

Proposal of an FTIR Methodology to Monitor Oxidation Level in Used Engine Oils: Effects of Thermal Degradation and Fuel Dilution

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Editor's Note: I have always wholeheartedly endorsed infrared analysis of used-oil samples, provided the measured parameter has been appropriately taken into account with the calibration of the instrument. At times, too much faith is put into the technology to provide a result without effectively accounting for variances in the oil's formulation or in the measure's own variances. This month's Editor's Choice paper delves into a longtime standard in the reporting of FTIR results and attempts to improve the accuracy of the result. The proposed methodology is based on the newly instated ASTM methods, which were decades in the making, and will perhaps aid in building momentum to approve new standards for other parameters.

Evan Zabawski, CLS
 Editor

KEYWORDS

Infrared; Spectroscopy; Oil Condition Monitoring; Lubricant Degradation; Internal Combustion Engine Oils

ABSTRACT

This article describes a procedure, based on ASTM standards D7214 and E2412, that has been defined to improve quantification of oil oxidation in used engine oils. Taking into account typical problems that can be found in this type of sample, including thermal oxidation and fuel dilution, Fourier transform infrared (FTIR) spectra were analyzed also considering the effect of the oil formulation. Two zones were considered inside the typical wave number range for quantification of oxidation, where those problems can be detected and assessed more easily: zone A between 1725 and 1650 cm^{-1} , where the main oxidation products, such as aldehydes, carboxylic acids, and ketones, occur due to thermal degradation of the oil; and zone B between 1770 and 1725 cm^{-1} , where esters due to potential biodiesel dilution problems are detected.

INTRODUCTION

Oxidation is the most predominant reaction of a lubricant in service and is therefore responsible for several lubricant-related problems, such as increasee viscosity and acidification, additive depletion, and so on (Macián, et al.¹). Therefore, controlling and monitoring oxidation levels (and other related parameters) should be considered apriority in order to assure good machinery performance and reliability (Macián, et al.²).

In all lubrication systems, including internal combustion engines, organic compounds exposed to oxygen, high temperatures, and pressures will partially oxidize into a large variety of by-products, such as ketones, esters, aldehydes, carbonates, and carboxylic acids, which exhibit characteristic infrared (IR) absorptions (Rudnick³; Malville, et al.⁴). The exact distribution and composition of these products is complex. Carboxylic acids contribute to the acidity of the engine oil and deplete its basic reserves as neutralization takes place. The net effect of prolonged oxidation is that chemically the oil becomes acidic, causing corrosion, and a physical increase in viscosity occurs.

One of the most common methodologies used to measure oxidation in used engine oils is Fourier transform infrared (FTIR) spectrometry (Van de Voort, et al.⁵). For many years it has been used to study lubricant degradation (Coates and Setti⁶; Powell and Compton⁷; Van de Voort, et al.^{5,8}) by measuring variations in the concentration profiles through the carbonyl (C=O) absorption region (1820–1650 cm^{-1} ; ⁹). All of the by-products previously mentioned have highly characteristic vibrations in this region: ketones (1725–1705 cm^{-1}), carboxylic acid (1725–1700 cm^{-1}), and ester (1750–1725 cm^{-1} ; Coates¹⁰).

Despite this fact and ASTM International's efforts to normalize oxidation measurements using this technique (ASTM E2412⁹ and ASTM D7214¹¹), many commercial labs still use their own internal procedures (usually variations based on the ASTM's standard practices). This may cause problems when comparing and analyzing results from different labs because a slight change in the considered band length of the carbonyl region will affect the final result.

This work has been developed in order to propose an FTIR methodology to monitor oxidation levels and to analyze the effects of thermal degradation, base oil formulation, and fuel dilution contamination. Two subzones (A and B) were identified to improve quantification and monitoring.

This study was performed using data obtained under real-world operating conditions and laboratory simulation tests. To isolate different effects, different types of engines were used: compressed natural gas engines (where the lubricant is expected to suffer higher thermal stress and no fuel dilution) and diesel engines (where fuel dilution problems and low thermal stress are predominant; Macián, et al.¹). Specific types of engine oils were used depending on the type of engine. Thermal stress and fuel contamination were simulated in the lab.

OVERVIEW OF THE EVOLUTION OF INFRARED SPECTROSCOPY AND RELATED METHODOLOGIES

FTIR spectroscopy is used to track relative changes in used oil by subtracting the spectrum of the fresh oil from its used or in-service oil counterpart. The molecular changes that occur can be spectrally visualized and associated to typical lubricant problems, such as additive depletion, oxidation, nitration, soot content, fuel dilution, etc.

Next an attempt was made to standardize the measurement of these changes in terms of absorbance or arbitrary units that can be correlated with machine faults or lubricant degradation level.

Perhaps the most important effort toward standardizing the methodology and analytical protocol was made by the U.S. Armed Forces in the frame of the Joint Oil Analysis Program (JOAP) and summarized in a JOAP report (Toms¹²). In this report, several fundamental aspects related to FTIR analytical condition monitoring protocol were presented, such as spectral regions and baselines based on standard addition experimentation for three oil categories: petroleum, synthetic (ester), and hydraulic oils.

Further research led to the development of ASTM E2412⁹. ASTM D7214 covers determination of the extent of a lubricant's oxidation using FTIR¹¹.

VARIABLES AFFECTING OXIDATION MEASUREMENTS

Temperature is one of the most important parameters affecting the oxidation process. Two related effects are governed by temperature: the reaction activation energy and the effect on the speed of the reaction, with greater speed associated with higher temperatures. This relationship is nonlinear, doubling

the rate of oxidation for every 10°C increase in temperature (Wooton¹³).

When lubricant oils are exposed to high temperatures in the presence of oxygen (air), oil begins to suffer a slow oxidation process in which the oil's hydrocarbons react with oxygen to form other substances, including organic acid derivatives such as ketones and aldehydes, with additional esters at lower concentrations. Engine oils are highly susceptible to oxidation, considering the high oil temperatures reached in the piston area, which results in thin-film oxidation (Adamczewska and Love¹⁴). Furthermore, the different combustion process and related temperatures of CNG engines, compared to diesel engines, result in a higher degradation rate in CNG engines, as observed in previous studies (Macián, et al.^{1,2}; Semin and Rosli¹⁵).

