A5EE-339

ASSESSMENT OF BITUMENS FOR EMULSIONS AND MODIFIED BINDERS: CHARACTERIZATION BY GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

Various techniques are available for an extensive analysis of bitumens. Usually, characterisation is performed in a first stage by classical tests such as penetration, softening point, Rolling Thin Film Oven Test (RTFOT). These tests give a first view on bitumens' properties but generally cannot be linked with their suitability for specific uses such as emulsions or polymer modified binders.

Additional information can be obtained from acidic index, SARA composition (Iatroscan), DSC (paraffin content, glass transition temperature), infra-red spectroscopy. However, the relationship between results obtained by these tests and bitumen end-use properties does not always appear clearly.

Further investigations through Gel permeation chromatography (GPC) permit a further step in bitumen knowledge. GPC, also named "Steric exclusion chromatography", consists of separating molecules according to their size, by injecting a solution of the sample through a porous matrix. This technique can be used in order to compare various bitumens according to different parameters: average molecular weight (Mp in Daltons), shape of the curve (qualitative information about molecular weight distribution), percentage of compounds with molecular weight above a given threshold. Criteria have been identified for bitumen assessment. Several practical cases are discussed; they are related to contexts where the aim was the evaluation of bitumen suitability for emulsions, or for polymer-modified binders either with or without crosslinking agent.

Keywords: bitumen, chemical composition, molecular weight, chromatography

1. INTRODUCTION

Building a road, upgrading an intersection or constructing a bridge are all vital for communications and involve a large number of parameters: traffic flow, safety, but also the quality and durability of roads. In relation to the goals of sustainable development, road construction companies attempt to build roads using the most effective technologies in order to limit environmental impacts. To do this, a number of different approaches are adopted such as emulsifying bitumens or the use of additives in bitumens, and more particularly the addition of polymers. In the case of polymer-modified binders, the many goals include:

- Reducing the thickness of the pavement layers, especially the wearing course,
- Improving pavement durability,
- Optimizing pavement maintenance.

The use of bitumen emulsions can also provide considerable energy savings and improve the safety of the laying gangs.

The bitumens for use in emulsions or modified binders must be selected from among those that are available on the market.
The formulation of emulsions requires extreme caution: two emulsions manufactured with two bitumens from a different source may have similar intrinsic properties (stability) but behave differently when mixed with aggregate.
Likewise, polymers, which are physically and/or chemically mixed with bitumen, contain molecular units that are approximately 100 times larger than the largest molecules in the bitumen, which may give rise to homogeneity problems in modified binders, depending on the source of the bitumens that are used.

In order to ensure our products have good performance and hence guarantee the durability of the road, it is necessary to make sure that the bitumens are emulsionable and compatible with the polymers.
The usual techniques used to characterize bitumens are the penetration, ring and ball softening point and RTFOT ageing tests. The results of these tests provide us with a first impression of the properties of bitumens but they may not be relevant for the use of the bitumens in question in emulsions or modified binders.
More comprehensive information may be obtained, for example, from the acid index, Iatroscan analysis (SARA), infra-red spectrometry or differential scanning calorimetry (DSC) (wax content, glass transition temperature). However, the relationship between the properties of the bitumen and the optimum end use is not always clear.

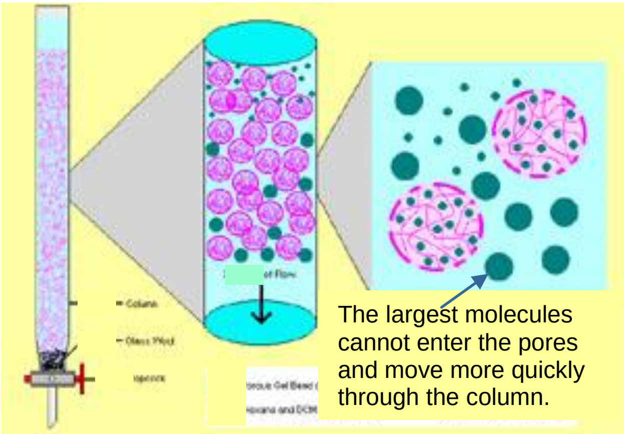
The objective of this work is to go further in the understanding of the relationships between bitumen chemical composition and its behaviour in emulsions and polymer modified binder.

