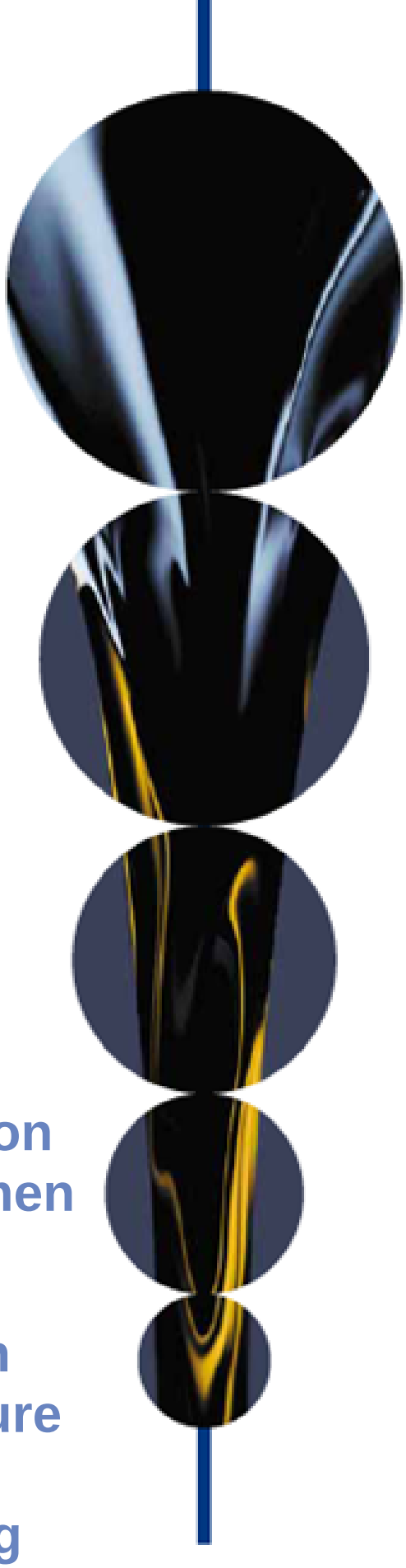

Assessment of Personal Inhalation Exposure to Bitumen Fume

Guidance for an Inhalation Exposure Metric and a Monitoring Strategy

Monitoring Method

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Acronyms and Abbreviations Used

CEN	Comité Européen de Normalisation (European Committee for Standardization)
CFC	Closed-Face Cassette
CRM	Certified Reference Material
CSF	Cyclohexane Soluble Fraction
DNEL	Derived No Effect Levels (REACH benchmark)
DCM	Dichloromethane (also called methylene chloride)
GSD	Geometric standard deviation.
HEG	Homogeneous Exposure Group (or Similar Exposure Group or SEG)
LoD, LoQ	Limits of Detection and Quantification
OEL	Occupational Exposure Limit (currently 8h-TWA)
PAH	Polycyclic Aromatic Hydrocarbon.
PBZ	Personal breathing-zone (sample or area)
PTFE	Polytetrafluoroethylene
RCR	Risk Characterization Ratio (REACH tool for risk assessment)
STD	Standard Deviation
STEL	Short Time Exposure Limits (usually set for 15 min)
THC	Total HydroCarbons (equivalent to Total Organic Matter or TOM)
TWA	Time Weighted Average; this is an average value of exposure over the course of a work shift (commonly an 8-hour TWA, which represents a full workday)
VF	Volatile Fraction

1. Scope and Purpose

This report gives practical guidance for the assessment and quantification of potential worker exposure to inhalable bitumen emissions. Recommendations for an appropriate sampling technique and parameters such as a preferred analytical measurement technique are given with a specific focus on the organic aerosol fraction. Due to the significant variability seen in capture and quantification of outdoor exposure situations (e.g. paving operations), not only the precision of the method used but the number of the samples dedicated to the measurement is discussed. As is usual in occupational hygiene, guidance regarding data interpretation is given and a recommended strategy dealing with existing exposure data or occupational limits is also considered.

2. Method Summary

Bitumen emissions comprise a mixture of particulates (mineral and organic) and organic vapours. The suitable sampling train used to capture these emissions is based on three in-line elements i.e. an individual sampler provided with an appropriate filter (capture of the particulates), a tube containing an adsorbent (capture of the vapours) and a portable pump. The recommended air flow rate is 2 L/min. The preferred sampler to capture the organic particulate fraction is the disposable 37-mm cassette in its closed-face configuration. The 2µ-pore size filter is made of PTFE and is suitable for anticipated airborne concentrations under normal circumstances. For specific purposes, that require a higher filter capacity, fibreglass filters can be used.

