Side-by-Side Comparison of Field Monitoring Methods for Hot Bitumen Emission Exposures: The German IFA Method 6305, U.S. NIOSH Method 5042, and the Total Organic Matter Method

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Field studies were conducted at paving and roofing sites to compare the German Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) Fourier transform infrared spectroscopy method 6305 with the National Institute for Occupational Science and Health (NIOSH) benzene soluble fraction method 5042 plus total organic matter. Sampling using both methods was performed in multiple bitumen-related workplace environments. To provide comparable data all samplings were performed in parallel, and the analytical data were related to the same representative bitumen condensate standard. An outline of the differences between the sampling and analytical methods is provided along with comparative data obtained from these site investigations. A total of 55 bitumen paving sampler pairs were reported and statistical comparisons made using the 35 pairs of detectable data. First, the German inhalable aerosol data and the NIOSH benzene soluble fraction (BSF) method showed a correlation coefficient of $R^2 = 0.88$ ($y_{(BSF)} = 0.60 \times_{(aerosol)}$). Second, the aerosol data compared with total particulate matter (TPM) show a R^2 of 0.83 ($y_{(TPM)} = 1.01 \times_{(aerosol)}$). Finally, total organic matter (TOM) and "aerosol + vapor" data yielded a R^2 of 0.78 ($y_{(TOM)} = 0.44 \times_{(aerosol+vapor)}$). Twenty-nine pairs of roofing data were also collected; 37% were below the limit of detection. When comparing the TOM data with the aerosol + vapor data, using the 13 of 29 pairs where both samplers showed detectable results, the relationship was $y_{(TOM)} = 0.74 \times_{(aerosol+vapor)}$ ($R^2 = 0.91$). The slopes within these equations provide predictive factors between these sampling and analysis methods; intended for use with large sets of data, they are not applicable to single point measurements.

Keywords asphalt, bitumen fume, IFA (BGIA) 6305, method comparison, NIOSH 5042

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INTRODUCTION

B itumen (asphalt), a product made from petroleum crude oil, contains a large and complex mixture of compounds and is used in a variety of applications, especially road construction, roofing, and other waterproofing applications. In the United States, "asphalt" refers only to the binder material, whereas in Europe, the binder material is called "bitumen" and the term "asphalt" refers to the final product mix of binder and mineral aggregates.

During placement of bitumen and its products, employees are potentially subjected to aerosol and vapor emissions consisting mainly of aliphatic hydrocarbons, cyclic alkanes, and low levels of polycyclic aromatic compounds.[1] These emissions can vary in composition and concentration (depending on the source of the bitumen), the application temperature, manufacturing conditions, and weather and other environmental variables that often complicate the task of monitoring bitumen fume exposure. Elucidation of all of the individual compounds present with bitumen fumes is not a practical measure for exposure monitoring. Therefore, summation measures have been employed to estimate the exposure.

The International Agency for Research on Cancer (IARC) conducted a comprehensive nested case control study of bitumen workers in Europe that showed no evidence of an association between bitumen emissions and lung cancer in bitumen workers.[2] The Fraunhofer Institute of Toxicology and Experimental Medicine completed a 2-year inhalation study that showed no statistically significant increase in total and organ-specific tumor incidence for the bitumen emission exposed group as compared with a clean air control group.[3] Although bitumen fumes were not considered tumorigenic to rats, this study did show signs of irritation effects in the nasal

passages and the lungs.[3] This is consistent with other research that has identified acute eye and upper and lower respiratory irritation associated with bitumen emission exposure.[4,5]

Internationally, there are different approaches used to collect emissions from bitumen. Occupational exposure limits (OELs) are related to the Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA, formerly, German Berufsgenossenschaftliches Institut für Arbeitssicherheit [BIA], and Berufsgenossenschaftliches Institut für Arbeitssicherheit [BIA]) Institute for Occupational Safety and Health of the German Social Accident Insurance method 6305[6] and NIOSH method 5042.[7] In Germany, the OEL covers both the aerosol and vapor components of emissions, whereas only the aerosol fraction is taken into account for the U.S. threshold.

Results of exposure monitoring studies are often used within occupational and environmental epidemiologic studies and risk assessment. For example, the International Agency for Research on Cancer (IARC)[3,8,9] conducted an international epidemiologic mortality study among European bitumen workers on almost 80,000 people with mortality follow-up during 1953–2000. Studies of pavers and roofers have suggested increased cancer risks in these occupations. Although these workers may have had exposure to bitumen, many also had confounding exposure to coal tar pitch. The IARC database included methods of assessing worker exposure that varied, making it difficult to directly compare exposure data. Quantification and characterization of exposure to bitumen fumes has suffered from a lack of standard sampling and analytical procedures.[10] Modeling programs have been designed to account for some of these parameters,[11] but it is important to understand the differences between analytical methods to interpret exposures.

German threshold limits for vapors and aerosols of bitumen were assigned in 1996[12] to 15 mg/m^3 for working outside but were reduced to 10 mg/m^3 on January 1, 2000. In 2005, the limit value was deleted as well as all other technically based values not medically derived.[12] In the United States, the National Institute for Occupational Science and Health (NIOSH) has issued a recommended exposure limit of 5 mg/m^3 based on the total particulate matter (TPM) as a 15-min ceiling. In addition, the ACGIH® has a threshold limit value of 0.5 mg/m^3 for bitumen fumes measured as benzene extractable inhalable particulate as an 8-hr time-weighted average,[13] shown to be equivalent to the benzene soluble fraction (BSF) for bitumen fumes.[14−16] This variety in international approaches presents a problem when subsequent measurements are compiled for epidemiologic studies, since each method may be measuring different fractions of bitumen emissions.

An international study by Ekström et al.[16] has already determined relationships between side-by-side samplers using a laboratory fume generation system; the German method reported lower values compared with U.S. data for the aerosol portion, but higher values for the aerosol + vapor or total organic matter (TOM). Four out of five laboratories used gas chromatography with flame ionization detection (GC/FID) for

quantitation of these parameters, whereas the German lab employed Fourier transform infrared spectroscopy (FTIR). Every sampler was slightly different, in addition to many of the analytical methodologies. Specifically, the German sampling method was the only FTIR-based method and used mineral oil as a reference standard. The aerosol fraction was lowest compared with all other data reported from the five other samplers as benzene solubles.

Ekström and colleagues speculated that the higher sampling flow rate and the use of mineral oil as a reference standard may have been contributing factors to these differences. Conversely, the TOM was within the range of the other samplers. High and low levels of fume generation were collected in triplicate runs; both levels were higher than seen in the field, and the authors acknowledged that field studies may show different results.

The current study was designed to evaluate and compare methods of bitumen fume exposure monitoring using various types of bitumen and application conditions *in the field* focusing on IFA method 6305 and NIOSH method 5042. An XAD-2 sorbent tube is frequently used in conjunction with the NIOSH method and was included for comparison in this study. This combination sample collection system is similar to that described in NIOSH method 5800[17] and has been used in numerous studies in combination with NIOSH method 5042 for bitumen fume studies[18−21] to allow collection of the aggregate volatiles and semivolatile compounds present in bitumen emissions.

METHODS

Workplace samples were collected in parallel at various bitumen operations in Europe and in the United States. In this current study, the aerosol values reported from the IFA method were compared with the BSF data reported from the NIOSH method. Similarly, the aerosol + vapor data reported from the IFA method were compared with the TOM data reported from the Heritage method.[18,19]

Field Collection and Analysis
Field Information

The paving process between the two countries is very similar, with comparable equipment used for the application process. Sampling was conducted on a variety of projects, including conventional paving, paving within a tunnel, and polymer-modified bitumen paving. Sample collection occurred both on the workers and in work areas. Workers wore the two sampling systems, seated right and left on the shoulders to have nearly the same height within the breathing zone.

Specific to Germany, some samples were collected during paving of mastic asphalt (manual application).[22] The mastic asphalt was delivered in mobile transportation mixers (up to where the work site is accessible) then transferred into carts, depending on the distance to the processing site. Mastic asphalt was spread manually to the desired thickness and then leveled with a wooden float or screed. The average bitumen temperature during mastic sample collection was 250°C,

substantially higher than the typical hot-mix asphalt paving temperature ($\sim$149–177°C[1]). During this process, since workers were on their hands and knees to spread the mix, their inhalation zone was closer to the hot bitumen than their normal standing position during road paving applications.

