TDTS 49

Fenceline and ambient monitoring of benzene and other hydrocarbons using diffusive sampling and TD analysis

It is recommended that this Application Note is read in conjuction with Application Note TDTS 10 (on using diffusive samplers with TD–GC analysis for monitoring VOCs in ambient air).

Summary

This Application Note provides an overview of options for the diffusive sampling of benzene and other hydrocarbons in air. Topics covered include advice on sorbent selection, deployment of samplers, uptake rates, method detection limits and application/interpretation of data.

Introduction

Benzene is a known human carcinogen and is subject to exposure limits in both workplace and ambient air in most industrialised countries. European ambient (urban) air levels are controlled to an annual average of 5 µg/m^3 (1.7 ppb) under the Benzene Directive (2000/69/EC).

Vehicle emissions are a major source of benzene in ambient air, but there are also significant industrial sources such as oil refineries. Monitoring and control of benzene concentration levels around the perimeter of all US oil refineries has been proposed by the US EPA under the 'Residual Risk Program'. Similar steps are anticipated in Europe and elsewhere.

Though benzene is perhaps the most widely regulated compound, the concentrations of other hydrocarbons, particularly olefins (alkenes), are also of interest in ambient and industrial air. These include other known carcinogens such as buta-1,3-diene, the so-called ozone precursors (see Application Note TDTS 16), hazardous air pollutants (HAPs) (see Markes' Technical Support Document for US EPA Method TO-17), and those listed in the UK protocol for refinery emissions[3]. See Appendix A–D for a listing.

This Application Note describes a low-cost diffusive monitoring method for benzene at ambient concentrations, which can be extrapolated to other hydrocarbons. The method uses long-term (1–4 week) diffusive sampling with axial samplers followed by TD–GC(MS) analysis. It can be applied to both ambient and industrial air monitoring applications, and lends itself to the generation of reliable annual concentration data.

The method is based on prEN14662-4[1], ISO/EN 16017-2[2], an internal BP method and a UK Energy Institute/Environment Agency Monitoring Protocol[3]. Details of these standard methods are given in Application Note TDTS 3.

Because not all of the above-mentioned compounds are compatible with diffusive sampling, multiple samplers would be needed to cover the widest range of analytes. However, long-term diffusion followed by automated TD–GC(MS) analysis is such a low-cost option that parallel deployment of multiple samplers is still cost-effective relative to other active sampling or auto-GC options.

In this Application Note we describe the method, and present advice regarding sorbent selection for diffusive sampling, deployment of samplers, uptake rates, method detection limits and application/interpretation of data.

Selection of sorbent and determination of diffusive uptake rates

Industry-standard sorbent tubes (3½″ × ¼″ o.d. with 4.9 mm bore) are compatible with both pumped and diffusive sampling, and have a defined air gap at the sampling end to eliminate air-speed effects and ensure reproducible quantitative data. They are available in both stainless steel and inert-coated stainless steel.

When used for diffusive sampling, only the front (first) sorbent is effective during sampling. Therefore multiple samplers, each containing a different sorbent, will be required for parallel monitoring if the analytes of interest cover a wide boiling range.

Key issues for sorbent selection for diffusive sampling include sorbent strength (to minimise back-diffusion) (see Application Notes TDTS 2, 5 and 20), inherent background/artefact levels, recovery during desorption (which should be >95% according to standard methods), hydrophobicity (the ability to selectively eliminate water) and activity (analyte stability during storage).

Ideal uptake rates may be calculated from diffusion coefficients and can generally be applied directly to sorbent–sorbate interactions that are sufficiently strong, *i.e.* with retention volumes greater than 1000 L (see Application Note TDTS 2). In all of these cases, back-diffusion will be minimal and uptake rates will therefore remain constant over time. The long-term (1–4-week) uptake rates listed in Table 1 are either fully validated or derived from short-term rates, where sorbent–sorbate interactions are sufficiently strong.

N.B. Uptake rates vary slightly (within 10%) between various standard methods, but this small variation has minimal impact on monitoring data.

A procedure for full validation of uptake rates for ambient air is described in EN 13528-2[5]. Well-recognised standard/test institutes such as the UK National Physical Laboratory (NPL), the Netherlands Measurement Institute (NMI) and VITO in Belgium offer comprehensive standard atmosphere generation facilities suitable for validation of both diffusive and pumped sampling of organic vapours in air at ambient (ppb) levels.

Uptake rates can also be readily determined in the field using parallel pumped monitoring of the real air onto sorbent tubes at low flow rates. This requires a constant-flow pump capable of 1–2 mL/min flow rates (such as the FLEC® pump) and a tube with inlet and outlet restriction (such as SafeLok™ tubes) to prevent diffusive interference. Three to six such pumped-tube assemblies can be set up to sample the air in parallel with 12 or more diffusive samplers. Alternatively, an automated sequential sampler such as Markes' MTS-32™ can be set up to sample onto a series of up to 32 tubes^6. In this case, faster pump flow rates are applied for shorter periods of time through each tube (*e.g.* 15 mL/min for 12 hours). The sequence of pumped samples can be collected over two weeks in parallel, with sampling onto a set of 12 or more diffusive tubes.

