Sampling and Analysis of Bitumen Fumes: Comparison of German and French Methods to Determine a Conversion Formula

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Abstract

Bitumen is classed as possibly carcinogenic to humans according to the International Agency for Research on Cancer. Data on individual exposure to bitumen fumes is therefore required to highlight the exposing situations and develop methods to prevent them. The Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) and the French National Research and Safety Institute for the Prevention of Occupational Accidents and Diseases (INRS) have both developed methods to measure individual exposure. The objective of this study was to determine a conversion factor to allow interconversion of data acquired by the two methods. To develop this conversion factor, comparative laboratory and workplace tests were performed according to both the IFA method (No. 6305) and the INRS method (MetroPol M-2). The amounts of organic material collected on the filters and XAD-2 beds were compared. The results revealed differences between the sampling and analytical methods that could be linked to sampler design, extraction solvent, and the detection method used. The total quantification returned by the two methods—the sum of the masses quantified on filter and XAD-2 bed for each sampler—were correlated in both controlled and real-life tests. A conversion equation was therefore determined, based on field tests: $C_{IFA} = 1.76 C_{INRS} + 0.39 \text{ } (R^2 = 0.99)$ that is applicable to total quantification data. This formula can be applied to data acquired by the two institutes to increase the number of data points available on exposure to bitumen fumes in various conditions, and thus increase the statistical power of studies into occupational prevention.

Keywords: analysing method; bitumen; fumes; method comparison; sampling method; semi-volatile aerosol
Introduction

In 2013, the International Agency for Research on Cancer re-classified straight-run bitumens and their emissions as class 2B, possibly carcinogenic to humans (IARC, 2013). It has therefore become even more important to assess individual exposure to bitumen fumes in road construction workers. In addition, recommendations must be made on practices, products, or design of the material used on sites to limit worker exposure.

To assess exposure to bitumen fumes, the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) and the French Research and Safety Institute for the Prevention of Occupational Accidents and Diseases (INRS) developed independent sampling and analysis methods for their own use. The methods consist of non-specific measurement of the fumes amount in the sampled air. As bitumen fumes are a complex mixture of hundreds of compounds, results act as indicators of exposure which are compared to respective limit values or recommendations. Both methods were developed and fully validated in line with the requirements of the standards EN 482 (CEN, 2012) and EN 13936 (CEN, 2014) in terms of performance, reproducibility, sensitivity, and sample storage.

IFA and INRS collect their individual exposure assessment data in databases. The German database is called ‘Measurement data relating to workplace exposure to hazardous substances’ (Messdaten zur Exposition gegenüber Gefahrstoffen am Arbeitsplatz in German) (MEGA) and the French one named ‘System for collecting exposure data from regional health insurance funds’ (Système de COLlecte des données d’exposition CHImique des Caisses régionales d’assurance maladie). Today, these databases are exploited individually and therefore offer a low statistical power when attempting to correlate hygiene recommendations (reducing bitumen temperature, setting up engineering control systems, installing windshields on finishers, etc.) with effective bitumen fume exposure concentrations for different classes of workers. The statistical power of observations could be significantly increased by merging the databases, thus leading to a better understanding of the effect of various hygiene recommendations for bitumen producers and users.

In a previous study (Kriech et al., 2010), the IFA method was compared to a number of alternative methods, including benzene soluble fraction (BSF), total particulate matter (TPM), total organic matter (TOM), and the method 5042 from the National Institute for Occupational Safety and Health (NIOSH) (NIOSH, 1998). But the correlation for paving bitumen fumes between the IFA method and the TOM method was weak ($R^2 \leq 0.78$) due to the differences of treatment in collection and analysis of the vapour fraction. The vapour content in bitumen fumes was since found to be non-negligible (Breuer et al., 2011; Sutter et al., 2016) and to vary as a function of the composition of the fumes or sampling conditions (Sutter et al., 2010; Dragan et al., 2015). These results mean that the BSF, TPM, and NIOSH 5042 methods are no longer considered relevant methods to assess exposure to bitumen fumes due to the fact that they do not consider the vapour fraction of the fume. The omission of the vapour fraction explains why results obtained with these methods correlated poorly with IFA results. Thus, only results obtained with the TOM method were related to those obtained with the IFA method. The TOM method uses a similar sampling system to the INRS method, but the extraction solvents, the chromatographic method using a gas chromatography and flame ionization detector (GC-FID), and calibration, all differ. Thus, results from TOM and INRS methods are expected to be non-identical.

