ASSESSMENT OF PERSONAL INHALATION EXPOSURE TO BITUMEN FUME. DEVELOPMENT OF A RECOMMENDATION FOR AN INHALATION EXPOSURE METRIC AND A MONITORING STRATEGY

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ABSTRACT

Currently there are no international standards for measurement of worker exposure to bitumen fumes. Numerous different methods are in use which measure different fractions of the fumes and have different capture efficiencies making comparison of data measured using different samplers problematic. Eurobitume initiated a study in order to recommend an appropriate exposure metric.
The resulting paper discusses practical issues (measurement and quantification). Starting from a literature review, recommendations for a reliable sampling and analytical method are given as such as relevant monitoring strategy as it is required in occupational hygiene.
The bitumen fumes are made of particulates and vapours. The suitable sampling train used to capture these fumes is based on on-line elements i.e. an individual sampler provided with an appropriate filter (capture of the particulates) and backed-up with a tube containing an adsorbent (capture of the vapours). It is strictly recommended to separately express the two organic fractions, these two chemical groups likely not giving the same information on the exposure levels. The accuracy of the method can be expressed by an overall uncertainty of 30%.
Bitumen applications usually require outside operations. This leads to a variability observed in the measurements due to external factors. This also impacts the monitoring strategy by constituting homogeneous exposure groups (HEG). The paper shows that one job type will be preferably monitored several times over a given period than the whole team in a single day. Similarly, the field variability imposes a number of determinations to express annual levels of worker exposure.

Keywords: Bitumen fume metric, personal sampler, occupational exposure, monitoring strategy

INTRODUCTION

In 2000 a literature review conducted on levels of exposure in the road construction industry was published [1]. The review concluded that there was a lack of standard methods for bitumen fume sampling and analysis. For example, country or company-related personal breathing-zone (PBZ) samplers and protocols have been used to collect individual exposure data. Currently there are no international standards specifically dedicated to the measurement of worker exposure to bitumen fumes. Numerous different methods are in use which measure different fractions of the fumes and have different capture efficiencies, making comparison of data problematic.

Recognising this concern, Eurobitume initiated investigations to recommend an appropriate exposure metric and method for measurement that might be used to assess worker exposure. Consequently, a project was set up to describe the metric and measurement protocol that could be used across the bitumen industry to measure personal exposure to bitumen fumes in a consistent manner. In 2002, CONCAWE published a guidance document for monitoring the organic part of the fumes called "inhalable particulates" [2] with particular attention on the exposure threshold limit value established by ACGIH in 2000. Starting from the CONCAWE document, this report includes an update of the published literature and makes practical recommendations to facilitate standardisation.

A METRIC ISSUE: THE PARTICULATE ORGANIC FRACTION

Capture of the inhalable part of the individual exposure is usually conducted with the help of a sampling train based on the following three on-line elements: an individual sampler provided with an appropriate filter and backed-up with a tube containing a chemical adsorbent and an individual pump as depicted in Fig. 1. The filter traps the particulate fraction of organic fumes, whereas an adsorbent-packed tube captures the gaseous or vapour fraction. Together, the collected organic aerosol fraction and the volatile compounds make up the total organic compounds or total hydrocarbons (TOC or THC).

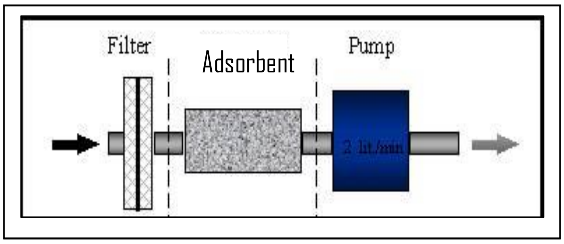

Fig. 1; the usual sampling train to capture fumes

Organic bitumen/asphalt fumes can be described as follows; [3]:

- The solvent soluble fraction of the particulate matter (SSF). This organic fraction was usually called Benzene Soluble Fraction or Matter (SSF/BSM) because historically benzene was used to extract the organic fraction of the total particulates. The organic particulates mainly comprise of organic aerosols containing droplets of condensed liquid bitumen (mist). As specified by CEN, the term aerosol is used to describe any suspension of particles in air, whether the airborne particles constitute airborne fibres or droplets, a fume or a mist [4].
- The vapour fraction (VF) which represents the organic vapour/gaseous phase of the fumes. The volatile emissions from hot bitumen include lower molecular weight petroleum compounds from the distillation process [5]. As such they exist in gaseous vapour form and require the help of a back-up adsorbent to be captured.

PBZ sampling is well suited to measure or monitor individual exposure of workers to airborne particles in a cost effective manner with the aerosol being sampled in the breathing zone of individual workers. However, there are no PBZ samplers specifically dedicated to bitumen/asphalt fumes. Currently PBZ samplers are multipurpose and sometimes are designed with regard to the particulate size being captured. Usually, the particulate fraction of the fumes is collected by means of a filter housed in the sampler.

In 1993, ACGIH, ISO and CEN adopted identical particle size-selective sampling conventions for inhalable, thoracic and respirable aerosols [6]. The purpose of these conventions was to provide a scientific basis for a new generation of particle size selective occupational exposure limits (OELs) for aerosols. The adoption of the convention (see Fig. 2) was based on measurements of human inhalation efficiency, and the notion of "inhalability" to particles up to 100 µm aerodynamic equivalent diameter (AED). The Inhalable Sampling Convention has also been published in an international standard, ISO 7708 [7].

