Catalysis Today 155 (2010) 255–260

Contents lists available at ScienceDirect

Catalysis Today

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

# Combination of mid-infrared spectroscopy and chemometric factorization tools to study the oxidation of lubricating base oils

N. Gracia [a,b,c,*], S. Thomas [a], P. Bazin [a], L. Duponchel [b], F. Thibault-Starzyk [a], O. Lerasle [c]

[a] *Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen, France*
[b] *Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), CNRS-UMR 8516, Université des Sciences et Technologies de Lille (USTL), bât C5, F-59655 Villeneuve d'Ascq, France*
[c] *Centre de Recherche de Solaize, TOTAL, BP22 – F-69360 Solaize Cedex, France*

ARTICLE INFO

*Article history:*
Available online 31 December 2009

*Keywords:*
Lubricants
Oxidation
FTIR
Chemometrics
Principal Component Analysis (PCA)

ABSTRACT

The effect of the presence of iron as a catalyst during base oil oxidation has been studied. Fourier transform infrared (FTIR) spectroscopy was combined to Principal Component Analysis (PCA) in order to extract chemical information during oil oxidation process. After 8 h, the presence of iron did not lead to significant change in the global chemical composition as revealed by the first principal component. However, the second principal component indicated clearly that the initial formation of alcohols and esters was favoured by the presence of iron. The influence of iron was highlighted by PCA analysis of on-line FTIR data.

## 1. Introduction

Motor lubricants oils are used to reduce the frictions of the mobile components and to keep the different elements clean, being able to work either as detergents or as dispersant agents. They play other functions as tightness improvement, cooling action by removing the heat produced by the contact of moving parts and prevention of corrosion and rust against weathering and contaminative agents such as oxygen, water, acids, glycol, fuel, sulphur. Maintaining the quality of lubricants is essential because of their key role in machine duration and performance. Oxidation is one of the main causes of oil degradation. To prevent and reduce the consequences of this phenomena in the best possible way, mechanisms must be determined and well understood.

Lubricants are a combination of base oils and additives, the former in a proportion ranging from 70 to 99%. Additives are used to strengthen the features of the base oil and/or to supply additional properties to the lubricating oils. In an engine, oils are in contact with metallic particles that catalyze oxidation [1], and some additives are used to prevent this oxidation, by passivating metallic particles for example or by acting directly on oxidation mechanisms.

The first step proposed for the oxidation of paraffins [2,3] is the formation of hydroperoxides, which get decomposed to give ketones and aldehydes on one hand, and alcohols on the other. Ketones are then oxidised in carboxylic acids, which react with alcohols to form esters. Oxidation on both sides of one paraffinic molecule may lead to the formation of one alcohol function on one part and of one carboxylic acid function on the other, and results, after intramolecular esterification, in the formation of lactones. Iron is known to favour the formation of alcohols during lubricating oils oxidation [4] and to catalyze the reaction of esterification [5].

In order to obtain analytical informations in a rapid and non-destructive way, mid-infrared spectroscopy has been largely applied to the study of motor oils with different purposes: quantifying contaminants [6] or oxidation [7], determining additives [8] and studying their interactions [9], estimating chemical properties [10] and classification according to their origins [11].

The main idea of Principal Component Analysis (PCA) is to project the data from a high dimensional space onto a lower dimensional space. If the data compression is sufficient, the large number of variables is substituted by a small number of uncorrelated latent factors which can explain sufficiently the data structure. The new latent factors, also called principal components (PCs) are obtained by maximizing the variance of the projected data, or in other words, by computing the eigenvalues of correlation or covariance matrix of the samples. The data structure can be visualized directly in a graphical way by projection of

---

* Corresponding author at: Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen, France.
*E-mail address:* nadege.gracia@ensicaen.fr (N. Gracia).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.11.012

objects onto the space defined by selected PCs. In this way, it is possible to detect the main observations' distribution [12,13].

Nevertheless, the combination of mid-infrared spectroscopy and chemometric factorization tools has been scarcely applied to study the oxidation of lubricating oils.