The organic particulates are extracted from the filter with cyclohexane and recovered by evaporating the solvent (sample recovery pre-determined). The extracted particulates are then preferably quantified by gravimetric methods. When quantification of the total particulate fraction is needed (ie. total mineral particulate), it is recommended either to wipe the inner walls of the cassette or to use an internal capsule in order to collect the whole mineral material making up the sample. In this case, pre-weighed blank samples are required.

The vapour fraction of the emissions 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 from the adsorbant material with the help of a solvent (Dichloromethane (DCM)) and is directly quantified by means of chromatography. The detector response is calibrated using a pure hydrocarbon having an equivalent molar mass in average (n-Tridecane). It is strongly recommended to separately report the two organic fractions (organic particulate and total organic vapour).

Sample labelling, sample transportation and storage, information recording during field surveys must be carefully conducted. The monitored period of time must be as representative as possible of the daily worker activities i.e. daily tasks (mostly set for reference periods of 6 or 8 hours). The accuracy of the method can be expressed by an overall uncertainty of less than 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 requiring homogeneous exposure groups (HEG). 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 limit on the number of determinations to report annual average levels of worker exposure (three minimum).

3. Apparatus

3.1. PBZ sampler

The recommended PBZ sampler is the disposable clear plastic (SAN or styrene acrylonitrile) 37-mm cassette in its closed-face configuration (CFC), with a 3-part body. CFC is preferred for practical considerations. This cassette has demonstrated advantages when operating: lower contamination risk, lower weight and better precision, lower sensitivity with respect to the airflow rate used, minimal loss of volatile organic compounds with IOM.

3.2. 2µm PTFE Filter

PTFE filters are preferred because they are hydrophobic (water sorption is very low), unlike fibreglass. PTFE is also known to be interference-free (inert) for chemical determinations (e.g. PAH determination in the organic fraction).

Each filter type has its own maximum collection capacity: the filter supplier usually recommends a filter capacity. The PTFE filter capacity was determined as 2 mg.

Filter capacity combined with pump flow rate will also influence the daily sampling time. Based on an 8-hour sampling period and a 2 L/min flow rate, a 2 mg capacity PTFE filter will establish a maximum airborne concentration of 2.1 mg/m^3.

A PTFE filter with a nominal pore size of 2µm is suitable.

Note: Fibreglass filters have demonstrated capacity up to 6 mg. Consequently, for specific purposes requiring a high filter capacity, a fibreglass filter can be used.

3.3. Adsorbent Tubes

The vapour fraction of the emissions is collected by means of a suitable adsorbent used for trapping gaseous compounds downstream from the filter. 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 surveys). There are several advantages to using polymeric sorbents. They are more consistent and can be desorbed more efficiently even at small loading rate. They are also not susceptible to the effects of high relative humidity. In addition, co-polymers are specifically dedicated to the capture of individual compounds (e.g. PAHs).

The adsorption of gases and vapours on sorbents is influenced by the gas and vapour concentrations in the sampled air and by the pumping flow rate (some adsorbent packaging limits the sampling flow rate). A maximum operating flow rate is recommended by the suppliers. 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.

Adsorbent tubes containing 100/50 mg XAD-2 resin are suitable. Some absorbent tubes with a heavier loading of resin cannot be used in series with a filter cassette/ sampler at a flow rate of 2.0 L/min.

3.4. Individual Sampling Pump

Sampling pumps used for particulate sampling should comply with the requirements of EN 1232 [CEN 1997]. They should have an automatic flow control (with indicator) which keeps the volumetric flow rate constant (within ± 5 % of the initial flow rate) in the case of changing back pressure; either a malfunction indicator, which following the completion of sampling indicates that the air flow has been reduced or interrupted during sampling or an automatic cut-out, which stops if the pump flow is reduced or interrupted. Usually, pumps have adjustable flow rates in the range 1 - 5 l/min. Along with the sampler geometry, the flow rate is a determining factor for the sampling efficiency.

3.5. Laboratory Apparatus

- Gas Chromatograph, equipped with on-column injector and flame ionisation detector.
- Gas chromatographic column, a 30 m * 0.32 mm id, DB-5MS, film thickness 0.25 micron column is suitable.
- Retention gap/ pre-column 1.5 m * 0.54 mm internal diameter, deactivated fused silica.
- Vacuum Oven, capable of maintaining a temperature of 40 ± 1°C and a vacuum down to 5 to 7 kPa (50 to 70 mbar). This should be vented into a fume hood (or equivalent).
- Sample Concentrator, heated, temperature-controlled block with nitrogen purge facility.
- Ultrasonic Agitation Bath, tank size approx. 150 x 135 x 100 mm.
- Electronic Microbalance with an appropriate accuracy (e.g. ± 0.001 mg).
- Gas Flow meter, capable of correctly indicating flow rates at pressure drops within the working range of the sampling pumps. 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. EN 482 gives details about the uncertainty of the flow rate measurement for different types of flow meters [CEN 2006].
- Flow Calibrator, with calibration certificate, covering the flow rate range of the sampling pumps.
- Gas-tight Syringe, 2.5 mL with luerlock injection needle equipped with a Millex-FH_{13} filter (13-mm diameter 0.45-μm pore size) are suitable.
- A range of syringes, e.g., 50, 100, 250, 500 µL for preparation and dilution of reference and sample solutions.