Gel permeation chromatography (GPC) provides a way of obtaining more in-depth knowledge about bitumens. In order to make progress in this area, a study has been conducted of bitumens that were intended for use in emulsions (7 bitumens) and modified binders (31 bitumens) to try to understand how they differ from a chemical point of view and see a connection between them and the performance of the products in which they are used. The aim was to identify a predictive criterion for the use of a bitumen as a modified binder and/or in an emulsion.

2. GEL PERMEATION CHROMATOGRAPHY (GPC) [1]

GPC, also known as "Steric exclusion chromatography", is a technique which consists of separating molecules according to their size, by passing a solution of the sample through a porous matrix. The largest molecules are not trapped and flow freely through the column at the same speed as the solvent (in this case, tetrahydrofurane), whereas the smallest molecules are trapped in the matrix pores. The retention time is inversely proportional to the log of the molecular weight.
This technique can be used to compare bitumens according to a variety of criteria:

- average molecular weight (Mp in Daltons)
- intensity of the peak (which may be linked with the presence of aromatic compounds)
- shape of the curve (qualitative information about the molecular weight distribution)
- percentage of compounds whose molecular weight is above or below a given threshold (e.g. 4000 Daltons).



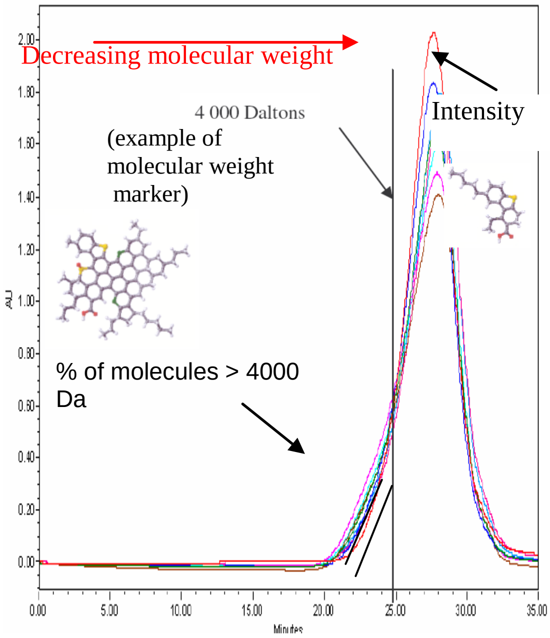


Figure 1 and 2: principle of the gel permeation chromatography

Operative conditions:
Column Styragel HR 2, HR 3 and HR 4, 7.8 x 300mm:

- Matrix material: 5 micron styrene divinylbenzene particles
- Effective molecular weight range : $10^1 – 6.10^5$g / mol

Mobile phase: THF (tetrahydrofuran)
Stationary phase: porous gel of styrene divinylbenzene particles
Flow rate: 0.7ml/min

3. ASSESSMENT OF BITUMENS FOR EMULSIONS [2], [3]

Our study of 7 bitumens was performed after an appraisal of an emulsion, which was carried out with a control emulsion formula and a control aggregate for a microsurfacing mix. Bitumen A, which has given satisfactory results both in the laboratory and at jobsites, was taken as a control bitumen. The other bitumens were divided into three groups:
Group 1: bitumens B, C and D, whose behaviour was as satisfactory as that of bitumen A.
Group 2: bitumen E, which can be used if blended 50/50 with bitumen A but not alone (at least not with the same emulsion formula).
Group 3: bitumens F and G which cannot be used, either pure or blended 50/50 with bitumen A (at least not with the same emulsion formula).
The problem encountered when using bitumen E, F or G was poor cohesion build–up : the emulsion took an hour or longer to break and the resulting mix exhibited poor or average performance in the Wet Track Abrasion Test (WTAT).

