

## DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY (DRIFTS) APPLIED TO THE CHEMICAL CHARACTERIZATION OF DIESEL SOOT

TAPIA A.<sup>1,\*</sup>SALGADO S.<sup>1</sup>SÁNCHEZ-VALDEPEÑAS J.<sup>2</sup>MARTÍN P.<sup>1</sup>RODRÍGUEZ J.<sup>2</sup>CABAÑAS B.<sup>1</sup><sup>1</sup>Physical Chemistry Department, University of Castilla-La Mancha

Avda. Camilo José Cela s/n

13071 Ciudad Real, Spain

<sup>2</sup>Grupo de Combustibles y Motores

Escuela Técnica Superior de Ingenieros Industriales

University of Castilla-La Mancha

Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

Received: 27/05/2015

Accepted: 11/04/2016

Available online: 19/05/2016

\*to whom all correspondence should be addressed:

e-mail: araceli.tapia@uclm.es

### ABSTRACT

In this work, diesel soot has been characterized chemically using a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique. Diesel soot samples were generated under combustion conditions reproducing the typical urban operating mode of a diesel engine. Initial experiments performed to ensure the repeatability of the DRIFTS analysis and the sample preparation method showed that the standard deviations were always lower than 20% for the DRIFTS analysis itself, and lower than 25% when sample preparation was included. This is of special interest as regards application of the DRIFTS technique for quantitative analysis. The functional groups on the soot surface were identified on the basis of the infrared bands observed in the spectra at room temperature, indicating that the diesel soot analyzed comprises a mixture of aromatic hydrocarbons, carboxylic compounds, hydroxyl species, ether groups, and methylene and methyl groups. Analyses were also carried out at different temperatures in the interval of 298-858 K in order to analyze the thermal stability of the functional groups, with carbonyl groups, lactones and ethers appearing to be the most thermally stable compounds.

**Keywords:** DRIFTS, chemical characterization, Diesel, soot, engine

### 1. Introduction

Incomplete combustion of fossil fuels in diesel engines releases particulate matter (PM) of different diameters into the environment. These particles are considered to be a pollutant due to the presence of polycyclic aromatic hydrocarbons (PAHs), which have been implicated in chemical and photophysical processes in the atmosphere and are thought to be the primary cause of several diseases, adsorbed onto a carbonaceous material (Vieria de Souza and Machado Corrêa, 2015). Cancer and cardiopulmonary diseases, for example, are known to be related to the redox activity of PM. The dithiothreitol (DTT) assay provides a measure of the ability of PM to catalyse electron transfer between DTT and oxygen, and a high degree of correlation has been found between the redox activity of particulate emissions and physical and chemical characteristics of PM emitted by an engine running on diesel (Geller *et al.*, 2006). Diesel exhaust particles (DEP) are also known to be involved in atmospheric processes as a result of the absorption of light by the black carbon and the organic matter present in it, thus affecting the radiation balance in the atmosphere (Guo *et al.*, 2014; Schnaiter *et al.*, 2003). As regards chemical processes, diesel

soot particles in urban and rural environments play an important role in the formation of SOA (secondary organic aerosol) under certain photochemical conditions, thereby affecting the chemical composition of the atmosphere (Lee *et al.*, 2004).

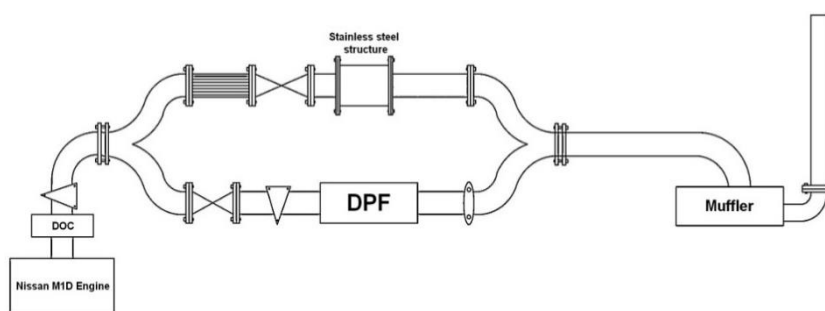
Diesel engine emissions have gained considerable attention due to their health risks and environmental concerns, especially particulate matter and NO<sub>x</sub> (Górski *et al.*, 2013). As such, after-treatment devices and in-engine techniques such as diesel particulate filters (DPFs) and exhaust gas recirculation (EGR), have been implemented in diesel engines in recent years to decrease particulate matter and NO<sub>x</sub> emissions (Lapuerta *et al.*, 2012; Beatrice *et al.*, 2012). As a result, it is of interest to characterize the soot collected from a DPF and to assess the impact of the type of soot generated on the behaviour and regeneration of a DPF (Zouaoui *et al.*, 2014). Some studies in this regard have focused on evaluating the PM generated from conventional and alternative fuels in terms of their chemistry and morphology (Salamanca *et al.*, 2012). It is also of particular interest to investigate the ability of soot to be oxidised by exhaust gases such as NO<sub>2</sub> (Tighe *et al.*, 2012) in different parts of the after-treatment assembly of the diesel engine in light of the morphological features of soot particles in relation to the temperature (Liati *et al.*, 2013).