In this paper, we describe a study performed by the IFA and INRS comparing their bitumen fume sampling and analysis methods. The aim of this study was to determine a conversion factor that could be applied to results to harmonize German or French quantification data.

To compare the methods, the study was performed in two parts. The first part was a laboratory comparison, where fumes were generated in perfectly controlled conditions from representative bitumen samples. This facet of the study allowed comparison of the methods in terms of sampler design and solvent extraction effect, as well as relative detector response/sensitivity. In the second part, the methods were subsequently tested in situ on German and French road construction sites, to determine the impact of uncontrolled environmental conditions and unknown bitumen products on the results returned by each method.

Material and methods

Sampling and analysis methods

The IFA and INRS methods are based on the same sampling principle: particles are collected on a filter and vapours passing through the filter are adsorbed on a bed of XAD-2 resin. However, the nature of the filter, the extraction, and analytical methods differ.

IFA method n°6305

IFA method No. 6305 ‘Bitumen (Dämpfe und Aerosole, Mineralölstandard)” (Breuer, 2008) has been used
in Germany to sample bitumen fumes since 2008. The inhalable dust-gas-sampling ‘Gesamtsstaub-Gas-Probenahme’ (GGP) system used by IFA to sample bitumen fumes is composed of an inhalable particle sampler, that includes a glass-fibre depth filter (1 µm liquid nominal pore size) for particle collection, and a 10-g XAD-2 amberlite resin cartridge (0.5–0.9 mm) to adsorb organic vapours. The method indicates a sampling flow rate of 3.5 l/min associated with a pressure drop of 2500 Pa.

As recommended in the method, material collected on the filter and XAD-2 cartridge were extracted separately in 10 ml of tetrachloroethylene (C₂Cl₄) for a minimum of 16 h. Extracts were stored at 4°C until analysis. Elements contained in bitumen fumes were detected by infrared absorption at the C-H aliphatic stretch frequencies (from 2800 cm⁻¹ to 3000 cm⁻¹). Predominantly aliphatic compounds or aliphatic chemical functions are detected at these frequencies by the infrared detector. A pool of four bitumen fume condensates was used for signal calibration.

INRS method MetroPol M-2
MetroPol method M-2 (INRS, 2015) is the current French method for sampling and analysis of bitumen fumes in workplaces; it was published by INRS in 2015. The sampling system includes a 37-mm polystyrene cassette (Millipore) containing a Polytetrafluoroethylene (PTFE) membrane (Zefluor™ 1.0 µm, 37 mm, Pall Life Science), and an XAD-2 amberlite sorbent tube (Orbo™ – 609, 400/200 mg, Supelco Analytical). The sampling flow rate was 1 l/min. Due to the pressure drop of about 12,400 Pa, a Sensidyne Gilian 5000 personal pump was used to manage the high-pressure drop induced by the sampler in all sampling situations.

In MetroPol method M-2, it is recommended that the extraction step be performed simultaneously on the PTFE membrane and the first bed of the XAD-2 sorbent tube, by placing them in the same extraction vial. However, to allow comparison with the IFA method No. 6, in this study, material was extracted from the collection substrates separately. Each substrate was extracted in n-heptane (n-C₇H₁₅) and the extract analysed by gas chromatography and flame ionization detector (GC-FID). N-hexadecane (C₁₆H₃₄) was used as a standard for the calibration of the GC-FID. More details on the analytical method are provided in Sutter et al. (2016).

