Evaluation methods of chemical additives used in warm and recycled asphalts Mixtures

Juan Gonzalez-Leon[1, a], Françoise Achard[1], Olivier Falletti[1]

[1] *Centre de Recherche de Rhones Alpes, ARKEMA, Pierre Benite, France*

[a] juan-a.gonzalez@arkema.com

Digital Object Identifier (DOI): dx.doi.org/10.14311/EE.2016.188

ABSTRACT

After several years of field trials and millions of tons of asphalt mix produced using warm mix asphalt (WMA) technologies, the chemical additive technology has been identified as the most robust, economical and simple to use.
It has already been reported in multiple occasions that the mechanical properties of asphalt mixtures using surfactant-based additives are similar or better than those obtained in regular hot mix asphalts. There are, however, some aspects of their implementation that are still studied, mainly due to the lack of simple laboratory evaluation methods. Here, two important issues related to the use of chemical additives in asphalts mixtures are discussed.
The first is related to the environmental concerns that the use of such additives can generate. A relatively simple analytical method is shown to be capable of identifying changes in the gaseous emissions due to the addition of chemical additives. The method is based on the chromatographic analysis of the emissions produced by hot asphalt binder. Through this method, differences in emissions between bitumens, their usage temperatures and the presence of additives are shown.
The second is about the assessment of the workability of asphalt mixtures in the laboratory. Evaluating the workability is important for the selection of the proper additive for WMA and also for hot mix asphalt that needs compaction aids due to its high stiffness or because of its particular handling requirements. This is a subject that has been studied for many years and, although there have been important advancements; there is still no standardized method for evaluating the workability of asphalt mixtures in the laboratory. In this work, a simple method based on the use of the gyratory compactor is shown to be able to help in the evaluation of the asphalt mixture workability. The method is capable of demonstrating the effects on the mix workability of different bitumen grades, different temperatures and surfactant additives, as those used in the production of WMA.

Keywords: Additives, Compatibility, Emissions, Warm Asphalt Mixture

1. INTRODUCTION

Warm mix asphalts (WMA) are asphalt mixtures that are produced and paved at temperatures below those usually required in asphalt mixtures. The targeted reduction in temperature is usually between 30 to 40°C, relative to the regular asphalt production temperature. However, the reduction in temperature may vary according to the WMA technology used to produce the mix.[1,2] One of the most simple and reliable WMA technologies consist on the use of surfactant-based chemical additives. These additives are used in amounts around 0.4wt% with respect of the bitumen (about 200g of additive per ton of asphalt). They do not change the rheological properties of the bitumen but have a significant effect on the workability of the mix. [3,4] Workability additives are also used when it comes to Reclaimed Asphalt Pavement (RAP) recycling. For every hot mix production plant, there exists an upper limit of cold or warm RAP content above which the heating power is not enough to produce a hot mix, increasing the RAP content above this limit leads to the production of an asphalt at lower temperature.

WMA are now widely used around the world due to their many practical advantages in terms of emission reduction, energy savings and worker improved safety and comfort during paving.[5,6] Their mechanical properties have been shown in several occasions to be similar to those of regular hot mix asphalt mixtures (HMA). The study of WMA in the laboratory is however not that simple. Although the confection of asphalt mixtures in the laboratory is practically the same, in particular with the use of surfactant-based additives, the evaluation of some of their most important advantages is not easily carried out, such as the reduction of emissions and the asphalt workability.

In order to evaluate the actual reduction in emissions, sampling during an actual paving work on site is usually done. This kind of measurements are the most relevant to the actual use of WMA and their additives.[6] Nevertheless, sampling during a job on site requires a lot of effort (material and human) and comparisons between different procedures or temperatures are difficult to make. Laboratory methods have been developed, where analytical material have been fitted to measure the emissions produced by asphalt mixtures at different conditions.[7] The work presented here describes a simple laboratory test, using standard gas chromatography equipment, that compares the potential emissions produced by bitumen, and their additives as a function of temperature. Although certain elements of the actual emissions in asphalt are not accounted for example, the presence of the mineral surface from the aggregate), it is enough to easily compare different kind of conditions, bitumens and additives.

Surfactant-based WMA additives are actually workability improvers for asphalt mixtures. This improved workability is what is actually used to reduce temperature (and achieve the same compaction level as a HMA). These kind of additives do not change the rheology of the bitumen, contrary to waxes, whose effect can be observed in a reduction of bitumen viscosity. There has been a lot of effort consecrated to measure the workability of asphalt mixture in the laboratory, however no simple or standard test has been really established to this end. Many universities and private construction companies have end up building their own devices and/or methods for the evaluation of workability.[8] Many of these devices are based on the torque necessary to turn a stirrer inside the mix. Others are based on the actual displacement (pushing) of asphalt. [9] Although many of these methods have been shown to capture well enough the differences between different kind of aggregates and temperatures, they remain tests that are not easily available to all road constructors (need special equipment, many of the times not commercially available). A couple of years ago, the U.S. Federal Highway Administration published a report, where they suggested that the compaction measured with a gyratory press could be used to evaluate asphalt additives for temperature reduction. [10] In this work the results based on this kind of tests are shown, where differences in workability were actually measured with relative ease. It is not a test that can be directly used to define field job parameters, but can make comparisons easier, with a machine, the gyratory press compactor, which is widely available by road constructors.