Chemometric methods allow valuable information to be extracted from multivariate data arrays, which are difficult to handle using classical univariate statistical methods [14]. IR monitoring studies provide in our case large amounts of data, containing multiple parameters whose interpretation is far from simple. Chemometric methods provide tools for finding relationships between groups of analyzed samples and/or related variables or parameters. Moreover PCA has shown interest in the extraction of the underlying factors that cause the variation in the spectra during the oxidation of lubricant oil [15].

In this article on-line infrared spectroscopy was combined to PCA to better understand the role of iron as catalyst of base oils oxidation.

## 2. Experimental

### 2.1. Experimental setup

A sample of lubricating base oil (27 g) with 120 ppm of iron (III) acetylacetonate ($[CH_3COCH{=}C(O)CH_3]_3Fe$ in chloroform solution) was heated at 170 °C with a silicon oil bath (Fig. 1, A and B) under an argon flow (part C). After stabilization at the desired temperature, flow was switched to oxygen (30 cc/min). The oxidation was carried out during 8 h. The oil was circulated inside the infrared transmission cell ($CaF_2$ windows, 100 μm pathlength) (part D) by an electromagnetic pump (part E). Condensation products were collected in a trap (part F). Infrared transmission spectra (32 scans) were recorded at room temperature using a Nicolet Magna 750 II spectrometer, with a DTGS detector, with 4 $cm^{-1}$ spectral resolution, between 4000 and 980 $cm^{-1}$. A spectrum was recorded every 45 s. Each experiment was performed five times, with no significant spectral difference observed.

The use of iron as a catalyst is based upon lubricants standard test methods, in order to take into account the presence of metallic particles and soluble iron in engines. The concentration is based upon ASTM International Standard Test Method D 7214-07 [16]. A preliminary study was done, showing that an increased amount of catalyst has no influence on the results.

Experiments were stopped after 8 h, before the complete oxidation of the sample to avoid the introduction of high viscosity samples in the pump and in the transmission cell. Furthermore no other change than global intensity occured after 200 min or so.

### 2.2. Peak Area Increase

Peak Area Increase is used as a criterion evaluating the state of oxidation during the study, and is determined along the ASTM International Standard Test Method D 7214-07 [16]: FTIR spectra of the fresh oil and of the used oil are recorded in a transmission cell of known pathlength. Both spectra are converted to absorbance and then subtracted. Using this resulting differential spectrum, a baseline is set under the peak corresponding to the carbonyl region around 1650 and 1820 $cm^{-1}$ and the area between this baseline and the carbonyl peak is calculated. The area of the carbonyl region is divided by the cell pathlength in millimetres and this result is reported as Peak Area Increase (PAI).The PAI is representative of the quantity of all the compounds containing a carbonyl function that have formed by the oxidation of the lubricant (aldehydes, ketones, carboxylic acids, esters, anhydrites, etc.). The PAI gives representative information on the chemical degradation of the lubricant which has been caused by oxidation.

This method of integration was also applied for the $\nu$(O–H) vibrations region, between 3284 and 3587 $cm^{-1}$, and will be called as "3500 band area" in the next sections.

### 2.3. Chemometric analysis

PCA transforms a multivariate data array into a new data set in which the new variables are orthonormal and explain maximum