As one moves from Group 1 to Group 2 then finally to Group 3, it is noticeable that the behaviour of the bitumens differs more and more from the control bitumen (A). The study therefore focused on identifying a change in chemical composition which led to a classification of the bitumens in the same order.

2.1 "Classical" characterizations

To begin with, all the bitumens were subjected to testing for penetration, softening point, acid index (a high acid index usually indicates rapid cohesion build-up), wax content by Differential Scanning Calorimetry, and 'SARA' analysis with calculation of the colloid index. This index is usually considered as a predictive parameter for the compatibility of a bitumen with polymers. The purpose of this study was to try to identify a link between colloid index and the way a bitumen behaves in an emulsion. The index is calculated as follows:

$$CI = \frac{(\%Saturates + \%Asphaltenes)}{(\%Resins + \%Aromatics)}$$

The correlation with the asphaltene content was also considered.
The results are set out in the table next page.

Table 1: Results of the "classical" characterizations

		Control bitumen	1. Satisfactory results, can be used alone as an alternative to the control bitumen			2. Can be used in a 50/50 mix with control bitumen but not alone	3. Cannot be used, even when mixed with the control bitumen	
Bitumen		**A**	**B**	**C**	**D**	**E**	**F**	**G**
Penetration at 25°C	**(1/10mm)**	62.0	84.0	55.0	71.0	67	57	59
Softening point	**(°C)**	48.6	45.4	50.0	47.0	47.8	48.4	48.6
Acid index*	**(mg/g)**	0.9	1.1	1.1	0.8	0.9	0.3	0.5
Wax content* ***(by DSC)***	**(%)**	0.44	0.07	0.09	0.92	0.95	01/01/67	0.93
SARA analysis*								
Asphaltenes	**(%)**	17,8	18,0	18,6	16,5	17,1	11,9	14,9
Resins	**(%)**	11,1	12,5	13,8	11,3	10,7	13,9	11,2
Saturates	**(%)**	6,2	6,4	5,9	5,1	6,8	6,0	6,9
Aromatics	**(%)**	64,9	63,1	61,7	67,0	65,4	68,3	67,0
Colloid index		0,32	0,32	0,32	0,28	0,31	0,22	0,28

*All the test methods are in the appendices at the end of the report

The results obtained during this first part of the study showed that none of "classical" tests provides the desired classification: there was no logical progression in the results between the control and the bitumens in groups 1, 2 and 3. We therefore performed additional physical and chemical characterisation of the bitumens.

2.2 Gel Permeation Chromatography (GPC)

The second phase was to subject all the bitumens were subjected to GPC. It was found that the bitumens with similar molecular weight distribution curves also had similar performance in microsurfacing emulsions.
Moreover, we observed that binders which performed poorly in microsurfacing emulsions also had the lowest polydispersity.

Table 2: Results of gel permeation chromatography on the bitumens

Bitumen	Mp (Daltons)	Polydispersity
A	550	5,6
B	548	6,2
C	586	6,1
D	499	5,3
E	630	5,3
F	719	3,8
G	718	4,4

2.3 Conclusion

Some of the characteristics have been identified as suitable for classifying bitumens with regard to their behaviour in microsurfacing emulsions.
The relevant results are summarized in the table next page.

Table 3: Summary of the results

	Control and bitumens with same behaviour (A, B, C, D)	Can be used in 50-50 mix with control bitumen but not alone (E)	Cannot be used in mix either with control bitumen or alone (F, G)
Asphaltene content (heavy compounds)	higher (>16 %)		lower (12 to 15 %)
GPC on bitumens: - Mp (Daltons) - Polydispersity	lower (500 – 585 Daltons) high (5.3-6.2)	medium (630 Daltons) 5.3	higher (>700 Daltons) low (3.8 - 4.4)

The most significant parameter appears to be the polydispersity of the molecular weights, which was determined by combining two analytical techniques: SARA analysis (asphaltene = heavy compound content), and Gel Permeation Chromatography (polydispersity).
The more highly dispersed a bitumen's molecular weights and the higher the percentage of heavy molecules (asphaltenes) it contains, the more suitable it is for use in microsurfacing, as is the case with the control bitumen (A).

