	0
334.884	Ni	II	146341
334.884	Sc	I	18750
334.894	Mo	II	1500
334.895	Th	II	0
334.904	Ti	II	1500000
334.906	Nb	I	35000
334.907	Cr	I	1200
334.917	Hf	II	1500
334.921	Sc	I	93750
334.921	Ta	II	5000
334.924	Ni	II	146341
334.932	Cr	I	1000
334.936	Nb	II	9600
334.941	Ti	II	5000000

1 CalibStd1
2 CalibStd3
3 Sample-1
4 spike

WL 334.898
Intensity 5955.62

Ti 334.941 {101}

☑ Left Bkg 1315.14
☑ Right Bkg 1301.19
Average Bkg 1309.91
Peak 1901.07
Corrected Peak 591.16

Figure 3: A sub-array plot for Ti 334.941 nm showing the presence of a chromium peak which could cause a possible interference on the background correction point. Moving the left background correction point to a new position avoids this problem.

The instrument was then calibrated with the prepared calibration standards and the samples and spikes analyzed. A detection limit and quantification limit study was carried out by analyzing a ten replicate blank solution (prepared in the same manner as the calibration blank). The standard deviation of these ten replicates was then multiplied by three (3-sigma) and by the dilution factor (2) to ascertain the detection limit. For the quantification limit study, the standard deviation was multiplied by ten and then by the dilution factor. These studies were repeated three times and the average detection and quantification limits determined using the mean of the values obtained. A two-hour stability study continuously analyzing spiked sample, was also conducted to demonstrate the long-term precision of the method.

Results and discussion

Table 3 gives the results of the sample, spike recovery, detection and quantitation limit studies. The results of the stability run are presented graphically in Figure 4.

	Sample	Spike	Recovery	Method Detection Limit	Method Quantification Limit
	mg/kg	mg/kg	%	mg/kg	mg/kg
Ag 338.389 nm	0.04	0.89	102	0.017	0.056
Al 308.215 nm	<DL	0.94	107	0.095	0.316
B 208.595 nm	0.08	1.11	127	0.061	0.203
Ba 223.527 nm	0.01	0.87	100	0.007	0.024
Ca 184.00 nm	0.75	0.93	107	0.041	0.137
Cd 214.438 nm	0.01	0.82	94	0.003	0.009
Cr 267.716 nm	0.01	0.86	99	0.010	0.035
Cu 324.754 nm	0.02	0.87	100	0.009	0.031
Fe 238.204 nm	<DL	0.89	102	0.017	0.057
Mg 279.553 nm	0.07	0.89	101	0.001	0.002
Mn 293.930 nm	0.01	0.87	100	0.009	0.032
Mo 281.615 nm	<DL	0.89	102	0.022	0.074
Ni 231.604 nm	<DL	0.87	100	0.028	0.094
P 178.284 nm	0.52	0.94	108	0.061	0.205
Pb 220.353 nm	<DL	0.86	98	0.038	0.127
Si 212.412 nm	<DL	0.88	100	0.032	0.108
Sn 289.999 nm	<DL	0.86	99	0.110	0.366
Ti 334.941 nm	0.01	0.85	98	0.004	0.012
V 309.311	0.01	0.90	103	0.005	0.016
Zn 213.856 nm	0.56	1.01	105	0.003	0.009

Table 3: Results of the analysis

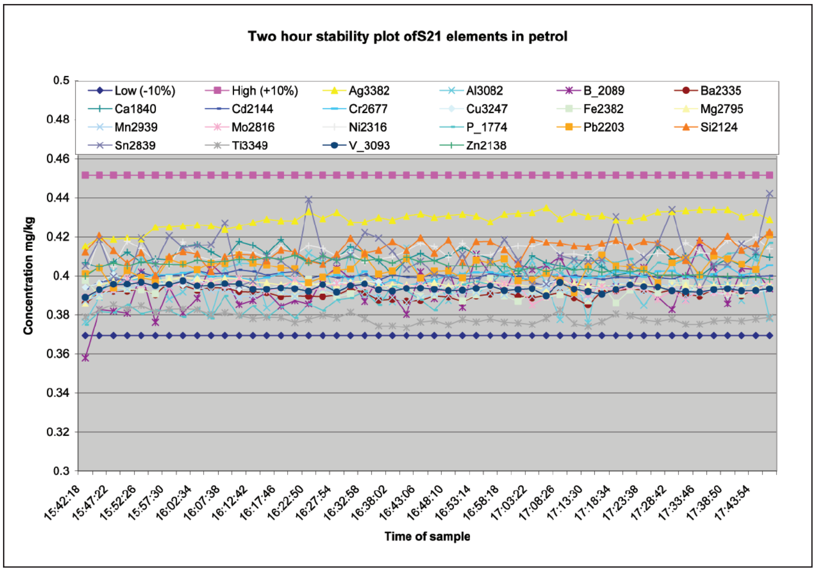


Figure 4: A two-hour stability plot of the continuous analysis of S21 elements in gasoline at 0.4105 mg/kg, showing that the results stay within 10% of this value (a lower limit of 0.369 mg/kg and a upper limit of 0.452 mg/kg).

The results of the analysis given in Table 3 show that spike recoveries for all elements determined were well within acceptable limits of +/- 10% of the prepared value of 0.87 mg/kg, with the exception of boron for which the recovery was somewhat high. This is likely to be due to the instability of boron in this matrix and the addition of a stabilizer may solve this problem. The method detection limits are also acceptable with most of the method detection limits in the low µg/kg range. The results of the stability study are also within acceptable limits. The first sample of this study is within 10% of the prepared value of 0.4105 mg/kg and for the duration of the study, deviation from within these limits is not seen.

Conclusions

The iCAP 6000 Series Radial enables the analysis of gasoline with a simple dilution of the sample with kerosene with the use of the volatile organics kit (p/n 8423 120 51711) with the IsoMist temperature controlled spraychamber set to -15 °C. The use of an internal standard corrects for any differential transport effects arising from volatility variation and of the differential concentration effects arising from evaporation. The simple optimization process and the use of the enhanced matrix tolerance torch (EMT torch) reduces carbon build up on the torch and reduces the frequency of user maintenance.

The study demonstrated that the iCAP 6000 Series Radial is capable of producing lowe detection limits, good long-term stability and excellent accuracy, proving that it is an ideal choice for the routine analysis of gasoline samples.

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