Analysis of diesel using the 4100 MP-AES

Application note

Energy and fuels

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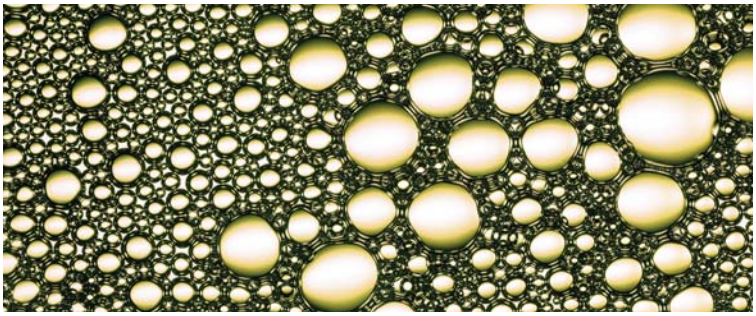

Introduction

The presence of certain trace elements in petro-diesel and biodiesel fuels can cause corrosion and deposition on engine or turbine components, especially at elevated temperatures. Some diesel fuels therefore specify the maximum levels of these elements to guard against the occurrence of engine deposits. For instance ASTM method D6751 specifies a limit of 5 ppm for the combined concentration of Ca and Mg, and 5 ppm for the combined concentration of Na and K [1]. Trace elemental analysis is used to determine the level of contamination of diesel fuels.

The Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. This stable plasma is capable of analyzing not only aqueous solutions, but also challenging organic matrices. When compared to conventional flame AA, the 4100 MP-AES eliminates expensive and dangerous gases such as acetylene, resulting in lower running costs, unattended operation, and improved productivity.

This application note describes the determination of trace elements in diesel fuels using the Agilent 4100 MP-AES.

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Experimental

Instrumentation

The Agilent 4100 MP-AES was fitted with an 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 the Organics kit comprising of the EGCM, the inert OneNeb nebulizer [2] and solvent resistant tubing, along with a double pass 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, whilst maintaining excellent sensitivity.

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.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4100 MP-AES operating conditions

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 s
Number of replicates	3
Sample uptake delay	15 s
Stabilization time	30 s
Fast pump during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte viewing positions, nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	240	High
Ca 422.673	240	High
Na 588.995	240	High
K 766.491	240	High

Samples and sample preparation

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.

Results and discussion

Detection limits

Method detection limits were calculated as the concentration equivalent to 3 standard deviations of 10 blank diesel measurements. The detection limits reported in Table 2 are in solution, and are sufficiently low for the requirements of the analysis. 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.

Table 2. Method detection limits (ppb) for Mg, Ca, K, and Na

Element	Wavelength (nm)	MDL (ppb)
Mg	285.213	2.7
Ca	422.673	8.2
Na	588.995	18.7
K	766.491	2.7

Spike recoveries

The spike recoveries in diesel fuel are shown in Table 3. The spike concentration was 0.55 ppm and 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 in the diesel fuel samples. A typical spectrum and calibration graph for K are shown in Figures 1 and 2 respectively.

Table 3. Results of spike recovery test

Element and 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

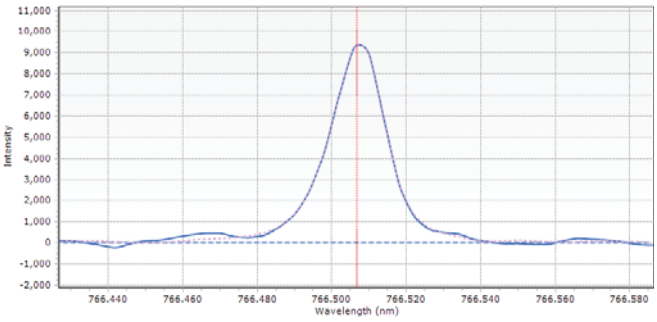

Figure 1. Signal for K 766.491 at 0.5 ppm showing the excellent sensitivity of the 4100 MP-AES when analyzing fuel samples

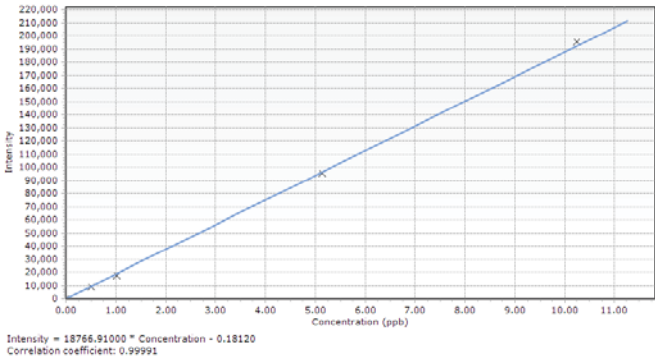

Figure 2. Calibration curve for K 766.491 showing excellent linearity across the calibrated range and a correlation coefficient of 0.99991

Conclusions

The Agilent 4100 MP-AES equipped with the OneNeb nebulizer and the EGCM provides an ideal solution for the routine analysis of semi-volatile organic samples such as diesel. 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 diesel fuel samples at levels likely to be encountered in this analysis (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.

Reference

1. ASTM D6751 – 11b, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, www.astm.org

2. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

3. EN 14538:2006, Fat and oil derivatives – Fatty acid methyl ester (FAME) – Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES), European Committee for Standardization, www.cen.eu

www.agilent.com/chem

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