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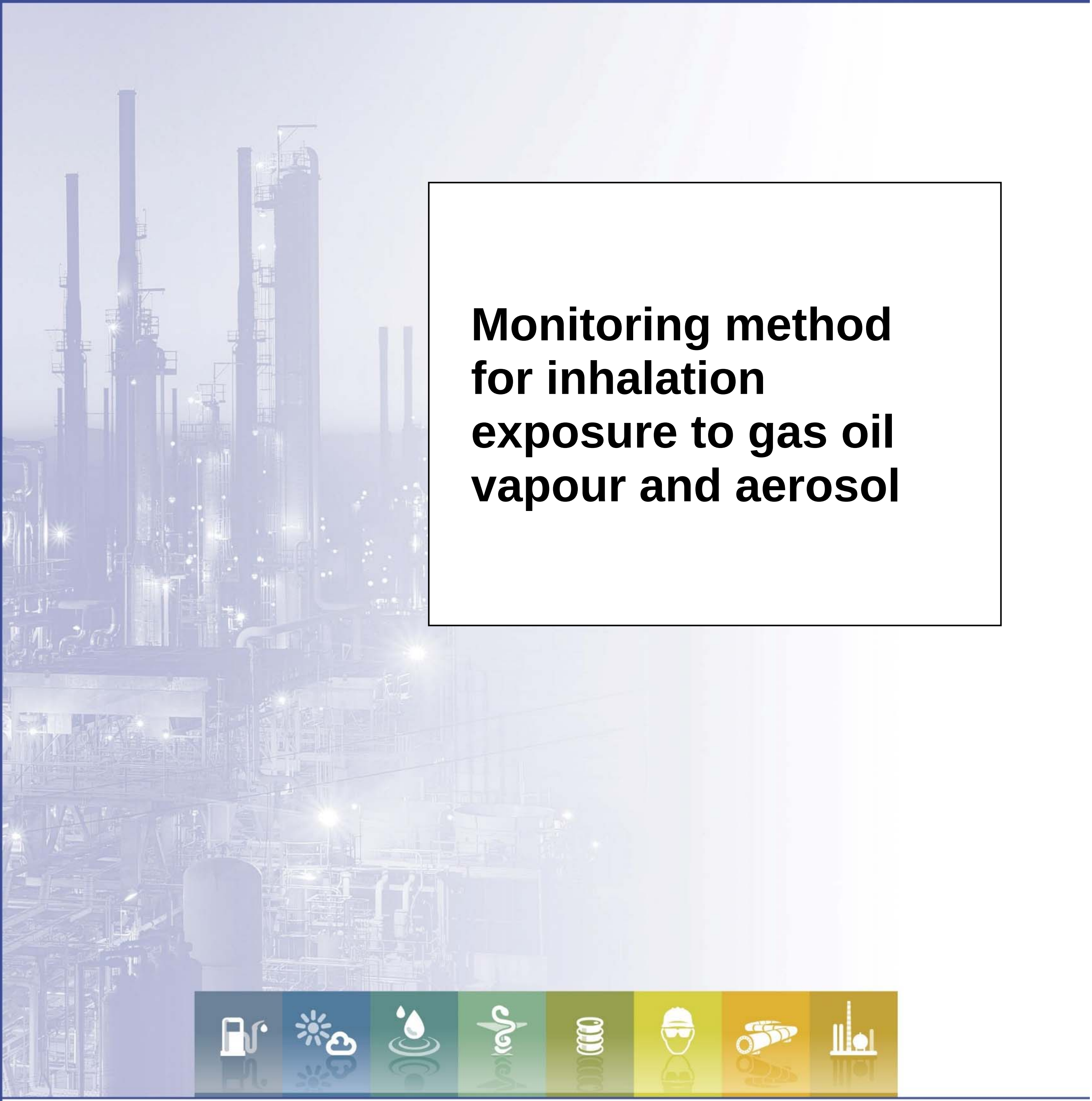

Monitoring method for inhalation exposure to gas oil vapour and aerosol

Environmental science for the European refining industry

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Monitoring method for inhalation exposure to gas oil vapour and aerosol

Prepared for the Concawe Health Management Group by its H/STF-29 Exposure Assessment Task Group and Fraunhofer ITEM:

J. Urbanus (Chair)
M. Banton
M. Carter
T. Dudzina
B. Geudens
R. Jones
G. Niemeck
G. Pizzella
R. Tibaldi
S. Williams

A. Rohde (Science Executive)
H. Ketelslegers (Science Executive)

E. Berger-Preiß (Fraunhofer ITEM)
W. Koch (Fraunhofer, ITEM)
S. Schuchardt (Fraunhofer ITEM)

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SUMMARY

A study was conducted to characterize sampling and analysis methods for the measurement of the personal workplace exposure concentration of gas oil vapours and aerosols and in particular, to describe their ability to quantify the aerosol-vapour partitioning. This project aims to address a deficiency identified in current monitoring methods where the principle focus has been on the aerosol phase of exposure to mists.

Two sampling methods for the total concentration of gas oil atmospheres and aerosol-vapour partitioning were investigated in a laboratory set-up:

- BIA-method: a filter and XAD-adsorbent cartridge operated in series
- VI-method: a virtual-impactor combined with filter-XAD cartridges

In conclusion, the BIA method allows for sampling and measuring the total concentration of the gas oil atmospheres for concentrations larger than $0.5 mg/m^3$ for 8-hour sampling. In the BIA sampling system, evaporation effects can cause a shift of the aerosol-vapour partitioning towards the vapour phase. The magnitude of these effects depends on the material being sampled, thermodynamic conditions during sampling and sampling duration. In contrast, in the VI-method, the aerosol-vapour fraction is nearly independent of the thermodynamic conditions and the sampling time. However, the partitioning coefficient can be influenced by smaller aerosols with diameters less than the critical cut-off diameter; this aerosol fraction is falsely recorded as vapour phase. The VI method has some other limitations (e.g., wall losses of up to 15-30% total concentration), however, it bears potential for further improvement.

1. INTRODUCTION

1.1. GENERAL

Gas oils are semi-volatile substances that can volatilise slowly at ambient temperature and pressure. When dispersed in air they can be present as a mixed atmosphere of aerosol and vapour. In order to address the potential health risks associated from the use of these materials it is therefore important to be able to measure both phases (aerosol and vapour) of the exposure. However, the available methods for monitoring exposures to mists have tended to only focus on the aerosol phase (NIOSH, 1996; HSE, 1997), largely because the methods were developed for higher boiling point substances, such as lubricating base oils, where the fraction of the vapour phase is extremely low. This project aims to address this deficiency as exposures to aerosols (and hence also to vapours) of gas oils can reasonably be anticipated during certain activities associated with the use of these products i.e. circumstances under which significant amounts of energy, whether kinetic or thermal, are applied to the substance.

Exposure of workers to gas oil mists are characterized by the presence of aerosols, determined by the high boiling compounds of the gas oil brand and volatile organic vapours. Upon inhalation, the aerosol fraction is absorbed differently in the lung compared to the vapour phase. The particle deposition pattern in the lung is primarily determined by particle transport mechanisms in the breathing air flow such as gravitational settling, impaction and diffusion. Particles are sticking to the epithelial lining fluid upon hitting the surface. In contrast, the uptake of vapours is limited by the interaction of the compound with the lung lining fluid such as its solubility or reactivity (Asgharian et al., 2012). Therefore, it is desirable to distinguish between the vapour fraction and the droplet fraction when analysing work place exposure of oil mists.

The particle-vapour partitioning of semivolatile compounds has been discussed widely in the literature. Volckens and Leith (2003), for example, compare different methods for the measurement of the partitioning of PAH and alkanes in Diesel exhaust. Different sampling trains are described in their paper and the accuracy regarding the measurement of the partitioning coefficient under the prevailing sampling conditions has been discussed for each of the methods. The combinations tested in their paper are: Filter-adsorbent, filter-filter-adsorbent, denuder-filter-adsorbent, electrostatic precipitator adsorbent.

In Germany, the filter adsorbent method is introduced in the BIA 6305 document for exposure to asphalt fumes at work places (Rühl et al., 2006). The sample collection method uses glass fibre filters for collection of the aerosol phase and XAD-2 tubes (37 mm filter cassette and adsorbent cartridge with 3 g XAD-2 resin: macro-porous polystyrene-divinylbenzene copolymer, size 0.5-0.9 mm) for the adsorption of the volatile compounds. The analysis is carried using IR-absorption calibrated by a standard mineral oil mixture. In Germany there is only a workplace limit value for the total concentration. Therefore, a distinction between aerosol and vapour phase that can be done in principal with the sampling unit, was not in the focus and the BIA method has not been evaluated regarding the measurement of the aerosol-vapour partitioning when used under real workplace situations. Three existing methods for asphalt fume sampling and analysis have been investigated by Kriech et al. (2010) under field conditions. Asphalt fumes emitted at high temperatures contain a great number of higher boiling compounds than gas oil mists and vapours. Therefore, the results of this study cannot be directly extrapolated to the sampling of gas oil emissions, particularly regarding the aerosol-vapour partitioning.

1.2. AIM OF THE STUDY

The aim of this study was to characterize sampling and analysis methods for measurement of the personal exposure concentration of gas oil vapours and aerosols, $c_{tot}=c_a+c_v$ at workplaces and, in particular, to discuss their ability to measure the aerosol-vapour partitioning, $\phi_a = c_a / c_{tot}$. Here c_a is the aerosol concentration and c_v is the vapour concentration.

Regarding workplace sampling, special emphasis should be directed to the simplicity of the sampling procedure and its reliability in view of allowing for a separation between the aerosol and vapour phase at conditions of fluctuating concentrations and thermodynamic non-equilibrium, generally present at work places.

The analytical procedure should be applicable for gas oils of different chemical compositions and, hence, boiling point distributions. Since the BIA-method is based on IR-absorption of the CH-vibration, it is likely to be suitable to measure gas oil mists and vapours dominated by alkanes. Therefore, only this method was selected as the analytical method considered for workplace analysis.

For testing purposes, a test stand for a reproducible generation of gas oil atmospheres from liquid samples had to be established. Two sampling devices were tested for their sampling characteristics and their ability to separate the vapour and aerosol phase.

Finally the investigated methods should be critically evaluated regarding their limitations and accuracy for their intended use under field conditions.

2. RATIONALE OF THE TESTING PROCEDURE

The test procedure follows the rational outlined below:

1. Generation of controlled, reproducible gas oil test atmospheres, at thermodynamic equilibrium characterized by the total concentration, c_{tot}, and the aerosol fraction ϕ_a at equilibrium.

2. Characterization of the equilibrium test atmosphere using a filter/adsorbent sampling method regarding the total concentration and the partitioning of the aerosol phase (filter) and the vapour phase (adsorbent). This is the concentration reference.

3. Testing of the candidate sampling methods at equilibrium conditions and comparison with the reference.

4. Testing of the candidate sampling methods by intermittently sampling from the equilibrium atmosphere and clean air for well-defined time periods to judge shifts in particle-vapour partitioning, ϕ_a .

5. Repetition of all tests with gas oils of significantly different boiling point distributions.

6. Carrying out chemical analysis following the BIA-6305-method for asphalt fumes and aerosols.

3. GAS OIL SAMPLES SELECTED FOR TESTING

Three test samples were selected for final testing from in total nine samples provided by the sponsor. The decision was made according to the boiling point distributions which were measured for all the samples. Results are shown in Tab. 3-1 and in more detail in Fig. 3-1. The samples A 143/11, A091/11 and A141/11, named **A**, **B**, and **C**, respectively were selected for further testing in this study. Their chromatograms are shown in Fig. 3-2. They were stored at +8°C in a cooling room for the period of analysis.

Tab. 3-1 Characteristics of the samples provided by Concawe, highlighted samples were selected for further testing.

