Talanta 109 (2013) 191–196

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

Rafael Rodrigues Hatanaka [a,*], Rodrigo Sequinel [a], Carlos Eduardo Gualtieri [a], Antônio Carlos Bergamaschi Tercini [a], Danilo Luiz Flumignan [a,b], José Eduardo de Oliveira [a]

[a] *UNESP–São Paulo State University, Institute of Chemistry, Center for Monitoring and Research of the Quality of Fuels, Biofuels, Crude Oil and Derivatives–CEMPEQC, 14800-900 Araraquara, SP, Brazil*

[b] *IFSP-São Paulo Federal Institute of Education, Science and Technology-Campus Avançado Matão, 15990–040 Matão, SP, Brazil*

ARTICLE INFO

Article history:
Received 1 November 2012
Received in revised form
4 February 2013
Accepted 5 February 2013
Available online 27 February 2013

Keywords:
Ethanol content
Lubrication oil
Validation
Infrared spectroscopy

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.

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].

---

* Corresponding author. Tel.: +55 16 33019504, +551633019666.
E-mail addresses: rrhatanaka@gmail.com, rrhatanaka@yahoo.com.br (R.R. Hatanaka).

0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.02.047

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

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

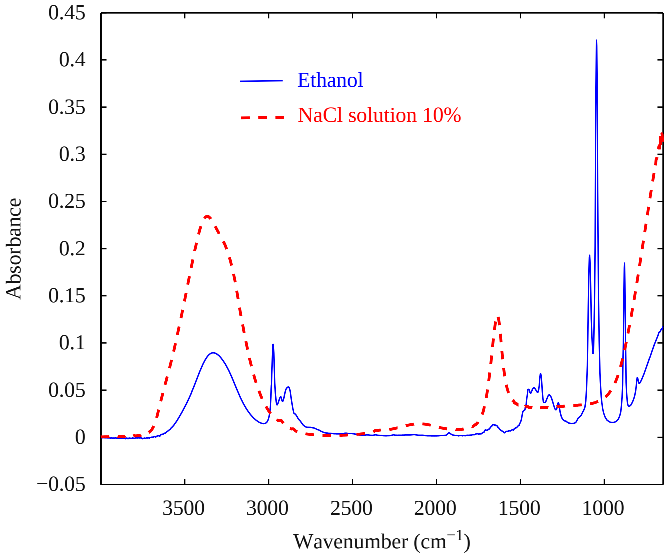

Fig. 1. Overlaid spectra of NaCl solution 10% (w/v) and absolute ethanol.

where n is the total number of reference values used in the calculation.

Next, the standard deviation of the validation errors (SVD) was calculated as

$$SDV=\sqrt{\frac{\sum\left[(y_i-\hat{y}_i)-bias\right]^2}{n-1}} \tag{2}$$

and the t value was calculated as

$$t=\frac{|bias|-\sqrt{n}}{SDV} \tag{3}$$

The t value was compared to critical t values (95%) for n degrees of freedom.

3. Results and discussion

3.1. Preliminary studies: attempt to quantify ethanol in lubricant oil using HS-GC-FID and ATR-MIR without sample pre-treatment

The initial aim of this work was to obtain an analytical method to quantify ethanol in lubricant oil without sample pre-treatment. Two techniques were tested: gas chromatography with flame ionization detection and headspace sampling (HS-GC-FID) and ATR-MIR. However, both techniques produced poor results. The first technique was ineffective due to the presence of water in the samples in concentrations from 0.02% to 5.89% (w/w) (Table 4), which causes physical interference in the HS analysis because the total pressure of the vapor phase in the headspace is equal to the sum of the partial pressures of all volatile compounds present in the sample. Practical experience has shown that the influence of volatile matrix components present at concentrations of less than approximately 1% can generally be ignored, whereas volatile matrix components above this concentration can significantly modify the composition of the headspace [23]. Table 1 shows the ethanol amount quantified by HS-GC-FID of three artificial samples with different amounts of water.

Next, the ATR-MIR technique was used for samples without pre-treatment; however, the results were also unsatisfactory. With the goal of studying the viability of this technique, the addition of different amounts of ethanol to the samples was achieved under vigorous agitation; however, the 1065 cm^{-1} band (alcohol C–O stretching vibrations) did not show significant changes in the absorbance values for the samples with high water content. This result can be explained by the degradation of dispersants in the lubricant oil, hindering the samples homogeneity.

