Available online at www.sciencedirect.com

ScienceDirect

Fuel 87 (2008) 1428–1434

FUEL

www.fuelfirst.com

Short communication

Characterization of asphalt fume composition by GC/MS and effect of temperature

E. Gasthauer [a,*], M. Mazé [a], J.P. Marchand [b], J. Amouroux [c]

[a] Centre de Recherche Eurovia Management, 22 Rue Thierry Sabine, BP 20067, 33703 Mérignac, France
[b] Eurovia Management, Direction Technique, 18 Place de l'Europe, 92565 Rueil-Malmaison, France
[c] Laboratoire de Génie des Procédés Plasmas et Traitement de Surface, Université Pierre et Marie Curie, ENSCP, 11 Rue Pierre et Marie Curie, 75231 Paris cedex 05, France

Received 26 July 2006; received in revised form 17 June 2007; accepted 19 June 2007
Available online 30 July 2007

Abstract

The aim of this work is to identify the volatile organic compounds (VOC) from asphalt by developing a process at atmospheric pressure under air flow in order to qualify and quantify the asphalt emissions by a standard analytical protocol with gas chromatography coupled to mass spectrometry. VOC formation depends on various parameters such as the asphalt temperature, the asphalt oxidation, and the humidity of air. This research contributes to improve knowledge of asphalt emissions. A decrease in VOC is mainly correlated with the asphalt temperature.

Keywords: Asphalt; Fumes; VOC; GC/MS

1. Introduction

Millions of tons of asphalt are produced every year and are used in the paving [1] industries mainly in the hot mix plants. Asphalt is a residue of oil vacuum distillation [2]. It is an extremely complex and variable mixture with carbon, hydrogen, nitrogen, oxygen and sulphur elements. It contains aliphatic, polycyclic aromatic and heterocyclic compounds.

In order to mix asphalt with aggregates and some additives, the asphalt viscosity must be reduced by increasing its temperature. So when the asphalt coating takes place, oxidation takes place at the interface and asphalt fume is emitted: gaseous emissions and volatile organic compounds (VOC) [3]. European guidelines 1999/13/CE [4] transcribed in French law by the decree of May 29, 2000 [5] impose a limit on VOC emission for binder plants and hot mix plants: 110 mg/m^3 (at 273 K and 1 atm) for a flow higher at 2 kg/h.

The first step is to characterize the volatile organic compounds and the temperature effect on VOC emission. A technical process has been developed in order to produce asphalt emission. Then, VOC are analysed by Gas Chromatography coupled with Mass Spectrometers (GC/MS), allowing the identification and quantification of these complex carbon compounds.

2. Glossary of terms used in the studies of pavers

Aggregate: Graduated fragments of hard, inert mineral material that are mixed with asphalt. Aggregate includes sand, gravel, crushed stone and slag.

Asphalt: The product of the nondestructive distillation of crude oil in petroleum refining; it is a dark brown to black cement-like semisolid or solid. Depending on the crude oil used as a feedstock, the distillation residuum may be further processed, typically by air blowing

---

[*] Corresponding author.

E-mail addresses: gasest@yahoo.fr (E. Gasthauer), mmaze@eurovia.com (M. Mazé), jpmarchand@eurovia.com (J.P. Marchand), jacques-amouroux@enscp.jussieu.fr (J. Amouroux).

0016-2361/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2007.06.025

(sometimes with a catalyst) or solvent precipitation, to meet performance specifications for individual applications. It is a mixture of paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulfur, nitrogen and oxygen.

Asphalt, hot mix (HMA): Paving material that contains mineral aggregate coated and cemented together with asphalt.

Bitumen: The term more commonly used in Europe to refer to asphalt.

