

MURE National Project: FTIR spectroscopy study to assess ageing of asphalt mixtures

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ABSTRACT

The French national project MURE, a collaborative research and development programme, started in March 2014. Two main issues are addressed: coupling of recycling and warm-mix asphalt technique and multi-recycling of bituminous mixtures. It gathers the national road federation, academic laboratories, road contractors and project contracting officials. The objective of the first working group (WG1) of MURE is to validate an accelerated ageing process for bituminous mixtures as well as on site than in laboratory.

To achieve this goal, it is first necessary to characterize the ageing using a reliable and reproducible method valid for laboratory and plant-made mixtures. Many studies from the literature showed the efficiency of FTIR spectroscopy for ageing identification. In particular, carbonyl and sulfoxide groups found in binders are appropriate ageing markers. Meanwhile, no common FTIR protocol does exist at present. The first step of the experimental work performed by the WG1 was to compare seven FTIR methods, differing from sample preparation and approaches for calculating spectroscopic indexes. One given bitumen was aged eight times successively by RTFOT method (75 min – 163 °C). Two IR spectrum acquisition modes were tested: attenuated total reflectance (ATR) and transmission (spreading of bitumen on an IR transparent plate and bitumen dissolution in a solvent). The second step of the study was to verify the repeatability of FTIR tests on neat and aged bitumen according to sample preparation and calculation methods.

The results allow confirming the relevance of FTIR spectroscopy for qualifying bitumen ageing. A single methodology and a common tool for harmonizing the calculation of indexes are proposed. The whole procedure can be used to follow the ageing properties on site at short and long times.

Keywords: Ageing, Chemical properties, Industrial application, Reclaimed asphalt pavement (RAP) Recycling, Warm Asphalt Mixture

1. INTRODUCTION

In 2009, after the Grenelle Environment Roundtable, a Voluntary Agreement was signed by the French Ministry of Ecology, the USIRF (Union of French road industry associations) and the companies involved in public works. This convention required environmental objectives: recycling of bituminous materials, promotion of WMA (Warm Mix Asphalt) techniques; and target figures (60% of recycled materials in plant in 2012).

In this framework of sustainable development, the French national project MURE (Multirecycling and warm mix asphalts) [1], a collaborative research program, started in 2014. It gathers about thirty partners (national road federation, academic laboratories, road contractors, additive suppliers and project contracting officials) and is organised in ten working groups (WGs). The main objectives of this project are the coupling of recycling and WMA techniques and the multirecycling of bituminous mixtures.

The first working group (WG1) is composed of eight partners. Its mission is to develop an accelerated ageing process for bituminous mixtures at industrial scale in order to obtain Reclaimed Asphalt Pavements (RAP) rapidly, without waiting 20 or 30 years. To this purpose, it is first necessary to propose a reliable, repeatable and reproducible method of bitumen ageing characterisation in laboratory. The FTIR (Fourier Transform InfraRed) spectroscopy was the selected technique because of its efficiency. Meanwhile, no standardised protocol exists at present to exploit the IR peaks.

In this paper, a brief state of the art about ageing characterisation by FTIR spectroscopy is introduced. Then, the experimental program is described. Many laboratories of WG1 tested the same bitumen after progressive ageing with its own FTIR protocol. Moreover, one laboratory tested neat and aged bitumen by varying preparation and calculation methods in order to define a common procedure. Finally, the FTIR results are discussed.

2. LITERATURE REVIEW

According to the type of layer (wearing or base course), the long term ageing of a bituminous mixture is due to temperature, air exposure, traffic-loadings or UV effect. All these factors could be combined and depend on time. From a chemical point of view, ageing is caused by irreversible oxidation, itself due to the presence of oxygen in air, thus creating carbonyl (C=O) and sulfoxide (S=O) groups, modifying bitumen composition (increase in molecule size, bitumen polarity and aromaticity) and hardening the bituminous binder which becomes more brittle [2,3]. Carbonyl and sulfoxide groups are considered as relevant markers for qualifying bitumen ageing and their monitoring by FTIR spectroscopy is often used [4]. Sulfoxide groups can be present before ageing, according to the origin of crude oil. They form faster and at higher temperature than carbonyl groups [2].

The determination of carbonyl or sulfoxide indexes (noted I_{CO} and I_{SO} respectively throughout this paper) by FTIR spectroscopy is used as a scientific tool in many research works to follow during time the ageing evolution of unique bitumen. Nevertheless, it seems difficult to estimate the degree of ageing for a given bitumen at a time t [2]. Consequently, far specifications on I_{CO} and I_{SO} cannot be implemented for qualifying RAP (Reclaimed Asphalt Pavements). According to European standard 13108-8 [5], the requirements for a binder extracted from RAP concern penetration, Ring & Ball softening point and viscosity.

In a FTIR spectrum, carbonyl and sulfoxide peaks are located at wavenumbers of 1700 and 1030 cm^{-1} respectively [6] (cf. Figure 1).