3.2. Liquid–liquid extraction

The liquid–liquid extraction (LLE) was first performed with 10% NaCl solution alone; however, emulsions formed, most likely because of the presence of an emulsifying additive in the lubricant oil. Because of the high viscosity of the samples (kinematic viscosity at 40 °C, ~80 cm^2/s), heptane (kinematic viscosity at 40 °C, 0.52 cm^2/s) was used as a viscosity-reducing solvent. A 2^3-factorial experimental design was implemented to optimize the heptane amount, agitation and decantation times. The Pareto chart (Fig. 2) shows that only the agitation time is significant; therefore, the other three factors were fixed at their lower levels (heptane amount=2 g; decantation time=1 h), and the agitation time was optimized. Fig. 3 shows that the difference in ethanol content is not significant after 30 s of agitation; therefore, this time was used.

Table 1
References and HS-GC-FID values for ethanol content for three standards with different water contents.

Sample	Ethanol content [% (w/w)]	Water content [% (w/w)]	HS-GC-FID ethanol content [% (w/w)]
1E1W	1.00	1.00	0.99
1E3W	1.00	3.00	0.32
1E5W	1.00	5.00	0.17

3.3. ATR-MIR spectra

Fig. 4 shows the spectra of different samples that were recorded in the range of 4000–650 cm^{-1}. It is possible to observe bands at approximately 1180–840 cm^{-1} that correspond to C–O and C–C–O stretching modes. C–H stretching absorption can be observed at 2900 cm^{-1}, and water bands are observed at 3450 cm^{-1} and 1650 cm^{-1} [24].

3.4. PLS regression

The best model was obtained using the C–O and C–C–O stretching region (between 1250 cm^{-1} and 808 cm^{-1}) and multiplicative scatter correction (MSC) pre-processing data. Only two latent variables were selected based on the RMSECV value calculated by the cross-validation leave-one-out procedure. Only a few latent variables are observed due to the LLE pre-treatment and the variable selection, which removes most of the interferents.

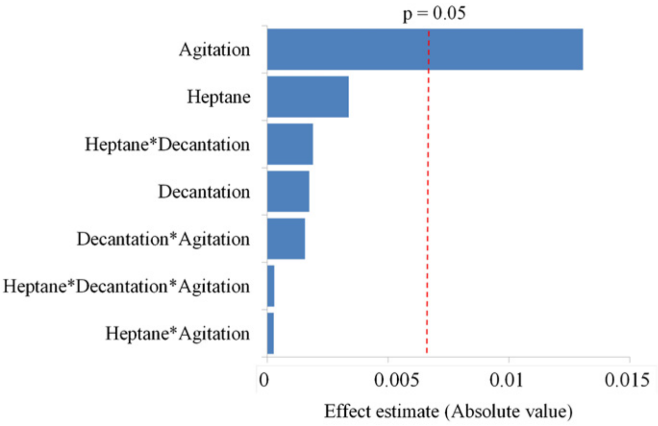

Fig. 2. Pareto chart for the full factorial design.

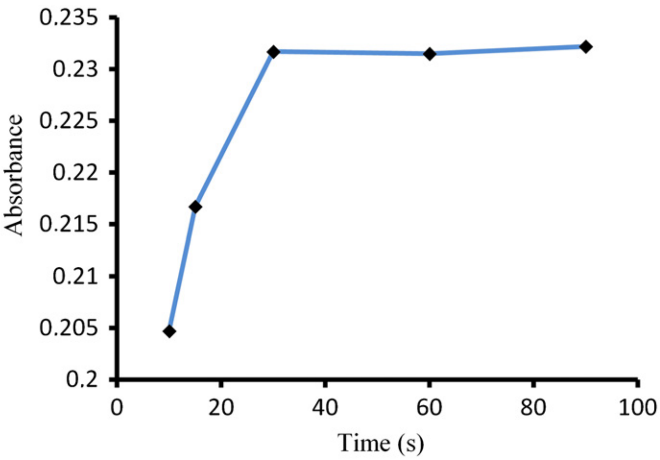

Fig. 3. Optimization of agitation time.