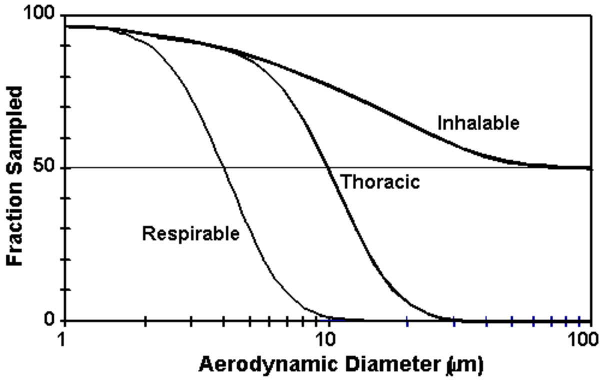

Fig. 2; the ISO/ACGIH/CEN sampling conventions. An ideal sampler should have a sampling efficiency curve that matches one of these curves as closely as possible under all wind directions and a velocity up to 4 m/s (from Baron, 2003).

Various samplers have been tested for their aspiration efficiency against the ISO 7708 model and a collaborative study of personal sampler performance demonstrated that the range of the aerosol size distribution greatly influenced the sampler performance [8]. Previous laboratory and field particle size determinations on bitumen fumes demonstrated that more than 96% to 99% mass had an aerodynamic diameter below 12.5 µm [9-11]. In research specifically dedicated to the analysis of bitumen fume, most of the particles were found to be less than 3.5 µm [12]. Similarly, in a field study particle size was measured to be from 0.5 to 20 µm [13]. This corresponds to the respirable convention established and the 50% cut point of 4 µm [7, 14]. Consequently, the inhalable and respirable aerosol fractions can be regarded as similar for bitumen fumes and any samplers able to collect organic materials having an aerodynamic diameter below ca. 10 µm could be regarded as suitable

PBZ Samplers

PBZ samplers described in the literature as having been used in the bitumen industry are based on three samplers: the 37-mm cassette from the USA used in either its closed-face or open-face configurations (CFC or OFC), the IOM sampler specifically designed in the UK (Institute of Occupational Medicine (IOM), Edinburgh) to capture the inhalable fraction and the GGP sampler developed in Germany. Historically, the 37-mm cassette is more popular in the USA than in Europe especially in its disposable form. Also, UK and Germany developed the IOM and GGP samplers in accordance with their occupational areas of interest.

The CFC, which houses 37-mm diameter filters, was developed in 1956 for clean-room analysis [15]. The early filter holders that exposed the whole filter to the air had the drawback of leaving it free to be contaminated by non airborne matters. The addition of a lid equipped with a 4-mm entry inlet made the filter much less likely to be accidentally damaged, which contributed to its popularity. Various methods for dust and particulate collection were validated using this cassette. In 1998, NIOSH published a specific method (NIOSH Method 5042) for determining asphalt fume particulates. Due to convenience, this CFC has historically been called "37 mm" due to the diameter of the cassette. This is a method specifically dedicated to bitumen fume capture and analysis and is widely used in the United States [16]. Regarding the two configurations (CFC and OFC), experience has shown that the closed-face configuration gives better protection against contamination and this is of major benefit in the field, where samples can be spoilt by splashing or touching the filter medium. On the lab scale, comparative testing showed behaviour similar to capture laboratory generated fumes [9]. In the field, the data suggest that the closed-face configuration might be size selective against large particles [17]. However, the open configuration operating under windy conditions (wind tunnel) showed efficiency up to 150% with high wind velocities (4 m/s) meaning an overestimate of exposure due to use of the 37-mm diameter open face [8]. Consequently, the closed-face configuration is preferred. As a non size-specific sampler, the 37 mm cassette was referred to as a “total” aerosol sampler (collection of "total" matter). However, the data now available suggest that such a description was a misnomer. Studies have been conducted to evaluate the CFC adequacy with regard to the inhalable convention [8, 18-23]. Overall, CFC shows a poor ability to fully satisfy the requirements for particle sizes above ca. 50 µm but a sampling efficiency above 95% could be reached for particles having up to 20 µm AED [22, 24, 25]. As such, a near 100% sampling efficiency was expected for bitumen particulates [9] and finally demonstrated on the lab scale in an international sampler comparative study [26].

In 1986, based on specific recommendations about inhalable particulate matter, the IOM designed a size-specific sampler specifically to collect the inhalable fraction [27]. This reusable sampler has been increasingly used to determine exposure to inhalable particulates (called "inhalable" aerosol sampler). The sampler contains a reusable stainless steel cassette fitted with a 25-mm diameter filter. The sampler was designed in order to weigh the entire filter cassette before and after sampling [28]. As already specified in the CONCAWE report, some laboratory investigations conducted on the mass stability of the IOM sampler demonstrated that only the stainless steel body housed in the sampler body was suitable for gravimetric measurement when compared to the plastic body [2, 29].

In Germany, BIA developed a personal sampling system called GGP (Gesamtstaub-Gas-Probenahme) to sample inhalable dust. Usually, the GGP is equipped with a specific sampling head called GSP (GeSamtstaub-Probenahme) which was designed for a specific flow rate (for instance, the GSP used to catch bitumen particulates is designed for a 3.5-L/min flow rate). In order to trap the vapour fraction in specific areas (combined vapour/aerosol sampling), investigations were conducted and led to the addition of a sorbent tube to make the GGP head system [30].

PBZ Sampler’s Comparison in Various Industrial Sectors

In many areas and especially in metal working, individual samplers have been compared and assessed. On the other hand, these are a few field studies specifically dedicated in comparison to various samples for bitumen fumes. As has been previously shown, bitumen fumes are a particular case in terms of inhalable / respirable aerosols. This is probably why CFC does not appear in a dedicated CEN technical report where samplers for the aerosol fractions are recommended following a literature survey [4]. Overall, the listed samplers have the potential to meet the requirements for several environmental conditions [31]. However, no sampler fulfils the requirements for all possible environmental conditions. The extent of the validations performed on the listed samplers differs considerably.