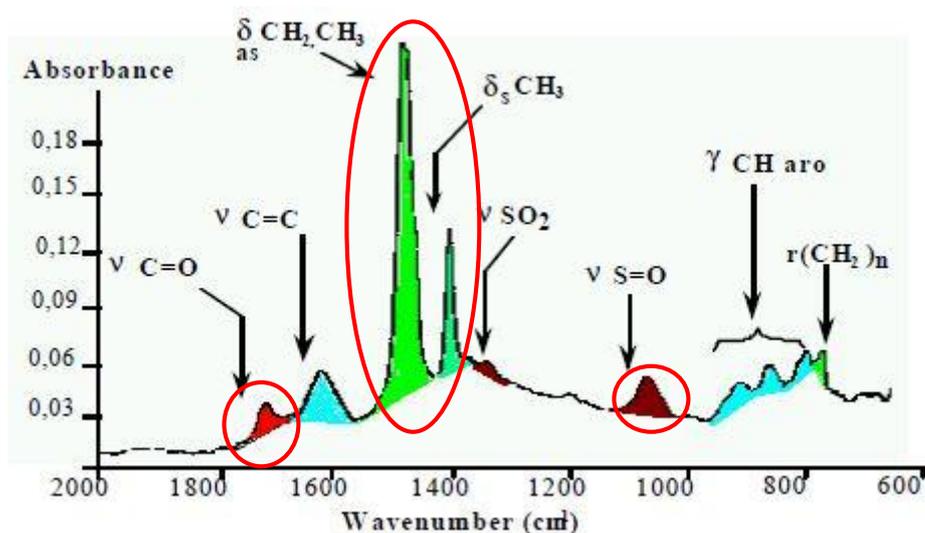


Figure 1: FTIR bitumen spectrum – presentation of carbonyl, sulfoxide and reference peaks (circled in red) [7]

I_{CO} is calculated according to equation 1:

$$I_{CO} = \frac{A_1}{A_0} \quad (1)$$

A_1 is the peak area of carbonyl group centred at 1700 cm^{-1} , A_0 is the area of peaks referred to ethylene and methyl groups (reference peaks) and centred at 1460 and 1375 cm^{-1} respectively (cf. Figure 1).

I_{SO} is calculated according to equation 2:

$$I_{SO} = \frac{A_2}{A_0} \quad (2)$$

A_2 is the peak area of sulfoxide group centred at 1030 cm^{-1} [6].

For these calculations, the spectrum is plotted in absorbance expressed following Beer-Lambert equation [2]:

$$\text{Abs}(\nu) = \epsilon_i(\nu) \times c_i \times l \quad (3)$$

Abs is the absorbance of a species i for the wavenumber ν , ϵ_i is the molar absorption coefficient of the species i for the wavenumber ν , l is the optical path length and c_i is the concentration of the species i . Then, I_{CO} is deduced from equations 1 and 3:

$$I_{CO} = \frac{\epsilon_1}{\epsilon_0} \times \frac{c_1}{c_0} \quad (4)$$

In 2010, Mouillet and al. [6] listed two methods for the analysis of bitumen samples using FTIR spectroscopy: transmission mode and attenuated total reflectance (ATR) mode. The transmission mode can be performed following several methods of bitumen sample preparation: spreading of hot bitumen on a transparent plate (KBr, NaCl, CsI...) or bitumen dissolution in a solvent. In this latter case, the bitumen solution can be either introduced into an appropriate cell, or deposited onto a transparent plate until the solvent evaporates.

In the literature, many methods are described for the calculation of carbonyl index:

- The RILEM method was implemented by the TG5 group of RILEM [2,8]. It consists of calculating I_{CO} with fixed area limits and a baseline drawn between the values of these limits (fixed carbonyl limits: 1660 and 1753 cm^{-1} ; fixed reference limits: 1350 and 1525 cm^{-1}). It was derived from IFSTTAR method no. 69 [6];
- The BRRC method [2] takes into account the peak height at 1700 cm^{-1} and the area defined at fixed limits (1770 and 1530 cm^{-1}). For this purpose, the baseline of each spectrum is corrected and each peak is brought to an absorbance coefficient of 1.2. This method was used by the BRRC laboratory (Belgium) in the framework of European project Re-Road (WP1) [9];
- The valley to valley method [10]: the peak area of carbonyl group is not delimited by fixed limits, but by the closer valleys located around the peak. Then the limits can differ from a spectrum to another;
- The deconvolution method [2,10] fits the spectrum with Lorentzian functions centred on chosen wavenumbers and a parabolic function.

From all these statements, it is deduced that the determination of I_{CO} and I_{SO} by FTIR spectroscopy is not standardised. Therefore, each laboratory has its own procedure, which leads to a scattering in the results. This observation was noted in the work of Marsac *et al.* [2].

The objective of this present study is to propose a common method for the preparation and analysis of bitumen samples by FTIR spectroscopy and the calculation of I_{CO} and I_{SO} .

3. CONTEXT OF THE EXPERIMENTAL STUDY

MURE is a collaborative programme gathering many laboratories which participate for all the analyses on binders. The members involved in the work of WG1 are presented in Table 1.

Table 1: Participants in bitumen characterisation tests for WG1, June 2015

Participant	Type of research structure
CEREMA/DTerMed	Academic laboratory
COLAS	Road contractor
EIFFAGE TP	Road contractor
ESTP	Academic laboratory
EUROVIA CRM	Road contractor
HONEYWELL	Additive supplier
IFSTTAR	Academic laboratory
MALET	Road contractor
TOTAL*	Bitumen supplier

* TOTAL is not a member of WG1, but it took part in several tests presented in this work.

