



## Reliable Determination of Copper, Phosphorus and Sulfur in Bioethanol Using Inductively Coupled Plasma Spectrometry

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The increased strain on existing fossil fuels has led to a rise in demand for alternative fuel production. Bioethanol is ethanol produced from the fermentation of sugar derived from plants such as sugar cane or beet, maize or cassava. The production of bioethanol for use as either a fuel substitute or a blending agent for gasoline has increased dramatically over the past few years. The USA produced an estimated 23.3 billion liters of bioethanol in 2007 compared with 16.2 billion liters in 2005.

Bioethanol production is not a new industry. Brazil has been producing it since the 1970s and has replaced 50% of its gasoline usage with bioethanol. In order for a car to run on pure ethanol, modification of the engine is required. In the USA and Brazil, all new cars must have converted engines, known as fuel flex engines, which can run on 100% ethanol, 100% gasoline or any combination of the two.

The use of bioethanol as a fuel substitute for gasoline offers a number of important benefits. Bioethanol can be blended with gasoline to reduce cost and increase fuel supplies while decreasing demand on fossil fuel supplies. Being an oxygenate additive, bioethanol improves the octane rating of fuels while also reducing green house gas emissions. A further benefit is that blends of 5% ethanol and 95% gasoline (E5) can be used in modern engines with no modification.

However, it has been found that organic and inorganic contaminants may be present in bioethanol fuels, leading to undesirable effects. Copper, phosphorus and sulfur are three contaminants that must be rigorously monitored, since they are associated with a number of problems. The analysis of sulfur in ethanol is necessary to ensure that emissions produced when the fuel is burnt comply with environmental legislation. The level of sulfur must be controlled to prevent the formation of sulfur dioxide which can lead to acid rain.

The concentration of copper and phosphorus must be also controlled as these two elements can cause adverse effects on the operation of an engine. Copper acts as a very efficient catalyst for the low temperature oxidation of hydrocarbons. Concentrations above 0.012 mg/kg rapidly increase the rate of oxidation leading to gum formation, which can deposit on engine components such as fuel injectors. Phosphorus can poison the catalyst used in the exhaust systems of engines leading to increased emissions of environmentally harmful gases as the catalyst becomes ineffective.

Global regulatory bodies have therefore introduced stringent legislation to specify the maximum allowable concentrations of various contaminants in ethanol, including copper, phosphorus and sulfur.

### Regulations

The American Society for Testing and Materials (ASTM) International enforces the D4806-09<sup>1</sup> standard specification, covering nominally anhydrous denatured fuel ethanol intended for blending with unleaded or leaded gasoline at 1 to 10% volume for use as a spark-ignition automotive engine fuel. Among others, the standard mandates that denatured fuel ethanol must conform to the specified performance requirements for copper and sulfur content.

The ASTM has also published D5798-09B<sup>2</sup> standard specification, covering a fuel blend, nominally 75 to 85% volume denatured fuel ethanol (Ed75-Ed85) and 25 to 15% additional volume hydrocarbons for use in ground

vehicles with automotive spark-ignition engines. According to the specification, fuel ethanol must conform to the performance requirements prescribed by the D4806-09 standard.

In Europe, EN 15376<sup>3,4,5</sup> standard specifies requirements and test methods for marketed and delivered ethanol to be used as an extender for automotive fuel for petrol engine vehicles. This standard specifies ethanol as a blending component at up to 5% and includes specific requirements in relation to low water content, range of non-harmful denaturants and level of impurities that will not harm exhaust gas treatment systems.

The International Organisation of Standardisation (ISO) is also expected to publish a standard for the analysis of ethanol for copper, phosphorus and sulfur in the future.

In order to comply with these regulations, the industry requires a dependable analytical method capable of providing reliable quality control of ethanol.

### Analytical Technologies

Fourier transform near infrared (FT-NIR) spectroscopy can analyse key bioethanol process streams for multiple components in seconds. The use of FT-NIR simplifies the testing protocol for biofuel plants since it can replace multiple pieces of equipment, eliminate disposable laboratory supplies and significantly reduce equipment maintenance. In addition, the ability of the technique to analyse samples in-line, on-line, at-line or in the laboratory allows each biofuel production facilities to set up the ideal monitoring protocol for their process. However, FT-NIR is best suited for quantifying the level of sugars and ethanol in the bioethanol fermentation broth, rather than monitoring the presence of contaminants.

Inductively coupled plasma (ICP) spectrometry is an ideal technique for the analysis and quantification of a combination of trace contaminants in ethanol due to its multi-element capability and ability to reach the required levels of detection. ICP is a rapid method, providing time-efficient, repeatable analyses of any sample type. Further key advantages of the technology include excellent stability, flexibility, sensitivity and precision.

### Experimental

A Thermo Scientific iCAP 6000 Series ICP emission spectrometer was used for this analysis, enabling full wavelength coverage from 166 nm to 847 nm with Fullframe capability offering full spectrum trend analysis and contamination identification. The dedicated radial view mode of the spectrometer was chosen for this analysis due to its freedom from interferences which are likely to be present in this matrix, such as carbon and oxygen-based molecular emissions derived from the ethanol.

A Glass Expansion IsoMist temperature controlled spray chamber was also used for this analysis. Ethanol is much more volatile than water resulting in higher sample transport efficiency from the nebuliser to the plasma compared with an aqueous sample. The higher vapor pressure causes the plasma to move upwards into the load coil and can cause plasma instability. To overcome this problem, the sample can be cooled immediately prior to introduction to the plasma by using a temperature controlled spray chamber. The selected spray chamber temperature depends upon the vapor pressure of the sample. For a sample to be introduced into a plasma successfully, it must exhibit a vapor pressure of 30 mm Hg or less. The temperature at which the vapor pressure of ethanol falls below this value is approximately 14 °C.