2. METHODS

2.1 Laboratory bitumen emissions measurements

Measurements of the emissions generated by hot bitumen were made through a gas chromatography technique. A head space sample preparation was carried out to make measurements. Head space sample preparation for gas chromatography analysis is commonly used for volatile samples (perfumes for example), but can be used for other samples if the sample is heated before the sampling. [11] Bitumen samples were prepared in hermetically closed vials that were heated for a given time at a given temperature. Then, only the top gaseous phase of the sample is collected and analyzed.

Volatile compounds generated by hot bitumen are identified using gas chromatography coupled with mass spectrometry detection (GC/MS). They also can be followed using gas chromatography coupled with a flame ionization detector (GC-FID). An Agilent 6890 gas chromatograph (Agilent Technology, Santa Clara, USA) coupled with a Waters GCT mass spectrometer (Waters, Millford, USA) was used for GC/MS experiments. An Agilent 6890N gas chromatograph equipped with a flame ionization detector was used for GC-FID experiments (Agilent Technology, Santa Clara, USA). The gas chromatographs were equipped with a CombiPAL head space sampler (CTC analytics, Zwingen, Switzerland) for samples heat and collection.

Figure 1 shows and schematic of the measurement procedure and an example of the chromatographic result.

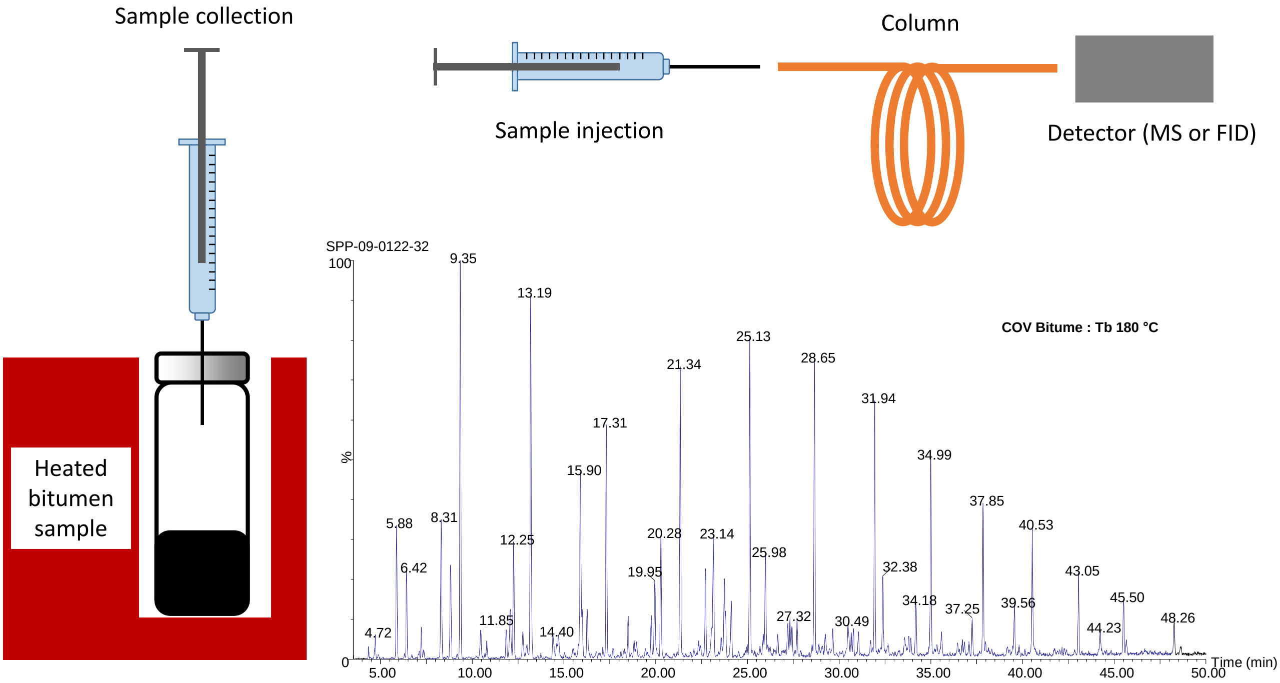

Figure 1: Schematic of the headspace chromatography technique applied to bitumen samples and a sample GC/MS chromatogram of a bitumen at 180°C.

