

# **assessment of personal inhalation exposure to bitumen fume**

# **guidance for monitoring benzene- soluble inhalable particulate matter**

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Brussels  
September 2002

## ABSTRACT

This report discusses practical issues in relation to the assessment of occupational exposure to bitumen fume as benzene-soluble inhalable particulate matter. A detailed sampling and analytical method is presented. This report supersedes guidance given previously by CONCAWE in report 6/84.

## KEYWORDS

Bitumen fume, inhalable particulate matter, occupational exposure

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## SUMMARY

Exposure limits of different types have been set for occupational exposure to bitumen fume by various organisations. Limits have either been set for all airborne particulate matter, or for a fraction thereof. Monitoring methods have been published which followed the concepts of these limits.

CONCAWE report 6/84 provided guidance for monitoring occupational exposure to bitumen fume. The procedure involved collection of airborne particulate onto a filter, extraction of organic material with benzene, and gravimetric quantification.

In 2000 a new limit value was issued by the American Conference of Governmental Industrial Hygienists (ACGIH) for bitumen fume defined as the benzene-soluble fraction of inhalable airborne particulate matter. The requirement to sample inhalable particulate matter was adopted in response to a new European standard for biologically relevant airborne particulate. The ACGIH guideline is used in a number of European countries.

This report reviews issues associated with inhalable particulate matter exposure assessment as it relates to bitumen fume, including comparative studies of old and new methodologies. Practical considerations, on the basis of application of a recommended new methodology are discussed. A detailed method is provided as an appendix.

## 1. SCOPE AND PURPOSE

This report gives practical guidance for the assessment of potential worker exposure to inhalable bitumen fume, in particular in relation to the exposure threshold limit value (TLV) specified by the American Conference of Governmental Industrial Hygienists (ACGIH). It is not intended as a comprehensive assessment guide or for other types of occupational exposure. It is recommended that exposure assessments for bitumen fume are conducted with the assistance of a suitably qualified and experienced occupational health advisor such as an industrial hygienist or an occupational physician.

When issuing their revised TLV for bitumen fume in 2000, the ACGIH adopted a new concept, of European origin, for size-selective sampling of airborne particulate matter. When a hazardous material is dispersed in air as particulate matter, only a fraction thereof is capable of reaching those areas of the respiratory tract where it can have adverse health effects. The new concept takes this into account. The previous approach to limit setting for hazardous particulate matter was not based on this type of biological consideration, but rather on the use of a common type of sampling equipment.

Chapter 2 provides some general notes in relation to the underlying assumptions for occupational exposure assessment. Chapter 3 provides information on exposure limits for bitumen fume, in particular the ACGIH TLV and the issue of size-selective sampling criteria, and sampler requirements and performance. Chapter 4 includes practical recommendations for measuring exposures to bitumen fume. A method suitable for the determination of personal inhalation exposure to bitumen fume is presented in the Appendices.

Similar guidance was produced by CONCAWE in 1984; the resulting report, 6/84, is now superseded by the present report.

## **2. ASSESSMENT OF OCCUPATIONAL EXPOSURE TO BITUMEN FUME – SOME GENERAL ISSUES**

### **2.1. INTRODUCTION**

Modern occupational health practice is aimed at maximising the availability of the workforce for work whilst minimising any adverse effects of work activities. In order to do so information is required on the health risks associated with work activities. A systematic approach of recognition, evaluation and control of hazards and risks to health in the workplace therefore forms an inherent part of an occupational health programme. Guidance on occupational health programmes appropriate to the needs of the oil industry has been given in an earlier CONCAWE report [15].

A comprehensive overview of the health, safety and environmental data on bitumens and their derivatives was published by CONCAWE in 1992 [16]. It is recognised that all workers using bituminous materials at elevated temperatures may be exposed to bitumen fume by inhalation and by skin deposition. They may also be exposed to other organic materials, which may be determined as part of, and be indistinguishable from, bitumen fume using a specific monitoring method.

This chapter focuses on the general principles of the assessment of personal inhalation exposures to bitumen fume. More detailed information on the exposure limit, bitumen fume and practical aspects are covered in the later chapters.

### **2.2. OCCUPATIONAL EXPOSURE DETERMINATION**

Occupational exposure may be determined for several reasons, such as:

- to compare the measured exposure with a limit value,
- to assess the effectiveness of adopted control measures,
- to document 'typical' exposure for current or future health surveillance.

Each of these reasons may require different measurement strategies as briefly explained in the following sections.

#### **2.2.1. Workplace factors affecting potential exposure**

All workers using bituminous materials at elevated temperatures may be exposed to bitumen fumes by inhalation. They may also be exposed to other organic materials which will be included in "bitumen fume" measurement results when determined according to the method given in this report. The magnitude of exposure will depend on workplace factors and protective measures.

Factors which may affect the potential exposure to "bitumen fume" include:

- the temperature of the bituminous material,
- the type of application e.g. paving, roofing,
- the type of bitumen used e.g. volatility,
- workplace geometry, distance from source,
- ventilation (or weather),

- the job/ task,
- exposure times,
- working habits,
- worker hygiene and worker protection.

Some of these parameters are inherent to the work being carried out, others vary at random. It is important that these factors are assessed to determine which are likely to be most important with respect to the risk of worker exposure.

One of the most important factors for potential exposure is the bitumen temperature, and temperature control has been widely advocated to reduce exposure levels. Factors of a more random nature are e.g. wind speed, the amount of product used and worker productivity.

Historical exposure data analysed in the context of the International Agency for Research on Cancer study of European asphalt workers [21] suggested that the following operations might lead to statistically significant increased exposure:

- mastic laying, especially in indoor environments,
- re-paving and hot *in-situ* recycling.

Information obtained earlier and/or calculations can be useful to determine which factors should be taken into account. Wherever possible it is recommended that these factors are used in selection of workers and conditions under which personal exposures are to be determined. The factors should, in any case, be recorded during personal exposure studies.

### **2.2.2. Measurement strategy**

The objective of any monitoring is to obtain the “best estimate” of worker exposure in a cost-effective manner in order to allow an evaluation that addresses the principal reason for the exposure determination. The selection process and numbers involved will depend on the exact situation. The preferred approach involves allocating workers to groups carrying out identical or very similar tasks. An assessment of the influence of the various workplace factors may be available or should be made for each group. This enables sampling to be focused on the worker groups that are most relevant. For example, when assessing compliance with the exposure limit in the case of asphalt paving operations, it is recommended that the paver driver and the screedman are selected for monitoring.

One or more representative worker(s) can be selected from a group; the number will depend on the size of the group. The CEN EN 689 guideline is to select at least one in 10 workers per group [13].

Since most exposure limits are based on an 8-hour time-weighted average (TWA) it is recommended that sampling for limit compliance monitoring covers the duration of the work. If the sampling period does not cover the complete period of exposure then the number of samples required will increase. CEN EN 689, Annex A, contains a guide for determining the number of samples; the number increases as the sampling duration decreases.