	Copper		Phosphorus		Sulfur	
	mg/L	mg/kg	mg/L	mg/kg	mg/L	mg/kg
Blank	0	0	0	0	0	0
Standard 1	0.05	0.063	0.1	0.127	1	1.27
Standard 2	0.1	0.126	0.5	0.635	5	6.34
Standard 3	0.2	0.252	1.0	1.270	10	12.67
Standard 4	0.4	0.504	1.5	1.905	20	25.35
Standard 5	-	-	-	-	30	38.02
Check Standard	0.15	0.189	0.75	0.9525	7.5	9.525

Table 1: Calibration and check standard concentrations. The values are shown in both mg/L and mg/kg to be applicable to both the ASTM standard and the expected ISO standard.

	Detection Limit mg/L	1 hour check		2 hour check		3 hour check		4 hour check	
		Measured mg/L	Recovery %	Measured mg/L	Recovery %	Measured mg/L	Recovery %	Measured mg/L	Recovery %
Cu 324.754 nm	0.0015	0.150	100.0 %	0.160	106.7 %	0.161	107.3 %	0.156	104.0 %
P 177.495 nm	0.011	0.701	93.5 %	0.709	101.3 %	0.713	95.1 %	0.741	98.8 %
S 180.731 nm	0.021	7.427	99.0 %	6.826	91.0 %	6.911	92.1 %	7.015	93.5 %

Table 2: The wavelengths used for the analysis, the results of the detection limit and stability studies.

A Thermo Scientific V-groove nebuliser was used in conjunction with the temperature controlled spray chamber to reduce the amount of solvent reaching the plasma. This helped to reduce the background emissions resulting from the molecular-carbon and oxygen-based emissions in the plasma.

### Method

Multi-element calibration standards were prepared from 1000 mg/L single element solutions (Fisher Scientific, Loughborough, UK), which were diluted to the required concentrations (Table 1) with analytical reagent grade ethanol (Fisher Scientific, Loughborough, UK). A check standard was also prepared using the same procedure used for the preparation of the calibration standards.

A method was developed containing the wavelengths of interest (Table 2). The plasma parameters were optimised to provide the best possible detection limit. The parameters obtained are shown in Table 3 in addition to the details of the sample handling kit used.

The instrument was calibrated and the sub-array plots for each of the wavelengths were examined. Adjustments to the central integration and background correction points were made, as necessary, to minimise the impact of interferences. A detection limit study was

performed by measuring a ten replicate analysis of a matrix-matched blank. The standard deviation of the results of the ten replicate readings were multiplied by three to provide the detection limits. The check standard was then analysed at an hourly interval over a four-hour period.

### Results

The results of the detection limit study and analysis of the check standard are shown in Table 2. The detection limits were as expected for this matrix, slightly higher than an aqueous matrix and well below the maximum permitted levels of the current legislative standards. This can be attributed to the dedicated radial view, which allows for the optimisation of the radial viewing height to minimise interferences from matrix-based emissions. The elevation in the detection limits can be attributed to the increased background structure resulting from oxygen- and carbon-based emissions in the regions of interest.

The results of the stability test were within acceptable limits, with all of the recoveries within 10% of the prepared value. The stability of the sample introduction system was enhanced by the use of the temperature controlled spray chamber, isolating the spray chamber from temperature effects within

Parameter	Setting
Pump tubing	Sample Tygon – Orange/white Drain Tygon – White/white
Pump rate	40 rpm
Nebulizer	V-groove
Nebulizer gas flow	0.4 L/min or 0.14 MPa
Spray chamber	IsoMist – glass cyclonic
Spray chamber temperature	10 °C
Centre tube	1 mm
RF Power	1400 W
Coolant gas flow	12 L/min
Auxiliary gas flow	1 L/min
Integration times	Low 10 seconds High 5 seconds
Radial viewing height	12 mm

Table 3: The parameters used for the analysis.

the laboratory. The accuracy was also well within acceptable limits. Overall, ultimate optimisation, sensitivity and analytical robustness were achieved.

### Conclusion

The presence of contaminants in ethanol has a number of detrimental effects, including environmental pollution and engine corrosion. This has triggered the introduction of strict regulations, specifying the maximum allowable concentrations of various contaminants in ethanol. Experimental data demonstrate that ICP spectrometry operated in radial view is capable of performing trace multi-element analysis of copper, phosphorus and sulfur in ethanol in compliance with current legislation. The method delivers excellent detection limits, stability, accuracy, sensitivity and analytical robustness.

### References

1. ASTM D4806 - 09 Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel, <http://www.astm.org/Standards/D4806.htm>
2. ASTM D5798 - 09B Standard Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engines, <http://www.astm.org/Standards/D5798.htm>
3. Automotive fuels – Ethanol as a blending component for petrol, <https://www.astandis.at/shopV5/Preview.action%3b%3bsessionid=4A5AEFC67BB7C0977DC9DC9A1EF055C7?preview=&dockey=295906&selectedLocale=en>
4. [http://www.evs.ee/Checkout/tabid/36/screen/freedownload/productid/136699/doclang/en/preview/1/EVS\\_EN\\_15376;2008\\_en\\_preview.aspx](http://www.evs.ee/Checkout/tabid/36/screen/freedownload/productid/136699/doclang/en/preview/1/EVS_EN_15376;2008_en_preview.aspx)
5. [http://ec.europa.eu/energy/res/events/doc/biofuels/presentation\\_cahill.pdf](http://ec.europa.eu/energy/res/events/doc/biofuels/presentation_cahill.pdf)

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