The manufacture of bitumen rolled-roofing products is essentially the same in both countries. Production takes place in a partly enclosed, exhaust-ventilated production line. After delivery, the bitumen or polymerized bitumen is mixed with filler to form the desired coating material. In the coating phase, the felt or glass fiber mat is passed through a bitumen bath for impregnation and coating. Finally, the respective surface protection (i.e., sand, slate, tallow, granulate) is added. The finished membrane is cooled down and then packaged into rolls. Measurements for this study took place at two stationary points at the open bitumen bath.

During roofing applications, the bitumen membranes are rolled out and torched with a propane/butane gas burner or an electric gas heater, allowing the bitumen to liquefy to allow adhesion to the roof deck while the membrane is unrolled slowly. On some work sites the whole membrane was heated. On other work sites only part of the overlapping membrane (10 cm to 20 cm) was heated. These types of application processes are common to both countries and produce minimal exposures compared with hot bitumen mopping applications (built-up roofing bitumen) performed in the United States.

For direct comparison of the different measurement techniques, harmonization of sampling times, and placement of samplers and reference substances occurred during this study. In the United States, the sampling period included the entire work shift. In Germany, the sampling time was consistent with the exposition period. In this study all sampling at the construction sites in both Europe and the United States were done in parallel and simultaneously (average paving time 5.6 $\pm$ 1.79 hr; roofing 4.31 $\pm$ 1.62 hr). For worker sampling, the parallel position of the NIOSH and IFA samplers was randomly distributed on the left and the right side of the worker to minimize possible influence of the sampler position (e.g., right-hander–left-hander, wind speed and direction, position to the source of emission). In the same way, stationary parallel measurements were performed at places with the highest potential of bitumen emissions.

IFA Method

Using the German sampler (PGP-System GGP;[23] GSA Messgerätebau GmbH, Neuss, Germany), aerosols of bitumen were sampled on a glass fiber depth filter (1 μm liquid nominal pore size) and the vapors on 3 g of XAD-2 resin (0.5–0.9 mm size) according to IFA method 6305.[6] This closed-face sampler was used for measuring substances occurring in both particle and vapor phases where the inlet air passes through an inlet cone. After the collected aerosols and vapors were extracted with tetrachloroethylene, the extracts were analyzed using FTIR. Bitumen is a residue of crude oil distillation processes and emissions upon heating contain mainly straight-chain aliphatic hydrocarbons. Therefore, the characteristic C-H-stretch absorption region between 2800–3000 cm^{-1} was used for FTIR quantification.

Mineral oil (CAS 8042-47-5) was used for calibration of the FTIR. However, since the composition of this standard differs significantly from that of the bitumen fume condensate, a correction factor was calculated during this study and applied to the IFA measurement.[24] Worldwide, no certified reference material for bitumen emissions is available. In this study, a paving and roofing fume condensate that had been validated to field exposures[25] was compared with the mineral oil response. The infrared response of the bitumen condensates was less than the mineral oil calibration standard. As a result, the calibration for this study was related to a paving bitumen condensate (factor 1.425) and a roofing bitumen condensate (factor 1.292). All three calibrations (mineral oil, bitumen paving, and roofing fumes) showed a linear response > 0.9985 for five concentrations between the limit of quantification (LOQ) and the upper working range.

NIOSH Method 5042

Using NIOSH method 5042,[7] the aerosols of bitumen plus particulate dust were sampled on a SKC 2.0-μm, 37-mm PTFE filter (225-27-07, and opaque cassettes 225-4; SKC Inc., Eighty Four, Pa.) and analyzed gravimetrically for TPM and BSF. After equilibration of the filter to minimize effects of moisture, the filter was weighed to determine TPM. Next, the filter was extracted with 3 mL benzene (cat. no. 270709; Sigma-Aldrich; St. Louis, Mo.) then filtered (Whatman 6-mL filter tube, 1.0 μm pore size made of PTFE; cat. no. 09-930-30c; Fisher Scientific; Pittsburgh, Pa.). One and one-half mL of the filtered extract were transferred to a pre-weighed weighing boat and gently evaporated to dryness to provide a gravimetric measure of the benzene soluble fraction of that particulate, reported as the BSF. Sampling pumps were operated at 2 L/min, and five cassette blanks were analyzed with each set of samples.

Addition for TOM sampling (Heritage Method)

In addition to collecting the BSF, Heritage and others have included an XAD-2 (SKC Inc. 226-30-04) tube after the PTFE filter to capture the volatile components of the fume.[18–21] The combination of the BSF and the more volatile compounds from the XAD-2 is defined here as TOM, referred to as the Heritage method. To accommodate the addition of a sorbent tube, NIOSH method 5506[26] prescribes a cellulose support spacer ring (SKC, cat no. 225-23) in place of the solid pad to allow easy flow of the volatile exposures into the connecting sorbent tube.

To analyze the TOM, an XAD-2 sorbent tube was attached in series with the NIOSH filter to capture the more volatile components that get stripped from the filter during a typical workday sampling event. These tubes (SKC, 226-30-04) contain a total of 150 mg of XAD-2 (100 mg front section/50 mg back section). The sorbent tube was extracted with 10 mL

TABLE I. Differences between IFA (BGIA) 6305 and NIOSH 5042 Plus Heritage Methods

	IFA (BGIA) 6305/2 Aerosol	Vapors	NIOSH 5042 TPM, BSF	Heritage TOM
Media	Glass fiber filter (37 mm) 1 μm pore size	XAD-2 cartridge (3 grams)	PTFE (37 mm) 2 μm pore size	XAD-2 tube (150 mg)
System	PGP-GGP system		Closed-face filter cassette	Tube connected in series with the filter
What it measures	C-H stretch region (2800-3000 cm^{-1})		Total dust, then benzene soluble portion of the dust	Total organic matter ~(C7-C42)
OELs	10 mg/m^3 as aerosol + vapors (withdrawn 2005 - based on mineral oil standard)		0.5 mg/m^3 as benzene soluble inhalable particulate (8-hr TWA)	No threshold
Solvent	Tetrachloroethylene		Benzene	Methylene chloride
Analysis	Fourier transform infrared (FTIR)		Gravimetric	Gas chromatography with flame ionization detection (GC/FID)
Calibration Standard	Mineral oil (used bitumen condensate since this study)		Class S weights	Bitumen fumes of similar boiling point range or gasoline, kerosene and/or diesel fuel standards
Intake opening	7.7 mm		4.0 mm	
Flow rate	3.5 L/min		2.0 L/min	
Intake velocity	1.25 m/s		2.6 m/s	
Typical collection time with one sampler	2–5 hr (for this study up to 8 hr)		6–10 hr (for this study can be less)	
Information provided	Determines organic, TCE soluble substances containing C-H stretch captured on the filter	Determines organic, TCE soluble substances containing C-H captured on the XAD-2	Non specific. TPM measures all dust; BSF measures benzene soluble portion of dust	Hydrocarbon chromatogram produced
Advantages	Easy procedures. Differentiates between aerosol and vapor phases		Easy procedures	More specific information provided such as simulated distillation and patterns. Can differentiate bitumen fume from some other organic matter
Disadvantages	Bitumen particulates and other organic confounders could be included in the results	Other organic confounders could be included in the bitumen fume results	Uses carcinogenic extraction solvent; bitumen particulates and other organic confounders could be included in the results, doesn't collect volatiles, spurious high blank values, variable LODs and LOQs	Requires a higher level of operator expertise for quantification. Standards used for quantification may vary depending on boiling point range
Range	0.2–100 mg/m^3		TP = 0.13–2 mg/sample BSF = 0.14–4 mg/sample	1.36–100 mg/sample
Precision	0.006–0.068 in a range from 0.2 to 25 mg/sample		TP = 0.048 at 0.1 mg/sample BSF = 0.061 at 0.21 mg/sample	1.34
Estimated LOD	0.10 mg/sample^A		0.04 mg/sample^B	0.420 mg/sample
Estimated LOQ	0.20 mg/sample^A		0.04 mg/sample^B	0.924 mg/sample

^{A}All performance data are calculated for the overall method to measure bitumen vapor and particulates, LOD = yB + 3 SD$_B$; LOQ = yB + 10 SD$_B$.

