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Un sistema di laboratorio per lo studio degli aspetti igienico-sanitari legati all'esposizione dei fumi di bitume

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A laboratory rig for studying health aspects related to bitumen fume exposure

Un sistema di laboratorio per lo studio degli aspetti igienico-sanitari legati all'esposizione dei fumi di bitume

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Summary

To study bealth matters related to worker exposure to PA Cs (polycyclic aromatic compounds) in between-containing materials, the Authors bave developed a laboratory fume generation rig in which bitumen fumes can be reproducibly generated and sampled. This paper summarises the main items of this development.
An explanation is given why a laboratory method has been developed.
The lay-out of the fume generation rig and the sampling train used for collecting the fumes (particulates and semi-volatiles), the subsequent analysis for total particulate matter and benzene soluble matter (BSM) and the method used for analysis of PACs in the BSM and in the semi-volatiles are briefly described.
BSM emission is quantified as a function of the volatility and the temperature of the bitumen (the fuming index). It is demonstrated that the fuming index can also be used to predict the contribution of asphalt temperature and bitumen volatility to personal exposure.
It is demonstrated that the laboratory fumes generated at a standard temperature of 160 °C are representative of fumes emitted in the temperature range relevantfor road paving and those generated at 250 °C for roofing.
Being representative of actual bitumen operations, the laboratory rig is an excellent tool for comparing the fuming tendencies of bitumen and for assessing the nature of the bitumen fume condensate in terms of PAC content.

Riassunto

È stato sviluppato un sistema per generare e campionare in laboratorio i fumi emessi dai bitumi; ciò per studiare gli aspetti igienico-sanitari correlati all'esposizione dei lavoratori ai fumi emessi dai materiali asfaltici. I risultati ottenibili sono riproducibili. Vengono descritti brevemente l'apparecchiatura messa a punto per generare i fumi, il sistema di campionamento, e le analisi successive del particolato, dei solubili in benzene (BSM), degli aromatici policiclici (PAC).
Le emissioni di BSM sono quantificate come funzione della volatilità e della temperatura del bitume (l'indice di fumo) Si dimostra che l'indice di fumo può essere usato per predire il contributo della temperatura e della volatilità del bitume all'esposizione personale.
Si dimostra altresì che i fumi generati in laboratorio a 160 °C sono rappresentativi dei fumi emessi durante i lavori stradali e di impermeabilizzazione (fino 250 °C).
Al presente lavoro è stato conferito il premio SITEB per lo sviluppo di metodi e processi per lo studio degli aspetti igienico-sanitari relativi alla produzione e uso dei materiali bituminosi.

Introduction

Crude oils contain traces of polycyclic aromatic compounds (PACs), which partly end up in the bitumen. During handling at elevated temperatures of bitumen-containing materials, like asphalt, airborne particulates (fumes) can be emitted. These fumes consist of an inorganic part, dust from the minerai aggregates etc., and an organic part, the benzene soluble matter (BSM), which mainly originates from the bitumen and contains PACs. Although the PAC concentrations are small, worker exposure to bitumen fumes is of potential concern, because some four- to six-ring PACs have been found carcinogenic in, for example, animai skin painting tests [1]. The principal routes of worker exposure to bitumen fumes are inhalation and skin deposition.
The current occupational exposure limits to bitumen