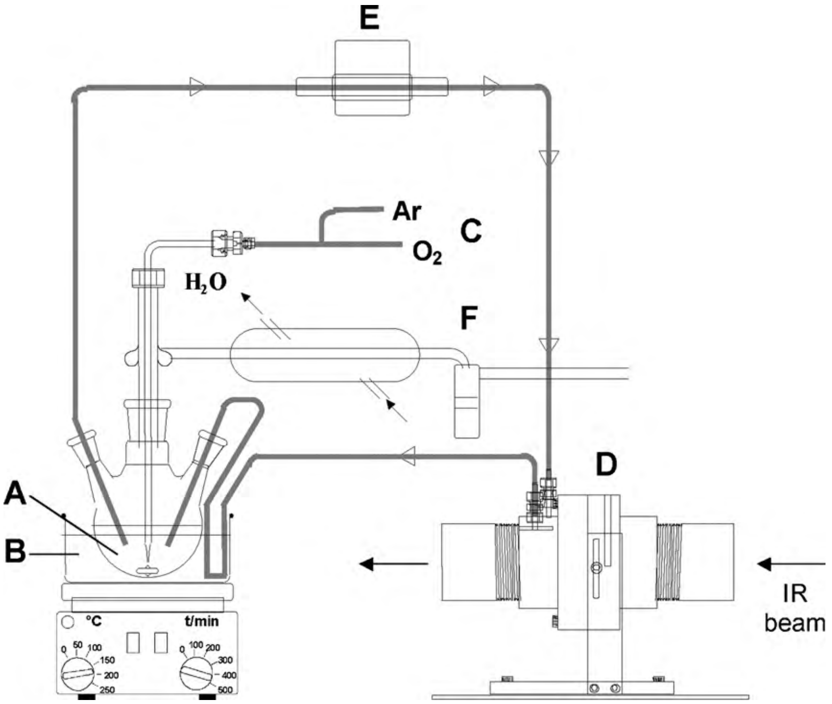

**Fig. 1.** Experimental setup.

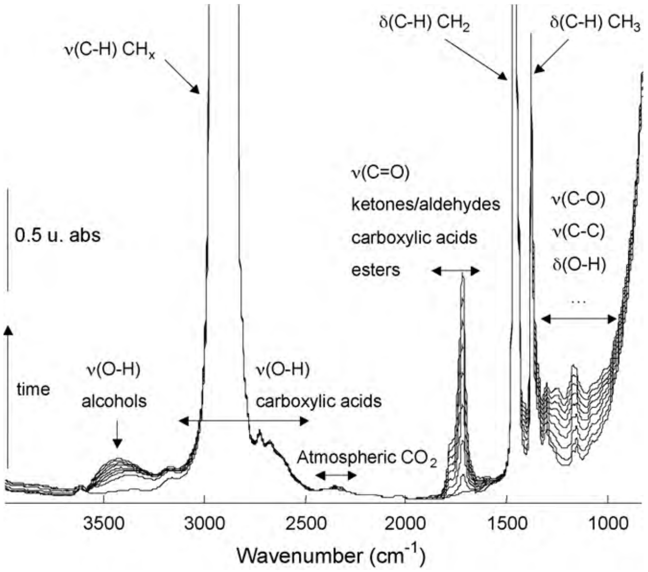

**Fig. 2.** Typical spectra observed during a base oil oxidation (one spectrum every hour).

variance [14]. It is based on the bilinear decomposition of the original data set:

$$D_{(I\times J)} = U_{(I\times N)}V^{\mathrm{T}}_{(N\times J)} + E_{(I\times J)}$$

where $D$ is the original data array, with $I$ rows (observations or here spectra) and $J$ columns (variables or here wavenumbers); $U$ is the matrix of scores of dimensions $I \times N$, where $N$ is the reduced numbers of components; $V^{\mathrm{T}}$ is the matrix of loadings with dimensions $N \times J$, and $E$ is the matrix of residuals that are not modeled by the $N$ principal components. $N$ is determined by examining the variance expressed by each PC and the cumulative variance captured by the PCs.

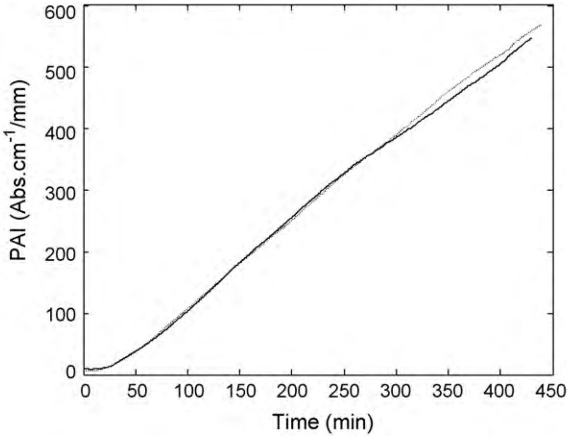

**Fig. 4.** PAI evolution for oxidations led without (dashed line) and with iron (solid line).

Thus, a reduced set of components are found that synthesize all the information from the original matrix. These new variables can be expressed as linear combination of the original ones. PCA provides the analyst with useful tools for data exploration, like the scores $U$ (sample-related, here evolution in time) and the loadings $V^{\mathrm{T}}$ (variable-related, here homogeneous to spectra), which quantify how much of each of the original variables are used to define each PC and which best describe the sources of variance in the data. The scores $U$ are the projections of the original data onto the new vector space, defined by the loadings. Their plots reveal the sample clusters and groups.