The three samplers described were regularly compared in the past with regard to the inhalable convention [8, 18, 19, 32]. In general, the samplers behave differently in calm and moving air. IOM has the best behaviour regarding the inhalable convention. The GSP and CFC sampling efficiency decreases as the particle size increases (from about 20/30 µm). In addition, the wind speed can alter the sampler capability to a lesser extent with the IOM for which even some overestimates were noted [8, 21, 32]. However, under moderate wind velocity, this sampler has given experimental sampling efficiency curves that best fit the CEN/ISO inhalable convention [23]. This higher IOM sampling efficiency for collecting dust may be related to the fact that there is no inner particle loss because the filter and the casing are taken into account [33, 34]. Internal wall deposits depend on the particle AED [27]. Under specific conditions, inner wall deposits were found to represent up to half of the collected matters [23]. However, when the sample includes wall deposits, the CFC performances more closely match the inhalable convention for which the IOM sampler was designed and the use of the 37-mm cassette can be recommended for the dust collection [8, 23, 34, 35]. Similarly, the addition of an internal capsule significantly reduces the IOM/CFC gap [36].

The intra-sampler variation was assessed for IOM and CFC samplers in a dedicated study [34]. With a flow rate of 2 L/min, the average dispersion for the mass concentration including walls was found to be 50% and 34% for IOM and CFC respectively. The slightly lower accuracy for the IOM sampler is likely due to the larger open face and the reduced possibility to handle the specimen during field operations. The body of this sampler is weighed after sampling as splashing can occur during the experiment. Also the significantly higher weight of the IOM steel body decreases with regards to the quite low collected matters. Sometimes, a better precision is observed for IOM when compared to CFC in specific environments [37]. Comparative GSD were determined from a set of field data collected from several countries in the rubber industry [38]. Overall, the average GSD values showed a slight advantage for CFC when compared to IOM (2.11 and 2.37 respectively). Additionally, it has been shown that a loss of volatile organic compounds from the IOM cassette after sampling can occur, unlike the closed 37-mm cassette [33]. CFC also demonstrated a lower sensitivity with respect to the airflow rate used to sample (from 1 to 2 L/min) [23].

There are a few comparative studies about GGP versus the two other samplers probably because GGP was designed only recently (1999). Some comparative tests using mineral oil and metal working fluids demonstrated that the GGP sampling system can underestimate the aerosol concentration due to an aerosol/vapour partitioning even if the total quantity of vapour and aerosols was recovered [30]. During these investigations, a comparison was made with the 37-mm cassette as the reference (configuration not specified) at two flow rates (0.5 and 1.2 L/min) and equipped with a back-up adsorbent tube. The total collected hydrocarbons were found to be similar for both samplers irrespective of the flow rates. However, a partitioning effect was observed in relation to the pump flow rate. Results showed a VF/SSF ratio at 1.2 L/min of 80/20 for metal working and 90/10 with the mineral oil and for paving operations at 2 L/min, the VF/SSF ratio was around 85/15 [39, 40]. However with GGP, these ratios were determined as being 92/8 and 100/0 respectively. This oil mist partitioning was imputable to the higher volume flow conventionally used with GGP (3.5 L/min) which increased the stripping rate.

Since particulate/gas partitioning effects are related to the operating flow rate, previous investigations conducting during the development of the IOM design demonstrated that 2 L/min was a good compromise [27]. The rationale is that the inspirability criterion is upheld when a personal sampler mounted on the body gives the same measured particulate concentration and size distribution as that inspired by its wearer (e.g. representative of the calibrated airborne concentrations in tunnel tests).

Comparative Capability regarding Bitumen Aerosols

An international study using lab-generated bitumen fumes was set up to compare “particulate samplers” [26]. Fumes from the bitumen were generated at two concentration levels. VF/SSF ratio was found similar for IOM and CFC (i.e. 89/11 and 87/13 respectively for the lowest fume concentration, 80/20 and 76/24 respectively for the highest fume concentration). GGP significantly differed. VF/SSF ratio was also found to be significantly different in favour of VF (95/5 and 87/13 respectively). Again, the higher flow rate was suspected as the cause of the VF difference. This study also demonstrated that the geometry of CFC and IOM was not an important factor for bitumen fume sampling under laboratory conditions (no wind).

Three papers more specifically describe paired CFC and IOM field experiments. The first paper relates to investigations which were conducted in bitumen production and bitumen roofing manufacturing sites in the United States [10]. Results confirmed the previous lab outcomes with comparable results for an aerosol concentration up to 10 mg/m^3. However, use of CFC was regarded as preferable because the IOM sampler has been designed and optimized for coarser aerosols (< 100 µm) than bitumen fumes. Another paper focuses on paving operations and asphalt worker exposures [13]. Again, data supported a 1:1 ratio between samplers for organic aerosols. A third paper discusses field trials conducted in Europe [39]. These field data demonstrate that both IOM and CFC can reliably collect SSF with a wind speed up to approximately 5 m/s (ratio of 1.02). Interestingly, the vapour fractions were found to be similar whatever the sample (ratio of 0.96). This demonstrates that the two sampler designs do not influence the capture of the gaseous / vapour fraction.

The validation steps of the Fraunhofer inhalation study in rats was an opportunity to conduct comparative field collection using GGP [41]. During these investigations, personal samples were collected at road paving sites using GGP and CFC with different protocols. In order to compare the total organic fractions obtained, variance analysis was conducted with the help of t-testing (comparison not originally made in the paper). The calculations show that CFC and GGP do not statistically differ. GSD calculations show a lower variability for CFC (1.5 and 1.8 respectively). For SSF, calculations can only be conducted on three actual comparative measurements, the limit of detection of the BIA method used with GGP being higher than the one used with CFC. The results significantly differ with three times more of captured aerosols with GGP. This reinforces partitioning issues with GGP most likely due to sampling conditions. A study conducted in the USA describing comparative field surveys using CFC and GGP confirms this tendency [40].