The bitumen samples were prepared in hermetically closed vials that were heated for 1 hour before a sample of the emissions can be taken (through a septum placed in the cap of the vial). The bitumen samples used in this study were regular distillation bitumens, as those usually used for the road applications. Bitumens with 10/20, 35/50 and 160/220 1/10mm penetration were used. They were heated to the lowest temperature possible in order to be able to pour them into the vials. This was done to limit the loss of volatile components in bitumen before the analysis. In the case of the bitumen containing a WMA additive (Cecabase RT®), 0.4wt% was introduced to bitumen at 120°C and stirred for just a couple of minutes in order to minimize loss of volatiles.

Chromatographic settings optimized for the detection of volatile molecules were used. A DB624 gas chromatography column (60m x 0.32mm i.d., film thickness 1.8µm) from Agilent Technology combined with an adapted oven temperature range are used to carry out the measurement. Those conditions allowed detection of volatile molecules up to boiling point of about 280°C.

2.2 Laboratory asphalt mix workability measurements

The workability test used in this work, as mentioned in the introduction is based on a report published by the TRB in 2011 [10]. In this document, it is suggested that a gyratory press can be used to check the effectiveness of a WMA additive when the number of gyrations to a fixed void percentage is compared at the desired compaction temperature and 30°C lower. Figure 2 shows an example of a compaction curve obtained with a gyratory press. The void percentage of the sample, which was calculated geometrically from the densities of the materials, weight and volume of the sample, is plotted against the number of gyrations during compaction.

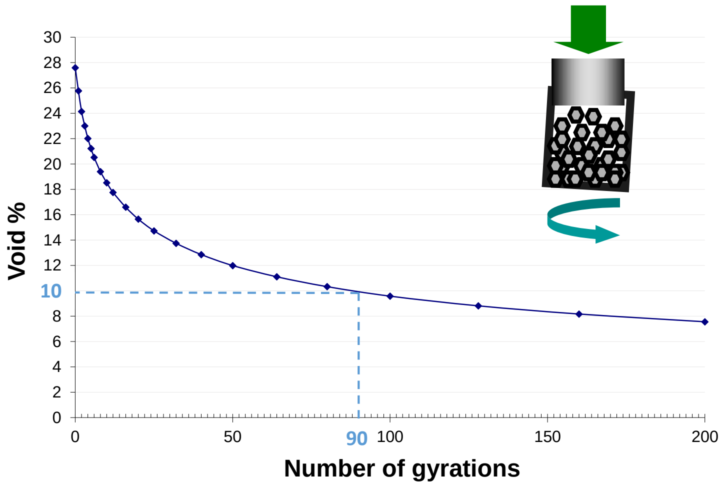

Figure 2: Compaction curve of an asphalt mixture: void percentage as a function of compactor gyrations.

It can be seen that the curve slope changes quickly at the beginning of the compaction. The slope decreases as it requires more and more gyrations to decrease the void content. An arbitrarily value of voids was chosen for comparison so that sample is not at the very beginning of compaction, while not being into a zone of a large number of gyrations. In the case shown in Figure 2, 10% void is chosen so a number of gyrations equal to 90 is recorded for this sample.

The results shown in this work were completed from asphalt mixtures of the type known in France as BBSG (Béton Bitumineux Semi-Grenu), usually used as a rolling surface in roads. It consists of aggregates going from 0 to 10mm. The composition and granulometric curve are shown in Figure 3.

	wt%
0/2	45
2/4	20
4/6	10
6/10	24
Filler	1

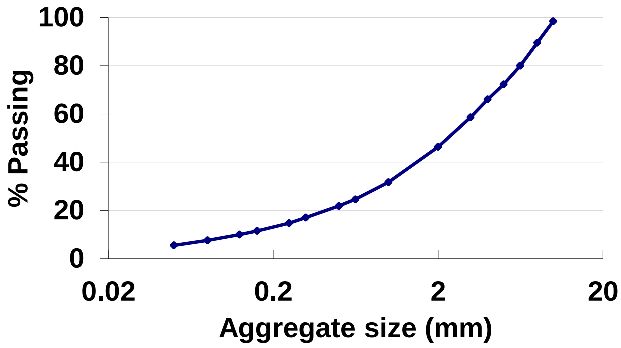

Figure 3: Asphalt mix composition and granulometric curve.