^{B}Determined using field blanks. LOD = 3 × SD of field blank weight differences (FBWD). LOQ = 10 × FBWD.

dichloromethane (HPLC Grade OmniSolv High Purity; cat. no. DX0831-1; EMD; Gibbstown, N.J.), and 5 mL of the extract was combined with the BSF residue and used for TOM analysis by GC/FID. This followed the SW 846-8015 protocol,[27] modified to accommodate bitumen fume quantification. A Varian model 3400 GC with a 1077 split/splitless injector (set at 250°C) and a flame ionization detector (set at 310°C) were used, along with a 5% phenyl /95% methylpolysiloxane column (30 m × 0.33 mm ID, 0.25 μm film thickness, RTX-5; Restek US, Bellefonte, Pa.); helium was the carrier gas set at 2 mL/min. The injection volume was 2.0 μL, and the oven temperature started at 40°C held for 3 min, increased to 120°C at 9°C/min and held for 0.5 min, ramped up to 305°C at 11°C/min, held for 10.89 min. Flame ionization detectors are advantageous in that they exhibit a uniform response to hydrocarbons. Calibration occurred using a kerosene standard (FU-005N Neat; AccuStandard, Inc., New Haven, Conn.) to determine the concentrations of the TOM samples. Kerosene is compositionally similar to bitumen fumes. Both contain primarily aliphatic hydrocarbons, with lesser amounts of branched chain hydrocarbons and even lower levels of polycyclic aromatic compounds (alkylated > parent).

Table I provides a detailed outline of the differences between the NIOSH (plus TOM) and IFA sampling and analytical protocols, including the range, precision, LOD, and LOQ.

Statistical Analysis

Statistical analysis and graphs were obtained using Sigma Plot software (Version 12; Systat Software, Inc., San Jose, Calif.) and "analyse-it" (Version 2.20, Analyse-it Software, Ltd., Leeds, UK). The regression was forced through the origin to allow calculation of a factor between the two sampling systems. Both models with and without intercept were calculated. All models were significant. Because of plausible considerations, only models without intercept are presented. The underlying assumption is that without exposure, any measurements result has to be zero. The intercept is significant only for TOM vs. aerosol + vapor for paving results.

Calculations for the paving data were made only on the pairs of data that had detectable results for all parameters, allowing comparison of 35 of 55 pairs. Since the roofing data had only three detectable pairs of data for all parameters; data that were detectable for the TOM and aerosol + vapor were used for the analysis (13 of 29 pairs).

RESULTS AND DISCUSSION

All results are shown for both samplers. However, only those pairs where both samplers show results above the respective method detection limits are used in the correlation and data analysis.

Paving Samples

Sites were sampled over a 2-year period from June 2006 until May 2008 for a total of 55 pairs of data from paving-related job functions. Figure 1 shows GC/FID chromatograms from two of the exposures collected using the TOM fraction. In addition to providing quantitative data, these chromatograms show qualitative differences. The bottom chromatogram labeled "machine" is typical of unconfounded bitumen paving fumes showing a normal Gaussian-shaped petroleum distillate pattern. The top chromatogram, labeled "bystander" is similar but contains additional peaks in the 8–11 min region, likely from a nonpetroleum based source. Table II provides the paving data from all sites. Statistical analysis of the paving data is provided in Table III for the 35 detectable pairs. Overall, only 17 of 55 filters for BSF had reasonable loading defined as ≤0.2 mg/filter (below 0.2 yields poorer precision[7]). Table II shows a GSD of 3.95 for the BSF; slightly higher than the variation seen by Deygout et al.[28] at 2.77.

As shown in Figure 2A, TPM was generally similar to the aerosol portion with the relation described by the function $y_{(TPM)} = 1.01 \times_{(aerosol)}$ ($R^2 = 0.83$). BSF, the organic portion of the TPM, showed a slightly stronger correlation ($R^2 = 0.88$) with the aerosol data, which also represents organic matter (Figure 2B), described by the function $y_{(BSF)} = 0.60 \times_{(aerosol)}$. TOM, the organic portion of the bitumen fume as determined by GC/FID, shows a reasonable correlation ($R^2 = 0.78$) to the aerosol + vapor data analyzed by IR (Figure 2C), described by the function $y_{(TOM)} = 0.44 \times_{(aerosol+vapor)}$.

Examination of the percentage of volatiles (compounds captured on the XAD-2) of the total fume showed an average value of 84.8% and 84.4% for the German and U.S. samplers, respectively. The IFA method measures this parameter separately, whereas the "volatiles" for the U.S. sampler is a calculated value (TOM–BSF). This is based on the 35 pairs of data in Table II that show detectable results for both parameters shown to be statistically similar. Because the sampling times were the same for each sampler type, this close relationship is not surprising.

Roofing Samples

All roofing industry sampling occurred in Europe from November of 2005 until May of 2008 on sites in the Netherlands, Italy, Sweden, and Germany during torch-applied or blower-applied application of rolls of bitumen. A total of 29 pairs of data from roofing applications were sampled and compared.

Concentrations of bitumen fumes collected during these roofing processes are listed in Table IV; results are generally low and often below the LOQ (59%). Since the purpose of this study was to examine the differences between results using two different samplers, 25 nondetectable samples (determined using the FTIR method) taken were not sent to the United States for analysis. In Table IV there are six instances where BSF is detectable but TOM is not. This is a function of the difference in detection limits between the gravimetric vs. GC/FID methods (~10-fold higher).