- 5 μL syringe for on-column injection.
- Weighing Cups, Teflon cups, mass about 0.05 g.
- Borosilicate Vials, 4 mL, with screw cap in combination with Teflon faced discs.
- Glassware, miscellaneous beakers etc. for extractions.
- Glass tube cutter.
- Flexible plastic tubing must have a suitable internal diameter for connecting pump with sampler.

4. Reagents & Materials

- Cyclohexane containing max 3 mg/L evaporation residue. CAUTION: this compound has been classified as an irritant to skin, highly flammable and toxic for the environment. Read the supplier SDS carefully.
- n-Tridecane analytical standard. CAUTION: this compound has been classified as an irritant to eyes, respiratory system and skin. Read the supplier SDS carefully.
- Dichloromethane, pro analyse grade. CAUTION: There are possible risks of irreversible effects with dichloromethane. Read the supplier SDS carefully.
- Aluminium foil.
- Nitrogen, dry and free from extraneous matter, e.g. oil and particles.

5. Preparation of the Apparatus

5.1. Glassware

- Wash all extraction glassware with a detergent solution, rinse with tap water and distilled water before allowing to dry.
- Clean and rinse the Teflon weighing cups in cyclohexane with ultra-sonic agitation, then dry in the vacuum oven at about 40°C and 5 to 7 kPa (50 to 70 mbar) for one hour.

5.2. Filter Cassette Assembly

- Assemble carefully to avoid any leak the 3 parts of the filter cassette + filter using dust-free gloves. SKC can provide SureSeal™ leak free cassettes.
- Put a label on the sampler with identification.
- Seal the filter cassettes before transport.

5.3. Pump Calibration

- Adjust the sampling pump to the 2 L/min flow rate (2.0 ± 0.1 L/min) with sampler, adsorbent tube and filter in line, using a gas flow meter calibrated with the certified flow calibrator. The flow calibrator must take place in series between the sampler / adsorbent tube and the pump. For this purpose use filter cassettes & cut tubes other than

those meant for monitoring to avoid premature collection of particulates.

Note: A flow rate of 2 l/min is strongly recommended as representative for sampling of airborne particulate matter. 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.

6. Sampling Protocol

The assessment of the potential worker exposure to chemical agents in workplace atmospheres often requires the measurement of the concentration of the agent 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 whether the exposure level is acceptable or not. In Europe, CEN has published general performance requirements for procedures for determination of the concentration of chemical agents in workplace atmospheres as required by the Chemical Agents Directive 98/24/EC [CEN 2006]. 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.

6.1. Assembly the Sampling Train

- The adsorbent tubes must be clearly labelled prior to monitoring.
- Break the sealed ends of the XAD-2 tube using the glass tube cutter. *CAUTION: Wear safety glasses and gloves when breaking the adsorbent tube.*
- If not used immediately, cap the tube with the red caps provided.
- Unseal the filter cassette.
- With the help of a short piece of tubing attach the adsorbent tube directly behind the filter cassette assembly making sure that the arrow on the adsorbent tube is pointing towards the sampling pump.
- Connect the cassette / adsorbent with the pump using a piece of flexible plastic tubing.

6.2. Field Blanks

Blank samples are required when gravimetric analysis is used. The use of blanks is the most important practical tool for reducing uncertainty due to filter weight instability. Correction for weight instability depends on the specific application. In general, blank sampling media are exposed, as closely as possible, to the same conditions as the active sampling media, without actually drawing air through the sampling cassette. Correction is effected by subtracting the average blank mass change from the mass change of the active collection substrates plus aerosol samples.

Generally, at least one blank is recommended for every 10 samplers. Measurement schemes in current use require between one and four blanks per batch or per day

6.3. Place the Sampling Train

- Affix the sampler in the breathing zone of the worker to be monitored. A clip can be used or a specifically designed belt. In order to be representative of the worker exposures, the PBZ sampler must be placed and maintained as close as possible to the face (breathing zone) of the worker e.g. on the shoulder (see picture). According to a NIOSH study, no effects due to the position of the sampler (left or right side) were noticed.
- Adjust the pump to a belt. The belt-adjusted portable pump should be placed as not to interfere with worker operations and/or endanger the worker (currently at the back).