TECHNICAL RECOMMENDATIONS FOR APPROPRIATE SAMPLING INSTRUMENTS & PROTOCOL

The assessment of worker exposure to chemical agents in workplace atmospheres often requires the measurement of the concentration of agents in the air in the worker's breathing zone. The procedures used for such measurements must give reliable and valid results so that a correct decision can be made as to whether the exposure level is acceptable or not. In Europe, CEN has published general performance requirements for procedures used to determination of the concentration of chemical agents in workplace atmospheres as required by the Chemical Agents Directive 98/24/EC [42]. These requirements apply to all measuring procedures, irrespective of the physical form of the chemical agent (gas, vapour, suspended matter) and of the sampling method and analytical method used. More specifically, some local methods are dedicated to bitumen fume capture and analysis like the NIOSH NMAM 5042 protocol established in 1998 for the USA and also adopted as an ASTM standard[1] [43]. This protocol is a good starting point to organize field monitoring because all the key practical aspects to consider are discussed more in depth when compared to CEN. However, regardless of the protocol selected, it will only differ in a few basic considerations which are discussed in the following paragraphs.

PBZ Samplers

The CFC and IOM sampler designs are recognized today to have good adequacy with regard to estimation of the organic particulates corresponding to the respirable/inhalable convention (< 20 µm AED). For instance, NIOSH NMAM 5042 specifies use of another sampler than the 37-mm cassette (configuration not specified) for particles larger than 30 µm. Hence, a sampling efficiency near 100% can be expected with regard to bitumen organic aerosols. On the other hand, GGP does not appear as a suitable PBZ sampler due to the partitioning effect of the two organic fractions of bitumen fumes resulting from the airflow rate used (non-representative capture of the two organic fractions when compared to CFC and IOM). In conclusion, CFC is preferred for practical considerations. This cassette has demonstrated a better convenience when operating: lower contamination risk, lower weight and better precision, lower sensitivity with respect to the airflow rate used, and reduced loss of volatile organic compounds with IOM.

Filters

From the literature, it appears that two types of filter have been commonly used: fibreglass and Polytetrafluoroethylene (PTFE) with a nominal pore size of 2µm. Preference is given to use of PTFE because it is hydrophobic (its water sorption is very low) unlike fibreglass [44]. Moisture sorption is the most common cause of weight instability even if blank samples are used and fibreglass filters require special preparation to eliminate moisture as a factor [45]. In addition, experiments show that during filter weighing fibre loss can occur with potential impact on the total particulate mass [9, 33]. PTFE is also known to be interference-free (inert) for chemical determinations (e.g. PAH determination in the organic fraction). Glass fibre filters are often used for their higher capacity. For example, the PTFE filter capacity was determined as 2 mg [16] and fibreglass filter demonstrated capacity up to 6 mg [9].

Adsorbents

The vapour fraction of the fumes is collected by means of a suitable adsorbent used for trapping gaseous / vapours compounds downstream from the filter. Inorganic support (mainly charcoal), silica gel and organic polymers are usually used as solid sorbents. The preferred nature for organic gas/vapours is organic polymers (e.g. commercially available XAD-2 tubes made of styrene-divinyl benzene co-polymer are widely used in road paving exposure studies). XAD-2 demonstrated better collection efficiency compared to silica gel [46]. There are several advantages of using the polymeric sorbents over charcoal-based material. They are more consistent and can be desorbed more efficiently even at small loading rates. They are not generally susceptible to the effects of high relative humidity [47]. In addition, some co-polymers are specifically dedicated to the capture of individual compounds (e.g. PAHs). Adsorbent tubes must have front and back sections to check for any breakthrough effect (the two sections are separately extracted and analyzed). The sampled mass is kept below the experimentally established breakthrough mass, in which case the sampling efficiency is 100 % and the uncertainty of the sampling efficiency does not need to be taken into account. The connection between the CFC and the adsorbent tube is critical. A small piece of (Teflon) tubing can be used in order to minimize the distance between the outlet of the cassette and the inlet of the sorbent tube. The tubes are not necessary of uniform size, so the connection needs to be checked to assure a tight fit.

Individual Pump and Flow Rate

Sampling pumps used for particulate sampling should comply with the requirements of EN 1232 [48]. They should have an automatic flow control (with indicator) which keeps the volumetric flow rate constant (within ± 5 % of the initial flow rate). To avoid changing back pressure, either 1) a malfunction indicator, which, following the completion of sampling, indicates that the air flow has been reduced or interrupted during sampling or 2) an automatic cut-out, which

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[1] The NIOSH protocol is sometimes preferred to ASTM D6494 that requires an evaporation step at 85°C. This is a sensitive step when volatile individual compounds are wanted (e.g. Naphthalene).

stops if the pump flow is reduced or interrupted, should be in included. Usually, pumps have adjustable flow rates in the range 1 - 5 l/min. Along with the sampler geometry, flow rate is a determining factor for sampling efficiency. As previously discussed, a flow rate of 2 l/min is recommended as representative for sampling of airborne particulate matter [27]. On a basis of a full 8h-working day, this corresponds to 0.96 m^3 of sampled air which is representative of an occupational atmosphere. Flow rates have to be calibrated before each trial and checked after sample collection (combination of filter and adsorbent tube). There are three main ways to calibrate an individual pump: by using an electronic soap bubble flow meter (film flowmeters), by using a calibrated rotameter or an electronic calibrator based on volume displacement. EN482 gives details about the uncertainty of the flow rate measurement for different types of flow meters [42].

Personal Sampler Position

In order to be representative of the worker exposures, the PBZ sampler must be placed and maintained as close as possible of the face of the worker e.g. on the shoulder (see Fig. 3). Placed as this, the CFC cassette has demonstrated similar performances than the IOM sampler to collect the inhalable fraction of the fumes [39]. According to a NIOSH study, no effects due to the position of the sampler (left or right side) were noticed [11].