Table V outlines the statistical data for the roofing samplers where comparative data were obtained. For aerosol and BSF, only three pairs of data were detectable for both samplers; only two of 29 filters for BSF had reasonable loading. Table IV
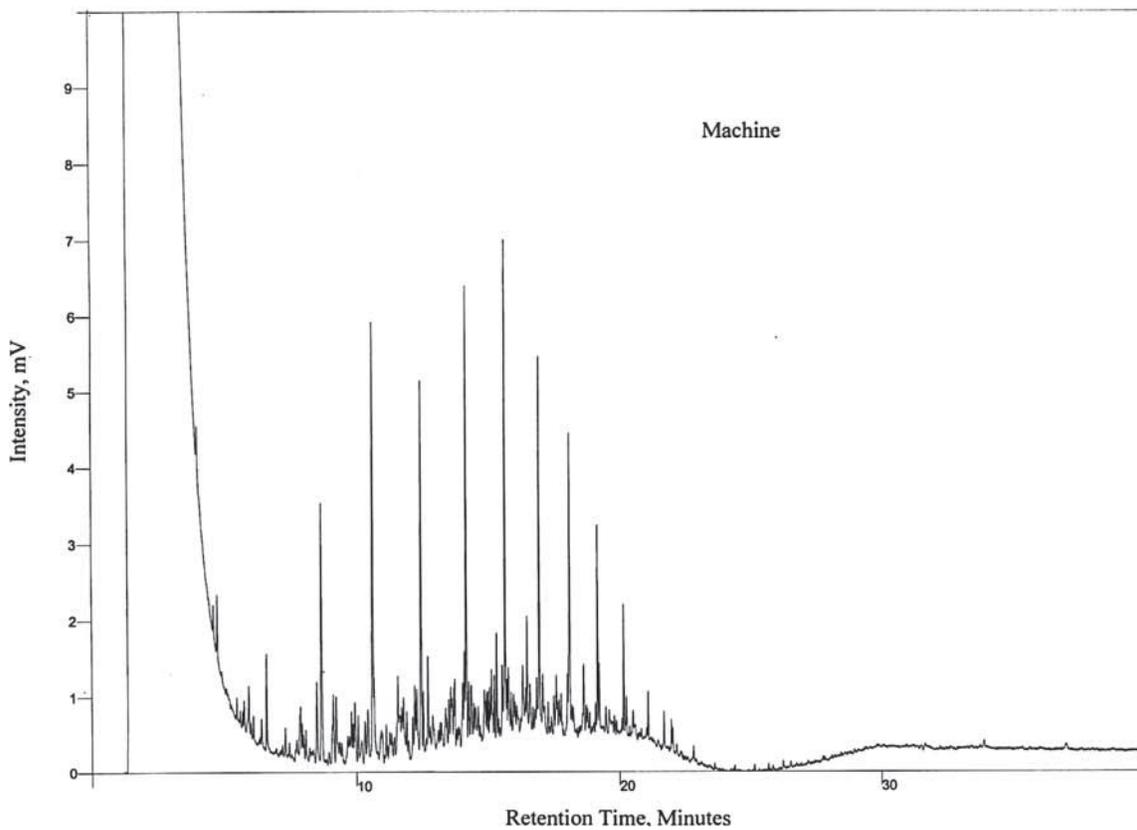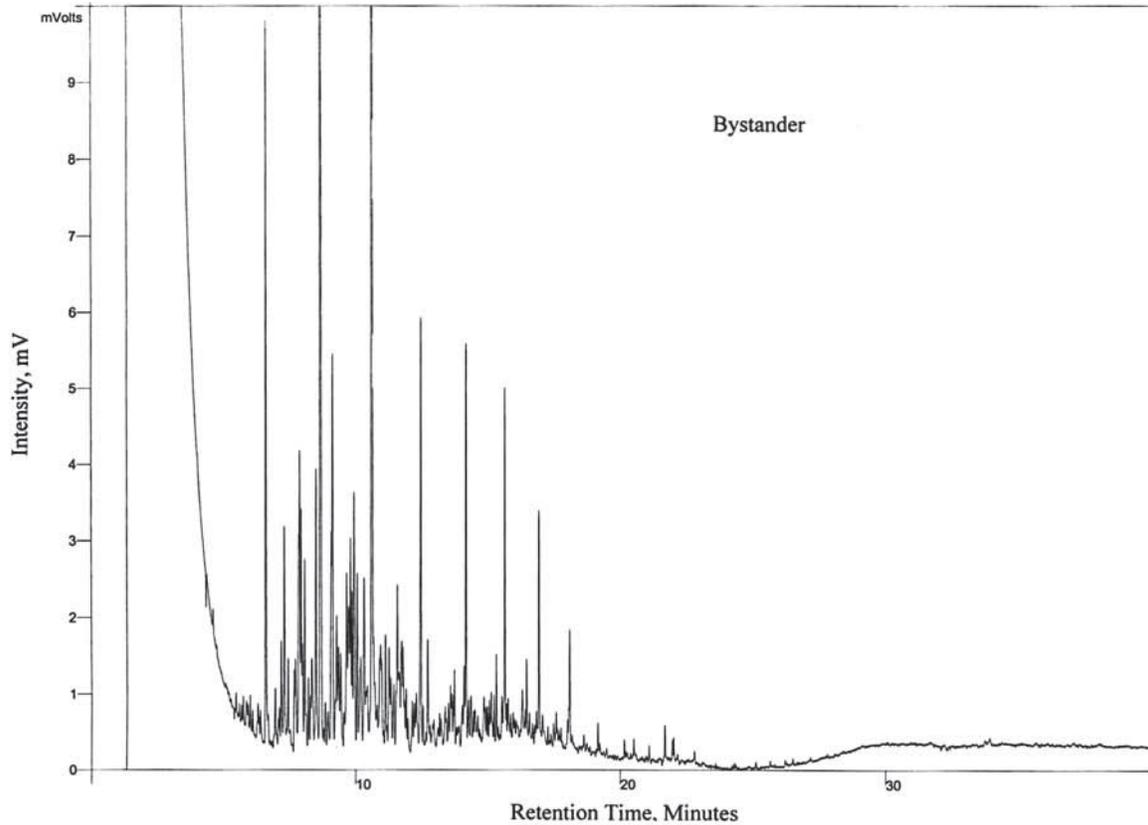
FIGURE 1. GC/FID example chromatograms of paving site emissions. The bottom chromatogram is typical of unconfounded bitumen paving fumes, whereas the top chromatogram contains additional peaks in the 8- to 11-min region.

TABLE II. Paving Site Comparison Data (n=55 pairs)

Site Location/Date	Description	Sampling Time (hr)	Flow Rate (L/min)	TPM (NIOSH) mg/m³	BSF (NIOSH) mg/m³	TOM (Heritage) mg/m³	Aerosol (IFA) mg/m³	Aerosol + Vapor (IFA) mg/m³
Gelsenkirchen, Germany, April 11, 2006	Mastic asphalt	3.37	2.00	2.31	1.61	7.01	3.12	4.26
Dresden, Germany, June 27, 2006	Indoor flooring	3.37	2.00	4.30	3.52	6.67	4.83	6.39
		5.00	2.00	4.55	0.82	0.93	2.10	3.80
		5.17	2.00	2.15	0.17	1.91	0.98	2.40
Bottrop, Germany, July 3, 2006	Conventional bitumen paving	5.17	2.00	3.40	1.01	2.28	2.10	3.60
		2.50	2.00	0.14	0.03	< 0.84	1.10	3.20
		2.50	2.00	0.25	0.04	< 0.84	0.80	3.10
Dillenburg Tunnel, Germany, November 22, 2006	Paving machine	2.50	2.00	0.24	0.08	< 0.84	0.56	1.80
		8.00	3.50	0.29	0.09	0.39	0.29	2.35
		2.00	3.50	0.41	0.16	4.81	1.03	4.55
		4.00	3.50	0.25	0.11	1.01	0.44	2.79
	Bystander left	4.00	3.50	0.23	0.13	0.58	0.44	3.08
	Bystander right	2.00	3.50	0.20	0.06	2.36	< 0.74	7.05
Indianapolis, Indiana May 4, 2006	Screed area	2.00	3.50	0.31	0.23	0.98	< 0.74	6.90
		6.00	1.99	1.61	1.19	6.98	0.88	10.07
		6.00	1.99	1.46	1.02	5.44	1.61	17.81
	Operator area	6.00	2.01	1.19	0.88	7.56	1.31	19.86
		6.00	2.02	0.31	0.14	1.51	0.58	3.07
		6.00	2.00	0.37	0.11	1.66	0.29	2.92
Indianapolis, Indiana May 5, 2006	Screed area	6.00	2.00	0.33	0.09	1.44	0.29	2.77
		5.42	2.03	0.65	0.50	6.75	0.58	5.99
		5.42	2.00	1.03	0.88	7.78	1.61	13.9
	Operator area	5.42	2.01	1.00	0.85	7.41	1.17	16.9
		5.42	1.95	0.14	0.05	1.15	0.28	2.19
		5.42	2.01	0.20	0.08	1.20	0.29	2.34
Indianapolis, Indiana May 8, 2006	Screed area	5.42	2.02	0.13	0.04	1.43	0.28	1.90
		6.00	2.01	0.13	< 0.04	0.70	< 0.24	1.31
		6.00	2.00	0.31	0.07	0.95	< 0.24	1.17
	Operator area	6.00	2.02	0.40	< 0.04	0.67	< 0.24	1.46
		6.00	2.02	0.10	0.06	< 0.50	< 0.24	0.58
		6.00	2.01	0.10	0.06	< 0.50	< 0.24	0.73
Indianapolis, Indiana May 9, 2006	Screed area	6.00	2.00	0.07	< 0.04	< 0.50	< 0.24	1.17
		6.00	1.97	0.24	0.06	2.15	< 0.24	3.21
		6.00	2.00	0.20	< 0.04	2.05	0.29	3.21
	Operator area	6.00	2.01	0.22	< 0.04	1.84	0.29	3.36
		6.00	2.01	0.50	< 0.04	1.01	< 0.24	1.61
		6.00	2.02	0.65	< 0.04	0.94	< 0.24	1.46

TABLE II.   Paving Site Comparison Data (n=55 pairs) (Continued)