A first industrial accelerated ageing process was conducted in Switzerland in December 2013. Five laboratories assessed oxidation indexes on four bitumen samples referred as follows:

- Bit 1: 50/70 penetration grade neat bitumen;
- Bit 2: bitumen extracted from the hot mixture applied on site (referred as E0) and manufactured with Bit 1;
- Bit 3: bitumen extracted from the mixture E0 passed three times through a drum mixer (mixture obtained referred as AE3). This operation was performed in order to accelerate the ageing of bituminous mixtures in plant;
- Bit 4: bitumen extracted from the mixture E0 stored at loose state for a long period. Then, the “natural” ageing was observed on site and compared to the accelerated ageing.

Bit 3 and Bit 4 are supposed to be the most aged bitumen samples.

Amongst the participants, two laboratories qualified oxidation without calculation (by answering yes or no). Three other laboratories (referred as Lab 1, Lab 2 and Lab 3) quantified the indexes with their own method. The results are displayed in Figure 2.

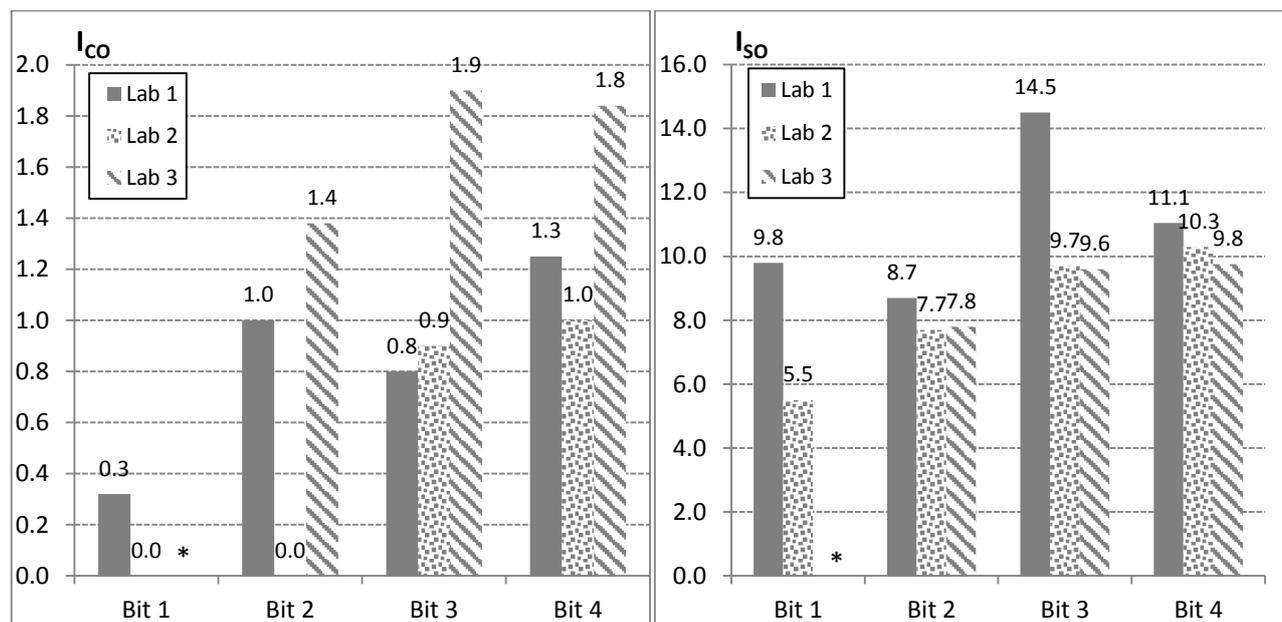


Figure 2: Carbonyl and sulfoxide indexes of four bitumen samples measured by three laboratories

* Not measured.

The following conclusions can be withdrawn from Figure 2:

- I_{SO} values are higher than I_{CO} values. Moreover, the four bitumen samples show high values of I_{SO}. It is assumed that this index is a less appropriate marker for bitumen ageing than I_{CO};
- For Labs 2 and 3, I_{CO} and I_{SO} increase from Bit 1 to Bit 4. The results from Lab 1 do not show the same tendency;
- Low values of I_{CO} are found for Bit 3 and Bit 4, whatever the laboratory performing the experiment (maximum I_{CO} value for Bit 3 = 1.9%). Furthermore, the indexes of Bit 4 are higher than those of Bit 3 (except the case of I_{SO} found by Lab 1);
- For a same bitumen sample, both I_{CO} and I_{SO} values are scattered. For example, I_{CO} of Bit 3 assessed by Lab 1 equals 0.8%, while the same index evaluated by Lab 3 equals 1.9%.

Even though the results indicate an increase in I_{CO} and I_{SO} from Bit 1 to Bit 4, the industrial process tested (introduction of mixture E0 three times in a drum mixer) did not accelerate enough the ageing of bituminous mixture. These results are confirmed by penetration and Ring and Ball values (~ 35 1/10 mm and $\sim 56^\circ\text{C}$ with targeted values of ~ 17 1/10 mm and $\sim 70^\circ\text{C}$ respectively). Therefore, another process of accelerated ageing on site must be defined by WG1. It is also deduced from Figure 2 that it is necessary to harmonise all the FTIR methods of laboratories.

From these conclusions, two actions were decided:

- A round robin test with each own FTIR method on one given bitumen sample;
- For one selected laboratory, an optimisation of the method by comparison of sample preparation and calculation methods.

