Analysis Of Fuel Samples By Microwave Plasma - Atomic Emission Spectrometry

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Introduction

The presence of certain trace elements in gasoline and petro-diesel fuels can cause corrosion and deposition on engine or turbine components, especially at elevated temperatures. The performance of engine or turbine components can therefore be compromised over time through exposure to these trace elements if they are present. Some standards specify the maximum levels of these elements that can be present in fuels to reduce the occurrence of engine deposits. For example, ASTM method D6751 specifies a maximum limit of 5 ppm for the combined concentration of Ca and Mg, and 5 ppm for the combined concentration of Na and K in biodiesel. Therefore routine monitoring of these elements is essential to ensure the fuel quality satisfies the applicable requirements and to guard against corrosion and deposition on moving parts. Trace elemental analysis is used to assess the level of contamination of petroleum and diesel fuels. This paper describes the analysis of trace elements in gasoline and diesel fuels using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). Microwave Plasma-Atomic Emission Spectrometry provides an ideal, low-cost solution for multi-element analysis of fuel samples with excellent long-term stability, reduced running costs, and improved lab safety.

The 4100 MP-AES is a fast sequential atomic emission spectrometer that uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. This stable plasma is capable of analyzing both aqueous and challenging organic matrices. This technique produces linear dynamic range, detection limits and analysis speed superior to conventional flame AAS. Based on an atomic emission technique, this elemental analysis technique also produces greater sensitivity than flame AAS. In addition, it eliminates the need to use hollow cathode lamps. This innovative elemental analysis technique also eliminates the need for argon or indeed, any bottled gas. It operates from a compressed air supply, using the Agilent 4107 Nitrogen Generator, producing a significant reduction in operating costs and reduced infrastructure costs. By using a nitrogen plasma, the 4100 MP-AES eliminates the need for expensive and dangerous gases, such as acetylene, resulting in lower running costs, unattended operation, and removing any safety concerns associated with use of acetylene and nitrous oxide when compared with traditional elemental analysis techniques like flame atomic absorption spectrometry.

The 4100 MP-AES equipped with a OneNeb nebulizer, the EGCM and the IsoMist cooled spray chamber provides an ideal solution for the routine and direct analysis of highly volatile gasoline. The nitrogen-based plasma excitation source exhibits a high tolerance level to organic solvent loading, and the powerful features of the MP Expert software such as standard addition enables analysis of tough samples. By injecting a controlled flow of air into the plasma using the EGCM, carbon buildup in the injector is eliminated. Excellent calibrations, detection limits, and recoveries were achieved in spiked gasoline samples at levels likely to be encountered in this analysis (low ppm).

Experimental

Instrumentation

The Agilent 4100 MP-AES was fitted with an optional External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and reduce background emissions. The instrument was set up with Organics kit comprising the EGCM, the inert OneNeb nebulizer, along with a double-pass glass cyclonic spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity.
Due to the high volatility of gasoline samples, an IsoMist cooled spray chamber from Glass Expansion was used to reduce the solvent loading on the plasma, resulting in a more stable plasma and further reducing background emissions.
The instrument was controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected. Also, the powerful Auto background correction mode easily and accurately corrects for the emission background arising from the organic matrix.
The instrument operating conditions for both petroleum and diesel analysis can be found in Tables 1 and 2 respectively.

Experimental

Table 1. Operating conditions for gasoline analysis

Instrument Parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double pass glass cyclonic
Sample tubing	Orange/Green solvent resistant
Waste tubing	Blue/Blue solvent resistant
Read time	3 sec
Number of replicates	3
Stabilization time	45 sec
Fast pump during sample uptake (80 rpm)	On
Background correction	Off-peak
Pump Speed	5 rpm
Calibration	Standard Additions
Cooled spraychamber temperature	-10°C

Table 2. Operating conditions for diesel analysis

Instrument Parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double pass glass cyclonic
Sample tubing	Orange/Green solvent resistant
Waste tubing	Blue/Blue solvent resistant
Read time	3 sec
Number of replicates	3
Stabilization time	30 s
Fast pump during sample uptake (80 rpm)	On
Background correction	Auto
Pump Speed	5 rpm

Method EN 14538 [3] was followed for the analysis of the diesel samples. Calibration standards were prepared at concentrations of 0.5 ppm, 1 ppm, 5 ppm and 10 ppm by diluting a 500 ppm S21+K solution (Conostan) with Shellsol (Shell). All standards were matrix matched with Blank Oil 75 (Conostan).
A commercial diesel sample was spiked with S21+K at the 0.5 ppm level and the spikes were measured to validate the method.
Gasoline fuel standards were prepared by spiking a sample with an oil-based metal calibration standard, S21+K (Conostan), giving final concentrations of 0.89 ppm, 1.92 ppm and 3.94 ppm.
The gasoline samples were directly analyzed, without any sample preparation.
For the spike recovery test, gasoline samples were spiked with S21+K to give spike concentrations of 1.1 ppm.

Results and Discussion

Detection limits

Method detection limits were calculated as the concentration equivalent to 3 standard deviations of 10 blank sample measurements. The detection limits for both petroleum and diesel can be seen in Table 3 and in both cases they are sufficiently low for the requirements of the respective analyses.