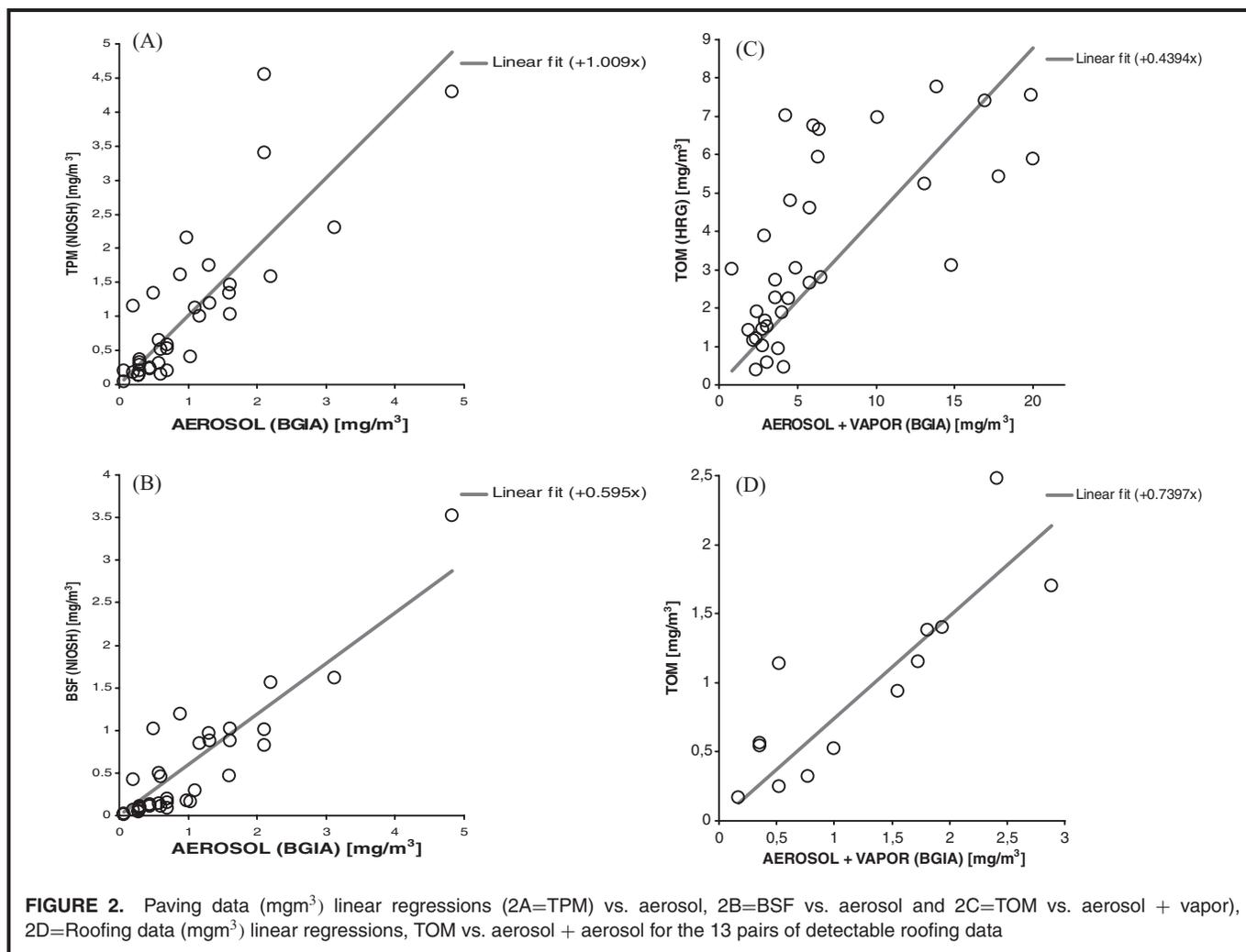| Site Location/Date	Description	Sampling Time (hr)	Flow Rate (L/min)	TPM (NIOSH) mg/m^3	BSF (NIOSH) mg/m^3	TOM (Heritage) mg/m^3	Aerosol (IFA) mg/m^3	Aerosol + Vapor (IFA) mg/m^3
Dusseldorf, Germany August 14, 2007	Conventional asphalt Paving	6.00	2.02	0.71	< 0.04	1.00	< 0.24	1.31
		8.00	2.00	0.04	0.01	2.73	0.07	3.60
Ueberherrn, Germany August 21, 2007	Conventional asphalt paving	8.00	2.00	0.20	0.02	2.66	0.07	5.80
		8.00	2.00	0.21	0.09	1.89	0.70	4.00
		8.00	2.00	1.58	1.56	5.23	2.20	13.1
Mainz, Germany, May 6 2008	Tunnel	8.00	2.00	1.34	1.02	3.88	0.50	2.90
		8.30	1.95	1.12	0.29	5.88	1.10	20.0
		8.27	1.95	1.34	0.47	3.12	1.60	14.8
		7.98	1.95	0.56	< 0.04	1.25	0.20	5.00
Feldmoching, Germany May 7–8 2008	Polymer modified asphalt	7.70	1.95	1.15	0.42	2.80	0.20	6.50
		3.50	2.07	0.08	< 0.10	1.64	0.50	2.70
		4.55	2.05	0.07	< 0.08	1.37	0.30	1.80
		2.97	2.07	0.15	0.11	3.04	0.60	4.90
Gross-Gerau, Germany May 13-16 2008	Open air	5.00	2.05	0.51	0.45	2.24	0.60	4.40
		7.62	1.95	1.75	0.96	4.62	1.30	5.80
		7.55	1.95	0.53	0.15	0.46	0.70	4.10
		7.45	1.95	0.58	0.19	5.94	0.70	6.30
Dresden, Germany, June 27, 2006	Indoor flooring	7.45	1.95	0.17	0.06	3.02	0.20	0.80
		3.37	2.00	2.31	1.61	7.01	3.12	4.26

shows a GSD of 3.64 for the BSF, similar to the paving GSD of 3.95. Thirteen pairs are above the detection limit for both aerosol + vapor and TOM. These 13 pairs show an R^2 of 0.91 ($y_{(aerosol+vapor)} = 0.74 \times _{(TOM)}$) (Figure 3). Evaluation of the percentage of volatiles in the total fume yielded similar results to that of the paving data set (79.7% German, 83.5% U.S.).

TABLE III. Statistical Data-Paving Sites (n=35 pairs)

mg/m^3	NIOSH		HRG TOM	IFA/(BGIA/2)	
	TPM	BSF		Aerosol	Aerosol + Vapor
Average	1.06	0.55	3.53	1.00	6.57
Std. dev.	1.13	0.69	2.39	0.97	5.51
Geometric mean	0.61	0.26	2.65	0.66	4.91
Geo std. dev.	3.11	3.95	2.32	2.65	2.14
Minimum	0.04	0.01	0.39	0.07	0.80
Maximum	4.55	3.52	7.78	4.83	20.0

It was observed that when examining the GC/FID chromatograms from samples collected during production of roofing bitumen-membrane (Figure 4), two samples contained detectable levels of TOM, whereas the torch-applied roofing sites produced TOM values < 1 mg/m^3, and the chromatographic patterns were unremarkable. Two distinctly different patterns are seen in Figure 4, yet both samples were collected during production of roofing bitumen membrane. Neither pattern reveals a typical distillate pattern as normally seen for bitumen fumes (Figure 1, bottom chromatogram). As it is hypothesized that these compounds may be from materials other than bitumen in the roofing sheets released during production, future research is planned to investigate the composition.

IFA aerosol concentrations are consistently larger than BSF for the paving samples, both related to the organic fraction of the aerosol. BSF determinations involve evaporation of solvent, whereas no evaporation occurs during the IFA method, possibly contributing to some loss. Despite these differences, the percentage of volatile organics of the TOM was similar between samplers averaging 85%, consistent with previous studies.[29]

FIGURE 2. Paving data (mgm³) linear regressions (2A=TPM vs. aerosol, 2B=BSF vs. aerosol and 2C=TOM vs. aerosol + vapor), 2D=Roofing data (mgm³) linear regressions, TOM vs. aerosol + aerosol for the 13 pairs of detectable roofing data

Both for paving and roofing samples, linear regressions were calculated to prove an association between the IFA and U.S. measurements (Table VI). It is shown that there are conversion factors for the different measurements (Figures 2A–D). To demonstrate the quality of the conversion factors, Bland-Altman plots were also calculated (Figures 3A–D) and include the bias and 95% limits of agreement.

Log-normal distribution was tested for TOM, BSF, TPM, aerosol, and aerosol + vapor. In all cases, results differ significantly from a normal distribution but not from a log-normal distribution. Therefore it was assumed that the values are distributed log-normally.

Although no difference in solubility was observed for bitumen emissions in the different solvents within a spiking study, solubility of bitumen particulates may be slightly different for benzene than for tetrachloroethylene, which may contribute to differences in results. European countries do not use benzene in their methods due to its carcinogenicity; it is also not suitable for IR use. Bitumen does not elute during the GC/FID TOM program due to its high molecular weight. Bitumen is, however, detected by IR.

