APPLICATION NOTE

ICP-Optical Emission Spectroscopy

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Direct Analysis of Ethanol for Phosphorus, Sulfur, Copper, and Iron with the Avio 550 Max ICP-OES

Introduction

Ethanol is an important blending component in fuels commonly used in gasoline/petrol. Depending on the ultimate use of the fuel, the ethanol concentration can vary from < 10% up to 85%. Because of its wide use, it is important to monitor the concentrations of impurities in the ethanol which can negatively impact the performance of the resulting fuel. As a result, standards have been created for the phosphorus (P), sulfur (S), and copper (Cu) content in fuel.

A European Standard has been established for the direct determination of P, S, and Cu in ethanol in the concentration ranges listed in Table 1. ASTM D4806 is a specification for a number of components in anhydrous denatured ethanol intended for blending with gasoline at 1-15% by volume, including S and Cu.

Table 1. IP 581 Concentration Ranges for Phosphorus, Sulfur, and Copper in Ethanol.

Element	Concentration (mg/kg)
P	0.13 – 1.90
S	2.0 – 15.0
Cu	0.050 – 0.300

Ethanol analysis by ICP-OES can be challenging both due to volatility and high carbon content. The low boiling point of ethanol (78 °C) means that a large volume of ethanol in the gaseous form enters the plasma, which may cause plasma instability and ultimately extinguish the plasma. The high carbon content can also deposit on the instrument interface or injector during analysis, which can lead to signal degradation over time. However, with the right choice of sample introduction components and a robust plasma, ethanol can be measured with ease. This work discusses the analysis of P, S, Cu, and Fe in ethanol using PerkinElmer's Avio® 550 Max fully simultaneous ICP-OES.

Experimental

Samples and Sample Preparation

All ethanol samples and standards were prepared by the addition of 2% HNO_3 (5 mL 2% HNO_3 to 45 mL ethanol) to keep the analytes in solution. Because of the polar nature of ethanol, aqueous stock standards could be used for the preparation of the calibration standards and spikes. The calibration scheme employed was the method of additions-calibrate. In this calibration mode, the calibration curve is prepared in a representative sample matrix, and all subsequent samples are measured against this calibration curve. Calibration standards were prepared in ethanol and 2% HNO_3 (v/v) at the concentrations shown in Table 2 from intermediate standards (1 mg/L Cu, Fe and 5 mg/L P, S). To check for accuracy, the ethanol sample was spiked at the same concentrations as the calibration standards and measured. Ytterbium (Yb) was added to all standards and samples as an internal standard. In addition, Ar 420.069 nm was also monitored. The comparison of Yb and Ar signals were used to assess the stability of the plasma.

Instrumental Conditions

The analyses were performed on an Avio 550 Max fully simultaneous ICP-OES (PerkinElmer, Shelton, Connecticut, USA) using the parameters shown in Table 3. All instrumental conditions were optimized to allow for low-level determination of the elements of interest. To decrease solvent loading to the plasma, the spray chamber was chilled to 2 °C and a 1.2 mm injector was used. Enhanced sensitivity and stability were gained by using a torch position of -5 and viewing the plasma in axial mode. Most Avio 550 Max applications run at a plasma flow of 8 L/min, although this may vary with organic analyses, depending on the sample introduction components used.

The elements and wavelengths appear in Table 4; multiple wavelengths were monitored for each element to confirm the results. Due to the fully simultaneous nature of the Avio 550 Max ICP-OES, adding extra wavelengths does not add time to the analysis.

Results and Discussion

First, the low-level calibration standard was analyzed, and the peaks for each element examined. It was observed that a peak for almost all wavelengths was present and could be integrated, verifying the ability to measure low levels. The exception was S 180.669 nm, where a high background was observed. The upper spectra in Figure 1 show the calibration blank and standards; the black vertical line indicates the location of the S 180.669 nm peak. As is evident, the peak is on the shoulder of a background peak, which is most likely a carbon band originating from the ethanol. As a result, low-level sulfur measurements are difficult.

Table 2. Calibration Standards in Ethanol.

Element	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)
P, S	100	250	500
Cu, Fe	20	50	100

Table 3. Instrumental Parameters for the Low-Level Analysis of Ethanol.

Parameter	Value
Sample Uptake Rate	1 mL/min
Nebulizer	MEINHARD® K1
Spray Chamber	PC³ Baffled Glass Cyclonic
Spray Chamber Temperature	2 °C
Injector	Alumina, 1.2 mm
Torch Position	-5
RF Power	1500 W
View Mode	Axial

Table 4. Elements and Wavelengths.