Flow rate control pumps and sample storage conditions
GSA SG5100 personal pumps were used in tests performed in German workplaces. Sensidyne Gilian 5000 personal pumps were used to ensure the sampling flow rate for laboratory tests of both systems, and in French workplaces. Laboratory samples were stored at 4°C and field samples were stored at ambient temperature until analysis with a maximum storage time of 21 days.

Bitumen fume generation for laboratory test series
The bitumen fume-generation system was the one developed and validated by Sutter et al. (2016) in which the fume-generation conditions (temperature, concentration, and hygrometry of the fumes) and the temperature of the bitumens were fully controlled to ensure homogeneous exposure of the samplers (coefficient of variation [C.V.] = 3% for 12 samplers).

IFA samplers (n = 6) and INRS samplers (n = 6) were placed inside the exposure chamber for simultaneous exposure to the same humidified fumes. The system generated bitumen fumes at 170°C with a concentration ranging from 0.01 to 9.36 mg/m³ and a relative humidity ranging from 22 to 80%. The particle size of the fumes was consistent with values measured in workplaces. Details of the comparison between laboratory and workplace fumes can be found in Sutter et al. (2016).

Bitumen samples
The composition of bitumen fumes can differ depending on multiple parameters such as temperature, grade, fluxing additives, refinery, origins, etc. Therefore, the sampling and analysis methods must be tested on many different bitumens currently used in Germany and France.

For this study, four 35/50 grade hot road-paving bitumens, numbered 1 to 4, were provided by the French trade union of bitumen producers [Groupement Professionnel des Bitumes (GPB)]. Two other 25/55 and 70/100 grade hot road-paving bitumens, numbered 5 and 6, were provided by German producers. Since these bitumens were produced in the refineries that supply French and German road-paving companies, they were considered to be representative of the bitumen used on road construction sites in the two countries.

Equivalence of samplers
The aerosol sampling efficiencies of the two different samplers had previously been evaluated with non-volatile particles (Kenny et al., 1997; Kenny et al., 1999). Results of these studies demonstrated that the closed-face 37 mm cassette is less efficient than the GPP sampler for sampling of airborne particles measuring over 10 µm in calm air. Below this diameter threshold, the two samplers display close performances. Since bitumen fume particles, mainly fall below 10 µm (Brandt
and de Groot, 1999; Calzavara et al., 2003; Herrick et al., 2007), the total amounts (particles + vapours) collected in both type of samplers in this study is expected to be similar.

The first part of this study was to confirm this hypothesis and verify that the German and French sampling methods displayed equivalent sampling efficiencies for bitumen fumes. To do this, four IFA and two INRS samplers were exposed to the same fumes produced in the fume-generation setup described above, and in which bitumen type 4 was used as the source of fumes. The collection substrates from two of the IFA samplers and both INRS samplers were analysed using the INRS analytical method, with \( n \)-heptane as extraction solvent; collection substrates from the other two IFA samplers were extracted with tetrachloroethylene. The masses of organic compounds extracted were then determined by the INRS method and compared as a function of sampler type and extraction solvent.

**Method comparison**

The first part of this study also aimed to compare the two analytical methods in a laboratory generation system. The second part of this study was a field comparison where the samplers were exposed to real bitumen fumes on road construction sites.

**Laboratory comparison**

During each sampling session, six IFA samplers and six INRS samplers were placed inside the exposure chamber. Target fumes concentrations were 0.5, 2, and 5 mg/m\(^3\) for all bitumens and bitumen 4 was used for two supplementary concentration targeted at 0.1 and 20 mg/m\(^3\). Sampling times were adapted to keep the mass collected in the samplers above the quantification limit. A total of 20 different generation conditions were developed to determine effects on results due to the identity of bitumens, fume concentrations, and analytical methods. Initial results indicated that bitumens 1, 2, and 6 produced no quantifiable material on the filters for either sampler. This observation was confirmed in additional experiments. Thus, a total of 34 sampling sessions were performed.

**Workplaces comparison**

In field tests, six IFA and six INRS samplers were systematically placed as static samplers on the finisher used at the road construction site. Each sampler was identified and placed as close to the others as technically possible. Figure 1 shows where the samplers were placed during field samplings. Samplers were placed close to an emission source to collect a maximum of fumes over a minimum of 2 h. Thus, sampling could be repeated up to three times during a working day.