Based on triplicate injections of a kerosene standard, a paving fume condensate[25] and a roofing fume condensate,[25] the GC/FID response (area/concentration) was 11790.97, 12262. 26, and 8732.08, respectively. The fume condensate materials are not commercially available. However, the bitumen paving fume response was within 3.9% relative standard deviation (RSD) of the kerosene standard, whereas the roofing fume response was only 74.1% of the kerosene response (an RSD of –29.8%).

Based on this data, the kerosene standard was used as reference standard for quantification of the bitumen fumes for this study (all patterns were within the boiling point range of the kerosene). Patterns from the roofing bitumen samples were unlike those of the roofing fume condensate standard based on built-up roofing asphalt (BURA) processes in the United States. Since European roofing does not generally use BURA, this difference was not surprising. It is hypothesized that the few peaks detected in the bitumen roofing samples may be from other additives and not from bitumen.

Although not a part of the NIOSH method, advantages of adding the GC/FID approach include its ability to provide
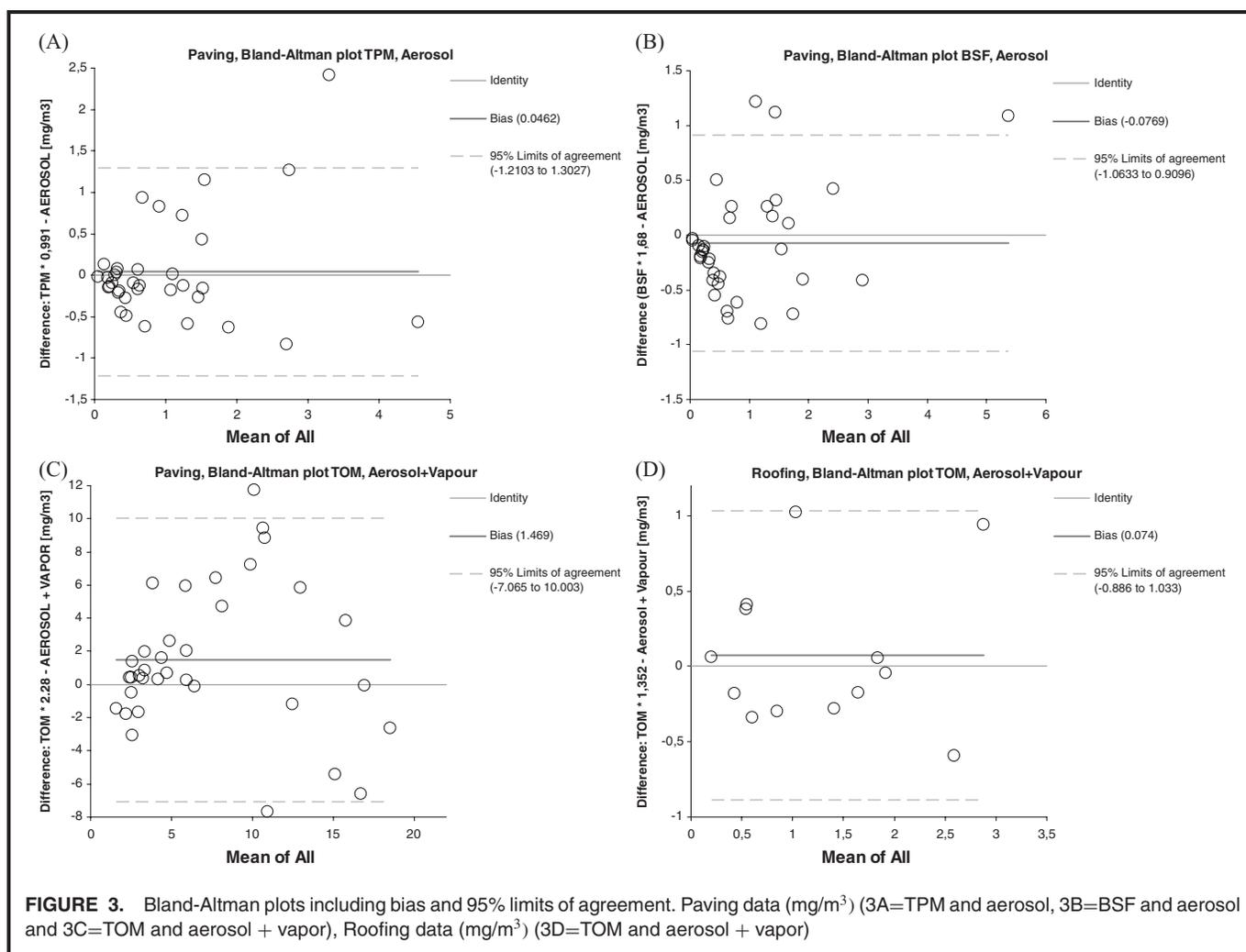
TABLE IV. Roofing Site Comparison Data (n=29 pairs)

Site Location/Date	Description	Sampling Time (hr)	Flow Rate (L/min)	TPM (NIOSH) mg/m^3	BSF (NIOSH) mg/m^3	TOM (Heritage) mg/m^3	Aerosol (IFA) mg/m^3	Aerosol + Vapor (IFA) mg/m^3
Burbach, Germany 11/18/2005	Production of bitumen-membrane	4.00	2.00	1.56	0.14	0.52	0.27	1.00
Ijlst, Netherlands 2/28/2006	Production of bitumen-membrane	6.00	2.00	0.72	$\leq$0.04	2.48	0.35	2.41
Groningen, Netherlands 3/1/2006	Production of bitumen-membrane	6.00	2.00	1.46	$\leq$0.04	1.40	0.26	1.94
Verona, Italy 9/29/2006		6.00	2.00	0.44	$\leq$0.04	$\leq$0.69	0.52	0.77
Helsingborg, Sweden 10/18/2006	Production of bitumen-membrane	3.92	2.00	1.36	$\leq$0.04	1.70	0.61	2.89
Bremen, Germany 3/31/2008	Roofer	5.33	2.00	0.98	$\leq$0.04	1.38	0.52	1.81
Altenstadt, Germany 4/4/2008	Roofer	5.25	2.00	0.92	$\leq$0.04	0.94	0.39	1.55
Augsburg, Germany 4/11/2008	Roofer	1.50	2.00	2.78	$\leq$0.04	$\leq$2.77	2.58	3.61
Pfullingen, Germany 4/17/2008	Roofer	2.50	2.00	0.54	0.13	0.25	$\leq$0.52	0.52
Düsseldorf, Germany 4/23/2008	Roofer	4.00	2.00	0.82	0.05	0.32	$\leq$0.32	0.77
Neuss, Germany 4/30/2008	Roofer	2.00	2.00	0.18	0.13	$\leq$2.75	$\leq$0.43	$\leq$0.43
Leipzig, Germany 4/28/2008	Roofer	2.00	2.00	0.12	$\leq$0.33	$\leq$2.75	$\leq$0.43	$\leq$0.43
Braunschweig, Germany, 5/6/2008	Roofer	5.80	2.00	0.10	$\leq$0.05	$\leq$0.44	0.26	0.52
Gersthofen, Germany 5/9/08	Roofer	6.40	2.00	0.12	$\leq$0.05	$\leq$0.44	0.26	0.43
Neumünster, Germany 5/5/08	Roofer	6.00	2.00	0.69	0.17	$\leq$0.68	0.26	0.35
Gehrden, Germany 5/13/08	Roofer	2.58	2.00	0.27	0.07	$\leq$1.10	0.69	1.12
Strasbourg, France 5/27/08	Production of bitumen-membrane	3.92	1.95	0.19	$\leq$0.09	$\leq$0.72	$\leq$0.22	$\leq$0.22
Strasbourg, France 5/28/08	Roofer	3.80	1.95	0.18	$\leq$0.09	$\leq$0.74	$\leq$0.22	$\leq$0.22
Strasbourg, France 5/29/08	Roofer	3.92	2.00	0.13	$\leq$0.09	$\leq$0.70	$\leq$0.22	$\leq$0.22

a chromatogram showing the boiling point characteristics of the exposures, possibly distinguishing between bitumen fumes and other confounders. Neither the IFA method 6305-2 (aerosol only) nor the NIOSH method 5042 (TPM/BSF) is selective for bitumen fumes. When the FTIR data are nondetected, that absence of fume is generally substantiated with the NIOSH and TOM data. To avoid false positives, confirming the presence of bitumen fumes using the GC/FID method may be helpful.

