

Methods for Identifying Organic Compounds in Bituminous Emissions

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Bitumen is a major construction material that can emit harmful fumes when heated. These fumes pose health risks to workers and communities near construction projects or asphalt mixing plants. The chemical complexity of bitumen fumes and the increasing use of additives add to the difficulty of analytically quantifying the harmful chemicals emitted using a single technique. Research on bitumen emissions consists of numerous sample preparation and analytical methods. There are a range of considerations to be made when deciding on an appropriate sample preparation method and instrumental configuration to optimise the analysis of specific organic contaminants in emissions. Researchers investigating emissions from bituminous materials may need to consider a range of analytical techniques to quantify harmful chemicals and assess the efficacy of new additives.

Keywords: bitumen ; asphalt ; emissions ; fumes ; sample preparation ; VOCs

1. Introduction

At room temperature, bitumen is still considered a liquid but is solid for all practical purposes. Due to the material's high viscosity, high temperatures are used when working with it to allow mixing with the aggregate. When used in paving applications the working temperatures can vary widely. There are four commonly defined types of asphalt relating to operation temperature: hot mix asphalt (HMA) (150–190 °C), warm mix asphalt (WMA) (100–140 °C), half-warm mix asphalt (HWMA) (60–100 °C), and cold mixes (0–40 °C) [1][2][3][4]. The mixing and laying temperatures can also go as high as 200 °C when bitumen is overheated in certain situations or during spray sealing operations [5]. When the bitumen is heated, particularly to the upper temperature ranges, it releases fumes, the volume of these fumes is reported to increase with temperature [6][7][8][9][10][11][12][13]. These emissions contain an extensive range of organic compounds. Among these emissions are volatile and semi-volatile organic compounds (VOCs/SVOCs); polyaromatic hydrocarbons (PAHs); and heterocyclic compounds containing nitrogen, oxygen, or sulfur, as well as inorganic gases such as hydrogen sulfide [2][3][5][7][14][15][16][17][18][19][20][21]. These are broadly categorised in **Table 1**. PAHs comprise a large proportion of the chemical classes investigated in laboratory-generated fumes due to their carcinogenicity [22] (**Table 1**). However, compounds from various chemical classes besides PAHs may also be of concern given their adverse health effects [23][24].

Table 1. List of broadly classified organic chemicals identified in bitumen fumes using laboratory testing.

Chemical Class	References
Polycyclic aromatic hydrocarbons	[2][3][12][25][26][27][28][29][30]
Nitrogen-containing polycyclic aromatic hydrocarbons	[26]
Oxygen containing polycyclic aromatic hydrocarbons	[29]
Sulfur-containing polycyclic aromatic hydrocarbons	[2][25][26][29]
Nitrogen-containing volatile organic compounds	[15]
Volatile organic compounds	[15][31]
Sulfur-containing volatile organic compounds	[15][31]

2. Sample Collection and Sample Enrichment Methods

Research investigating fuming can either be performed in the field, where samples of fumes are taken on a work site to measure worker exposure [3], or sampling can be performed in the laboratory in a closed system as a controlled

experiment ^[4]. When focusing on the laboratory setting, there is a range of methods to assess fumes accurately. Each sample preparation method seeks to collect the chemical components of the fumes before moving them to an analytical instrument for identification. The methods of collection that have currently been used in this area of research can be split into three main categories: filters ^{[2][3][4][12][25][27][30][32][33][34][35][36][37]}, headspace sampling ^{[15][38][39]}, and direct evolution of fumes into analytical instruments ^{[14][31][35][40]}. Each of these techniques has unique advantages and disadvantages.

2.1. Filter Sampling

The collection of fumes via filtering is a commonly used technique in the laboratory ^{[2][3][4][12][25][27][30][32][33][34][35][36][37]}. The use of filters allows for large volumes of bitumen fumes to be concentrated onto a series of filters significantly increasing the concentration of trace compounds that are able to be collected. Once the collected analytes are extracted with a solvent, the extract can then be separated using gas or liquid chromatographic (LC) instruments before being identified with methods such as mass spectrometry (MS) ^[41].

When using filters in the laboratory, a mixing apparatus is often used to stir while heating the bitumen. The agitation and heating are intended to mimic in-field conditions and facilitate the release of particulates ^[4]. However, it is not a complete simulation of such conditions, and reproducibility is difficult because factors such as container size, bitumen surface area, agitation, air flow, wind, environmental temperature, etc. can affect the results ^{[4][11]}.