Due to design differences between German and French finishers, samplers could not be placed in identical positions on the finishers. On German finishers, the samplers were fixed to the outer wheel-covering of the finisher, whereas on French finishers they were fixed on the engine-cover.

Two additional samplers were used as the environmental blanks for each sampling session; they were placed at least 50 m from the construction site.

Environmental parameters, such as temperature, humidity, and atmospheric pressure were recorded for both German and French workplaces; wind speed was also recorded for German sites. All these data were acquired at 1 Hz throughout sampling sessions. A GRIMM aerosol spectrometer (model 11-A) was also used to measure the mass median diameter (MMD) and the geometric standard deviation (SD) \((\sigma_g)\) of the airborne particles in the air close to samplers; samples were taken every 6 s.

A first group of sampling sessions was scheduled for the 1st, 2nd and 3rd of December 2015 around the city of Arras in northern France; a total of 24 samples each were produced for the IFA and INRS methods over four sampling sessions. Bitumens having a 20/30 and 35/50 grade were applied at hot temperatures from 140 up to 190°C. A second group of sampling sessions was scheduled from the 2nd to the 4th August 2016, producing 42 samples for each method over seven sessions. Bitumens having a 50/70 grade were used at hot temperature from 180 up to 210°C. The environmental conditions recorded for these two groups of samplings were different, thus, any effect due to environmental conditions should be observable in the results.

**Statistical analysis**

All statistical analyses were performed using Statgraphics Centurion software.

**Method comparison**

Each of the 34 sampling sessions was composed by six IFA samplers and six INRS samplers producing two analyses by sampler for filters and adsorbents. Once the collection substrates were analysed by the corresponding IFA and INRS methods, the concentrations of fumes were statistically tested for normality using the Shapiro-Wilk test \((n = 6)\). For all sampling sessions, \(P\)-values were above 0.05 demonstrating the normality of the experimental data. Moreover, since the samples were generated inside a homogenized exposure chamber leading to less than 3% variability of the concentration on 12 samplers, the homoscedasticity of the data is assumed. Finally, the six concentrations are averaged for each sampling...
session: the studied data is composed of 34 averages for IFA and 34 for INRS.

For comparing IFA and INRS data, linear regressions were used as employed by Kriech et al. (2010). First, the possibility of removing the intercept so the slope of the linear regression would be a conversion factor was assessed. For this, regressions with intercept were computed and the 95% confidence intervals (CI) of the intercepts were compared to zero. All intercept values were included within the 95% CI except for the bitumen n°2 where the zero intercept value was included in the 97% CI of the intercept. Consequently, all regressions used for the later comparisons of the methods were performed without constant.

Since several linear regressions were computed, the assessment of the statistical differences between the slopes is performed by the analysis of covariance (ANCOVA). This procedure used the protocol described by Andrade and Estevez-Perez (2014), implemented in the Statgraphics software.

Field comparison

Regarding the field comparison, the variability of all collected data was assessed separately for France and Germany. The variables were tested for similarity using a t-test and F-test for averages and SD with the H₀ hypothesis that the parameters measured in Germany and France were similar (P > 0.05). The tested variables are temperature and humidity, aerosol characteristics measured by the Grimm spectrometer on field (MMD, σₔ), and concentrations in bitumen fumes analysed by both the methods.

Linear regressions on field data were done with the same procedure than for laboratory data, including the ANCOVA.

Results and discussion

Laboratory tests

Equivalence of samplers and extraction solvents

The data produced in laboratory on the amounts collected on the different sampler substrates are shown in Fig. 2. As n = 2 for each conditions, averages were directly compared taking into account a CI defined as ±3% of the average, corresponding to the variability of the concentration determined on 12 samplers exposed simultaneously to a fume generated inside the generation system.