3. Experimental set up

3.1. Asphalt composition

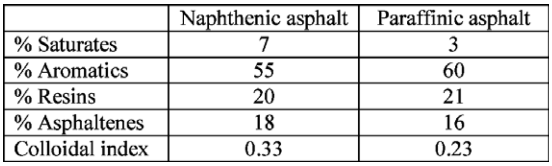
Asphalt is mainly composed of carbon and hydrogen compounds and of less than 3% oxygen, nitrogen, sulphur and metal atoms. Asphalt is fractionated by SARA analysis, a chromatography method, into four fractions: Saturates, Aromatics, Resins, Asphaltenes [6]. The saturates are hydrocarbons (paraffinic compounds: saturated chains) and naphtenic cycles with low molecular mass and low polarity. The aromatic fraction contains aromatic cycles with paraffinic and naphtenic carbons including sulphur elements. The resins [7] fraction contains more cyclic structures (aromatic, naphtenic and heterocycle) joined by aliphatic bridges than the aromatic fraction and it possesses more polar chemical groups bearing oxygen, nitrogen or sulphur atoms. The asphaltenes fraction contains the most complex molecules of asphalt with large aromatic cycles substitute for aliphatic, naphtenic and heterocycle groups [8,9]. Asphaltene contains porphyrine with metal atoms like Vanadium, Nickel etc. We give an example of this kind of molecules in Fig. 1.

Asphalt used to generate fume are naphtenic and paraffinic (grade 50/70). The SARA distribution (Fig. 2) indicates that naphthenic and paraffinic asphalt are almost the same while the most important chemical family is the aromatic fraction.

However, naphtenic asphalt exhibits specific carbonyl function detected by Infrared. The acidity index determined by potassium hydroxide measure is 4.5 mg KOH/g for naphthenic asphalt and 1.5 mg KOH/g for paraffinic asphalt. Finally, paraffinic asphalt contains 1.5% paraffin.

3.2. Experimental process and reactor

An asphalt layer of 30 mm (1100 g asphalt) is laid down in a cylindrical reactor (Ø*h (mm^2) 204 × 224) and heated in an oven with a controlled temperature. A dry air flow at 3.7 l/min (humidity content is trapped on two cold traps



	Naphthenic asphalt	Paraffinic asphalt
% Saturates	7	3
% Aromatics	55	60
% Resins	20	21
% Asphaltenes	18	16
Colloidal index	0.33	0.23

Fig. 2. SARA (saturates, aromatics, resins, asphaltenes) chromatography analysis.

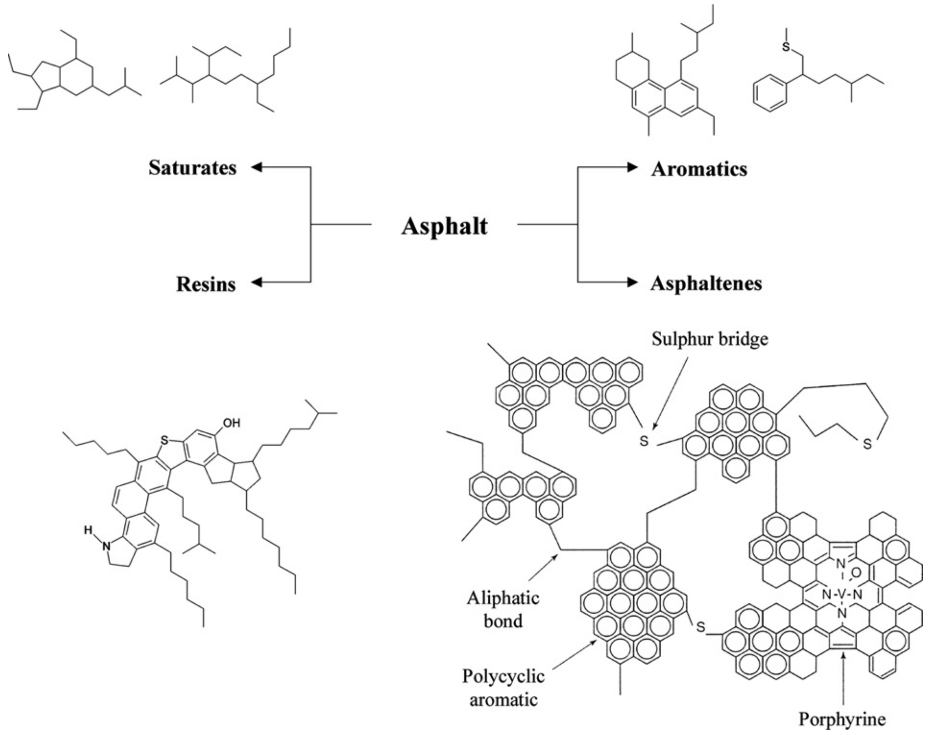


Fig. 1. Type of asphalt composition SARA (saturates, aromatics, resins, asphaltenes).