Oxidation due to oil temperature leads to important changes in the effectiveness of the oil as a lubricant, increasing the acidity (Oliveira, et al.¹⁶) and viscosity of the oil (Owringa, et al.¹⁷), among other changes. Consequently, the lubricant becomes more aggressive toward metal surfaces, especially nonferrous surfaces, and modifies its ability to form a lubricant film, leading to potentially higher engine wear. Many analytical techniques (FTIR, potentiometric acid-base titrations, voltammetry, sealed capsule differential scanning calorimetry, gas chromatography, etc.) have been used to try to more precisely quantify the by-products and effects of oil oxidation.

Fuel dilution problems have long been studied and different alternative measurement methods have been used for detection, including gas chromatography, flash point, "fuel sniffer," or viscosity excursions (Hiltz, et al.¹⁸; Tormos¹⁹; Mortier, et al.²⁰). Automotive fuels can consist of a wide variety of branched aliphatic compounds, aromatic compounds, and many other compounds blended to produce a desired set of physical properties. Typical conventional fuel dilution problems⁹ can be identified mainly in the spectral range between 815 and 745 cm⁻¹. This absorbance band is typical for out-of-plane bending of two adjacent hydrogens in a para-substituted aromatic ring. This range is quite far from the range associated with oxidation measurements, thus avoiding interference problems. This situation changing due to the introduction and extensive use of biofuels (according to European regulations, which allow up to 7% v/v content of biofuels; UNE EN 590), and especially in diesel engines where biodiesel blends are being used. Constituents of biodiesel (methyl esters from vegetable oils) present spectral interferences in the oxidation quantification area (approximately at 1745 cm⁻¹). This interference could be worse in association with higher biodiesel blends.

CHARACTERISTICS OF METHODOLOGY AND SAMPLES

Methodology Measurement

A methodology based on ASTM D7214¹¹ and ASTM E2412⁹ and considering the type of machine to be monitored (internal combustion engines) was developed using FTIR (A2

Table 1 | Characteristics of FTIR Equipment

Characteristics	
Spectral range	4700–590 cm ⁻¹
Resolution	4 cm ⁻¹
Sample scan	128
Background scan	128
Path length mm (μm)	0.1 (100)
Sampling cell material	Zinc selenide (ZnSe)
Interface	Transmission-TumbIIR
Apodization	Triangular

Table 2 | Engine Characteristics

Characteristics	CNG Vehicle Type	Diesel Vehicle Type
Type ^a	II/TC	DI/TC
Number of cylinders	6	6
Bore/stroke (mm)	115/125	128/155
Engine displacement (cc)	7,790	11,967
Power (kW)	200 @ 2,000 rpm	220 @ 1,900 rpm
bmp (bar)	15.4	11.6
Power/displacement (kW/L)	25.67	18.38
Oil drain period (km)	15,000	35,000
Oil sump capacity (L)	23	31
Oil type in use	Oil A and B	Oil C

^aII = indirect injection; DI = direct injection; TC = turbocharged.

Equipment Technologies PAL Series, CT, USA). The characteristics of the FTIR equipment are provided in Table 1.

Measurements of the oxidation levels were performed in the range between 1770 and 1650 cm⁻¹ and reported as peak area increase (PAI; unit, Abs·cm⁻¹/mm), following ASTM D7214, or peak high (PH; unit, Abs). Both measurements were performed using a single baseline starting at 1850 cm⁻¹ and ending at 1620 cm⁻¹.

Table 3 | Characteristics of Fresh Oils

Characteristic	Oil A	Oil B	Oil C	Oil D
SAE grade	15W/40	10W40	15W/40	5W50
Density at 15°C (kg/m ³)	885	865	881	859
Viscosity at 40°C (cSt)	112.0	91.8	108.0	105
Viscosity at 100°C (cSt)	14.5	14.3	14.5	17.3
Viscosity index	125 min	160	130 min	153
Total Base Number (mg KOH/g)	10	13.2	10	9.0
Flash point, open cup (°C)	215	>220	215 min	236
Pour point (°C)	-27	<-33	-27 max	-51
Service Classification	API CF-4	IVECO 18-1809	API CI-4/CH-4/SL	API SM, SL, CF

SAMPLE CHARACTERISTICS

Different types of samples were used, including samples obtained from engines under real working conditions in an urban transport fleet and samples that were lab degraded.

Vehicles tested in the urban fleet were powered by two different types of engines: diesel and CNG engines. The main characteristics of each type of engine are presented in Table 2. For CNG engines, two types of engine oil were used—a 15W40 mineral oil (oil A) and a 10W40 synthetic oil with higher antioxidant additive package (oil B)—in order to check the performance of the oils under similar working conditions. A 15W40 mineral oil (oil C) was used for diesel engines. Additionally, a synthetic engine oil 5W50 (oil D), base oil API group IV, was used for lab tests. The main characteristics of all of the oils employed in the present study are summarized in Table 3.

Samples of used oil were taken for analysis every 5,000 km. Additional samples were taken at the end of the oil drain period 15,000 km for CNG engines and 30,000 km for diesel engines. Vehicles have frequent stop and go service, long periods of engine idling, and average speed of 12.7 km/h. Vehicles were equipped with automatic fresh oil refilling systems.

A second group of samples was evaluated in the laboratory after a specific degradation process using the same types of fresh oils (A,B,C, and D).

Two degradation processes were considered, one representing thermal degradation, which was simulated using a thermal bath at 270°C for 48 h. To avoid possible external factors affecting degradation such as the catalysis effect of metal components, this process was performed in a glass beaker and samples were collected every 6h. The temperature range selected for this experiment was higher than temperature ranges used in other lab oxidation tests (Adamczewska and Love¹⁴; Bowman and Stachowiak²¹; Cerny, et al.²²; Moehle, et al.²³). The selection was made in order to simulate situations in which the engine oil temperature can rise to over 250–260°C in real operations due to hot spots in the engine in contact with the lubricant, or in the first piston groove near the combustion chamber (Maleville, et al.⁴).

