Petrochemistry / Biofuels

Bio-ethanol

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Instrument: ULTIMA 2

1 Introduction

Ethanol fuel is used as a biofuel alternative to gasoline (as a side benefit improving engine performance), when it is obtained from the conversion of carbon based renewable feedstock. Currently, it is produced by fermentation of starch or sugar from a wide variety of agricultural feedstocks (sugar cane, corn and switchgrass, are examples). Prior to fermentation, some crops require pre-production steps. Depending on the production method, ethanol contributes then to the reduction of greenhouse CO_2 emissions. Although CO_2 is emitted during fermentation and combustion, the production of the biomass compensates or cancels out the emission by a greater uptake.

Depending on the engine configuration, ethanol is used directly as a fuel or is mixed with unleaded gasoline (E85 Ethanol Fuel for example contains 85 % ethanol). Flex-fuel vehicles are designed to run on E85, whereas E10 (90 % gasoline) does not require modification of the engine.

This application flash describes the analytical procedure for analysis of ethanol with the ULTIMA 2 ICP-AES instrument. Another application flash deals with biodiesel[1].

2 Operating conditions

Ethanol is a volatile solvent and needs special operating conditions for ICP-AES analysis.
The procedure may be dilution of ethanol with a lower volatility solvent, or with water. However, to avoid sample preparation and risk of contamination, the analyst would prefer analyzing pure ethanol. The best alternative is to use a cooled spray chamber to minimize solvent load in the plasma and maintain robust conditions. This procedure also has also the advantage of improving the limits of detection.

• Sample introduction system

The classical way to minimize the sample load in the plasma, when a volatile solvents are analyzed, is to use a refrigerated cyclonic (or Scott) spray chamber with a dedicated cooling system.
A new approach consists of using a cyclonic spray chamber cooled by the Peltier effect. Such a system incorporates a cyclonic spray chamber featuring a central transfer tube, which is encapsulated in a conductive resin for intimate contact with the Peltier heat transfer block. The solid-state Peltier device controls the temperature in the range of – 10 to + 60 °C, in 1 degree increments.
The big advantage is that the system is one-piece and is very compact and compatible with the sample introduction compartment of the instrument (as shown in Image 1). The transfer tube between the spray chamber and the torch is minimal. The temperature is computer controlled and the stabilisation is very fast.

Image 1: cooled cyclonic spray chamber (Peltier effect), below the torch compartment.

Tables 1 and 2 give plasma and instrument parameters.

Table 1: Plasma parameters

Parameter	Specification
Power	1200 W
Plasma gas	16 L/min
Auxiliary gas	0.8 L/min
Sheath gas	0.35 L/min
Nebuliser gas	0.35 L/min (1.7 bar)
Sample uptake	0.8 mL/min (15 rpm)
Plasma view	Radial*

* Total Plasma View (observation of the complete NAZ, Normal Analytical Zone), for minimised matrix effects and optimum sensitivity.

Table 2: Specifications of the ULTIMA 2 ICP spectrometer

Parameter	Specification
Generator	40.68 MHz, solid state, water-cooled
Optical System	Czerny-Turner (1 m Focal)
Gratings	2400 g/mm double order
Spectral range	120 - 800 nm (Far UV option)
Resolution	5 pm in 120 - 320 nm range 10 in 320 - 800 nm range
Sample introduction	parallel flow (inert) nebulizer /cooled cyclonic
Pump tubing	Black/black Viton (sample) Grey/grey Viton (drain)
Torch design	Vertical demountable, 3 mm i.d injector

For ethanol applications, the temperature of the cooled spray chamber is set at – 10 °C.

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3 Analytical results

Calibration is performed with pure ethanol (analytical grade, Merck) as the blank and standards prepared in ethanol from Précis mono-element stock solutions (HORIBA Jobin Yvon).