(253 K)) is injected into the asphalt (in liquid phase) to produce the oxidation mechanisms and the fume emission (Fig. 3). Asphalt fumes are collected on quartz fiber filters (2500 QAT-UP, 25 mm, particle retention >0.3 μm: 99.9% put in a stainless steel filter holder) and trapped in a glass tube. The temperature of the first filter (343 K) is fixed by a thermal exchanger while the temperature of the second one is about 305 K. Filtration of gas emissions depends on both particle retention capacity and filtration temperature. In fact, the temperature of the traps is controlled in order to collect VOC by condensation and to separate asphalt fume molecules versus their molecular mass: the heaviest fractions of VOC are trapped on filter F1, then the others VOC are collected on filter F2 and the lightest molecules are condensed on cold trap called P3 (253 K). Each test lasts 2 h.

3.3. Analytical process

The mass of the deposit collected on filter and on cold trap permits us to determine the mass of VOC trapped and to calculate VOC concentration with gas flow (mg/m^3 gas at 293 K and 1 atm).

Some processing steps are required to manipulate the asphalt fume sample for its analysis. So, VOC trapped by filter are extracted into liquid phase (CH_2Cl_2) with an Accelerated Solvent Extractor (ASE) at 393 K under 100 bar for 10 min of static time. The extracted solution is concentrated by an evaporation of the solvent into the sample solution under a nitrogen flow before GC/MS analysis.

Asphalt fumes are characterized by GC/MS [10]: GC 8000 TOP (Thermo electron), with a spilt/splitless injector and a mass spectrometer Automass II, quadrupole Voyager (Thermo electron). The determination of asphalt fume composition is carried out using positive electron ionisation (EI). Separation is performed using a column BPX5, 5% phenyl polysilphenylene-siloxane, 0.25 μm 30 m × 0.25 mm. The GC/MS analysis was performed with an oven temperature program from 333 (held for 2 min) to 513 K at 25 K/min then to 573 K at 5 K/min and finally to 593 K at 3 K/min (held for 3 min). The analysis parameters were: column head pressure of 80 kPa, injector temperature of 523 K, interface temperature of 593 K, source temperature of 523 K and helium as carrier gas with a split flow of 100 mL/min. The injector was in the splitless mode, the split valve being closed for 30 s. The parameters used are particularly adapted to analyse heavy compounds.

The limits of detection of each compounds are calculated using a statistical method, precisely a linear regression and using the calibration straight line of different compounds. This method permits us to calculate the limits of detection with a margin of error. Employing this approach, the limits of detection were obtained for some of the VOCs of interest. GC/MS has a high sensitivity detection