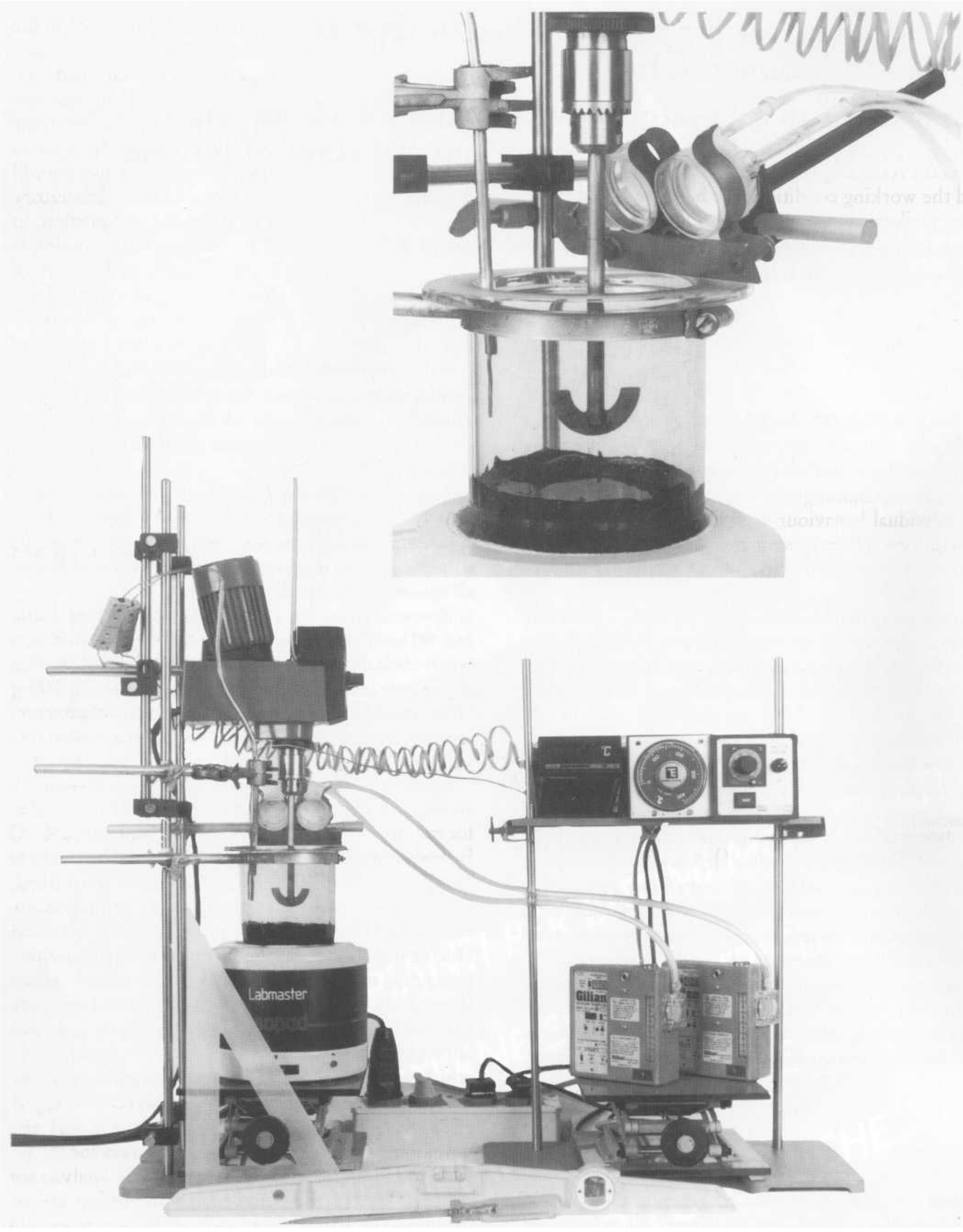


Fig. 1 - The laboratory rig and the position of the filter cassette (close up).

fumes are expressed as total particulate matter, hence including the inorganic part. The hazard however is related to the exposure to benzene soluble matter (as pan of the total particulate matter exposure) and to the PAC content of the bitumen fume condensate. Therefore we will concentrate on benzene soluble matter and PACs. Depending on the type of application and the working conditions the benzene soluble matter contribution can range from a few percent to 90% of the total particulate matter. Generally at higher exposures higher percentages of benzene soluble matter are found.

Personal exposure is measured in actual working situations (field surveys). These are very costly and labour-intensive and many factors can influence the outcome. Some of the factors are listed below.