Supplier	FhG-No.	Name	Density [g/mL]	Boling points		
				Min [°C]	Max [°C]	50% [°C]
S_A	**A:** A143/11	097 Galosio Auto	0.827	186	380	287
S_A	A144/11	UN/3A1/Y13/190	0.826	165	381	280
S_B	**B:** A091/11	Oil 2602R CAS 68814-87-9 category: straight-run gas oil	0.838	250	344	302
S_B	A092/11	Risella oil 907 CAS64742-79, category: other gas oils	0.856	226	288	260
S_C	A138/11	TGO-63ATM	0.847	204	398	300
S_C	A139/11	ARDSGO	0.881	234	401	331
S_C	A140/11	LGOLSH	0.831	194	391	294
S_C	**C:** A141/11	VGO	0.881	264	399	339
S_C	A142/11	TGO-53ATM	0.856	232	385	305

Fig. 3-1 Graphs of the boiling point distributions

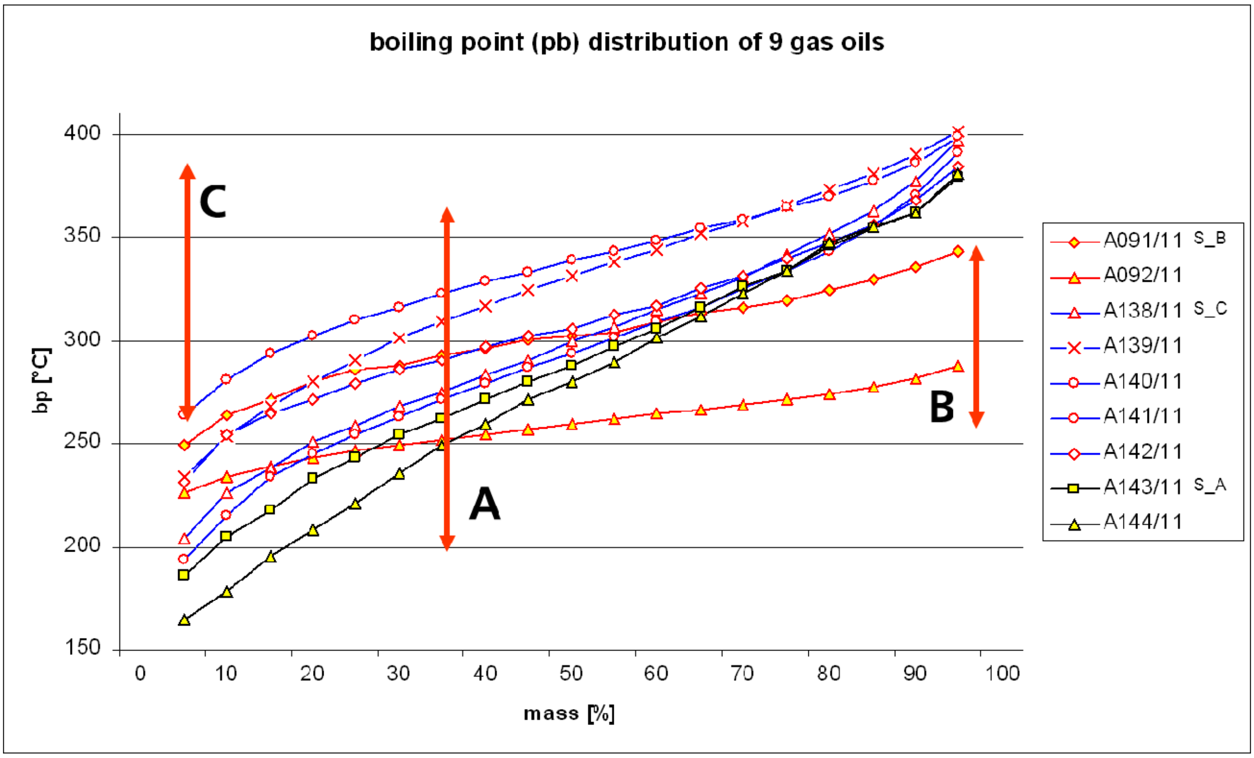
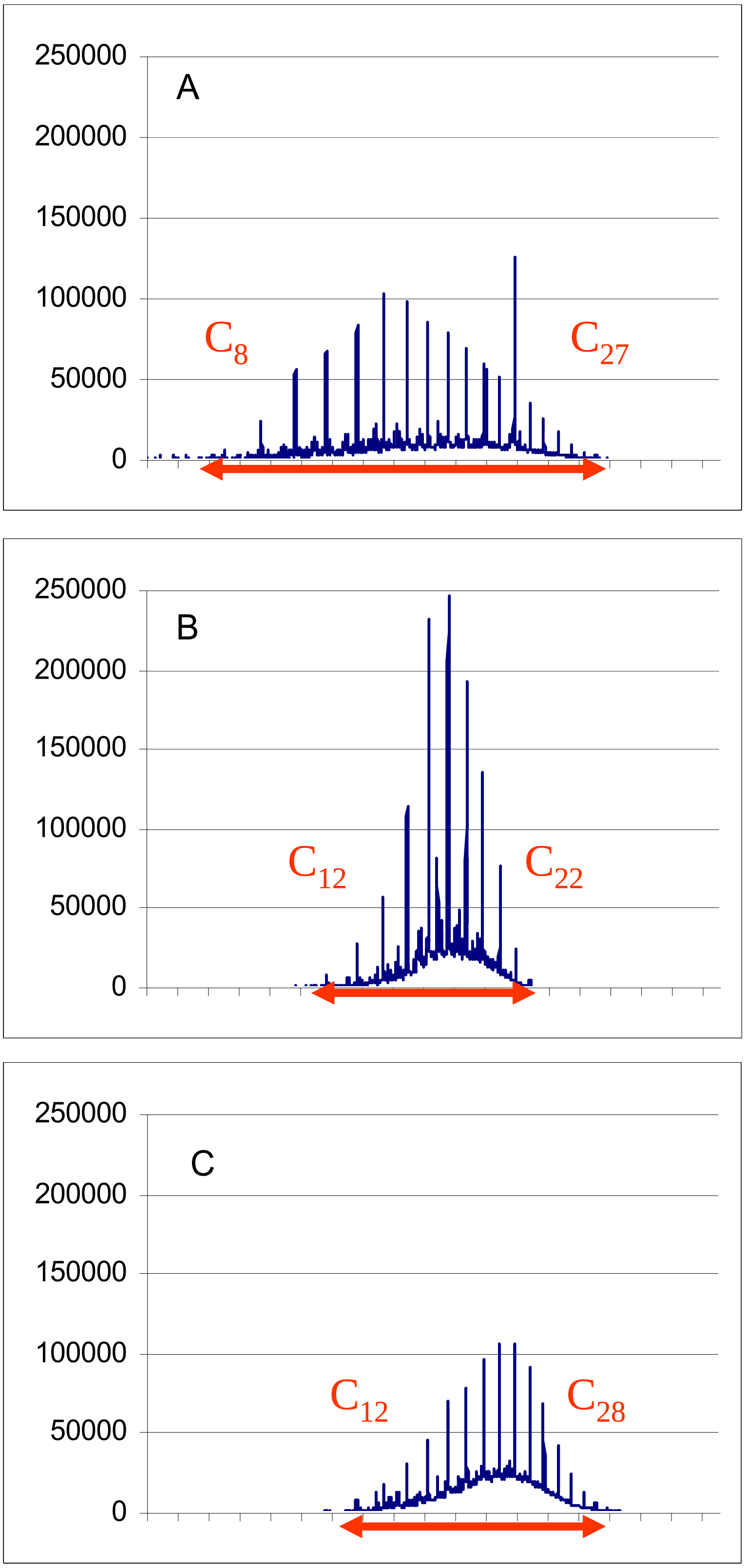


Fig. 3-2 C-number range of the test samples

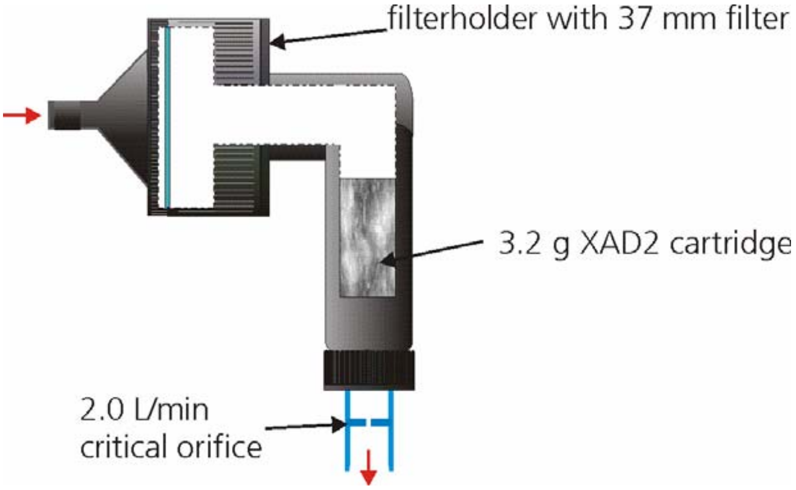


4. SAMPLING METHODS SELECTED FOR TESTING

4.1. BIA SAMPLING METHOD

The standard BIA sampler (Fig. 4-1) consists of the GSP (Gesamtstaubprobenahmesystem) with a 37 mm filter holder and cartridge for 3 g adsorbent (GSA Messgerätebau D41469 Neuss GmbH). In the filter holder 37mm glass fiber filter without adhesives (Art.No. Munktel 3.1105.037) is placed. 3.2 g of XAD-2-88 (Amberlite ® 20-60 mesh, Supelco Art. No 1-0357) were weighed into the cartridge. Before use the XAD-2-88 was purified by alternate drying (50°C) and washing (2 x methanol, 2 x dichloromethane and 2 x tetrachloroethene). The final drying was performed at 70°C and 30 mbar vacuum. The filter holder with the cartridge was then inserted into the sampling system. The air flow, Q, was set to 2 L/min by using a critical orifice. The filter and the XAD-2-88 were analyzed separately.

Fig. 4-1 The BIA sampling unit consists of a filter and an adsorber cartridge



The concentrations in the aerosol phase, c_a, and the vapour phase, c_v, are calculated from the two analytical values determined by IR analysis of deposits on the filter, m_f, and on the XAD-tube, m_v using:

$$c_a = \frac{m_f}{Q \cdot T}, \quad c_v = \frac{m_v}{Q \cdot T} \tag{1}$$

It is expected that the aerosol fraction, $c_a / (c_a + c_v)$, is measured correctly when the sample is taken at conditions where aerosol and vapour phase are in thermodynamic equilibrium during the entire sampling time, T. When operated under these conditions, the BIA method is a reference method. However, in realistic work place settings, equilibrium is usually not the normal case. There will be a mass transfer from the filter to the XAD during sampling conditions where the gas phase is not saturated. This will lead to evaporation of material sampled on the filter. Therefore, in general the BIA method is expected to underestimate the aerosol phase, particularly for light boiling mixtures and at low concentrations (Breuer, 1999; Harper, 2004).

4.2. VIRTUAL IMPACTOR SAMPLING METHOD

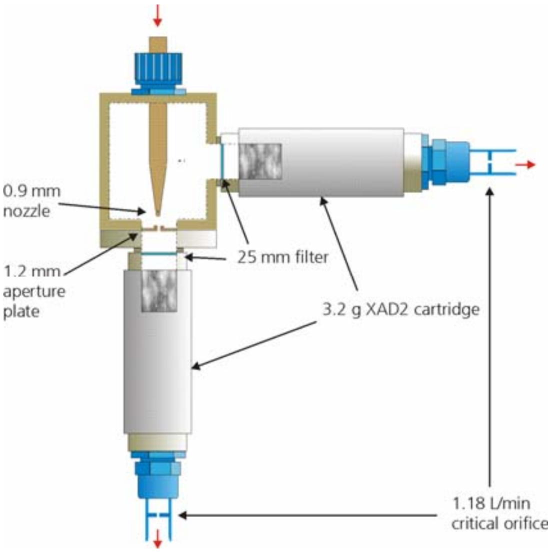
The virtual impactor (Fig. 4-2) consists of a nozzle (∅ = 0.9 mm) that is located on-axis in 5 mm distance from an aperture plate ∅ = 1.2 mm. Perpendicular to the nozzle (off-axis) and below the aperture plate are two 25 mm glass fiber filter without adhesives (Sartorius no. 13400-25) located in the gas stream. Both filters are in series with cartridges filled with 3.2 g of XAD-2-88 (see BIA method). The air flow is controlled on and off-axis by critical orifices which adjust the flow rate to Q =1.18 L/min (total sampling flow rate: 2.36 L/min). The filters and the XAD-2-88 cartridges were analyzed separately.

In the virtual impactor the aerosol is collected on the on-axis as well the off-axis sampling column. In the ideal case, when the diameters of all aerosol particles are above a certain critical diameter, determined by the nozzle size and the air velocity in the nozzle, the particulates will be entirely captured on-axis (due to their inertia) while the off-axis column samples only vapour. If we designate by m_{on} and m_{off} the mass collected in the two sections of the virtual impactor the aerosol and vapour phase concentrations are calculated by:

$$c_v = \frac{m_{off}}{Q \cdot T}, \quad c_a = \frac{m_{on} - m_{off}}{2Q \cdot T} \tag{2}$$

Here, Q =1.18 L/min is the flow rate through each of the two sampling columns. This would give the desired information on the total concentration and the partitioning between the vapour phase and the particulate phase. Non equilibrium sampling conditions would not affect the results since they are based on the total mass sampled on-axis and off-axis. Material that eventually evaporates from the filters in the respective channel will be collected by the corresponding downstream XAD column.