Several techniques, such as titration with a probe gas using a Knudsen reactor (Tapia *et al.*, 2015), Raman spectroscopy (Sadezky *et al.*, 2005), X-ray scattering and absorption spectroscopy (Braun *et al.*, 2005), transmission electron microscopy (Wentzel *et al.*, 2003; Yehliu *et al.*, 2012) and diffuse reflectance infrared Fourier transform spectroscopy (Steiner *et al.*, 2013), have recently been used to characterize the structure and composition of diesel soot. IR spectroscopy provides important information about the identity of molecular functional groups on the soot surface as a result of the characteristic vibrational frequencies of a functional group after absorbing infrared radiation (Jäger *et al.*, 2007; Russo *et al.*, 2012). Moreover, soot structure can be analyzed in relation to the spectral shift of the infrared band positions due to the chemical environment (Pino *et al.*, 2008). The DRIFTS technique is based on the infrared light reflected in all directions after incidence on the sample surface and collected by use of an ellipsoid or paraboloid mirror onto the detector. As such, this technique can be extremely useful for non-transparent materials such as soot and/or for *in situ* measurements at elevated temperatures. For example, Liu *et al.* (2010) investigated the structural changes in soot during heterogeneous reaction with O<sub>3</sub> at room temperature using an *in situ* DRIFTS technique. Similar experiments were carried out by Muchenhuber and Grothe (2007), who used DRIFTS to investigate the products of the reaction of soot with NO<sub>2</sub> at different temperatures. Improved sensitivity and accuracy can be achieved by using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), a technique derived from FTIR that has been used to quantify the functional groups of organic and inorganic compounds present in environmental aerosol particulate samples (Courty and Dillner, 2008).

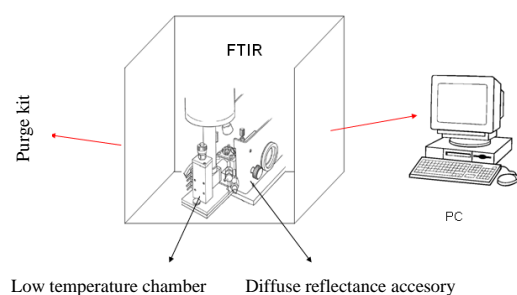
The aim of this work was to apply the DRIFTS technique for the chemical characterization of samples of diesel soot obtained under a fixed engine condition.

## 2. Methods

Soot obtained from diesel fuel was analyzed using the DRIFTS technique in order to investigate the composition thereof and the functional groups present on the particles' surface. A Nissan Diesel engine 2.0L (Model MID), fulfilling EURO 5 emission standard, equipped with a cooled EGR, diesel oxidation catalyst (DOC) and regenerative wall-flow type DPF was used to obtain the soot. A stainless steel mesh was used to retain soot particles at the exhaust (figure 1). The experimental set-up used for analysis was a DRIFTS device consisting of a Fourier transform infrared spectrometer (Model Prestige-21, SHIMADZU), a diffuse reflectance spectroscopy accessory (model DRP-M-05, HARRICK SCIENTIFIC), a catalytic support for low temperature studies (Model CHCCHA-3, HARRICK SCIENTIFIC) and an automatic temperature controller (Model ATC-024-2, HARRICK SCIENTIFIC) (figure 2). KBr was selected as the non-absorbent compound for dilution of soot samples. Dilution samples of 1:1000, 1:500 and 1:200 were analyzed to check the signal sensitivity, and the 1:500 proportion was found to offer the best signal-to-noise ratio. Spectra were recorded in the spectral range 4000 to 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.