The PCA analyses were made using the Matlab 6.5 for Windows and the corresponding PLS Toolbox [17], with mean-centered data.

## 3. Results and discussion

Spectral evolution for a base lubricating oil oxidation process (Fig. 2) exhibits a progressive increment in the analytical signal

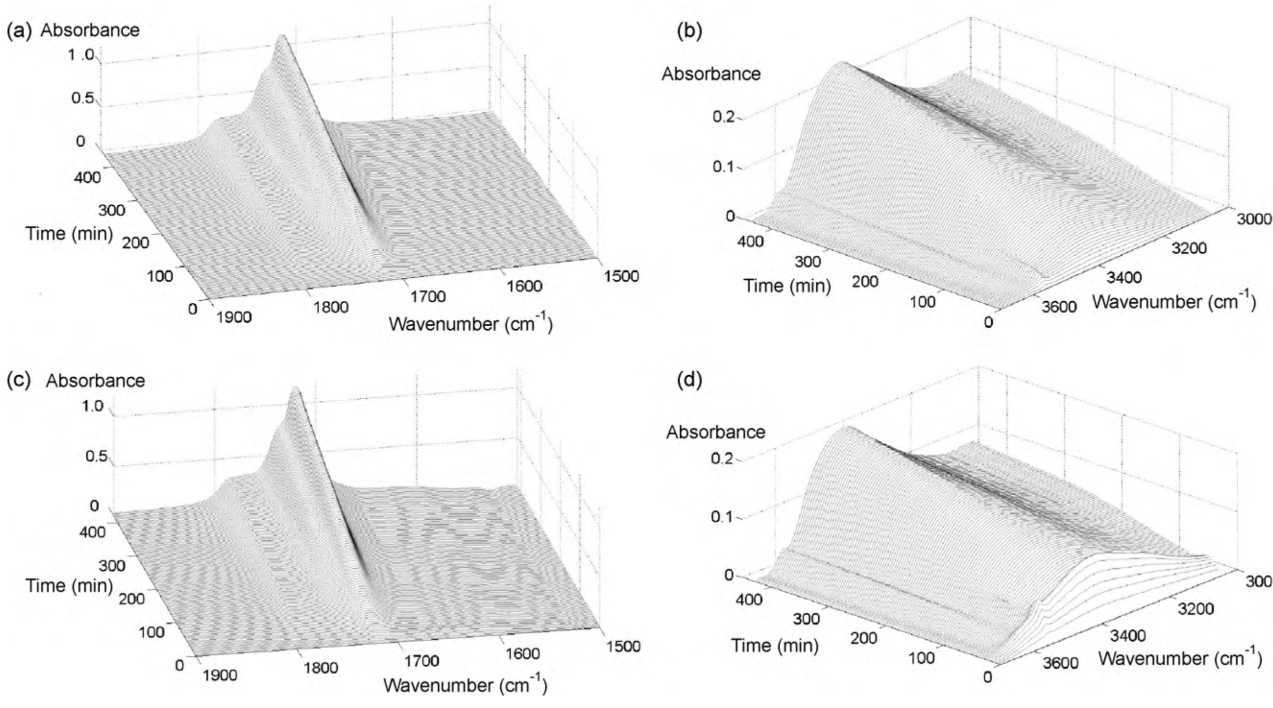

**Fig. 3.** Spectra evolution along time (1500–1900 and 3050–3700 cm$^{-1}$) for oxidation experiments: without iron: (a) and (b) and with iron: (c) and (d).

registered caused by the chemical transformation occurred during the oxidation.