Fig. 4-2 Schematics of the virtual impactor.



In this study, the filters and the XAD columns were measured separately in order to be able to analyse the influence of possible errors such as losses of particles on the inner walls of the virtual impactor, and a non-zero mass fraction of droplets in the size range below the critical size of the separation stage. In the version used in this study the cut-off diameter was 0.7 µm (Schwarz, 2007).

5. MATERIALS AND METHODS

5.1. SET-UP FOR GENERATION OF THE TEST ATMOSPHERES

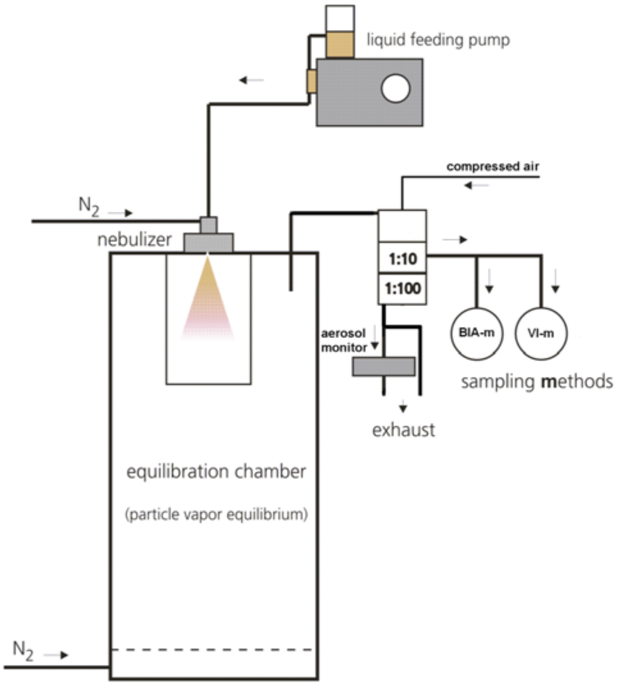
As a source for different gas oil atmospheres, a set-up as shown in Fig. 5-1 was built. The test atmospheres are generated by single path nozzles. A pneumatic nozzle developed by ITEM and operated with compressed nitrogen is used. The liquid oil is fed into the nozzle at constant flow rate by a syringe pump. Further dilution with nitrogen takes place in the equilibration chamber. The aerosol-vapour partitioning is controlled by the ratio of the liquid feed rate to the total volumetric flow rate of the nitrogen. A cascade of dilution stages operated with compressed air is used to reduce the total gas oil concentration of the equilibration chamber by a factor 1:10 and 1:100, respectively.

Since the nitrogen flask and the tubes of the compressed air system are in equilibrium with the room air, the temperature in the generation system was equivalent to the room temperature. This was recorded for every test and covered a range between 20 and 22°C.

Losses of aerosol on the walls of the chamber and inside the dilution system could not be avoided. Depending on the test substances the percentage of losses was between 30 and 40% in comparison to the mass balance. Therefore the unit serves only as a reproducible source for gas oil atmospheres generated from different liquids. Reproducibility was assured by controlling the feed rate of the syringe pump and by on-line measurement of the aerosol concentration after the second dilution stage using an aerosol photometer.

Samples were taken either after the 1:10 or at the 1:100 port of the dilution cascade. In the dilution system and the sampling line the atmosphere is given sufficient time to adjust to thermodynamic equilibrium.

Fig. 5-1 Set-up for generation of the gas oil test atmospheres



5.2. ANALYTICAL PROCEDURES

5.2.1. IR analysis

The IR analysis was carried out in accordance with the BIA-6305 method and the Fraunhofer ITEM SOP150246. Therefore, a calibration graph in a range from 0 to 10 mg/mL of a standard mineral oil (Aldrich No. 16.140-6) in tetrachloroethene was recorded (Merck No. 1.00965.2500). The integral absorption of the CH vibrations between 2800-3000 cm^{-1} was measured against the concentration of the standards. This calibration was further processed by the IR spectrometer software. The integral absorption of unknown samples is converted into so called ‘mineral oil equivalents’ (ME). In section 6.1 a description is given to calculate an individual correction factor. This substance specific correction factor was used to calculate the actual mass of the gas oil samples. All further evaluations refer to these actual masses.

The glass fibre filter and the XAD-2 granulate were analysed separately. Each sample was placed in a 50 mL glass jar with vessel stopper. 10 mL tetrachloroethene was added via pipette and the samples are then treated in an ultrasonic bath for 10 min and allowed to equilibrate overnight. The next day the sample solutions were measured in a 1 cm quartz cuvette in a Fourier-transform infrared spectrometer (Vector 22, Bruker). The solvent spectrum of tetrachloroethene served as the base reference.

5.2.2. GC analysis

In addition to the standard IR analysis GC analysis was carried out for selected samples in order to get a better understanding of the particle-vapour partitioning and the influencing parameters. After IR-analysis 5 mL of selected 10 mL BIA samples were evaporated to 0.5 mL at 50°C under 40 mbar vacuum. The solution was then transferred with dichloromethane (Merck No. 1.6054.2500) into a 5 mL volumetric flask and filled to the calibration mark. 2 µL of this solution was injected into a HP-GC (model 5890). GC-conditions: column: DB-5ms (J & W) 30x0.32 mm, fth = 0.25 µm, injection volume: 2 µL, injector temperature: 250°C, FID detector temperature: 330°C, split: 25 mL/min, splitless: 0.5 min, carrier gas: He (3 mL/min constant flow mode), temperature program: initial 40°C for 3 min, heating rate 1: 9°C/min, final temperature 1: 120°C, hold: 0.5 min, heating rate 2: 11°C/min, final temperature 2: 320°C, hold: 9.5 min.

5.2.3. Marple impactor

The droplet size distributions of the aerosolized gas oil samples were measured at equilibrium conditions using a cascade impactor. In this study an 8-stage Marple impactor (Series 190) was employed. The instrument covers a size range between >21 µm (pre-stage) and < 0.5 µm (back-up filter). The total pressure drop of the impactor is smaller than 20 mbar at a flow rate of 2 L/min. After disassembly of the impactor device the impaction plates were rinsed immediately with 5 mL tetrachloroethene into a volumetric flask to minimize evaporation losses. The concentration of mineral oil equivalent was then determined by IR analysis.

5.3. AEROSOL PHOTOMETER

The aerosol photometer (Type SAD, development of Fraunhofer ITEM) uses the principle of light scattering at small particles to detect aerosols. Near infrared light (0.63 µm) from a laser diode is scattered at the dust particles inside a measuring volume. The amount of scattered light is detected under an angle of 70° by a solid state infrared detector. The signal is amplified to an output voltage between 0 and 4 V available at the output pins. The aerosol is sucked in by a small pump. The pump also creates a sheath air current which is flowing concentrically to the sample flow though the measuring cell. The sheath air flow protects the optics from being contaminated by particles.

5.4. CARRYING OUT THE TESTS

The tests were carried out by connecting the sampler to the 1:10 or 1:100 sampling port of the dilution apparatus via a 6 mm tube of non-conducting plastic material. Tubes of the same length were used for all the tests. The flow through the sampler was established via the in-house vacuum system and was controlled using calibrated critical orifices. The nitrogen flow rate and the feed rate of the syringe pump were set to fixed values which were not changed throughout the study. The signals of the aerosol photometer measuring the aerosol atmosphere at 1:100 dilution was recorded by a data logger. The photometer readings were taken into account in the statistical analysis of the analytical data obtained from the filter and XAD samples.

6. RESULTS AND DISCUSSION

6.1. RESPONSE IR-FACTORS

IR analysis was selected to be the analytical method of choice to be used throughout the study. In order to characterise the error related to the standard calibration method when measuring gas oil samples of unknown composition the IR response factors were measured for the three known gas oil samples and compared to the response factor of the standard mineral oil. A known quantity of gas oil was dissolved in the solvent and the concentration was compared to the concentration given by the IR-method calibrated with the standard mineral oil equivalent (ME). The results are shown in Tab. 6-1.

Tab. 6-1 Correction factors to be used when measuring the concentration of gas oils using IR absorption (CH-vibrations) with standard ME calibration.

Sample No.	Gravimetric concentration [mg/10 mL]	IR: mineral oil equivalent (ME) [mg/10 mL]	Correction factor
A	6.502	5.648	1.151
B	6.648	5.772	1.152
C	6.992	5.398	1.295

The correction factors are all larger than one since, in comparison to the pure paraffin compounds of the standard mineral oil mix, there are additional C-H bonds in gas oils due to compounds like aromatics, cyclic, olefinic and hetero hydrocarbons. Taking for example for unknown environmental (gas oil) samples an average value of 1.2 for the correction factor, the maximum error related to the determination of the concentration by the IR method is smaller than 10 %. The concentration data presented in this study are based on the actual response factors obtained for each gas oil brand.

6.2. PHOTOMETER SIGNALS

For every test the photometer signal was recorded in order to check for reproducible generation of the mist. Fig. 6-1 shows an example of a series of seven measurements carried out with sample **A**. The average value of the daily means of the voltages is 0.28 V with a deviation of 0.01 V, i.e. 3.7 %.

6.3. MASS SIZE DISTRIBUTION OF THE AEROSOL FRACTION OF THE GAS OIL ATMOSPHERES

The mass size distribution of the aerosol of the different diesel-oils was measured with the Marple cascade impactor after both dilution stages. The recovery of all measurements was 56(±12) % of the BIA (filter) aerosol measurement. At the high concentrations (1:10 dilution) mass fractions of between 11 and 25 % were recorded in the particle size range smaller than 0.5 µm. These fractions increase when the gas oil atmosphere is further diluted.

Fig. 6-1 Photometer signals for seven tests carried out on consecutive days with the gas oil sample 143-11.

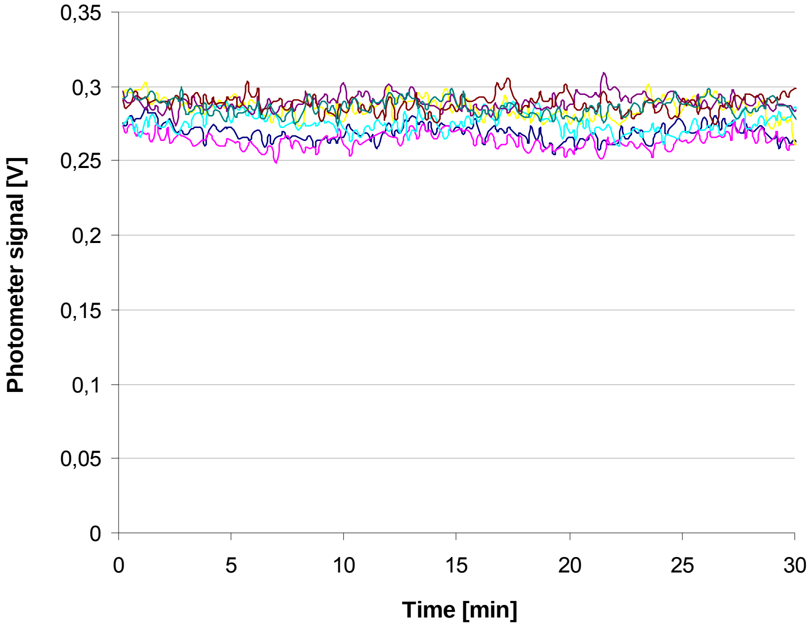
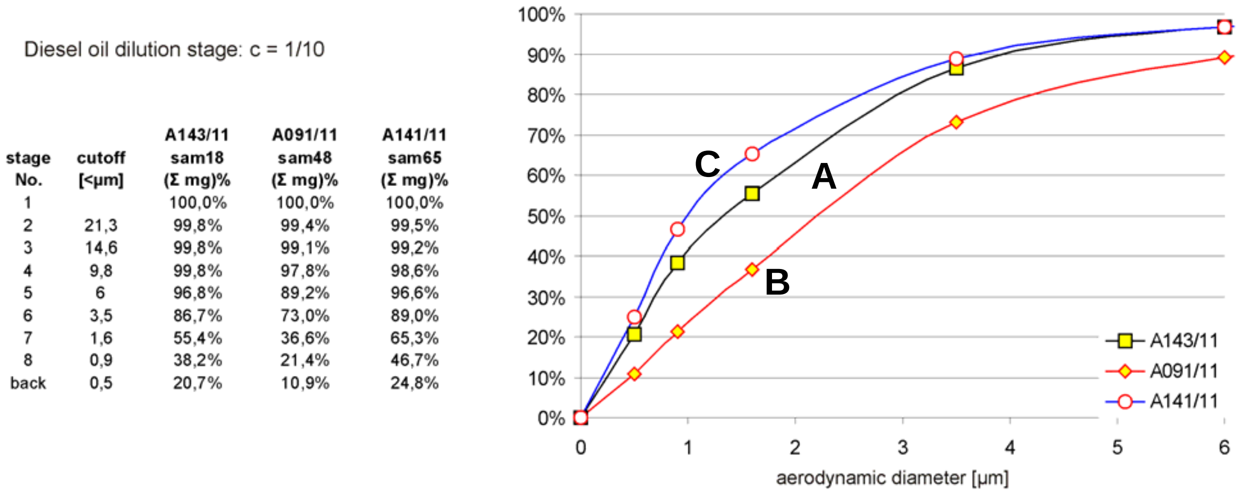


Fig. 6-2 Mass size distribution of the aerosol fraction of the gas oil atmospheres at the 1:10 dilution port.