The recommended position of the sampler and the adsorbent tube

6.4. Sampling

- Switch on the pump.
- Check the stabilisation of the flow rate via the pump display.
- Draw a known volume of air through the filter cassette and adsorbent tube, using the personal sampling pump at a flow rate of 2.0 L/min for the full shift or a shorter term when appropriate.
- Check the pump, including displayed flow rate, at periodic intervals during sampling.

Note 1: The monitored period of time must be as representative as possible of the daily worker activities i.e. daily tasks (for instance, workplace occupational exposure levels [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, a full-shift sampling is required to determine compliance with OELs. Usually, long breaks (e.g. lunch time) are excluded.

Note 2: 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 are not representative of the working day because this leads to biased estimates of both variability and mean shift-long exposure.

6.5. Record Keeping

Experience shows that any recorded information in the field during the monitoring can be useful afterwards especially for the data treatment (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 [CEN 2005] based on industrial hygiene considerations

An example of an established document specifically dedicated to road paving is given in Appendix 1. The form needs to report all basic

information regarding the survey and a chronological order of the key tasks/events of the monitored individual(s).

6.6. Disassembling

- When the test sample has been taken, check the displayed flow rate, and switch off the pump.
- Record the sampling time.
- Dissemble the sampling train.
- Seal the filter cassette and cap the tube with the red caps provided.
- Wrap the cassette tightly in aluminium foil.
- Place the sealed cassette and tube in airtight plastic bags.

6.7. Sample Transportation and Storage Stability

Transport and storage of a sample shall be carried out in such a way that the physical and chemical integrity is maintained between sampling and analysis. To prevent any compound re-volatilisation, archived collection substrates shall be individually stored immediately after sampling and refrigerated before analysing (< 10°C). Samplers and samples must be covered with aluminium foil if further analysis of light-sensitive compounds is requested (e.g. PAHs).

7. Sample Recovery & Analysis

7.1. Control of the Flow Rate

Check the sampling pump to the 2 L/min flow rate (2.0 ± 0.1 L/min) with sampler, adsorbent tube and filter in line, using a gas flow meter calibrated with the certified flow calibrator. If the flow rate values differ by more than 0.1 L/min, calculate the average value.

7.2. Recovery & Quantification of the Fractions

7.2.1. Total Particulate Fraction (TPF)

TPF is quantified by gravimetric methods. Particulate matter is collected on pre-weighed PTFE filters and determined by weight difference after sampling (filter weighing). Several blank samples are required. The use of blanks is the most important practical tool for reducing uncertainty due to filter weight instability. Because transfers of mass between filters and the 37-mm cassettes can occur during sampling and storage (inner wall deposits), 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.

The tared filters are reweighed preferably using the same balance or a balance having an equal precision and stability. Workplace-air sampling typically requires a balance capable of weighing to a resolution of 1 µg or 10 µg. The balance shall be regularly calibrated using reference masses (check weights) traceable to International Standards

7.2.2. Organic Particulates (Cyclohexane Soluble Fraction)

- Allow the samples to reach room temperature before unpacking.
- Disassemble carefully the filter cassette.
- Remove the filter carefully from the cassette and place it in a 50 mL beaker and add 3 mL cyclohexane.
- Cover the beaker with a piece of aluminium foil and allow to vibrate in the ultrasonic bath containing water for 20 min. Maintain the water level in the bath higher than the cyclohexane level in the beaker.
- Weigh a Teflon cup to the nearest 0.001 mg.
- Place the cup in the sample concentrator at ca. 60°C under a stream of nitrogen.
- Switch off the ultrasonic bath and transfer the extract, as completely as possible, into a 2.5 mL syringe-driven PTFE.
- Remove the needle and attach a Millex-FH_{13} filter unit, add the needle and transfer about half of the extract through the filter into the pre-weighed Teflon weighing cup.
- When most of the cyclohexane has evaporated, inject the remainder of the extract into the Teflon cup and evaporate to near dryness.
- Repeat the extraction procedure by adding 3 mL cyclohexane and for 5 min in the ultrasonic bath (two-step extraction).
- Evaporate the final cyclohexane extract to near dryness at 60°C in the sample concentrator. Place the cup in the vacuum oven at about 40°C and 5-7 kPa (50 to 70 mbar) for two hours.
- After cooling and equilibrating for 30 minutes, reweigh the Teflon cups, to the nearest 0.001 mg, and determine the amount of CSF.
- Calculate the emission in mg/m^3 by means of the following equation:

  $$\text{Emission, } mg/m^3 = (m * 1000) / (Q * t)$$

  Where:

  m = amount of weighed CSF, mg

  Q = pump flow rate, L/min

  t = sampling time, min
- Report the concentrations to the nearest 0.01 mg/m^3.