The comparison of the averages indicated that INRS samplers extracted with n-C₇H₁₆, GGP extracted with n-C₇H₁₆, and GGP extracted with C₂Cl₄ all gave significantly different total concentrations as no interval is overlapping others. The mean total concentrations were determined at 7.39 ± 0.22, 8.04 ± 0.24, and 9.15 ± 0.27 mg/m³, respectively.

The effect of sampler design on the concentration measured was assessed by analysing the differences between IFA_n-C₇H₁₆ series and INRS_n-C₇H₁₆. The effect of extraction solvent on the concentration measured was assessed by comparing IFA_n-C₇H₁₆ and...
IFA-C2Cl4 series. The quantitative differences, expressed as percentages are reported in Table 1.

Focusing on filters, the design differences between the samplers (GGP versus 37 mm cassette), in terms of geometry and sampling flow rate, resulted in 4.5% higher quantification values with GGP than with the cassette. This result is consistent with the data from Görner et al. (2010), where differences in sampler design and sampling flow rate were reported to alter the particulate fraction sampled compared to the conventional inhalable particulate fraction.

The different extraction solvents also produced differences in the concentrations measured, with C2Cl4 extraction resulting in 8.6% higher values than n-C7H16. This result contrasted with the data reported by Sutter et al. (2015), where no significant differences were found between extraction solvents used to extract particles collected on filters.

Combining the effects of sampler design and extraction solvent, quantification of particles collected on filters by the IFA method returned values 13.5% higher than those determined with the INRS method. As already demonstrated by Dragan et al. (2015), the flow rate of the GGP, which is 3.5 times higher than that for the 37 mm cassette, causes the transfer of more semi-volatile material from the filter to the XAD-2. Differences in extraction efficiency for these solvents were also observed on XAD-2 beds (Sutter et al., 2015), but with a lower difference between n-C7H16 and C2Cl4 in comparison of the previous study (+ 24.3% against + 38%).

The values for total difference indicated in Table 1 are closely linked to the conditions in which fumes were generated (source bitumen, temperature, concentration, etc.). Therefore, they are not transferable to a general case.

### Laboratory comparison of methods

All data produced by the laboratory assay can be found in the Table 1 of the Supplementary Material.

### Total quantification of bitumen fumes

Total quantifications for all bitumen types, relative humidities, and bitumen temperatures are presented in Fig. 3.

A linear regression without constant could be fitted to the 34 observations (Fig. 3a). The slope of this curve

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**Table 1.** Mean percentage differences in concentrations ± max absolute differences, measured by the IFA method compared to the INRS method. Results are classed according to sampler type and extraction solvent.

<table>
<thead>
<tr>
<th>Type of sampler associated to the extraction solvent</th>
<th>Filter gap</th>
<th>XAD-2 gap</th>
<th>Total gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter gap</td>
<td>4.5 ± 1.1%</td>
<td>18.2 ± 8.4%</td>
<td>8.7 ± 1.8%</td>
</tr>
<tr>
<td>XAD-2 gap</td>
<td>8.6 ± 1.9%</td>
<td>24.3 ± 8.3%</td>
<td>13.9 ± 2.3%</td>
</tr>
<tr>
<td>Total gap</td>
<td>13.5 ± 0.9%</td>
<td>46.9 ± 2.3%</td>
<td>23.8 ± 1.2%</td>
</tr>
</tbody>
</table>
was 1.69 with $R^2 = 0.93$ demonstrating a correlation between the methods. The maximum dispersion was observed for values greater than 10 mg/m$^3$ according to the IFA method or 5 mg/m$^3$ as measured by the INRS method. In workplaces, values such as these would be encountered only exceptionally; therefore, the graph was redrawn excluding the highest concentrations (Fig. 3b).

The slope of the low values' linear regression was equal to 1.82 with $R^2 = 0.97$. Both regressions were not determined as significantly different (ANCOVA with $F$-test, $P = 0.74$).