In order to obtain a reliable estimate of typical exposures it may be necessary to perform measurements on both a sufficient number of representative workers per

group, with a suitable sampling duration, and during a sufficient number of shifts with variable exposure conditions.

If the objective is to determine whether worker “worst-case” exposures comply with the occupational exposure limit (OEL) then not only the worker (group) but, if possible, also exposure conditions should be selected with this objective in mind. This may involve identifying times when higher exposures occur and determining the exposure for these periods. Conditions should not be changed such that they are unrepresentative and could expose the worker(s) to a greater risk than the anticipated “worst-case” situation.

### 2.2.3. Measurement procedure

A proposed measurement procedure consists of the following steps:

- Select the workers/ group of workers as per required measurement strategy.
- Wherever possible, determine worker exposure by taking breathing zone samples for the entire working period.
- Use a standardised sampling method (see also method given in appendix).

It is recommended that a suitable template be used to record actual details and workplace conditions. An example of a Monitoring Record Sheet Template is given in **Appendix 1**.

## 2.3. INTERPRETATION OF MEASUREMENT RESULT

### 2.3.1. Compliance with a limit value for full-shift exposure

The method presented in the Appendices describes determination of airborne exposures in mg/m<sup>3</sup>, averaged over the measurement duration. The results may need to be compared with a limit value, which is usually given on an 8-hour time-weighted average (TWA) basis.

This basis is defined by e.g. the ACGIH as “the time-weighted average concentration for a conventional 8-hour workday and a 40-hour work week, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect” [2].

The occupational exposures in a shift are normally (CEN EN 689) treated [13] as being equivalent to a single uniform exposure for 8 hours (the 8-hour TWA exposure).

The 8-hour TWA exposure can therefore be represented mathematically as:

$$\frac{\sum c_i t_i}{8}$$

where  $c_i$  is the measured occupational exposure concentration for task  $i$

$t_i$  is the exposure time in hours of task  $i$



Note that  $\sum t_i$ , the actual total exposure time, is not necessarily equal to 8 hours.

This means that the actual worker exposure is normalised to 8 h/d. This is the value that should be compared to e.g. the TLV-TWA.

### **2.3.2. Compliance with a short-term exposure limit**

No Threshold Limit Value-Short-Term Exposure Limit (TLV-STEL) has been set by any limit-setting body for bitumen fume. In some cases, a short-term limit can be derived from the full-shift limit value. ACGIH recommends that the duration of peak exposures at levels up to 3 times the numerical value of the 8-hour limit should not exceed 30 minutes per workday, whereas a level of 5 times the numerical value of the 8-hour limit should never be exceeded, not even for very short periods [2].

## **2.4. ASSESSMENT REPORT**

A suggested format for the report includes:

- (Executive) summary

- Objective

  - Published data, legislation and company policy

- Measurement strategy

- Collected data

  - Summary of work carried out

  - Summary of job types, worker numbers, description of workplace factors

  - Summary of sampling conditions

  - Measurement procedure used

  - Summary of results

- Conclusions (where relevant also recommendations),

- Appendices

  - Raw data

### 3. PARTICLE SIZE-SELECTIVE SAMPLING OF BITUMEN FUME

#### 3.1. OCCUPATIONAL EXPOSURE LIMITS FOR BITUMEN FUME

Historically, some European countries have specified limits for bitumen fume exposure, others have specified limits for benzo(a)pyrene or the sum of other Polycyclic Aromatic Compounds (PACs) that are present in fume, while some have no specific limit - although generic limits for dust may be applicable. Some of these countries have also specified a measurement method in conjunction with the limit value. It is noteworthy that the results of bitumen fume measurements depend on the type of method used, and that there is no 'gold standard' method available for comparison.

Examples of currently applicable limit values are:

United Kingdom	:	5 mg/m <sup>3</sup> as TPM
The Netherlands	:	None, although a standard of 5 mg/m <sup>3</sup> as TPM is advised
Germany	:	10 mg/m <sup>3</sup> as total hydrocarbons
France	:	None (there are limits for "dust" of 5 and 10 mg/m <sup>3</sup> as TPM)

Where countries do not specify limits for bitumen fume exposure they often use ACGIH recommendations as guidelines. ACGIH annually re-issues its TLV list, which may contain some revised recommendations. Some countries immediately incorporate these recommendations into legislation. Any change in the ACGIH TLV therefore has international implications.

For many years the ACGIH recommended a TLV-TWA of 5 mg/m<sup>3</sup> Total Particulate Matter (TPM) for bitumen fume. At the beginning of 2000 the ACGIH published a new TLV-TWA for Asphalt (Petroleum; Bitumen) fume of 0.5 mg/m<sup>3</sup> <sup>(1)</sup> as benzene-soluble aerosol (or equivalent method). The notation <sup>(1)</sup> refers to Inhalable Particulate Matter. The ACGIH has adopted the criteria for size-selective airborne particulate matter monitoring of the European standard EN 481 [12]. These criteria are based on potential deposition, upon inhalation, of particles in areas of the human respiratory tract where they may cause health effects. Inhalable particulate mass TLVs are set for those materials that are hazardous when deposited anywhere in the respiratory tract [2]. The collection efficiency as a function of particle diameter, defined for this mass fraction is fixed and independent of the method used. TPM results, in contrast, are linked to a given dust sampling method. The shift from 'total particulate' to the benzene-soluble fraction was made to make the limit more specific to bitumen fume. Thus both the value and the basis for measurement have been changed simultaneously.

The basis of the TLV value is mucous membrane and eye irritation. The ACGIH's TLV Committee, in its documentation in support of the TLV for bitumen fume, has not addressed the possible contribution of vapours to irritation [1]. In addition, most of the past exposure data for airborne particulate, reviewed for the establishment of the TLV, were obtained with methodologies different from the current recommendation. Insufficient data are as yet available to determine how those results relate to data obtained with a method meeting the inhalable particulate matter definition.

### 3.2. IMPLICATIONS OF THE TLV CHANGE

In order to understand the implications of the TLV change it is necessary to consider the nature of emissions from bitumen when heated to elevated temperatures and how the emission and exposures can be determined.

When bitumen-containing materials such as asphalt are handled at elevated temperatures, fumes, i.e. vapours and particulate matter, are emitted to the air. Particulate matter can be sampled by pumping air through a particulate matter filter. When sampling bitumen fume, the materials collected on the filter may also include inorganic and organic matter from other sources, such as mineral aggregates, diesel exhaust particles etc. The organic part is soluble in organic solvents, e.g. benzene; this is **Benzene Soluble Matter (BSM)**. Depending on the type of application and the working conditions the BSM contribution can range from a few percent to ca. 90% of the total airborne particulate matter [6].

In addition to the particulate matter, other compounds are emitted from hot bitumen in vapour form and are not retained on a particulate matter filter. These materials, called **Semi-Volatiles (SV)**, can be trapped by an adsorbent tube attached in series behind the filter. Together the BSM and SV are the **Total Organic Matter (TOM)** that has been collected. The relative amounts of BSM and SV in the TOM vary depending on the type of application. Only the German exposure limit relates to combined particulate matter and volatiles.