**Figure 1.** The exhaust configuration of the diesel engine used, which features a by-pass system for soot collection

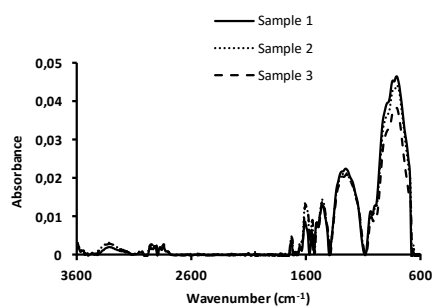


**Figure 2.** Experimental DRIFTS system

### 3. Results and Discussion

#### 3.1. Validation of the technique and experimental procedure

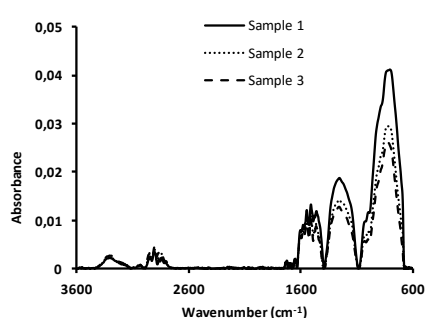
The DRIFTS technique is normally used only for qualitative analysis of solid samples. As such, the repeatability of the infrared spectroscopy analysis and the sample preparation process were investigated with the aim of validating the technique for quantitative analysis. The experimental procedure comprises weighing fixed quantities of KBr and soot depending on the dilution level for the analysis, followed by mixing and grinding for thirty minutes.



**Figure 3.** DRIFTS spectra of diesel soot at 298 K from 3600 to 600  $\text{cm}^{-1}$  for three replicates of the same sample

The mixing and grinding times were also optimized in initial experiments. A quantity of sample was then placed in the reaction chamber under vacuum and infrared spectra recorded in the range 4000 to 600  $\text{cm}^{-1}$ . The same sample was analyzed five times under the same conditions and the relative standard deviation in the spectral areas calculated was determined to assess the repeatability of the detection process.

Figure 3 shows the spectra for three replicates of the same sample analyzed in the repeatability study. As can be seen, the quantification of the spectral band between 1080  $\text{cm}^{-1}$  and 675  $\text{cm}^{-1}$  presents lower precision than the others. The values of the areas for the different infrared bands checked in the spectrum are shown in table 1 for all experiments performed. The relative standard deviations (RSD%) were subsequently calculated, with the values obtained also being presented in the table. As can be seen, the repeatability of the IR analysis is high, with errors always lower than 20%. Although there are currently no established guidelines for evaluation of the precision of soot measurements using the DRIFTS technique, relative standard deviations of less than 20% for IR analysis have been considered to be acceptable given the maximum value of 25% established for other types of analytical methods (USEPA, 2013).



**Figure 4.** DRIFTS spectra of diesel soot at 298 K in the 3600 - 600  $\text{cm}^{-1}$  range for the three samples used in the repeatability analysis

The repeatability study was completed by considering the procedure for preparing soot samples and its associated experimental errors. For this study, five different samples of diesel soot in KBr, in a proportion of 1:500, were prepared and analyzed to determine the relative standard deviation in the computed integrated absorbances. Figure 4 shows the typical infrared spectra obtained upon analysing diesel soot in the range from 3600 to 600  $\text{cm}^{-1}$  after correcting the baseline for three replicates. As can be seen in this figure, the spectral areas obtained are very similar for the different samples. Table 1 lists the RSD values for these experiments. When including sample preparation in the error evaluation, the relative standard deviation values obtained are higher due to errors resulting from the dilution process, although they remain acceptable for the analytical method. The infrared band between 2890 and 2775  $\text{cm}^{-1}$  shows an RSD value higher than 25%, possibly due to the low intensity of the signal detected in this case.

Given our experimental results, we can conclude that the DRIFTS technique allows us to obtain reproducible results when applied to diesel soot characterization and could therefore be an appropriate method for conducting comparative quantitative studies of different kinds of soot in light of the experimental errors in infrared band intensity obtained here.