1. The application temperature
2. Bitumen volatility
3. Operator training
4. Individuai behaviour such as smoking
6. The type of equipment used
7. The type of application
8. Non-bitumen sources, such as exhaust gases, vapours from diesel
9. The weather

1 and 2 will be discussed in detail in this paper.

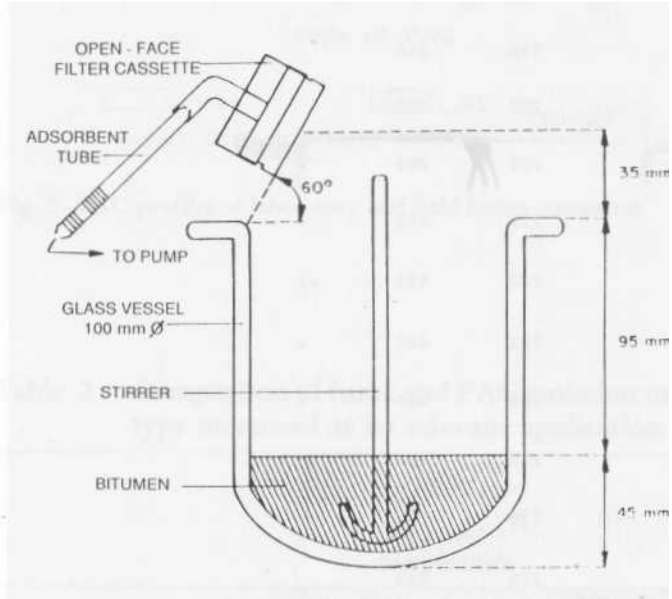


Fig. 2 - Detail of the laboratory rig. Vessel containing the bitumen and position of the filter cassette and adsorhent tube.

Shell as a major bitumen producer is interested in the bitumen contribution to the PAC exposure. Because of the many contributing variables this bitumen contribution is very difficult to study with field exposure studies. Therefore wc have developed a laboratory fume generation rig in which we can reproducibly generate fume under controlled conditions. In this paper we will demonstrate the representativeness of our laboratory rig with respect to assessing the bitumen contribution to personal exposure to PACs and its value as a simple tool for comparing PAC-emission-related aspects of bitumens in the laboratory. Because many parts of this development have already been reported elsewhere we will only give a brief description of the main issues and refer to the relevant publications for detailed descriptions and validations of the various parts.

2. Experimental

2.1 Short description of the fume generation rig and sampling equipment

The heart of the fume generation rig (Figures 1 and *2)* consists of a 700 ml round-bottomed glass reaction vessel with flanged rim, which is placed in a heating mantle. The fumes are generated by heating *200* g bitumen to the chosen, well controlled temperature. During heating and sampling the bitumen is stirred at a constant rate (10 rev s^{-1}). The standard temperatures for fume generation were chosen by analogy with practical applications of the various grades: for example 160 °C for paving grade bitumen, *250 °C* for oxidised grades. Sampling of the fume is started as soon as the temperature of the bitumen has stabilised. The fumes are collected with the same sampling equipment as used for field exposure studies: using standard 37 mm Gelman filter cassettes, with a filter combination consisting of a 37 mm Gelman A/E-type glass fibre followed by a 37 mm 0.8 .tm silver membrane, supported by a Gelman cellulose ester back-up pad. The positioning of the filter cassettes is very important for obtaining reproducible results, therefore a simple holder has been designed that guarantees exact positioning. A detailed description of the laboratory rig and the development and validation of the method for sampling of bitumen fumes and the subsequent analysis for total particulate and benzene soluble matter can be found in [2], Pan 1. The method for sampling and analysis for total particulate and benzene soluble matter has been adopted by CONCAWE and the fully detailed method can be found in CONCAWE Report 6/84 [3].