The new ACGIH TLV is defined for the benzene-soluble fraction of the inhalable particulate. This means that it is analogous to BSM but has to be collected using a suitable, size-specific sampler. It is the Benzene-Soluble fraction of the **Inhalable Particulate (IP)**. For convenience, the term **Benzene-Soluble Inhalable Particulate (BS-IP)** will be used to describe the substance in this document. The term BE-IP (benzene-extractable inhalable particulate) has also been used to describe the same substance.

Few sampling surveys using a BS-IP approach have been published so far for bitumen fume. Therefore, the exact implications of the change in TLV remain uncertain. The basis for the previous TLV was TPM, i.e. including organic, as well as any inorganic airborne particles. There is no simple correlation between results from the methods associated with the new and old ACGIH recommendations. BSM data, however, are considered more specific for bitumen fume than TPM data.

The mathematical equation for the capturing efficiency of a sampling device to meet the IPM convention is given in **Appendix 2**. The capturing efficiency should decrease with increasing particle size; e.g. only 52.5% of the airborne particles with aerodynamic diameter of 50 µm should be captured. This equation is a reflection of what is actually inhaled beyond the human nose, as assessed in laboratory studies.

### 3.3. SAMPLER PERFORMANCE STUDIES

Although the ACGIH considers the task of a TLV and its source documentation [1] to include informing the user on *what* to sample, ACGIH does not consider its role to include specifying *how* to sample it. The ACGIH does not, therefore, specify any particular sampler or procedure.

### 3.3.1. Samplers historically used to determine bitumen fume

In 2000 a literature review of levels of exposure in the road construction industry was published [10]. The review contains details of the samplers used, when these were included in the original publication. From this it appears that particulate filters have normally been used to determine exposures to organic fume, and that the most commonly used sampler was the 37 mm cassette with a glass fibre or PTFE filter. Other samplers, not included in the literature review include the 7-hole inlet [22] and the PGP-System GGP [5].

NIOSH method 5042 for determining asphalt fume as benzene-soluble fraction and Total Particulate, published in 1998, specified the 37 mm cassette with a PTFE filter [29]. The 37 mm cassette is frequently referred to as a “total” aerosol sampler.

Other samplers, which have been used to determine exposure to dust during road construction, include cyclones and cascade impactors [10].

### 3.3.2. Sampler performance - inhalable convention

Some of the samplers mentioned in 3.3.1 were included in a collaborative European study of personal sampler performance [23]. Data from this study were used to calculate the performance characteristics of the samplers enabling comparison between samplers and with the inhalable sampling convention. The sampler types were the Institute of Occupational Medicine (IOM) sampler, the seven-hole sampler, the GSP sampler, the PAS-6 sampler, the PERSPEC, the CIP10-I, the open-faced 37 mm cassette and closed-face 37 mm cassette. In this study the samplers were mounted on a full-size mannequin rotating in a wind tunnel. Sampler efficiencies were determined for monodisperse aerosols of aluminium oxide at 9 different particle sizes in the range between 6 µm and 100 µm, and at 3 different wind speeds, 0.5, 1.0 and 4.0 m/s.

The general trend was for the sampling efficiency to decrease as wind speed increased. The samplers could be grouped into broadly similar classes. At low external winds 6 of the samplers performed adequately, viz. IOM (although over-sampling slightly), seven-hole, GSP, PAS-6, PERSPEC and 37 mm closed-face. As the wind speed increased only two samplers, the IOM and GSP, maintained adequate performance. At high wind speeds (4.0 m/s) none of the samplers performed very well.

The IOM sampler was designed specifically to collect the inhalable fraction [28,34]. It has been increasingly used to determine exposure to inhalable particulate [35]. In addition to the comparative laboratory study, paired exposure studies comparisons have been carried out for the IOM and 37 mm cassette in several industries [35]. The results showed that the level of exposure based on inhalable aerosol consistently exceeded that for “total” aerosol. The observed ratios between the inhalable and “total” aerosol, collected using the closed-face cassette, ranged from ca. 1.2 to > 3. The ratio was greater for workplaces where the aerosol was coarser or denser. No asphalt paving or roofing operations were included in these workplace comparisons.

The potential difference in performance between inhalable aerosol samplers used for personal and for area sampling was evaluated recently [27]. Sampler performance was shown to depend on particle size, wind speed and also on sampler orientation with respect to wind direction.

### **3.3.3. Efficiency for bitumen fume (laboratory studies)**

The performance of the IOM, closed-face 37 mm cassette, 7-hole and the PGP-System GGP samplers has been compared using lab-generated bitumen fumes [18]. For both TPM and BSM (BS-IP) the ratio between the IOM and the average for the other samplers was close to 1. This implied that the geometry of the samplers was not an important factor for bitumen fume sampling under laboratory conditions. The German method used did not enable determination of the TPM.

In a more extensive laboratory comparison, again at low wind speed, of the IOM and the open-faced 37 mm cassette, the IOM sampled slightly, but statistically significantly more bitumen fume than the 37 mm cassette. The ratio was 1.10 for paving grade bitumen at ca. 160°C and ca. 1.04 for roofing grade bitumen at 210 - 250°C [20].

These findings are consistent with the small particle size of bitumen fume. Particle size determinations on bitumen fumes showed that more than 96% by mass was below 12.5 µm [9].

The slightly higher IOM sampling efficiency in the later study may, in part, be related to the fact that there is no inner particle loss because the filter and filter cassette are analysed together. With the 37 mm sampler only the filter is weighed; there are reports that the material deposited on the (inner) walls of the cassette may be a significant percentage of the material sampled [25].

### **3.3.4. Efficiency for bitumen fume (field studies)**

Laboratory studies have shown that at low particle size and under certain conditions, aerodynamic factors may not significantly affect sampler performance. Field studies may show differences as other factors, e.g. wind and its effect on sampling efficiency, and also particulate matter originating from sources other than bitumen are involved. No comparative field studies for bitumen fume have been reported yet in the literature. Field studies to compare the performance of the 37 mm cassette and IOM sampler for sampling bitumen fume are currently underway in both Europe and the USA.

### **3.3.5. Quality of bitumen fume (lab studies)**

The studies reported above have, in general, focused on sampler efficiency, i.e. the quantity of material sampled related to the particle size of the material. Bitumen fume is a complex chemical mixture and parameters such as the Polycyclic Aromatic Hydrocarbon (PAH) content of fumes, or boiling point distribution have been used in comparisons of laboratory and field fumes as part of the validation of laboratory generated fume [8,24]. As a supplement to the quantitative study on bitumen fume, qualitative examinations were carried out.

For laboratory-generated fume, the composition of the BS-IP sampled using an IOM sampler was compared to that of the BSM sampled using a 37 mm cassette. Fumes were generated from paving and roofing grade bitumens, and PAH contents and profiles of the BS-IP and BSM compared. For the paving grade bitumen the PAH emission was slightly greater when sampled with the IOM sampler compared to the 37 mm sampler, i.e. a similar relationship as for the fume sampling. No significant difference was observed in PAH emission from the roofing grade bitumen. There

was no significant difference in the PAH profiles for fumes from either grade of bitumen [31].