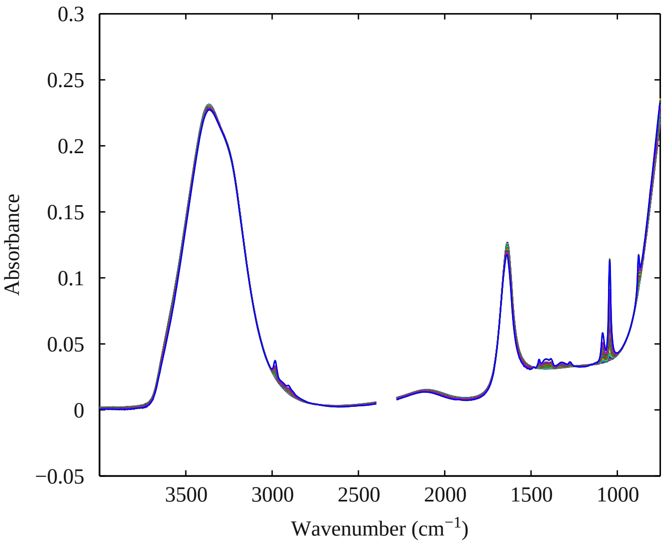

Fig. 4. Spectra of different samples recorded in the range of 4000–650 cm^{-1}.

Table 2
FOM of the proposed method.

FOM	Parameter	Value
Accuracy	RMSECV	0.082%
	RMSEC	0.084%
	RMSEP	0.089%
Precision	RSD repeatability	0.05% (w/w)
Linearity	Correlation coefficient	0.9997
	Slope	0.996
	Intercept	0.0062
Measure interval		0.16–10%
Selectivity		0.047
Sensitivity		0.011% (w/w)$^{-1}$
Analytical sensitivity (γ)		61.24% (w/w)
γ^{-1}		0.016% (w/w)$^{-1}$
Limit of detection		0.049% (w/w)
Limit of quantitation		0.16% (w/w)
Signal-to-noise ratio	Maximum	812
	Minimum	201
Bias	*t* value	0.627
	t critical	2.36

Table 3
Replicates of three real samples to estimate the precision at the level of repeatability.

Sample	Ethanol content [% (w/w)]	Average [% (w/w)]	RSD (%)
OL32	1.45	1.52	0.04
	1.54		
	1.50		
	1.55		
	1.52		
	1.56		
OL18	4.69	4.68	0.05
	4.60		
	4.66		
	4.69		
	4.70		
	4.77		
OL41	7.53	7.58	0.04
	7.62		
	7.53		
	7.60		
	7.61		
	7.57		

Outliers were not observed in the model, most likely because of the LLE pre-treatment.

3.5. Validation

Table 2 shows the main FOM of the proposed method. The accuracy was measured using the model's errors values, RMSECV, RMSEC and RMSEP, which show that the predicted values for ethanol were in accordance with the reference values.

Precision, at the level of repeatability, was calculated by analyzing three real samples at different levels (Table 3). The relative standard deviation (RSD) values obtained were 0.05%, which represents the good repeatability of the multivariate model.

The fitting of the model was evaluated by the correlation coefficient of the line adjusted between the reference and predicted values (Fig. 5). The value of the correlation coefficient is

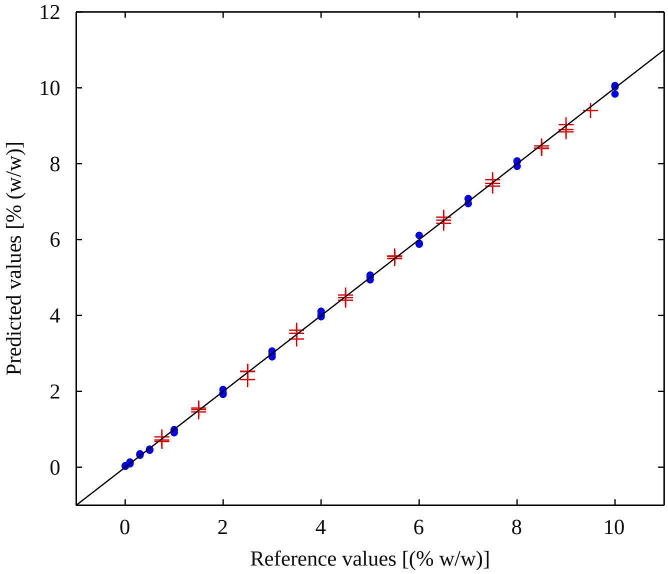

Fig. 5. Plot of reference versus predicted values for the calibration (circles) and validation (crosses) samples.