Because the aim of the survey was to compare samplers, many area samples were taken but with no intention for the data to draw conclusions about typical full-shift exposures to workers.

In addition to the complicated nature of bitumen fumes and work environments, variation in field measurements from one sampler to another make comparison using the same methodologies difficult. The situation represents a worst-case scenario for comparing analytical results given that (1) there are various combinations of three different analytical instruments/methods (FTIR, gravimetric, GC/FID); (2) there are three different solvents used across the methods to desorb or dissolve the samples at some stage of analysis (tetrachloroethy-

FIGURE 3. Bland-Altman plots including bias and 95% limits of agreement. Paving data (mg/m³) (3A=TPM and aerosol, 3B=BSF and aerosol and 3C=TOM and aerosol + vapor), Roofing data (mg/m³) (3D=TOM and aerosol + vapor)

lene, benzene, dichloromethane); (3) there is uncertainty regarding the equivalence of different calibration standards (mineral oil, bitumen condensate, or other hydrocarbon standards); and (4) a significant number of the samples were below detection limits of one or more methods.

The presence or absence of solid bitumen particulates on the filters and the chemical composition of the fumes also affected the quantification of exposure. Bitumen fumes involve sufficiently small particle size (<1 μm) such that either sampler should provide capture of this exposure.[14,30] The German sampler may allow entry of more nonfume particles in air,

TABLE V.   Statistical Data-Roofing Sites (n = 13 pairs)

| mg/m³ | NIOSH | | HRG | IFA/(BGIA/2) | |
	TPM	BSF	TOM	Aerosol	Aerosol + Vapor
Average	0.85	0.16	0.97	0.25	1.23
Std. dev.	0.41	0.20	0.67	0.18	0.88
Geometric mean	0.76	0.08	0.74	0.20	0.91
Geo std. dev.	1.66	3.64	2.23	2.10	2.42
Minimum	0.32	0.02	0.17	0.08	0.17
Maximum	1.56	0.71	2.48	0.61	2.89

TABLE VI.   Correlation Coefficients and Slopes Between the NIOSH Methods, IFA Method, and Heritage (TOM) Method for Paving and Roofing

Type of Bitumen	Parameters	Formula	R²
Paving	IFA aerosol vs.TPM	y = 1.01 ×	0.83
	IFA aerosol vs. BSF	y = 0.60 ×	0.88
	IFA aerosol + vapor vs. TOM	y = 0.44 ×	0.78
Roofing	IFA aerosol + vapor vs. TOM	y = 0.74 ×	0.91

Note: For data sets generated prior to 2008,[24] slopes must be multiplied by 1.4689 to normalize to bitumen fume condensate.
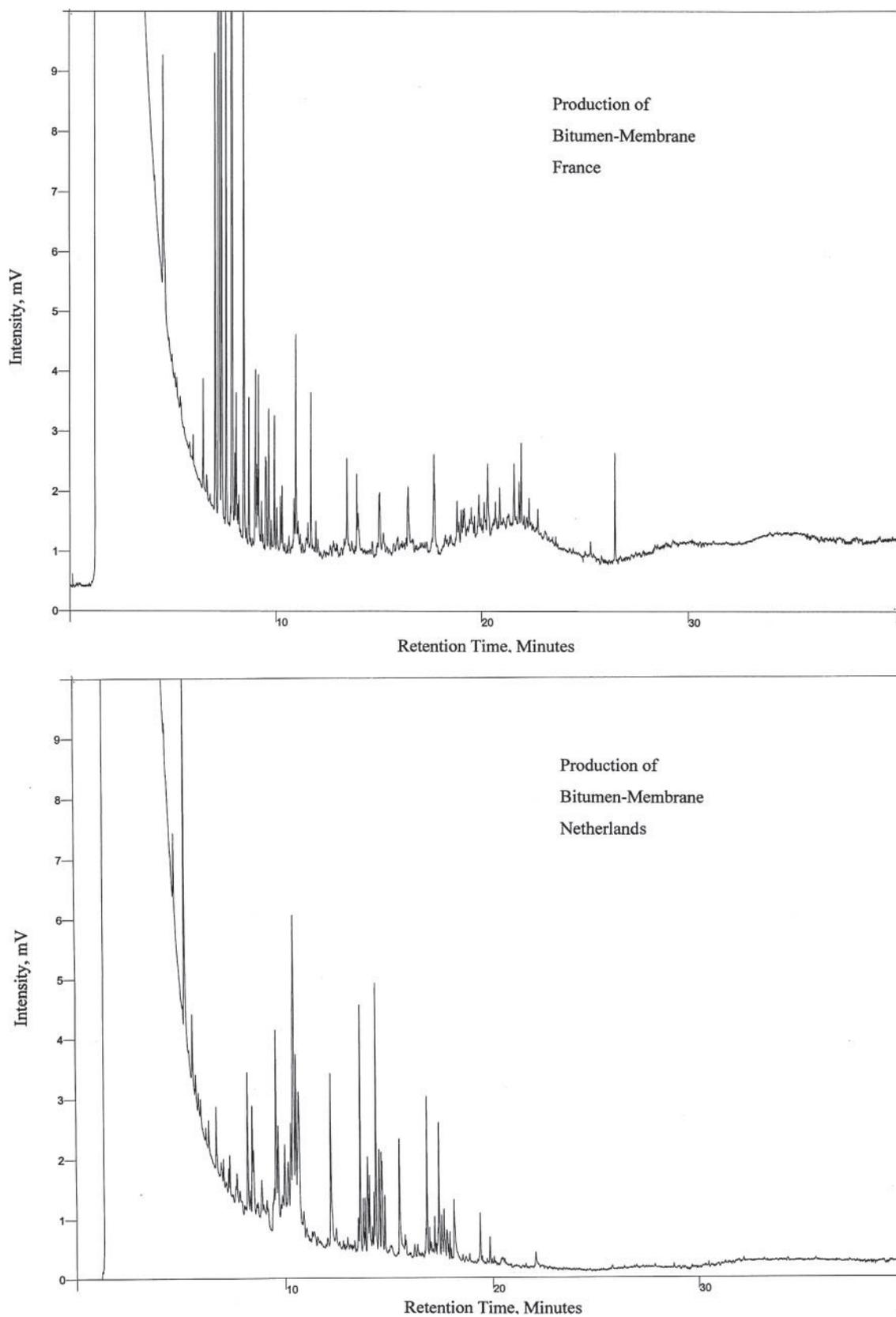
FIGURE 4. GC FID chromatograms from samples collected during production of roofing bitumen-membrane. Typical asphalt fume peaks are more like those shown in Figure 1. Torch-applied roofing sites produced < 1 mg/m³ of TOM.

whereas the NIOSH sampler may have a negative bias for large particles, appropriate for bitumen fumes with an average size of 0.89 μms, but not for particulates larger than 1 μm.[14] Kriech et al.[14] showed that the BSF for the NIOSH sampler (4-mm orifice) was 0.05 mg/m^3 on average compared with the IOM sampler (15-mm orifice) at 1.37 mg/m^3 for a milling site where bitumen particulates were the primary exposures (no fumes present). By extrapolation, the German sampler would have detected 0.50 mg/m^3 based on its 7.7-mm orifice, all of which was due to bitumen particulates from the milling process.

Historically, data collected using the IFA sampler are related to an occupational exposure limit value that includes both aerosols and vapors, whereas the data collected with the NIOSH sampler are related to limit values that refer only to aerosols. Therefore, a comparison between the different systems is reduced to a comparison of the aerosol vs. TPM and BSF data.

CONCLUSIONS

Despite significant method differences there appears to be a relationship between samplers. Within the paving data, there is a high correlation coefficient (R ^{2} = 0.88) between the aerosol and BSF data with a calculated correlation of $y_{(BSF)} = 0.60 \times_{(aerosol)}$. A similar correlation coefficient existed between the aerosol data and the TPM data (R^2 = 0.83) with a comparison of $y_{(TPM)} = 1.01 \times_{(aerosol)}$. Finally, a slightly weaker correlation coefficient existed between the aerosol + vapor data and the TOM data derived with the Heritage method (R^2 = 0.78: $y_{(TOM)} = 0.44 \times_{(aerosol+vapor)}$).

