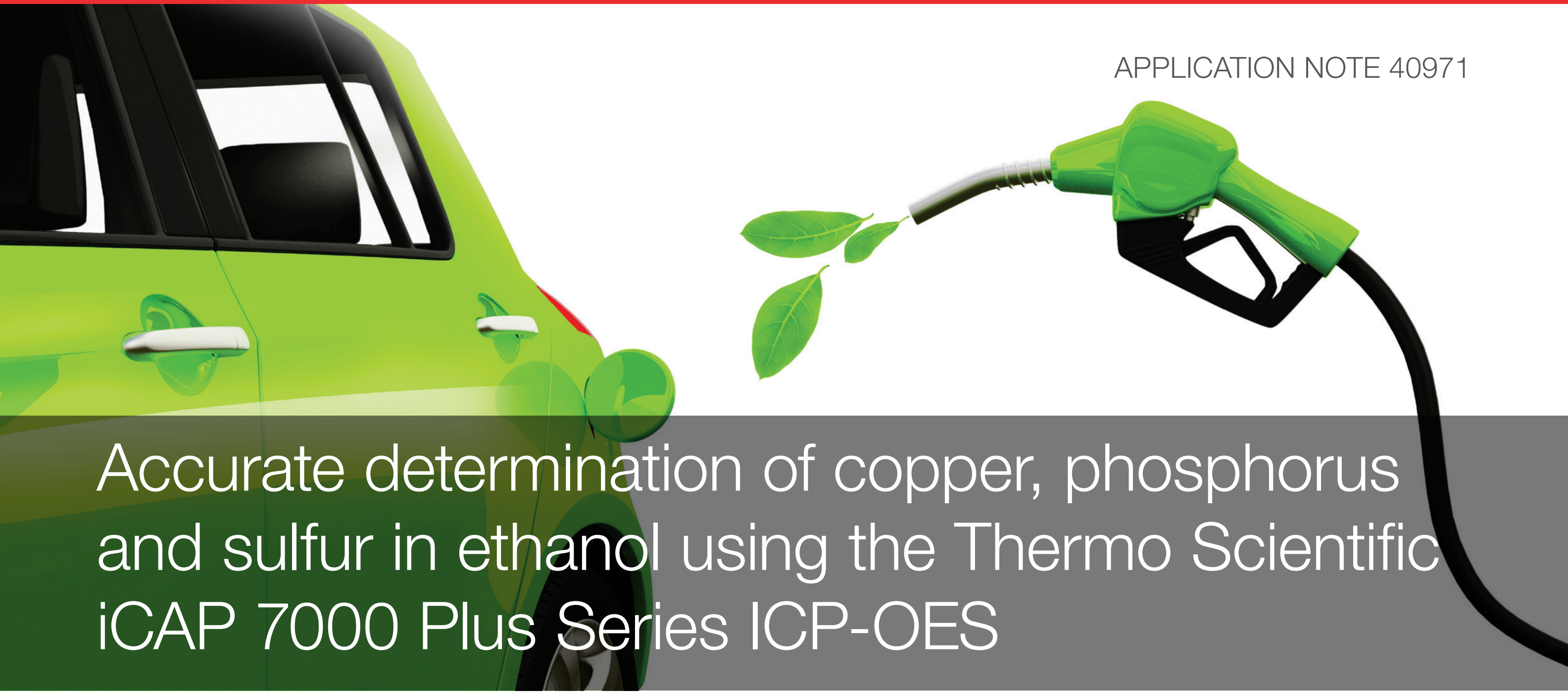
APPLICATION NOTE 40971



Accurate determination of copper, phosphorus and sulfur in ethanol using the Thermo Scientific iCAP 7000 Plus Series ICP-OES

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Keywords

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Goal

This application note demonstrates how volatile organic solvents like ethanol can be easily analyzed with the Thermo Scientific iCAP 7000 Plus Series ICP-OES fitted with a temperature controlled spray chamber to reduce volatility of the solvent. Cooling down the spray chamber to 10 °C reduces the solvent load on the plasma and allows straight forward analysis of ethanol with a more stable plasma and reduced background emission.

Introduction

The production of bioethanol (ethanol produced from the fermentation of sugar derived from plants such as sugar cane or beet, maize, or cassava) 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 to 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 – but the global increased strain on fossil fuels is necessitating alternative fuel production. For a car to run on pure ethanol, some modification of the engine needs to take place. In the USA and Brazil, all new cars sold must have converted engines known as fuel flex engines which can run on 100% ethanol, 100% gasoline or any combination in between.

Some of the benefits of bioethanol as a fuel are:

- Greenhouse gas emissions are reduced when bioethanol is substituted for gasoline
- It can be blended with gasoline to reduce the cost and increase fuel supplies/decrease demand on fossil fuel supplies
- Blends of 5% ethanol and 95% gasoline (E5) can be used in modern engines with no modification
- Ethanol is an oxygenate additive which improves the octane rating of fuels

The current ASTM standard for the copper and sulfur content of denatured fuel ethanol is D4806-17. The details of the permitted concentrations of these elements are shown in Table 1. In addition to this ASTM standard, ISO (International Organization of Standardization) have published a standard for the analysis of ethanol for copper, phosphorus and sulfur (ISO EN 15837:2009), the analysis range for this standard is shown in Table 2.

Table 1. The maximum permitted levels of S and Cu in ethanol according to ASTM D4806-17.

Element	Maximum permitted concentration (mg·kg^{-1})
S	30
S (in the state of California, USA)	10
Cu	0.1

Table 2. The expected concentration range of Cu, S and P according to ISO standard 15837:2009.