Oxidation of hydrocarbon molecules introduces functional groups such as alcohol, ketone, aldehyde, carboxylic acid, ester and lactone that provide characteristic FTIR spectral bands. Therefore oil oxidation should generate visible changes in the following vibration bands: $\nu$(O–H) (3100–3600 cm$^{-1}$ for alcohols and 2500–3200 cm$^{-1}$ for carboxylic acids in polar environment), $\nu$(C=O) (1650–1730 cm$^{-1}$ for aldehydes and ketones, 1680–1710 cm$^{-1}$ for carboxylic acids, 1700–1740 cm$^{-1}$ for esters, 1780 cm$^{-1}$ for lactones), $\nu$(C–O) between 1050 and 1450 cm$^{-1}$, $\nu$(C–C) between 1000 and 1250 cm$^{-1}$ and $\nu$(C=C) for aromatic compounds between1440 and 1650 cm$^{-1}$.

$\delta$(C–H$_x$) and $\nu$(C–H$_x$) are expected between 1370–1550 and 2750–3000 cm$^{-1}$. Due to the sampling technique absorbance saturation was reached and the regions could not be used for PCA analysis. Moreover $\nu$(O–H) bands for carboxylic acids overlap with $\nu$(C–H$_x$) so we did not expect to extract much information on carboxylic acids evolution.

### 3.1. Influence of the presence of iron

Spectral evolutions along time for oxidations led without and with iron as a catalyst (Fig. 3) exhibit the progressive apparition of molecules with carbonyl (Fig. 3(a) and (c)) and alcohol functions (Fig. 3(b) and 3(d)). The differences in the behavior of alcohols led us to study the "3500 band area" as a counterpart of PAI.

PAI evolution for oxidations with and without catalyst is very similar (Fig. 4). In order to check this, the two spectra corresponding to a 500 Abs cm$^{-1}$/mm PAI value for each experiment are overlaid (Fig. 5), no major difference appears and we can conclude that the composition of the system is the same after approximately 7 h of oxidation, no matter the presence or not of iron.

Considering the 3500 band area evolution for both experiments (Fig. 6) we observe differences induced by the presence of iron: alcohols formation is much more important during the first 30 min of oxidation, then a sudden decrease occurs until the 50th minute,

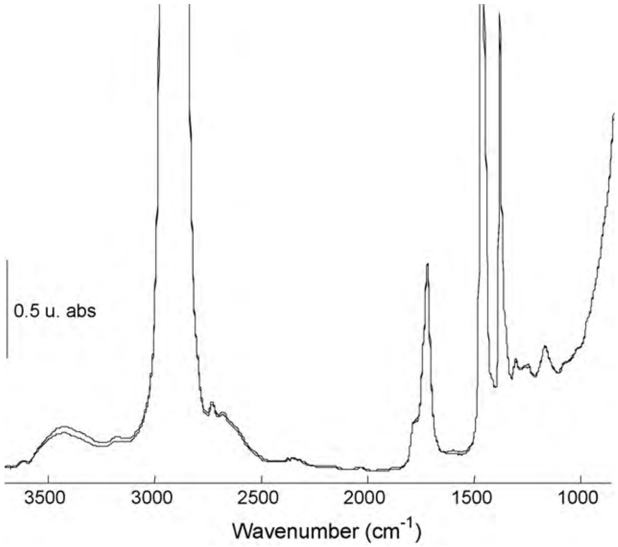

**Fig. 5.** Superposition of spectra (one for oxidation without iron and one for oxidation with iron) for PAI value = 500 Abs cm$^{-1}$/mm.

