Measurements of Ethanol Traces in Natural Waters Using a DMFC Enzymatic Device and Chemometric Application

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Abstract

The use of ethanol in fuels and biofuels, in variable amounts, in some cases even higher than 10%, especially in countries such as Brazil, Australia, US, etc., appears to result in benefits, from the point of view of air pollution decrease, however, at the same time, it seems to cause problems in some natural waters, since it was noted that ethanol increases the solubility of BTX in natural waters, and, at the same time, exert diauxic effects during BTX biodegradation, slowing the bioremediation process. The research of new methods for the measurement of ethanol, inexpensive and able to operate in situ, are thus increasing. An original method, which uses a enzymatic direct catalytic fuel cell (DMFC) for the analytical determination of methanol and ethanol in all natural waters, for instance in rain and river waters, is proposed and applied in the present communication. The measurement, on the same water samples, also of other analytical parameters, has allowed the application of PCA on all the obtained experimental analytical data.

Introduction

The ethanol enrichment of unlead gasoline, but also other fuels as diesel and biodiesel, is a problem of considerable importance. In fact, although there are many arguments in favor of fuels ethanol enrichment, such as a purported reduction in air pollutant emissions during engine cars combustion and a purported reduction in gas emissions and dependence of fossil fuels, however one of the aspect of the ethanol enrichment which is debated is the potential impact that ethanol-enriched gasoline has on natural waters, even for ethanol level of 10% in the gasoline (so called E10), taking into account that there are also close variations, such as E15 and E20, but even great variations, i.e. E85 (an 85% ethanol fuel), used in ethanol-fuelled and certain hybrid vehicles. In fact some studies, carried out in contaminated hydrocarbons sites of Brazil, shown that ethanol can enhance the solubilization of BTX (i.e. Benzene, toluene, xylene hydrocarbons) in natural waters and it might exert diauxic effects, i.e. a preferential substrate utilization, during BTX biodegradation [1]. Really it was reported that if the gasoline contain 22% ethanol (i.e. an easily degradable substrate) a lay period has been observed, during which ethanol is degraded before any significant BTX degradation occurs [1]. Therefore, since their introduction one or two decades ago, gasoline oxygenates such as ethanol has been mired in controversy. Following a protracted public debate (which, in a first time, mainly focused on the potential damage to car engines and components) the Australian government demanded that from July 2003 it would limit the ethanol content of gasoline to 10%. On the other hand the political dimensions of the ethanol-in-gasoline debate are broadly similar to the US and Canada.

Materials & Methods

For ethanol (really total alcohols) measures, a DMFC H-TEC Model F111 small fuel cell, weighing about 100 g, was obtained from the Fuel Cell Store (College Station, TX, USA). The electrode area was about 4 cm^2 and maximum generated power 10 mW. The fuel cell frame was made in Plexiglas®, while the electrode end plate was made in Pt-Ru black catalyst, assembled with Nafion™ membrane. The dehydrogenase enzyme was placed in the anodic section of the cell, rinsed in a small dialysis membrane bag. For potentiostatic format measurement, Palmsens mod. EmStat potentiostat was used, connected to fuel cell. The current supplied to the cell was recorded and collected with data interface by PSTrace Software ver. 4.6 to Compaq Presario PC. Using the fuel cell working in potentiostatic format mode [2], an optimized potential (OAP) [2], was applied,

experimentally established in a previous paper [2] (i.e., OCV minus 100 mV). The dissolved oxygen in the analyzed water samples was measured using an amperometric electrode Amel 332/P and a dissolved oxygen meter Amel 360; the pH measurements were carried out by a pH meter GLP 22 Crison using a pH electrode 52-02 Crison. Lastly temperatures measurement were performed by internal temperature probe TC-100, connected to dissolved oxygen meter Amel 360.

Results

To better clarify the above cited controversial aspects few authors have been conducted a series of experimental studies on the effect that, the presence of ethanol, produces in the natural bioremediation perspective for BTX in natural waters [1]. The most of these studies concerns the transport and contemporary degradation of ethanol overall in groundwater [3]. These studies are mainly of "modellistic type", because in effects little or nothing it is reported in the literature on real ethanol concentrations in natural waters, also owing its rapid and large variability. Since recently our research group has experienced the possibility to use for analytical purposes, a small enzymatic direct catalytic fuel cell for methanol, or ethanol determination [2, 4], obtaining good results and performing numerous applications operating in real hydroalcoholic matrices, using this device, that were more than satisfactory [3], we considered that maybe interesting to use this analytical device, both to determine the ethanol content in different samples of natural waters (in effects what was measured it was the sum of the ethanol and methanol eventually contained) and to verify if the method can be applied throughout the field of concentrations of ethanol content used in the modellistic works cited above [1, 3]. To this end we carried out a number of different ethanol standard additions to rain and river water samples (that were totally devoid of traces of alcohols), by controlling the values of recoveries obtained, with the standard addition method, using the enzymatic catalytic fuel cell above described. Finally, as on the different samples of the analyzed waters, were measured also pH, the dissolved oxygen content (by a Clark electrode) and temperature values, we used all the obtained values, coming from the measures of the four different considered parameters, for a chemometric application, processing them by the Principal Components Analysis (see Fig. 1).
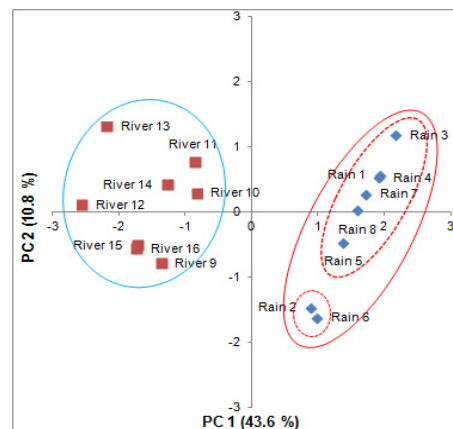

Fig 1: Scores representation

Conclusions

The "scores" of PCA representation showed that two first principal components are able to separate all the samples into two clusters, one of which groups together the samples of rain water, the other groups the river water samples, while the loadings representation showed that the pH values give the main contribution to two clusters separation, and the ethanol content single out two subclusters. The results obtained using the standard addition method, on analyzed rain and river water samples, cannot be called perfect, but certainly acceptable, in fact, do not deviate more than 15% from the expected nominal values (one have to take into account besides the high volatility of ethanol, which greatly affects the measurement accuracy), while the repeatability of the measure has generally been more than satisfactory. This confirms the validity of the proposed method, which is also inexpensive, quick and simple to apply.

References

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