7.2.3. Organic Volatile Materials (Volatile Fraction)

Extraction procedure

- Cut and break the adsorbent tube near the glass wool plug in the centre. *CAUTION: Wear safety glasses and gloves when breaking the adsorbent tube.*
- Remove the plug with the puller/inserter and collect the collecting adsorbent in a 4 mL vial.
- Add 1.5 mL dichloromethane.
- Close the vial with the screw cap.
- Shake the vial occasionally during the next 30 minutes.
- Repeat the procedure for the backup adsorbent.

- Filter the solutions using the 2.5 mL gastight syringe and the Millex-FH filter unit.
- Proceed with chromatographic analysis or store the solutions in a refrigerator.

Preparation of reference solutions

- Prepare at least 2 stock solutions of the selected reference material (n-Tridecane) by dissolving e.g. ca. 20 mg and ca. 50 mg, weighed to the nearest 0.001 mg in 2 mL of dichloromethane.
- Dilute the stock solutions to cover the range ca. 0.1 mg/mL to ca. 2.5 mg/mL using gas-tight syringes. It may be necessary to prepare additional dilutions of the stock solutions to determine detector response for the range covering that of the sample solutions. Based on an 8hr-sampling period the reference material concentrations given above relate to an exposure range of 0.15 to 4 mg/m^3.

Note: the stock solutions may be stored in a freezer at –20 °C for no longer than 6 months. Alternatively they may be stored in a refrigerator at ca. 4°C for up to 2 weeks.

Chromatographic analysis

- Set up the GC equipment (see suitable operating conditions given in the following table) and allow to stabilise.

Column	30 m * 0.32 mm id, DB-5MS, film thickness 0.25 micron
Pre-column / retention gap	Deactivated fused silica, 1.5 m * 0.54 mm id
Carrier Gas	Helium at constant pressure (ca. 75 kPa)
Detector	Flame Ionisation Detector at 375°C
Temperature programme	1. initial temperature 35/45°C for 5 min
	2. 10°C / min to 350°C
	3. final temperature, 350°C for 15 min
Injection	On column injection of 2μL

Inject one of the reference solutions and one of the sample solutions to determine the initial and final retention times of the materials to be chromatographed.

Inject dichloromethane to determine any column bleeding and also the solvent blank value S_b. Determine the area for a time range including both the initial and final retention times determined. Repeat the dichloromethane injection and compare the areas determined. Repeat, if necessary, until system is stable. Determine the mean.

- Inject the reference solutions in random order. For each reference solution determine the area S for the same time range as used to determine the blank.
- Calculate the detector response F_n for each solution as follows:

$$F_n = (S_n – S_b) / M_n$$

Where:

S_n = area for reference solution.

S_b = mean blank value for blanks injected before & after calibration solution(s).

M = amount of reference material in solution injected.

- Determine the mean detector response factor F. The detector response should be linear for the range used to quantify the volatile fractions.
- Inject the sample solutions. Determine the area S for each solution for the same time range as used to determine the blank and reference solutions and calculate the amount of semi-volatiles in each sample solution by using the mean detector response factor.
- Determine the solvent blank value at regular intervals during sample analysis. The stability of the system and the area of the blank compared to sample solution areas will determine the frequency at which the blank should be re-determined.
- Calculate the emission in mg/m^3 by means of the following equation:

  Emission, mg/m^3 = (m * 1000) / (Q * t)

  Where:

  m = amount of semi-volatiles in sample, mg

  Q = pump flow rate, L/min

  t = sampling time, min

- Report the emission of semi-volatiles to the nearest 0.01 mg/m^3.

7.2.4. Mineral Particulates

The mineral fraction is quantified by weight difference (TPF - CSF).

Note: an estimate of the whole mineral fraction can be made by calculation when the mineral fraction was only based on the materials collected on the filter (walls excluded). In that case, it is recommended to multiply by a factor of 1.8 the mineral mass collected on the filter.

7.2.5. Total Hydrocarbons

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

8. Precision about Measurements

8.1. Method Validation

The extraction step requires a sample recovery determination with the help of spiked samples at several concentrations e.g. from 0.05 to1.5 mg per filter. Recovery depends on the collected mass and usually ranges from 80% to 100%. Therefore, determined correction factors can be used to express the results with regard to the collected masses.

To assess the acceptability of the selected method, results can be compared using the requirements of the European Standards. For instance, EN 482 [CEN 2006] 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 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 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 [CEN 2006] discussed later in this paper.