The test used in this work consisted on preparing asphalt mixtures at different conditions, filling the compactor moulds, and compacting them using the gyratory press. In the case of standard hot mix asphalts, the mix was prepared at 160°C (aggregates and bitumen) and compacted at 130°C. The gyratory compactor used was an ICT100 (Invelop) with 10cm diameter moulds. The aggregates and the bitumen were mixed using a laboratory planetary mixer for 45s. For the WMA asphalts, the mix was prepared at 120°C (aggregates at 120°C, while the bitumen remains at 160°C) and compacted at 90°C. In the case of WMA with additives, 0.4%wt of additive was added to the hot bitumen (160°C) and mechanically stirred for 10 min while controlling the temperature. The additive used is the Cecabase RT® additive commercialized by CECA. Six specimens for each condition (temperature and/or additive) were prepared in order to calculate average values of the number of gyrations required for a given void percentage.

3. RESULTS

3.1 Laboratory bitumen emissions measurements

It has been already shown that changes in asphalt temperature can have a large impact on its amount of volatile organic component emissions [6]. Measurements were carried on a pure 35/50 1/10mm bitumen using the above mentioned headspace technique at different temperatures. The samples were heated for 1 hour at 120°C, 160°C and 180°C before they were injected in to the column for GC/MS analyses. Figure 4 shows the three GC/MS chromatograms obtained for these measurement. A relative percentage of the signal (%) is plotted against the elution time (minutes). This relative percentage of the signal is normalized for the three samples, in a way that the peak intensities of each detected molecule is directly comparable between samples. Low boiling point molecules are detected at shorter times while high boiling point molecules are detected latter. The increase of the signal baseline from the time 40 min is caused by GC/MS column bleeding.

For all samples, the first peaks around 3.5 min (between 3.44 and 3.59min) are related to air (O_2, CO_2, N_2) trapped in the sample during sample preparation. As it can be observed, at 180°C there are several peaks that appear along the measurement coming from the bitumen.

At 160°C most of the peaks are still present, but are harder to identify. From this comparison it is clear the strong influence of the temperature in the amount of volatile organic components that are generated by the bitumen. The advantage of reducing the asphalt production temperature by about 40°C (120°C for WMA with a 35/50 1/10 mm bitumen asphalt) is clear from these measurements.

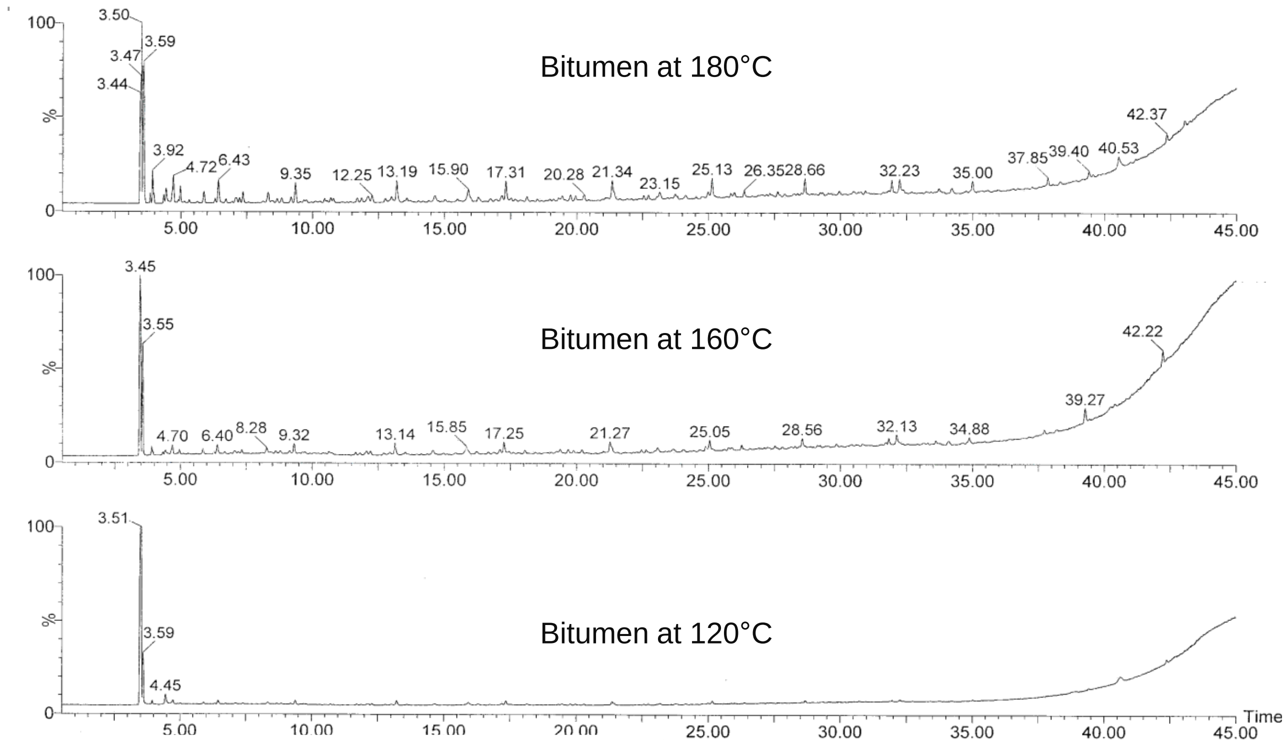

Figure 4: GC/MS chromatograms of a 35/50 1/10mm bitumen at different temperatures