• Limits of quantification

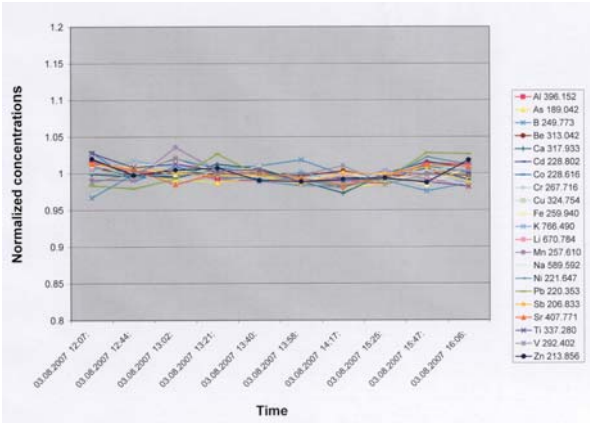
The limits of detection are estimated using the formula LOD = 3 x SD. SD is the Standard Deviation of the blank concentration from an analysis of 10 replicates.

Table 3: LODs and LOQs in pure ethanol (in ppb unit)

Element	LOD(ppb)	LOQ(ppb)	Element	LOD (ppb)	LOQ (ppb)
Ag 328.028	0.47	1.56	Mo 202.030	0.45	1.47
Al 167.020	0.15	0.50	Na589.592	4.96	16.36
Al 396.152	2.68	8.84	Ni 221.647	0.30	0.99
As 189.042	2.22	7.31	P 177.440	4.92	16.24
B 249.773	1.42	4.69	P178;229	4.32	14.26
Ba 455.403	0.04	0.13	P 213.618	2.63	8.68
Be 313.042	0.21	0.68	Pb 220.353	1.68	5.54
Ca 317.933	1.56	5.15	S 180.676	5.13	16.94
Cd 228.802	0.17	0.55	Sb 206.833	2.30	7.59
Co 228.616	0.32	1.06	Se 196.026	39.63	130.76
Cr 267.716	0.35	1.16	Si 251.611	1.84	6.07
Cu 324.754	0.28	0.92	Sn 189.989	2.83	9.33
Fe 259.940	0.52	1.72	Sr 407.771	0.01	0.05
Hg 194.163	1.80	5.94	Ti 337.280	0.13	0.42
K 766.490	29.67	97.93	Tl 190.864	2.66	8.79
Li 670.784	0.65	2.14	V 292.402	3.59	11.86
Mg 279.806	4.01	13.22	Zn 206.200	0.53	1.74
Mn 257.610	0.13	0.44	Zn 213.856	0.60	1.97

The performance is very similar to what the ULTIMA 2 can achieve in water, excepted for K, Na and Se which are higher because of the presence of molecular bands.

• Stability



Graph 1: Stability test on 1 ppm in ethanol

The limit of quantification is then LOQ = 3.3 x LOD. Both LODs and LOQs are listed in Table 3.

Table 4: Recovery of 10 ppb

Element	Conc (mg/L)	SD (mg/L)	RSD(%)	Recovery(%)
Ag 328.068	10.06	0.07	0.69	100.6
Al 167.020	10.91	0.20	1.85	109.1
As 189.042	10.76	0.22	1.87	107.6
Ba 455.403	10.11	0.06	0.58	101.1
Be 313.042	10.32	0.10	0.93	103.2
Cd 228.616	10.46	0.30	2.57	104.6
Cr 267.716	10.31	0.15	1.50	103.1
Cu 324.754	9.82	0.13	1.32	98.2
Fe 259.940	9.90	0.06	0.64	99.0
Li 670.784	10.13	0.18	1.79	101.3
Mn 257.610	9.86	0.09	0.88	98.6
Mo 202.030	10.27	0.14	1.36	102.7
Ni 221.647	10.23	0.28	2.72	102.3
Pb 220.353	9.31	0.80	9.21	93.1
Sr 407.771	10.08	0.02	0.21	100.8
Ti 337.280	9.88	0.03	0.27	98.8
Tl 190.864	10.47	1.19	11.38	104.7

A spike of 10 ppb in the blank has been done for some elements (from Précis mono-element solutions) to show the efficiency of the methodology in terms of sensitivity and accuracy criteria (Table 4).

The 4 hours stability test in Graph 1 shows the efficiency of the cooling system as well as the benefit of the torch configuration and plasma observation.

Reference:
(1) Application Flash, PETRO 01, "Biodiesel", Agnès Cosnier, Sophie Lebouil, Sébastien Vélasquez, HORIBA Jobin Yvon, Longjumeau, France

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