Sampling Time Duration

The monitored period of time must be as representative as possible of the daily worker activities i.e. daily tasks (for instance, OELs are mostly set for reference periods of 8 hours). Field experience shows that in most cases, this requires a full-shift sampling time including direct exposures and ancillary tasks (daily TWA concentrations). In any case, full-shift sampling is required to determine compliance with OELs [49]. Usually, work breaks (e.g. lunch time) are excluded. However, it can be pertinent to determine a specific level of exposure for a given task in order to prevent expected immediate/acute adverse effects on health (e.g. 15min-STEL). In that case, spot exposure concentrations can be calculated. Such concentrations should not be seen as representative of the working day because this leads to biased estimates of both variability and mean shift exposure [50].

Fig. 3: the recommended position of the sampler and the adsorbent tube.

Sample Transportation and Storage Stability

The samplers must be clearly labelled prior to the monitoring. Transport and storage of a monitoring sample shall be carried out in such a way that the physical and chemical integrity is maintained between workplace sampling and analysis. To prevent any compound re-volatilisation, archived collection substrates shall be individually stored immediately after sampling and preferably refrigerated or frozen before analysing. Samplers and samples must be covered with aluminium foil if further analysis of light-sensitive compounds is requested (e.g. PAHs).

Record Keeping

Practical experience has shown that any information recorded in the field during the monitoring can be useful afterwards especially for the data analysis (e.g. determination of correlations) or for establishing new surveys. All necessary information needed to identify samples and trials shall be recorded via a form. The Annex A of the technical report CEN/TR 15230 contains a list of the basic information needed for such report [4] based on industrial hygiene considerations [51, 52]. Basically, the form needs to report all of the essential information regarding the survey and a chronological order of the key tasks/events of the monitored individual(s).

Regarding Wind Effect

Wind is a key determinant regarding the capture efficiency of the inhalable fraction of the particulates with a lower IOM sensitivity for the largest particles [8]. However, inside particle losses for closed-face 37-mm cassette have been reported to be insignificant for particles < 20 µm at several wind orientations and low wind speeds (1.1 m/s) i.e. at wind speed and particle size consistent with a laboratory study [21]. This was confirmed in the field where the results show that both cassettes collect organic particulates similarly, with such an aerodynamic diameter range and with a wind speed up to approximately 5 m/s [39]. Consequently, current wind speed encountered in the field (up to 4-5 m/s) can be considered as having no significant influence on the particle capture (aerosols).

PROPOSED ANALYTICAL MEASUREMENT TECHNIQUE

SSF Recovery and Characterization

There are several key elements to consider regarding the sample recovery: the nature of the solvent, the extraction and evaporation steps. Historically, benzene was used for the extraction efficiency. As a carcinogen, benzene is going to be replaced by safer solvents such as dichloromethane (DCM, also called methylene chloride) or cyclohexane. In any case, the solvent efficiency must be quantified (extraction recovery). For instance, in a preliminary asphalt fume spiking experiment, NIOSH compared benzene and DCM as extraction solvents [16]. Asphalt fume was spiked on tared PTFE filter media at the following concentrations: 3.38, 0.68, 0.14, and 0.034 mg per filter. Benzene gave recoveries greater than 100% for all concentrations while DCM gave recoveries greater than 96% for the two highest levels spiked, at the two lower levels the recoveries were less than 67%. Many laboratories which routinely used this solvent have investigated other products to extract and recover organic particulates. Cyclohexane was tested for this type of extraction and has been found to have solvent properties similar to those of benzene according to their solubility parameters [53, 54]. Consequently, cyclohexane can be regarded as a suitable benzene substitute. A two-step extraction process is preferred for the filter extraction due to higher effectiveness especially when substantial mineral matters are on the filter [39]. The extraction step requires a sample recovery determination using spiked samples. Recovery depends on the collected mass and usually ranges from 80% to 100%. For instance, NIOSH gives an average of 90% recovery with benzene from 0.02 to 2 mg of collected SSF for a PTFE membrane [16]. Therefore, the determined correction factor can be used to express the results with regard to the collected masses. To prevent any compound volatilization, the solvent is usually evaporated in a sample concentrator at about 40°C under gentle nitrogen flow or under vacuum.

Gravimetric methods appear to be the most reliable way to quantify SSF (better efficiency/cost compromise). When the collected organic aerosols are the only fraction desired, blank samples are not required because the organics are extracted from the filter (no filter weighing is needed). Comparative characterization between gravimetric and GC-FID techniques were previously conducted [41]. Overall, SSF was found to be 20% less with GC-FID even if comparable FID response/mass calibration materials were used (generated bitumen fume standards). Similarly, FTIR can be used for quantifying SSF. But, a calibration material is required for the infrared determination (the aliphatic C-H stretch at 2800-3000 cm^{-1} is usually chosen). For instance, the German BIA methods use two materials (either a mineral oil or bitumen condensates) and a factor must be applied to compare the two methods [55]. This demonstrates that the calibration material is very sensitive for either GC-FID or FTIR. For instance, previous investigations using either FTIR or GC-FID showed that collected organic matters were probably underestimated [56]. Only 15% of SSF were found in total particulates when a 50/50 ratio is expected for current road paving applications [39]. The paper discusses this concern and the cause was thought to be the calibration standards which were different in nature from bitumen condensates (saturated aliphatic hydrocarbons). This underestimation is also recognized with FTIR and some authors recommend the use of correction factors for cross-reading [41, 57] which makes sense if a reader wants to compare published results.

VF Recovery and Characterization

The front and back sections of the adsorbent tube are separately extracted using dichloromethane (DCM). No breakthrough must be observed (back section). The analysis of the vapour phase extracts is usually conducted by means of GC-FID. The FID response could be calibrated using field or laboratory-generated VF samples, which have comparable FID response/mass. However, the carbon number range of the volatile fractions has been determined as being ca. C5 to C20 and is primarily straight chain and alkylated alkanes and, to a lesser extent, alkenes [5, 58-60]. Therefore, an equivalent-in-mass pure compound such as n-tridecane can be used as standard (as having a molar mass similar to the average one observed with VF profiles, see Fig. 4). The GC-FID linearity range must be checked by using calibration curves at several concentration levels. The front and back sections of the adsorbent tube are separately solvent extracted (DCM). No breakthrough must be observed (back section).

