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SAMPLING AND ANALYSIS OF BITUMEN FUMES

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Abstract—Processes which involve the use of bitumen-containing materials at elevated temperatures can release airborne particulates into the workplace. The organic part of the particulates. characterized by the benzene-soluble matter (BSM), mainly stems from the bitumen and contains small amounts of polycyclic aromatic hydrocarbons (PAHs).

A sampling and analytical procedure for the determination of total particulate matter (TPM)and BSM for bitumen fume in the atmosphere has been developed and validated. Its suitability for sampling PAHs has been investigated.

The sampling package consists of a glass-fibre–silver membrane combination supported by a back-up pad. all contained in a standard 37 mm Gelman-type filter cassette. The glass-fibre–silver membrane filter combination was shown to have a maximum capacity of 6 mg. Some loss of BSM was shown to occur owing to evaporation during sampling, but for a 5 mg sample losses are not expected to be greater than 2% mass per hour of sampling under normal operating conditions. The sampling procedure has also been shown to be suitable for PAHs, although evaporative losses may lead to a relative deficiency of the lower molecular weight PAHs in samples containing small amounts of material.

By this method personal breathing-zone samples of the mixed aerosol have been taken for analysis, giving TPM, BSM and information on the content of certain three- to seven-ring PAHs. Airborne concentrations have been measured for 17 jobs in six processes in manufacturing, road application, roofing, and indoor mastic laying. The materials contained bitumen, stone and cutback solvent, giving rise to potential exposure by inhalation and skin contact. Time-weighted average exposures over 8 h (TWA (8 h)) ranged from 0.2 to 18 mg m^{-3} for TPM, 0.1 to 14 mg m^{-3} for BSM and 4 to 2508 ng m^{-3} for a total of eleven selected PAHs. The BSM varied from 0.5 to 84% of the TPM depending on the materials being used. Exposures are compared showing the effects of material, temperature, job and indoor working: the findings are in general agreement with other published work. Generally, the exposure to PAHs is related to the amount of BSM.

For laboratory studies of the emission of fumes from hot bitumens and the analysis of three- to seven-ring PAHs in those fumes, a laboratory rig has been developed and validated, in which we can reproducibly generate and sample bitumen fumes under controlled conditions. The results obtained with the laboratory rig are shown to be related to those obtained in the field from the same product.

Condensed bitumen fumes are characterized briefly in terms of their chemical composition, boiling-point distribution and viscosity. Total fume emissions, measured as BSM and the concentrations of a number of individual PAHs in the BSM have been determined for penetration (paving) grade bitumens and for oxidized (roofing)grade bitumens at temperatures relevant for the practical applications. A comparison is made between bitumens and coal-tar pitches and the fumes generated from them.

The PAH contents of fumes from penetration grade bitumens and oxidized grade bitumens were similar. The major factor controlling variations in PAH emissions from hot bitumens was the amount of fume generated, measured as BSM, and this is shown to be markedly dependent on the bitumen temperature. The coal-tar fumes contained far more PAHs than the bitumen fumes.

BSM exposure provides a good indication of relative exposure to PAHs in bitumen fume particulates released from normal bitumens under typical application conditions.

INTRODUCTION

PROCESSES which involve the use of bitumen-containing materials at elevated temperatures can release airborne particulates into the working area. As bitumen consists essentially of hydrocarbons and their derivatives, the emissions can be expected to be made up of complex organic mixtures, arising from the parent bitumens or from diluents such as kerosine. The organic mixture contains small quantities of. polycyclic aromatic hydrocarbons (PAHs). Although the PAH concentrations are small, they are of potential concern because some four- to six-ring PAHs have been shown to be carcinogenic in, for example, animal skin painting studies (BINGHAM et al., 1979).

The overall objective of the present study was to obtain information on fume emissions and PAH emissions from hot bitumens, both as a function of the type of application and as a function of bitumen characteristics.

Although bitumen itself is of a mainly organic nature, in many work situations there may also be inorganic materials present such as stone or sand, forming an essential ingredient of the product, and/or unspecified particulates, e.g. dust, from the environment.

The aerosol which is generated by heat may contain organic droplets and inorganic particulates, which may be amorphous or crystalline, plus organic vapour and steam. The concentrations of emissions in air can be expected to vary over a wide range, depending on process, temperature and working method.