4. ROUND ROBIN TEST

For the round robin test, 50/70 penetration grade pure bitumen was aged eight times successively by RTFOT method (75 min – 163°C). Then, nine samples were obtained and analysed by FTIR spectroscopy.

Two methods of preparation were tested: transmission mode and ATR mode. As described previously (cf. Paragraph 2.), the transmission mode can be either performed on a IR transparent plate (KBr or NaCl) or by bitumen dissolution. In the first case, the bitumen was heated at a sufficient temperature (around 100°C) to be spread on the plate with a spatula and to obtain a translucent film. The spectrum of the sample was obtained after subtraction of the background. Bitumen film was thin [2] in order to avoid spectrum saturation. The variation of thickness (and thus optical path length) has no influence on I_{CO} and I_{SO} , since these are calculated as a function of the proportion of reference groups used as internal standard. In the second case of preparation, 5% bitumen was dissolved in organic solvent (perchloroethylene or cyclohexane). The solution was then deposited between two transparent IR plates. The method using bitumen dissolution (deposition of a bitumen solution drop on a transparent plate and analysis after solvent evaporation) was not tested in the round robin test.

Concerning the ATR mode, the sample was directly deposited on the diamond reflection crystal heated at high temperature or remained at room temperature. One of the characteristics of this ATR method is that the signal needs to be processed to get the spectrum.

Seven laboratories participated to this round robin test. According of each laboratory, different spectrometers were used (from Perkin Elmer Inc. or Thermo Fisher Scientific Inc.). The data processing was conducted directly using the spectrometer software of each laboratory. The resolution of the spectra was 4 or 2 cm^{-1} , according to the practices of each laboratory. The spectra of bitumen samples were means of 32 scans. Concerning the calculation methods, the determination of I_{CO} and I_{SO} were defined according to equations 1 and 2. To this purpose, fixed limits of carbonyl, sulfoxide and reference peaks were chosen. The fixed limits homogenise the area calculation with a minimum time spent (especially when a multitude of spectra must be interpreted) but can conduce to wrong results because of a negative area taken into account in the calculation (cf. Figure 3). Meanwhile, these limits differ from a laboratory to another.

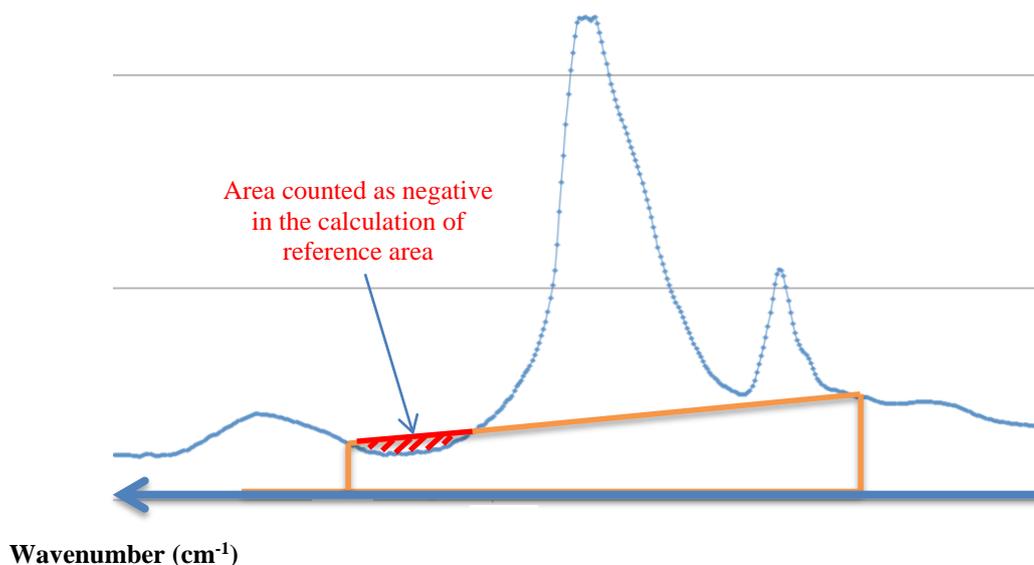


Figure 3: Possible issue when using the method of fixed limits on reference peaks

The experimental conditions for sample preparation and integration limits in transmission and ATR mode are gathered in Tables 2 and 3 respectively.

Table 2: Integration limits for calculation of areas in transmission mode

Laboratory	Method of preparation	Integration limits (cm ⁻¹)					
		Carbonyl peak (1700 cm ⁻¹)		Sulfoxide peak (1030 cm ⁻¹)		Reference peaks (1460 and 1375 cm ⁻¹)	
1	Spreading of hot bitumen on NaCl plate	1719	1678	1070	983	1524	1350
2	Spreading of hot bitumen on KBr plate	1721	1665	1098	980	1505	1330
3*	Spreading of hot bitumen on KBr plate	1723	1645	1082	980	1538-1399	1399-1349
4	Bitumen dissolution in cyclohexane	1731	1680	1055	1028	1532.9	1317.6
	Bitumen dissolution in perchloroethylene	1724	1673	1070	1014	1532.9	1317.6
5	Spreading of hot bitumen on KBr plate	1753	1635	1082	980	1538	1349
		1750	1660	1075	979	1539	1325

* Areas of ethylene and methyl groups were calculated separately.

