# Direct measurement of metallic impurities in petroleum fuels using the 4100 MP-AES

Application note

Energy and fuels


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## Introduction

The performance of engine or turbine components can be compromised over time through exposure to certain trace elements that may be present in gasoline (petrol) and petro-diesel fuels. It is important to monitor these elements in order to ensure the quality of the fuel and to guard against corrosion and deposition on moving parts. 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 [1]. Even though the method relates to biofuels, it is equally relevant to other petroleum fuels such as gas turbine fuel oil [2].

This application note describes the determination of trace elements in gasoline, without dilution or digestion, using the innovative Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 is a fast sequential atomic emission spectrometer that uses magnetically-coupled microwave energy to generate a robust and stable nitrogen plasma. This stable plasma is capable of analyzing both aqueous and challenging organic matrices. 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 improved productivity when compared with traditional elemental analysis techniques like flame atomic absorption spectrometry.

## 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 [3], 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 the gasoline sample, 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.

MP Expert also provides Standard Addition Calibration to allow the analysis of samples where finding a matrix matched set of standards is difficult. A further feature of the software, which simplifies analysis and method development, is the easy-to-use off-peak background correction markers that can be directly modified on the spectra in real time.

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 |
| Stabilization time | 45 s |
| Fast pump during sample uptake | On |
| Background correction | Off-peak |
| Pump speed | 5 rpm |
| Calibration | Standard additions |
| Cooled spray chamber temperature | -10 °C |

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

| Element & wavelength (nm) | Nebulizer pressure (kPa) |
|---|---|
| Mg 285.213 | 240 |
| Ca 422.673 | 240 |
| Na 588.995 | 240 |
| K 766.491 | 240 |

### Samples and sample preparation

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 gasoline measurements. The detection limits for gasoline are sufficiently low for the requirements of the analysis. These detection limits demonstrate the ability of the Agilent 4100 MP-AES to handle tough organic samples when coupled with the EGCM, the OneNeb nebulizer and the cooled spray chamber.

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

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

### 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 3, 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.

**Table 3.** Calibration correlation coefficients for Mg, Ca, Na and K

| 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 |

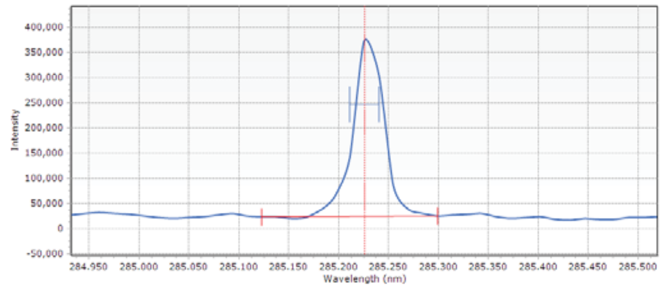


**Figure 1.** Representative spectrum for Mg 285.213 in the spiked sample

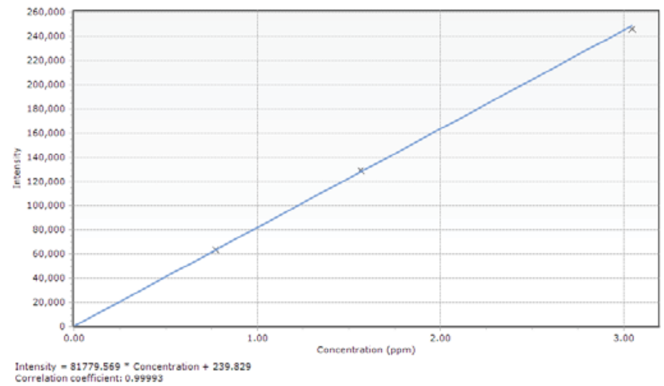


**Figure 2.** Calibration curve for Mg 285.213

### Spike recoveries

The spike recovery results for the gasoline samples are shown in Table 4. The spike concentration was 1.1 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 gasoline samples.

**Table 4.** Spike recovery results for Mg, Ca, Na and K in gasoline

| Element & wavelength (nm) | Sample (ppm) | Spiked sample (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 |

## Conclusions

The Agilent 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 via the EGCM to prevent carbon buildup in the injector, excellent calibrations, detection limits, and recoveries were achieved in spiked gasoline 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 Agilent 4100 MP-AES also improves sample throughput and removes the need for hollow cathode lamps.

## References

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

2. ASTM D2880 – 03, Standard Specification for Gas Turbine Fuel Oils, ASTM International.

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

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