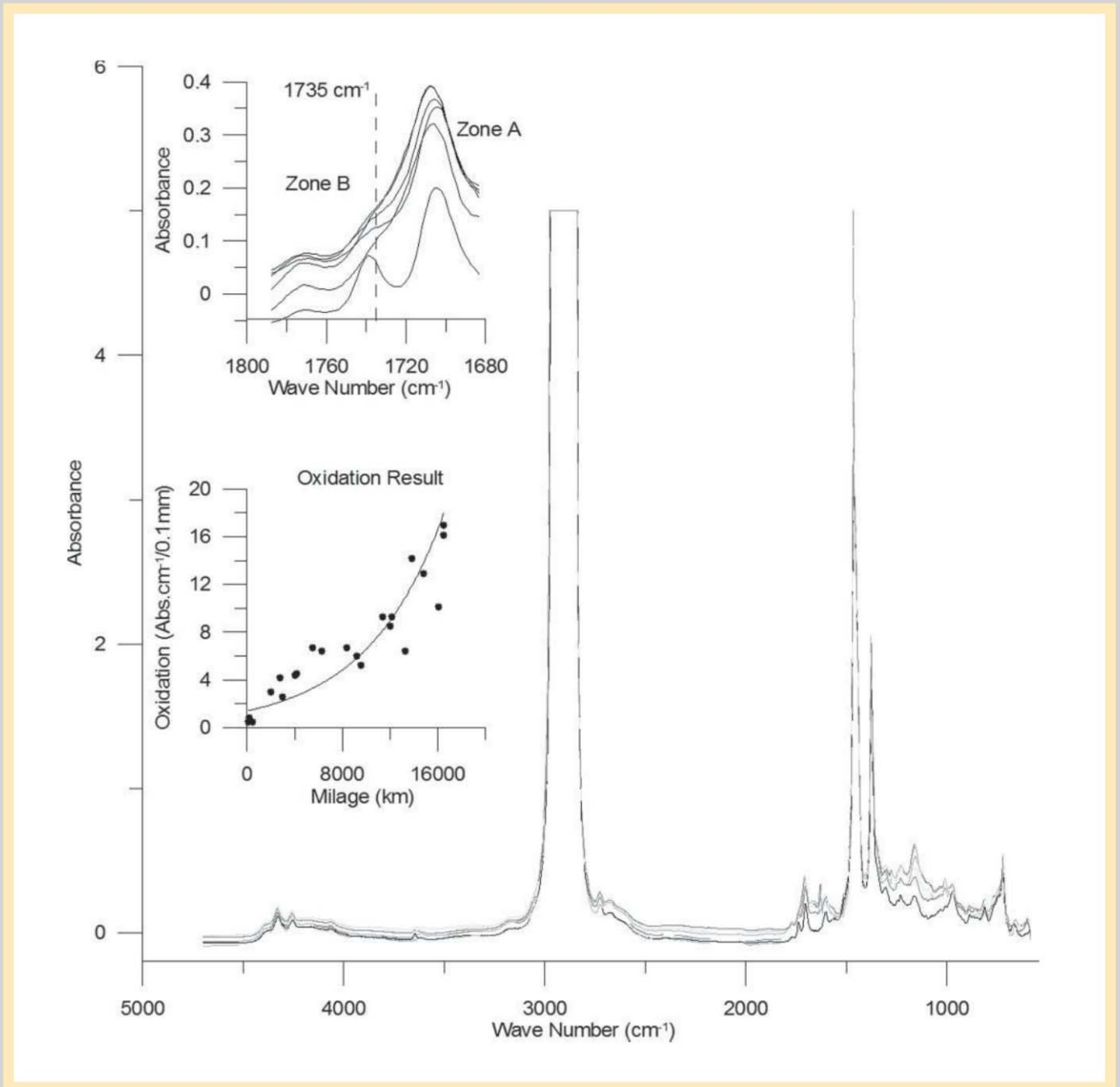


Figure 1 | Results for CNG engines using mineral oil A.

To assess the effects of fuel contamination, the oils specifically formulated for diesel engines (types C and D) were diluted (1, 3, 5, 7, 10, 15, and 20%) using two different biodiesel fuel blends: B10 and B20.

RESULTS

Samples from Engines in Real Service

Figures 1 and 2 show the results for CNG engines in real operating conditions in a transport fleet. Figure 1 shows the complete FTIR spectra for the five most representative samples from CNG engines using oil A, including the fresh oil sample, which is depicted with a dark color. The graph on

the lower left-hand side of Fig. 1 represents the extreme values computed in absorbance values and measured as a PH. As can be seen in the range between 1780 and 1680 cm^{-1} , fresh oil had absorbance values around 0.2 Abs in zone A, and samples representing maximum oil degradation reached values up to 0.4 Abs. In addition, the initial peak present in zone B associated with fresh oil gradually disappeared in used oil samples as a direct consequence of oil degradation related to thermal stress.

The bottom left area of Figure 1 presents the results of oxidation quantification using the PAI method for all 30 samples pertaining to this group. Maximum values of 18