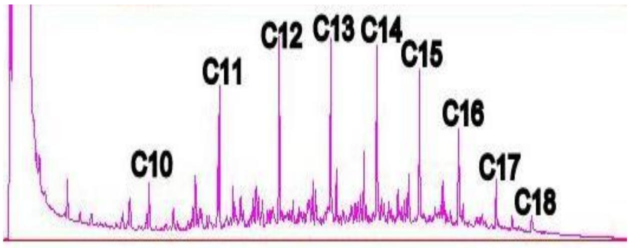

Fig. 4 : typical GC profile of field volatile fractions

Total Hydrocarbons

The total organic matter or total hydrocarbons (TOM or THC) is the sum of the aerosol and vapour fractions. It is strictly recommended to separately express the SSF and VF results.

Precision about Measurements

Method Validation

To assess the acceptability of the method employed, results can be compared using the requirements of the European Standards. For instance, EN 482 [42] gives the general requirements for the performance of procedures for the measurement of chemical agents (e.g. validation process with the help of Round-Robin tests). For comparison with occupational limit values, it requires the Relative Overall Uncertainty (ROU or bias plus twice the standard deviation) to be less than 30%, when used in range 0.5 to 2 times a limit value, including sampling and analytical errors. In many cases, ROU found significantly above 30% during the validation process allows the identification of technical problems. Further to the method validation, variation of exposure to chemical agents in the workplace can be significantly greater than indicated by the uncertainty of a single measurement calculated. This is due to the temporal and spatial variability of workplace exposures [42] discussed later in this paper.

Uncertainty

For complete measurement procedures for airborne particles, the expanded uncertainty is a combination of the uncertainty of the sampled volume and fraction, the uncertainty of the transportation, storage, sample preparation, and the uncertainty of the analytical method employed. Sampling instruments usually have accuracy given at about 30% [31] which is the figure already determined for CFC (from 31 to 34%) [9, 34]. Relevant standards give details of the analytical bias and precision. For instance, ISO 15767 gives some recommendations for controlling and characterizing uncertainty in weighing collected aerosols [44]. The non-random uncertainty component associated with the analytical method bias can be estimated by the replicate analysis of certified reference materials (CRMs). CRMs are generally useful (spiking) for methods that involve sample dissolution, solvent extraction and evaporation (recovered SSF and VF).

Limit of Detection and Limit of Quantification

When analysing the same substance several times at concentrations near or below the measuring range, and when any systematic error is excluded, the mass of the analysed substance can be determined along with its standard deviation (STD). The analytical limit of detection (LoD) is conventionally considered to be three times the STD (post-sampling weight minus tare weight). Similarly, the analytical limit of quantification or quantitation (LoQ) is conventionally considered to be ten times STD. Both the LoD and LoQ of the methods depend on the volume of air sampled, and on the analytical method used to quantify the collected materials. For instance, NIOSH NMAM 5042 determined LoD and LoQ for TPF and SSF using field blanks [16]. The calculated LoD/LoQ for the two fractions were 0.04/0.13 mg and 0.04/0.14 mg per sample, respectively. In another study, lower values were determined (0.006/0.02 mg/m^3) due to a better precision of the balance used [39]. If the measured mass value result falls between the two limits, then it should be reported that the measured mass is between the values of LoD and LoQ. An estimate of the average concentration can be made in the presence of non-detectable values (i.e. the determined amount of material is below LoD). There are two situations: either a set of experimental values are available but not relevant (because < LoD) or only a single value or no value available (some instruments do not distinguish between values below LoD and background noise). In the first case, it is recommended to use the median value (50th percentile) of the actual data set [61]. In the second case, the use of the more conventional LoD/2^{½} for GSD below 3 or LoD/2 for GSD above 3 (highly skewed distribution) is advised [62].

Minimum Sampling Time

The collected mass “m” on the media can be basically calculated from the estimated aerosol concentration “C” of the atmosphere, the flow rate “Q” and the sampling time “t” : $m = C \times Q \times t$. If the collected mass is given as LoQ, a minimal sampling time to collect a detectable amount of a substance can be calculated. Note that an estimate of the concentration is required (previous available data sets).

REGARDING THE MINERAL PARTICULATES

Previous comparisons made between IOM and CFC showed a lower efficiency for CFC which collects fewer mineral materials especially when the particulate size increases [8, 18, 19, 21, 32-34]. The observed IOM/CFC ratios were greater for workplaces where aerosols were coarser or denser. Experimental efficiencies for coarse particles (> 50 µm AED) are still decreasing and are never constant as predicted by the CEN-ISO inhalable convention [23]. It is commonly observed that the IOM identifies about twice the amount compared with CFC, due to the latter not taking into account inner wall deposits. These deposits are likely reinforced by the CFC plastic holder which can increase the electrostatic charges [14]. In this case, it is recommended either to wipe the inner walls of the cassette or to use an internal capsule in order to collect the whole material making up the mineral sample. When these deposits are taken into account the ratio is close to 1 for CFC and IOM (total particulates). Total particulates are quantified by gravimetric methods. Particulate matter is collected on pre-weighed filters and determined by weight difference after sampling (filter weighing, blank samples required). The mineral fraction is quantified by difference between the total particulates and SSF.

