



## Characteristics of volatile organic compounds emission profiles from hot road bitumens



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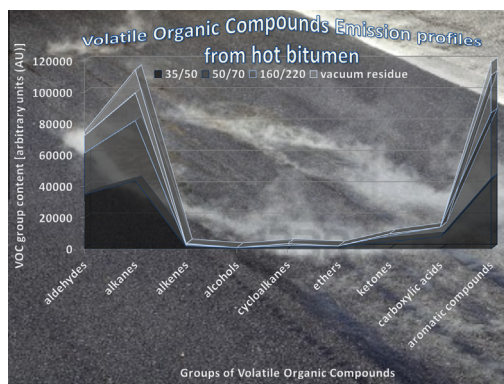
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### HIGHLIGHTS

- New procedure for comparison of VOC emission profiles from hot bituminous materials.
- Very complex chemical composition of bitumen fumes.
- The content of VOC strongly depends on the degree of bitumen oxidation.
- Useful tools for optimization of the bitumen manufacturing processes.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A procedure for the investigation and comparison of volatile organic compounds (VOCs) emission profiles to the atmosphere from road bitumens with various degrees of oxidation is proposed. The procedure makes use of headspace analysis and gas chromatography with universal as well as selective detection, including gas chromatography–mass spectrometry (GC–MS). The studies revealed that so-called vacuum residue, which is the main component of the charge, contains variable VOC concentrations, from trace to relatively high ones, depending on the extent of thermal cracking in the boiler of the vacuum distillation column. The VOC content in the oxidation product, so-called oxidized paving bitumen, is similarly varied. There are major differences in VOC emission profiles between vacuum residue and oxidized bitumens undergoing thermal cracking. The VOC content in oxidized bitumens, which did not undergo thermal cracking, increases with the degree of oxidation of bitumens. The studies revealed that the total VOC content increases from about 120 ppm for the raw vacuum residue to about 1900 ppm for so-called bitumen 35/50. The amount of volatile sulfur compounds (VSCs) in the volatile fraction of fumes of oxidized bitumens increases with the degree of oxidation of bitumen and constitutes from 0.34% to 3.66% (w/w). The contribution of volatile nitrogen compounds (VNCs) to total VOC content remains constant for the investigated types of bitumens (from 0.16 to 0.28% (w/w) of total VOCs). The results of these studies can also find use during the selection of appropriate bitumen additives to minimize their malodorousness. The obtained data append the existing knowledge on VOC emission from oxidized bitumens. They should be included in reports on the environmental impact of facilities in which hot bitumen binders are used.

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## 1. Introduction

The occurrence of volatile organic compounds in bitumen binders constitutes a serious technological and environmental problem, taking place from the moment of their formation during production until their utilization in road paving and other applications. Over 250 examples of bitumen application have been reported (Read and Whiteoak, 2003). In most cases bitumens have to be heated prior to use in order to lower viscosity enabling their application. The production of bitumens involves oxidation of residue from vacuum distillation of petroleum to obtain products with desired properties. During operations yielding the raw material for bitumen production (vacuum distillation) as well as the process of oxidation with hot air, the bitumen mass deposited on heating elements undergoes partial thermal cracking, which results in the formation of unsaturated and aromatic compounds as well as hydrogen sulfide, water vapor, carbonyl sulfide, carbon disulfide and others. These compounds undergo further transformations yielding a variety of volatile compounds: ketones, aldehydes, organic acids, phenols and their derivatives, as well as organosulfur and organonitrogen compounds. A fraction of the resulting volatile compounds is removed from the reactor with hot air, yielding so-called exhaust gases, which undergo scrubbing in a basic aqueous solution or absorption in wash oil (Boczkaj et al., 2010, 2014). VOCs remaining in the bitumen mass are emitted during storage (Deygout, 2011; Davie et al., 1993a, 1993b; Trumbore, 1999), transport (EPA, 2000a), making mineral-bitumen mixtures (EPA, 2000b; Ventura et al., 2007; Ruehl et al., 2007; Gasthauer et al., 2008; Chauhan et al., 2010; Jullien et al., 2010), roof impregnation (Rogge et al., 1997; Trumbore, 1998; Franzen and Trumbore, 2000; Kriech et al., 2004; Ruehl et al., 2007; Parker et al., 2011) and road paving (Brandt et al., 1985; Monarca et al., 1987; Greenspan et al., 1995; Hicks, 1995; Gamble et al., 1999; Burstyn and Kromhout, 2000; Burstyn et al., 2003; Posniak, 2005; Preiss et al., 2006; Hugener et al., 2010; Breuer et al., 2011; Spickenheuer et al., 2011; Raulf-Heimsoth et al., 2011).