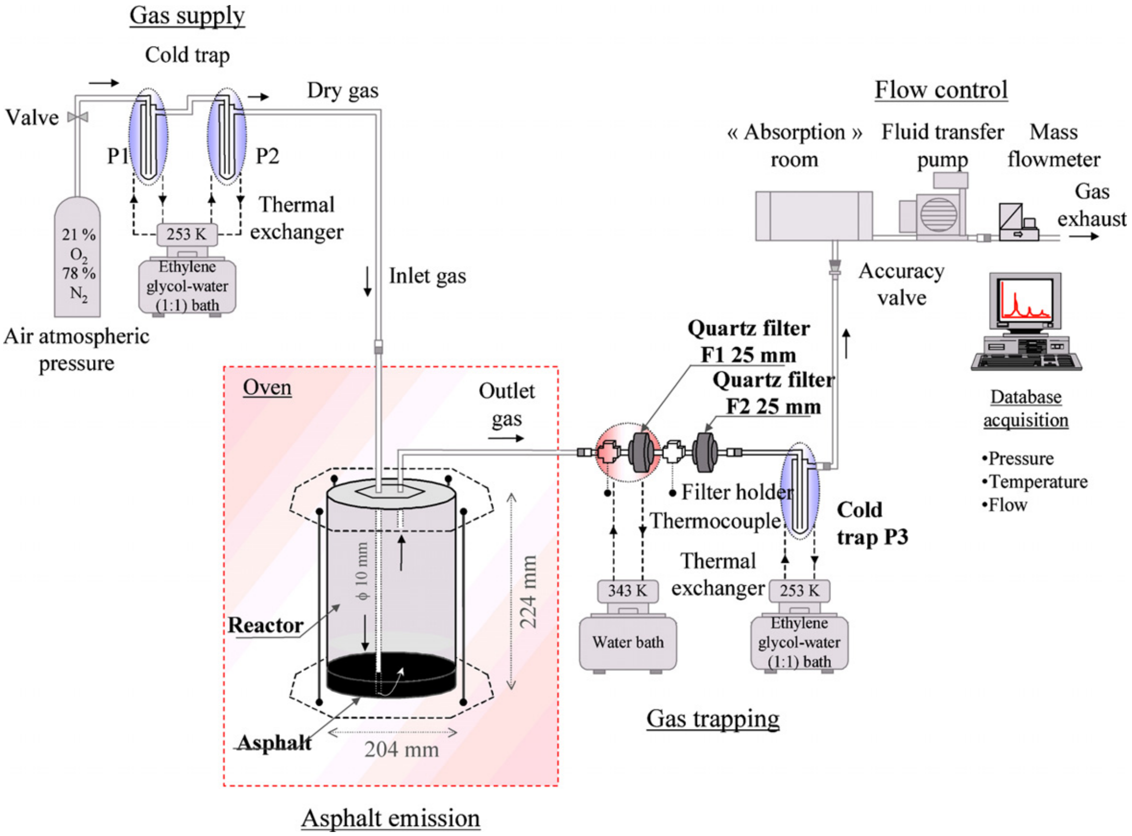
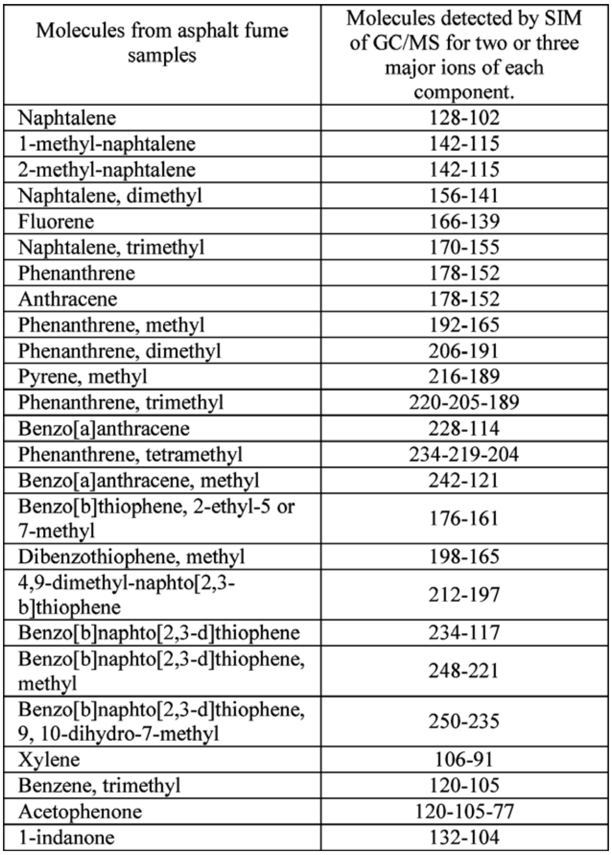


Fig. 3. Experimental process at atmospheric pressure for asphalt emission post analysis.



Molecules from asphalt fume samples	Molecules detected by SIM of GC/MS for two or three major ions of each component.
Naphtalene	128-102
1-methyl-naphtalene	142-115
2-methyl-naphtalene	142-115
Naphtalene, dimethyl	156-141
Fluorene	166-139
Naphtalene, trimethyl	170-155
Phenanthrene	178-152
Anthracene	178-152
Phenanthrene, methyl	192-165
Phenanthrene, dimethyl	206-191
Pyrene, methyl	216-189
Phenanthrene, trimethyl	220-205-189
Benzo[a]anthracene	228-114
Phenanthrene, tetramethyl	234-219-204
Benzo[a]anthracene, methyl	242-121
Benzo[b]thiophene, 2-ethyl-5 or 7-methyl	176-161
Dibenzothiophene, methyl	198-165
4,9-dimethyl-naphto[2,3-b]thiophene	212-197
Benzo[b]naphto[2,3-d]thiophene	234-117
Benzo[b]naphto[2,3-d]thiophene, methyl	248-221
Benzo[b]naphto[2,3-d]thiophene, 9, 10-dihydro-7-methyl	250-235
Xylene	106-91
Benzene, trimethyl	120-105
Acetophenone	120-105-77
1-indanone	132-104

Fig. 4. Targeted compounds and their monitoring ions.