Similar measurement were carried at 170°C and 130°C with two different grades of bitumen. In this case, a 10/20 1/10mm and a 160/220 1/10mm bitumens. The GC/MS chromatograms presented in Figure 5 show the signal pics obtained for the two bitumens when they were heated at 170°C. A relative percentage of the signal (%) is plotted against the elution time (minutes). GC/MS chromatograms are zoomed between 5.20min to 37.50min; thus the peak around 3.5 min (related to air: O_2, CO_2, N_2) do not appear in presented chromatograms. The relative percentage of the signal is normalized for the two samples so peak intensity of each detected molecules is directly comparable between samples. The increase of the signal baseline from the time 35 min is caused by GC/MS column bleeding.

A large difference between the two bitumen grades can be observed. More and larger signal pics were found for the 10/20 1/10 mm bitumen than the 160/220 1/10 mm one. The measurement for 130°C (not shown in this work) had smaller signal peaks for both cases, however there 10/20 1/10mm bitumen presented two more pics than the softer bitumen grade. While 170°C is an unusual temperature for the 160/220 1/10mm bitumen it is a common temperature for the 10/20 1/10mm.

This is a relative surprising result, since it could be expected that a softer bitumen contains more volatiles, thus having more and larger signal pics in this analysis. It should be noted that the two bitumens tested here are shown as an illustration of an analytical technique. The hard and soft bitumens tested do not come from the same refinery, which would be a necessary requirement to carry out a more quantitative comparison between them and further understand this results. In any case, these results demonstrated the sensibility of the headspace measurements to different kinds of bitumen and that differences in emissions can be expected from different bitumen grades.

