Application Note: 40971

Petrochemical Series – Accurate determination of copper, phosphorus and sulfur in ethanol using the Thermo Scientific iCAP 6000 Series ICP

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Key Words

- ICP
- iCAP Radial
- Volatile solvents
- Organics
- Ethanol
- IsoMist
- Cooled spray chamber

Benefits in Brief

- Peltier temperature controlled spray chamber enables simple analysis of volatile samples such as ethanol
- Dedicated radial view with adjustable viewing height offers ultimate optimization, sensitivity and analytical robustness

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:

- Green house 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 D4806–07a. The details of the permitted concentrations of these elements are shown in Table 1 below. In addition to this ASTM standard, ISO (International Organization of Standardization) are expected to publish a standard for the analysis of ethanol for copper, phosphorus and sulfur in the future and the anticipated analysis range for this standard is shown in Table 2 below.

Element	Maximum permitted concentration mg/kg
Sulfur	30
Sulfur in the state of California	10
Copper	0.1

Table 1: The maximum permitted levels of sulfur and copper in ethanol according to ASTM D4806-07a

Element	Lower limit of Calibration range mg/L	Upper limit of Calibration range mg/L
Copper	0.05	0.4
Phosphorus	0.1	1.5
Sulfur	1	20

Table 2: The predicted lower and upper calibration limits of the expected ISO standard.

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 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 due to its multi-element capabilities and ability to reach the required levels of detection.

Thermo SCIENTIFIC

Method

Instrumentation

The Thermo Scientific iCAP 6000 Series ICP 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 of the iCAP 6000 Series 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 IsoMist temperature controlled 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

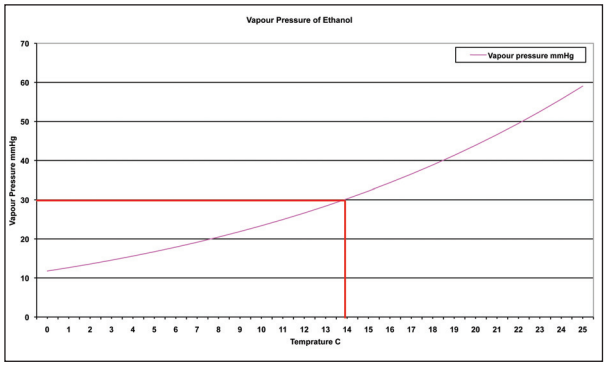

Figure 2: Graph of ethanol vapor pressure as a function of temperature.

The V-groove nebulizer was used in conjunction with the IsoMist 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 single element solutions (Fisher Scientific, Loughborough, UK) which were diluted to the required concentrations (Table 3) with analytical reagent grade ethanol (Fisher Scientific, Loughborough, UK). A check standard was also prepared using the same procedure as described for the preparation of the calibration standards.

	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 3: 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.

Method development

A method was created containing the wavelengths of interest (Table 5 below). The plasma parameters were optimized using the Optimize Source function of iTEVA (available on the iCAP 6500 Series only) 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.

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 4: The parameters used for the analysis.

The instrument was calibrated and the sub-array 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 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 analyzed 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 5 below.

	Detection Limit	1 hour check		2 hour check		3 hour check		4 hour check	
	mg/L	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 5: The wavelengths used for the analysis, the results of the detection limit and stability studies.

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 with 10 % of the prepared value.

Conclusions

The analysis of copper, phosphorus and sulfur in ethanol can be performed in a simple multi-element method by utilizing the radial view iCAP 6000 Series. The detection limits achieved are well below the maximum permitted levels of the current ASTM standard D4806-07a and the expected ISO method. 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 with acceptable limits. The stability of the sample introduction system is enhanced by the use of the IsoMist, isolating the spray chamber from temperature effects within the laboratory. This shows that the radial view iCAP 6000 Series is ideal for this type of analysis.

Plasma Capabilities from Thermo Fisher Scientific

The use of an Inductively Coupled Plasma source (ICP) is the accepted and most powerful technique for the analysis and quantification of trace elements in both solid and liquid samples. Its applications range from routine environmental analyses to the materials industry, geological applications to clinical research and from the food industry to the semiconductor industry.

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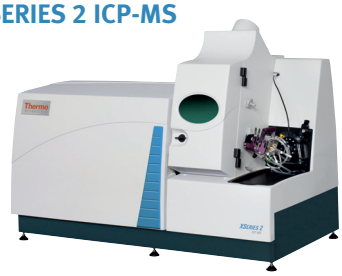
Thermo Scientific iCAP ICP

Thermo Scientific XSERIES 2 ICP-MS



Thermo Scientific ELEMENT2 HR-ICP-MS

Thermo Scientific NEPTUNE Multi-collector ICP-MS

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