Representing data points in Fig. 3b as a function of the different bitumen identities (Fig. 4) gives regression lines with $R^2$ of 0.94 or greater. The dispersion of x, y values observed for total bitumen fumes in Fig. 3b was statistically explained by the bitumens' identity (ANCOVA with $F$-test on the six regressions, $P = 0.0382$). Consequently, the different bitumen identities, in other word the individual compositions of the bitumens with different origins, lead to different methods performances. A maximum difference of 20.3% was calculated between the extreme slopes and the average slope of 1.82. Thus, in workplaces, the two methods are expected to return different quantification results if the bitumens used are identical to the ones tested in laboratory.

Filter and XAD-2 quantifications

Quantification data for samples collected on filters are shown in Fig. 5a. Quantifiable organic material was recovered from filters after sampling for only three of the six bitumens tested. The slope of the linear regression fitted to this data (1.12; $R^2 = 0.97$) was less than the slopes determined for total quantification data. Conversion of the slope to a percent difference would give +12.0% for the IFA method, which is very close to the difference between the two methods determined during the sampler equivalence test (+13.1% for the IFA method). Thus, the detection techniques (FT-IR and FID) had the same response for the material collected on filters.

Quantifications of the material collected on XAD2 beds (excluding high concentrations above 10 and 5 mg/m$^3$ for IFA and INRS, respectively) are shown in Fig. 5b. For all bitumens tested, organic matter was collected in quantifiable amounts on XAD-2 beds. The same quality of data fitting ($R^2 ≥ 0.94$) was obtained for data from XAD-2 and for total quantifications (Fig. 4). The average slope calculated from the XAD-2 quantifications represented in Fig. 5b is 1.95, which is equivalent to a percent difference of +94.8% between the two methods. As differences in sampler design and extraction solvent resulted in 42.5% higher values determined by the IFA method compared to the INRS method, the remaining +52.3% must be linked to differences in detector sensitivity for the material collected on XAD-2.

To understand this difference in detector sensitivity, the chromatographic method used in the INRS method was calibrated with a mixture of $n$-alkanes from $C_8$ to $C_{40}$. Based on this calibration, the chromatographic retention times for compounds collected on filters and XAD-2 could be converted to an equivalent carbon number (ECN). This conversion is a rough estimate of the molecular weight of the different compounds detected.
Each chromatogram was then integrated point-by-point to determine an area that was compared to the total area for each ECN and bitumen number (Fig. 6).

These data for material collected on filters indicate that 80% of the total matter corresponds to compounds with equivalent carbon numbers (ECN$_{80}$) ranging from C$_{25}$ to C$_{28}$. In contrast, the ECN$_{80}$ of the material collected on XAD-2 differed widely (C$_{13}$ to C$_{19}$). ECN$_{80}$ and the slopes determined in Fig. 5b were correlated by a linear model:

$$ECN_{80} = -11.56 \text{slope} + 36.82; R^2 = 0.89.$$

Based on these results, it appears that the difference in response between the IFA and INRS methods can mainly be explained by differences in detector response. These differences increase in magnitude for low ECN$_{80}$ values. In other words, the FT-IR detector quantifies much more material than FID when the material analysed has a low ECN$_{80}$.

To conclude on the comparison of laboratory results, sampler design, extraction solvent, and detector all significantly influence the amount of material quantified on filters or XAD-2. As the quantities of material collected on each collection substrate are expected to change as a function of the concentration of particles and vapours, the semi-volatile character of the fumes and thus, the nature of the bitumen, it was not possible to determine a correction factor for interconversion of results obtained by the different methods for each collection substrate. Thus, only the total quantification (filter + XAD-2) can be converted.

Field tests: comparing methods using data collected in workplaces

Environmental conditions

All data acquired in workplaces, including the atmospheric temperature, humidity, wind speed and pressure, particle count, the MMD, and the geometric SD calculated from the GRIMM spectrometer data can be found in the Table 2 of the Supplementary Material. To resume, the environmental condition of the German and French sessions were significantly different (all $P$-values < 0.05). The averaged environmental temperature was 29.8°C.
for German sampling sessions and 13.4°C for the French ones. The granulometry of the fumes and the concentration in particles were also significantly different.