### 3.2. Analysis of diesel soot at room temperature

As mentioned above, the DRIFTS technique has been used to chemically characterize samples of diesel soot obtained under fixed engine conditions. The total spectral range has been divided in three zones to a better observation of the identified bands. Then qualitative analysis was carried out in the following ranges: 4000–2000  $\text{cm}^{-1}$ , 2500–1000  $\text{cm}^{-1}$  and 1500–600  $\text{cm}^{-1}$ . The spectra used for baseline correction are shown in figures 5, 6 and 7. Infrared bands of different intensity were found in each region, thus meaning that different functional groups are present on the surface of diesel soot, as has been demonstrated using other analytical techniques (Tapia *et al.*, 2015). Table 2 lists the infrared bands identified for diesel soot

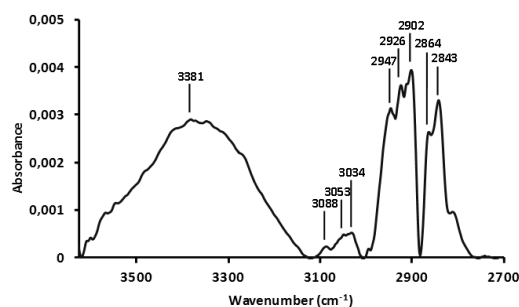
in bibliographic references compared with data obtained in this work. Another column with the corresponding functional groups in accordance with standard infrared spectroscopic assignments and literature data has been included in the table for comparison. Polycyclic aromatic hydrocarbons are a group of compounds with low volatility that mainly appear adsorbed onto the surface of soot as a result of incomplete fuel combustion (Ballesteros *et al.*, 2010).

**Table 1.** Relative standard deviation (RSD) values for the infrared absorption bands selected for DRIFTS analysis.

Wavenumber (cm <sup>-1</sup> )	Repeatability of IR analysis (n=5)			Repeatability including sample preparation (n=5)		
	Experiment	Area	RSD (%)	Experiment	Area	RSD (%)
3425-3125	1	-	8.0	1	0.324	16.8
	2	0.427		2	0.367	
	3	0.437		3	0.378	
	4	0.487		4	0.458	
	5	0.502		5	0.487	
3000-2890	1	0.134	18.4	1	0.14	12.4
	2	0.178		2	0.169	
	3	0.181		3	0.139	
	4	0.209		4	0.172	
	5	0.222		5	0.183	
2890-2775	1	0.136	13.9	1	0.061	26.6
	2	0.132		2	0.097	
	3	0.106		3	0.085	
	4	0.156		4	0.055	
	5	0.146		5	-	
1664-1525	1	-	4.3	1	0.347	5.6
	2	0.936		2	0.369	
	3	0.882		3	0.388	
	4	0.845		4	0.372	
	5	0.874		5	0.337	
1525-1390	1	1.02	6.5	1	0.568	15.4
	2	1.162		2	0.445	
	3	1.118		3	0.428	
	4	1.179		4	0.601	
	5	1.211		5	0.576	
1390-1080	1	4.524	3.2	1	3.721	16.8
	2	4.402		2	2.793	
	3	4.272		3	2.427	
	4	4.187		4	3.496	
	5	4.233		5	3.277	
1080-675	1	11.261	9.2	1	9.641	22.4
	2	10.641		2	6.606	
	3	9.007		3	5.38	
	4	9.475		4	8.793	
	5	10.729		5	8.482	

Oxygenated functional groups are generated during the same process, and appear bonded to these aromatic compounds. Thus, the bands at 3381 cm<sup>-1</sup> (figure 5) and 1244 cm<sup>-1</sup> (figure 7) are associated with hydroxyl group and ether C-O-C group stretching, respectively (Zawadzki and Wisniewski, 2003; Cain *et al.*, 2010). Similarly, the carbonyl functional group is associated with the band at 1718 cm<sup>-1</sup> (Santamaría *et al.*, 2010). The value of the wavenumber for this C=O group varies depending on the chemical nature of the molecule, with molecules such as quinones, lactones and carboxylic acids exhibiting carbonyl bands at wavenumbers of 1604, 1701, 1685 and 1670 cm<sup>-1</sup> (Coury and Dillner, 2008) signals observed in the spectrum of figure 6. Bands corresponding to the C-H stretching vibration in aromatic structures are found

at 3053 and 3034  $\text{cm}^{-1}$  (figure 5), whereas bands at 2947, 2926, 2902, 2864 2843  $\text{cm}^{-1}$  are assigned to the asymmetric and symmetric C-H stretching vibrations of aliphatic  $\text{CH}_3$  and  $\text{CH}_2$  groups (Santamaría *et al.*, 2006).