Apart from the PACs in the particulates phase attention is given to compounds that are in the gas phase, called semi-volatiles, and which are not retained on the particulates filter. Components present in these semi-volatiles are suspected of causing irritancy effects in asphalt workers [4]. Therefore the filter cassettes bave been backed up with an adsorbent tube as described in NIOSH method 5506 [5] that retains PACs in the semi-volatiles.

2.2 PAC analysis

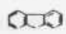
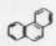
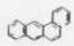
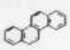
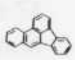
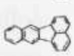
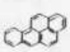
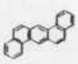
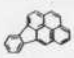
Currently we analyse for the 16 PACs listed by the US Environmental Protection Aeencv "EPA method 630" [6], to which coronene has been added to mark the end of the three- to six-ring area of the chromatogram (Table 1).

PACs are analysed with reversed-phase high-performance liquid chromatography (HPLC) with UV- fluorescence detection.The benzene soluble matter is directly injected as a 0.5% solution in tetrahydrofurane.

2.3 *Presentation of data*

In order to prevent confusion, laboratory generated data are expressed as weight per hour (e.g. mg/h) and personal exposure measurements, measured in actual field situations, are expressed as weieht per cubic metre (e.c.

Table 1 - List of EPA PACs, structural formulas and selected physical constants.

Code	Analyte	Structural formula	Molecular weight	Approx. Boiling Point *	Carcino-genicity
1	Naphthalene		128	218	-
2	Acenaphthene		154	279	-
3	Fluorene		166	294	-
4	Phenanthrene		178	338	-
5	Anthracene		178	340	-
6	Fluoranthene		202	383	-
7	Pyrene		202	394	-
8	Benz(a)anthracene		228	425	+
9	Chrysene		228	431	+/-
10	Benzo(b)fluoranthene		252	481	+
11	Benzo(k)fluoranthene		252	481	+
12	Benzo(a)pyrene		252	496	+
13	Dibenzo(a,h)anthracene		278	535	+
14	Benzo(g,h,i)perylene		276	542	-
15	Indeno(1,2,3-cd)pyrene		276	534	+
16	Coronene**		300	590	-

Acenaphthylene is undetectable and hence not listed.
* Ref 13
** Analyte added to EPA PAC to mark 3-7 ring area of chromatogram
- negative, + positive,

mg/m^3). Quantification of some of the PACs on the EPA list is obscured by high background levels from matrix fluorescence, leading to bad repeatability, whilst other PACs, especially those with less than four rings, are retained on the particulates filter either not at all or only incompletely. Therefore only the PACs that can be determined with enough precision bave been presented in Figure 3, where a comparison has to be made nn hasis nf nnly a few exnerimentc_