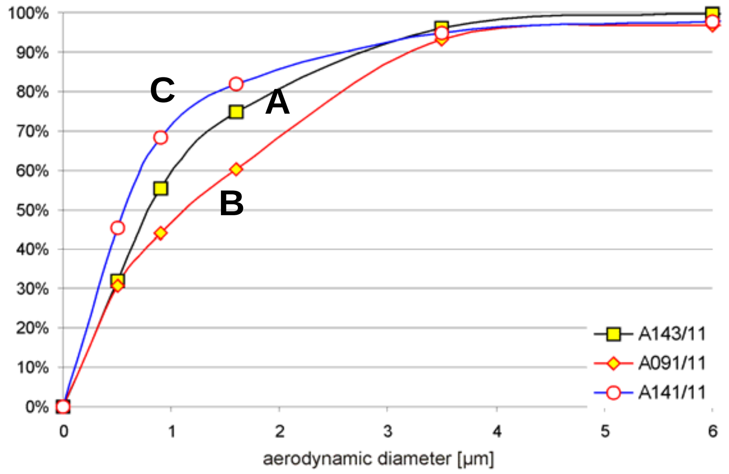

Diesel oil dilution stage: c = 1/10

stage No.	cutoff [<µm]	A143/11 sam18 (Σ mg)%	A091/11 sam48 (Σ mg)%	A141/11 sam65 (Σ mg)%
1		100,0%	100,0%	100,0%
2	21,3	99,8%	99,4%	99,5%
3	14,6	99,8%	99,1%	99,2%
4	9,8	99,8%	97,8%	98,6%
5	6	96,8%	89,2%	96,6%
6	3,5	86,7%	73,0%	89,0%
7	1,6	55,4%	36,6%	65,3%
8	0,9	38,2%	21,4%	46,7%
back	0,5	20,7%	10,9%	24,8%

Fig. 6-3 Mass size distribution of the aerosol fraction of the gas oil atmospheres at the 1:100 dilution port.

Diesel oil dilution stage: c = 1/100

stage No.	cutoff [<µm]	A143/11 sam20 (Σ mg)%	A091/11 sam49 (Σ mg)%	A141/11 sam67 (Σ mg)%
1		100,0%	100,0%	100,0%
2	21,3	99,8%	99,2%	99,4%
3	14,6	99,8%	98,9%	99,1%
4	9,8	99,8%	98,1%	98,7%
5	6	99,6%	96,9%	97,8%
6	3,5	96,1%	93,3%	94,8%
7	1,6	74,7%	60,3%	82,0%
8	0,9	55,2%	43,9%	68,4%
back	0,5	31,9%	30,9%	45,4%



6.4. FILTER ADSORBENT METHOD (BIA)

6.4.1. Sampling at conditions of thermodynamic equilibrium

One of the aims of this part of the study was to determine the influence of the concentration level and the sampling time. The sampling time should cover short term (10-20 min) as well as long term sampling (4-8 h). More specifically, questions like the detection limit on the one hand and the capacity of the adsorbent columns on the other hand have to be addressed. Therefore, the BIA sampling train was evaluated at two different concentrations and for various sampling times. The reproducibility was controlled by monitoring the aerosol fraction using the aerosol photometer. The results are summarized in Tab. 6-2 as well as in Fig. 6-4 and Fig. 6-5 for the gas oil **A**.

No influence on the analytical determined concentration was found. For example the standard deviation of the total concentration obtained for the test runs at 1:10 dilution is 2 % and the standard deviation of the measured aerosol fraction is 3 %. This is smaller than the uncertainty of 10 % associated with the use of a standard calibration factor for the IR analysis of the samples. The measured total concentration at the sampling port is considerably lower than the concentration expected from mass balance due to losses of gas oil fume to the inner surfaces of the generation system, particularly in the equilibration chamber. These losses cannot be avoided. However, due to the use of the photometer the generation system can be operated in a very reproducible manner. The findings of this part of the study suggest the BIA sampling method together with the IR analysis should be regarded as the reference method for the measurement of the total concentration and the aerosol fraction at thermodynamic equilibrium.

Tab. 6-2 Performance tests of the sampling device for different parameters (sample A)

C set, photometer [mg/m³]	Sampling time [min]	Flow rate [L/min]	Total concentration [mg/m³]	Aerosol concentration [mg/m³]	Vapour concentration [mg/m³]	Aerosol fraction [%]
172.3	20	2	86.80	41.9	44.9	48.3
172.3	10	2	89.00	42.4	46.6	47.6
172.3	15	2	89.00	42.4	46.6	47.6
172.3	15	2	87.90	44.4	43.5	50.5
172.3	120	0.2	83.00	40.2	42.8	48.4
172.3	360	0.2	85.00	41.0	44.0	48.2
172.3	20	2	86.40	43.4	43.0	50.2
175.0	15	2	87.00	45.6	41.4	52.4
17.2	360	2	7.47	1.65	5.82	22.1
17.2	100	2	6.74	1.63	5.11	24.2

Fig. 6-4 BIA-method at equilibrium: gas oil sample A at 1:10 dilution port.

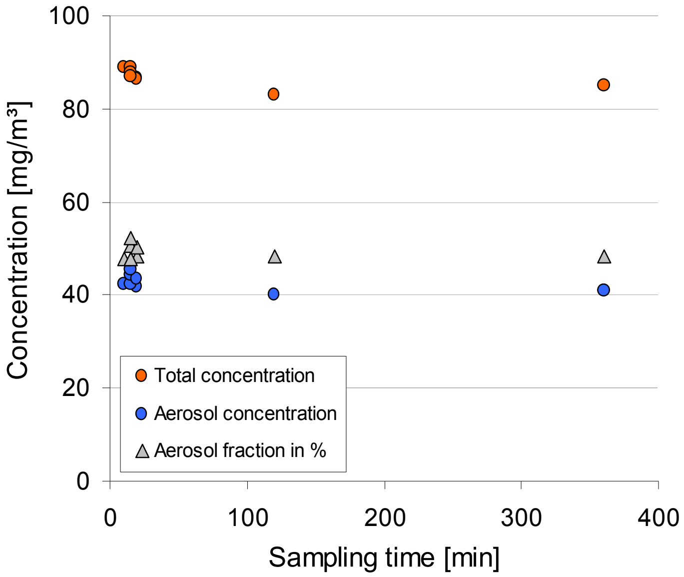
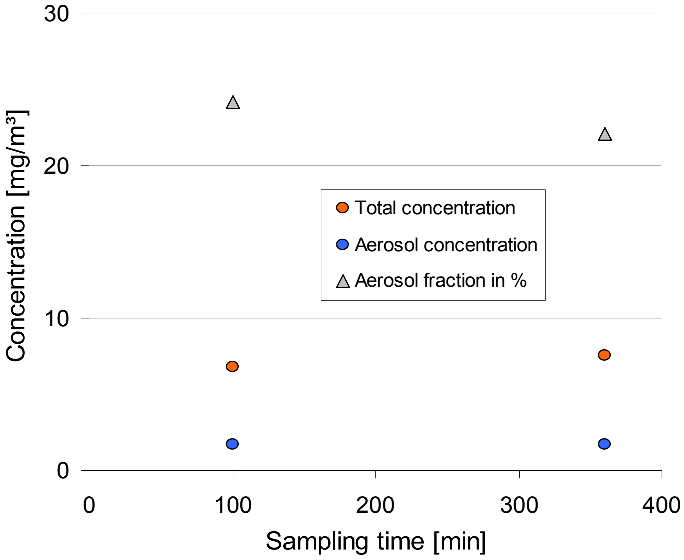


Fig. 6-5 BIA-method at equilibrium: gas oil sample A at 1:100 dilution port.



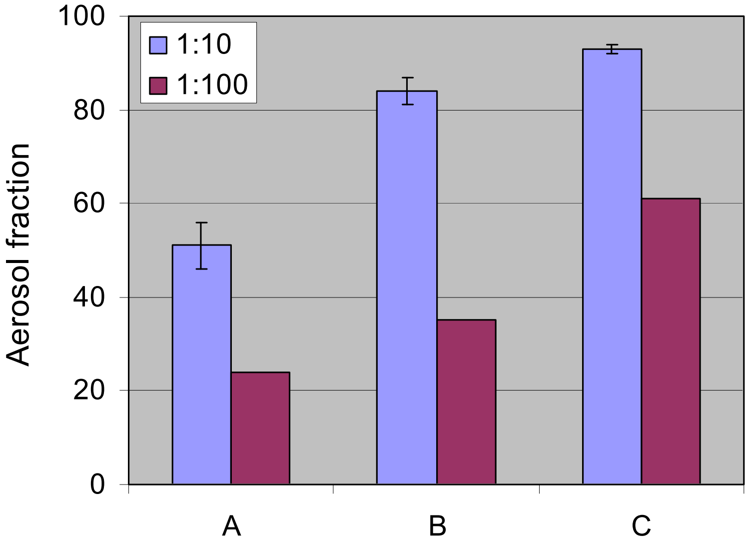
After the pre-evaluation part, a series of experiments were conducted under standardized sampling conditions. The partitioning between vapour phase and aerosol phase given by the percentage of aerosol of the total concentration is shown in Tab. 6-3 for the three different gas oil products. The first column indicates the so called set concentration, calculated from the mass balance of nitrogen flow and liquid flow and the dilution factors of the dilution cascade. The concentration ratio between the 10-fold and 100-fold diluted sample is nearly 12.3, 9.6, and 13.8 for the gas oil products **A**, **B** and **C**, respectively, indicating some aerosol losses in the dilution cascades. However, the standard deviations indicate good reproducibility of the test conditions (see also Fig. 6-6).

As is to be expected the aerosol fraction increases with the 50 %-value of the boiling temperature for the three products: 287°C, 302°C and 339°C. When the total concentration decreases (by dilution) the aerosol fraction decreases as well because the vapour saturation concentrations of the single compounds constitute a higher fraction of the atmosphere. This can also be seen from the chromatograms taken separately for the vapour collected on the XAD column and the aerosol fraction sampled on the filter (see Appendix Fig. 10-1 and Fig. 10-2) The quantitative evaluation of the sum of peak areas agrees within 10 % with the results of the IR absorption. From the results of these measurements it is concluded that separation in the vapour phase and aerosol phase depends only on the vapour pressure and concentration (molar fraction) of the single components in the gas oil (nearly ideal solution mix). For a given concentration and temperature, but independently of the type of the gas oil used, the separation between vapour and aerosol phase (separation point) occurs at the same n-alkane. (e.g., C = 100 mg/m³ at n-C15, C = 10 mg/m³ at n-C17). This conclusion was drawn from a series of tests where the variation of the temperature was 0.5°C.

Tab. 6-3 Total concentration an aerosol fraction of the gas oil atmosphere

C_set [mg/m³]	A	B	C	A	B	C
	Total concentration [mg/m³]	Total concentration [mg/m³]	Total concentration [mg/m³]	Aerosol fraction [%]	Aerosol fraction [%]	Aerosol fraction [%]
75 - 187	86(±2)	93(±7)	138(±4)	51(±5)	84(±3)	93(±1)
17.5 – 18.7	7	9.7	10	24	35	61

Fig. 6-6 Aerosol fractions (in %) at equilibrium for the test samples. The aerosol fractions shift to lower values as the total concentration decreases.