Element	Concentration range (mg·kg^{-1})
Cu	0.05 - 0.3
P	0.13 - 1.9
S	2 - 15

The analysis of sulfur in ethanol to be used as a fuel is to ensure emissions produced when the fuel is burnt comply with environmental legislation. The level of sulfur is controlled to prevent the formation of sulfur dioxide which can lead to acid rain. The concentration of copper and phosphorus is 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^{-1} 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. An ideal method of analysis for this combination of elements is ICP-OES due to its multi-element capabilities and ability to reach the required levels of detection.

Instrumentation

The Thermo Scientific™ iCAP™ 7400 ICP-OES Radial was used for the analysis. This has full wavelength coverage from 166 nm to 847 nm with Fullframe capability which offers full spectrum trend analysis and contamination identification. The dedicated radial view model was chosen for the 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). The Glass Expansion IsoMist™ temperature cooled spray chamber (Figure 1) was also used for the analysis. Ethanol is much more volatile than water resulting in higher sample transport efficiency from the nebulizer to the plasma compared to 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 the use of a temperature controlled spray chamber such as the IsoMist. 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, as indicated in Figure 2.

Figure 1. The IsoMist temperature controlled spray chamber.

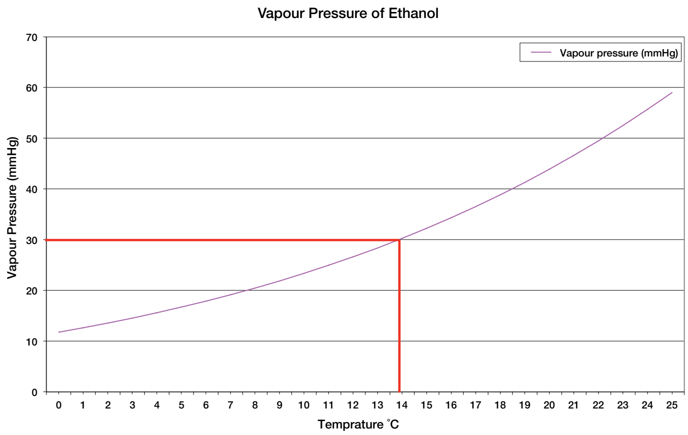

Figure 2. Graph of ethanol vapor pressure as a function of temperature.

A V-groove nebulizer was used in conjunction with the IsoMist 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.

Standard preparation

Multi-element calibration standards were prepared from 1000 mg·L^{-1} single element solutions (Fisher Scientific™, Loughborough, UK) which were diluted to the required concentrations (Table 3) with analytical reagent grade ethanol (Fisher Scientific). A check standard was also prepared using the same procedure as described for the preparation of the calibration standards.

Table 3. Calibration and check standard concentrations in mg·L^{-1}.

	Cu	P	S
Blank	0	0	0
Standard 1	0.05	0.1	1
Standard 2	0.1	0.5	5
Standard 3	0.2	1.0	10
Standard 4	0.4	1.5	20
Standard 5	-	-	30
Check standard	0.15	0.75	7.5

Method development and analysis

A LabBook was created in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software containing the wavelengths of interest (Table 5). The plasma parameters were optimized using the Plasma Optimization function of the Qtegra ISDS Software which automatically optimizes the plasma conditions to give the optimum detection limit. The parameters obtained are shown in Table 4 in addition to the details of the sample handling kit used.

The instrument was calibrated and the subarray plots for each of the wavelengths were examined and adjustments to the central integration and background correction points were made, as necessary, to minimize the impact of interferences. A detection limit study was performed by analyzing a matrix-matched blank with ten repeats. 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 analyzed at an hourly interval over a four hour period.

Table 4. Instrument parameters.

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Tygon® orange/white Drain Tygon® white/white
Pump Speed	40 rpm
Nebulizer	V-groove
Nebulizer Gas Flow	0.4 L·min^{-1}
Spray Chamber	IsoMist
Spray Chamber Temperature	10 ˚C
Auxiliary Gas Flow	1 L·min^{-1}
Coolant Gas Flow	12 L·min^{-1}
Center Tube	1 mm
RF Power	1400 W
Radial Viewing Height	12 mm
Exposure Time	UV 10 s, Vis 5 s

Results

The results of the detection limit study and analysis of the check standard are shown in Table 5.

Table 5. The wavelengths used for the analysis, the results of the detection limit and stability studies.

Element and wavelength (nm)	Detection limit (mg·L^{-1})	1 hour check		2 hour check		3 hour check		4 hour check	
		Measured (mg·L^{-1})	Recovery (%)	Measured (mg·L^{-1})	Recovery (%)	Measured (mg·L^{-1})	Recovery (%)	Measured (mg·L^{-1})	Recovery (%)
Cu 324.754	0.0015	0.150	100.0	0.160	106.7	0.161	107.3	0.156	104.0
P 177.495	0.011	0.701	93.5	0.709	101.3	0.713	95.1	0.741	98.8
S 180.731	0.021	7.427	99.0	6.826	91.0	6.911	92.1	7.015	93.5

The detection limits are as expected for this matrix, which is slightly higher than an aqueous matrix. 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 are within acceptable limits, with all of the recoveries within ±10% of the expected value.

Conclusion

The analysis of copper, phosphorus and sulfur in ethanol can be performed in a simple multi-element method by utilizing the Thermo Scientific iCAP 7400 ICP-OES Radial. The detection limits achieved are well below the maximum permitted levels of the current ASTM standard D4806-17 and ISO standard 15837:2009. This can be attributed to the dedicated radial view, which allows for the optimization of the radial viewing height to minimize interferences from matrix-based emissions. The accuracy and stability are also well within acceptable limits. The stability of the sample introduction system is enhanced by the use of the IsoMist temperature controlled spray chamber, isolating the spray chamber from temperature effects within the laboratory. This shows that the iCAP 7400 ICP-OES Radial is ideal for this type of analysis.

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