The gaseous emissions from bitumen during heating and agitation are pumped through tubing into filters to collect the sample. Various configurations of this system are used throughout the research and there is no universally standardised system ^{[2][3][4][12][25][27][30][33][34][36][41][42][43]}. In general, the system consists of a PTFE or glass wool filter to physically remove particulates and downstream of this there is at least one filter to collect the gaseous chemicals; this is often a charcoal filter for VOCs and an XAD-2 filter for PAHs. Often a combination of both filters is used to analyse a broader range of chemicals in the emissions ^{[4][42]}. Once the emissions have been collected, the filters can be extracted with minimal amounts of solvent to produce a concentrated extraction of the sample. This extract can then be separated using a gas chromatogram (GC) or LC techniques and identified using a range of detectors such as a MS ^[27].

2.2. Headspace Sampling

Headspace (HS) sampling can generally be categorised into static headspace (SHS) or dynamic headspace (DHS) sampling. SHS sampling involves using a speciality syringe to draw a gas sample from the HS of a vial containing a small mass of the sample, which is then injected into a GC.

SHS is a non-exhaustive extraction and takes a small sample of the gas phase with a gas tight syringe. This sample is from a single point in time and the analytes extracted will represent the equilibrium between the sample matrix and the HS when the extraction occurs. Taking an extraction while the HS is not at equilibrium can lead to inconsistent results ^[44].

For DHS sampling, instead of taking a single sample of gas from the HS of a vial, the gases are continuously extracted along with a carrier gas through capillaries to the GC. The gases are often concentrated onto a sorbent trap to allow detection of trace level gases. This concentration of analytes allows for much greater detection of chemicals that would be in too low of a concentration in a single small volume sample. This method is an exhaustive technique that depletes the sample during extraction ^[45].

2.3. Headspace Solid Phase Microextraction Sampling

Headspace solid phase microextraction (HS-SPME) is a non-exhaustive technique similar in principle to the previous example of HS; however, instead of taking a gas sample of the HS a SPME device is exposed to the gaseous analytes in the headspace where the chemicals will absorb into the solid phase of the device. The device itself consists of a thin silica needle-like structure covered in a solid phase coating. An example of this coating is the nonpolar coating, polydimethylsiloxane, which is one of the most common coating materials utilised in HS-SPME. The coating allows chemicals in the HS to be concentrated onto the fibre; the fibre is then removed from the headspace and inserted into the inlet linear to the GC. The analytes are then desorbed in the heated liner and the gas flow carries the analytes into the column ^[45].

2.4. Nonseparative Real Time Sampling

These methods involve the continuous flow of gases from the sample into an analytical instrument. The gases are passed from the sample container into an instrument. This provides the advantage of detecting any changes in the chemicals being emitted from the sample over time or varying temperature ranges.

Work by Cui et al. [40] employed this analytical technique using a thermogravimetric analyser (TGA) coupled with MS to continuously qualitatively analyse the emissions produced by bitumen samples with varying concentrations of layered double hydroxide additives to investigate the effect of this additive on the emission of volatile species. The TGA records the mass loss by using a temperature program that increases temperature over time at a rate of 10 °C/min from room temperature to 300 °C. Piping carries gasses from the TGA to the MS, where selected molecular ions of VOCs are monitored. The intensity of the response for each molecular ion can be used to determine the relative abundance of the molecule passing the detector.

The advantages of this method allow for the identification of a wide range of compounds. In this work the researchers can identify small volatiles including hydrogen sulfide and larger PAHs such as fluoranthene. The real-time monitoring of sample emissions means that the variation in fume composition can be tracked over time or with temperature changes. However, the procedure described by the researchers does not quantify the chemical concentrations. The results are described using current intensity measured in amperes (A). The researchers use this as a qualitative measure of volatile emissions in different bitumen samples.

2.5. Summary of Sample Preparation Techniques

The sample preparation methods available based on the current research provide a range of tools for researchers when analysing bitumen emissions. When designing an analytical analysis, selecting an appropriate sample preparation method is vital if working with a complex material such as bitumen. Due to the range of organic compounds that are present in the emissions the choice of whether to investigate acetone [31] or benzo[a]anthracene [25] would reasonably require different analytical procedures. There are both advantages and limitations to the methods described in this work. Some of these are outlined in **Table 2**.

Table 2. Comparison of sample preparation techniques.

Sample Technique	Comment
Filter sampling	The most representative of industrial application Requires solvent extraction of analytes
Headspace sampling	Fast sampling Suited for large sample sets Solventless
Headspace solid-phase microextraction	Fast sampling Suited for large sample sets Solventless
Nonseparative real-time sampling	Solventless Possible to measure organic emissions rates over time

Historical techniques, such as filter sampling, have proved essential in analysing trace PAHs in bitumen due to the concentration of large emission volumes onto filters [41][30]. However, this method requires solvent extraction of filters, large sample volumes, and a timely extraction process involving ad hoc mixing apparatuses. Future technologies such as novel SPME materials designed for selective adsorption of aromatic compounds could prove crucial for analysing trace PAHs in bitumen using fast, automated methods that have become a mainstay in analytical chemistry [46][47][48][49].

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