8.2. 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% [CEN 2001] which is the figure already determined for CFC (from 31 to 34%).

Relevant standards should be consulted for details of the analytical bias and precision. For instance, ISO 15767 gives some recommendations for controlling and characterizing uncertainty in weighing collected aerosols [ISO 2009]. The non-random uncertainty component associated with the analytical method bias can be estimated by the replicate analysis of CRMs. CRMs are generally useful (spiking) for methods that involve sample dissolution, solvent extraction and evaporation (recovered CSF and VF).

8.3. 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 STD. The analytical limit of detection (LoD) is conventionally considered to be three times the value of 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 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 determined LoD and LoQ for TPF and CSF using field blanks [NIOSH 1998]. The calculated LoD/LoQ for the two fractions was 0.04/0.13 mg and 0.04/0.14 mg per sample, respectively. In another study, lower values were determined (0.006/0.020 mg/m^3) due to a better precision of the balance used. Note that field sample values should be compared to the LoD and LoQ values only after the field samples have been blank corrected.

If the reported 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 not available (some equipments do not make the difference 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. 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 accurate.

8.4. 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, provided an estimate of the concentration is available.

9. Impact of the Variability on the Data Interpretation

9.1. Variability in the Measurements

They are situations where measurements on work sites are location-specific and require consideration of the effect of external factors, called determinants. The bibliography study shows that asphalt workers are non-uniformly exposed. 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 usual GSD determined in field surveys (around 2), the percentage of variability due to the measurement error is about 15% only [AIHA 2008].

As a consequence, when expressing the results of occupational exposure measurements, it is important to take account of the way in which emissions were collected and all potential confounding factors; should include task, 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 whatever the level of exposure is. 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.

9.2. 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 period of the year and whatever the site due to the observed variability, occupational hygienists recommend grouping the exposed individuals in task groups defined as homogeneous (HEG).

Currently the variability is expressed by means of GSD which describes the scatter of the measurements. Usual GSD encountered in occupational hygiene to express HEGs ranges from 2.0 to 2.5 [AIHA 2008]. Overall, a cost-effective air sampling strategy can be established with a GSD value below 3 meaning that a GSD above 3 requires a split of the monitored group in subgroups.

9.3. Result Interpretation (Means)

When a set of data is available, there are two ways to express the data, either use 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. For such distribution, GM is the best way to represent the averaged level of exposure. The weight in the calculations given by the highest values always gives higher AM's.

However, the number of measurements has an impact on the decision with regard to the actual distribution. How to be sure that a few data fully represent the actual distribution? Following the precautionary principle used in industrial hygiene, the higher average should be used (AM). 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 approach.

An example of calculation (concentrations, AM, GM, GSD, confidence interval and comparison of exposed groups) is given in Appendix 2.

10. Impact of the Variability on the Monitoring Strategy

10.1. Usual Strategies in Occupational Hygiene

Industrial hygienists usually describe measurement strategies taking into account between-worker variability in long-term exposure. These strategies use an observational group approach and recognise that exposure varies both within and between workers. This is especially suitable for situations where the evaluation and control of long-term exposures is required, due to possible chronic health effects. When there is no specific strategy (e.g. initial assessment), systematic or arbitrary sampling is required.

Screening measurements of 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 occupational exposure limit values (OEL) 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.

10.2. Recommended Strategy

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 requiring homogeneous exposure groups (HEG). The comparison between the within-worker variability and the between-worker variability usually shows that the first can be significantly higher. Consequently, one job type will be preferably monitored several times over a given period rather than the whole team in a single day. Similarly, the field variability imposes a limit on the number of determinations to express annual levels of worker exposure (three being the minimum).

Three key steps can summarize the full worker exposure assessment:

1. Selection of the worker exposer groups (HEG).
2. Field measurements and analytics.
3. Data analysis (statistics), exposure level interpretation (HEG confirmation) and possibly risk assessment (occupational exposure limit comparison).

10.3. 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, a complete assessment would require five measurements per day with duplicates which is obviously limited by cost. AIHA recommends at least six random measurements per HEG in order to have representative means without a large variability [AIHA 2006]. Similarly, REACH makes the same recommendation in Europe. Six data points should be presented to adequately describe the exposure of a single work activity within one company [ECHA 2010]. 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 this is to say the comparison of an exposure level with a relevant OEL.

11. Cross-reading with existing exposure data

The comparison of original data with previous issued values is key. For large applications such as road paving, the average levels of exposures have been published on a regular basis. This comparison is also a way to check if the operating conditions are well managed. 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 literature shows overall homogeneous data for the last decade (GSD around 1.3).