Similarly, there was no significant difference between the boiling point range nor PAH profile of Total Organic Material sampled using IOM and 37 mm samplers, both in combination with XAD-2 adsorbent tubes, as determined by the same laboratory [18].

### **3.3.6. Sampler selection**

Any sampler meeting the size-specific efficiency criteria for inhalable particulate may be used for sampling bitumen fume for comparison with the ACGIH TLV. Although not exclusively written for the IOM sampler, the method in **Appendix 3** contains information that is applicable for an IOM sampler. The inclusion of information on the IOM sampler in the method and in the next chapter is based on the sampler performance in the European collaborative study, its wide availability and use in other industries, and experience from ongoing exposure studies.

## **4. PRACTICAL CONSIDERATIONS FOR MEASURING PERSONAL INHALATION EXPOSURE TO BITUMEN FUME**

This chapter aims to provide information and recommendations based on practical experience of sampling and analysis of bitumen fume. The information below, where based on use of the IOM sampler, has been used in the development of the method presented in **Appendix 3**.

### **4.1. SELECTION OF PERSONNEL AND RECORDING OF DETAILS**

Identification of important workplace factors and relevant worker groups for measuring exposures was discussed in Chapter 2. An important, but random factor between studies is wind speed and direction. Recording the position of workers relative to wind direction is critical for understanding the measurement results. This can be demonstrated from personal exposures measured on two consecutive days at the same road paving job. There was a strong wind on day 1 and no wind on day 2. Average BSM exposures on day 2 were a factor 2 higher than on day 1. On day 1 the exposure of the upwind screedman was a factor 6 lower than the downwind screedman [31].

It should be noted that sampler performance was not studied in the laboratory at wind speeds higher than 4.0 m/s, which equates to a gentle breeze. Thus, no information is available on how well the inhalability criterion is met at stronger wind speeds.

The hygiene and working practices of the workers should be closely observed and recorded for subsequent interpretation of exposure data. An example of working practice significantly affecting exposure was observed during loading of bitumen into road tankers. One tanker driver continuously monitored the filling operation from a position close to, and directly above the filling point. This behaviour was in contrast to other drivers who kept the frequency and duration of the checks to a minimum. There was a difference of more than a factor 3 in exposures; this led to revised recommendations for drivers [31].

### **4.2. PUMPS AND FLOW RATE**

Requirements and test methods for pumps for personal sampling have been incorporated in a CEN standard EN 1232 [11]. This European standard is applicable to pumps whose nominal volumetric flow rate is within the range 5 ml/min to 5 l/min. The standard classifies the pumps according to their intended use as pumps for personal sampling of particulate matter (type P) or of gases and vapours (type G). For the sampling of bitumen fumes a type P pump is used; when vapours are also sampled an adsorbent tube is included in series after the particulate filter.

Type P pumps have adjustable flow rates in the range 1 - 5 l/min. A flow rate of 2 l/min is commonly used for sampling of airborne particulate matter, but in any event the sampler manufacturer's instructions should be followed. The German BIA method stipulates a flow rate of 3.5 l/min. NIOSH 5042 stipulates a flow rate between 1 and 4 l/min.

Pump flow rate should be calibrated with a representative sampler in line. For a combination of filter and adsorbent tube, use of a flow rate higher than 2 l/min can give problems in terms of the back pressure and/or the length of time for which the battery of the pump can operate. At 2 l/min a pump can typically operate for at least 8 hours, with or without a suitable adsorbent tube in series with an IOM or 37 mm cassette, thus covering a normal work shift. At a higher flow rate this time is likely to be reduced (pump dependent).

An adsorbent tube containing 2 sections of 100 and 50 mg of adsorbent, e.g. XAD-2 can be used in series at 2 l/min. An adsorbent tube containing 2 sections of 150 and 75 mg has been used in series with both an IOM sampler and a 37 mm (PTFE filter) sampler in limited laboratory experiments at 2 l/min, but has not been used for exposure measurements. An adsorbent tube containing 2 sections of 400 and 200 mg could not be used in series at a flow rate of 2 l/min [31].

A flow rate of 2 l/min is recommended for the IOM sampler. Along with the sampler geometry, this is the determining factor for the sampling efficiency to approach the inhalability curve. The inventor, Dr Vincent, estimated that a suitable range is limited to 1.8 - 2.1 l/min [3]. Laboratory studies have indicated a non-linear sampling relationship with flow rate [31].

### **4.3. IOM SAMPLERS**

#### **4.3.1. Suitability of cassette material**

The IOM sampler body is made from conductive plastic that dissipates electrical charges thus preventing static electricity influencing the collection of aerosols. The cassettes (front and rear parts) are available in plastic, aluminium or steel.

Both the aluminium and steel cassettes are suitable for TPM and BS-IP measurements. The steel cassette has proven more robust in practice although the aluminium cassette is lighter (ca. 1.2 g compared to ca. 4.6 g).

The plastic cassette is unsuitable for the determination of BS-IP for two reasons. Particles deposited on the filter and the inner cassette walls are intended to be part of the sample. Studies have shown that the tare-weight of the plastic cassette is not stable and it is suggested that this may be because it is hygroscopic [26,32]. Furthermore, the plastic cassette appears to both absorb benzene and to release materials into the benzene [31] (see also Analytical Work-up requirements below).

#### **4.3.2. Filter capacity**

The capacity of a 37 mm glass-fibre/silver membrane filter combination is 6 mg (total particulate matter) [9]. The capacity of a 37 mm PTFE filter, recommended by NIOSH, is 2 mg [29]. In laboratory studies with a 25 mm glass fibre filter in an IOM sampler, the capacity was determined as  $\geq 5$  mg [31].

Based on an 8-hour sampling period and a flow of 2 l/min, i.e. 960 l, these capacities translate to the following exposures:

37 mm glass-fibre/ silver membrane, 6.3 mg/m<sup>3</sup>  
37 mm PTFE, 2.1 mg/m<sup>3</sup>  
IOM, 5.2 mg/m<sup>3</sup>



Filter capacity combined with pump flow rate will influence the sampling time. For example, the potentially suitable German sampler is operated at 3.5 l/min. In personal exposure studies the maximum advised sampling time is therefore fixed at 5 hours to avoid exceeding filter capacity [33].

#### 4.3.3. Transport and storage of samples

Losses from the filter and cassette are dependent on the loading and on the storage conditions. It is essential that the samplers are properly sealed and placed in airtight plastic bags. They should be stored in the dark, if possible in a cool or cold place and transferred to a refrigerator, or freezer, as soon as possible and retained there until analysis. The use of a (food) cool-bag with (frozen) cool-pack has proven a practical solution to the temporary storage and transport of samplers taken during exposure studies.