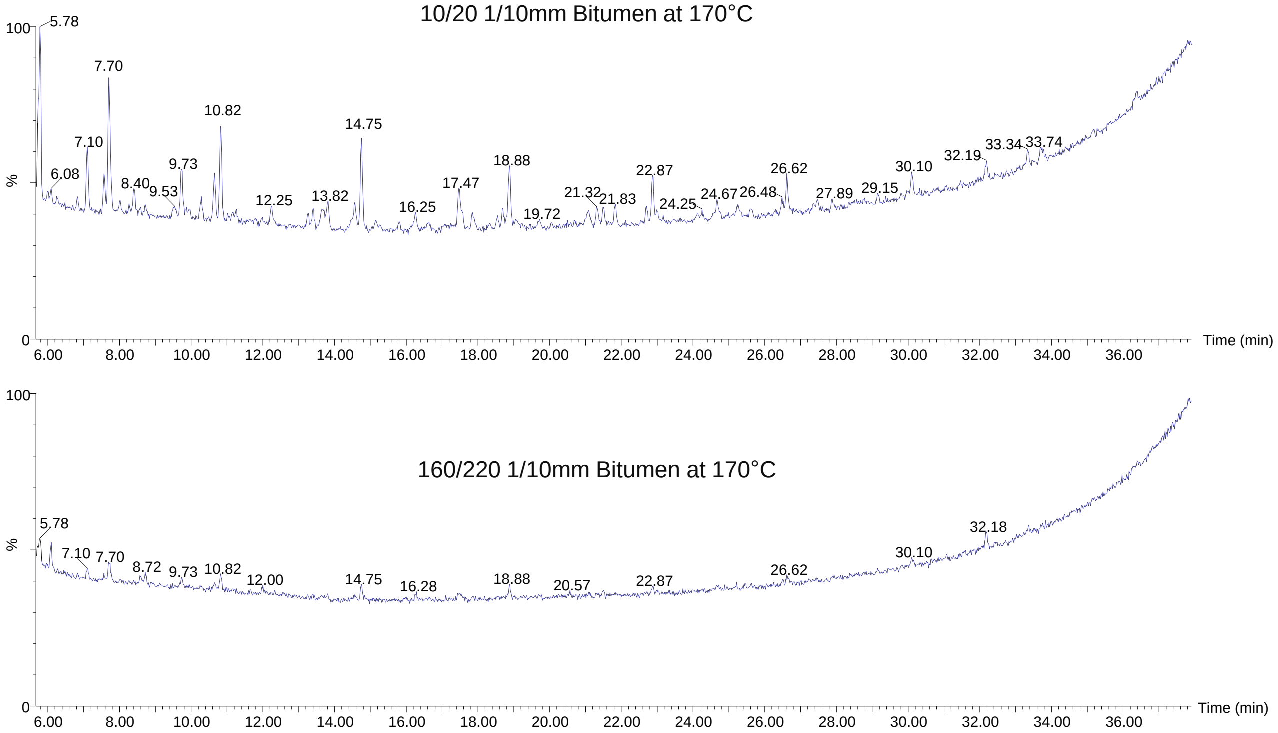

Figure 5: GC/MS chromatograms of a 10/20 and a 160/220 1/10mm bitumen at 170°C

A final comparative measurement was carried out between a 35/50 1/10mm bitumen with and without a WMA additive using head space sample preparation with GC-FID detection. Figure 6 shows the two GC-FID chromatographic curves (with and without additive) superimposed after being heated for 1 hour at 160°C. A flame ionization signal (expressed in µV) is plotted against the elution time (minutes). The signal is normalized for the two samples so the peak intensity of each detected molecule is directly comparable between samples

As it can be seen the curves are almost identical, with no significant difference in the signal pics obtained. This demonstrates that the WMA additive tested, do not generate new volatile components, at the tested conditions.

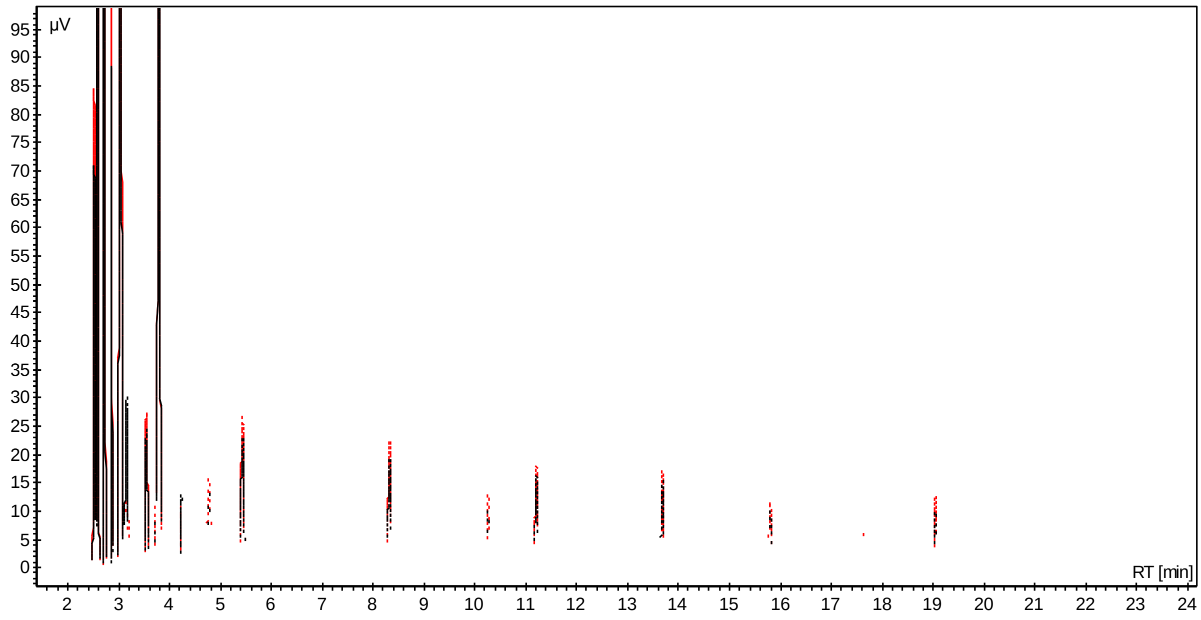

Figure 6: GC-FID chromatograms of a 35/50 1/10mm bitumen without (black) and with a WMA additive (red) at 160°C

The analytical method used in this study is quite sensitive as it is capable of detecting traces (at the ppm level) of volatile organic components (VOC). The VOC measured through this technique are in a very low concentration in the actual field job as has been confirmed through measurements on the field. [6].

The results presented here are qualitative (no specific quantities of each detected molecule are obtained), since the peaks areas are relative to a detector signal. It should be noted however that the head space sample preparation associated with GC/MS or GC-FID detection can be used for quantitative measurements of a targeted molecule (that has been previously calibrated).

3.2 Laboratory asphalt mix workability measurements

The number of gyrations necessary to obtain 10% voids was compared between different asphalt mixtures. Figure 7a shows a comparison between asphalts prepared with different bitumen grades. In this case, the same aggregate composition was used with 35/50 1/10mm and 50/70 1/10mm grade bitumens. The same amount of bitumen was used in each case (5.2wt%). Both asphalt mixtures were produced and compacted at 160°C. As expected, the asphalt mix with the softer bitumen (50/70 1/10mm) required a lower number of gyrations to achieves the 10% void percentage. This shows that the method is indeed sensitive to changes in the workability of the mixtures (in this case cause by the differences in viscosity of the bitumens used).