Table 3. Method detection limits (ppb) for fuels samples

Element	Wavelength (nm)	MDL Gasoline (ppb)	MDL Diesel (ppb)
Mg	285.213	2.7	2.7
Ca	422.673	4.3	8.2
Na	588.995	5.3	18.7
K	766.491	29.4	2.7

Table 4. Calibration coefficients for gasoline analysis

Element	Wavelength (nm)	Correlation coefficient
Mg	285.213	0.99993
Ca	422.673	0.99934
Na	588.995	0.99939
K	766.491	0.99975

These detection limits demonstrate the ability of the 4100 MP-AES to handle tough organic samples, provide excellent detection limits at low sample flow rates, and handle the challenging background from carbon emissions using the power and simplicity of auto background correction.

Results and Discussion

Calibration

When measuring gasoline samples, the high volatility of the samples makes finding matching standards difficult, even if samples have been diluted with kerosene. For this reason, standard additions calibration was used for this analysis.
Standard addition also means that the gasoline samples can be directly analyzed, without the need for further sample preparation. The stable nitrogen plasma of the MP-AES can easily handle these volatile samples and, as shown in Table 4, excellent correlation coefficients were found for the elements measured in this analysis. A typical spectrum for Mg 285.213 with off-peak background positions, and a calibration curve for Mg 285.213 are shown in Figures 1 and 2.

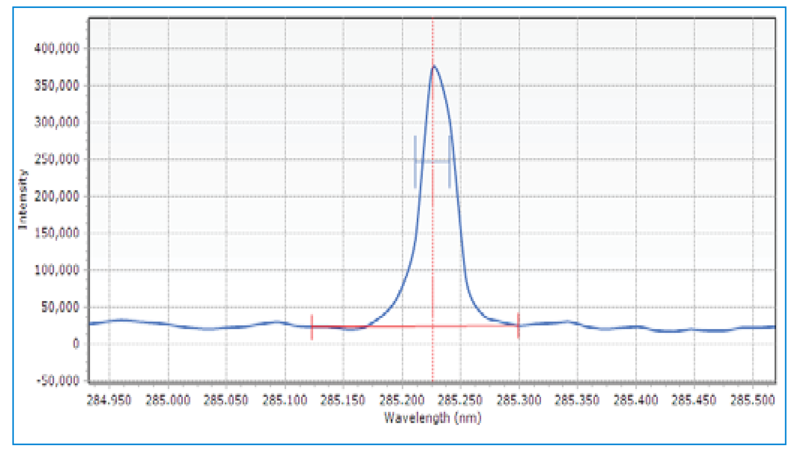

Figure 1. Representative spectrum for Mg 285.213 in a spiked gasoline sample

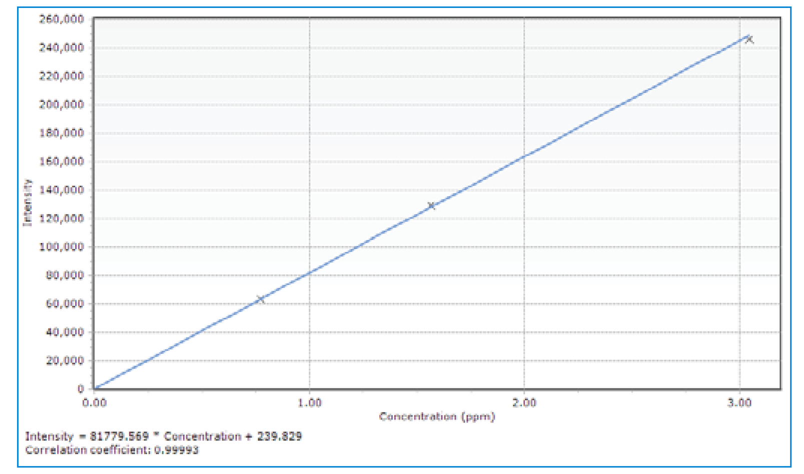

Figure 2. Calibration curve for Mg 285.213

Spike recoveries

The spike recovery results for the gasoline and diesel samples are shown in Tables 5 and 6 respectively.

Table 5. Spike recovery results for elements in gasoline

Element & wavelength (nm)	Sample (ppm)	Spike (ppm)	Recovery (%)
Mg 285.213	< MDL	1.11	100
Ca 422.673	< MDL	1.06	95
Na 588.995	< MDL	1.11	100
K 766.491	0.05	1.12	96

Table 6. Spike recovery results for elements in diesel

Element & wavelength (nm)	Sample (ppm)	Spike (ppm)	Recovery (%)
Mg 285.213	< MDL	0.53	97
Ca 422.673	< MDL	0.51	93
Na 588.995	< MDL	0.51	93
K 766.491	< MDL	0.51	93

The spike concentration was 1.1 ppm for the gasoline samples and 0.55 ppm for the diesel samples. All recoveries were within ±10% of the target value. The excellent recoveries demonstrate the ability of the 4100 MP-AES to accurately determine Mg, Ca, Na and K at the levels required for both gasoline and diesel analysis.

Conclusions

The Agilent 4100 MP-AES equipped with the OneNeb nebulizer and the EGCM provides an ideal solution for the routine analysis of fuel samples. Whether it is the direct analysis of highly volatile gasoline samples, or the routine analysis of semi-volatile diesel samples, the 4100 MP-AES has been proven to the an ideal solution.
The nitrogen-based plasma excitation source exhibits a high tolerance to the organic solvent load and the easy-to-use yet powerful features of the MP Expert software, such as the auto background correction mode, ensure excellent detection limits. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent calibrations, detection limits, and recoveries were achieved in spiked fuel samples at levels likely to be encountered in these analyses (low ppm).
Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. The 4100 MP-AES also improves sample throughput and removes the need for consumables like hollow cathode lamps.