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Analysis of Bioethanol Impurities with the Spectrum Two FT-IR Spectrometer

Figure 1. The Spectrum Two FT-IR Spectrometer.

Introduction

The intensifying global emphasis on developing sustainable fuel supplies has led to increasing use of fuels derived from biological sources. The most important of these are biodiesel (produced by transesterification of plant and animal oils and fats) and bioethanol, which is produced by fermentation of sugars, starches and, increasingly, cellulose from a range of crops including corn, sugarcane, wheat and sugarbeet.

The fermentation produces a complex mixture of ethanol and byproducts, from which the ethanol is isolated by distillation. The performance of the ethanol as a fuel is dependent on its purity, and international standards such as ASTM® D4806 and EN 15376 limit the allowable concentrations of impurities in fuel ethanol and specify the test methods to be used. At present, the specified tests are time-consuming chromatographic and titrimetric methods, so a rapid spectroscopic method such as FT-IR could provide an attractive alternative.

In this note we show that the Spectrum Two™ FT-IR spectrometer (Figure 1) can be used to develop a quantitative method with sufficient sensitivity to meet the required detection limits for methanol, water, C_3–C_5 alcohols and gasoline denaturant, while requiring less than two minutes of analysis time per sample.

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Experimental

A feasibility study was conducted by preparing 60 mixtures of ethanol with water (0–1% m), methanol (0–1% m), 1-propanol (0–1.7% m), 1-butanol (0–1.7% m), 1-pentanol (0–1.7% m) and petroleum spirit (0–7% m). The experiment was designed to cover a large number of levels of each analyte and to account for 2-factor interactions; higher-order interactions were not considered.

The spectra were measured on a PerkinElmer Spectrum Two™ FT-IR spectrometer, using a 0.1 mm liquid flow cell with BaF_2 windows. The flow cell allowed samples to be injected and drained to waste rapidly, for a total analysis time of ~2 minutes per sample, with negligible carryover.

Results and Discussion

Some of the measured spectra are shown in Figure 2. Due to the long pathlength, the strong bands of ethanol are saturated. Small absorption features due to the impurities are evident throughout the spectrum. Due to the large number of species present, the bands are overlapped and it is not reasonable to build calibrations based on single wavelengths.

Spectrum Quant+ software was used to build and cross-validate full-spectrum PCR models for all of the analytes. The default software settings were used, and good results were obtained without any manual adjustment of the model parameters. The results of the cross-validation are shown in Figure 3 below.
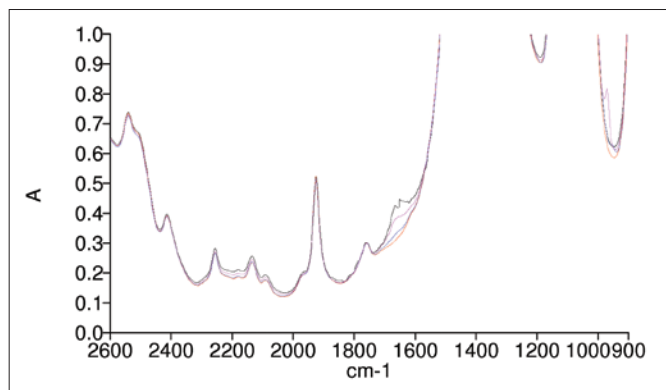