The atmospheric temperature and humidity were significantly different between German and French workplaces, mainly due to normal variations between summer and winter. These differences could affect concentrations of particles and vapours, increasing the vapour quantity and reducing the airborne particle number at higher air temperatures.

The MMD confirmed this trend with a significant difference between data for the two countries, with an MMD of 1.31 µm for France associated with the lowest temperatures (13.4°C), compared to 0.44 µm for Germany, where the hottest temperatures were recorded (29.8°C). These MMD were similar to values measured during the laboratory comparison step.

The particle count (PC) was also significantly different between countries, with 34 times greater values measured for German workplaces than for French ones. The main reason for this difference is the bitumen temperature used in the workplaces—around 150°C in French workplaces compared to 190°C in German ones. A correlation between total particulate matter and bitumen temperature was previously reported (Brandt and de Groot, 1999; Brandt et al., 2000; Cavallari et al., 2012; Bolliet et al., 2015), although the PC was not measured in these previous studies. As demonstrated in the Quantification Comparison section of this paper, the total quantifications on the samplers were significantly higher for German samples than for French ones. As the MMD was lower for Germany than for France, the only way to obtain this result is to significantly increase the PC and the vapour concentration. This was confirmed by the PC determinations and also by the XAD-2 quantifications.

**Quantification comparison**

All quantification data related to workplace samples are reported in the Table 3 of the Supplementary Material. For all sampling sessions, the environmental blanks showed no quantifiable material, even though road traffic was not stopped in some workplaces. Thus, the values measured by the two methods correspond to bitumen fumes only.

The average quantifications for all sampling sessions were compared keeping data for the different methods separate (Fig. 7). The average concentrations, as determined using the INRS method, ranged from 0.51 to 4.9 mg/m³. A linear regression without constant gave an excellent fit with the dispersion of the averages, with a slope of 1.76 and $R^2$ of 0.99. The laboratory regression was very similar to the regression determined on workplace data, and is within the 95% CI for variations in workplace data. Thus, the two regressions are equivalent and agree well.

Significant differences between the medians and averages of the concentrations determined in Germany and France were identified. The concentrations measured in Germany were significantly higher than those measured in

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**Figure 6.** Relative cumulative mass determined from GC-FID chromatograms for material collected on filters (a) and XAD-2 (b) as a function of the equivalent carbon number for the different bitumen number.
France, with an average of 5.97 versus 2.77 mg/m³ determined by the IFA method (t-test, \( P = 2.97 \times 10^{-12} \)) and 3.37 versus 1.50 mg/m³ determined by the INRS method (t-test, \( P = 1.77 \times 10^{-11} \)). This difference could be explained by the very different environmental conditions between the two periods but also by the differences between the bitumens used during road construction operations and the conditions of use (e.g. temperature, finisher).

The SD of the concentrations determined in Germany were 1.58 for the IFA method and 1.01 for the INRS method, while SD were 1.21 and 0.65, respectively for the French sampling sessions. The greater SD for German sampling sessions can be explained by the dispersion between results for the six quantifications performed during each sampling session with a concentration gradient linked to the position of the samplers on the fixation system. In French workplaces, in contrast, the dispersion between samples taken at the same time was low and homogeneous around the average.

The samplers were placed on the finisher at variable distances from the bitumen distribution screw, where fumes are emitted in high quantity. Despite the gradation of the concentrations measured for the different sampler positions, all individual quantifications were well fitted by the workplace regression.

Figure 8a, b compares the average and individual concentrations determined for material collected on filters and XAD-2 by the two methods.

Unlike during German sampling sessions, no quantifiable material was detected on filters for any of the French sampling sessions performed in December, regardless of the method used. Although some types of bitumen produced particles that could be counted with the GRIMM spectrometer, these particles evaporated during the sampling time causing them no longer to be present on filters.