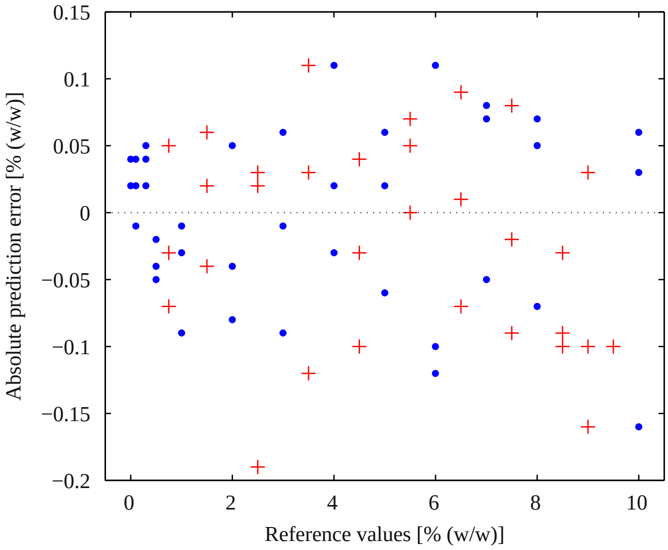

Fig. 6. References values for ethanol versus the absolute prediction error. Calibration samples (circles) and validation samples (crosses).

close to unity, indicating an excellent fit of the model to the real values.

The selectivity of the method indicates the part of the measured signal that is unique to the analyte of interest and is used for the multivariate calibration model [9,25]. The result presented in Table 2 shows that 4.7% of the signal was used in the calibration of ethanol.

Sensitivity can be defined as the fraction of an analytical signal that is responsible for a unit increase in the concentration of a particular analyte. In inverse multivariate calibration models (such as PLS), the sensitivity can be calculated as the inverse of the vector of the regression coefficients or by taking into account the net analyte signal. Conversely, the analytical sensitivity (γ) is a simpler and more informative FOM for assessing the sensitivity of an analytical method. The analytical sensitivity is calculated using the relationship between the sensitivity and the estimate of the instrumental noise. The minimum concentration difference discernible by the analytical method can be estimated by the inverse of this parameter (γ^{-1}) [9,14,15,25]. Based on this result, it is possible to differentiate samples with a 0.016% ethanol concentration difference (Table 2).

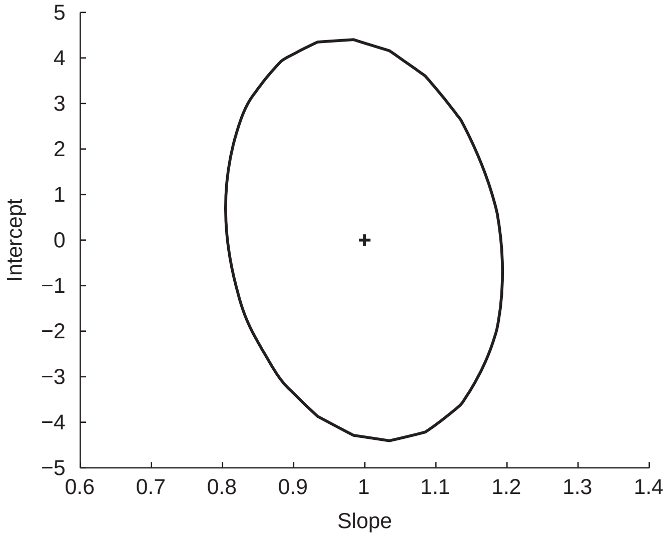

Fig. 7. Elliptical joint confidence region (at 95% confidence level) for the slope and intercept of the regression line of predicted versus reference values.

In the case of this study, it is not possible to construct traditional calibration curves for evaluating linearity, which are meant for univariate methods. Thus, the linearity is evaluated qualitatively by the observation of the distribution of the residuals in both calibration and validation samples, which should be random [15]. Fig. 6 shows an approximately random behavior in the distribution of errors.

Table 2 shows the maximum and minimum signal-to-noise ratios observed for the method. The fraction of signal related to the analyte is at least 201 times greater than the noise.

Fig. 7 shows the elliptical joint confidence region [26] (at 95% confidence level) for the slope and intercept of the regression line of predicted versus reference values. The ellipse contains the ideal point (1,0) for slope and intercept, respectively, showing that the reference and predicted values are not significantly difference at the 95% confidence level. Also, it is possible to conclude that no systematic errors were observed in the calibration.