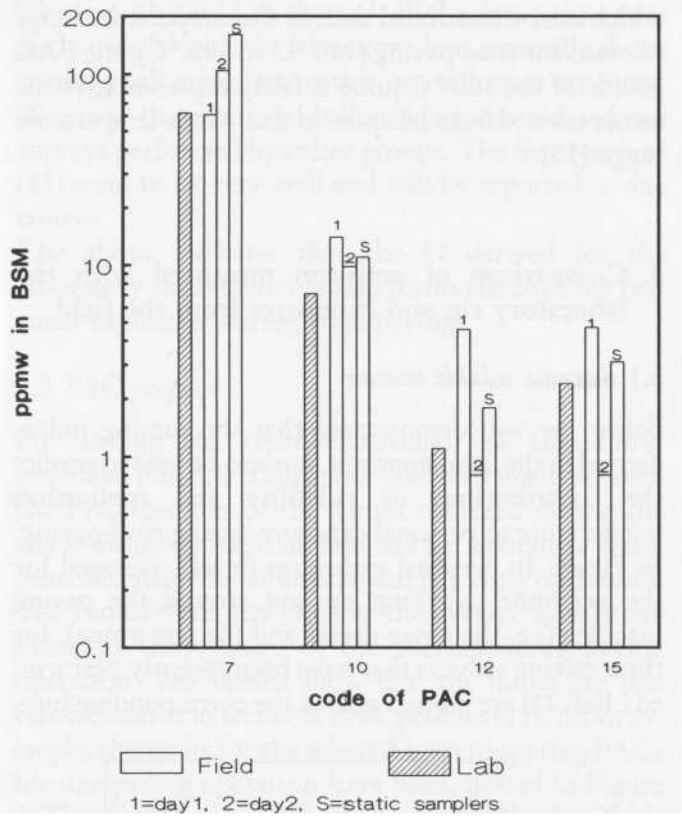


Fig. 3 - PAC profiles of laboratory and field fumes compared.

3. Validation of laboratory fume generation method

The detailed validation of the laboratory fume generation method can be found in [2]. The most relevant observations are summarised here. For up to 7 hours the fume generation rate is independent of time. Depending on the amount collected on the filter (1-6 mg) between 0.15 to 0.4% of the bitumen has evaporated in the sampling period. These amounts generally correspond to less than 20% of the material (and PACs with three or more rings) that theoretically could evaporate, which means that at the end of the test the bitumen is far from depleted. Particle size distributions of laboratory generated fumes were similar to those measured during field surveys and for all: 96-99.7% mass was below 12.5 µm, which means that all the fume particulates can enter the respiratory tract.

4. Laboratory results

4.1 *PAC emission*

PAC emission is the product of total benzene solubles emission and of the PAC concentration in the benzene soluble matter.

$$PAC_{emission} = BSM_{emission} \times [PAC]_{in\ BSM}$$

The main variation in PAC emissions is the benzene soluble matter emission. PAC concentrations differ less (Table 2), although a spread in PAC contents has been found which appeared to be bitumen-dependent [7], indicating possible differences in carcinogenic potential between bitumen fume condensates originating from different bitumens. Table 2 also shows that the PAC contents of BSM from paving bitumen, generated at 160 °C, and those from oxidised-grade bitumens,

Table 2 - Comparison of fume and PAC emission rates for penetration- and oxidised-grade bitumens, each type measured at its relevant application temperature.

	Fume generation temperature	BSM mg/h	Σ 11 (4-,5-and 6-ring) PACs in BSM ppmw	Σ 11 (4-,5-and 6-ring) PACs emission ng/h
Penetration-grade bitumens	160°C	0.16-1.3	212-316	35-395
Oxidised-grade bitumens	250°C	27-201	138-220	3 700-44 000

generated at 250 °C, are very similar. The factor of approximately 100 times higher PAC emission rate for oxidised grades relative to penetration grades almost completely originates from the approximately hundred-fold higher BSM emission rate for the oxidised grades.

4.2 Benzene soluble matter emission

In our laboratory rig, fume was generated at three temperatures from a wide variety of bitumens. Linear regression of the logarithm of the fume emission rate (mg/h benzene soluble matter) with the fuming index (FI), a linear function of bitumen volatility, expressed as percent mass recovery at 450 °C measured by TBP/GLC (Rec450) *[8, 9],* and the reciprocal of the fume generation temperature (in kelvin), gives a fair correlation (Figure 4a) of the form:

$$\log[BSM] = 0.134(Rec450) - 5039(1/T) + 10.81 \quad \text{(Eq. 1)}$$

In the temperature range relevant for paving applications (140 to *190* °C) the fume emission rate increases by a factor of 2 for about every 11-12.5 °C temperature increase. In the temperature range relevant for roofing applications (210 to 270 °C) it is a factor of 2 for every 14 to 17 °C. At a fixed temperature, the fume emission rate increases by a factor of 2 for an increase in Rec450 of 2.3%. To give an idea of the range usually encountered: for *80/100* pen bitumens the Rec450 generally is found to Ile between 1 and 12.

