Analysis of ethanol fuel according to standard methods using the Agilent 5100 SVDV ICP-OES

Application note

Energy & chemicals, biofuels

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Fossil fuels have been the main source of energy in industrial applications and transportation for decades. However, depleting reserves, environmental concerns and economic issues have led to the development of renewable, cheaper and cleaner alternatives. Bio-ethanol is one of those alternatives and is derived by fermenting the sugar and starch components of plant by-products.

Different purities of bio-ethanol are used as fuel sources. Hydrated ethanol fuel has not had treatment to remove moisture and contains between 93-96% ethanol. It is often used in flexible (flex-fuel) or dual fuel engines. Anhydrous ethanol has been treated to remove moisture and has a purity of at least 99%. It is blended at up to 25% v/v with gasoline.

High purity fuel can be contaminated with elemental impurities during production, stockpiling and transportation, so accurate quantitation of metal content is important. According to ASTM D4806 specification [1] and the Brazilian National Agency of Petroleum, Natural Gas and Biofuels

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(ANP) Resolution number 19/2015 [2], the presence of Cu, Fe, Na and S in ethanol must be controlled. Limit concentrations for Cu are 0.1 and 0.07 mg/kg (ASTM and ANP respectively), 5 mg/kg Fe (ANP), 2 mg/kg Na (ANP), and 30 mg/kg S (ASTM).

In this study, the accuracy, precision and long term stability performance of the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES was evaluated for the determination of Cu, Fe, Na and S in ethanol fuel samples according to ASTM D4806 and ANP Resolution 19/2015 methods.

Experimental

Instrumentation
All measurements were carried out using an Agilent 5100 SVDV ICP-OES, which is equipped with a Dichroic Spectral Combiner (DSC). The 5100 SVDV uses the DSC to facilitate both axial and radial view emissions from the plasma to be measured at the same time, in a single reading, over the entire wavelength range. This increases the linear working range, improves sample throughput and ensures that the amount of argon consumed per sample is lower than conventional simultaneous DV ICP-OES systems. The 5100 ICP-OES uses a vertically orientated torch and a solid-state radio frequency (SSRF) system operating at 27 MHz to deliver a plasma with the stability and robustness necessary for the analysis of organic samples. Data acquisition times are the same for the 5100 operating in SVDV or axial view mode.

The 5100 was fitted with a standard sample introduction system comprising a glass concentric nebulizer and a glass single-pass cyclonic spray chamber. Although this configuration is typically used for the analysis of aqueous solutions, it is also suited to the analysis of diluted organic samples. A standard dual view torch (1.8 mm ID injector) was used. Black/Black Solva Flex tubing was used for the sample, and Grey/Grey Solva Flex tubing was used for the waste.

The 5100 SVDV ICP-OES features a three port gas module allowing an Ar/O_2 gas mix to be routed automatically through the auxiliary gas line. The addition of oxygen to the plasma is sometimes necessary during the analysis of organic samples to eliminate carbon build up in the torch. Oxygen wasn't added in this work and no carbon deposition was observed. Instrument operating conditions are listed in Table 1.

Table 1. Agilent 5100 SVDV ICP-OES operating parameters

Parameter	Setting
RF applied power (kW)	1.50
Auxiliary gas flow rate (L/min)	1.0
Plasma gas flow rate (L/min)	12
Nebulizer gas flow rate (L/min)	0.60
Ar/O_2 addition	Not required
Viewing height (mm)	8
Pump speed (rpm)	12
Stabilization time (s)	15
Read time (s)	20
Replicates	3
Viewing mode	SVDV
Background correction	Fitted
Elements and emission wavelengths (nm)	Cu – 324.754; 327.395 Fe – 238.204; 259.940 Na – 588.995; 589.592 S – 180.669; 181.972

Standards and sample preparation
Multi-element calibration standards containing 0, 0.01, 0.05, 0.1, 0.5, 1.0, 5.0 and 10.0 mg/L Cu, 0, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0 and 40.0 mg/L Fe and Na, and 0, 1.0, 5.0, 10.0, 20.0, 50.0, 75.0 and 100.0 mg/L S were prepared in 10% v/v ethanol by dilution with 1% v/v HNO_3. Hydrated ethanol fuel samples were prepared by simple 10-fold dilution with 1% v/v HNO_3.

In order to check accuracy and precision as stated in the ASTM and ANP methods, ethanol fuel samples were spiked at half of the target concentration and at the target concentration. Spikes were added at 0.03 and 0.07 mg/kg Cu, 2.5 and 5.0 mg/kg Fe, 1.0 and 2.0 mg/kg Na, and 15 and 30 mg/kg S. Long-term stability (150 min) was evaluated using a solution containing 0.5 mg/L Cu, 5 mg/L Fe and 20 mg/L S in 10% v/v ethanol.

Results and discussion

Table 2. Linear calibration range, sensitivity and method detection limits (MDL) for Cu, Fe, Na and S in ethanol fuel using the 5100 SVDV ICP-OES according to ASTM D4806 and ANP Resolution no. 19.

Element	Wavelength (nm)	Calibration range (mg/L)	Sensitivity (counts per sec./ppm)	MDL (mg/kg)	ASTM limits* (mg/kg)	ANP limits** (mg/kg)
Cu	324.754	0 – 10.0	45615	0.02	0.1	0.07
	327.395	0 – 10.0	45105	0.003	0.1	0.07
Fe	238.204	0 – 40.0	32350	0.003	-	5.0
	259.940	0 – 40.0	12247	0.006	-	5.0
Na	588.995	0 – 40.0	16071	0.27	-	2.0
	589.592	0 – 40.0	8097	0.06	-	2.0
S	180.669	0 – 100.0	83	1.7	30.0	-
	181.972	0 – 100.0	139	12.7	30.0	-

* The maximum concentration allowed by ASTM D4806 **The maximum concentration allowed by ANP Resolution no. 19.