Bias was tested using the prediction results for the validation samples according to the *t* test established in ASTM E1655 [22]. The results showed that the bias included in the model was not significant because the *t* value obtained (see Eq. (3)), 0.627, was lower than the critical value, 2.034. This result indicates that the predicted and reference values have essentially the same average result as measurements conducted by the reference method (weighing in this work).

3.6. *Quantification in real samples*

After the validation of the method, real samples were analyzed to study the applicability of the proposed method. Fifty-nine real samples were analyzed according to ASTM D6304 and the proposed method to quantify water and ethanol content, respectively. The results are shown in Table 4. The measurement interval of the proposed method covers 84.7% of the range of ethanol content in the samples. The remaining 15.3% were below the LOQ (nine samples: OL9, OL11, OL14, OL23, OL34, OL38, OL46, OL52 and OL56).

Table 4
Determination of water content by ASTM D6304 and ethanol content in used lubricant oil by the proposed method.

Sample	Water content [a]	Ethanol content [a]	Sample	Water content [a]	Ethanol content [a]	Sample	Water content [a]	Ethanol content [a]
OL01	1.24	1.04	OL21	4.82	2.20	OL41	3.52	7.53
OL02	2.22	1.81	OL22	3.27	2.71	OL42	0.04	0.20
OL03	3.43	2.13	OL23	0.17	0.08 [b]	OL43	1.56	3.51
OL04	0.18	0.19	OL24	1.34	3.33	OL44	2.27	4.98
OL05	1.34	3.17	OL25	2.28	4.16	OL45	0.05	0.10 [b]
OL06	2.17	5.55	OL26	4.02	9.41	OL46	1.34	2.79
OL07	0.16	0.47	OL27	0.13	0.19	OL47	2.46	4.47
OL08	3.71	5.09	OL28	1.93	2.18	OL48	1.07	1.98
OL09	0.18	0.03 [b]	OL29	2.61	1.81	OL49	2.03	3.26
OL10	2.73	4.59	OL30	0.10	0.35	OL50	3.83	6.15
OL11	0.10	0 [b]	OL31	1.29	2.97	OL51	0.08	0.04 [b]
OL12	1.20	2.34	OL32	1.51	1.03	OL52	1.36	2.82
OL13	2.49	3.54	OL33	2.91	1.32	OL53	2.24	4.22
OL14	0.17	0.08 [b]	OL34	0.16	0.11 [b]	OL54	3.61	5.86
OL15	1.33	3.08	OL35	1.32	2.54	OL55	0.04	0.04 [b]
OL16	2.39	4.40	OL36	2.22	3.39	OL56	2.63	4.11
OL17	1.52	2.62	OL37	3.56	5.58	OL57	2.13	4.11
OL18	3.23	4.69	OL38	0.08	0.08 [b]	OL58	2.28	4.11
OL19	3.53	3.43	OL39	1.16	2.86	OL59	4.54	4.76
OL20	1.30	2.79	OL40	1.61	3.84			

[a] [% (w/w)]
[b] Below LOD

Table 5
Results of the addition and recovery study.

Sample	Ethanol content [% (w/w)]	Added ethanol (%)	Detected ethanol (%)	Recovery (%)
OLAZ	0.28	0.30	0.65	112.0
OL48	1.07	1.00	1.93	93.5
OL43	1.56	1.50	3.28	107.1
OL10	4.49	4.50	8.76	97.4

Because the used lubricant oil samples are complex mixtures, a study was conducted by addition and recovery (Table 5) to determine the potential interference of the matrix in the described method.

The results obtained for the FOM and the real samples show that the proposed method based on ELL-MIR and multivariate calibration can be implemented generally for the quality control of lubricant oils.

4. Conclusions

Because of the complexity of the samples, it was not possible to perform determinations by HS-GC-FID or ATR-MIR without pretreatment. Instead, a method based on ATR-MIR-PLS with LLE was developed and validated for ethanol determination in used lubricant oil samples. The developed method afforded a simplified and low-cost procedure with low generation of chemical waste, making it environmentally friendly because the miniaturized LLE extraction was conducted using aqueous NaCl solution. This method was validated and considered linear, precise, accurate and sensitive in the range of 0.16% to 10.0% (w/w) ethanol. It was also applied to the practical determination of real samples from automobile industry tests, indicating its wide applicability.