4.3 *PA* Cs

The standard temperatures adopted in our laboratory rig (160 °C for paving and 250 °C for roofing) represent only one temperature in the range of application temperatures observed in real applications. If the temperature differences are large (say 100 °C), the influence of the temperature on the PAC distribution in the bitumen fume condensate is noticeable [7]. However, laboratory tests bave been performed from which can be concluded that, in the temperature range relevant for road-paving (140 °C to *190* °C), the PAC profile of the 160 °C fume is fairly representative for fumes emitted from bitumen in that whole temperature range [10].

5. Comparison of emission measured with the laboratory rig and exposures from the field

5.1 *Benzene soluble matter*

Below we will demonstrate that the fuming index, derived in the laboratory test, can also be used to predict the contributions of volatility and application temperature to personal exposure during road-paving. In Figure 4b personal exposures (level), averaged for the personnel working on and around the paving machine (Le. the paver driver and the screwmen), for three paving surveys that bave been recently performed (Ref. 11) are plotted against the corresponding fum-

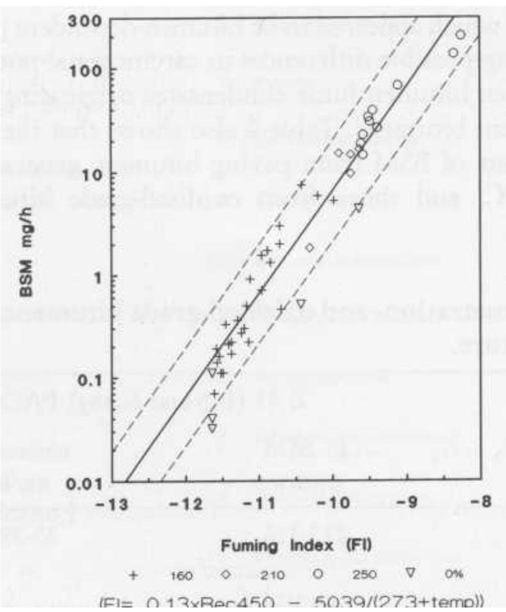


Fig. 4a - Prediction of laboratory fume emission (BSM) from bitumen temperature and volatility.

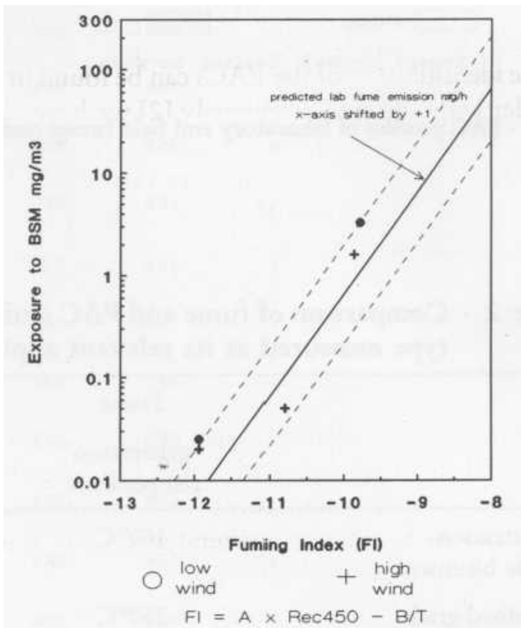


Fig. 4b - Paving: Measured personal exposure vs. asphalt temperature and bitumen volatility.

ing index (FI) calculated from the bitumen volatilities and the asphalt temperatures (FI = A x Rec450 - B/T), using the coefficiente from equation 1. In the same figure the predicted laboratory fume emission and the 95% confidence limits for the prediction are also given. To enable a fair comparison of the data, the set has been split into two groups: the data collected on the days with a low wind speed (o sign) and the other data which refer to days with a relatively high wind speed (+ sign). The hypothetical line through all the data points runs fairly parallel with the laboratory line, especially if one considers all other factors that can influence exposure. We are in the process of collecting exposure data from surveys performed by other groups. The first received [12] seem to fit very well and will be reported in due course.