Element	Wavelength (nm)
P	213.617, 214.914
S	180.669
Cu	327.393, 324.752, 224.700
Fe	238.204, 239.562, 259.939
Yb	328.937

However, the effect of the interference can be eliminated through the use of Multicomponent Spectral Fitting (MSF), a simple-to-use, robust algorithm, only available on Avio ICP-OES instruments, which uses all the information available in the spectra and does not rely on background or integration points. The MSF model is built from the spectra of a blank (2% HNO_3), standard (500 µg/L S), and interference (ethanol). These spectra are defined, and the software automatically applies the MSF algorithm, yielding an interference-free spectrum for sulfur, as shown in the lower spectrum in Figure 1. With the MSF model entered in the method, it is automatically applied to all standards and samples analyzed with the method, allowing for interference-free low-level analysis.

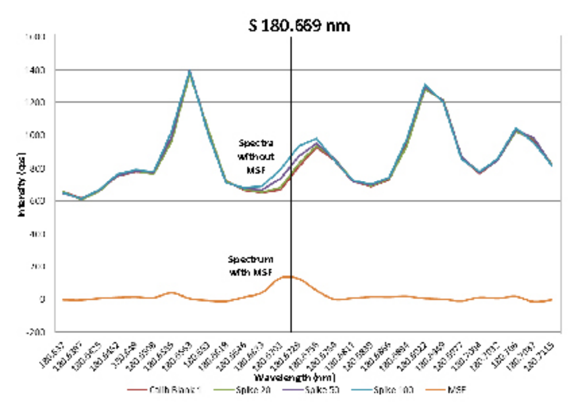

Figure 1. Spectra of blank, 100, 250, and 500 µg/L sulfur standards in ethanol without MSF applied, and the resulting spectrum for the 100 µg/L standard after MSF is applied.

With MSF applied to S, the calibration curves for all elements at all wavelengths yielded correlation coefficients of 0.999 or greater. Next, to determine the accuracy of the methodology, a second-source ethanol sample was analyzed, along with spike additions at the concentrations of the calibration standard. Table 5 shows the quantitative results for P and S, while the results for Fe and Cu appear in Table 6. Each element was present at less than the detection limit in the sample, with the exception of sulfur, which is present at 20 µg/L. The agreement between multiple wavelengths of each element confirms the quantitative results. The spike recoveries are all within 5% of their true values for all wavelengths and all spike levels of P, Cu, and Fe.

Table 5. Results for Phosphorus and Sulfur in Ethanol.

Sample	P 213.617 (µg/L)	P 214.914 (µg/L)	S 180.669 (µg/L)
EtOH	< 5	< 5	20
EtOH + 100 µg/L	99	98	121
EtOH + 250 µg/L	254	255	248
EtOH + 500 µg/L	483	496	500

Due to direct spectral overlaps (as seen in Figure 1), only one S wavelength is available for analysis: 180.669 nm. As discussed above, even though a carbon interference is present on S 180.669, MSF removes the interference, allowing S 180.669 nm to be measured interference-free, with spike recoveries within 10% of their true values.

With the accuracy established, a petrochemical ethanol sample was analyzed. The results are shown in Table 7 and correlate with the known values for this sample. In addition, the agreement between multiple wavelengths for all analytes (except S) further confirms the accuracy of the results.

The stability of the plasma was assessed by monitoring the signal from both Yb and argon (Ar). Since Ar originates from the plasma, it is a true measure of the plasma stability, as it is not affected by sample introduction (i.e. peristaltic pump, nebulizer, spray chamber, aerosol transport, etc.). Since Yb was added to all blanks, samples, and standards, its signal is affected by both sample introduction and the plasma. Figure 2 shows the stability of both Yb and Ar over a 35-minute analytical run consisting of the calibration standards, samples, and QC checks. Ar varied by less than 2% over the run, demonstrating exceptional plasma stability with the introduction of ethanol, a volatile organic solvent. The Yb signal recovered within 4% of the blank value, showing that sample introduction and transport had very little impact on the stability. The relative standard deviation of the signals are also shown in Figure 2, further confirming the robustness of the methodology and instrumentation.

Table 7. Concentrations in a Petrochemical Ethanol Sample.

Element	Wavelength (nm)	Concentration
Cu	327.393	< 2
Cu	324.752	< 2
Cu	224.700	< 2
Fe	238.204	21.0
Fe	239.562	19.4
Fe	259.939	20.6
P	213.617	< 5
P	214.914	< 5
S	180.669	263

Table 6. Results for Copper and Iron in Ethanol.