6.4.2. Sampling at conditions of thermodynamic non-equilibrium

The prevailing situation for real workplace sampling is thermodynamic non equilibrium with respect to the gas oil atmospheres. Emissions might be subject to changing dilution with fresh air due to variation of the emission rate. It is also quite likely that during a shift the device will sample air without any gas oil atmosphere. Since air is continuously drawn through the filter it may “dry” out by evaporation of deposited material causing an apparent under-representation of the aerosol fraction compared to the real workplace situation. In order to simulate these effects the following sampling scheme was used.

For each gas oil product, 4 samples were taken at the 1:10 dilution port for a sampling time of 15 minutes under thermodynamic equilibrium. One of the samples was analysed to give the total concentration and the true partitioning between aerosol and vapour. Since the reproducibility of gas oil generation was checked by aerosol photometry the loading of the remaining three samples is assumed to be the same. These samples were then exposed to air of zero gas oil concentration. This was done by sampling compressed air during time periods of 10 min, 30 min and 90 min, respectively through the remaining three samples corresponding to sampling volumes of 20, 60 and 180 L. These filter and XAD samples were analysed in the same way as the equilibrium samples. The total concentration is obtained by summing the loading of the filter and the XAD.

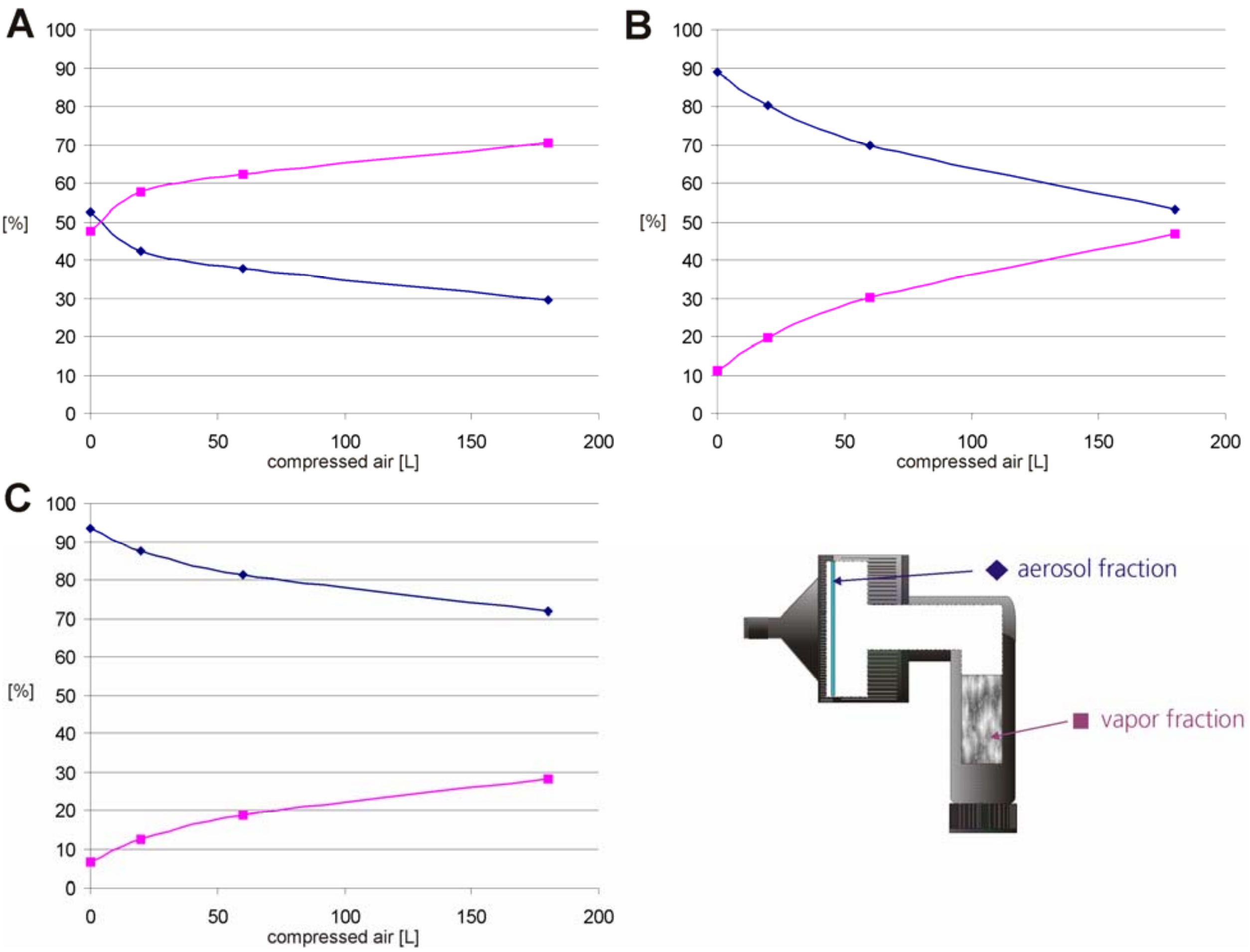
The results are shown in Tab. 6-4 and Fig. 6-7. For all samples the total concentration is constant within ±5 %. However, the aerosol-vapour partitioning changes significantly when clean air is drawn through the sampling device. At non-equilibrium conditions the aerosol fraction is always underestimated when using the BIA sampling method for workplace sampling, especially at long sampling times. In order to stay within an uncertainty of 20 % the volume sampled at non-equilibrium should be less than 30 L.

In conclusion, for sample periods of up to 8 hours the BIA method can be used in the loading range 0.03 to 10 mg for the filter and 0.06 to 10 mg for the XAD to measure the **total concentration**. The detection limit for 8 h sampling is 0.5 mg/m^3. A tolerable accuracy (20 %) of the measurement of the **aerosol fraction** is only possible for short sampling times at non-equilibrium conditions (15 minutes).

Tab. 6-4 Total concentrations and aerosol-vapour partitioning for non-equilibrium sampling conditions.

Clean air sampling volume [L]	**A**			**B**			**C**		
	Total [mg/m³]	**Aerosol fraction [%]**	**Vapour fraction [%]**	**Total [mg/m³]**	**Aerosol fraction [%]**	**Vapour fraction [%]**	**Total [mg/m³]**	**Aerosol fraction [%]**	**Vapour fraction [%]**
0	87.0	52	48	154.4	89	11	135.7	94	6
20	90.8	42	58	160.8	80	20	138.9	88	12
60	90.6	38	62	151.7	70	30	136.4	81	19
180	94.8	29	71	156.9	53	47	142.2	72	28

Fig. 6-7 Change in aerosol-vapour partitioning for non-equilibrium sampling conditions. Diamonds: aerosol fraction, squares: vapour fraction. Upper left: A ; upper right: B; lower left: C.



6.5. VIRTUAL IMPACTOR (VI) METHOD

6.5.1. Sampling at conditions of thermodynamic equilibrium

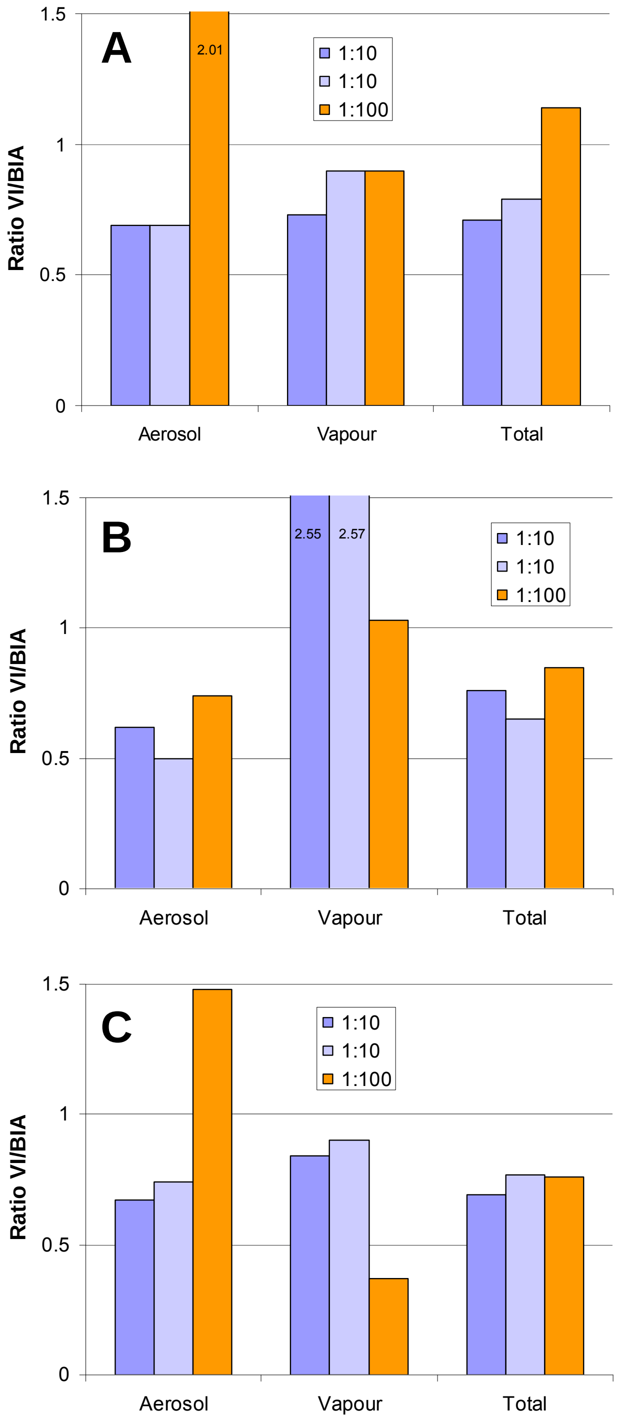
The virtual impactor was selected as the second sampling device for testing since the principle of operation suggests that evaporation losses are less pronounced compared to the BIA method, at least when the aerosol mass is mainly determined by the size fraction above the critical diameter of the virtual separation stage. In this test phase three samples were taken for each of the gas oil samples, two at the 1:10 dilution and one sample at the lower concentration from 1:100 dilution port. In addition to each of the virtual impactor samples a BIA sample was taken serving as a reference (thermodynamic equilibrium!). Gas oil material collected on the filter and the XAD of the two sampling columns of the virtual impactor was analysed separately. However, the first intention was to use the simple evaluation routine given by Eq. 2 to calculate aerosol and vapour concentration based on the integral analysis of the on-axis and off-axis samples. In Tab. 6-5 and Fig. 6-8 the so-defined aerosol and vapour concentrations as well as the total concentration are compared with the BIA reference.

Tab. 6-5 Performance of the virtual impactor at thermodynamic equilibrium sampling conditions.

Gas oil	C_BIA [mg/m³]		C_VI [mg/m³]		C_VI / C_BIA		
	Aerosol	**Vapour**	**Aerosol**	**Vapour**	**Aerosol**	**Vapour**	**Total**
A	47.6	41.4	33.0	30.2	0.69	0.73	0.71
	47.6	41.4	33.0	37.3	0.69	0.90	0.79
	1.68	5.92	3.38	5.32	2.01	0.90	1.14
B	152.0	19.3	101.5	16.2	0.67	0.84	0.69
	110.4	21.7	82.0	19.5	0.74	0.90	0.77
	5.50	10.20	8.13	3.79	1.48	0.37	0.76
C	129.1	10.1	80.2	25.8	0.62	2.55	0.76
	129.1	10.1	64.1	26.0	0.50	2.57	0.65
	6.13	3.87	4.55	3.98	0.74	1.03	0.85

The efficiency of the VI-sampler for measuring the total concentration of the gasoil-atmospheres is 79 (±14) % when sampling takes place at thermodynamic equilibrium. The efficiency is related to losses of vapour and aerosol onto the internal surfaces of the separation stage. The internal losses evaporate and are sampled on the XAD cartridges when sampling clean air through the device and thus, can almost be completely recovered. This will be shown in the next section of this report.

Fig. 6-8 Sampling efficiency of the virtual impactor method at thermodynamic equilibrium.