For the roofing data, results were too low in concentration for the samples to statistically assess aerosol vs. BSF fractions. However, for the aerosol plus vapor (TOM) fraction, a strong positive correlation is shown between the samplers (R^2 =.91: $y_{(TOM)} = 0.74 \times_{(aerosol+vapor)}$).

To correlate the data determined by the NIOSH method with the data determined by the old IFA method 6305, the factor 1.4689 has to be considered (IFA 6305/2[31]). This accounts for the response differences between mineral oil and bitumen fume condensate.

Although the factors generated within this study will be useful as predictors of results among the three sampling and analysis methods for large data sets, they should not be applied to single-point measurements because of the variability.

ACKNOWLEDGMENTS

REFERENCES

1. **National Institute for Occupational Safety and Health (NIOSH):** Hazard Review: *Health Effects of Occupational Exposure to Asphalt*. DHHS (NIOSH) Pub. No. 2001-110. Cincinnati, Ohio: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, NIOSH, 2000.

2. **Olsson, A., H. Kromhout, M. Agostini, et al.:** A case-control study of lung cancer nested in a cohort of European asphalt workers. *Environ. Health Perspect.* 118:1418–1424 (2010).

3. **Fuhst, R., O. Creutzenberg, H. Ernst, et al.:** 24 months inhalation carcinogenicity study of bitumen fumes in Wistar (WU) rats. *J. Occup. Environ. Hyg. 4(Suppl. 1)*:20–43 (2007).

4. **Tepper, A.L., G.A. Burr, H.A. Feng, et al.:** Acute symptoms associated with asphalt fume exposure among road pavers. *Am. J. Ind. Med.* 49:728–739 (2006).

5. **Ma, J.Y.C., M.W. Barger, A.J. Kriech, et al.:** Effects of asphalt fume condensate exposure on acute pulmonary responses. *Arch. Toxicol.* 74:452–459 (2000).

6. **Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA):** *Measurement of Hazardous Substances—BGIA Arbeitsmappe [BGIA working Folde], Method 6305: Determination of Exposure to Chemical and Biological Agents*. Bielefeld, Germany: Erich Schmidt Verlag, 1997.

7. **National Institute for Occupational Safety and Health (NIOSH):** Method 5042, Benzene-soluble fraction and total particulate (asphalt fume). In *NIOSH Manual of Analytical Methods*, 4th ed., No. 98-119. P.M. Eller and M.E. Cassinelli (eds.). Cincinnati, Ohio: NIOSH, 1998.

8. **Burnstyn, I., P. Boffetta, D. Heederik, et al.:** Mortality from obstructive lung diseases and exposure to polycyclic aromatic hydrocarbons among asphalt workers. *Am. J. Epidemiol.* 158:468–478 (2003).

9. **Boffetta, P., I. Burstyn, T. Partanen, et al.:** Cancer mortality among European asphalt workers: An international epidemiological study: I. Results of the analysis based on job titles. *Am. J. Ind. Med.* 43:18–27 (2003).

10. **Burstyn, I., H. Kromhout, and P. Boffetta:** Literature review of levels and determinants of exposure to potential carcinogens and other agents in road construction industry. *Am. Ind. Hyg. Assoc. J.* 61:715–726 (2000).

11. **Burstyn, I., P. Boffetta, G.A. Burr, et al.:** Validity of empirical models of exposure in asphalt paving. *Occup. Environ. Med.* 59:620–624 (2002).

12. *German Ordinance on Hazardous Substances* (Verordnung zum Schutz vor Gefahrstoffen (Gefahrstoffverordnung), BGM1. I S 3758. Berlin, Germany, December 23, 2004.

13. **ACGIH:** *2010 TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*. Cincinnati, Ohio: ACGIH, 2010.

14. **Kriech, A.J., L.V. Osborn, H.L. Wissel, et al.:** Total versus inhalable sampler comparison study for the determination of asphalt fume exposures within the road paving industry. *J. Environ. Monit.* 6:827–833 (2004).

15. **Calzavera, T.S., C.M. Carter, and C. Axten:** Air sampling methodology for asphalt fume in asphalt production and asphalt roofing manufacturing facilities: Total particulate sampler versus inhalable particulate sampler. *Appl. Occup. Environ. Hyg.* 18:358–367 (2003).

16. **Ekström, L., A. Kriech, C. Bowen, et al.:** International studies to compare methods for personal sampling of bitumen fumes. *Environ. Monit.* 3:439–445 (2001).

17. **National Institute for Occupational Safety and Health (NIOSH):** Method 5800. Polycyclic aromatic compounds, total (pacs). In *NIOSH Manual of Analytical Methods* (*NMAM*), 4th ed., No. 98-119, P.M. Eller and M.E. Cassinelli (eds.). Cincinnati, Ohio: NIOSH, 1998.

18. **Kriech, A.J., J.T. Kurek, H.L. Wissel, et al.:** Evaluation of worker exposure to asphalt paving fumes using traditional and nontraditional techniques. *Am. Ind. Hyg. Assoc. J.* 63:628–635 (2002).

19. **Kriech, A.J., L.V. Osborn, D.C. Trumbore, et al.:** Evaluation of worker exposure to asphalt roofing fume: Influence of work practices and materials. *J. Occup. Environ. Hyg.* 1:88–98 (2004).

20. **McClean, M.D., R.D. Reinhart, L. Ngo, et al.:** Inhalation and dermal exposure among asphalt paving workers. *Ann. Occup. Hyg. 48(8)*:663–671 (2004).

21. **Herrick, R.F., M.D. McClean, J.D. Meeker, et al.:** Physical and chemical characterization of asphalt (bitumen) paving exposures. *J. Occup. Environ. Hyg. 4(Suppl 1)*:209–216 (2007).

22. **Rühl, R., U. Musanke, K. Kolmsee, et al.:** Vapours and aerosols of bitumen: Exposure data obtained by the German Bitumen Forum. *Ann. Occup. Hyg. 50(5)*:459–468 (2006).

23. **Buchwald, K.:** Device for sampling substances, which are present in particle and vapor form. In *BGIA Folder*, Sheet 3040. Bielefeld, Germany: Erich SchmidtVerlag, 2005. pp. 1–3.

24. **Breuer D.:** Bitumen (Dämpfe und Aerosole, Bitumenkondensat-Standard) Method 6305-2. In *Measurement of Hazardous Substances—BGIA Arbeitsmappe (BGIA Folder), Determination of Exposure to Chemical and Biological Agents*. Bielefeld, Germany: Erich Schmidt Verlag, 2008.

25. **Kriech, A.J., L.V. Osborn, H.L. Wissel, et al.:** Generation of bitumen fumes using two fume generation protocols and comparison to worker industrial hygiene exposures. *J. Occup. Environ. Hyg. 4*:1,6–19 (2007).

26. **National Institute for Occupational Safety and Health (NIOSH):** Method 5506. Polynuclear aromatic hydrocarbons by HPLC. In *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed., No. 98-119. P.M. Eller and M.E. Cassinelli (eds.). Cincinnati, Ohio: NIOSH, 1998.

27. **U.S. Environmental Protection Agency (EPA):** Method SW846-8015B, Nonhalogenated organics using GC/FID. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846*, 3rd rev. ed. Washington, D.C.: EPA (1996).

28. **Deygout, F., and P. Couronne:** Field sampling investigations within the road paving industry. *J. Occup. Environ. Hyg. 7*:103–108 (2010).

29. **Walter, D., and U. Knecht:** Standardized investigation of percutaneous absorption of bitumen emission in humans. *J. Occup. Environ. Hyg. 4(Suppl. 1)*:144–153 (2007).

30. **Kenny, L.C., R. Aitken, C. Chalmers. et al.:** A collaborative European study of personal inhalable aerosol sampler performance. *Ann. Occup. Hyg. 41*:135–153 (1997).

31. **Breuer, D., and C. Engel:** Bitumen (vapour and aerosol). In *The MAK-Collection for Occupational Health and Safety, Part III: Air Monitoring Methods, Volume 11*. H. Parlar and H. Greim (eds.). Weinheim, Germany: Wiley-VCH, 2010.