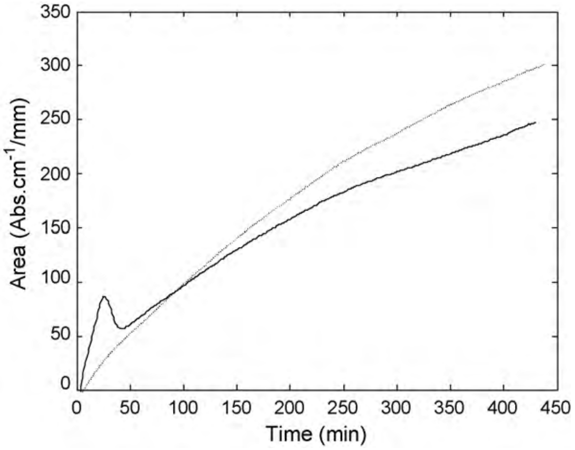

**Fig. 6.** 3500 band area evolution for oxidations led without (dashed line) and with iron (solid line).

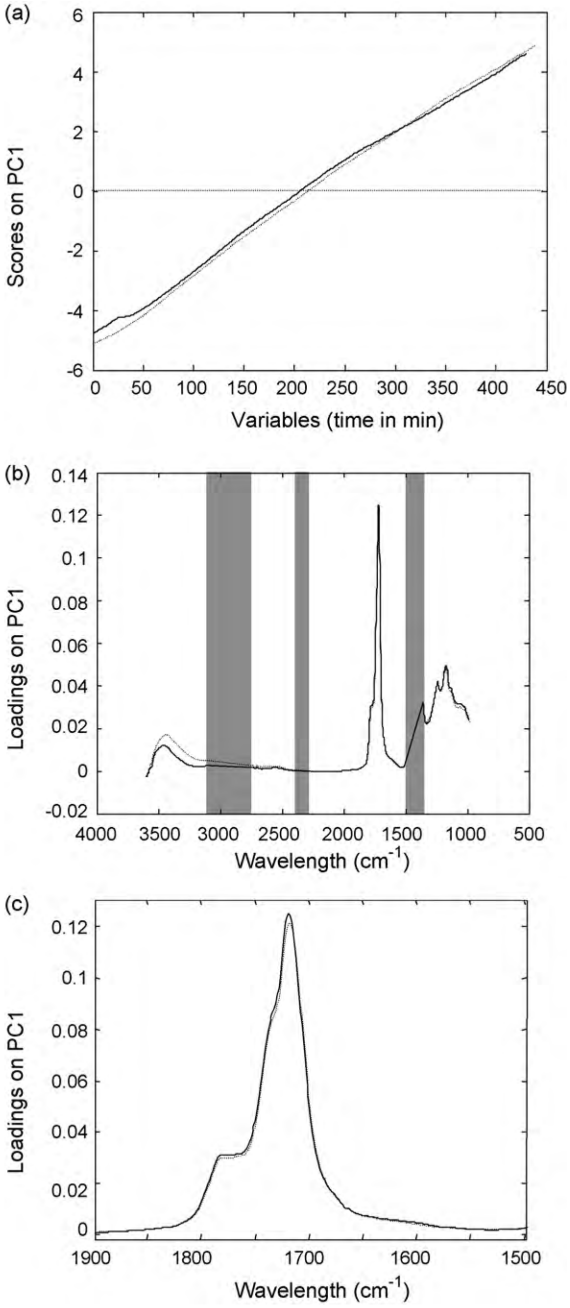

**Fig. 7.** Scores versus time (a) and loadings (b) of the first PC. Zoom (c) on 1500–1900 cm$^{-1}$ spectral zone of PC1. Experiments without (dashed lines) and with iron (solid line).