For **A** and **B** the aerosol fractions determined by the VI sampler in combination with the simple evaluation routine match rather well the values obtained with the reference (a BIA sample). For the third gas oil sample (**C**) the aerosol fraction of the VI method is considerably smaller compared to the reference; on the other hand the VI delivers a vapour phase concentration more than twice as high as the reference concentration. It is quite reasonable to assume, that for this gas oil product a part of the aerosol is collected off-axis because of its size distribution. From Fig. 6-2 and Fig. 6-3 it is seen that the sample **C** has the largest fraction of aerosol material in the size range smaller than 0.5 µm. This material will be collected on the off-axis filter and will therefore be attributed to the gas phase concentration which then apparently increases. In addition, for sample **C** about 90 % of the mist at the high concentration is attributed to the aerosol and only 10 % to the vapour phase (as determined by the BIA method). This means that a 10 % aerosol transfer to the off-axis filter would result in an increase in the calculated gas-phase concentration by a factor of 2.

A more detailed analysis can be made when using the additional information available from the test device by distinguishing between the filter and XAD samples in the on- and off-axis sampling column. Using the additional analytical data aerosol and vapour phase concentrations can be calculated for the on-axis and the off-axis sample. The vapour concentrations were calculated from the masses collected on the two XAD columns. For the on-axis aerosol concentration it was assumed that the entire aerosol fraction was sampled here and the reference volume flow rate was twice the value of Q actually drawn through it (see 4.2). This is shown in Tab. 6-6 for the absolute concentration values and in Tab. 6-7 for the concentration ratios.

The vapour concentration measured from the off-axis samples is always smaller than the value obtained from the on-axis XAD-samples although, ideally, it should be identical. Internal losses by condensation/adsorption of the inner surfaces of the separation stage most likely account for this. The total pressure drop through the orifice is of the order of 50 mbar. Assuming adiabatic expansion in the nozzle the temperature decrease is 6°C which can result in condensation of the vapour phase on the inner surfaces. In addition, it is known that there are losses of droplets particularly of those droplets with diameters close to the critical separation diameter. For each test under equilibrium conditions a liquid film was observed on the nozzle plate. Vapour can also be dissolved in this film according to the thermodynamic conditions.

Tab. 6-7 shows that the reference vapour concentration determined by the BIA method is approximately reproduced by the on-axis vapour concentration of the virtual impactor method. The average ratio is 0.91 with a standard deviation of 0.13 i.e. 14 %. For the aerosol fraction when off-axis and on-axis aerosol concentrations are summed up to give the total aerosol concentration (see column 6 of Tab. 6-7) the corresponding ratio is 0.85 with a standard deviation of 20 %.

Tab. 6-6 Results of the detailed analysis of the VI-samples

Gas oil	C_BIA [mg/m³]		On-axis [mg/m³]		Off-axis [mg/m³]	
	Aerosol	Vapour	Aerosol	Vapour	Aerosol	Vapour
A	47.6	41.4	32.4	30.8	5.3	24.9
	47.6	41.4	32.4	37.9	5.4	31.9
	1.68	5.92	1.70	7.00	0.30	5.02
B	152.0	19.3	103.5	14.1	7.1	9.1
	110.4	21.7	82.4	19.1	6.6	12.9
	5.50	10.20	3.50	8.42	0.11	3.68
C	129.1	10.1	95.1	10.9	18.9	6.9
	129.1	10.1	80.9	9.2	19.6	6.4
	6.13	3.87	4.74	3.79	1.57	2.41

Tab. 6-7 Ratios of the concentrations obtained by VI and BIA method

Gas oil	**On-axis VI /BIA**		**Off-axis/On-axis VI**		**Total VI/BIA**
	Aerosol	**Vapour**	**Aerosol**	**Vapour**	**Aerosol**
A	0.68	0.74	*0.16*	*0.81*	*0.79*
	0.68	0.92	*0.17*	*0.84*	*0.79*
	1.01	1.18	*0.18*	*0.72*	*1.19*
B	0.68	0.73	*0.07*	*0.65*	*0.73*
	0.75	0.88	*0.08*	*0.68*	*0.81*
	0.64	0.83	*0.03*	*0.44*	*0.66*
C	0.74	1.08	*0.20*	*0.63*	*0.88*
	0.63	0.91	*0.24*	*0.70*	*0.78*
	0.77	0.98	*0.33*	*0.64*	*1.03*

Furthermore, it is seen from column 4 of Tab. 6-7 that the three gas oil products are ranked A141/A143/A091 in the order of decreasing relative amount of aerosol sampled off-axis. This is exactly the order of the aerosol fraction smaller than 0.5 µm of the mass size distribution measured for each of the products at equilibrium conditions: 25 % for sample **A**; 21 % for **B** and 11 % for **C**. Since the critical separation diameter of the separation stage is approximately 0.7 µm the off-axis aerosol is simply the fraction not separated in the virtual impaction stage.

6.5.2. Sampling at conditions of thermodynamic non-equilibrium

The reason for evaluating the virtual impactor as a sampling device was its ability in the ideal case to measure the concentration of the total gas oil atmosphere and, separately, the concentration of the vapour phase without interference of aerosol evaporation. This would allow for an accurate distinction between the aerosol and gas phase even for non-equilibrium sampling conditions. To check for this, a similar series of experiments was conducted as for the BIA sampling method. At first, samples were taken at thermodynamic equilibrium. The non-equilibrium condition was simulated by drawing 47, 121, and 424 L of clean air through the pre-loaded devices. Approximately the same amount of clean air as for the BIA method is sucked through the individual sampling columns of the virtual impactor. The results are shown in Tab. 6-8 and Fig. 6-9.

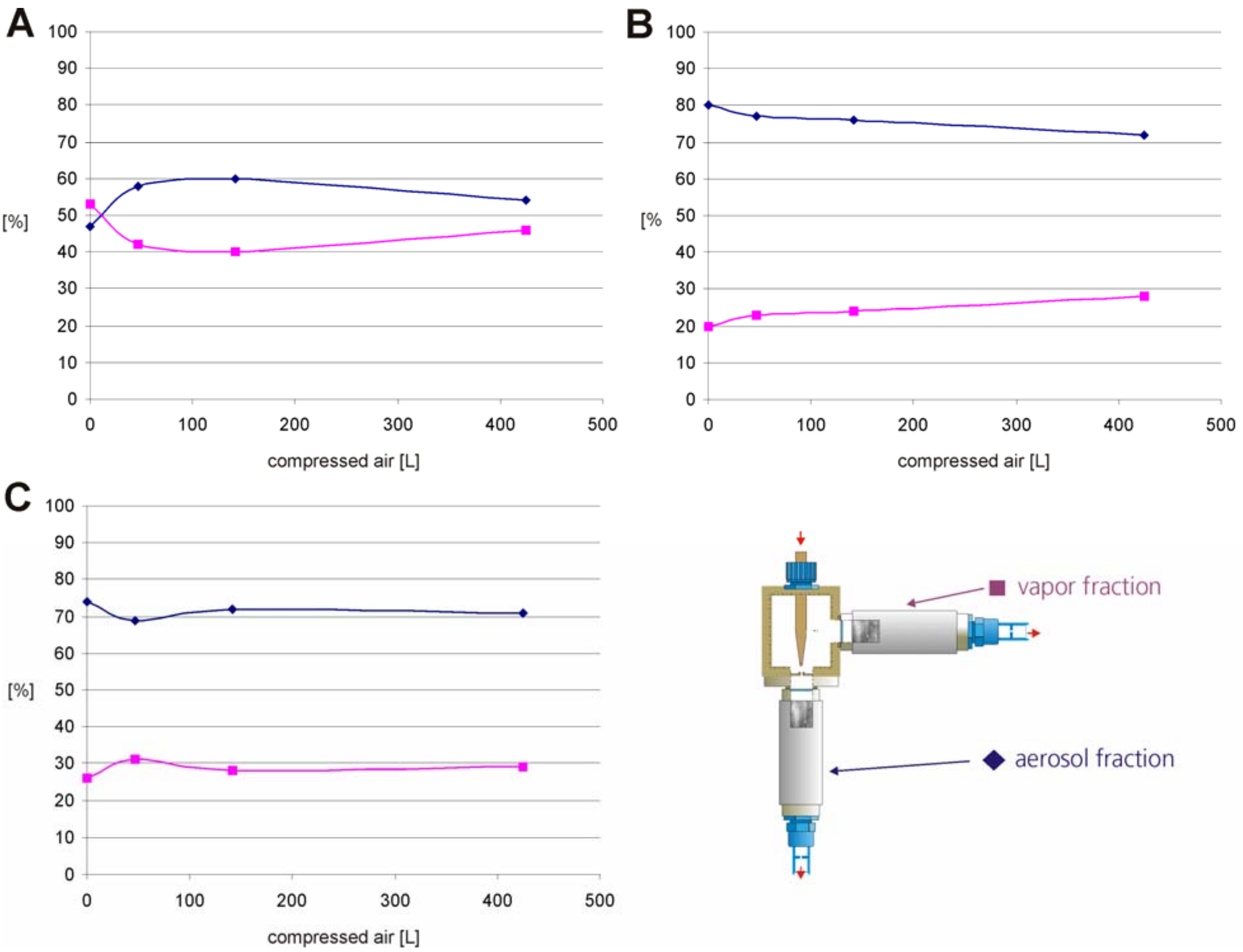
Tab. 6-8 Total concentrations and aerosol-vapour partitioning for non-equilibrium sampling conditions.

Clean air sampling volume [L]	A			B			C		
	Total [mg/m³]	Aerosol [%]	Vapour [%]	Total [mg/m³]	Aerosol [%]	Vapour [%]	Total [mg/m³]	Aerosol [%]	Vapour [%]
0	69.9	47	53	99.2	80	20	95.8	74	26
47	73.9	58	42	108.5	77	23	94.5	69	31
121	80.0	60	40	107.2	76	24	100.8	72	28
424	83.3	54	46	125.1	72	28	118.7	71	29
0 BIA	90.8	51	49	131.7	84	16	135.7	94	6

It is seen again that the initial efficiency of the virtual impactor is about 70 % of the efficiency of the BIA sampler. In contrast to the BIA sampler, the aerosol fraction does not change when clean air is drawn through the sampling device. This is because the calculations (Eq. 2) are based on the total gas oil masses collected in each of the two sampling columns which are not affected by evaporation of the fraction sampled on the corresponding filters.

The total concentration of the gas oil atmosphere increases with increasing sampling volume of clean air (see Tab. 6-8) because material deposited on the inner surfaces evaporates and is mainly collected in the off-axis XAD cartridge. Thus, from a practical point of view the efficiency of the virtual impactor could be increased by clean air sampling after the workplace sampling. Otherwise the inner surfaces of the virtual impactor could be rinsed with solvent which would be added in equal parts to the solutions obtained from the on-axis and off-axis column, respectively.

Fig. 6-9 Change in aerosol-vapour partitioning for non-equilibrium sampling conditions. Sampling device: virtual impactor. Diamonds: aerosol fraction, squares: vapour fraction. Upper left: A, upper right: B, lower left: C.



7. DISCUSSION

Two methods were investigated for their suitability for measuring the concentration of gas oil atmospheres and their ability to distinguish between the aerosol fraction and the vapour fraction. Three gas oils products were selected as test compounds for the investigations. Regarding their boiling point distribution the products were considered to represent the extremes, i.e. low and high boiling petroleum fractions and an average distribution.

Two aspects had to be considered in the study: the analytical method for the analysis of the sampled gas oil material and the method of collection of gas oil atmospheres with separation of the aerosol and the vapour phase. The characterization of the aerosol aspiration efficiency of the sampling devices was not the purpose of this study.

7.1. ANALYTICAL METHOD

Regarding the analytical method the IR-absorption at wave numbers probing the CH-vibrations was investigated in detail. This method is used in existing procedures for monitoring asphalt fumes at workplaces (BIA, 6305). The calibration factors for these three gas oil samples covering the extremes of the boiling point distributions of the samples varied by a factor of 1.13. When using a standard mineral oil mixture for calibration, the average conversion factor from standard mineral oil to the gas oil atmospheres was 1.20. Note that all actual masses presented here were calculated from the individual conversion factors. These are smaller than the value of 1.66 found as conversion factor between the standard mineral oil and the bitumen fume used for example in an inhalation study with re-aerosolized bitumen condensate (Pohlmann, et al., 2006) where the atmosphere was measured with the BIA 6305-method. In a recent field study carried out by Kriech et al. (2010) the BIA method was compared to two other methods for workplace monitoring of asphalt fumes: 1) the NIOSH method 5042 measuring the benzene soluble fraction of filter samples quantified by gravimetry, and 2) the Heritage Method combining filter sampling and XAD-collection for total organic matter (TOM) using GC-FID calibrated with kerosene. In this study the conversion factor for the BIA method was 1.425 for the paving bitumen and 1.292 for the roofing bitumen. The results obtained by the three different methods correlated, but partly with considerable scatter of the individual data pairs. For the total asphalt fume atmosphere (aerosol + vapour) the correlation between the Heritage (y) and BIA (x) method was $y=0.44x$ ($R^2=0.78$) for the paving bitumen and $y=0.74x$ ($R^2=0.91$) for the roofing bitumen.