In either case, all samples (pumped and diffusive) can be analysed by TD–GC(MS) under identical analytical conditions. Having determined the actual average air concentration from the pumped tubes, the mean diffusive uptake rate can readily be determined from the diffusive tube sampler results.

Diffusive sampler deployment

General requirements

Whatever the application, diffusive samplers should invariably be housed in some sort of open box (see Figure 1) or inverted funnel-type arrangement (EN 13528-3) constructed of an inert, non-outgassing material. This gives the monitors some protection from direct sunlight and adverse weather conditions. The samplers themselves should be attached upside-down, with the sampling end pointing downwards and fitted with a diffusive sampling cap (Figure 2) to protect the sampler from particulates and air turbulence.

Figure 1: Example of a monitoring station used at a BP petrochemical site in the UK.
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Figure 2: A sampling tube, brass cap and diffusion cap.

Note that the non-sampling end of the sorbent tube must remain firmly sealed. The sampling end of the tube should project from the underside of the open box or funnel by about a centimetre in order to maintain ambient air movement past the diffusion cap. Wind speed and direction measurements may be required at each monitoring location. If so, this equipment should be taken into consideration when designing the sampler housing.

The monitoring station shown in Figure 1 is widely used in the UK by BP on the perimeter of their sites and in adjacent populated areas. It consists of a telescopic stainless steel pole (which is usually set to be 1.5 m high), set into a concrete base. The shelter is an 18″ diameter stainless steel flat top with a ~3″ rim on the edge to give some rain protection. Four connectors underneath are each capable of holding at least four tubes. It is also possible to attach other equipment, including sample pumps if required, to the central pole when necessary.

Samplers should be positioned away from any obvious local emission source or large buildings, which may cause wind funneling or other spurious effects.

N.B. Diffusion caps with a silicone membrane fitted in order to minimise water ingress are designed for short-term (8 hour monitoring) and have limited utility for long-term (7–28 day) monitoring. Note also that different uptake rates apply if a silicone membrane type cap is used.

Ambient/urban air monitoring

Samplers should be dispersed around the area of interest as illustrated in Figure 3. The placement of multiple samplers (100–200) enables generation of pollution isopleths.

Perimeter monitoring at refineries and petrochemical works

Sampling options for refinery perimeter monitoring vary depending on monitoring objectives, but samplers are typically deployed at evenly spaced angular intervals around the refinery perimeter. Recommendations range from every 15° around the plant (24 sampling locations) to every 22.5° (16 sampling locations) and every 40° (9 sampler locations).

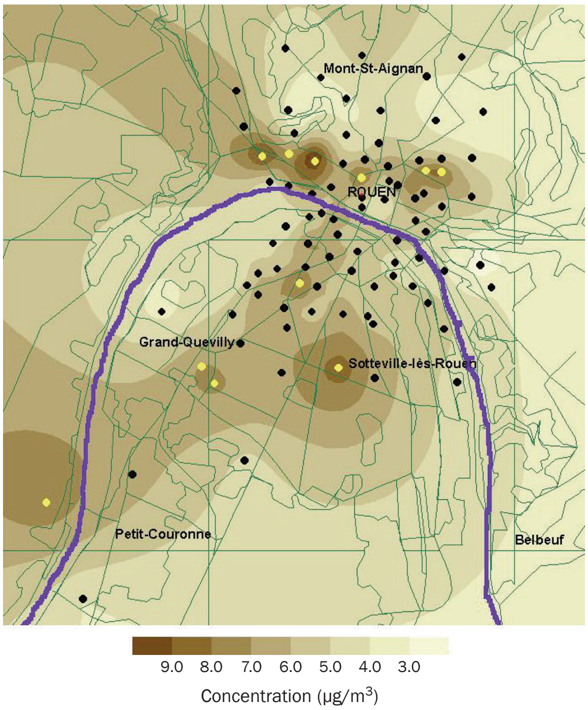

Figure 3: Locations of diffusive samplers during a monitoring exercise around Rouen, France, and the resulting benzene concentration map[7].

Additional sampling locations may also be required:

- around satellite installations (if these are thought to be responsible for >10% of total refinery emissions)
- points upwind/downwind of the plant
- in local centres of population.

Figure 4 shows a typical deployment of samplers around the 400-acre BP Hull petrochemical site in the UK. There are nine perimeter monitoring stations, sited to take account of prevailing wind, access and the nearest population centres, and a further four monitoring stations in local villages.

It is normally good practice to place replicate samplers in some locations. At least two field blanks should also be deployed for each monitoring period. These should be identical to sampling tubes, except that the caps must remain sealed at both ends throughout the monitoring period.