The above indicates that the FI derived for the laboratory fume emission also forms the basis for personal exposures during road-paving.

5.2 PA C profiles

For testing the representativeness of laboratory-generated fumes, a comparison has been made between the PAC profiles of the fumes collected during the above-mentioned field surveys and the laboratory fumes generated from the bitumens used in paving operations. The fumes were generated at the average asphalt application temperature of the corresponding paving operation. The results show that the fumes are also representative in terms of PAC profiles [11]. As an example, theresults for the selected four- to six-ring PACs for one paving operation have been plotted in Figure 3. The identification of the PACs can be found in Table 1 under code. Because previously [2] we have already demonstrated the representativeness for roofing and indoor mastic laying operations, we can conclude that with regard to PAC profiles the laboratory fumes are representative for all major bitumen applications.

6. Conclusions

A simple laboratory fume generation rig has been developed in which bitumen fumes can be generated reproducibly under well controlled conditions.

The laboratory fumes generated at a standard temperature of 160 °C are representative for fumes emitted in the temperature range relevant for road-paving, those generated at 250 °C for roofing.

The PAC profiles of the laboratory fumes fit the PAC profiles of the fumes sampled ori the operators.

The current and previously published work demonstrates that for personal exposure to benzene soluble matter and to PACs, the laboratory rig test is representative of commercial bitumen applications and that the fuming index derived can be used to predict the contributions of asphalt temperatures and bitumen properties to personal exposure.

Being representative of actual bitumen operations, the laboratory rig is an excellent tool for comparing the fuming tendencies of bitumen and for assessing the nature of the bitumen fume condensate in terms of PAC content.

This work has been awarded the SITEB prize on "Methods and processes for the investigation of health aspects of bituminous materials in their production and use".

References

[1] E. Bingham, R.P. Trosset and D. Warshawsky, *J. Environ. Pathol. Toxicol.*, 3, 1979, 483-563.
[2] H.C.A. Brandt, P.C de Groot, M.K.B. Molyneu and P.E. Tindle, *Ann. Occup. Hyg.*, 29, 1985, 27- 80.
[3] CONCAWE, *Review of bitumen fume exposures and guidance on measurement*, CONCAWE, The Hague, Report No. 6/84, 1984.
[4] T. Norseth, J. Waage and I. Dale, Am. J. Ind. Med., 20, 1991, 737-744.
[5] NIOSH method 5506: *Polynuclear Aromatic Hydrocarbons*, NIOSH 1985.
[6] US EPA SW846-8310: *Polynuclear Aromatic Hydrocarbons.*
[7] H.C.A. Brandt, Symposium on *Health Aspects of Asphalt Production and Paving* of the European Asphalt Pavement Association (EAPA), Stockholm, June 7-8, 1990, Proceedings, pp. 171-183.
[8] SMS 2551-89, *Boiling range distribution of residue-containing petroleum products (GLC with FID)*, Shell Method Series.
[9] G. van Gooswilligen, F.Th de Bats and T. Harrison, *Quality of paving grade bitumen - A practical approach in terms of functional tests*, Eurobitume 1989, Appendix I-4.
[10] H.C.A. Brandt and N. Cordingley, *Personal exposures to bitumen fumes and PAC during road paving and in laboratory simulations*, EAPA -5th Eurasphalt congress, The Hague, September 14-18, 1992.
[11] H.C.A. Brandt, C.D.M. Beverwijk and T. Harrison, *Health aspects of hot bitumen application* Eurobitume, Stockholm, 1993, paper 2.09.
[12] L.G. Ekström, *An overview of workers exposure studies*, EAPA - 5th Eurasphalt congress, The Hague, September 14-18, 1992.
[13] *Spectral Atlas of Polycyclic Aromatic Compounds*, Vol. 2, editor W. Karcher. Kluwer Academic Publishers for the Commision of the European Communities, 1988.