To conclude, we suggest that bitumens with a more “homogeneous” composition (fewer molecules at both extremes of molecular weight) give more stable emulsions. This makes it more difficult to obtain breaking rapidly after mixing with the aggregate, leading to very slow setting and cohesion build-up.

3. ASSESSMENT OF BITUMENS FOR POLYMER MODIFIED BINDERS [4], [5]

For a given formula of modified binder and a given manufacturing process, major differences in performance (softening point, storage stability,…) are observed according to the nature and the source of the bitumen used. The purpose of the two cases that are described here is to study the influence of the chemical composition of bitumens on their performance and their compatibility during modification of SBS-modified binders. The study only considers non-crosslinked modified binders.

Two practical cases are considered. They are related to 2 series of bitumens ; each series is used in a given geographical zone, which will be referred to as zone A and zone B.

3.1 Practical case n°1 (from geographical zone A)

The detailed analysis of 25 bitumens from different sources and intended to manufacture the same number of modified bitumens, was carried out following on from a study that set out to improve our knowledge about bitumens, particularly with regard to the relationship between the results of Iatroscan SARA analysis and the compatibility of the bitumen with SBS.
The compatibility study, which mainly focused on the softening point and storage stability of the modified binder led to the identification of 3 groups:
Group 1: bitumens 1 to 14, with satisfactory compatibility
Group 2: bitumens 15 to 18, with moderate compatibility
Group 3: bitumens 19 to 25, with poor compatibility
The study set out to determine a chemical composition criterion which led to the same classification of the bitumens as that given above.

It should be noted that 70/100 and 50/70 pen bitumens were mainly considered here.

3.1.1 “Classical” characterizations

Initially, all the bitumens were analyzed to determine their penetration, R&B temperature, acid index and Iatroscan SARA composition. As mentioned above, the colloid index was also calculated as it is considered to be a selection criterion for bitumens with regard to their compatiblility with polymers (a low CI indicates better compatiblility with SBS).
The CI is calculated as follows:

$$CI = \frac{(\%Saturates + \%Asphaltenes)}{(\%Resins + \%Aromatics)}$$

The results are presented in the Table next page.

Table 4: Results of the "classical" characterizations

		1. Satisfactory compatibility	2.Moderate compatibility	3. Poor compatibility
Bitumen		**1 to 14**	**15 to 18**	**19 to 25**
Penetration at 25°C	**(1/10mm)**	62 - 89	70 - 78	57 - 77
Softening point	**(°C)**	45.8 - 49.0	48.4 - 49.0	48.0 - 52.8
Acid index	**(mg/g)**	0.2 - 4.6	0.6 - 2.5	0.2 - 1.2
SARA analysis				
Asphaltenes	**(%)**	3.3 – 20.9	18.8 - 28.8	20.8 - 27.0
Resins	**(%)**	5.5 - 26.4	9.6 - 16.2	5.1 - 9.6
Saturates	**(%)**	3.0 - 14.5	5.6- 12.9	3.9 - 15.5
Aromatics	**(%)**	56.4 - 71.7	52.0 - 57.1	54.5 - 64.6
Colloid index		0.13 - 0.59	0.36 - 0.55	0.36 - 0.68

We were not able to identify any criterion that linked the results of the "classical" tests that were obtained during the first phase of the study with the compatibility of the bitumen with polymers.
In view of the highly variable saturate contents of the different bitumens (between 3 and 15%) the usual CI criterion (a low CI indicates better compatibility with SBS) is obviously invalid here.