Method detection limits (MDLs) were calculated from background equivalent concentrations (BEC) and signal-to-background ratios (SBR) of ten replicate measurements of the 10% v/v ethanol blank solution using the 5100 in SVDV mode. The linear calibration range, sensitivity (slope of the calibration curves) and MDLs for Cu, Fe, Na and S are shown in Table 2. For all emission lines, the MDLs (considering the 10-fold dilution) were below the limits specified in ASTM D4806 and ANP Resolution 19/2015.

Calibration linearity

The calibration curves for Na and S (Figure 1) show excellent linearity across the calibrated range, with correlation coefficients of 1.00000 and 0.99997 respectively.
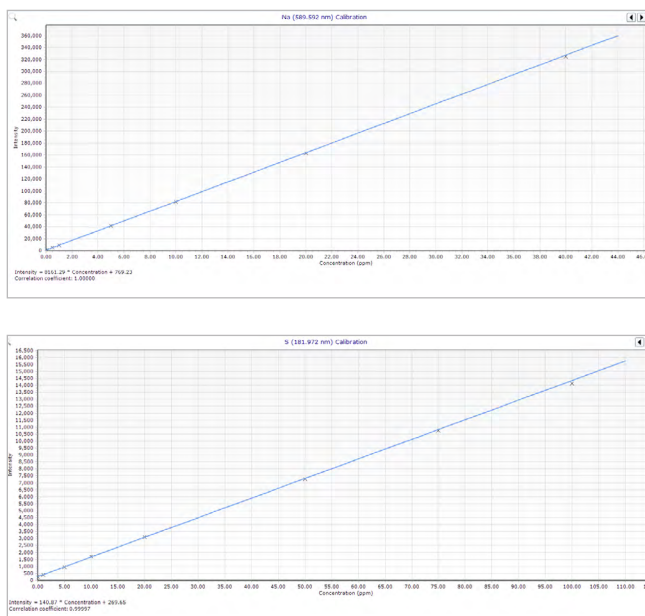
Figure 1. Calibration curve for Na (upper) and S (lower) by using the 5100 SVDV ICP OES

Long-term stability

The long term stability of the Agilent 5100 SVDV ICP-OES was evaluated by analyzing a solution containing 0.5 mg/L Cu, 5 mg/L Fe and 20 mg/L S in 10% v/v ethanol over 150 min. Good stability was achieved for Cu, Fe and S, with recoveries within ±10% over the sequence. No changes in plasma stability were observed during this study.

Spike recoveries

Table 3. Mean spike recoveries for Cu, Fe, Na and S in three ethanol fuel samples.

Element	Wavelength (nm)	Spiked level 1			Spiked level 2		
		Spike conc. (mg/kg)	Measured (mg/kg)	Recovery (%)	Spike conc. (mg/kg)	Measured (mg/kg)	Recovery (%)
Cu	324.754	0.030	0.027 ± 0.001	90	0.070	0.069 ± 0.001	99
	327.395	0.030	0.032 ± 0.001	107	0.070	0.070 ± 0.001	100
Fe	238.204	2.50	2.54 ± 0.02	102	5.0	5.4 ± 0.1	108
	259.940	2.50	2.58 ± 0.02	103	5.0	5.3 ± 0.1	106
Na	588.995	1.00	0.88 ± 0.02	88	2.00	1.98 ± 0.03	99
	589.592	1.00	1.01 ± 0.02	101	2.00	2.05 ± 0.03	103
S	180.669	15.0	15.7 ± 0.2	105	30.0	31.7 ± 0.2	106
	181.972	15.0	15.9 ± 0.2	106	30.0	31.0 ± 0.2	103

For all analytes, spike recoveries ranged from 88 to 108 % with precision (relative standard deviation) better than 3.3 % (n = 3) in SVDV mode (Table 3). Similar results (not shown) were obtained in axial-view mode. The recoveries demonstrate the ability of the 5100 SVDV ICP-OES to accurately determine Cu, Fe, Na and S at the required levels in the ethanol fuel samples.

Only S (0.37-1.65 mg/kg) and Na (0.11-0.17 mg/kg) were detected in the diluted samples.

Conclusions

The method detection limits demonstrated that the Agilent 5100 SVDV ICP-OES meets industry requirements for the analysis of Cu, Fe, Na and S in hydrated ethanol fuel after a simple 10-fold dilution with HNO_3, as specified in both ASTM D4806 and ANP resolution no. 19. Excellent accuracy was achieved, as illustrated by the spike recovery results, which were within expected limits. Precision was better than 3.3 % RSD and stability remained within ±10% of expected value over the 2.5 hours of analysis.

The 5100 operating in Synchronous Vertical Dual View (SVDV) mode combines the robustness of a vertically-oriented torch and plasma with the sensitivity of axial view ICP-OES. Advanced DSC technology allows both the axial and radial views of the plasma to be captured in one reading. This enables fast simultaneous data acquisition and ensures that the amount of argon consumed per sample is low and no more than single-view ICP-OES.

References

1. American Society for Testing and Materials – ASTM D4806 – Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel. 2015.

2. Brazilian National Agency of Petroleum, Natural Gas and Biofuels, Resolution ANP Resolution number 19, D.O.U. April 16, 2015.

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