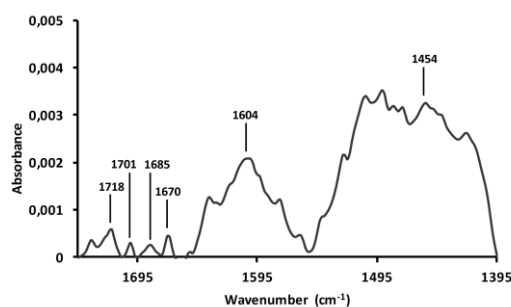
**Figure 5.** DRIFTS spectra of diesel soot at 298 K from 3625 to 2700  $\text{cm}^{-1}$  range

**Table 2.** Assignment of infrared bands to functional groups on diesel soot at 298 K. Second column shows typical wavenumber values found in soot bibliographic references, third column shows values for standard infrared spectroscopic assignments for functional groups and fourth column values found in this work.

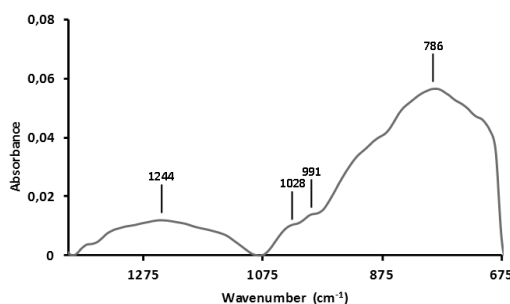
Assignment	Wavenumber <sup>a,b,c</sup> ( $\text{cm}^{-1}$ )	Wavenumber <sup>d</sup> ( $\text{cm}^{-1}$ )	Wavenumber ( $\text{cm}^{-1}$ )
O-H	3620-2500	3650-3200	3381
Aromatic C-H stretch	3050, 3030	3080-3030	3053, 3034
Asymmetric and symmetric C-H stretching of $\text{CH}_3$ and $\text{CH}_2$ aliphatic groups, respectively	2975, 2925, 2850	3000-2840	2947, 2926, 2902, 2864, 2843
Carbonyl C=O stretching	1720	1765-1645	1718
Quinones	1680-1550	1675	1604
Lactones	1790-1675	1790-1650	1701, 1685, 1670
Carboxylic acids	1760-1665	1800-1650	
Asymmetric $\text{CH}_3$ and scissor $\text{CH}_2$ deformations and symmetric $\text{CH}_3$ deformation and cyclic $\text{CH}_2$	1450-1380	1470-1430 1395-1365	1454
Ether C-O-C stretching	1260	1310-1000	1244
C-H bending out-of-plane of condensed aromatic systems	890, 840, 750	900-650	786

<sup>a</sup>Santamaría *et al.*, 2006, <sup>b</sup>Cain *et al.*, 2010, <sup>c</sup>Figueiredo *et al.*, 1999, <sup>d</sup>Pretsch *et al.*, 2009.

Bands at 1454  $\text{cm}^{-1}$  (figure 6) correspond to asymmetric and symmetric  $\text{CH}_3$  and scissor  $\text{CH}_2$  deformations, thus meaning that aliphatic structures are also present on the soot's surface. The band at 786 (figure 7) can be assigned to the presence of C-H stretching out-of-plane vibrations of substituted aromatic and alkene systems (Daly and Horn, 2009).



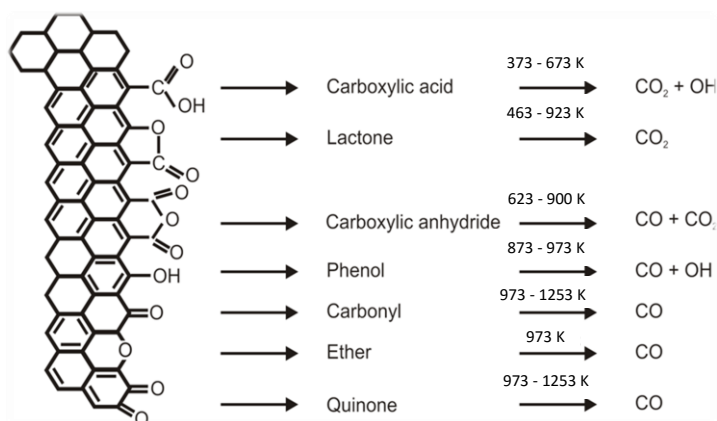
**Figure 6.** DRIFTS spectra of Diesel soot at 298 K from 1745 to 1395  $\text{cm}^{-1}$  range



**Figure 7.** DRIFTS spectra of diesel soot at 298 K in the range 1400 - 675  $\text{cm}^{-1}$  range

### 3.3. Analysis of diesel soot at different temperatures

Oxygenated functional groups on the surface of soot are desorbed at different temperatures depending on their thermal stability. Thus, Muckenhuber and Grothe (2006) have used temperature programmed desorption mass spectroscopy (TPD-MS) to distinguish and assign functional groups in commercial soot samples on the basis of their thermal stability (figure 8).