The studies on characteristics of fume emissions from hot bitumen binders under real conditions published thus far have mostly dealt with control of total parameters, i.e. total VOC content, total PAHs, particulate matter (PM), benzene soluble matter (BSM). Hydrogen sulfide emission has also been determined. Individual polycyclic aromatic compounds have been determined in bitumen fume condensate (Blomberg et al., 1999; Brandt et al., 2000; Burstyn et al., 2002; Ventura et al., 2007; Rasoulzadeh et al., 2011; Trumbore et al., 2011). A detailed investigation of the determination of unsubstituted PAHs, considered to be carcinogenic, revealed that for bitumen samples the analytical problem is very complex and requires a two-step sample preparation procedure prior to the final determination step by chromatographic analysis (Gilgenast et al., 2011). The distribution of distillation temperature of fume condensate characterizing their volatility range can be determined using simulated distillation (SIMDIS) technique (Kriech et al., 1999; Ekstrom et al., 2001; Preiss et al., 2006; Kriech et al., 2007). For hydrocarbon mixtures containing significant amounts of aromatic compounds more accurate results are obtained by empty-column gas chromatography (EC-GC) (Boczkaj et al., 2011; Boczkaj and Kamiński, 2013).

Relatively little is known on detailed characteristics of the presence of VOCs in bitumen fumes. So far, despite information on the possibility of formation of hydrogen sulfide and volatile sulfur compounds (VSCs) during the production of oxidized bitumens (Davie et al., 1993a; Boczkaj et al., 2010; Deygout, 2011; Davie et al., 1993b), no papers are available on the identification of VSCs released at elevated temperatures from bituminous materials. The information on the presence of volatile nitrogen compounds (VNCs) in bitumen fumes is also scarce. Screening tests for VOCs

were carried out using static headspace analysis combined with solid-phase microextraction/gas chromatography/mass spectrometry (SHS-SPME-GC-MS). Using this technique, 25 polycyclic aromatic compounds (PACs) occurring in bitumen fumes were identified (Agozzino et al., 1999). Determination of individual components in very complex hydrocarbon matrices by one-dimensional gas chromatography often fails (Boczkaj et al., 2013). The SHS-SPME-GC-MS technique was also used for the identification of volatile components of asphalt release agents (Tang and Isacson, 2005; Tang and Isacson, 2006) and bituminous sealants (Tang et al., 2006).

Emission of VOCs from hot bitumens has several consequences. One of the most important environmental problems is the direct effect of fumes on workers pouring asphalt, making and transporting asphalt mixes and road construction. Such an exposure is of a long-term nature. The effect of bitumen fumes on human health has been investigated in numerous studies. The emission of VOCs from bitumens also impacts the quality of air at the emission site. In addition, global impact of VOC emissions from bitumens should be considered: pollution of the atmosphere by volatile organic compounds and their transformation products, especially the depletion of the ozone layer and formation of secondary aerosols (Andreae and Crutzen, 1997).

This paper presents a new procedure for the comparison of VOC emission profiles from hot bituminous materials. The studies enabled detailed characteristics of volatile fraction of bitumen fumes.

## 2. Materials and methods

### 2.1. Materials

Please see [Supplementary Data – Section S1](#).

### 2.2. Apparatus

Please see [Supplementary Data – Section S2](#).

### 2.3. Procedure

#### 2.3.1. Identification of volatile components by dynamic headspace and gas chromatography–mass spectrometry (DHS–GC–MS)

Samples of bituminous materials (ca. 0.1 g weighed accurately on an analytical balance to convert GC peak areas per unit mass of bitumen) were placed in 22-mL headspace vials, which were then capped with caps with a PTFE-lined silicone septa using a crimper. Two fused silica capillaries were then introduced through the septum – one of them fed helium purging the bitumen sample (1 cm above the bituminous material – the intended position of the capillary relative to the vial bottom was marked with a marker on the outer wall of the vial prior to the experiment) while the other one transported the gas with the analytes to a sorbent trap (please see [Supplementary Data – Fig. S1](#)).

The sample was placed in a heating block and thermostatted for 30 min at 180 °C. Next, the flow of the purge gas was turned on and the volatile analytes released from bitumen were passed to the sorbent trap maintained at 30 °C. The purging was carried out for 11 min. During thermal desorption of the analytes trap was initially heated to 260 °C, and the analyte desorption from the trap was performed at 270 °C for 4 min. The desorbed analytes were passed through a fused silica transfer line heated to 200 °C directly to the gas chromatograph.

For conditions of separation and detection please refer to [Supplementary Data – Section S.3.1](#).

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