12. Risk Assessment by Using the REACH Strategy

REACH places obligations on registrants (manufacturers and importers) to develop DNELs as benchmarks for determining safe levels of exposure for each defined scenario. 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 safety factors based on case-by-case expert judgement (since DNELs are being established as benchmark values for registration and risk management, national OELs remain the legal workplace control values).

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 (RCR = exposure value / DNEL) which must be below 1 [ECHA 2008]. 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 [ECHA 2010].

13. References

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14. Appendix 1: Typical Document for the Monitoring Survey

Date:	dd/mm/yy
Name of the company:	xxx
Trial :	xxx
Worksite:	xxx
Work purpose:	Road paving (motorway)
Worker name:	xxx
General weather conditions:	Sunny
Pump identification / Total pumping time:	xxx
Filter no.:	x
Adsorbent no.:	x
Worker-related conditions	
Worker protection (PPE)	Shoes, gloves & adapted clothes
Specific worker hygiene practices (e.g. hand washing)	Hand washing before eating
Smoking habits	5 cigarettes a day
Work clothing: bare parts of the body	Face only
Worker seniority in asphalt	16 years
Worker body mass index (height, weight, BMI)	1.80m, 85kg, 26.2
Job/task-related conditions	
Job class/title	Paver driver, senior
Dominant task (actual exposure duration)	Driving (200 min in total)
Distance between the source & worker (e.g. 1,5,10m)	4m

Process/material/equipment-related conditions	
Work process conditions	Paving with a large size paver
Source machinery/tool	2 pavers equipped with a feeder
Engineering controls (e.g. ventilation)	No
Production rate for the task / day	1600 tons
Paved area, layer thickness & length	6000 m^2, 13 cm, 500m
Average application temperature / Observed emissions	150°C, no blue smoke
Type of parent material	35/50 pen grade
Asphalt type & binder content	0/20 road base layer, 3.7% of binder
Used of tack-coat in priming road surface	Yes
Additional sources of contaminants	Use of diesel fuel
Fuel type used to power the machinery	Diesel fuel
Location-related conditions	
Workplace geometry especially the degree of enclosure	Countryside
Traffic	No (closed area)
Weather/season-related conditions	
Outdoor temperature (min/max/average)	14 / 28 / 24.5°C
Wind (up/down/cross/none; min/max/average direction)	Cross (West to East)
Wind speed (min/max/average)	0.5 / 2.0 / 1.0 m/s
Relative humidity (min/max/average) / precipitation	45 / 75 / 50 (no)
Atmospheric pressure (min/max/average)	1014 / 1018 / 1017
GPS coordinates/Elevation	T0383323 / UTM5386447 / 157m
Remarks	Paving direction: North-South

Date: dd/mm/yy	Name: xxxx
Time	**Event**
8.00 am	Arrival of the staff on site
8.30 am	Set-up of the individual equipment for monitoring
8.45 am	Start of the pumping time
9.00 am	Paver engine started
9.15 am	Paver in position
9.25 am	Arrival of the 1st truck (asphalt temperature: 145°C)
9.35 am	Start of paving operations; few fumes observed during asphalt pouring
9.45 am	Paving stopped; wait for the 2nd truck
9.55 am	Arrival of the 2nd truck (asphalt temperature: 155°C); paving restarts
10.10 am	Arrival of the 3rd truck (asphalt temperature: 160°C); paving continues
--------	*(repeated data removed in order to simplify this example)*
12.10 am	Cleaning of the paver
12.20 am	Arrival of the Xth truck; paving continues (asphalt temperature: 150°C)
12.35 am	Paving stops (break for lunch); paver engine stopped, pump stopped
1.00 pm	Pump restarted
1.15 pm	Arrival of the Yth truck; paving restarts (asphalt temperature: 170°C); blue fumes observed during paving
--------	*(repeated data removed in order to simplify this example)*
4.25 pm	Arrival of the last truck (asphalt temperature: 150°C)
4.40 pm	End of paving operations; paver cleaning
4.55 pm	End of the operations; pump stopped; individual equipment removed
Total monitored / pumping time	460 330 minutes

15. Appendix 2: Examples of Calculation

An operator spent 4 hours on a paver in the morning and 2.5 hours in the afternoon. The current working day was 8 hours included the journeys. The monitoring was conducted on site except for the lunch break. The sampling flow rate was 2 L/min (780 L pumped in total). The collected CSF on the filter is 0.10 mg.

Occupational Exposure Concentration (spot value)

The average exposure concentration to bitumen aerosols during the sampling periods is:

$$(0.10 / 0.78 \times 1) = 0.13 \text{ mg/m}^3.$$

Consequently, the 8h-TWA concentration is expressed as:

$$[(0.13 \times 4) + (0.13 \times 2.5)] / 8 = 0.10 \text{ mg/m}^3.$$

Within Worker Variability (GSD)

Similar monitoring is conducted for 6 days within 3 weeks. The six 8h-TWA concentrations are: 0.10, 0.12, 0.07, 0.19, 0.11 and 0.13.