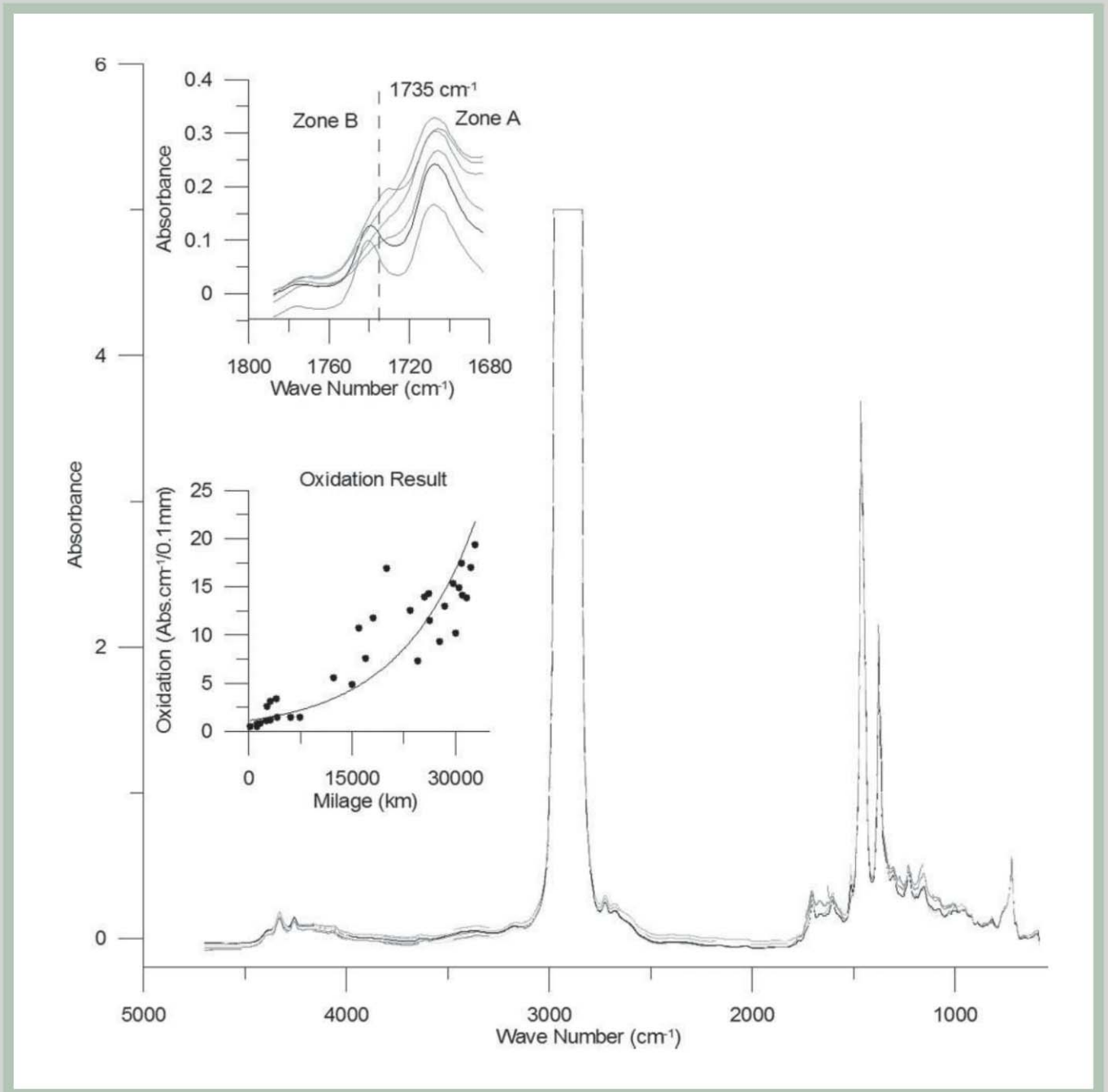


Figure 2 | Results for CNG engines using synthetic oil B.

Abs·cm⁻¹/0.1 mm were reached at the end of oil drain period, around 16,000 km. A direct relationship between oil degradation (oxidation) and oil mileage (Macián, et al.¹) was observed.

The main graph in Figure 2 shows the FTIR spectra for five samples considered representative out of the full group (30 samples), corresponding to CNG engines lubricated with synthetic oil B. As can be seen, the behavior was quite similar to the previous case. As can be seen in the zoomed graph, highlighting wave numbers range between 1780 and 1680 cm⁻¹, fresh oil presented absorbance values slightly lower than 0.2 Abs in zone A, and samples representing maximum

oil degradation reached values around 0.35 Abs. In this case the mileage was substantially higher, reaching more than 30,000 km, caused due to the use of improved antioxidant additive packages and base oil. The bottom left area of Figure 2 presents the results for oxidation quantification using the PAI method for these samples and it can be seen that values were 21 Abs·cm⁻¹/0.1 mm at the oil drain period.

Figure 3 represents the evolution of the oxidation of mineral oil (type C) samples from diesel engines. Similar behavior was observed as in the previous result but with lower oxidation values (PAI measurement) of about 12 Abs·cm⁻¹/0.1

