Determination of water in ethanol by near infrared spectrometry

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Introduction

Near infrared (NIR) spectroscopy has been used for the determination of ethanol in complex mixtures, for which multivariate modelling has shown to produce the best results in terms of reducing the standard error of prediction (*SEP*). The literature describes NIR-based methodologies for determination of ethanol in beverages[1,2] and at least two papers have been published aimed at the determination of low water content in solvents, including ethanol.[3,4] Also, a method was recently developed for determining ethanol in gasoline, demonstrating that the number of variables employed in a multivariate linear regression (MLR) could be reduced by using genetic algorithms and used with advantage in relation to PLS modelling employing all the available data.[5] All previous works employed multivariate calibration which is justified by the complex matrices shown by the beverages and mixed fuels where, among others, sugar and a series of hydrocarbons can be present in high concentrations, severely affecting the absorption spectrum in the NIR region.

In Brazil, most of the ethanol employed as fuel comes from the fermentation of sugar cane juice. Two main products result from fermentation and distillation; the anhydrous ethanol, containing 0.2 to 1.0 % (w / w) water and the azeotropic mixture, containing about 7.5% (w / w) of water.[6] These are, indeed, noble products with a high degree of purity. In fact, the amount of all the other substances that can be found in the final product is lower by 0.1%. Absolute ethanol is mixed with gasoline in proportions of up to 26% (v / v), while the hydrated product is employed directly as fuel. Adulteration of the fuel can easily be accomplished because water and ethanol are soluble in all proportions. In this way, the quality control of the fuel is based mainly on the determination of its water content. This content is also important in controlling the quality of the ethanol to be mixed with the gasoline because higher water content causes phase-splitting and can severely damage car engines.

The specifications for both fuel products ensure that the methodology employed should be capable of accessing the water content with absolute precision, equal or better than 0.1%[6]. The standard method employed in the distillery is based on the density measurement of the final product. However, this method is not suitable for use in process control and requires long thermal equilibration times before the final density reading can be obtained, even when modern densitymeters are used.

This paper describes a detailed investigation of the use of NIR spectroscopy for the determination of water in ethanol from the fuel industry in order to define the best procedure to be employed in its quality control involving in-line monitoring of the water content in distillates and in the final product sold by fuel stations.

Experimental

Instruments

NIR absorbance spectra, in the range from 900 to 2200 nm, were obtained by using a home-assembled, dual-beam spectrophotometer. Two acousto-optical tunable filters (AOTF) (Brimrose, models TEFUH.80-1.6 and TEFUH1.5-2.4) were employed in a configuration that exploits the two monochromatic beams which emerged from the device to produce the reference and measurement beams.[7] A quartz cuvette with 2 mm optical path was employed for the spectrum acquisition. The overall precision of the absorbance measurements was 0.00070 A.

Ethanol–water solutions

Twenty-six solutions containing water in ethanol, in the range 0.20–10.0% (w / w), were prepared by using 99.80% ethanol (Merck) and deionised water. Prepared solutions were labelled P1 to P26. The following concentration range and approximate concentration increment (CI) were selected, aiming to produce standards and validation solutions for the range of interest in which water is present in samples of absolute and hydrated ethanol: P1–P8, 0.20–1.95%, CI = 0.20%; P9–P26, 3.50–10.96%, CI = 0.50%.

Software and hardware facilities

For multivariate data analysis the software package, Unscrambler 6.0 (CAMO, Trondheim, Norway), was used. Origin 4.1 software was used for producing graphics. The computer facilities included an IBM compatible Pentium 233 MHz with a hard disc of 3 Gbytes and 32 Mbytes of RAM both for hardware control and data treatment.

Results and discussion

Figure 1 shows a collection of 26 spectra obtained for the solutions P1–P26 [water content in the range 0.20%–10.0%(w / w)]. The spectra are dominated by the combination band and first overtones of the water O–H group at 1929 nm and 1445 nm, respectively. In the range 1630–1900 the overtones of the various C–H groups can be observed.
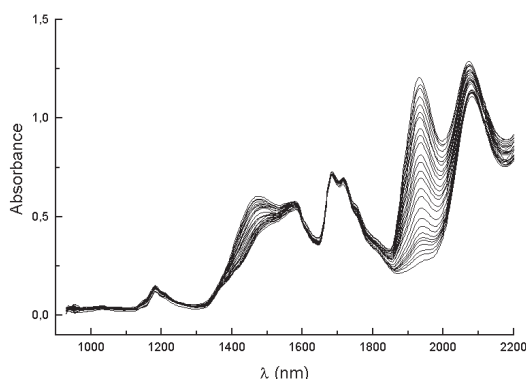

Figure 1. Set of 26 NIR absorbance spectra obtained for ethanol containing water in the the range 0.20–10.0% (w / w).