(average: less than 1 ppm) and is used to identify the volatile organic compounds.

To detect specific VOC at trace levels, a selective ion monitoring (SIM) mass spectrometry is used. Monitoring ions are listed in Fig. 4. The second column lists the two or three major ions that were monitored for each molecule. Multiple M/Z ratios and relative retention time (to an appropriate internal standard) are used for the identification of compounds. GC/MS analysis is adapted to follow compounds from mass 20 to 450.

The goal of this study is to identify VOC and quantify the compounds such as aromatic compounds in function of asphalt temperature in our reactor. An internal standard offers the additional benefit of qualifying the accuracy of the test. So, we use for that, a labelled molecule of anthracene with deuterium atoms; like this, it is possible to quantify the sampling procedure from the filter to the final solution and we do that by an introduction of 20 μl of deuterium anthracene (200 ng/μl) on each filter before the extraction procedure [11].

4. Results and discussion

4.1. VOC composition

First filter (F1) becomes yellow and brown after the collection of asphalt emission and its blue color under UV light signals that aromatic compounds are trapped.

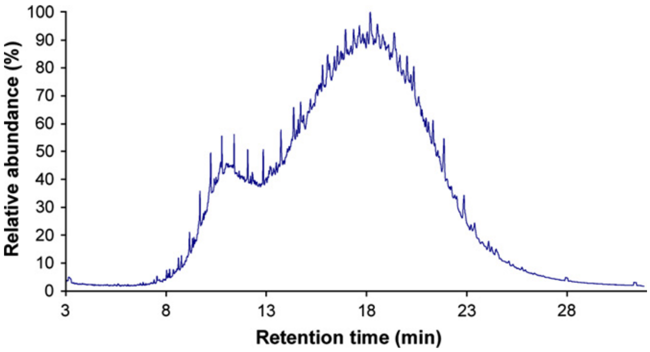


Fig. 5. Filter F1 chromatogram from positive EI detection with a GC/MS analysis for a naphthenic asphalt heated at 453 K.

At 453 K, our experimental results signal that the masses of trapped compounds in the three traps are largely different for a paraffinic asphalt or a naphthenic one. If we compare the mass of the first filter which corresponds to the trapped heavy molecules, it is clear that naphtenic asphalt produces much heavier molecules (140 mg/m^3) than the paraffinic one (63 mg/m^3). But it mainly differs from the second filter (F2) which collects the volatile compounds at room temperature. In F2, we observe that very few chemical species are produced for the naphtenic asphalt (7 mg/m^3) while the mass of organic compounds is very high for the paraffinic one (168 mg/m^3). The chemical reaction with the oxygen atom signals the weakness of asphalt molecules. The last trapping system (P3) at low temperature, 253 K, gives us the water content in the gas phase: this means the oxygen reacts with the different kinds of compounds of the asphalt. We can conclude that the paraffinic asphalt is richer in hydrogenated compounds (2189 mg/m^3) than the naphtenic one (1687 mg/m^3). This liquid solution P3 is characterized by its relative acidity pH 3–4.

The GC/MS analysis acquired by positive EI detection permits us to compare the chromatogram of the compounds from filter F1 for naphtenic (Fig. 5) and paraffinic (Fig. 6) asphalt.

The retention time depends on the mass of the molecules and their polarity, so that these two chromatograms signal that the maximum of compounds appears for 18 min for the naphtenic asphalt while the maximum is obtained for 10 min for the paraffinic study. Asphalt emissions of naphtenic asphalt contain chemical species with high molecular mass with a high boiling temperature contrary to paraffinic asphalt.

Thanks to GC/MS positive electron ionisation, the composition of asphalt fumes in the complex mixture of the first fraction could be identified: hydrocarbons asphalt emission is composed of 99% saturated hydrocarbons (like alcans) and a low quantity of aromatic hydrocarbons [12]. So in order to detect the minor compounds by mass spectrometers, selective ion monitoring (SIM) is used.