Sealing a (closed-face) 37 mm cassette by plugging the filter cassettes is relatively simple. An IOM filter cassette is supplied in a small transport container; this is not airtight. Experience has shown two ways of sealing the IOM samples - to wrap the complete sampler, including filter cassette, tightly in aluminium foil, or to remove the cassette from the sampler and wrap it tightly in foil.

Laboratory studies with bitumen fume samples showed that losses from an unprotected IOM cassette / filter were ca. 22% relative after a period of 2 weeks for a loading of ca. 0.7 mg, almost half, ca. 9%, being lost in the first 48 hours. For a higher loading of ca. 1.8 mg, the losses were ca. 12% and 4% relative respectively. Tightly wrapping the IOM cassette / filter in aluminium foil reduced these losses of bitumen fume by more than 50% in the first 3 days. During subsequent storage in a freezer at -20°C, the IOM cassette / filter did not show any additional weight loss in a period of ca. 2 weeks [31].

#### 4.4. USE OF FIELD (TRIP, TRANSPORTATION) BLANKS

The use of field blanks (also known as trip, or transportation blanks) is essential. A minimum of 3 blanks per group of samples should be used. If sampling takes place on more than one consecutive day then it is recommended that 3 blanks be taken per day. NIOSH recommends the use of 5 blanks [29].

The blanks should be treated in the same manner as the sample cassette / filter, except that air is not drawn through them. This includes exposing them to the same atmospheric conditions as the sample cassette / filter. The mean value for the blanks should be used to determine the amount of sample collected by correction for benzene residue, and traces of materials that may have been deposited during preparation and transport.

Typical values for IOM BS-IP replicates determined according to the method in **Appendix 3** are:

Day 1: 24, 17, 22; mean = 21 µg

Day 2: 30, 21, 32; mean = 28 µg [31]

These values are, naturally, highly dependent on the purity of the benzene used for extraction. For comparison, Benzene Soluble Fraction (BSF) background (blank)

contributions of  $29 \pm 6 \mu\text{g}$  and  $35 \pm 5 \mu\text{g}$  were reported for NIOSH method 5023 and OSHA method 58 respectively [17]. These methods, for the determination of coal tar pitch volatiles, were examined for their suitability for measuring asphalt fume exposures as benzene soluble matter.

#### 4.5. STUDY BACKGROUND (AREA) MEASUREMENTS

It is recommended that study background (area) measurements be taken if feasible, but they should not replace personal sampling. This can identify confounding materials, which do not originate from the bitumen-containing materials, but are present in the air at the sampling site and interfere with the bitumen fume analysis. These materials can originate from e.g. nearby (industrial) facilities, or heavy passing traffic. Wherever possible it is advised that “up” and “down”-wind samples are taken. This may of course not be possible with variable wind direction or mobile work sites.

Normally, dust samplers should be operated with the inlet either facing horizontally or downwards and manufacturers’ instructions should be carefully followed. Samplers should in any event not be operated facing upwards as this may lead to large particles falling into the inlet, thus creating high results, which do not relate to actual operator exposure.

It should be appreciated that sampler performance, both efficiency and internal losses, are dependent on the orientation of the sampler with respect to wind direction and wind speed [27]. For example, the IOM sampler over-sampled larger particles ( $> 20 \mu\text{m}$ ) when wind orientation is  $\sim 0^\circ$  (wind towards sampler) but under-sampled large particles when the wind orientation was  $90$  and  $180^\circ$ . Efficiencies for small particles ( $\leq 10 \mu\text{m}$ ) were independent of orientation at relatively low wind speeds ( $\leq 1.1 \text{ m/s}$ ). It is recommended that up- and down-wind samplers should face in the same direction.

#### 4.6. ANALYTICAL WORK-UP REQUIREMENTS

##### 4.6.1. Extraction of sample from sampler

###### Conventional filter cassettes

When using conventional (e.g. 37 mm) cassettes the filter is removed from the cassette and weighed to determine TPM. Material deposited on the inner cassette walls is not included in the sample.

When glass fibre filters are used, fibre losses can occur. If the amount of TPM collected is low then any fibre loss can significantly affect the TPM result and can even result in negative values. One method of minimising losses is to pre-load the filter into a cassette before removing and weighing. If fibres had adhered to the cassette they can then be removed carefully before replacing the filter [14]. Fibre losses of ca.  $6 \mu\text{g}$  were reported in a laboratory study [9]. During exposure studies higher values have occasionally been observed; this is manifested by BSM greater than TPM. When estimated from the difference between TPM and BSM data these losses were  $< 100 \mu\text{g}$ , i.e. well below 0.1% of filter weight [31]. These values are significantly lower than the losses of  $440 - 1510 \mu\text{g}$  (0.5 - 1.9% of filter weight) reported by Dunzik *et al.* [17]. It should however be noted that they also reported

BSM greater than TPM in more than 50% of the measurements. Only minimal loss of filter material has been recorded when a PTFE filter is used.

Although loss of fibres can significantly affect TPM results it has little effect on BSM results since the fume is deposited on the whole filter and only a very small part of the filter is lost. BSM is determined by extracting the organic material from the complete filter in a test tube or vial using benzene and evaporating the benzene (see also Quantification of BS-IP, below).

#### **IOM sampler**

As mentioned before, the IOM sampler body is designed to hold “snap together” reusable cassettes. Particles deposited on the filter and the inner cassette walls are intended to be part of the sample. Any particles deposited on the outside of the cassette are not intended to be part of the sample. The literature contains references to the cassette and filter being weighed together as a single unit after wiping off particles deposited on the outside of the cassette [4]. An alternative procedure is to swab off the particles deposited on the inside of the cassette with benzene and to include this with material extracted from the filter [18].

Experience has shown that little or no material is deposited on the outside of the filter cassette. Should IPM be determined, then fibre losses, which can occur from glass-fibre filters, are minimised when the filter is weighed in-situ in the cassette. For the extraction of BS-IP it has proved simple and convenient to disassemble the cassette, leaving filter in place in the cassette rear, and to place both parts in a beaker [31]. The filter and cassette rear are covered in benzene that has been used to rinse the inside of the cassette front while in the beaker. It is advised to pre-wash the cassette before (or between) use.

The plastic cassette is not suitable for this analysis. When extracting the total cassette and filter with benzene there is a significant increase in the weight of the plastic cassette. The plastic cassette absorbs benzene, which is released only very slowly. On evaporation of the benzene the residue (extract) is darkly coloured; this would be consistent with the extraction of material from the plastic [31].

#### **4.6.2. Extraction efficiency**

The choice of 3 x 2 ml for extraction is based on extraction efficiencies determined using a 37 mm glass fibre /silver membrane filter combination; ca. 70% was extracted in the first 2 ml, the extraction efficiency for 3 x 2 ml being > 93% [7].

#### **4.6.3. Quantification of BS-IP**

Benzene Soluble Matter has normally been determined gravimetrically, e.g. NIOSH 5042, since this is a widely applicable and relatively simple option. The method in **Appendix 3** for BS-IP is also written as a gravimetric method. The quality of the benzene used is important since a correction is required for any benzene residue. It is important that the residue is low since this will be reflected in field blank values. 6 ml of benzene with an evaporation residue of 3 ppm will contribute 18 µg.