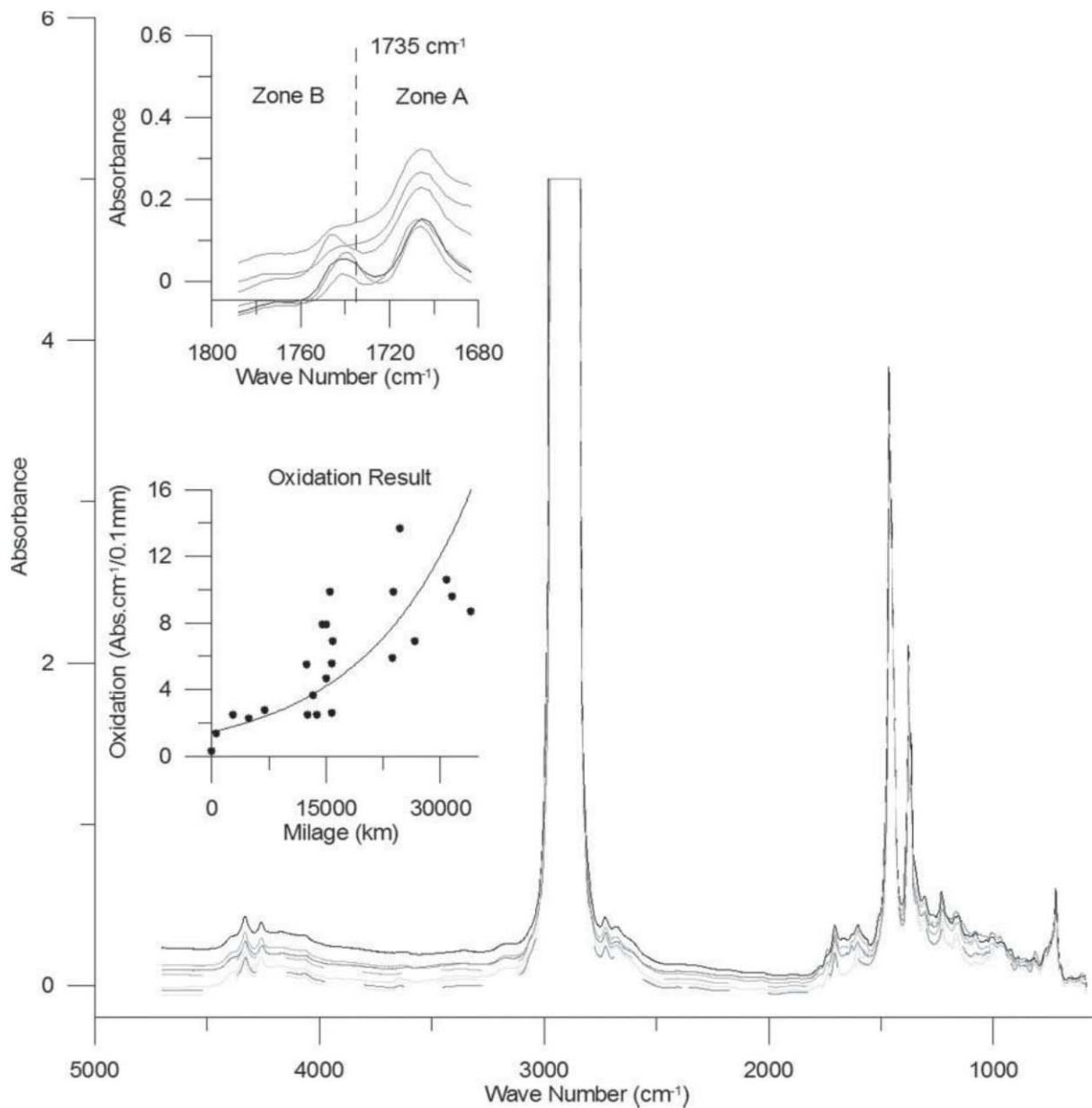


Figure 3 | Results for diesel engines using mineral oil C.

mm. This was a direct result of the lower thermal stress suffered by engine oil in diesel engines. Additionally, it can also be assumed that a certain reduction was associated with a lower PH value for fresh oil C compared to oils A or B. In all cases, the trend of the spectra of lubricating oils is the growth of zone A, in terms of both PH and PAI, as a direct result of thermal degradation suffered by engine oil. Oxidation levels in oil B were lower than those obtained in oil A due to its better base oil and higher additive package.

Figure 4 presents the results for samples from diesel vehicles that had severe fuel dilution problems (reaching al-

most 20% of fuel dilution in one sample). The fuel was the B20 biodiesel blend. Fuel dilution problems can be easily detected, showing the important peak increase reaching values of about 0.6 Abs in zone B (1770–1735 cm^{-1}).

The following equation has been used to quantify the fuel dilution percentage presented in Figure 4:

$$\text{Fuel Dilution (\%)} = 0.4984 \cdot \text{PH} + 3.6607$$

This equation was obtained as a calibration curve in laboratory tests using fresh oil and the B20 biodiesel blend.