This paper is part of the MSc dissertation of R.R. Hatanaka.

Acknowledgments

The authors would like to thank Capes, CNPq and Fundunesp for providing academic scholarships and Cempeqc for providing financial support and the samples.

References

[1] A. Borin, R.J. Poppi, Vib. Spectrosc. 37 (2005) 27–32.
[2] H.S.P. Carneiro, A.R.B. Medeiros, F.C.C. Oliveira, G.H.M. Aguiar, J.C. Rubim, P.A.Z. Suarez, Energy Fuels 22 (2008) 2767–2770.
[3] ASTM D3525-04,Standard Test Method for Gasoline Diluent in Used Gasoline Engine Oils by Gas Chromatography, ASTM International, West Conshohocken, PA, USA, 2010.
[4] ASTM D3524-04, Standard Test Method for Diesel Fuel Diluent in Used Diesel Engine Oils by Gas Chromatography, ASTM International, West Conshohocken, PA, USA, 2010.
[5] ASTM D6304-07, Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives by Coulometric Karl Fischer Titration, ASTM International, West Conshohocken, PA, USA, 2007.
[6] ASTM D2982-07, Standard Test Methods for Detecting Glycol-Base Antifreeze in Used Lubricating Oils, ASTM International, West Conshohocken, PA, USA, 2007.
[7] ASTM D4291-04, Standard Test Method for Trace Ethylene Glycol in Used Engine Oil, ASTM International, West Conshohocken, PA, USA, 2009.
[8] R.M. Balabin, R.Z. Safieva, Anal. Chim. Acta 689 (2011) 190–197.
[9] M.C. Sarraguça, J.A. Lopes, Anal. Chim. Acta 642 (2009) 179–185.
[10] F.V.C. de Vasconcelos, P.F.B. de Souza Jr, M.F. Pimentel, M.J.C. Pontes, C.F. Pereira, Anal. Chim. Acta 716 (2012) 10–107.
[11] M. Blanco, J. Coello, H. Iturriaga, S. Maspoch, R. González, Mikrochim. Acta 128 (1998) 235–239.
[12] E.-P. NG, S. Mintova, Microchem. J. 98 (2011) 177–185.
[13] Joint Committee for Guides in Metrology. International Vocabulary of Metrology–Basic and General Concepts and Associated Terms (VIM), third ed., 2012. Available at: 〈www.bipm.org/vim〉 (accessed 08.10.12).
[14] A.C. Olivieri, N.K.M. Faber, J. Ferré, R. Boqué, J.H. Kalivas, H. Mark, Pure Appl.Chem. 78 (2006) 633.
[15] M.A.M. Silva, M.H. Ferreira, J.W.B. Braga, M.M. Sena, Talanta 89 (2012) 342–351.
[16] M.A. Cantarelli, R.G. Pellerano, E.J. Marchevsky, J.M. Camiña, Anal. Sci. 27 (2011) 73–78.
[17] H.C. Goicoechea, A.C. Olivieri, Anal. Chem. 71 (1999) 4361–4368.
[18] A. Muñoz de la Peña, A. Espinosa-Mansilla, M.I. Acedo Valenzuela, H.C. Goicoechea, A.C. Olivieri, Anal. Chim. Acta 463 (2002) 75–88.
[19] 〈http://www.octave.org〉 (accessed 05.18.11).
[20] 〈http://guioctave.com/〉 (accessed 05.18.11).
[21] J. Ferré, S.D. Brown, F.X. Rius, J. Chemom. 15 (2001) 537–553.
[22] ASTM E1655-05, Standard Practices for Infrared Multivariate Quantitative Analysis, ASTM International, West Conshohocken, PA, USA, 2012.
[23] B. Kolb, L.S. Ettre, Static Headspace-Gas Chromatography: Theory and Practice, second ed., Wiley-Interscience, Hoboken, 2006.
[24] G. Socrates, Infrared and Raman Characteristic Group Frequencies, third ed., John Wiley & Sons Ltd, Baffins Lane, 2001.
[25] P. Valderrama, A.L. Romero, P.M. Imamura, I.R. Magalhães, P.S. Bonato, R.J. Poppi, Anal. Bioanal. Chem. 397 (2010) 181–188.
[26] J. Mandel, F.J. Linning, Anal. Chem. 29 (1957) 743–749.