Further investigations were therefore conducted in order to improve the chemical characterization of bitumens and identify an indicative criterion.

3.1.2 Gel permeation chromatography

In a second stage, all the bitumens were analyzed by GPC. The results reveal a criterion which is only detectable with GPC which can separate the bitumens into 2 categories:

- compatible bitumens
- incompatible or moderately compatible bitumens.

This criterion is the percentage of molecules with a molecular mass > 4000 Daltons (Da). It was correlated with two other parameters which are specific to GPC.

- Intensity of the peak (which is assumed to indicate the level of aromatic compounds)
- Percentage of molecules with a molecular mass < 4000 Da.

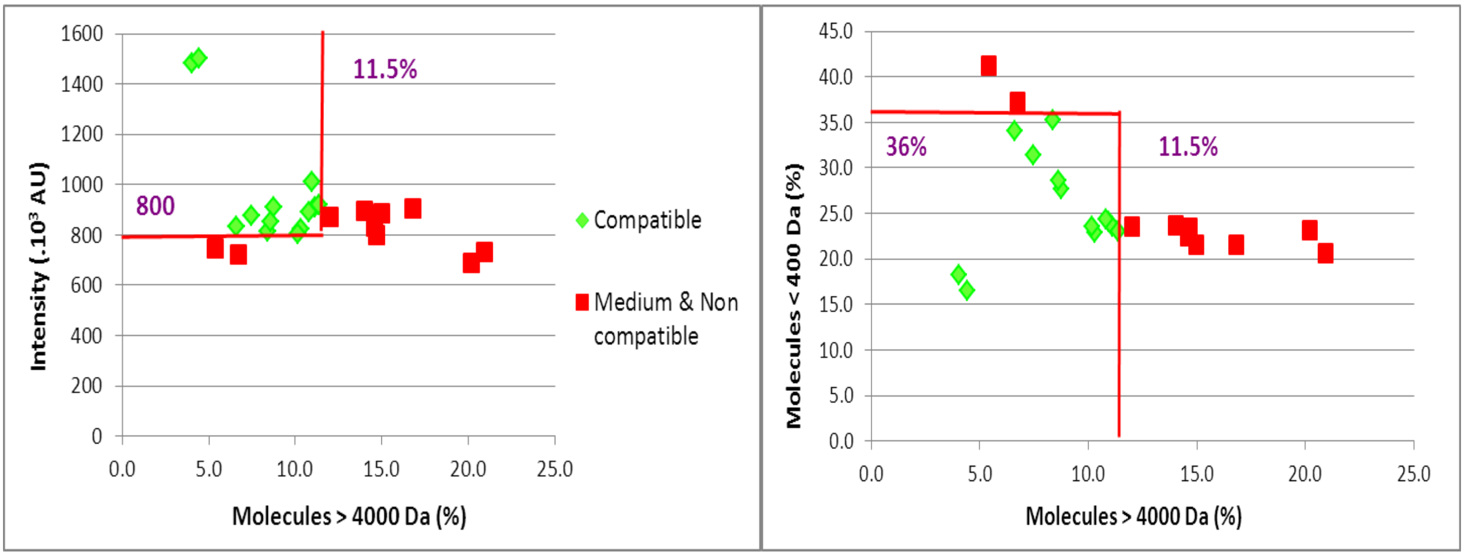


Figure 3 and 4: graphs about the % of molecules with a molecular mass > 4000 Da correlated with the intensity of the peak and with the % of molecules with a molecular mass < 4000 Da

The percentage of molecules > 4000 Da was also linked to the asphaltene content. As above, we observe the existence of two zones:

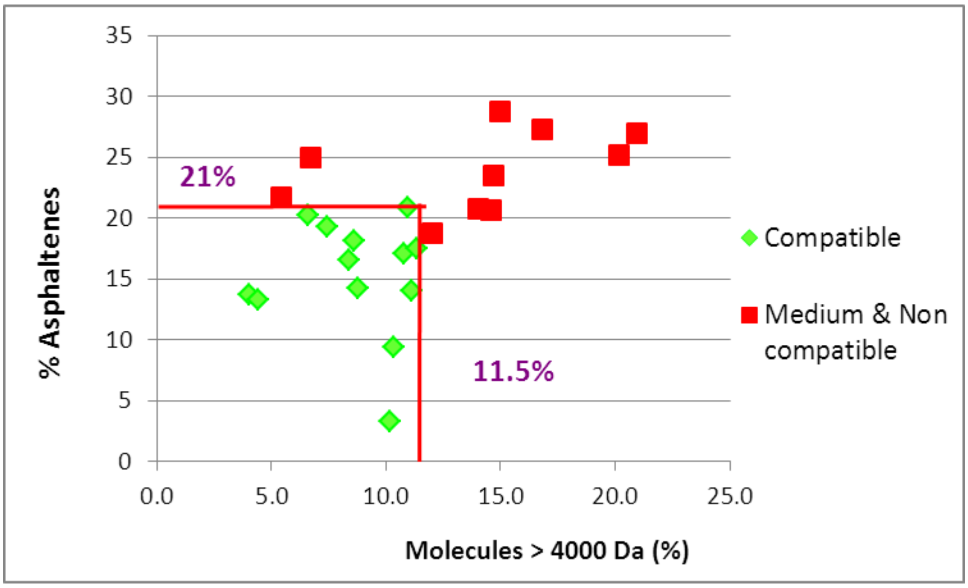


Figure 5: graph about the % of molecules with a molecular mass > 4000 Da correlated with the % of asphaltenes

Thus, some specific characteristics were selected in order to classify the bitumens according to their compatibility with SBS.

Table 5: Summary of the results

	Molecules > 4000 Da and **% Asphaltenes**
Compatible bitumens (1 to 14)	**IF Molecules > 4000 Da < 11.5%** AND IF % **Asphaltenes < 21%**
Bitumen that are moderately or poorly compatible (15 to 25)	Zone where one of the 2 above criteria is not met

The bitumens which are compatible with SBS have the following criteria in common:

➔ Compounds with a molecular mass > 4000 Da < 11.5 %

➔ % Asphaltenes ≤ 21%

The aim of the second case study, which also related to modified binders, was to see if the above criterion is applicable to the second series of samples obtained from a different geographical zone different from the first. If so, we will verify if the threshold values are the same.

3.2 Practical case n°2 (geographical zone B)

Compatibility with SBS was evaluated for the second series of samples (from a different origin from the previous one) on the basis of criteria that were similar to those used for the first series. It should be noted that 160/220 pen bitumens were mainly considered here.
As above, the compatibility study, which mainly focused on the softening point and the storage stability of the modified binder, allowed us to divide the bitumens into 3 groups:
Group 1: bitumens a, b and c: with satisfactory compatibility
Group 2: bitumen d: with moderate compatibility
Group 3: bitumens e and f: with poor compatibility

3.2.1 "Classical" characterizations

In contrast to the first series of samples, the classical tests allowed us to identify criteria for determining compatibility with polymers. Low asphaltene content combined with a low IC is characteristic of a bitumen which is compatible with SBS and vice-versa.

Table 6: Results of the "classical" characterizations

		1. Satisfactory compatibility	2. Moderate compatibility	3. Poor compatibility
Bitumen		**a, b et c**	**d**	**e et f**
Penetration at 25°C	**(1/10mm)**	172 - 199	190	168 - 197
Softening point	**(°C)**	38.6 – 40.4	38.4	40.6 – 40.8
Acid index	**(mg/g)**	0.2 – 0.6	4.0	0.3 – 0.4
SARA analysis				
Asphaltenes	**(%)**	10.1 – 10.9	13.1	20.0 – 20.6
Resins	**(%)**	11.4 – 16.5	17.0	5.1 – 7.8
Saturates	**(%)**	5.6 – 9.3	8.5	8.1 – 8.9
Aromatics	**(%)**	63.8 – 72.1	61.4	64.1 – 65.3
Colloid index		0.19 – 0.25	0.28	0.39 – 0.42

In order to validate the GPC results that were determined before, the second series of specimens was then analyzed by chromatography.