Indeed, asphalt fumes contain linear long saturated chains (like alcans and/or with alkyls: C13 to C22) or

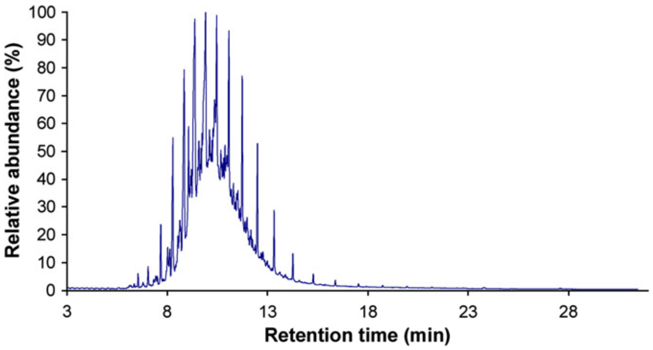


Fig. 6. Filter F1 chromatogram from positive EI detection with a GC/MS analysis for a paraffinic asphalt heated at 453 K.

unsaturated and also oxygenated compounds (like oxygened hydrocarbons: C12 to C15, or oxygened aromatic compounds), mono, bi-, tri-cyclic aromatic compounds and likewise sulphur compounds (like thiophenic) with their characteristic odour in asphalt emission. A nonexhaustive list for asphalt VOC is displayed in Fig. 7.

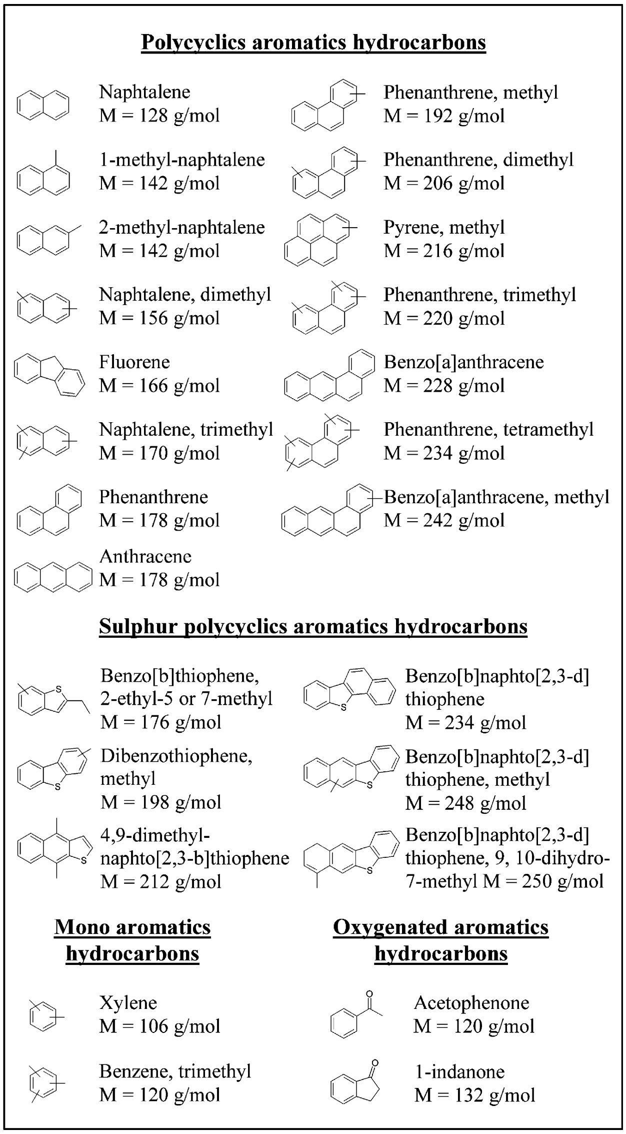


Fig. 7. Nonexhaustive list of compounds detected by GC/MS in asphalt emission.

Asphalt oxidation mechanisms give light VOC and oxygenated compounds. When water vapour is mixed with air gas flow, emissions of polycyclic aromatic hydrocarbons (PAH) and thiophenic compounds increase. So the two main parameters which control the asphalt emissions are the time spent in the reactor and the humidity of the mixture asphalt-air in the reactor.

