Development and validation of an environmentally friendly attenuated total reflectance in the mid-infrared region method for the determination of ethanol content in used engine lubrication oil

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ABSTRACT

Lubricating oils are crucial in the operation of automotive engines because they both reduce friction between moving parts and protect against corrosion. However, the performance of lubricant oil may be affected by contaminants, such as gasoline, diesel, ethanol, water and ethylene glycol. Although there are many standard methods and studies related to the quantification of contaminants in lubricant oil, such as gasoline and diesel oil, to the best of our knowledge, no methods have been reported for the quantification of ethanol in used Otto cycle engine lubrication oils. Therefore, this work aimed at the development and validation of a routine method based on partial least-squares multivariate analysis combined with attenuated total reflectance in the mid-infrared region to quantify ethanol content in used lubrication oil. The method was validated based on its figures of merit (using the net analyte signal) as follows: limit of detection (0.049%), limit of quantification (0.16%), accuracy (root mean square error of prediction=0.089% w/w), repeatability (0.05% w/w), fit (R^2=0.9997), mean selectivity (0.047), sensitivity (0.011), inverse analytical sensitivity (0.016% w/w^{-1}) and signal-to-noise ratio (max: 812.4 and min: 200.9). The results show that the proposed method can be routinely implemented for the quality control of lubricant oils.

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1. Introduction

Automotive lubricant oils are complex mixtures of hydrocarbons and additives. These formulations provide appropriate compositions that promote the reduction of friction between the parts, protection against corrosion and rust and coolant action, among others. Despite the need for high-quality lubricant to preserve engines, the lubricant can be contaminated during use with fuels and coolant agents. These contaminants interfere directly with the lubricant properties, altering its quality. These alterations could lead to irreversible engine damage [1].

The need to reduce greenhouse gases and dependence on fossil fuels has been increasing ethanol use because ethanol can be obtained from renewable resources [2]. Furthermore, ethanol fuel can be used in flexible-fuel automotive engines that work not only with gasoline but also with hydrous ethanol (such as in Brazil) or anhydrous ethanol blended with petrol fuel (such as in Brazil, the USA and Europe) in any ratio.

Many standard methods have been successfully applied to the routine analysis of lubricant oil contaminants, such as gasoline [3], diesel [4], water [5] and ethylene glycol [6,7]. However, to the best of our knowledge, no method has been described for ethanol quantification in used engine oils.

Infrared spectroscopic methods, both mid-infrared (MIR) and near-infrared (NIR), combined with multivariate analysis are being used to evaluate biofuels quality [8–10], as well as for determination of contaminants in lubricant oil [1,11] and quantification of moisture in lubricant oils, combined with solvent extraction approach [12].

According to the International Vocabulary of Metrology (VIM), the term "validation" refers to proving that the specified requirements are adequate for an intended use [13]. To validate a univariate method, the International Union of Pure and Applied Chemistry (IUPAC) introduced a well defined set of rules. For multivariate calibrations, the analytical division of IUPAC recommends the use of the net analyte signal (NAS) theory to calculate figures of merit (FOM) [9,14].

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The NAS is defined as the part of the analytical signal related to the analyte of interest alone and orthogonal to the space containing the interferences [9,15]. The validation of multivariate methods using the FOM calculated by NAS theory has been applied in the scientific literature [9,14,16–18].

Therefore, this work presents the development and validation of a model based on partial least-squares (PLS) multivariate analysis combined with attenuated total reflectance (ATR) in the mid-infrared region and a solvent extraction approach to quantify ethanol in used Otto cycle engines lubricant oil samples.

2. Experimental

2.1. Samples

Sixty-eight standard samples were prepared by adding appropriate amounts of ethanol between 0.1% and 10% (w/w) to CASTROL® SLX 5W40 automotive lubricant oil. Each sample was vigorously stirred to guarantee effective mixing. Real samples of used lubricant oils (from automotive tests) were provided by Cempeqc (Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil and Derivatives).

2.2. Karl Fischer analysis

The water content determinations were conducted according to ASTM D6304 [5] in a coulometric Karl Fischer titrator, model 831 (Metrohm, Herisau, Switzerland).

2.3. Chromatographic analysis

The analysis was carried out using a gas chromatograph model GC-2010 (Shimadzu, Tokyo, Japan) equipped with a split/splitless injector, a flame ionization detector (FID) and an AOC-5000 auto sampler. An Rtx-1 (30 m, 0.32 mm, 3 μm) column was used. The PTV and FID temperatures were 300 °C. The oven temperature was held at 50 °C. Helium was used as the carrier gas at a linear velocity of 50 cm/s. The headspace conditions were a 2 mL sample volume (placed in a 20 mL headspace vial) with incubation at 80 °C for 45 min. A volume of 500 μL was injected into the system using a split ratio of 1:50.