3.2.2 Gel permeation chromatography

The criterion determined for the first series of bitumens is also valid for the second series of bitumens. The threshold values were nevertheless different. The differences can at least partly be explained by the differences in the penetration grade of the bitumens: 160/220 pen for the second series of bitumens (Zone B) and mainly 70/100 and 50/70 pen for the first series of bitumens (Zone A).

Table 7: Results of gel permeation chromatography on the bitumens

	Compatibility with SBS	**% Asphaltenes**	**Intensity (.10^3 AU)**	**% Compounds with a molecular weight > 4000 Da**
a	Yes	10.5	1229	4.7
b	Yes	10.1	1299	7.2
c	Yes	10.9	1226	6.7
d	Moderate	13.1	821	8.3
e	No	20.0	897	9.2
f	No	20.6	830	9.9
Criteria for ZONE B	**Yes if**	**≤ 13%**	**> 1 000**	**< 8.0**
Criteria for ZONE A	Yes if	≤ 21%	> 800	< 11.5

Thus, the bitumens from zone B which were compatible with SBS shared the following criteria:

➔ [Compounds with a molecular mass > 4000 Da] < 8% (11.5% for zone A)

➔ % Asphaltenes ≤ 13 % (21% for zone A)

3.3 Conclusion

The available results allowed us to classify the bitumens according to their compatibility with polymers.
The table below summarizes the useful results.

Table 8: Summary of the results

	Compatibility with SBS	**% Asphaltenes**	**% Compounds with a molecular weight > 4000 Da**
1st series (1 to 25) Zone A 50/70 and 70/100	Yes both criteria are met (1 to 14)	≤ 21	< 11.5
2ème série (a to f) Zone B 160/220	Yes if both criteria are met (a, b and c)	≤ 13	< 8.0

In the case of the non-crosslinked modified binder formulations, GPC is therefore able to provide an indicative criterion **(% of compounds with a molecular mass > 4000 Da)** which, when combined with the asphaltene content of the bitumen, makes it possible to evaluate the bitumen's compatibility with SBS.

3. CONCLUSION

The cases that we have described above illustrate the added value provided by Gel Permeation Chromatography compared with conventional tests with regard to the detailed analysis of the bitumens.
This technique allows us to identify indicative criteria which link the chemical composition of the bitumens with their suitability for use in emulsions for microsurfacing and their compatibility with polymers for polymer-modified binders.

For both practical cases related to modified binders, gel permeation chromatography enables the definition of relevant criteria to predict compatibility of bitumens with polymers, whereas criteria based on SARA analysis (and more specifically, asphaltenes content) alone, as used previously, were not considered as relevant.
These criteria, whose levels depend on the geographic zone in question and the penetration grade of the bitumen, are the molecular mass, polydispersity, or the percentage of compounds with a molecular mass > 4 000 Daltons.

As regards bitumen use in emulsion, this technique is all the more interesting, that no criteria had been clearly identified before. The most significant parameter appears to be the polydispersity of the molecular weights, which was determined by combining two analytical techniques: SARA analysis (asphaltene = heavy compound content), and Gel Permeation Chromatography (polydispersity).
The more highly dispersed a bitumen's molecular weights and the higher the percentage of heavy molecules (asphaltenes) it contains, the more suitable it is for use in microsurfacing, as is the case with the control bitumen (A).
To conclude, we suggest that bitumens with a more "homogeneous" composition (fewer molecules at both extremes of molecular weight) give more stable emulsions. This makes it more difficult to obtain breaking rapidly after mixing with the aggregate, leading to very slow setting and cohesion build-up.