The arithmetic mean is:

$$[(0.10 + 0.12 + 0.07 + 0.19 + 0.11 + 0.13)] / 6 = 0.12 \text{ mg/m}^3.$$

The geometric mean (GM) requires the use of logarithms (log-normal distribution). Consequently, the log-transformed values are: -2.30, -2.12, -2.66, -1.66, -2.21 and -2.04.

GM is expressed as the exponential of the average of the log-transformed values:

$$\text{EXP}\ [(-2.30 + -2.12 + -2.66 + -1.66 + -2.21 + -2.04) / 6] = 0.11 \text{ mg/m}^3.$$

As both average exposure concentrations to bitumen aerosols during these periods are very close (arithmetic and geometric means), it can be already assumed that the data set is not very skewed and scattered (GSD likely below 2). 0.12 mg/m^3 will be retained as expressing the exposure level.

A standard deviation is calculated from the log-transformed values (STD = 0.30). The resulting GSD is its exponential value: 1.35. Consequently, the set of values can be regarded as homogeneous (GSD < 3, HEG constitution).

Between Worker Variability (GSD)

A monitoring of a paving crew is conducted for 1 day. The six 8h-TWA concentrations are:

- Paver driver: 0.15
- Screedman 1: 0.11
- Screedman 2: 0.08
- Raker 1: 0.07
- Raker 2: 0.09
- Roller driver: 0.02

The geometric mean is 0.07 mg/m^3.

A standard deviation is calculated from the log-transformed values (STD = 0.63). The resulting GSD is its exponential value: 1.89. This set of values can be regarded as homogeneous.

Confidence Interval (CI)

For the current level of confidence used in industrial hygiene (95%), the mean is delimited by:

$$\pm 1.96 \times (\text{STD} / \text{root square of the measurement number}) = 1.96 \times 0.30 / (6)^{½} = 0.24$$

The log-transformed limit is -2.165. Consequently, the CI limits are (in log):

-2.165 – 0.24 = -2.405 which gives in concentration of (EXP) 0.09 mg/m^3

-2.165 + 0.24 = -1.925 .. .. 0.15 mg/m^3

The paver driver exposures have 95% of probability to be between 0.09 and 0.15 mg/m^3 (note that a measurement exceeded this interval). In other words, the probability to exceed these limits is 5% i.e. 5 days of 100 working days, roughly two weeks per year.

Maximum Worker Uptake

Usually the breathing rate of individuals on work places is 1.5 m^3/h. With this information, it is possible to calculate the maximum worker uptake which is the maximum amount of pollutant the worker may inhale. The uptake is calculated from the average atmosphere concentration, the breathing rate and the exposure duration:

$$0.12 \text{ mg/m}^3 \times 1.5 \text{ m}^3/\text{h} \times 6.5 \text{ h} = 1.17 \text{ mg}$$

Comparison of Worker Exposures

Another paver driver was monitored in another location and the purpose now is to assess if this second set of measurements is or not distinguishable from the first set. The 7 determined exposure levels are (8h-TWA): 0.10, 0.05, 0.07, 0.13, 0.11, 0.05 and 0.08 mg/m^3. GSD from log-transformed data = 1.42.

The variability calculations are based on the Student test (t-Test Two-Sample) for mean comparison assuming equal or unequal variances. T-Test starts with the hypothesis that the means are not distinguishable in terms of variability. A p-value (error probability) is determined. Following this value (< or > 0.05 for usual 95% of confidence level), the hypothesis will be or not rejected.

As there are two types of Student test (for equal or unequal variances), a Fisher test (F-Test Two-Sample) is preferred first for the variance analysis of each group. Fisher test determines which t-Test type is preferred (tuned calculations).

With the two sets of log-transformed data, Fisher test gives log-transformed averages of -2.16 and -2.53 and variability values of 0.11 and 0.14 respectively. The calculated p-value is 0.39 (i.e. 39% of error level if we reject the hypothesis that the variances are equal). As this value is largely above the 0.05 usually set, the two variances can be considered as equal.

Consequently, a t-Test assuming equal variance is conducted. The obtained p-value is 0.04 meaning 4% of error level if we reject the hypothesis that the mean of each group are similar. The determined error level being below the usual 0.05, the two means can be regarded as statistically distinguishable and the two averaged levels of exposures for the two paver drivers are 0.11 and 0.08 mg/m^3 respectively. There are likely variables (determinants) which could be investigated in order to explain such statistically difference in exposure levels.

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