Table 3: Integration limits for calculation of areas in ATR mode

Laboratory	Temperature of diamond crystal (°C)	Integration limits (cm ⁻¹)					
		Carbonyl peak (1700 cm ⁻¹)		Sulfoxide peak (1030 cm ⁻¹)		Reference peaks (1460 and 1375 cm ⁻¹)	
3	Room temperature	1723	1645	1082	980	1538-1399	1399-1349
4	100	1731	1680	1055	1028	1532.9	1317.6
6	Room temperature	1731	1666	1079	976	1485	1326
7	140	1729	1664	1101	980	12 peaks between 3100 and 707	

The results are depicted in Figures 4 and 5.

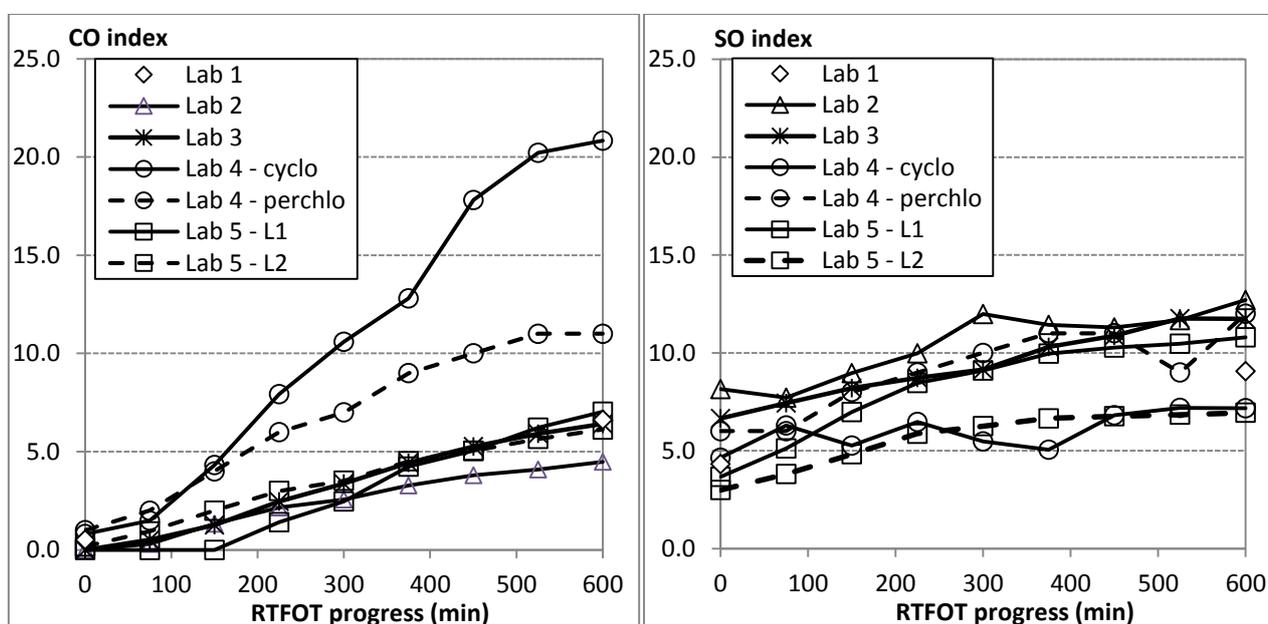


Figure 4: Evolution of I_{co} and I_{so} in transmission mode as a function of RTFOT progress

L1: 1st integration limits for Lab 5, L2: 2nd integration limits (cf. Table 2).

Note: for Lab 5, the first three oxidation results are negative, due to the calculation method. Since a negative value has no physical signification, the values were brought back to zero.