The workplace concentrations detected on filters therefore did not fit the laboratory regression (Fig. 8a). This discrepancy between laboratory and workplace data can be explained by different responses of the methods due to differences in composition of the material collected on the filters (Sutter et al., 2016). The material generated in the laboratory and collected on filters had higher molecular weights than the material generated in workplaces, with an equivalent median carbon number of 23 for laboratory samples compared to 14 for workplace samples. As the laboratory comparison test demonstrated, lighter material produces greater differences between the detectors used in the different methods, with a greater response of the FT-IR detector than the one of the FID detector for this class of particles. This difference produced steeper slopes in Fig. 5b.

The min and max slopes of the laboratory data are shown in Fig. 8b where the quantifications of material collected on XAD-2 and quantified by the two methods are compared. All the average workplace points fell between the extreme laboratory slopes. Thus, the responses of the methods were similar between laboratory and workplace assays. The dispersion of the individual data points indicates differences in the ECN80 between the sampling sessions leading to different responses of the methods.

As the ECN80 cannot be predicted for the materials collected on each samples, the responses of the methods cannot be corrected to account for the material collected separately on the collection substrates of the samplers. Furthermore, the INRS method recommends simultaneously quantifying material collected on both filter and XAD-2 substrates. Consequently, the ECN80 for the different collection substrates will not be available to correct the INRS quantifications based on the nature of the material collected.

Finally, even if some differences between the IFA and INRS methods were identified for different bitumen types/natures, the relationship between total quantification results is strong enough to allow conversion of the German and French data, making more exposure data available for statistical studies. This relation is defined by this unique equation at the 95% CI calculated on the averaged values as represented in Fig. 7:

\[
C_{\text{IFA}} = 1.76 C_{\text{INRS}} \pm 0.39
\]

where \( C_{\text{IFA}} \) and \( C_{\text{INRS}} \) are the total concentrations determined by the IFA and INRS methods, respectively.
Conclusion

IFA n°6305 and INRS MetroPol M-2 methods are similar in principle but differ in terms of sampler design, extraction solvent, and analysis method. The IFA method systematically gave higher quantifications than the INRS method.

Our results indicated that differences in sampler design account for 4.5 and 18.2% of the increase in quantification measured with the IFA method on filters and XAD-2 beds, respectively. This increase can be explained by differences in the particulate fraction sampled and by differences in the flow rate that enhance transfer of the semi-volatile material from filters to the XAD-2 bed during sampling.

Tetrachloroethylene extracts more material than n-heptane, leading to an increase of + 8.6% and + 24.3% of values determined by the IFA method on filters and XAD-2 beds, respectively.

A significant difference was also identified between the detectors used in the different methods. In laboratory conditions, the FT-IR detector and FID detectors returned similar results for material collected on filters with a stable difference of + 12%. In contrast, for material collected on XAD-2 beds, FT-IR systematically returned higher quantification results, with an average increase of + 52.3%. This difference can be explained by the quality of the material analysed by taking the equivalent carbon number into account. At low ECN, the FT-IR has a greater response than the FID, a trend that was confirmed in workplaces where the material collected on filter was lighter than the material collected during laboratory assays. In these conditions, FT-IR results were + 44% higher for material collected on filters in workplace assays compared to laboratory assays.

As the differences between the methods were well identified, it was possible to apply corrections to the results. However, the particle size distribution and concentration of the particles, the semi-volatile nature of the fumes and the equivalent carbon number for the material collected on filters and XAD-2 beds remain unknown during the sampling time. Consequently, it is not possible to specifically correct the results to account for those different effects. Thus, workplace quantification should only consider the total concentration, which is the sum of the material collected on the filter and XAD-2 bed.

In these conditions, a strong relationship was found between the two methods that can be summarized by this equation: $C_{IPA} = 1.76C_{INRS} \pm 0.39$. This relation was not affected by environmental conditions, even though they were drastically different in the workplace comparison step.

Therefore, the total bitumen fume concentrations measured using the IFA or INRS methods can be interconverted with a high level of confidence. Databases created in Germany and France should be combined to allow for more extensive analyses by type of work, equipment, engineering control equipment on finisher, and elaborate new hygiene recommendations.

Supplementary Data

Supplementary data are available at Annals of Work Exposures and Health online.

Declaration for Publication

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