Figure 2. Some typical spectra of contaminated ethanol samples.
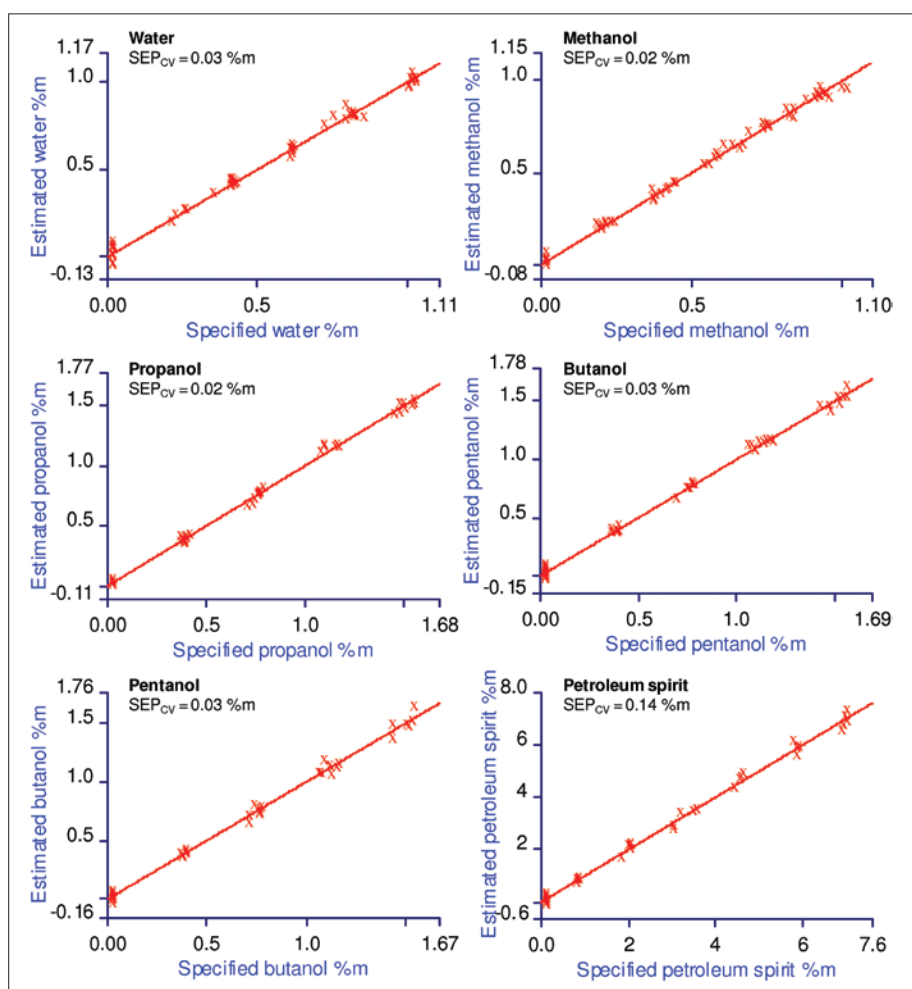

Figure 3. Cross-validation plots for quantitation of impurities in ethanol.

Conclusions

Defining the detection limit conservatively as 5× the SEP and comparing it with the maximum allowable impurity concentrations (see Table 1), it can be seen that the FT-IR method has promise. All of the impurities are detectable at levels well below the specified limits for both ASTM® D4806 and EN 15376. Furthermore, all of these impurities are detected simultaneously within a two-minute measurement.

The Spectrum Two instrument was designed with demanding quantitative applications like this in mind, and combines excellent sensitivity with a compact and robust chassis together with a full-featured software suite. The patented AVI™ technology standardizes the abscissa and lineshape of each instrument against a "virtual" reference, vastly reducing variation between instruments and in many cases permitting the application of a single calibration model across many instruments without the need for complicated calibration transfer procedures.

While the feasibility of this method has been demonstrated, it must be emphasized that, in a realistic application, greater variability among the samples may be encountered. For example, additional C_3–C_5 alcohols may be present. Gasoline, which may be present as a denaturant, is itself a highly variable mixture. Accordingly, implementation of the method will require careful development and maintenance of calibration models built on realistic, representative sets of accurately characterized samples.

Table 1. **Ethanol impurities: maximum levels compared with FT-IR detection limits.**

Parameter	ASTM® D4806	EN 15376	FT-IR LOD (5xSEP)
Water	1.0% v (1.3% m)	0.3% m	0.15% m
Methanol	0.5% v (0.5% m)	1.0% m	0.12% m
C_3–C_5 alcohols	N/A	2.0% m	0.48% m
Gasoline (denaturant)	1.96–5.0% v (~2-5% m)	N/A	0.7% m

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