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Analysis of bioethanol samples through Inductively Coupled Plasma Mass Spectrometry with a total sample consumption system

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ABSTRACT

Bioethanol real samples have been directly analyzed through ICP-MS by means of the so called High Temperature Torch Integrated Sample Introduction System (hTISIS). Because bioethanol samples may contain water, experiments have been carried out in order to determine the effect of ethanol concentration on the ICP-MS response. The ethanol content studied went from 0 to 50%, because higher alcohol concentrations led to carbon deposits on the ICP-MS interface. The spectrometer default spray chamber (double pass) equipped with a glass concentric pneumatic micronebulizer has been taken as the reference system. Two flow regimes have been evaluated: continuous sample aspiration at 25 μL min^{-1} and 5 μL air-segmented sample injection. hTISIS temperature has been shown to be critical, in fact ICP-MS sensitivity increased with this variable up to 100–200 °C depending on the solution tested. Higher chamber temperatures led to either a drop in signal or a plateau. Compared with the reference system, the hTISIS improved the sensitivities by a factor included within the 4 to 8 range while average detection limits were 6 times lower for the latter device. Regarding the influence of the ethanol concentration on sensitivity, it has been observed that an increase in the temperature was not enough to eliminate the interferences. It was also necessary to modify the torch position with respect to the ICP-MS interface to overcome them. This fact was likely due to the different extent of ion plasma radial diffusion encountered as a function of the matrix when working at high chamber temperatures. When the torch was moved 1 mm plasma down axis, ethanolic and aqueous solutions provided statistically equal sensitivities. A preconcentration procedure has been applied in order to validate the methodology. It has been found that, under optimum conditions from the point of view of matrix effects, recoveries for spiked samples were close to 100%. Furthermore, analytical concentrations for real samples following the preconcentration method and the direct determination were not significantly different. The quantification method was finally based on external calibration with standards containing 50% (v/v) ethanol content.

1. Introduction

Bioethanol is considered as a promising alternative to fossil fuels [1,2] and in its anhydrous form it is often blended to products such as gasoline thus giving rise to the so-called ethanol fuel. Nevertheless, this product may contain organic as well as inorganic pollutants, among them metals and metalloids [3]. The presence of these species may result detrimental from the point of view of engine performance and environmental quality. Although official methods have been developed to determine the metal and metalloid content in fossil fuels, a few methods exist in the case of ethanol fuel [4–6]. So far, there are only procedures for determining the content of Na, K, Ca, Mg, Fe, Cu, P and S in this kind of samples and no attention is paid to other heavy toxic metals.

Several spectrometric techniques have been employed to perform this kind of analysis. Recently, High Resolution Continuum Source Flame Atomic Absorption Spectrometry was applied to the sequential determination of nine metals in ethanol fuel samples [7]. Due to the low metal content usually present in bioethanol samples (*i.e.*, μg L^{-1}), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) appears as an excellent alternative to other spectrometric atomic absorption and emission techniques. However, some problems can be found when only bioethanol containing samples are introduced into the plasma. In fact, in its hydrated form, bioethanol may contain up to 7% of water. Moreover, the fermented solution present before the distillation step may contain ethanol volume percentages ranging from 12 to 15%. In addition, as much as 300 different organic compounds such as longer chain alcohols, ketones or aldehydes may be present in the matrix [1]. This may cause degradation in the accuracy of the determination if the matrix nature is not considered [6]. Obviously, the introduction of an organic specimen into the plasma induces severe ICP-MS spectral interferences thus making it difficult to quantify analytes such as ^{28}Si or ^{52}Cr [8]. An additional difficulty is that there are limited certified reference materials that hamper the method validation procedure [1,2].

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Studies trying to overcome some of these problems have been published based on the use of collision or reaction cells [9], dedicated sample introduction systems such as Electrothermal Vaporization [10], micronebulization [11] or flow injection [12]. Recently, Virgilio et al. proposed a method based on the use of ICP-MS/MS to carry out ethanol fuel analysis. In this methodology, samples were diluted with a nitric acid solution and matrix matching was employed for elemental quantification [13].

Non spectral interferences can be overcome by using well known methods such as sample dilution with water [14], matrix matching [15] or internal standardization [16]. All these procedures suffer from their own drawbacks such as loss in sensitivity, time consumption or the lack of appropriate elements to be used as internal standard. In a recent report, it was verified that it is possible to perform bioethanol analysis in ICP-OES by means of a high temperature total sample consumption system [17]. The basic principle of the so-called High Temperature Torch Integrated Sample Introduction System (hTISIS) consists of the complete aerosol evaporation before it enters the plasma. In this manner, analyte transport efficiency is virtually 100% regardless the sample matrix. Therefore, interferences originated in the sample introduction system are removed. In order to avoid plasma degradation caused by the introduction of organic matter, air segmented 5 μL injection or low liquid flow rates are employed [18]. Additional advantages of the hTISIS over conventional sample introduction systems include improved sensitivities and limits of detection and shorter wash out times.

So far, most of the existing studies have been focused on the analysis of ethanol fuel. The aim of the present work was thus to test the combination of hTISIS-ICP-MS as a rapid and direct way for performing multielemental determination in bioethanol samples. In a first step, analytical figures of merit were evaluated. Additional problems caused by the introduction of organic samples in ICP-MS such as non-spectral interferences were discussed and characterized. All the studies were done following two different flow regimes: (*i*) continuous sample aspiration at a 25 μL min^{-1} liquid flow rate, and; (*ii*) air-segmented (5 μL) injection mode.