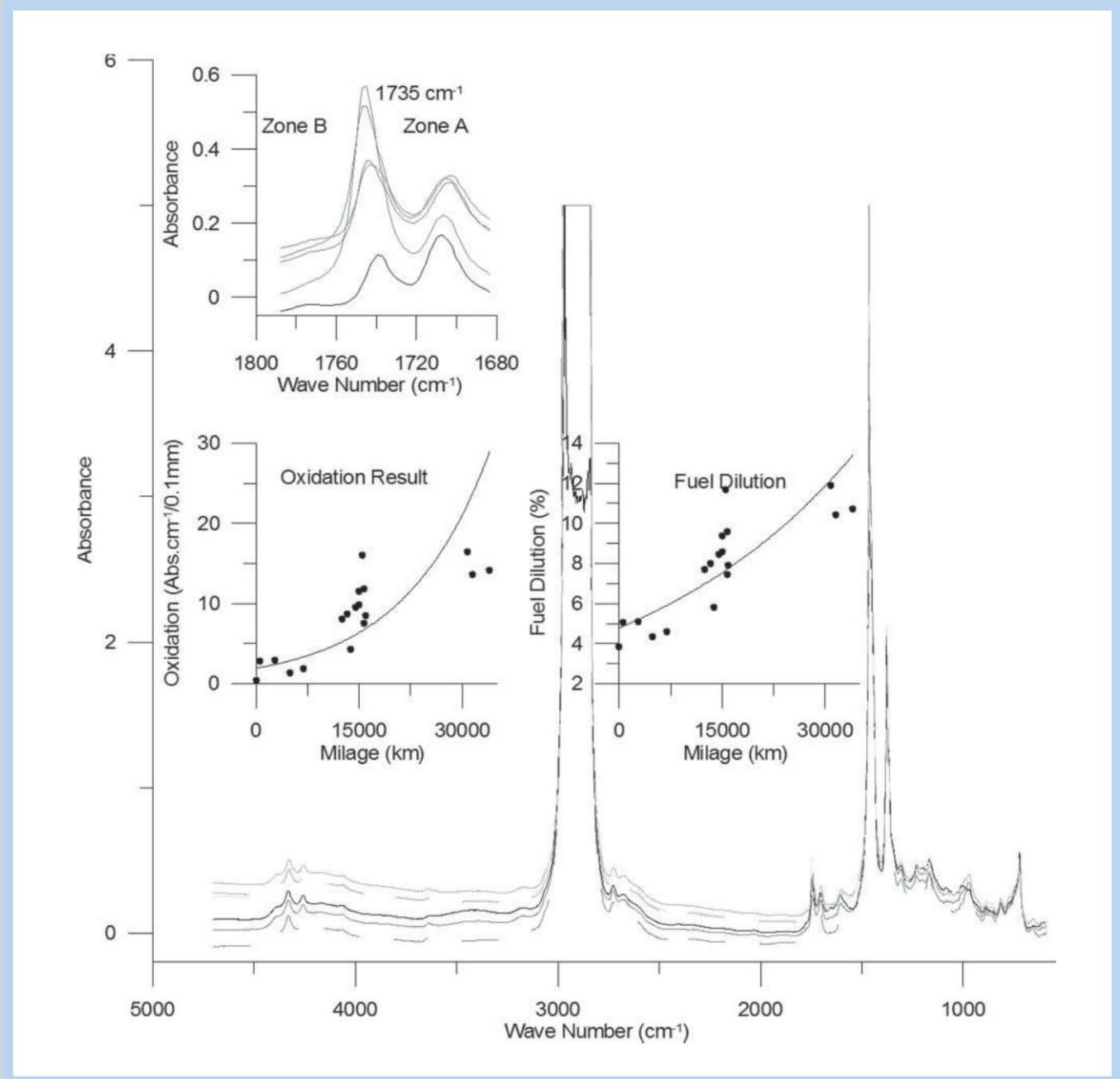


Figure 4 | Results for diesel engines (oil C) with fuel dilution problems.

Samples from Lab Degradation Tests

Figures 5–8 present the results for lab thermal degradation tests for the different types of engine oils considered. As can be observed, thermal degradation was mainly characterized by a peak increase in zone A (1725–1650 cm^{-1}). There was a clear difference between oil D (Figure 8), formulated using an API IV base oil, and the other types of engine oils considered. The same behavior observed in samples from engines in real service, related to the peak present in zone B and associated with fresh oil, gradually disappeared in degraded samples, was observed in these simulation tests. As can be clearly observed in Figures 5–7, peak in zone B disappear

gradually as a consequence of lube degradation.

Figures 9 and 10 show the results for lab fuel contamination tests. The fuel dilution effect was mainly reflected as a peak spectra increase in zone B (1770–1725 cm^{-1}). Oil D has a special behavior because the high absorbance in zone B (1.4 Abs), related to its synthetic origin (ester base oil), led to difficulties in detecting changes associated with fuel contamination. In most cases there was a decrease in absorbance in this area (Figure 10). In an uncommon scenario, where B20 biodiesel blend was used and high fuel dilution problems are present, a slight increase in absorbance values was observed (Figure 10). Oil C (degraded in the lab) had the

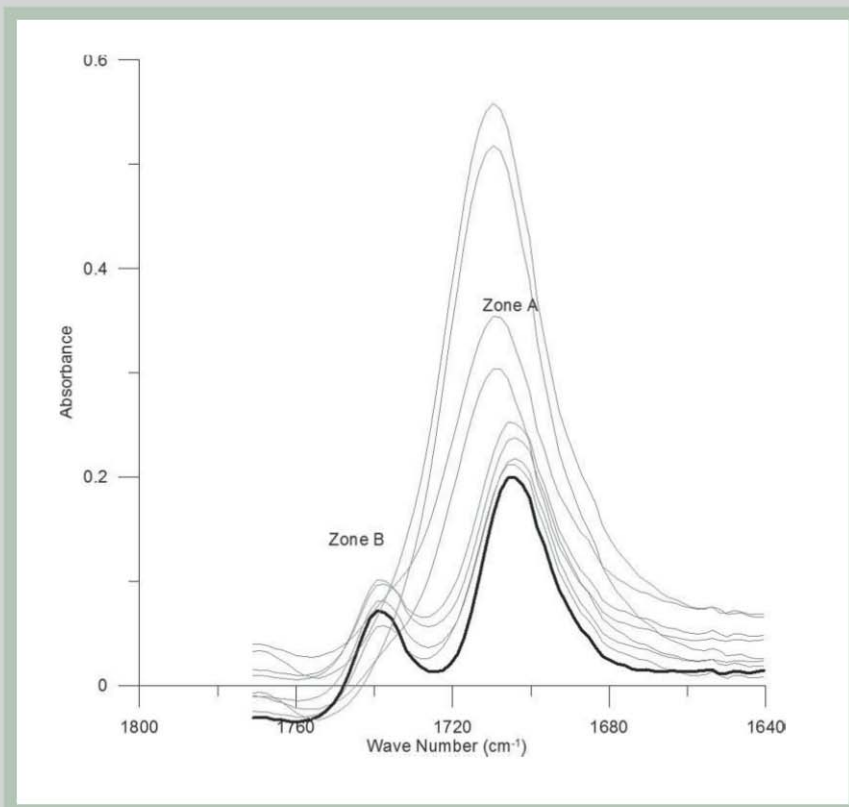


Figure 5 | FTIR spectra (range 1750-1640 cm^{-1}) for samples degraded by temperature. Engine oil type A.

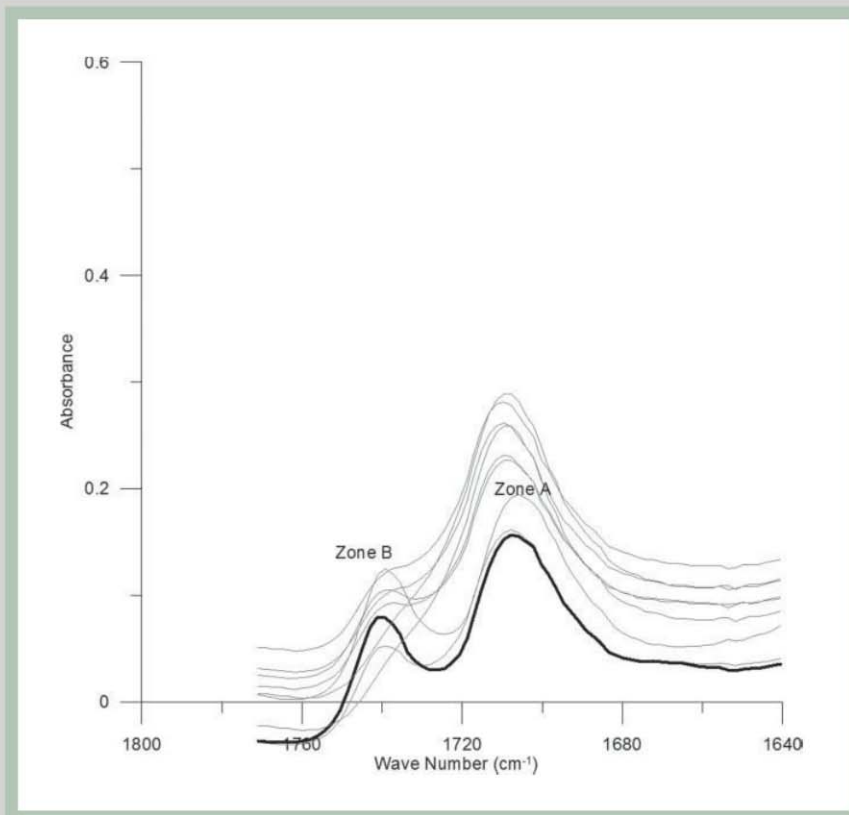


Figure 6 | FTIR spectra (range 1750-1640 cm^{-1}) for samples degraded by temperature. Engine oil type B.