Multivariate modelling results

The data set shown in Figure 1 was mean centred and processed by the Unscrambler software PLS1 modelling. The results showed a standard error of calibration (*SEC*) and a standard error of prediction (*SEP*), respectively, equal to 0.16% and 0.14% for the water content determination in the range 0.20–10.0%. The *SEP* value was obtained by using a group of samples external to calibration. The *SEP* value obtained is not suitable for the specifications of the Brazilian Petroleum Agency, which requires that the water content should be known to within 0.10%. However, the multivariate analysis revealed that the most significant regression coefficients are, as expected by observation of the spectra in Figure 1, those related to the absorbances at 1929 and 1445 nm. The relative importance of the absorbance at 1929 is about four times greater than that at 1445 nm. A multiple linear regression (MLR) was attempted, employing only two wavelengths, which showed a slight improvement in the *SEC* (0.12%) but a deterioration in the *SEP* (0.18%).

Univariate results

A univariate calibration was also evaluated for both wavelengths. The results for linear and quadratic models applied to the absorbances at 1445 nm were not suitable and the *SEP* was about 0.3%. On the other hand, the absorbances at 1929 nm fitted very well in a quadratic model, producing an *SEP* of 0.07% for the range 0.20–10.0% of water in ethanol, as shown in Figure 2(a). A detailed observation of the range of interest for the anhydrous ethanol [0.20–3.00%(w / w)] revealed that the absorbances at 1929 nm fit in a linear regression with an *SEP* of 0.03%, as can be seen in Figure 2(b).

Conclusion

Samples with complex matrices, such as alcoholic beverages, containing diverse specimens, certainly need power-statistical tools to produce reliable results for the determination of a given constituent. In these cases, multivariate calibration appears to be essential, although some authors advocate the
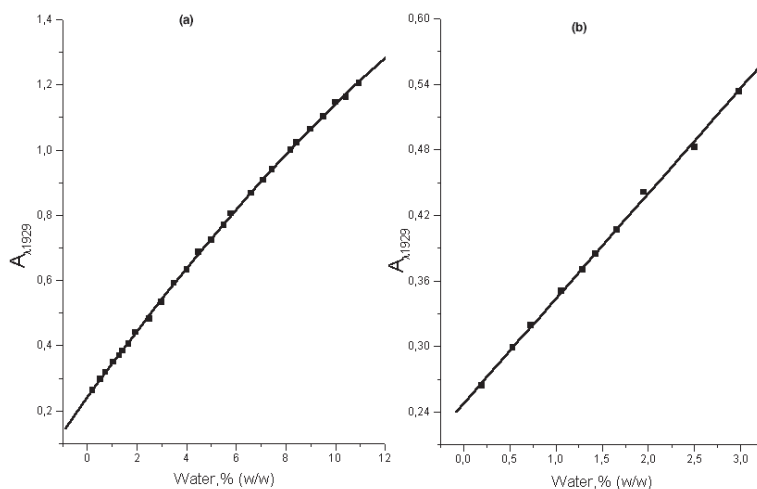

Figure 2. (a) Analytical curve for water determination in the range 0.20–10.0%, results of a quadratic regression applied to the absorbances at 1929 nm; (b) analytical curve for determination of water in the range 0.20–3.00% results for a linear regression of the absorbances at 1929 nm.

simpler and physical–chemical variably-driven selected calibration.[1,3] The determination of water in ethanol, produced for the fuel industry by the distilleries, requires a simple method capable of being used in-line in the distillation plant. The product has a high purity and spectral features, due the presence of water, are easily identified and provide enough information for its determination.

The results shown in this work allow us to conclude that, for the determination of water in fuel ethanol, the univariate method presents better results. The method is very simple and robust, being less affected by the precision on the wavelength because only a peak absorbance value is employed. These facts allow us to anticipate the production of a simple, filter-based instrument that can ensure the requirements for water determination in absolute and hydrated fuel ethanol are met.

Acknowledgements

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