An alternative to determining the BS-IP or BSM gravimetrically would be to determine it by e.g. gas chromatography. This would have the advantage of removing the need for an evaporation step and would also supply additional qualitative information, e.g. a boiling point profile. If this is carried out then an appropriate material should be used as calibration standard. Materials which have been used include a No. 2 diesel fuel standard and a vacuum distillate (40 cSt at 40°C) [19], and samples of BSM and TOM collected from a paving bitumen using a laboratory rig [31].

Although outside the scope of this document, information on the relative response of PACs and paraffinic hydrocarbons, based on the effective carbon number concept, is available [30].

## 5. REFERENCES

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## APPENDIX 1

### MONITORING RECORD SHEET TEMPLATE (EXAMPLE)

#### Part A: Survey data

Trial identification			
Date			
Location			
Product specific information			
Application			
Type of product			
Supplier			
Reference nos. product			
Temperature of product			
Other (confounding) materials used (e.g. cut-back materials, organic release agents)			
Engine exhaust entering work atmosphere		Passing traffic Y/N Busy road Y/N	
Weather conditions			
Time	xx:xx	xx:xx	xx:xx
Cloudy/clear/sun/rain			
Air temperature °C			
Humidity %			
Wind			
Speed. m/s			
Direction			
Pressure			
Site description			
Position of equipment / workers		(use sketch / photographs if possible)	
Tasks carried out			
Work schedule			
Work description			
time work started			
Interruptions			
time work stopped			
Work description			
time work started			
Interruptions			
time work stopped			
Static samplers		Yes/ no	
Position			
Field blanks		Yes / no	
No. of blanks			



**Part B: Sampler / worker specific detail**

Worker			
Job description			
Job particulars			
type of work			
Activity 1			
time work started			
Interruptions			
time work stopped			
work practices			
Protection			
Activity 2			
time work started			
Interruptions			
time work stopped			
work practices			
Protection			
Smoker	Yes / No	cigars/ cigarettes / pipe / other	no. smoked :
Pump			
Identification			
flow rate			
Start			
Stop			
Interruptions			
Sampler			
type			
Identification			
Filter			
type			
Identification			
Other			
ads tube	Yes / no	type :	

## APPENDIX 2

### PARTICLE SIZE-SELECTIVE SAMPLING CRITERIA OF ACGIH TLV

The new TLV is defined in size-specific terms, i.e. as Inhalable Particulate Mass (IPM) [1,2]. IPM guideline limits are set for materials that are hazardous when deposited anywhere in the respiratory tract.

Inhalable Particulate Mass consists of those particles that are captured according to the following collection efficiency regardless of sampler orientation with respect to wind direction:

$$SI(d) = 50\% \times (1 + e^{-0.06d})$$

$$\text{for } 0 < d \leq 100 \mu\text{m}$$

where:  $SI(d)$  = the collection efficiency for particles with aerodynamic diameter  $d$  in  $\mu\text{m}$  [1].

Collection efficiencies representative of particles in this mass fraction are shown in the table.

**Table 1:** Collection efficiencies for Inhalable Particulate

Particle Aerodynamic Diameter ( $\mu\text{m}$ )	Inhalable Particulate Mass (IPM) (%)
0	100
1	97
2	94
5	87
10	77
20	65
30	58
40	54.5
50	52.5
100	50

The ACGIH TLV therefore requires that Inhalable Particulate be collected using a sampler with collection efficiency as defined above and the benzene soluble fraction determined by appropriate means, e.g. gravimetric.

Other definitions have been developed for Thoracic Particulate Mass, i.e. for those materials that are hazardous when deposited anywhere within the lung airways and the gas-exchange region, and for Respirable Particulate Mass, i.e. those materials that are hazardous when deposited in the gas-exchange region. Also for these fractions mathematical equations have been developed for the appropriate sampler capture efficiency as a function of aerodynamic particle diameter [2].

**References:**

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## APPENDIX 3

### MONITORING METHOD - DETERMINATION OF PERSONAL INHALATION EXPOSURE TO BITUMEN FUME (AS BENZENE-SOLUBLE INHALABLE AEROSOL)

#### 1. SCOPE

This method describes the sampling of bitumen fume as benzene-soluble inhalable aerosol in work place atmospheres. It can be used for determining personal exposures and for area monitoring. Bitumen fume is collected using a personal inhalable-aerosol sampler and a glass fibre filter. Determination is gravimetric.

The method can also be used for the gravimetric determination of the inhalable fraction of airborne Total Particulate Matter. The method is compatible with the use of adsorbent tubes, which may be included, in series, in the system for the determination of volatile materials passing through the filter.

A lower limit of detection of  $0.05 \text{ mg/m}^3$  is estimated for an 8-hour sample, collected at a rate of 2 l/min. The filter has a capacity for bitumen fumes of ca. 5 mg total particulates.

#### 2. WARNING

Bitumen may, upon heating, present a health risk if incorrectly handled. Prevent contact with the skin. Avoid excessive fume inhalation. When sampling wear suitable personal protection.

Benzene is used in the analytical procedure of this method; benzene is classified as a human carcinogen. All procedural steps involving benzene should be conducted inside a fume cupboard; the fume cupboard's protective performance should be verified in line with the laboratory's safety management system. Also avoid any skin contact with benzene.

#### 3. METHOD SUMMARY

Personal monitoring should always be carried out with the sampler as close as possible to the breathing zone of the worker to be monitored.

Air is pumped at a fixed rate through a glass fibre filter in a personal inhalable-aerosol sampler. The filters and sampler cassette to be used are pre-extracted with benzene. They should be pre-weighed if the determination of inhalable particulate matter is also required.

Inhalable particles are deposited on the filter. If the IOM personal inhalable sampler cassette is used then particles deposited on the inner side of the sampler cassette are intended to be part of the sample; the material deposited on the outside of the cassette is wiped off before further analysis. After weighing (optional, used to determine particulate matter), filter and cassette are extracted as a single unit with benzene using an ultrasonic agitation bath. After evaporation of the benzene, the amount of benzene-soluble inhalable particulate matter (BS-IP) in the sample is determined gravimetrically. When required the BS-IP may be stored in a refrigerator for further analysis.

Note 1: The American Conference of Governmental Industrial Hygienists recommends a Threshold Limit Value - Time Weighted Average (TLV-TWA) for the substance "Asphalt fume as benzene-soluble aerosol (or equivalent method)" of  $0.5 \text{ mg/m}^3$  <sup>(1)</sup>. The <sup>(1)</sup> refers to Inhalable Particulate Mass i.e. this is a particle size-selective sampling criteria for Airborne Particulate Matter which is defined in terms of sample collection efficiency as follows:

$$SI(d) = 50\% \times (1 + e^{-0.06d}) \text{ for } 0 < d \leq 100 \mu\text{m}$$

and where

SI(d) = the collection efficiency for particles with aerodynamic diameter d in  $\mu\text{m}$ .