same behavior observed in samples from engines in real service related to the peak located in zone B and associated with fresh oil; this peak increased gradually in contaminated samples (up to 0.6 Abs measured as a PH with 20% of fuel dilution using a B20 blend; Figure 9).

CONCLUSIONS

A procedure based on ASTM standard D7214 was defined to improve oxidation quantification and problem detection in used oils from internal combustion engine. Two parameters were used depending on potential problems that can be present in samples: PH and PAI. The wavenumber range considered was between 1770 and 1650 cm^{-1} using a single baseline from 1850 to 1620 cm^{-1} . Two zones were defined inside the main wavenumber range taking into account where the studied variables (thermal degradation and fuel dilution) could be more easily detected in each zone. Zone A was defined between 1725 and 1650 cm^{-1} and zone B was defined between 1770 and 1725 cm^{-1} .

Oil degradation related to thermal stress was mainly studied in the range 1725-1650 cm^{-1} because, as observed in this work, this is the range where most of the by-products of the thermal oxidation degradation process present higher absorbance values. Carboxylic acids and ketones are the main products, where the C-O and O-H vibrations are highly characteristic in this frequency range.

Detection of fuel contamination could be performed in additional wavenumber ranges than those offered by the ASTM standard practice (835-735 cm^{-1}). Taking into account the increased use of biofuel blends, fuel dilution problems were much easier to identify in zone B (1775-1725 cm^{-1}). The ester content due to biofuel contamination had vibrations highly characteristic in the frequency range 1750-1725 cm^{-1} . This procedure presents more clear advantages when higher biodiesel blends are used.

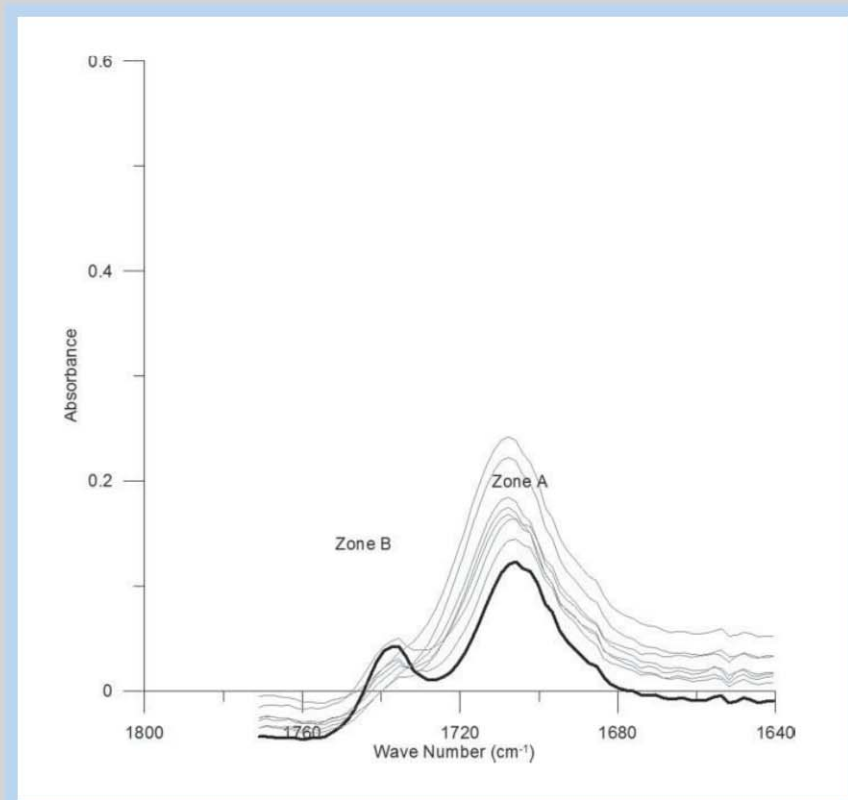


Figure 7 | FTIR spectra (range 1750-1640 cm^{-1}) for samples degraded by temperature. Engine oil type C.