APPENDICES: TEST METHODS [3]

Acid index

Purpose: this test is performed in order to determine the content of potassium hydroxide needed to neutralize the acids present in 1g of bitumen.

Method: An accurate weight of bitumen is dissolved in a chlorobenzene solvent. Then, an equivalent volume of ethanol is added to the solution and titrated with a potassium hydroxide solution. The end of the titration is determined by potentiometry and the equivalence volume is used to calculate the index acid.

Wax content by DSC (Dynamic Scanning Calorimetry)

Purpose: the wax contained in the bitumens constitute a class of saturated hydrocarbon compounds which have a low chemical reactivity and whose general chemical formula is C_nH_{2n+2} with n variable between 15 and 70. The strong proportion of linear chains enables them to crystallize and their melting point is lower than 70°C. During the analysis in DSC of the bituminous binders, the crystallisable fractions of the bitumens are defined as having a melting point being on a range of temperature of 0 to 95°C.

Method: a small weight (~20mg) of bitumen is placed in a crucible, sealed and then, the material is cooled and heated in order to detect any process endo or exothermic phenomenon which occurs during the heating (or the cooling) of this material.
Thanks to the melting latent heat (ΔH_m which is proportional to the surface of the peak related to melting and function of the quantity of wax), it is possible to calculate the wax content in a bitumen.

SARA analysis

Purpose: this test is performed in order to determine the chemical composition of the bitumen which is composed of 2 main families: the asphaltenes and the maltenes (which group together the saturates, the aromatics and the resins).

Methods: the test principle is to separate the asphaltenes from the maltenes by dissolution of those in the heptane. Then, the chemical composition of the maltenes is determined by silica gel bars chromatography and flame ionization detection after the elution of the saturates, the aromatics and the resins in several solvents (See Figure 5 below).

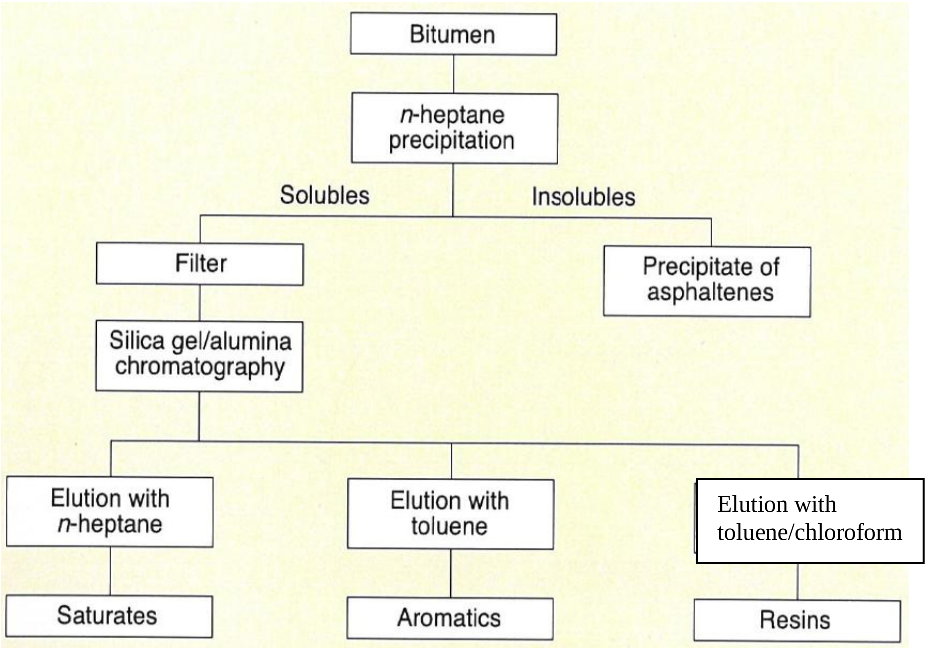


Figure 5: Schematic representation of the analysis for broad chemical composition of bitumen

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