For convenience, the term BS-IP will be used to describe the substance in this method.

The term BE-IP (benzene-extractable inhalable particulate) is often used, informally, to describe the same substance.

Note 2: All materials collected that are soluble in benzene will be included in the BS-IP. These may originate from sources other than asphalt (bitumen) fume.

#### 4. APPARATUS

##### 4.1. Personal Inhalable Aerosol Sampler meeting the ACGIH particle size-selective sampling criteria.

The IOM inhalable dust sampler is suitable. This consists of a 'snap together' reusable aluminium or steel cassette that holds the glass fibre filter (4.2) and a static dissipating plastic (or stainless steel) casing that holds the cassette during monitoring. For transport purposes plastic transport clips are provided. Available from, e.g. SKC ([www.skcinco.com](http://www.skcinco.com)) as Cat. nos. 225-70 (plastic sampler), 225-75 and 225-74 (stainless steel & aluminium cassettes, resp.).

Note 3: The plastic IOM cassette (225-71) is not suitable.

##### 4.2. Glass Microfibre Filter, 25 mm diameter, e.g. type GF/A, Cat. no. 1820 025, from Whatman.

##### 4.3. Personal Sampling Pump, intrinsically safe, capable of maintaining a flow rate 2.0 l/min for at least 8 hours. Calibrated before use. The model Escort ELF, Cat. no. 805558 from MSA, (or equivalent) is suitable.

Note 4: The recommended sampling flow rate for the IOM is 2.0 l/min.

##### 4.4. Weighing Cups, Teflon cups, mass about 0.05 g., Cat. no. 2034, from Cahn Instruments, Cerritos, CA, USA (or equivalent) are suitable.

##### 4.5. Ultrasonic Agitation Bath, tank size approx. 150 x 135 x 100 mm. The Sonicor, from Sonicor Instrument Corp., Copiague, NY, USA (or equivalent) is suitable.

##### 4.6. Electronic Microbalance, measuring accuracy $\pm 0.001 \text{ mg}$ , calibrated.

##### 4.7. Sample Concentrator, heated, temperature-controlled block with nitrogen purge facility. The Techne SC-3 sample concentrator from Techne Ltd., Duxford, Cambridge, UK (or equivalent) is suitable.

- 4.8. Gas-tight Syringe, 2.5 ml, with the option of attaching Millex-FH filter units (4.9). The gas-tight syringe No. 1002, capacity 2.5 ml, with Yale 23 luerlock injection needle from Hamilton Corp., Reno, Nevada, USA, is suitable.
- 4.9. Millex-FH<sub>13</sub> Filter Units, Non-sterile, diameter 13 mm, pore size 0.5 mm, e.g., Cat. no. SLFH 013 NL from Millipore Corp.
- 4.10. Vacuum Oven, capable of maintaining a temperature of  $40 \pm 1^\circ\text{C}$  and a vacuum down to 5 to 7 kPa (50 to 70 mbar). This should be vented into a fume hood (or equivalent).
- 4.11. Gas Flow meter, capable of correctly indicating flow rates at pressure drops within the working range of the sampling pumps.
- 4.12. Flow Calibrator, with calibration certificate, covering the flow rate range of the sampling pumps. The Hewlett-Packard model, Part No. 9301-1231 (or equivalent) is suitable.
- 4.13. Flexible plastic tubing, of suitable internal diameter for connecting pump with sampler.
- 4.14. Glassware, miscellaneous beakers etc. for extractions.

## 5. REAGENTS AND MATERIALS

- 5.1. Acetone, analytical grade
- 5.2. Aluminium foil
- 5.3. Benzene, containing <3 mg/l evaporation residue, e.g., Cat. no. 1792, "Benzol for organic trace analysis, Suprasolv", from E. Merck, Darmstadt, Germany (or equivalent).

Note 5: CAUTION. Benzene is a known carcinogen and presents a serious health risk if incorrectly handled. Avoid any contact by all routes by the best practical means. Extract vapour by working in a fume cupboard.

Note 6: The benzene evaporation residue of each batch should be checked before use.

- 5.4. Nitrogen, dry and free from extraneous matter, e.g. oil and particles.

## 6. APPARATUS PREPARATION

- 6.1. Glassware

Wash all extraction glassware with a detergent solution, rinse with tap water, distilled water and finally acetone before allowing to dry. Clean the Teflon weighing cups in benzene (CAUTION. See Note 5) or dichloromethane with ultrasonic agitation, rinse with acetone and then dry in the vacuum oven at about  $40^\circ\text{C}$  and 5 to 7 kPa (50 to 70 mbar) for one hour.

- 6.2. Filter Cassette Assembly

Pre-wash the glass fibre filters by placing them in a 50 ml beaker containing 10 ml benzene (CAUTION. See Note 5) or dichloromethane and extract ultrasonically as

described in 8.3. Dry in a vacuum oven at 40°C and 5 to 7 kPa (50 to 70 mbar) for two hours. Pre-wash the cassettes with benzene and dry in fume cupboard.

If using the IOM, assemble the filter cassettes using dust-free gloves and weigh the filter + cassette to the nearest 0.001 mg (optional, for determination inhalable particulate matter,  $m_1$ ). If using other samplers the filters should be weighed prior to assembling the cassette.

### 6.3. Transport

Seal the filter cassettes before transport. If using the IOM sampler, place the filter cassettes in the labelled transport clips using dust-free gloves.

### 6.4 Pump

Adjust the sampling pumps to the desired flow rate,  $2.0 \pm 0.1$  l/min in the case of the IOM sampler, with sampler and filter in line, using a calibrated gas flow meter (4.11). This calibration should be carried out away from exposure to avoid premature collection of particulates.

Note 7: If an adsorbent tube is to be used then flow calibration should take place with the adsorbent tube in series between the sampler and the pump.

## 7. **SAMPLING**

7.1. Unseal the filter cassettes. If using the IOM sampler, remove the filter cassettes from the transport clip and mount them into the labelled plastic casings (or stainless steel).

7.2. Connect the cassette / sampler with the pump using a piece of flexible plastic tubing. For personal sampling affix the sampler in the breathing zone of the worker to be monitored; for area monitoring place the samplers at selected positions.

Note 8: Samplers should be placed as not to interfere with worker operations and/or endanger the worker.

7.3. Switch on the pump. Draw a known volume of air through the filter for the full shift or a shorter term when appropriate. Verify that the pump is still running, and displaying the correct flow, at periodic intervals during sampling.

7.4. When the test sample has been taken, check the displayed flow rate, and switch off the pump. Record the time of sampling. If the displayed flow rate has varied by more than 0.1 l/min re-check the flow rate of the pump with the filter in line as described in 6.4. If the flow rate values differ by more than 0.1 l/min, calculate the average value.