For gas oils the compositions are dominated by alkanes and are closer to the composition of the mineral oil equivalent than the bitumen fume condensates resulting in a smaller value of the conversion factor as found in the bitumen studies. For some samples a quantitative mass evaluation of gas chromatograms (integration of the peak areas) generated from the gas oil samples was carried out. These results agree well (deviation <5%) with the results of the actual masses derived from the IR-method. Therefore, regarding the analytical procedure of sample analysis the IR-method is suggested as a suitable analytical method for gas oil atmospheres as well.

7.2. SAMPLING PROCEDURE

The sampling procedure was investigated by generating reproducible atmospheres in a laboratory set-up from the three gas oil products. Two different sampling methods were considered: 1) the filter absorbent set-up as used in the BIA method, 2) a combination of a virtual impactor and filter/absorbent cartridges. Due to losses of material in the test set-up, the reference concentration of the total gas oil atmosphere could not be derived from mass balance consideration. Furthermore, it is not possible to predict the aerosol-vapour partitioning from first principles. For the test conditions at thermodynamic equilibrium, the filter-adsorbent sampling method (BIA method) was therefore considered as a reference for the total concentration and the actual aerosol-vapour partitioning. The experimental matrix comprised: 1) testing the virtual impactor method at thermodynamic equilibrium by comparing with results from the BIA-method. 2) testing of both methods at simulated non-equilibrium conditions by first loading the sampling unit at equilibrium and subsequently drawing different volumes of clean air through the device. Aerosol and vapour phase concentrations were then compared with the reference concentrations taken at equilibrium. An independent aerosol monitor was used to check for reproducibility of the experimental conditions for the tests carried out consecutively.

The simple filter and adsorbent method as described in BIA method delivers reliable results for the **total concentration** of the gas oil atmospheres for concentrations larger than 0.5 mg/m³ for 8-hour sampling. This was shown in the laboratory tests where the aerosol size was in the range smaller than 5 µm.

The suitability for real workplace measurements of the **total concentration** when droplets larger than those used in this study are present can also be assumed. This is justified by the following arguments: The aerosol inlet of the BIA sampling device is the so called GSP-inlet, the aspiration efficiency of which was evaluated as being compatible with the CEN definitions of the inhalable aerosol fraction (CEN, 1993, Kenny et al., 1997). The flow rate of the original GSP head is 3.5 L/min. For combined aerosol and vapour sampling with a lower flow rate of 2 L/min the inlet cone can be modified to meet the sampling criteria for inhalable particles (see http://www.dguv.de/ifa/de/fac/ring/probenahme/pgp_koepfe/index.jsp). Therefore, even if large oil droplets (>10 µm) are present in the workplace air, the aspiration efficiency for the total gas oil atmosphere follows the guidelines for proper workplace sampling. In addition the BIA method has been proven to be robust for routine workplace sampling. In our test the aspect of aspiration efficiency was not addressed since the gas oil atmosphere was sucked into the device via a tube.

However, the BIA method has its drawback when the partitioning between aerosol and vapour phase has to be assessed. Evaporation losses from the aerosol phase collected on the filter leads to an underestimation of the aerosol phase and a shift of the partitioning ratio towards the vapour phase. This was quantified by following the evaporation kinetics of loaded aerosol filters by drawing clean air through the sampling device. Depending on the boiling range of the product and the sampling time, a decrease of the aerosol fraction of up to 43 % for sample **A**, 40 % for **B** and 24 % for **C** relative to the initial values was measured. The extreme values correspond to a ratio of 1:6 for the sampling times at equilibrium and (worst case) non-equilibrium sampling conditions. The aerosol losses correlate with the 50 % boiling temperature of 287°C, 302°C and 339°C for **A**, **B** and **C**, respectively, showing that obviously the lower vapour pressure compounds of the aerosol fraction cause primarily the losses. All evaporation curves show a decrease in aerosol loss rate with increasing clean air sampling time due to the fact that gas oil compounds with strongly decreasing vapour pressure remain on the filter as the sampling time increases. Initial loss rates are 10 % in 15 minutes non-equilibrium sampling time.

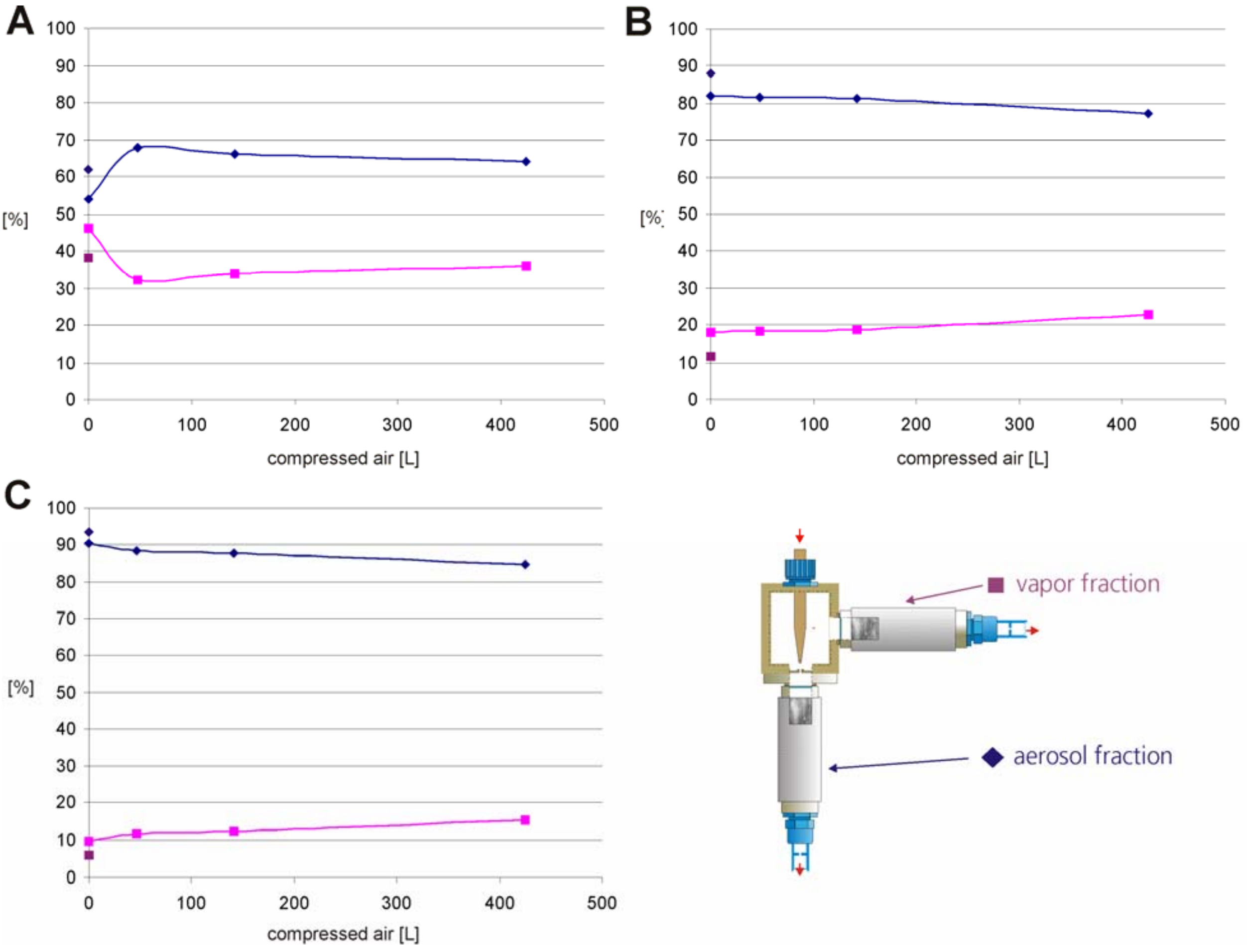
Therefore, in context of the analytical uncertainties of 10 % related to the use of a general calibration factor, the BIA method could be applied for the measurement of the aerosol-vapour partitioning (besides the total concentration) when the sampling times are short (<15 min). For longer sampling times the determination of the total concentration is still possible, but the aerosol fraction will be generally underestimated by up to 50 % with a corresponding overestimation of the vapour phase, except when high boiling mists are prevailing and the sampled atmosphere is in thermodynamic equilibrium.

An alternative sampling method also described in the literature (Kim and Raynor, 2009, 2010) that was used here is based on a technique separating vapour and particle phase in the airborne state before collection on substrates and sampling the vapour phase in a separate branch of the device which contains no oil droplets. This can be achieved by using the principle of virtual impaction. A prototype of the separation stage developed earlier at Fraunhofer ITEM was equipped with sampling cartridges intending to collect 50 % of the vapour phase sucked into the device in one (off-axis) cartridge and sampling the total aerosol phase and the other 50 % of the vapour phase in a second (off-axis) cartridge. Since the vapour phase concentration of the gas oil atmosphere is measured separately, the aerosol fraction can be calculated by subtracting the gas phase concentration from the total concentration. Like in the BIA method, this is possible with just two analytical values determined by IR spectroscopy.

The sampling technique implies that there is no shift in the partitioning coefficient irrespective of the thermodynamic state of the gas oil atmosphere. This was shown experimentally for all three gas oil samples. Comparison with the BIA method used as reference in the mode of thermodynamic equilibrium revealed losses up to 30 % for the virtual impactor sampler. However, these losses can be recovered either by rinsing the device with the solvent used for the IR technique or drawing clean air through the device to re-evaporate the deposited material.

Another possibility is given by a refined analysis when distinguishing between filter and XAD in each sampling axis. In this analysis the aerosol concentration is calculated from the filter values of the two channels and the vapour phase concentration from the off-axis XAD sample, only. The results for the non-equilibrium tests are shown in Fig. 7-1. Based on the arguments discussed in 6.5.1 a correction was applied to the first points (equilibrium) since we know the deficit in off-axis vapour phase sampling for these conditions (correction factors between 1/0.7 and 1/0.8). This correction was not applied for the rest of the data points. Obviously re-evaporation processes of material deposited on the inner surfaces partly compensate for this deficit. By comparison of Fig. 6-7 and Fig. 7-1 it is found that the refined, more laborious evaluation of the virtual impactor samples reproduce the equilibrium aerosol fractions quite well and, most importantly, do not lead to a decrease in aerosol vapour partitioning for non-equilibrium conditions. Since non-equilibrium is presumably the prevailing workplace situation, the correction is actually not needed.

Fig. 7-1 Change in aerosol-vapour partitioning for non-equilibrium sampling conditions with corrected values for L = 0 (the extra symbols at L = 0 represent the corresponding uncorrected values). Sampling device: virtual impactor. Diamonds: aerosol fraction, squares: vapour fraction. Upper left A, upper right: B, lower left: C.



Although this technique is promising to deliver both the total concentration and the partitioning coefficient for all atmospheric sampling conditions, limitations must be considered in view of the size distribution of the aerosol phase. The current device used for testing has a critical separation diameter of approx. 0.7 µm. This means that all aerosol material in the size range smaller than 0.7 µm will automatically be collected in the off-axis channel and, thus, will be allocated to the gas phase. Future development work has to aim at reducing the inner losses as well as the cut-off diameter of the separation stage and at a redesign in view of miniaturizing the overall dimensions and improving the handling.

8. CONCLUSIONS

Two sampling methods for the total concentration of gas oil atmospheres and aerosol-vapour partitioning have been investigated in a laboratory set-up: 1) a filter and XAD-adsorbent cartridge operated in series (BIA-method) and 2) a virtual-impactor combined with filter-XAD cartridges (VI-method). The material collected was analysed using a FTIR method calibrated with standard mineral oil. The following conclusions can be drawn from the results of the study:

- A conversion factor of 1.2 is suggested when calculating the gas oil mass of samples from FTIR results based on mineral oil calibration. The conversion factor is the mean of three factors determined from three gas oil products covering the upper and lower extreme of boiling point distributions of in total nine gas oil products.
- The BIA method allows for sampling and measuring the total concentration of the gas oil atmospheres for concentrations larger than 0.5 mg/m³ for 8-hour sampling.
- When using the VI-method losses of about between 15 and 30 % have been encountered when measuring the total concentration.
- Evaporation effects cause a shift of the aerosol-vapour partitioning towards the vapour phase in the BIA sampling system. The magnitude of this effect depends on the boiling range of the gas oil, the thermodynamic conditions during sampling and the sampling duration. Up to 50 % transfer of aerosol material to the gas phase has been measured in our tests. For sampling times smaller than 15 minutes the shift in the partitioning coefficient remains below 20 %. In the VI-method the aerosol-vapour fraction is nearly independent of the thermodynamic conditions and the sampling time. However, the partitioning coefficient can be influenced by small aerosol particles with diameters smaller than the critical cut-off diameter; this aerosol fraction is falsely counted as vapour phase.
- The VI method bears potential for further improvement towards reducing, the separation diameter, reducing internal losses, simplifying the layout and the handling.