Sample	Cu 327.393 (µg/L)	Cu 324.752 (µg/L)	Cu 224.700 (µg/L)	Fe 238.204 (µg/L)	Fe 239.562 (µg/L)	Fe 259.939 (µg/L)
EtOH	< 2	< 2	< 2	< 1	< 1	< 1
EtOH + 20 µg/L	19.4	20.3	20.3	20.6	19.7	20.6
EtOH + 50 µg/L	50.1	52.6	49.9	52.6	49.6	52.1
EtOH + 100 µg/L	99.9	99.5	98.7	98.7	99.9	98.7

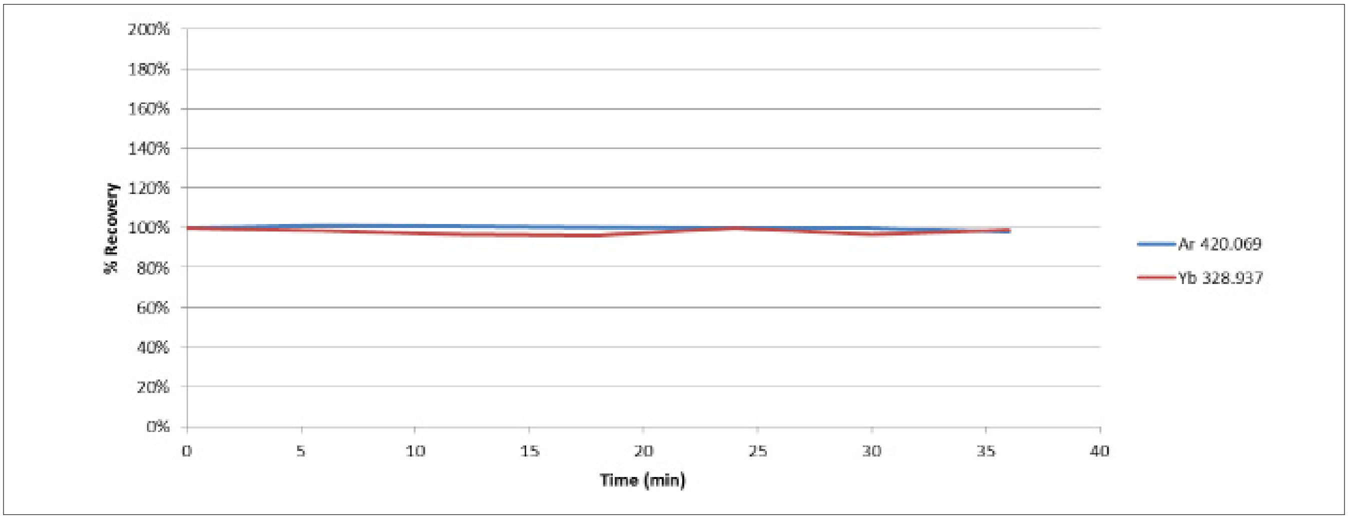

Figure 2. Stability of Ar and Yb during analysis of 100% ethanol.

Conclusions

This work demonstrates the ability of the Avio 550 Max fully simultaneous ICP-OES to measure low levels of P, S, Cu, and Fe in ethanol, in accordance with European Standard IP 581. By selecting the appropriate sample introduction and plasma conditions, low concentrations of P, S, Cu, and Fe can be accurately measured directly in ethanol, without the need for dilution. A spectral interference on S 180.669 is eliminated by the application of Multicomponent Spectral Fitting, allowing for accurate results to be obtained at concentrations as low as 100 µg/L.

Reference

1. *"Multicomponent Spectral Fitting"*, Technical Note, PerkinElmer Inc., 2017.

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043 (Flared) 09908587 (Non-flared)
Drain Tubing, Red/Red (1.14 mm id), PVC	09908585
Internal Standard Tubing, Orange/Green (0.38 mm id), PVC	N0773111 (Flared)
Copper Standard, 1000 mg/L	N9300183 (125 mL) N9300114 (500 mL)
Iron Standard, 1000 mg/L	N9303771 (125 mL) N9300126 (500 mL)
Phosphorus Standard, 1000 mg/L	N9303788 (125 mL) N9300139 (500 mL)
Sulfur Standard, 1000 mg/L	N9303796 (125 mL) N9300154 (500 mL)
Ytterbium Standard, 1000 mg/L	N9303811 (125 mL) N9300166 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)

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