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Metal and metalloid determination in bioethanol through inductively coupled plasma-optical emission spectroscopy

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ABSTRACT

A new method to carry out the elemental determination of metals in bioethanol through ICP-OES has been developed. The procedure is based on the use of a heated torch integrated sample introduction system (hTISIS) to directly introduce the vaporized sample into the plasma. Two injection modes (continuous liquid aspiration and air-segmented flow injection analysis) have been evaluated. In a first step, the matrix effects caused by several ethanol–water mixtures were removed by operating the hTISIS at 400 °C in segmented injection. Meanwhile, the results also proved that the system could be operated in continuous mode at 200 °C with the complete interference removal. Finally, twenty-eight real samples with bioethanol contents between 55% and 100% were analyzed with the methods previously developed. Regarding validation, recoveries from 80% to 120% were obtained for 18 analytes and the concentrations found with the proposed method were in agreement with those encountered with a preconcentration method, taken as a reference procedure. Limits of detection went from 3 ng mL^{-1} for manganese to about 500 ng mL^{-1} for calcium. This allowed to quantify Cr, Fe, Mg, Mn and Zn in segmented flow injection and Al, Cd, Cr, Cu, K, Mg, Mn, Na and Zn in continuous sample aspiration mode in bioethanol samples.

1. Introduction

Bioethanol is known as the alcoholic product obtained from the fermentation of carbohydrates present in a wide renewable feedstock (e.g. sugar cane, corn and switchgrass) using various types of microorganisms [1,2]. Among the possible species present in bioethanol, metals deserve special attention. Metals and metalloids can be present in the raw material [3–6]. Moreover, bioethanol may be contaminated with metals during its synthesis [4,5,7] and/or its storage and transport in metallic containers [5–8]. Finally, some metallic species can be incorporated as additives to promote the combustion process [9].

The quantification of metals and metalloids in bioethanol shows many difficulties as they are generally present at low concentrations (μg L^{-1}). Besides, commercially available bioethanol contains up to 7% of water and 300 different organic compounds. Both facts may cause a degradation in the accuracy of the determination if the matrix nature is not considered. An additional difficulty is that there are limited certified reference materials that hamper the method validation procedure [1,2].

Several analytical techniques have been proposed to determine metals in ethanol fuel [10], such as electrothermal atomic absorption spectroscopy (ETAAS) [5,11–16], microwave induced plasma optical emission spectrometry (MIP-OES) [6] or voltammetry [17–21]. Flame absorption atomic spectroscopy (FAAS) in turn has been widely employed for this purpose [4,22–26]. However, a preconcentration step is necessary due to the high limits of detection provided by this technique [24–26]. Therefore, inductively coupled plasma optical emission spectroscopy (ICP-OES) [27,28] and mass spectrometry (ICP-MS) [28–30] are highly appropriate to perform bioethanol analysis due to their low limits of detection and wide dynamic range. Unfortunately, ICP techniques suffer from non-spectral interferences caused by the ethanolic matrices that preclude the accuracy of the determinations.

In order to remove or to mitigate non-spectral interferences caused by ethanol in ICP-OES, samples should be diluted employing water [30,31]. An obvious limitation of this methodology is that LODs and sensitivity are severely degraded. Matrix matching has also been applied, although the chemical composition of the matrix is usually unknown [28,30]. Finally, the use of internal standardization has been recommended [28,30]. The most important drawback of this methodology is the selection of a suitable internal standard.

Additionally, alternative sample introduction systems can be proposed to remove the matrix effects. In previous works, a high temperature torch integrated sample introduction system (hTISIS) has been described. Basically, this device consists of a temperature programmable single-pass spray chamber. The hTISIS has been specially designed to work at liquid flow rates below roughly 100 μL min^{-1}. So far, this sample introduction system has been applied to the analysis of aqueous [32] as well as organic [33] samples through ICP-OES. Higher

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sensitivities, lower limits of detection and absence of interferences are among the benefits of the hTISIS over conventional sample introduction systems.

It should be noted that most of the studies previously mentioned have been developed for ethanol fuel analysis. The main goal of this work was thus to test the suitability of the hTISIS to perform metal determination in bioethanol samples through ICP-OES. In order to accomplish this, the matrix effects induced by the presence of variable ethanol contents were studied at different hTISIS spray chamber temperatures under continuous and air-segmented sample introduction modes.