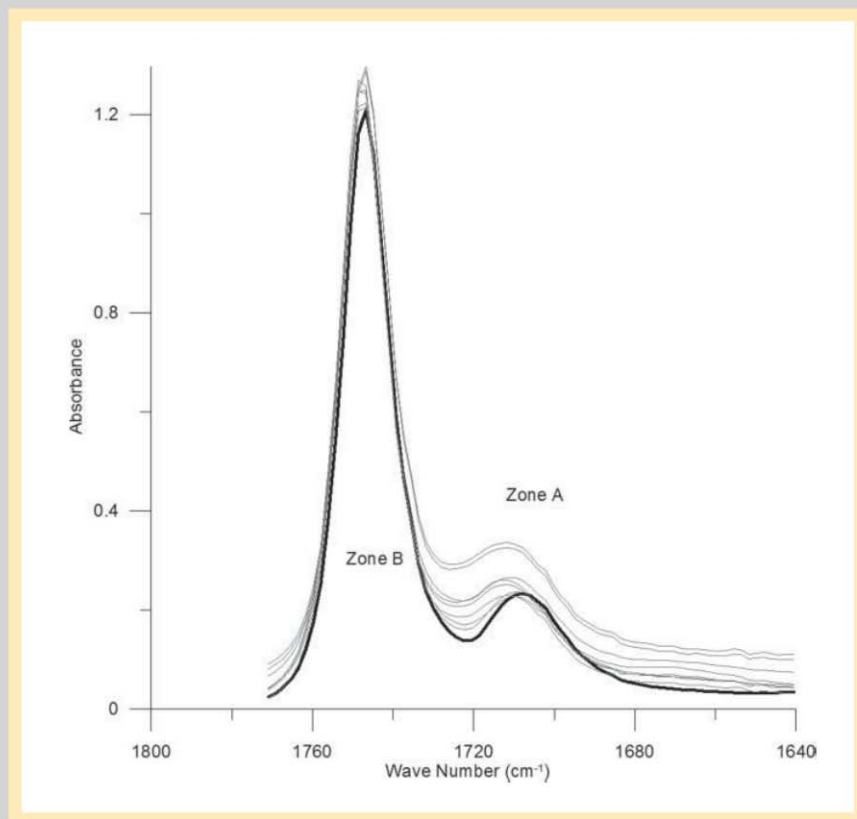


Figure 8 | FTIR spectra (range 1750-1640 cm^{-1}) for samples degraded by temperature. Engine oil type D.

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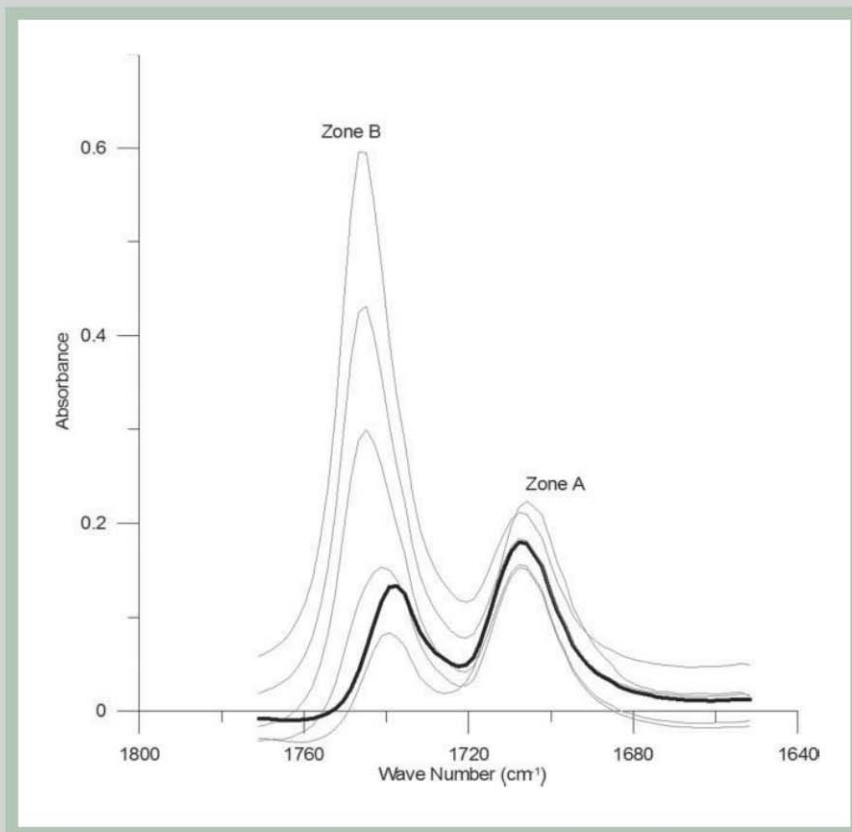


Figure 9 | Evolution of degradation by fuel dilution (B20). Engine oil type C.

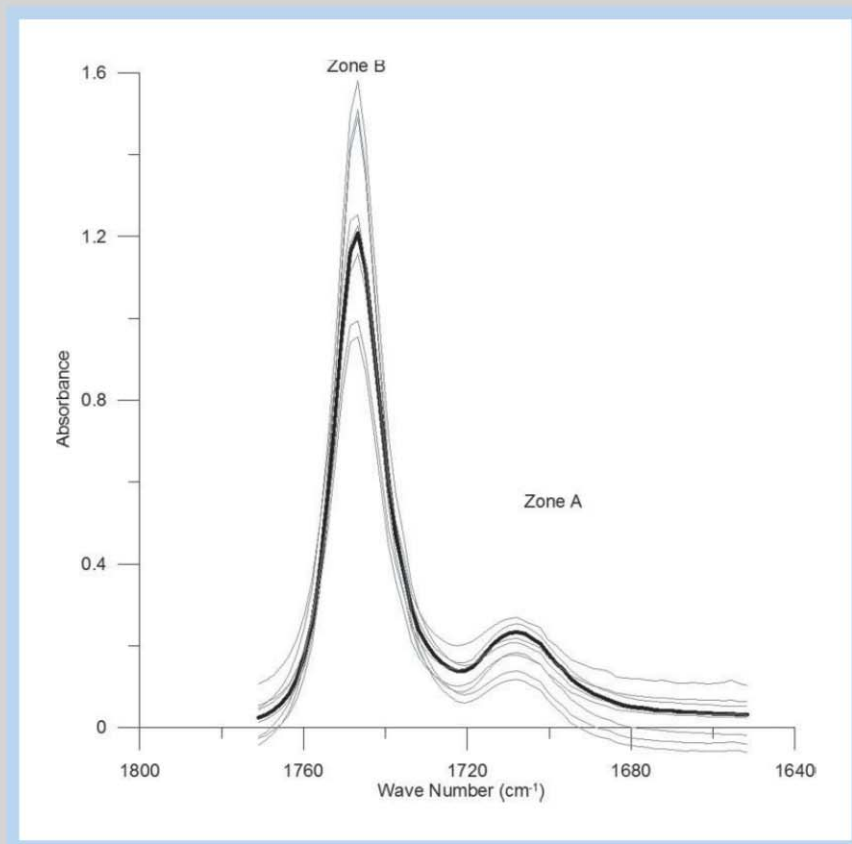


Figure 10 | Evolution of degradation by fuel dilution (B20). Engine oil type D.

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