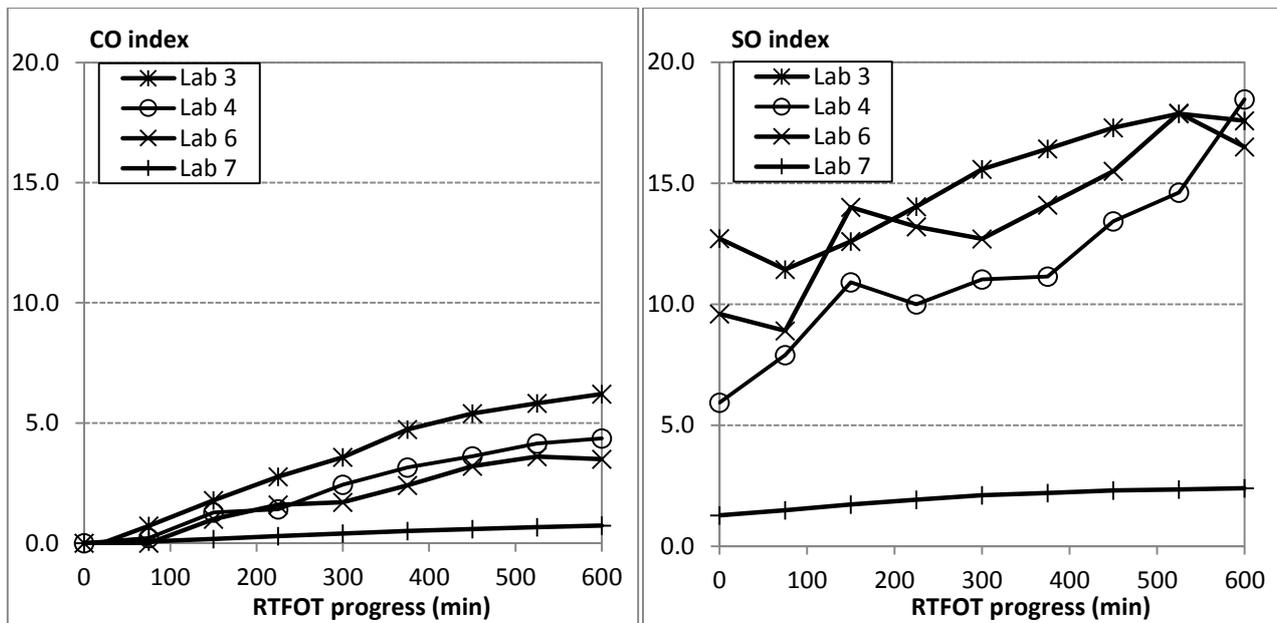


Figure 5: Evolution of I_{CO} and I_{SO} in ATR mode as a function of RTFOT progress

According to Figures 4 and 5, I_{SO} index is positive, whatever the preparation method. It is also the case for I_{CO} index, except for Lab 5 – L1, for which the first three values are negative. This is due to the chosen integration limits. For both preparation methods, I_{CO} increases constantly from 0 to 600 min, whereas I_{SO} increases, then reaches a plateau. For example, I_{SO} stabilises from 450 to 600 min for Labs 4 and 5 in transmission mode and from 300 to 600 min for Lab 7 in ATR mode. The results stress a difference in oxidation kinetics of carbonyl and sulfoxide groups. This is in accordance with the literature [8].

In transmission mode, the I_{CO} values are in the same range from 0 to 600 min, except for Lab 4. Labs 1, 2, 3 and 5 performed the FTIR tests by spreading of bitumen on KBr or NaCl plate. Even though various parameters were different from a laboratory to another (thickness of bitumen film, type of spectrometer, software used for the calculations), the discrepancies in I_{CO} values are low. Moreover, the integration limits taken by the three laboratories are in the same wavenumber range (cf. Table 2). The differences in I_{CO} values calculated with limits L1 and L2 (Lab 5) can be attributed to the presence of different limits between the peaks and the baseline. This is more visible with I_{SO} . On contrary to the other laboratories, Lab 4 performed the tests by bitumen dissolution. It is deduced that the solvent probably interacts with bitumen, thus modifying its chemical composition. This interaction seems more important with cyclohexane than with perchloroethylene.

In ATR mode, I_{CO} and I_{SO} values are in the same range for Labs 3, 4 and 6, but low for Lab 7. This is due to the calculation method employed by this laboratory. A multitude of peaks were taken for determining the area of reference groups (cf. Table 3). Therefore, the area found for these groups is high, and I_{CO} and I_{SO} are low.

After eight cycles of RTFOT, mean I_{CO} (excluding values obtained by Lab 4) is slightly higher in transmission mode than in ATR mode, whereas mean I_{SO} is higher in ATR mode.

According to the results from Figure 4, sample preparation by bitumen dissolution and direct FTIR analysis on the solution is discouraged. The I_{CO} and I_{SO} values obtained from transmission mode by spreading on KBr plate and ATR mode are in the same range. Meanwhile, the repeatability of these results must be verified. Moreover, the spectroscopic indexes depend on the calculation methods. It is also interesting to create a useful tool for calculating easily I_{CO} and I_{SO} and usable by any laboratory. For this purpose, calculations on two bitumen samples were performed using Excel.

5. REPEATABILITY OF FTIR TESTS IN TRANSMISSION AND ATR MODE

One laboratory (Lab 5) conducted FTIR tests on two samples: 35/50 penetration grade pure bitumen and the same bitumen aged by PAV (100 °C under air pressure of 2.1 bars).

Both transmission and ATR mode were used for sample preparation. In the case of transmission mode, only the spreading of hot bitumen on KBr plate was performed according to the procedure described in 4. Five tests were carried out on the same sample for each condition in order to get reliable results. In the case of ATR mode, bitumen samples were deposited on the diamond crystal at room temperature.

Both samples (neat and aged 35/50 penetration grade bitumen) were analysed in a Thermo Fisher Scientific spectrometer, at a resolution of 4 cm^{-1} . The spectra obtained were means of 32 scans.

The calculation of areas was lead using the software with data processing of the spectrometer and on an Excel worksheet (according to trapezoidal method, cf. Figure 6).