2. Experimental

2.1. Solutions and samples

Ethanol–water mixtures were prepared using analytical grade ethanol 96% (Panreac, Spain) and ultrapure water (R < 18.2 MΩ) obtained with a Millipore water purification system (El Paso, TX, USA). Blanks containing variable ethanol concentrations were also prepared. Multielemental solutions were obtained from a stock solution (Merck IV, Darmstadt, Germany) and filtered with a 0.45 μm PTFE filter pore size (Filabet, Barcelona, Spain).

Twenty-eight bioethanol 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 to obtain the calibration line were prepared in a 1:1 (v/v) ethanol/water matrix. Recovery studies were performed in which the diluted samples were spiked with the multielemental stock solution. In this case, non-spiked samples were taken as blanks.

Solution physical properties were measured. The viscosity was obtained with an Ostwald viscometer employing ultrapure water as the reference solvent. In order to measure the density, 5 mL of each standard was weighed. Finally, the surface tension was calculated by determining the weight of 30 drops provided by a peristaltic pump under controlled conditions using ultrapure water as reference solvent. The obtained data are summarized in Table 1 for eight representative situations: three water–ethanol mixtures and five real samples having variable ethanol contents. It was verified that density and surface tension decreased with the ethanol content whereas the viscosity depended on the water content. Interestingly, these physical properties significantly differed as a function of the real sample considered. Therefore, changes in the performance of the system were expected.

2.2. Instrumentation

Drop size distributions of the aerosols generated by the nebulizer (i.e., primary aerosols) were measured by means of a laser diffraction instrument (Model 2600c, Malvern Instruments, Malvern Worcestershire, UK).

An Optima 4300 DV Perkin-Elmer ICP-OES spectrometer (Uberlingen, Germany) was employed to axially take the intensities. The spectrometer was equipped with the hTISIS equipped with a 9 cm^3 single-pass spray chamber. The operating conditions are gathered in Table 2. In the present work, 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 segmented flow injection methodology 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 by means of the peristaltic pump. The sample plug was driven to the nebulizer thus avoiding sample dispersion, as the carrier stream was simply air.

Table 2
ICP-OES operating conditions.

	hTISIS in segmented injection flow	hTISIS in continuous aspiration
Ar flow rates/L min^{-1}	Plasma: 15 Auxiliary: 0.2 Nebulizer: 0.4	Plasma: 15 Auxiliary: 0.2 Nebulizer: 0.3, 0.4
Volume injected/μL	5	–
Liquid aspiration conditions	350 rpm (air)	25 μL min^{-1}

Emission lines/nm			
	Ag I 328.068	Cr II 267.716	Mg II 280.271
	Al I 396.153	Cu II 213.597	Mg II 279.077
	Ar 420.069	Cu I 324.752	Mn II 257.610
	Ba II 233.527	Cu I 327.393	Na I 589.592
	Ca II 317.933	Fe II 239.562	Ni II 231.604
	Cd I 228.802	Fe II 238.204	Pb II 220.353
	Co II 228.616	In II 230.606	Zn II 206.200
	Co II 238.892	K I 766.490	Zn I 213.857
	Cr II 205.560	Li I 670.784	Zn II 202.548
		Mg I 285.213	
RF power/W	1400		
Number of replicates	5		

3. Results and discussion

3.1. Drop size distribution

Fig. 1 plots the median of the volume drop size distribution (D_{50}) for the primary aerosols and the ethanol solutions considered in Table 1. It was verified that the higher the ethanol content the lower the D_{50} mainly because of the reduction in surface tension. Also interesting was the fact that the bioethanol samples provided aerosols with different D_{50} values. This was clearly due to a modification in the ethanol content and anticipated the appearance of a

Table 1
Physical properties for a series of samples with different ethanol contents.

Samples	Ethanol content (%, v/v)	Density (g mL^{-1})	Surface tension (mN m^{-1})	Viscosity (mPa s)
Water	0	1.0021 ± 0.0006	72	0.8909
Water/EtOH	50	0.942 ± 0.003	29.1 ± 1.0	2.131 ± 0.003
EtOH	96	0.814 ± 0.004	21.98 ± 0.09	1.249 ± 0.008
B5	70	0.882 ± 0.003	25.3 ± 0.8	2.038 ± 0.014
B2	93	0.827 ± 0.002	21.3 ± 0.5	1.412 ± 0.004
B7	98	0.825 ± 0.004	22.70 ± 0.14	1.359 ± 0.010
B3	100	0.801 ± 0.002	20.9 ± 0.5	1.240 ± 0.008
B8	55	0.910 ± 0.003	27.5 ± 0.2	2.19 ± 0.03