Figure 7b shows another comparison between the same asphalt mix formulas but prepared and compacted at different temperatures. One mixture was prepared and compacted at 120°C and another at 160°C. The two asphalts comprise of the same identical composition, the only difference was the aggregates temperature before mixing. It can be seen that a large increase in the number of gyrations to achieve the same compaction level takes place when the production and compaction temperature are reduced by 40°C. The difference is in fact larger than that observed before with a softer grade of bitumen. The observed sensitivity to temperature suggests that this test is suitable for comparing the compaction of HMA and WMA.

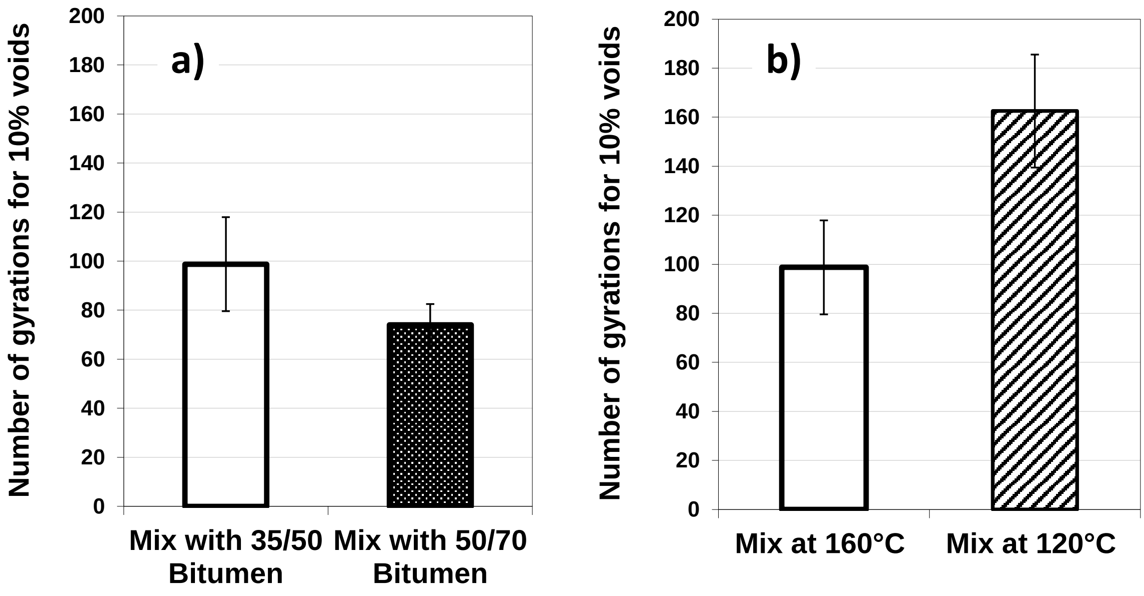

Figure 7: Number of gyrations for 10% void compaction of asphalt mixtures at the given conditions

Another comparison was made between HMA and a WMA containing a surfactant-base additive that improves the workability of the mix. In this case, the HMA mixture was prepared at 160°C and compacted at 130°C and the asphalt mixture containing 0.4wt% with respect to the bitumen of the additive was prepared at 120°C and compacted at 90°C. Figure 8a shows that the asphalt containing the additive does actually have a workability closer to that of the asphalt made at 160°C than the one made at 120°C without additive. This example, shows that the test based on the number of gyrations during compaction can be used to evaluate the effectiveness of a workability improving additive.

A similar comparison was made and the results are shown in Figure 8b but in this case the asphalt mixture contained 60wt% of reclaimed asphalt pavement (RAP). It is known that the addition of the RAP to a mixture can dramatically change the workability. This is mainly due to the presence of an oxidized, aged bitumen from the RAP that can have a significantly higher viscosity than a fresh bitumen binder. In this example, the same granulometric formulation of fresh aggregates was used (adjusted for 40%). Fresh binder, 35/50 1/10mm was also adjusted accordingly. All the asphalt mixtures in this example were mixed at 160°C, but the compaction was made either right away (compaction at 160°C) or after the temperature in the mold was 130°C. The fresh aggregates were at 200°C and the RAP was warmed to 130°C in an oven for 2 hours before mixing. Although there are changes on the aggregate composition between figures 8a and 8b that should be taken into account, the effect of adding 60% of RAP can be clearly observed. The number of gyrations goes from about 100 in the mix without RAP to about 135 with RAP (same mixing and compaction temperatures). The difficulty of compaction is more noticeable when the mix is compacted at 130°C, as the number of necessary gyrations increase to more than 250. This test represents the situation where a hot mix production plant is at full heating capacity with high RAP content, and producing a hot mix asphalt at 160°C that can be compacted at 160°C. However because of transportation cooling, this HMA will not be well compacted once at 130°C. In this case, the effect of the surfactant based additive was also observed. The number of gyrations is reduced significantly when 0.3wt% of additive (relative to the total weight of bitumen: fresh and aged) was used in the mix. Another mix containing 2wt % of a low viscosity mineral oil, similar to those reportedly used to soften mixtures with large contents of RAP, was tested at the same conditions as with the additive. It can be seen that an improvement in the compaction was also achieved, as expected from using an oil that reduced significantly the viscosity of the bitumen and increase its final penetration grade. The effect however, is similar to that obtained with a significantly lower amount of surfactant-based additive (about 7 times less).