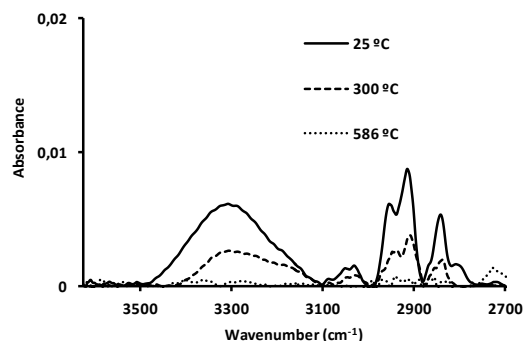
**Figure 8.** Temperature range for the thermal decomposition of functional groups on soot surfaces (Muckenhuber and Grothe, 2006)

Similarly, Setiabudi *et al.* (2004) have identified the role of  $\text{O}_2$  and  $\text{NO}_2$  in the reaction with soot at elevated temperatures using the DRIFTS technique. In our study, the sample was heated from 298 to 859 K using an automatic temperature controller and the evolution of the infrared bands was analyzed in order to identify signals coming from oxygenated functional groups on soot. Figure 9 shows the evolution of the infrared bands with increasing temperature in a typical experiment. As can be seen, the intensity of the infrared bands decreases with increasing temperature, with the exception of the bands at 1718, 1701 and  $1244 \text{ cm}^{-1}$ , which correspond to carbonyl, lactone and ether functional groups, the intensity of which does not change on heating from 298 to 573 K. This suggests that carbonyl, lactone and ether groups are thermally more stable than the other groups and are not desorbed until higher temperatures (859 K) are reached.

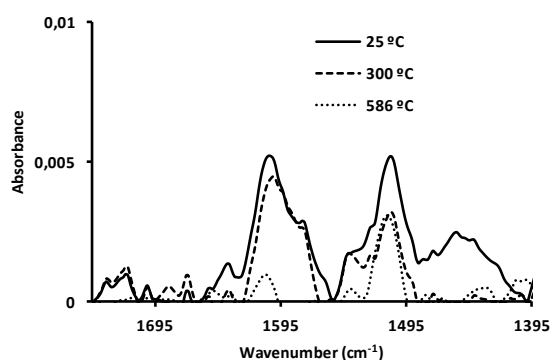
## 4. Conclusions

Diffuse Reflectance Infrared Fourier Transform Spectroscopy has been used to characterize the functional groups present on the surface of diesel soot. A validation study of the analytical method showed acceptable repeatability values considering both DRIFTS spectral acquisition and sample preparation. The IR spectra revealed the presence of aromatic polycyclic hydrocarbons containing oxygenated functional

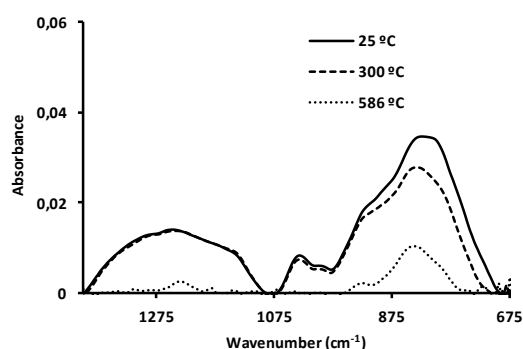
groups, such as phenols, quinones, lactones, carboxylic acids and ethers, on diesel soot as a result of the incomplete combustion of diesel fuel. Carbonyl, lactone and ether groups are desorbed from the soot surface at higher temperatures than other groups, thus meaning that they are thermally more stable. The presence of these compounds adsorbed on diesel soot is important from an environmental point of view as they could affect the heterogeneous processes that take place in the atmosphere.



(a)



(b)



(c)

Figure 9. DRIFTS spectra recorded for Diesel soot in several wavenumber ranges after heat treatment: (a) 3625 cm⁻¹ - 2700 cm⁻¹, (b) 1745 cm⁻¹ - 1395 cm⁻¹, (c) 1400 cm⁻¹ - 675 cm⁻¹

#### Acknowledgments

This work was supported by project ENE2007-67529-CO2-02 granted by the Ministerio de Educación y Ciencia.



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