4.2. Effect of asphalt temperature

The temperature of asphalt is a significant parameter for asphalt emissions. Our results (Fig. 8) signal the emission increase in function of the asphalt temperature. If we compare the emission flow for the three experimental thermal conditions: 413, 433, and 453 K, our results signal for both cases, naphtenic and paraffinic asphalt, that the emission law is in agreement with Arrhenius law and we can predict the emission flow through an equation such as $[COV] = ae^{bt}$. a and b parameters depend on the asphalt composition. It gives for F1 and F2: $a1 = 2 \times 10^{-5}$, $b1 = 8.75 \times 10^{-2}$ for naphtenic asphalt, $a2 = 6 \times 10^{-4}$, $b2 = 7.2 \times 10^{-2}$ for paraffinic asphalt. We have to remember that the decrease of the temperature by 20 K from 453 to 433 K decreases the mass of the asphalt fume of 80%. The water mass collected in the last trap P3 proves that OH radicals like O_2 molecules react with asphalt molecules that produce the fume.

The results of GC/MS analysis of filter F1 extract after naphthenic or paraffinic asphalt emission for different temperatures are displayed in Figs. 9 and 10 by following specific molecule targets. We use the ratio between the analytes and the internal standard, in that way, we can minimize the error and give quantitative results of the concentration of each one (ratios of the primary ion area of molecule to the primary ion area of internal standard).

According to the other experiments published regarding the effect of temperature in asphalt emission [13], asphalt fumes generated at high temperatures are more likely to generate polycyclic aromatic hydrocarbons (PAHs) than fumes generated at lower temperatures. Chemical composition of asphalt vapors and fumes varies and depends on crude petroleum sources, type of asphalt, temperature and mixing during the manufacturing process, and temper-

		Asphalt fume		
	Asphalt temperature	Collected by filter n°F1 (mg/m^3)	Collected by filter n°F2 (mg/m^3)	Collected by cold trapping P3 (mg/m^3)
Naphthenic asphalt	453K	140	7	1687
	433K	31	3	1129
	413K	4	1	801
Paraffinic asphalt	453K	63	168	2189
	433K	7	51	1162
	413K	0	13	1144

Fig. 8. The effect of temperature on VOC concentrations from naphthenic and paraffinic asphalt.

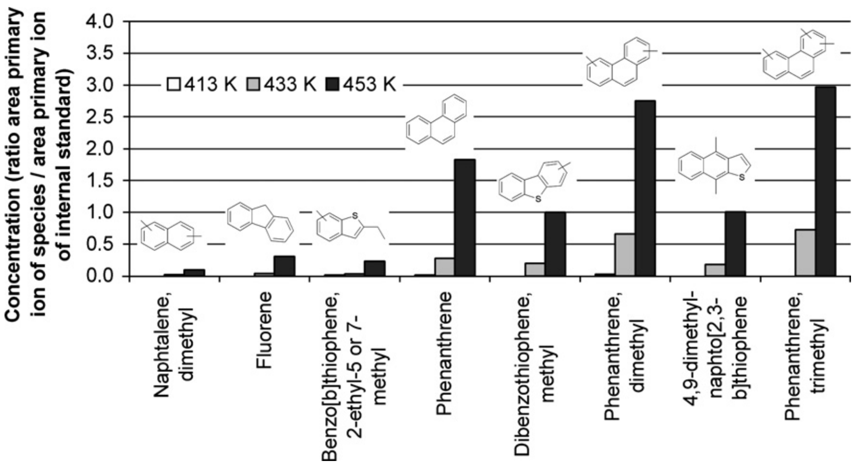


Fig. 9. Concentration (ratio of the primary ion area of molecule to the primary ion area of internal standard) of some chemical species on F1 filter in function of temperature effect on naphthenic asphalt.