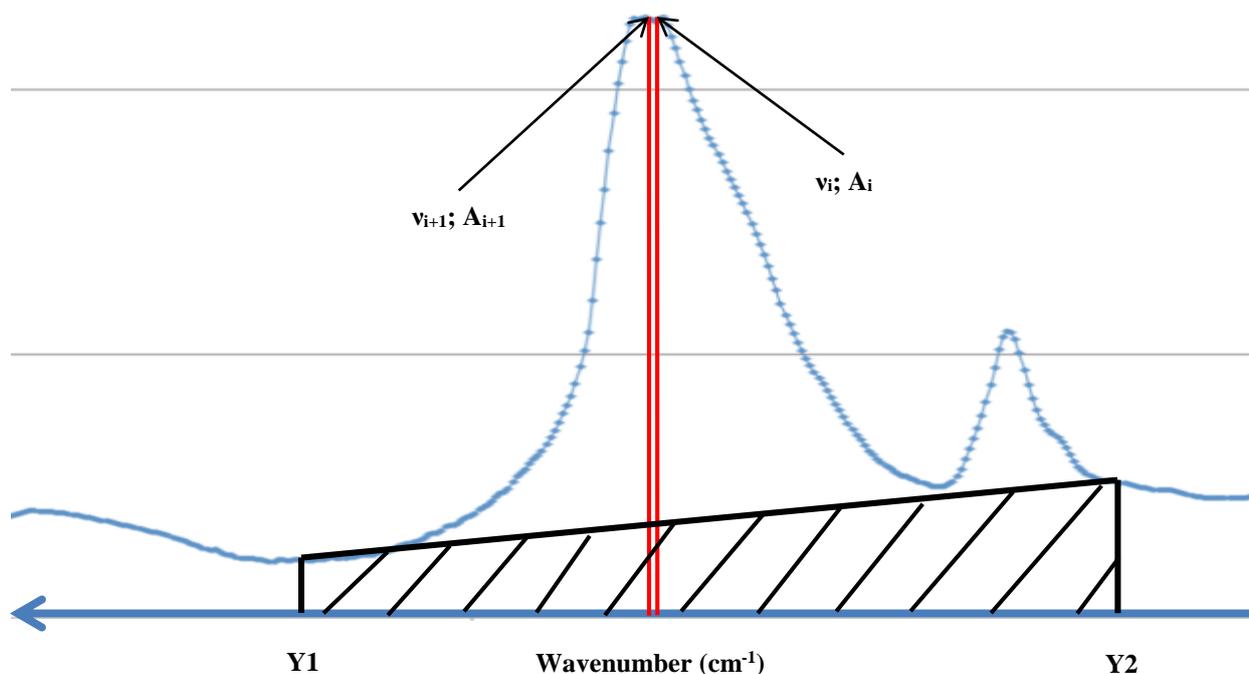


Figure 6: Trapezoidal method applied to reference peaks

Peak areas of carbonyl, sulfoxide and reference groups were calculated according to the following equation:

$$\text{Area} = \left(\sum_{i=Y1}^{Y2} \frac{A_i + A_{i+1}}{2} \times (v_{i+1} - v_i) \right) - (\text{Trapezoidal black area}) \quad (5)$$

A_i and A_{i+1} are the areas of peaks centred at the wavenumbers v_i and v_{i+1} respectively.

The two types of limits (L1 and L2) are given in Table 4 and were applied for transmission (referred as KBr) and ATR mode.

Table 4: Method integration limits for calculation of areas

Type of limits	Integration limits (cm ⁻¹)					
	Carbonyl peak (1700 cm ⁻¹)		Sulfoxide peak (1030 cm ⁻¹)		Reference peaks (1460 and 1375 cm ⁻¹)	
L1- Peak limits	1753	1635	1082	980	1538	1349
L1 - Baseline limits	1753	1635	1082	980	1538	1349
L2 - Peak limits	1720	1678	1070	980	1540	1350
L2 - Baseline limits	1720	1540	1100	980	1540	1200

Figures 7 and 8 show the results before and after ageing, as a function of the calculation methods (limits L1 and L2; spectrometer software or Excel).

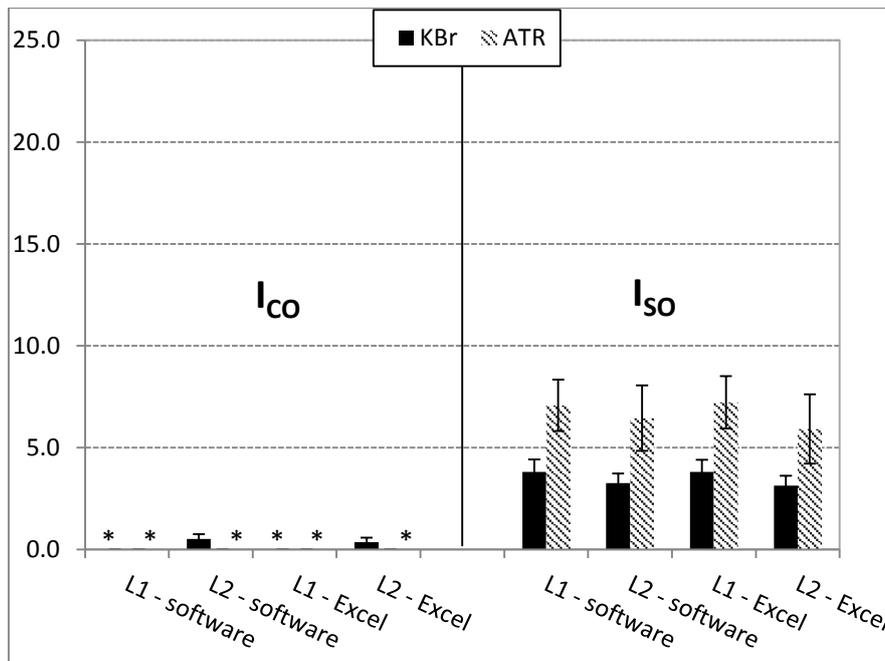


Figure 7: I_{CO} and I_{SO} values of 35/50 penetration grade neat bitumen according to analysis method

* indicates negative values due to the calculation method. Since a negative value has no physical signification, the values were brought back to zero.