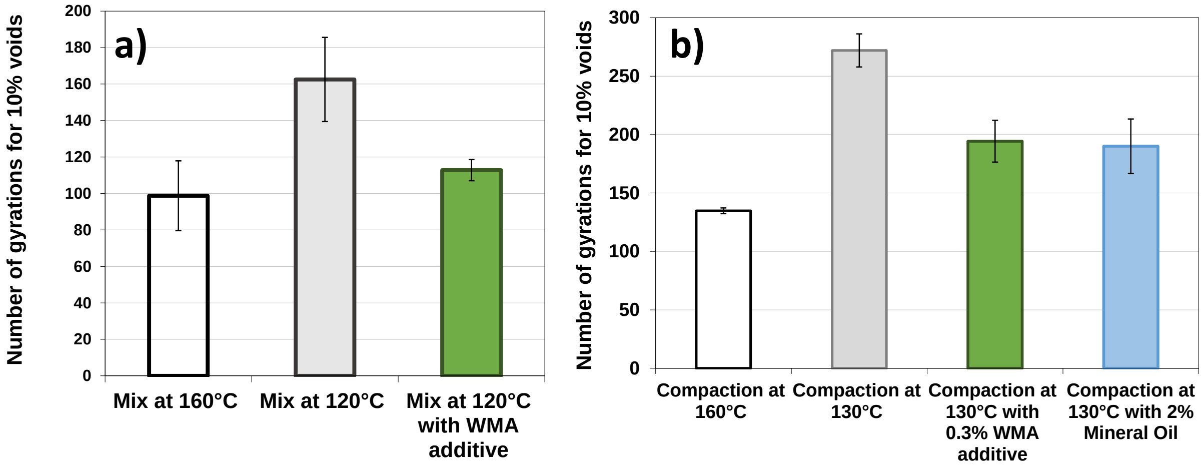

Figure 8: Number of gyrations for a compaction to 10% voids. a) Asphalt mixtures with and without additive, prepared at the given temperatures and compacted 30°C lower. b) Asphalt mixtures with and without additives containing RAP, prepared at 160°C and compacted at the given temperatures.

It should be noted that the differences in workability through this test may vary dramatically from one condition to another. An asphalt mix with a very high or very low workability will probably not show clear differences through this test (limits of the test probably related to the press itself and size of the experiment).

4. CONCLUSIONS

The chromatographic method known as "head space" can be applied to bitumens. It showed a significant reduction in VOC emissions from bitumen when the sample temperature was decreased. The method was also sensitive to the type of bitumen used. In this case, more VOCs were observed in a lower penetration grade bitumen (10/20) compared to a high penetration grade (160/220) under the same temperature conditions. Is was also shown to be useful to understand the possible contribution to VOC emissions in bitumen when an additive is used. In this case, the additive tested, did not add any additional VOC to the tested bitumen at 160°C.

The head space chromatography method is relatively simple and several samples at difference conditions can be easily tested. It is a useful tool to do comparison and first approach analysis on the impact on the VOC in bitumens. It is a very sensitive test, but only qualitative. Additional quantitative analysis should be carried out in order to draw conclusions about a specific VOC and how it compares to established expose regulations.

The proposed test based on the compaction using a gyratory compactor is shown to be sensitive enough to show differences in workability due to different factors. Differences in workability were observed between mixes prepared with different grades of bitumen. A significant increase in the number of gyrations needed to achieve an arbitrarily chosen compaction level was also observed when the compaction temperature was decreased by 40°C. The test also helps showing the effect of the surfactant based additives, claimed to increase the workability of the mix. As shown in the two examples presented here, the surfactant based additives can decrease significantly the number of gyrations for a certain compaction, even in the presence of large amounts of RAP in the mix (60 % RAP).

The compaction test, although not perfect, allows to compare the workability of different types of asphalt formulations and temperatures using a simple test carried on an equipment that is present in many asphalt laboratories around the world.

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