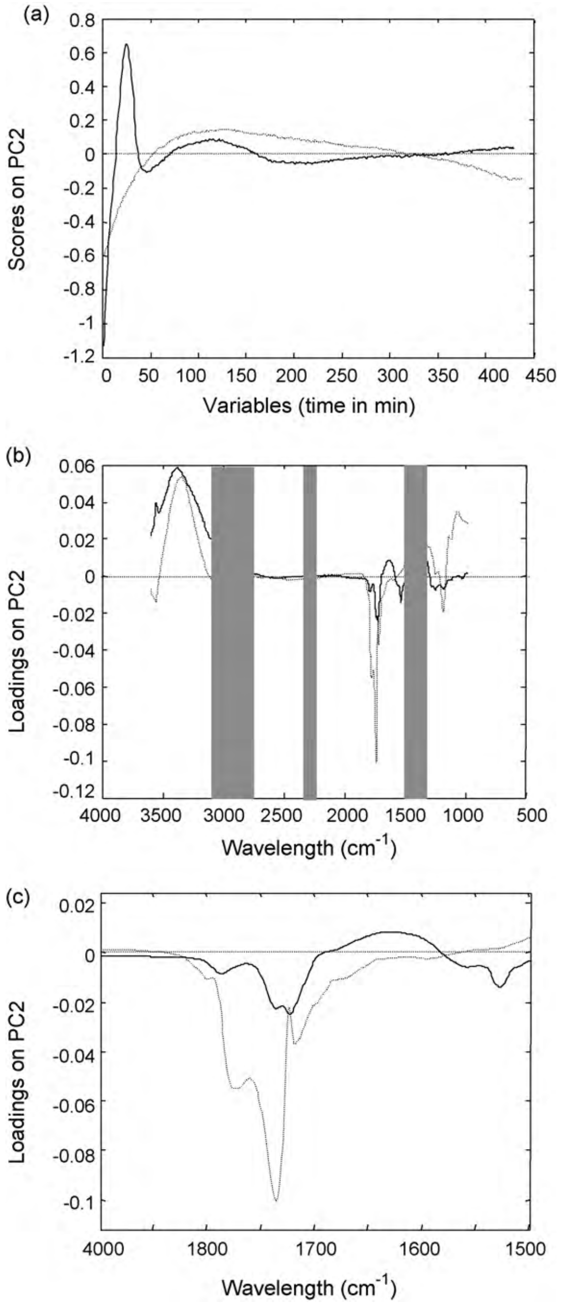

**Fig. 8.** Scores (a) and loadings (b) of the second PC. Zoom (c) on 1500–1900 $\mathrm{cm}^{-1}$ spectral zone of PC2. Experiments without (dashed lines) and with iron (solid line).

time after which the alcohols formation progresses more slowly than in the absence of iron.

### 3.2. Chemometric analysis

PCA analysis showed that two principal components allow to express more than 99% of the variance of the system in both cases of oxidation. Comparing the PCs in both cases allows to find similarities and differences in the behaviors.

The first PC (Fig. 7) presents very similar scores versus time and loadings for both experiments, without and with iron. We observe that the $\nu$(C=O) vibration bands are similar in both experiments whereas the $\nu$(O–H) vibration band for alcohols is slightly more intense in the case of oxidation without iron. Loading vectors are highly related to the spectra obtained at the end of oxidation experiment as can been inferred from comparing it with the last spectrum collected in each batch. Furthermore the variance explained by PC1 is 99.72% for the oxidation without iron and 99.48% for the oxidation with iron, we can conclude that the scores of the PC1 express the relative degree of oxidation and the loadings express the distribution of oxidised compounds reached after several hours of oxidation.

About the second PC (Fig. 8), expressing 0.21% and 0.34% (respectively for experiments led without and with iron) we observe that after 50 min, scores are almost equal to zero. Loadings associated show a large absorption band between 3100 and 3600 $\mathrm{cm}^{-1}$ for alcohols, and absorption bands for $\nu$(C=O) spectral area in opposite sign, corresponding to esters (1740 $\mathrm{cm}^{-1}$) and cyclic esters (lactones, 1780 $\mathrm{cm}^{-1}$). During the first 50 min, for the oxidation with iron, scores versus time exhibits a rapid increase followed by a decrease, whereas a slow increase is observed for experiment led without iron. In both cases, scores remain close to zero after 50 min. Considering the oxidation mechanism, esters are secondary products, not present at the first step of the oxidation. Moreover esters and lactones peaks are in opposite sign to alcohols band, meaning that this second PC involves inverse tendencies for these compounds. With this information we propose that PC2 introduces a correction towards PC1 about species present in greater amounts during the first steps (alcohols) or not present (esters) and which can be consumed or formed by secondary reactions. This PC underlines that iron led to more intense 3500 band area during the first steps indicating that alcohols are present in a greater amount when the oxidation is led in the presence of iron, as mentioned by Shilov and Shul'pin [4]. Furthermore esters bands are less intense in experiment led with iron meaning that the correction introduced by PC2 is less important in that region. Esters are produced in higher amounts during the first minutes which is in good agreement with the fact that esterification is favoured by the presence of iron, as demonstrated by Ishihara et al. [5]. This behavior of iron explains the 3500 band peak as alcohols are formed in large amount during the first steps and then consumed when carboxylic acids become present in the sample. We can conclude that the second principal component is mainly related to differences in the oxidation mechanism during the first hour of oxidation.