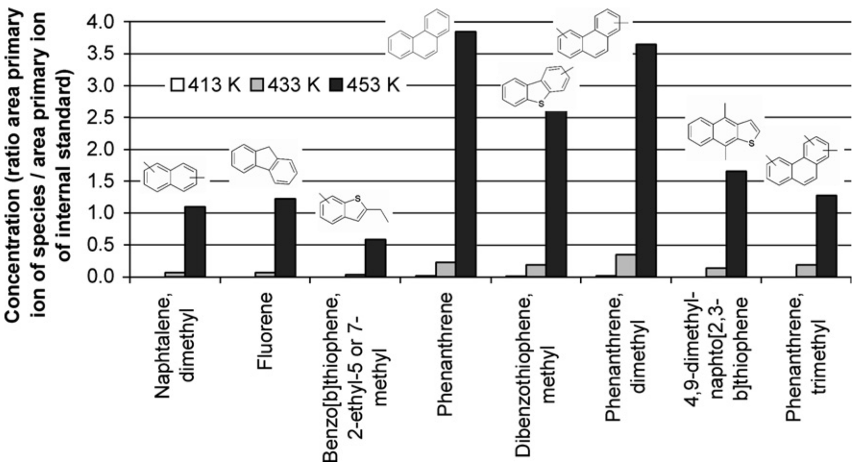


Fig. 10. Concentration (ratio of the primary ion area of molecule to the primary ion area of internal standard) of some chemical species on F1 filter in function of temperature effect on paraffinic asphalt.

ature and extent of mixing during either laboratory generation or field operations e.g., paving or roofing.

We can highlight that the temperature of asphalt is the key parameter in order to control the emission: the Arrhenius law gives us the possibility to simulate and to predict the mass of emission and to develop a process in agreement with the European guidelines.

5. Conclusions

A high reliable analytical method has been developed to qualify the asphalt fume composition produced. This study was performed with the goal that the temperature be an important key parameter for asphalt emission and odour reduction in agreement with Arrhenius law. Our work signals the oxidation mechanisms which are responsible for the emission of many chemical species mainly characterized by cyclic and polycyclic molecules with or without oxidized functions. Our work indicates a large difference between naphtenic and paraffinic asphalt in terms of concentration and nature of VOC. Finally, the decrease in VOC in the industrial process is mainly correlated with the temperature of industrial mixing and with the oxygen content.

References

[1] Asphalt in figures, European asphalt pavement association (EAPA), 2002.

[2] Sauterey R, Irastorza-Barbet D, Depetrini A, Ossola MF. Les enrobés bitumineux, Tome 1, USIRF, Dec 2001.

[3] Hot mix asphalt plants – Emission assessment report, Environmental protection agency, EPA 454/R-00-019, Dec. 2000.

[4] Directive du conseil n°1999/13/CE du 11 mars 1999 relative à la réduction des émissions de composés organiques volatils dues à l'utilisation de solvants organiques dans certaines activités et installations, JOCE n°L85 du 29 mars 1999.

[5] Arrêté du 29 Mai 2000 portant modification de l'arrêté du 2 Février 1998, relatif aux prélèvements et à la consommation d'eau ainsi qu'aux émissions de toute nature des installations classées pour la protection de l'environnement soumises à autorisation.

[6] Loeber L, Muller G, Morel J, Sutton O. Bitumen in colloid science: a chemical, structural and rheological approach. Fuel 1998;77(13): 1443–50.
[7] Murgich J, Rodriguez J, Aray Y. Molecular recognition and molecular mechanics of micelles of some model asphaltenes and resins. Energy & Fuels 1996(10):68–76.
[8] Calemma V, Rausa R, D'Antona P, Montanari L. Characterisation of asphaltenes molecular structure. Energy & Fuels 1998(12):422–8.
[9] Peng P, Morales-Izquierdo A, Hogg A, Strausz OP. Molecular structure of Athabasca asphaltene: sulfide, ether and ester linkages. Energy & Fuels 1997(11):1171–87.
[10] H.J. Hubschmann, Handbook of GC/MS, Ed. Wiley-vch, 2001.
[11] Air ambiant-Détermination des hydrocarbures polycycliques totales (phase gazeuse et particulaire)-Prélèvement sur filtres à sorption et analyses par chromatographie en phase gazeuse/spectrométrie de masse, Norme ISO 12884, 2000.
[12] Loi du 10 Juin 1999 relative aux établissements classeés_EXP-31No 31 Installation de fabrication d'asphalte, http://www.environnement.public.lu/guichet_virtuel/etabl_classes/index_formulaires/EXP-31.pdf, April 2003.
[13] Health Effects of Occupational Exposure to Asphalt, Hazard review; NIOSH Publication No. 2001–110, December 2000.