IMPACT OF THE VARIABILITY ON THE DATA INTERPRETATION

Variability in the Measurements

There are situations where measurements on a given work site are location-specific and require consideration of the effect of external factors, called determinants. The literature shows that asphalt paving workers are non-uniformly exposed. More specifically, the job environment has regularly been identified as having a greater influence than the job title [1, 63]. This is mainly due to the influence of variables called determinants, the between-group variability (sites S1, S2, S3, etc.) and the within-worker variability (days D1, D2, D3, etc.) which are generally observed to be significantly higher than the between-worker variability (individuals I1, I2, I3, etc. for a given group and a given day) regardless of the job task [64] [2]. Environmental & production factors showed distinct influences on the within-worker variability but not on the between-worker variability. Consequently, the variability due to the reproducibility of the measurement in industrial/ambient air measurements of the workplace can be regarded as significantly lower when compared to the total variability. Analytical bias and lack of precision generally have minor impact on the error in the measurement of airborne particle concentrations. For typical GSD determined in field surveys (around 2), the percentage of variability due to the measurement error is only about 15% [65]. As a consequence, when expressing the results of occupational

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[2] In the present case, the between-group and within-worker variabilities can be regarded as similar, since staff is working at the same site on the same day (sites & days 1, 2, 3).

exposure measurements, it is important to take into account the way in which the fumes were collected and all potential confounding factors, including task, and job environment. This also means that the influence of the number of samplings will have a greater influence on the final determination than the measurement accuracy for all levels of exposure. Currently, it is considered that the main source of lack of precision in the measurement of workplace contaminant concentrations is the non-uniformity in time and space of the contaminant cloud surrounding the worker.

Determination of HEGs (Use of GSD)

As it is not feasible to assess the level of exposure for all workers of a population, at all times of the year and whatever the site due to the observed variability, occupational hygienists recommend consolidating the individual exposure data into groups defined as Homogeneous / Uniformly Exposed Groups (HEG/UEG). Currently the variability is expressed by the geometric standard deviation (GSD) which describes the scatter of the measurements. In 1991, Rappaport introduced the concept of HEG [66]. Following Rappaport, 95% of the individual mean exposures in an HEG lie within a factor of 2 meaning a GSD value < 1.2 (between-worker variability below 1.2). Less restrictive, the UK HSE established that the individual mean exposures must lie in a range between half and twice the mean value of the group leading to a GSD below 1.45 [67]. Currently, in many industry sectors dealing with outside exposures, GSD are above these recommendations. Usual GSD encountered in occupational hygiene to express HEGs ranges from 2.0 to 2.5 [65]. Overall, a cost-effective air sampling strategy can be established with a GSD value below 3 [68] meaning that a GSD above 3 requires a split of the monitored group in subgroups.

Result Interpretation (Means)

When a set of data is available, there are two ways to express the data; either using the arithmetic or geometric means (AM and GM). Usually, for an exposed group, an average exposure level follows a lognormal distribution, which is the current distribution obtained with outside exposures such as asphalt workers [66]. For such distribution, GM is the best way to represent the averaged level of exposure. The weight in the calculations given to the highest values always yields higher AM's. However, the number of measurements has an impact on the decision with regard to the actual distribution. Applying the precautionary principle, the higher average should be used (AM). The basic principles are: for a significant number of measurements (e.g. > 20), GM can be regarded as reliable if all the field situations were included in the matrix. On the other hand, for data sets below 6, it is recommended to use AM. Between these two limits, field experience or available data sets can influence the choice.

IMPACT OF THE VARIABILITY ON THE MONITORING STRATEGY

Usual Strategies in Occupational Hygiene

Industrial hygienists usually describe measurement strategies taking into account between-worker variability in long-term exposure [66]. These strategies use an observational group approach and recognise that exposure varies both within and between workers. They are especially suitable for situations where evaluation and control of long-term exposures are required to prevent chronic health effects. When there is no specific strategy (e.g. initial assessment), systematic or arbitrary sampling is required. Screening measurements to evaluate variation of concentration in time and/or space can clearly identify episodes where higher exposures occur, e.g. high emissions due to certain working activities. Sampling periods can be selected containing these episodes. This approach is called worst-case sampling. Periodic measurements are used to determine whether exposure conditions have changed since the measurements were performed, or whether control measures remain effective. Measurement strategies are also established for comparison with OELs to obtain results of known precision and accuracy for the average concentration of a chemical agent in the air in a worker's breathing zone. Subsequently, monitoring can be required either as a screening measurement of time weighted average concentration or for comparison with limit values.

Recommended Strategy

The comparison between the within-worker variability and the between-worker variability shows that the first can be significantly higher. Consequently, this has a direct consequence on the monitoring strategy to express annual levels of worker exposure: it is more representative to monitor part of a crew (e.g. one job type) over a given period (e.g. several non-continuous days or weeks) than monitoring the whole team on a single day.

Three key steps can summarize the full worker exposure assessment:

1. Constitution of the exposed groups (HEG).
2. Field measurements and analytics.
3. Data treatment (statistics), exposure level interpretation (HEG confirmation) and possibly risk assessment (occupational limit comparison).

Determining the Number of Measurements Required

As already noted, the (limited) number of measurements by group impacts the expression of the exposure levels. For instance, an effective assessment would require five measurements per day with duplicates which is obviously limited by cost [66]. Already, NIOSH recommended a minimum sampling number in relation with the size of the group (e.g. 14 for a group larger than 50 people) [70]. AIHA recommends at least six random measurements per HEG in order to have representative means without a large variability [AIHA 2006]. Similarly, REACH Guidance documents make the same recommendation in Europe. Six data points should be presented to adequately describe the exposure of a single work activity within one company [71]. In the UK, BOHS advises to use three measurements per HEG but at least six for comparing true means with OEL [72]. Overall, three measurements are required as a minimum for assessing the exposure level (e.g. periodic measurements). This figure is in good agreement with the current designed strategies used for risk assessment when comparing an exposure level with a relevant OEL.