## 4. Conclusion

Combination of IR spectroscopy and factorization tools allows to extract more information about the role of iron on esterification and alcohols formation. Principal Component Analysis of the mean-centered data has revealed the principal components which explain 99.99% of the variance. The first PC is similar for oxidation led without or with iron, but the second PC shows that iron favours the formation of alcohols and esters. This influence is strong at the very first moments of the oxidation but no longer visible after a while. Formulation of antioxidants, which generally interact with the primary compounds of the oxidation process, must take this fact into account, and their efficiency should be evaluated in the presence of iron since it influences the first steps of oxidation. The PCA method is a preliminary and promising work and further investigations will be made using "curve resolution" methods such as Band-Target Entropy Minimization [18] and Multivariate Curve Resolution—Alternating Least Squares [19] to estimate the number of species, extract the kinetic profiles and the spectra associated.

## References

[1] T. Colclough, Industrial & Engineering Chemistry Research 26 (1987) (1888).
[2] H.H. Zuidema, Chemical Reviews 38 (1946) 197.
[3] H.S. Blanchard, A study of mechanism of cumene autooxidation. Mechanism of the interaction of t-peroxy radicals, Journal of American Chemical Society 81 (1959) 4548.

[4] A.E. Shilov, G.B. Shul'pin, Chemical Reviews 97 (1997) 2879.

[5] K. Ishihara, M. Nakayama, S. Ohara, H. Yamamoto, Tetrahedron 58 (2002) 8179.

[6] A. Borin, R.J. Poppi, Vibrational Spectroscopy 37 (2005) 27.

[7] Standard Test Conditions Monitoring of used Lubricants by Trend Analysis Using Fourier Transform Infrared (FTIR) Spectrometry, ASTM International, 2004 (E 2412-04).

[8] Z. Yin, Y. Sun, Spectroscopy and Spectral Analysis 19 (1999) 190.

[9] H.F. Shurvell, S. Meylan, A.D.H. Clague, V.L. Brookes, Canadian Journal of Analytical Sciences and Spectroscopy 43 (1998) 67.

[10] D. Wooton, S. Barry, S. White, R. Thomas, Practicing Oil Analysis 7 (2005) 31.

[11] H.L. Yip, Journal of Forensic Sciences 18 (1973) 264.

[12] I. Stanimirova, B. Walczak, D.L. Massart, V. Simeonov, Chemometrics and Intelligent Laboratory Systems 71 (2004) 83.

[13] D.L. Massart, B.G.M. Vandeginshe, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics. Part A, Elsevier, Amsterdam, 1997 (Chapter 17) p. 519.

[14] M. Felipe-Sotelo, R. Tauler, I. Vives, J.O. Grimalt, Science of the Total Environment 404 (2008) 148.

[15] A. Borin, R.J. Poppi, Journal of the Brazilian Chemical Society 15 (2004) 570.

[16] Standard Test Method for Determination of the Oxidation of Used Lubricants by FT-IR Using Peak Area Increase Calculation, ASTM International, 2007(D 7214-07).

[17] B.M. Wise, N.B. Gallagher, PLS Toolbox for use with Matlab, Ver. 2.1, Eigenvector Technologies, Manson, 1998.

[18] F. Gao, A.D. Allian, H. Zhang, S. Cheng, M. Garland, Journal of Catalysis 241 (2006) 189–199.

[19] R. Tauler, Chemometrics and Intelligent Laboratory Systems 30 (1995) 133–146.