7.5. Seal the filter cassettes to avoid loss of particulates. If the IOM sampler needs to be re-used then remove the filter cassettes from the plastic sampler and place them in the transport clips. Wrap the clips tightly in aluminium foil. Place the sealed cassettes in airtight plastic bags. Store the bags in the dark and, if possible in a cool or cold place; transfer to a refrigerator at the first opportunity. If the sampler does not need to be re-used during the same survey then it is preferable to leave the cassettes inside and to place a cap over the cassette and wrap in foil tightly, then chill in ice or dry ice immediately for shipment to the lab for analysis.

Note 9: Losses from the filter/ cassette are dependent on loading and on storage conditions.

- 7.6. With each group of samples (shift), three field, or transport, blanks should be used. These should be treated in the same manner as the sample filters, except that no air has been drawn through them; i.e. they should be opened then sealed and packed immediately.

## 8. SAMPLE RECOVERY

- 8.1. Allow the samples to reach room temperature before unpacking. If the IOM sampler has been used then, using dust-free gloves, wipe off the particulates adhering to the outside wall and weigh the filter cassettes plus filter after ca. 90 seconds stabilising in the balance chamber to the nearest 0.001 mg (optional, for determination inhalable particulate matter,  $m_2$ ). If using other samplers remove the filter carefully from the cassette before weighing.

- 8.2. Place the filter, plus disassembled filter cassette if using IOM sampler, in a 50 ml beaker and add 2 ml benzene (CAUTION. See Note 5). Cover the beaker with a piece of aluminium foil and vibrate for 5 minutes in the ultrasonic bath, containing water. Maintain the water level in the bath higher than the benzene level in the beaker.

Note 10: Take suitable precautions to maintain unique sample identification.

- 8.3. Weigh a Teflon cup (4.4) to the nearest 0.001 mg. Place the cup in the sample concentrator at ca. 60°C under a stream of nitrogen.

- 8.4. Switch off the ultrasonic bath and transfer the extract, as completely as possible, into a 2.5 ml syringe (4.8). Remove the needle and attach a Millex-FH<sub>13</sub> filter unit (4.9), add the needle and transfer about half of the extract through the filter into the pre-weighed Teflon weighing cup (4.4, 8.3). When most of the benzene has evaporated, inject the remainder of the extract into the Teflon cup and evaporate to near dryness.

- 8.5. Repeat the extraction procedure of 8.2 twice, followed each time by the filtration and evaporation steps of 8.3.

- 8.6. Evaporate the final benzene extract to near dryness at 60°C in the sample concentrator. Take care not to evaporate the extract completely. Place the cup in the vacuum oven at about 40°C and 5 to 7 kPa (50 to 70 mbar) for two hours.

- 8.7. After cooling and equilibrating for 30 minutes, reweigh the Teflon cups, to the nearest 0.001 mg, and determine the amount of BS-IP,  $m_3$ .

- 8.8. Store the BS-IP in a refrigerator.

- 8.9. Repeat the analysis described in 8.1 through 8.8 on the three transport blank filters (7.7) to determine the blank filter / benzene residue value  $m_4$  (and, optional, for determination inhalable particulate matter,  $m_5$ ).

## 9. CALCULATION

- 9.1. Total Particulates (optional)

Calculate the concentration of total particulates in the sample, in mg/m<sup>3</sup>, by means of the following equation:

$$\text{Total Particulates, mg/m}^3 = [(m_2 - m_1) / V] - [(m_5 - m_1) / V]$$



where  $m_2$  = mass of filter (combination) + sample (8.1), mg,  
 $m_1$  = mass of filter (combination) before sampling (6.2), mg,  
 $m_5$  = mass of (blank) filter (combination) after transport, (8.9) mg  
 $m_1'$  = mass of (blank) filter (combination) before transport (6.2), mg,  
 $V$  = sample volume,  $m^3$ , (at actual sampling conditions uncorrected for temperature and pressure).

Note 11: 2l/min is equivalent to 0.002  $m^3$ /min.

Note 12: Humidity changes in the laboratory will change the weight of both the samples and the field blanks. However, conditioning in a desiccator to compensate for humidity changes is not considered necessary provided that both samples and field blanks have been exposed to the same conditions.

9.2. Benzene-Soluble Inhalable Particulates (BS-IP)

Calculate the concentration of the BS-IP in the sample, in  $mg/m^3$ , by means of the following equation:

$$BS-IP, mg/m^3 = (m_3 - m_4) / V$$

where  $m_3$  = mass of benzene soluble matter, (8.7) mg,  
 $m_4$  = average mass of blank residue, (8.9) mg,  
 $V$  = sample volume,  $m^3$ , (at actual sampling conditions uncorrected for temperature and pressure).

**10. REPORTING**

Report the concentrations of total particulates (optional) and Benzene-Soluble Inhalable Particulates in the sample to the nearest 0.1  $mg/m^3$ , mentioning "according to this method".

**11. PRECISION**

Due to the nature of this analytical method (continuously changing conditions during field surveys) no true repeatability and reproducibility figures can be given for personal monitoring.

Using laboratory generated fume the following data were obtained for BS-IP: loading =  $965 \pm 74 \mu g$ ,  $\sigma = 53$ ,  $n = 5$ .

**Addendum to method****Determination of volatile material passing through an aerosol filter (“semi-volatiles”)**

A suitable adsorbent tube (commercially available or prepared in-house) can be added, in line, between the sampler and the pump.

When an adsorbent tube is used it is important that the flow is calibrated with both the filter and the tube in place.

An example of a commercially available adsorbent tube, which can be used for trapping volatile aromatic compounds, is the XAD-2 containing adsorbent tube (SKC 226-30-04). It should be noted that this will not completely retain compounds containing  $\leq 8$  carbons.

The XAD-2 tube can be extracted using dichloromethane.

The amount of these “semi-volatiles” captured by the adsorbent can be determined by GC-FID analysis. The FID must be calibrated using a suitable reference material, a material with a composition / boiling range which is as similar as possible to that of the “semi-volatiles”. Samples of laboratory generated semi-volatiles, BS-IP and “Total fume” have comparable FID response /mass.

Suitable conditions for the analyses of “semi-volatiles” and BS-IP (and hence total fume) are:

Column	: 30 m * 0.32 mm id, DB-5MS, film thickness 0.25 micron
Pre-column (retention gap)	: 1.5 m * 0.54 mm id
Initial temperature	: 45°C for 5 min
Temperature programme	: a) 10°/min to 250°C b) 5°/min to 350°C
Final temperature	: 350°C for 10 min.
Injection	: On-column injection of 2 µl
Detection	: FID at 375°C

**APPENDIX 4****GLOSSARY OF TERMS USED IN THIS REPORT**

ACGIH	American Conference of Governmental Industrial Hygienists
TLV	threshold limit value
TWA	time-weighted average
OEL	occupational exposure limit
IPM	inhalable particulate matter
TPM	total particulate matter
BS-IP	benzene-soluble inhalable particulate matter
BE-IP	benzene-extractable inhalable particulate matter
PAC	polycyclic aromatic compounds
PAH	polycyclic aromatic hydrocarbons
IOM	Institute of Occupational Medicine (Edinburgh, UK)
Eurobitume	European Bitumen Association