CROSS-READING WITH EXISTING EXPOSURE DATA

The comparison of original data with previously issued values is key. For large applications such as road paving, the average levels of exposure are known and have been published on a regular basis. This comparison is also a way to control if the operating conditions are well managed. Road paving is a sector where many studies were conducted leading to an abundance of published data. Table 1 summarizes some exposure values issued during the last decade for the main bitumen applications. From this, it appears that the exposure levels are comparable and can be regarded as guidance values in terms of risk assessment. For the organic particulate and volatile fractions, the calculated averages from the 5 studies show overall homogeneous data (GSD around 1.3).

Table 1: exposure values issued during the last decade for the main bitumen applications

Study	Burstyn [73]	Heikkila [63]	Kriech [13]	Rühl [74]	Deygout [39]	All
Type of published data	GM*	GM*	Original data set	GM*	Original data set	-
Particulates in mg/m^3 (GM*)	0.15 (n = 362)	0.12 (n = 53)	0.22 (n = 27)	0.24 (n = 298)	0.13 (n = 40)	0.17 (GSD = 1.32)
Volatiles in mg/m^3 (GM*)	1.50 (n = 222)	1.80 (n = 53)	1.44 (n = 27)	1.55 (n = 298)	0.78 (n = 38)	1.36 (GSD = 1.34)

(*) GM: geometric mean

RECOMMENDED STRATEGIES FOR RISK ASSESSMENT

A NIOSH guidance document, published in 1977, is regarded as a pioneer by occupational hygienists [70]. It was the first time that comparisons with OELs were investigated including probability of exceeding these occupational limits. However, the notions of environmental variability and homogeneous groups (HEG) were not tackled. Subsequently, others have attempted to design strategies and these are updated on a regular basis.

The AIHA strategy

AIHA suggests two categorization schemes for rating exposures. First, a threshold is defined using “minor” and “major” exposure scenarios if the exposure level is less or equal/greater than 1/10 of the OEL respectively [75]. Four exposure rating categorizations are then based either on an estimate of the arithmetic mean of the exposure level relative to the OEL (<10% OEL, 10-50% OEL, 50-100% OEL and > OEL) or on an estimate of the 95th percentile of the exposure level relative to the OEL (little to no exceedance of 0.1 x OEL, > 5% exceedance of 0.1, 0.5 and the OEL). More importantly, the first exposure rating categorization is recommended for agents exhibiting cumulative adverse health effects. Faced with the variability problem, hygienists have often regarded as satisfactory that the 95th percentile of the exposure distribution is probably below the OEL. Overall, a threshold of 10% of the OEL and the 95th percentile of the exposure level are suggested as triggers for beginning to collect exposure data and to support the exposure judgement. However, the 95th percentile is not very precise unless there are a significant number of measurements.

The EN689 strategy

The Comité Européen de Normalisation recommends a sole measurement per job as a starting point [76]. Similarly to AIHA, if the value is above the 10%-OEL threshold, two additional measurements are required. Several recommendations are given following the determined mean/OEL ratio, however, there is uncertainty regarding specific situations, such as when the mean of the measurements is above 50% of the OEL without exceeding it.

The REACH strategy

REACH places obligations on registrants (manufacturers and importers) to develop Derived No Effect Levels (DNELs) as benchmarks for determining adequate control of exposure for exposure defined scenarios. The methodology for deriving DNELs involves the systematic application of assessment factors (AF, uncertainty factors based on toxicological references). The concept of inhalation DNELs for workers is very similar to the concept of OELs although OELs are typically derived by applying rather small overall factors based on case-by-case expert judgement (since DNELs are being established for registration and risk management measures purposes, national OELs prevail). REACH states that for any exposure scenario the risk to humans can be considered to be controlled if exposure levels do not exceed the appropriate DNEL. REACH uses RCR (Risk Characterization Ratio = exposure value / DNEL) which must be below 1 [77]. If the available exposure data set is generally adequate for deriving an exposure estimate that reflects the conditions of use described in the exposure scenario, REACH recommends selecting the appropriate percentile i.e. the

90th percentile of an exposure distribution reflecting the whole spectrum of conditions of use described in a particular exposure scenario [71]. DNEL values may be significantly different from the OEL values (ca. one order of magnitude lower) and trigger much more stringent risk management measures. To resolve potential conflicts, the European Commission has proposed that for substances for which there are established national OELs, these could be used as a starting point for developing worker (inhalation) DNELs. DNELs are likely to be approximately one order of magnitude lower than the corresponding OELs [78]. Consequently, using a 10%-OEL threshold to achieve compliance with OELs due to variability effects or compare the 90th percentile with a given DNEL should lead to a similar risk assessment.

CONCLUSIONS

The organic part of bitumen fumes comprises a mixture of particulates and vapours. In the case of bitumen fumes, the inhalable fraction is equivalent to the respirable fraction (particulates having an aerodynamic diameter below 10 µm). The preferred sampler to capture these organic particulates is the disposable 37-mm cassette in its closed-face configuration. The organic particulates are extracted from the filter with cyclohexane and recovered by evaporating this solvent (sample recovery pre-determined). The extracted particulates are then quantified by gravimetric measurement. The vapour fraction of the fumes is collected by means of a two-section adsorbent tube packed with a co-polymer (XAD-2 type). Similarly to the organic particulates, the vapour fraction is extracted with the help of a solvent (DCM) and is directly quantified by means of chromatography (GC-FID). The detector response is calibrated using a pure hydrocarbon having an equivalent molar mass in average (n-tridecane). It is strongly recommended to separately express the two organic fractions.

Bitumen applications usually require outside operations. This leads to a variability observed in the measurements due to external factors. This also impacts the monitoring strategy by constituting homogeneous exposure groups (HEG). The study of the field variability shows that one job type will be preferably monitored several times over a given period rather than the whole team in a single day. Similarly, this variability imposes a limit on the number of determinations to express annual levels of worker exposure (three being the minimum).

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