2.4. Liquid–liquid extraction

A full factorial design (2^3) was performed to identify the significant parameters. The variables evaluated were heptane (viscosity reducer) content (2–4 g), agitation duration (5–15 s) and decantation duration (1–3 h). The absorbance in 1045 cm^{-1} was used as a response. NaCl 10% (w/v) aqueous solution was used as extractant. All experiments were performed using artificial lubricant oil samples with 3% (w/w) ethanol and 2% (w/w) water.

To ensure that the method was environmentally friendly, i.e., to use the least amount of solvent possible and make the method generally applicable, the extraction was performed in a miniaturized system comprised of a glass tube with 20 mL capacity capped with a silicon stopper. After agitation by vortexing, the lower aqueous layer was extracted using a syringe with a needle and measured in an ATR-MIR system.

2.5. ATR-MIR measurements

The samples infrared spectra were collected in the range of 4000 to 650 cm^{-1}, using 32 scans at 4 cm^{-1} resolution by a Nicolet 6700 FTIR (Thermo Scientific, Waltham, USA), equipped with the Smart ARK® (Thermo Scientific) ATR sampling accessory. The angle of incidence of the ZnSe crystal is 45°. The spectrum of 1 mL of extract added onto the crystal surface was collected. An air spectrum was used as the reference in the absorbance calculations.

2.6. Chemometric analysis

The quantitative evaluations were carried out using partial least squares (PLS) regression by Octave 3.2.4 [19], GUI Octave 1.0.14 [20] and TQ Analyst 8.0.1.30 software (Thermo Scientific). The selection of variables was made based on the differences between the spectra of absolute ethanol and the NaCl solution (Fig. 1) in the region between 1250 cm^{-1} and 808 cm^{-1}.

2.7. Validation

The validation was performed using the following FOM: accuracy, selectivity (SEL), sensitivity (SEN), analytical sensitivity (γ), linearity, precision, measuring interval, bias, limit of detection (LOD), limit of quantitation (LOQ) and signal-to-noise ratio (S/N). The FOM for multivariate calibration have been well described elsewhere [9,14,15] and are not described in detail here.

NAS theory was applied to calculate the SEL, SEN, LOD, LOQ and signal-to-noise ratio using the equations proposed by Ferré et al. (2001) [21]. Analytical sensitivity was calculated as (SEN/δx), where δx is the approximation of the instrumental noise estimated by the standard deviation of the NAS value for 15 spectra of the reference signal [17,18].

The relative standard deviation (RSD) of three real samples for different levels, with six replicates each of same-day measurements was used to represent the precision. The measuring interval was considered to be between LOQ and the highest concentration present in the calibration set of the model.

Bias is a term used to characterize systematic errors and was calculated using a *t* test to determine if the predicted values show a statistically significant bias according ASTM E1655 [22], as follows.

First, the average bias for the estimation of the validation set was calculated as

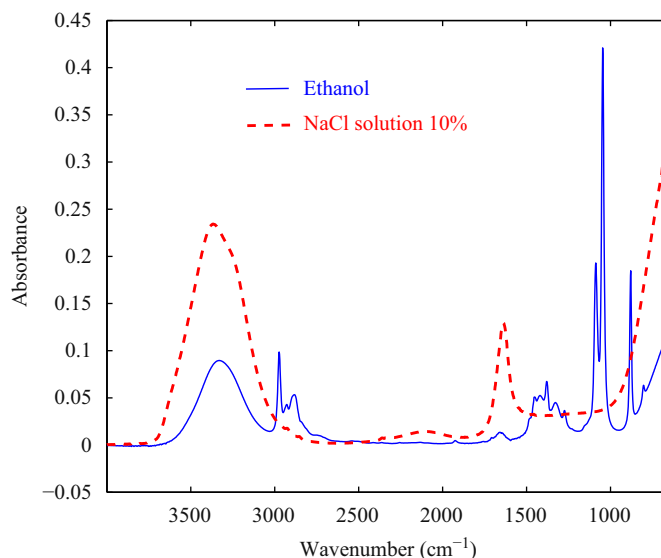$$bias = \frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i) \tag{1}$$

Fig. 1. Overlaid spectra of NaCl solution 10% (w/v) and absolute ethanol.