9. GLOSSARY

CEN	Comité Européen de Normalisation
GSP	Gesamtstaubprobenahmesystem
ME	Mineral oil Equivalent
NIOSH	National Institute for Occupational Safety and Health
PAH	Polycyclic Aromatic Hydrocarbon
TOM	Total Organic Matter

10. REFERENCES

1. Asgharian, B., Price, O.T., Schroeter, J.D., Kimbell, J.S. and Singal, M. (2012) A lung dosimetry model of vapor uptake and tissue disposition. *Inhalation Toxicol 24, 3, 182-193*

2. BIA (2004) Messung von Gefahrstoffen - BIA-Arbeitsmappe – Gefährdungsermittlung bei chemischen und biologischen Einwirkungen. Bitumen 6305. Berlin: Deutsche Gesetzliche Unfallversicherung

3. Breuer, D. (1999) Measurement of vapour-aerosol mixtures. *J Environ Monit 1, 299-305*

4. CEN (1993) Workplace atmospheres - Size fraction definitions for measurement of airborne particles. EN 481:1993. Brussels: Comité Européen de Normalisation

5. Harper, M. (2004) Assessing workplace chemical exposures: the role of exposure monitoring. *J Environ Monit 6, 5, 404-412*

6. Kenny, L.C., Aitken, R., Chalmers, C., Fabriès, J.F., Gonzalez-Fernandez, E., Kromhout, H., Lidén, G., Mark, D., Riediger, G. and Prodi, V. (1997) A collaborative European study of personal inhalable sampler performance. *Ann Occup Hyg 41, 2, 135-153*

7. Kim, S.W. and Raynor, P.C. (2009) A new semivolatile aerosol dichotomous sampler. *Ann Occup Hyg 53, 3, 239-248*

8. Kim, S.W. and Raynor, P.C. (2010) Optimization of the design of a semivolatile aerosol dichotomous sampler. *Aerosol Science and Technol 44, 2, 129-140*

9. Kriech, A.J., Emmel, C., Osborn, L.V., Breuer, D., Redman, A.P., Hoeber, D., Bochmann, F., Ruehl, R. (2010) 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. *J Occ Environ Hyg 7, 12, 712-725*

10. NIOSH (1998) Benzene-soluble fraction and total particulate (asphalt fume). NIOSH Method 5042. Cincinnati OH: National Institute for Occupational Safety and Health

11. Pohlmann, G., Preiss, A., Koch, W., Kock, H., Elend, M., Raabe, M. (2006) Collection, validation and generation of bitumen fumes for inhalation studies in rats. Part 3: Regeneration of bitumen fumes, inhalation setup, validation. *Ann Occ Hyg 50, 8, 813-819*

12. Rühl, R., Musanke, U., Kolmsee, K., Prieß, R., Zoubek, G., Breuer, D. (2006) Vapours and aerosols of bitumen: Exposure data obtained by the German bitumen forum. *Ann Occ Hyg 50, 5, 459-468*

13. Schwarz, K. (2007) Enrichment and separation of particles in the sub-micrometer size range, Diploma thesis (in German), Technische Universität Bergakademie Freiberg

14. Volckens, J., Leith, D. (2003) Comparison of methods for measuring gas-particle partitioning of semivolatile compounds. *Atmosph. Environm. 37, 23, 3177-3188*

APPENDIX FID-CHROMATOGRAMS

Fig. 10-1 Gas chromatograms for the gas oil atmospheres sampled at thermodynamic equilibrium (1:10) (blue: aerosol fraction, pink: vapour fraction). A: Gas chromatogram sample 7, B: Gas chromatogram sample 46, , C: Gas chromatogram sample 63.

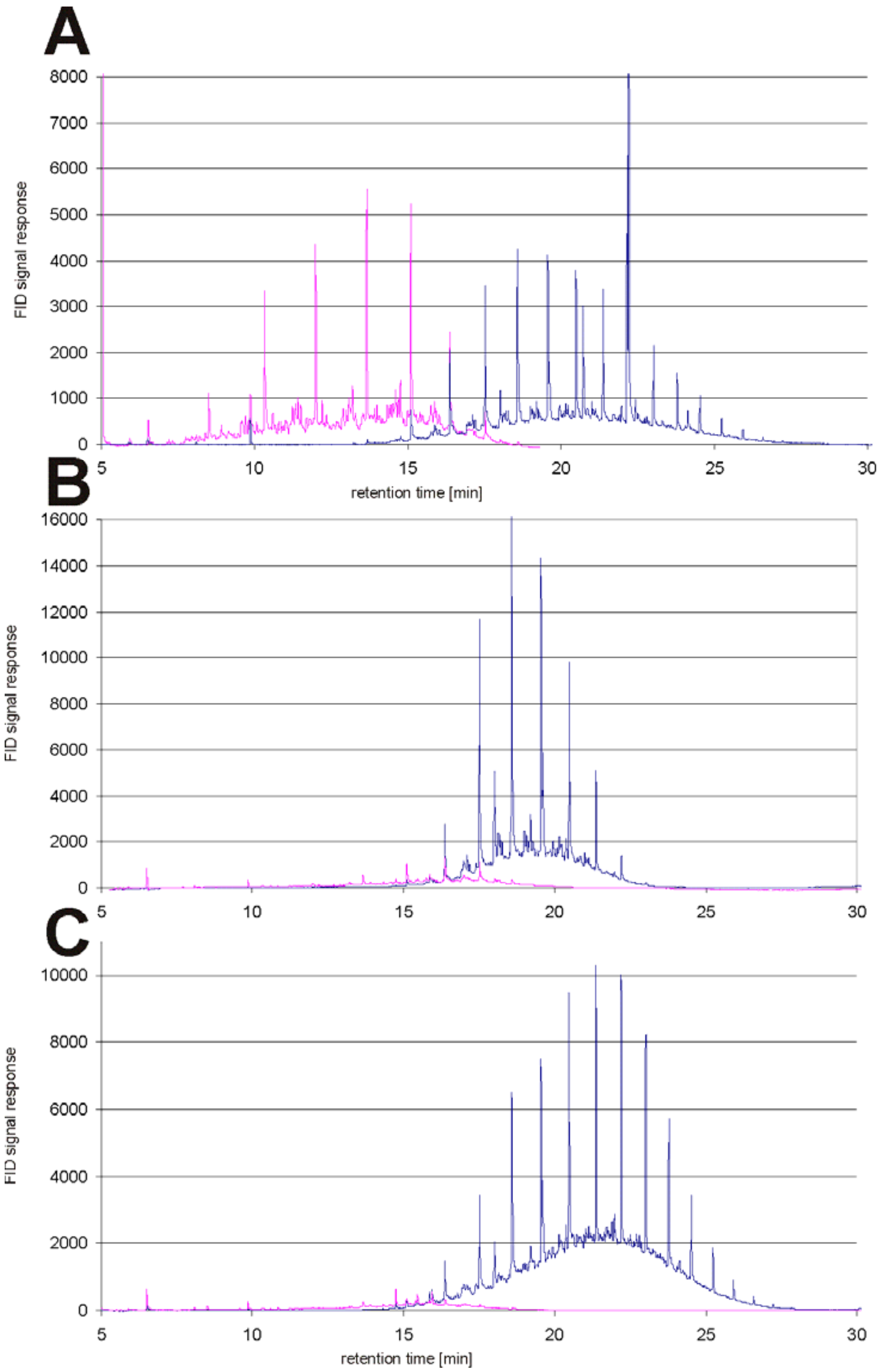
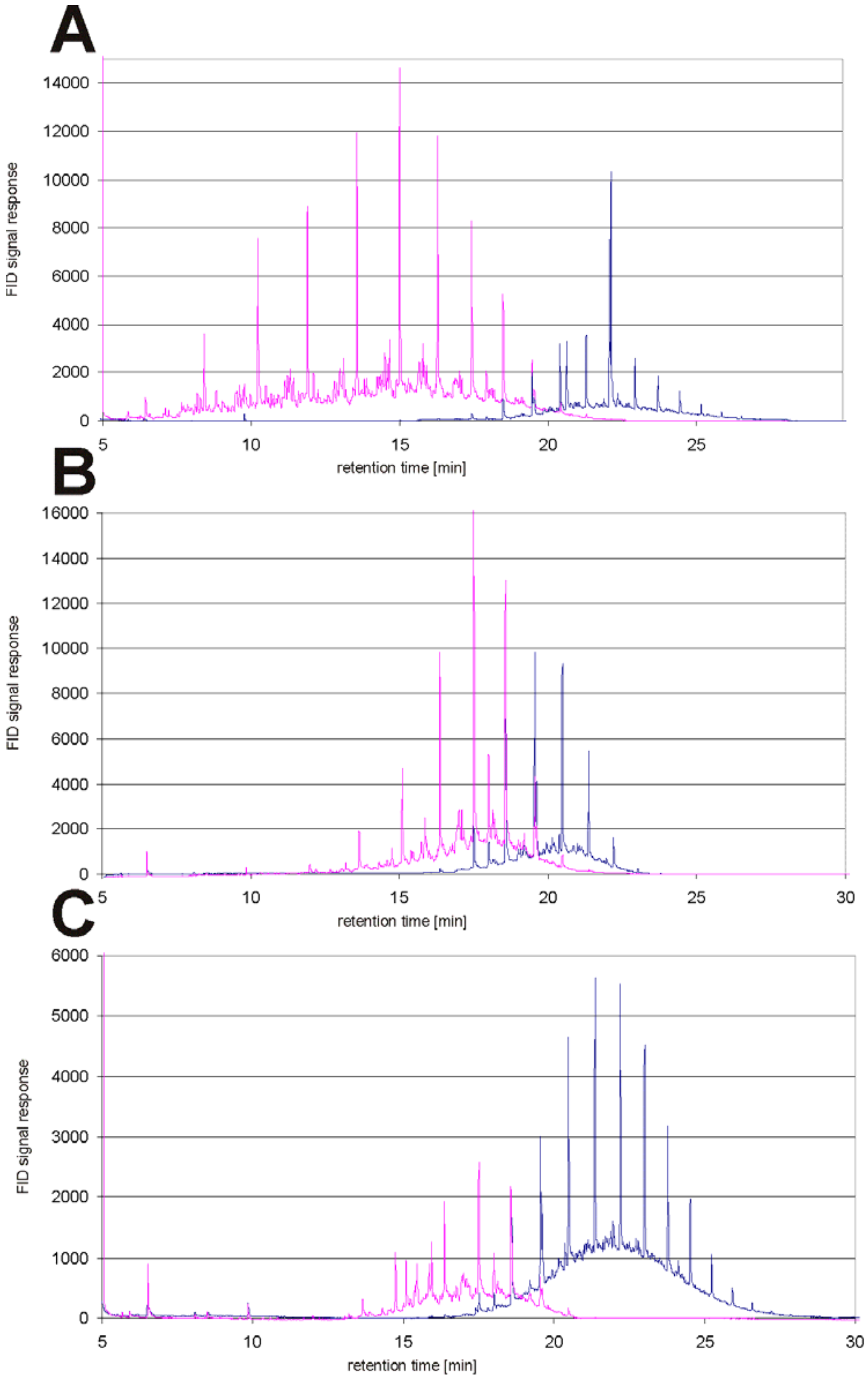


Fig. 10-2 Gas chromatograms for the gas oil atmospheres sampled at thermodynamic equilibrium (1:100) (blue: aerosol fraction, pink: vapour fraction). A Gas chromatogram sample 14, B: Gas chromatogram sample 50, C: Gas chromatogram sample 68.



Concawe
Boulevard du Souverain 165
B-1160 Brussels
Belgium

Tel: +32-2-566 91 60
Fax: +32-2-566 91 81
e-mail: info@concawe.org
website: http://www.concawe.org

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