The sampling package most widely used is designed primarily for the measurement of total particulate matter (TPM). The samples can subsequently be extracted to give 'benzene-soluble matter' (BSM) or 'bitumen fume', depending on the terminology and the solvent used. For practical reasons, the total concentration and the solvent-extracted fraction were used in this study as parameters for assessing exposure in manufacturing and in downstream applications. The literature contains several references which report TPM and the solvent fraction and in some cases the content of a number of individual PAHs in paving (PUZINAUSKAS, 1980; DANISH STATE INSTITUTE OF WORK HYGIENE. 1978; ASSOCIATION OF DANISH ASPHALT INDUSTRIES, 1979; AHONEN *et al.*, 1977), rooting (PUZINAUSKAS, 1979; DANISH STATE INSTITUTE OF WORK HYGIENE 1978; PRIHA et *al.*, 1980; MALAIYANDI *et al.*, 1981), indoor surfacing (DANISH STATE INSTITUTE OF WORK HYGIENE, 1978; VIRTAMO *et al.*, 1979). and production (DANISH STATE INSTITUTE OF WORK HYGIENE. 1978) for a variety of bitumen mixtures at temperatures ranging from 135 to 310°C. Several workplaces have been assessed with breathing-zone concentrations ranging from less than 0.2 to 39 mg m^{-3} for TPM, and less than 0.1 to 11 mg m^{-3} for the solvent fraction. These studies give valuable background information on workplace concentrations, subject to differences in sampling packages, quality control and sampling strategy and analysis methods.

With reference to sampling and analysis methods for bitumen fumes in the U.S.A.,

OSHA* (1971) and NIOSH† (1977 and 1978) published methods for bitumen fumes, but there was no consensus on filter combinations and sampler configuration to be used. PUZINAUSKAS (1980) doubted the suitability of the NIOSH procedure for bitumen.

CONCAWE (1981) published an outline of methods of sampling oil mist which is not intended for sampling bitumen fumes. In the coal-tar industry much work has been done on sampling and analysis of coal-tar pitch volatiles (CTPV). RICHARDS et *al.* (1967) describe a method using silver membranes and benzene extraction. Other authors report staining of back-up pads and filter clogging when using silver membranes for CTPV sampling (FANNICK et ai., 1972; JACKSON and CUPPS, 1978).

Our first task, therefore, was to establish a valid procedure for sampling and analysis of bitumen fumes. This procedure had to be suitable both for field use, for checking of occupational exposure to bitumen fumes in terms of TPM and BSM, and for laboratory studies of the factors controlling the emission of fumes and their PAH content.

The main principles of a standard procedure meeting these requirements, which involves the use of a personal sampler, together with its validation, forms the subject of Part 1 of this paper. Where possible, elements from existing methods have been used. The work has contributed to a critique by CONCAWE of the method of sampling and analysis and the detailed procedure is included in a report from CONCAWE (1984).

In Part 2 we aim to provide inter-correlatable data on exposure arising from the use of a number of bitumen materials in manufacturing and user industries. The standard sampling package described in Part 1 was employed in all surveys. Data are expressed as concentrations and time-weighted average exposure over 8 h (TWA (8 h)) for breathing zone samples for TPM and BSM. A number of the samples were also analysed for their content of a range of three- to seven-ring PAHs for the purpose of improving the understanding of the composition of bitumen fume in field situations. The results serve to complement the study described in Part 3.

During field studies, factors such as the nature of the application, the type of job Performed and external conditions such as the weather can have a considerable influence on emission and exposure. In actual field situations these conditions are difficult to reproduce from one survey to another. In order to study the influence on emissions of the type of bitumen, bitumen temperature, etc., we therefore considered it essential to conduct experiments in a laboratory rig under controlled conditions. This work is the subject of Part 3.

As the PAH emission is the product of total fume emission, measured as BSM, and of the PAH concentration in the BSM, we have investigated each of these two parameters and assessed their influence on PAH emission.

As possible detrimental effects of PAHs on biological tissues depend not only on PAH composition and concentration but also, for example, on the viscosity and chemical nature of the material, we deal briefly with general physical and chemical characteristics of bitumen fumes.

PAH contents and emissions of bitumen fumes are reported for various bitumens.

*OSHA, Occupational Safety and Health Administration, U.S.A.
†NIOSH, National Institute of Occupational Safety and Health, U.S.A.

Factors influencing BSM emission and the PAH content of the BSM such as bitumen temperature, type of bitumen and the influence of the blowing reaction are discussed.

In order to place the variations in values measured for bitumen fumes in a wider perspective, a comparison is made with coal tars and the fumes generated from them.

In the discussion an attempt is made to summarize the results of the study as a whole.