2. Experimental

2.1. Solutions and samples

Standards containing ethanol at concentrations ranging from 0 to 50% (v/v) were prepared using ultrapure water (R < 18.2 MΩ) obtained with a Millipore water purification system (El Paso, TX, USA) and analytical grade ethanol 96% (Panreac, Barcelona, Spain). Multielemental standards were obtained from a stock solution (Merck IV, Darmstadt, Germany). Blanks containing variable ethanol and water concentrations were also prepared. All these synthetic solutions were filtered with a 0.45 μm PTFE filter pore size (Filabet, Barcelona, Spain).

Twenty-eight real samples containing water concentrations from 0 to 45% were analyzed. These samples were 1:1 (v/v) diluted with ultrapure water (R < 18.2 MΩ) and the standards used for elemental quantification were prepared in a 1:1 (v/v) ethanol/water matrix. Recovery studies were performed in which the diluted samples were spiked to 250 μg L^{-1} by using a Merck IV multielemental stock solution. In this case, non spiked samples were taken as blanks.

Viscosity was obtained with an Ostwald viscometer employing ultrapure water as the reference solvent. For the tested real samples, this physical property ranged from 1.24 to 2.19 mPa s^{-1}. In order to measure the surface tension 30 drops provided by a peristaltic pump under controlled conditions were recovered in a polyethylene container and further weighed. The final value of this property was obtained using ultrapure water as reference solvent. Surface tension was included within the 20.9 to 27.5 mN m^{-1} range depending on the sample considered.

Real samples corresponded to bioethanol produced from beet (labeled as B9 to B16 and B19-B23), wheat (B2, B5, B7 and B17) and finally from sugarcane (B4) and wine (B18). Together with all these samples, an ethanol sample containing additives (B3) was also analyzed.

Table 1
ICP-MS Agilent 7700x operating conditions.

Plasma			
Ar flow rates/L min^{-1}	Plasma gas: 15.0 Auxiliary gas: 0.9		
RF power/W	1600		
hTISIS conditions			
Sample injection mode	Air Segmented injection		Continuous sample aspiration
Volume injected/μL	5		------
Liquid aspiration conditions	350 rpm (air)		25 μL min^{-1}
Nebulization flow rate/ L min^{-1}	0.4		
Number of replicates	5		
Integration software	Transient (TRA)		Spectrum
Integration time/s	0.1		0.3
Sweeps per replicate	1		100
Total acquisition time/s	300 s (for 5 peaks)		------
Collision cell			
He flow rate/mL min^{-1}	4.3		
OctP Bias/V	−18		
Oct RF/V	200		
Energy discrimination/V	3.0		
HMI System Conditions			
ArHMI flow rate/ L min^{-1}	0.56		
Measured isotopes			
^{7}Li	^{11}B	^{43}Ca	^{44}Ca
^{27}Al	^{55}Mn	^{56}Fe	^{60}Ni
^{52}Cr	^{66}Zn	^{75}As	^{88}Sr
^{63}Cu	^{111}Cd	^{115}In	^{136}Ba
^{107}Ag	^{140}Ce	^{208}Pb	^{209}Bi
^{137}Ba	$^{156}CeO^{+}$	$^{68}Ba^{2+}$	$^{70}Ce^{2+}$
$^{154}BaO^{+}$	^{23}Na	^{24}Mg	

2.2. Instrumentation

An Agilent Technologies 7700x ICP-MS spectrometer (Santa Clara, California, USA) equipped with a high matrix introduction system (HMI) was employed to take the ionic intensities of the analytes shown in Table 1. A hTISIS equipped with a 9 cm^3 single-pass spray chamber was adapted to the spectrometer. The operating conditions are also gathered in Table 1. A glass pneumatic concentric nebulizer, TR-50-C0.5 (Meinhard Glass Products, Santa Ana, USA) was employed. Strictly speaking this is not considered as a 'micro nebulizer', however it was able to work in a stable fashion, thus leading to satisfactory analytical figures of merit, when liquid flow rates on the order of tens of microliters per minute were selected.

The solutions were delivered to the nebulizer by means of a peristaltic pump (Perimax 16 antiplus, Spetec) and a 0.19-mm id flared end PVC-based tubing (Glass Expansion, Melbourne, Australia) was employed. In the air segmented injection mode, the peristaltic pump continuously aspirated air. A given sample volume was measured with an automatic pipette (Eppendorf, Hamburg, Germany). Then, the nozzle was adapted to the flared end tubing and the solution was aspirated. The sample plug was driven to the nebulizer thus avoiding sample dispersion, as the carrier stream was simply air.

3. Results and discussion

3.1. Analyte transport efficiency

Experiments were performed in order to verify the impact of the chamber temperature and ethanol content on the mass of analyte leaving the single-pass spray chamber. To achieve this goal, twenty 5 μL standard (200 mg L^{-1} multielemental solution) volumes were consecutively injected and delivered to the nebulizer under the liquid aspiration conditions and nebulizer gas flow rate indicated in Table 1. The