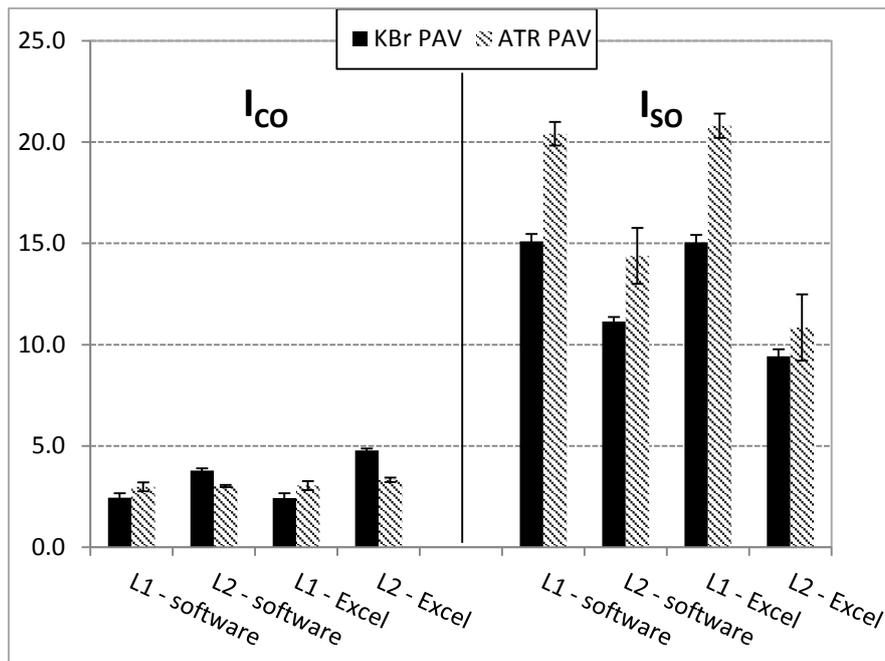


Figure 8: I_{CO} and I_{SO} values of 35/50 penetration grade aged bitumen according to analysis method

The presence of sulfoxide groups is confirmed in neat bitumen, whatever the method employed. It is deduced that I_{SO} is a less appropriate marker for qualifying bitumen ageing. In the case of neat bitumen, I_{CO} is negative when it is assessed with limits L1 (KBr and ATR mode) and limits L2 in ATR mode. This confirms that the choice of integration limits is important for the calculation.

After PAV, an increase in the values of indexes is observed, thus confirming bitumen oxidation.

It is also noticed that I_{SO} is always higher in ATR mode. Moreover, the standard deviation of I_{SO} is higher in ATR than in transmission mode ($\sigma_{mean} \sim 0.3\%$ and $\sigma_{max} \sim 0.6\%$ in transmission, $\sigma_{mean} \sim 1.3\%$ and $\sigma_{max} \sim 1.6\%$ in ATR). It is concluded that the calculation with transmission mode is more repeatable than with ATR mode.

Regarding limits, differences in index values is remarked, especially with aged bitumen. In particular, I_{SO} is lower when calculated with limits L2. As the integration limits of the baseline are broader than the integration limits of the peaks, the peak area is higher. In particular, the area of reference group is overestimated. Meanwhile, limits L1 conduct to negative results for neat bitumen.

There are no significant differences between Excel and spectrometer methods, except with limits L2. This is due to the discordance between the integration limits of the peaks and the limits of their baseline, thus conducting to a misleading increment with Excel. It is assumed that the spectrometer software uses a method close to trapezoidal method with a comparable precision.

As a conclusion, transmission mode by spreading of bitumen on KBr plate is more favoured than ATR mode, since the results obtained using this preparation are more repeatable. Calculation of indexes with Excel provides the same results as the spectrometer software. Then, a macro of Excel sheet was implemented in order to facilitate and harmonise the calculation of indexes with a complete control. At present, this tool is operational and usable by any laboratory.

6. CONCLUSIONS

This project, part of the collaborative national project MURE, is focused on FTIR spectroscopy study to assess ageing of asphalt mixtures. It allows confirming that this technique is relevant to qualify bitumen ageing and to quantify ageing evolution with time. The I_{CO} is more appropriate than I_{SO} for evaluating bitumen oxidation.

In this work, ATR and transmission modes have been compared. It was shown that ATR mode was less appropriate, since it is less repeatable and the spectra obtained are first mathematically treated. Concerning transmission mode, two methods were tested: spreading hot bitumen on transparent plate and bitumen dissolution and direct analysis of the solution. The second method is discouraged because of chemical interaction between bitumen and solvent. Moreover, it requires a long preparation. The method of hot bitumen spreading on transparent plate is fast and does not depend on the thickness of bitumen film. This method is the one selected for analysing bitumen samples throughout the national project MURE.

This study highlighted discrepancies in the index values due to the calculation methods. The method of fixed limits is practical when a multitude of spectra must be interpreted. Meanwhile, it can lead to misleading results, since negative areas can be taken into account in the calculation. Furthermore, each laboratory does not choose the same limits for the peaks as for their baseline. A perspective of this work is the use of the valley to valley and the deconvolution methods for calculating I_{CO} and I_{SO} .

This project also allowed proposing an Excel macro to simplify and harmonise the calculation of indexes. To finish, this work allows proposing a single and reliable methodology to qualify bitumen ageing for all laboratories participating to the national project MURE.

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