If compounds of interest cover a wide range of analytes, multiple samplers may be required at each monitoring location – for example Carbosieve™ SIII for $C_{2/3}$ hydrocarbons, Carbograph™ 5TD for buta-1,3-diene, and Carbograph 1TD for benzene, toluene and xylene. In this case, replicates of each sampler type will be required, and two field blanks of each type of tube should also be included in each monitoring period.

Fenceline monitoring data, together with ancillary results from upwind/downwind of the plant and in local population centres, may simply be used to demonstrate that a particular industrial installation is not contributing significantly to ambient hydrocarbon concentrations and is thus presenting minimal risk to human health. Perimeter measurements can also be used alongside wind speed and direction data, to determine emission levels and distribution of emitted hydrocarbons[3].

Sampling procedure

Urban/ambient air monitoring should be carried out over a 1–4-week period, and can be continuous if annual-average concentration data is required.

Fenceline monitoring of refineries or other industrial plant can also be continuous, but should at a minimum be carried out twice annually, in winter and summer, to determine concentrations under these different ambient conditions.

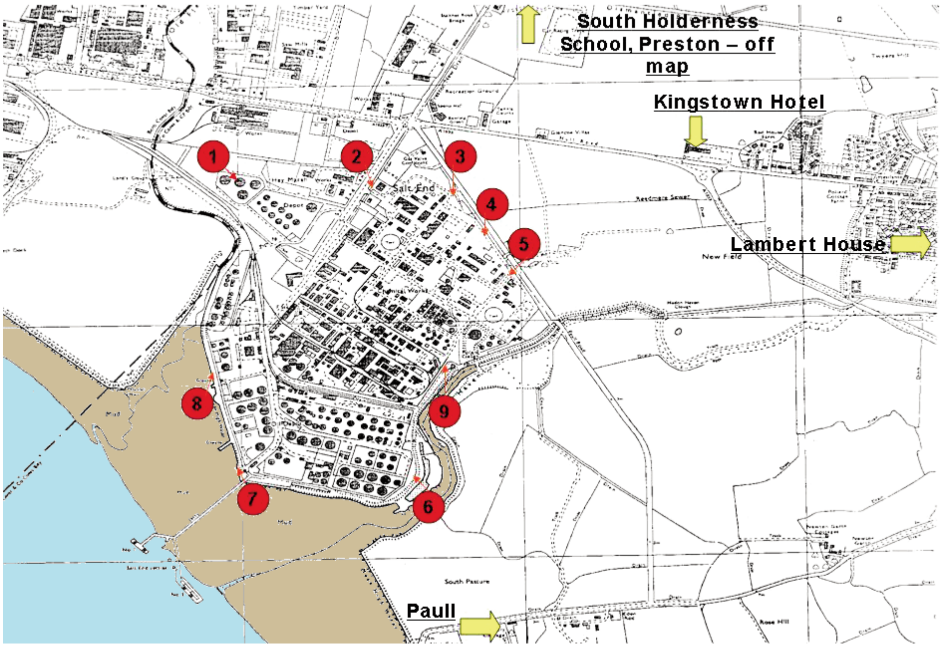

Figure 4: Location of monitoring stations at the BP Hull petrochemical site, UK. Red circles mark perimeter stations, and yellow arrows mark stations in local villages. Grid lines are 1 km apart. ***Image reproduced with the kind permission of BP.***

Diffusive monitors comprise conditioned sorbent tubes capped with long-term, SwageLok-type caps with combined PTFE ferrules (see ASTM D6196-3[8], EPA Method TO-17[9], ISO 16017[2] and other standards). A corresponding number of diffusion caps will also be required. All sorbent samplers should be fixed into or under the weather-proof box/shield without disturbing the seal at the non-sampling end. The identification number etched into the side should be noted, together with the time and date, before removing the brass cap at the sampling end using spanners or a customised tool such as Markes' CapLok™ tool (Figure 5). The diffusion cap can then be fitted. All samplers should be deployed as rapidly as possible at the start of a monitoring period to synchronise the start time.

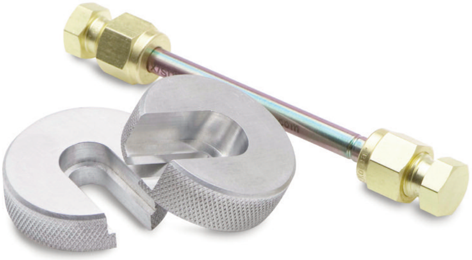

Figure 5: A CapLok tool for removal of ¼″ brass caps from sampling tubes.

A replicate sampler or set of samplers should be installed at one or more sampling locations to provide information regarding measurement uncertainty/variability. At least two field blanks of each of the types of sampler (sorbent) in use should be deployed at randomly selected sampling points to ensure that no contamination occurs during storage or transport of the tubes. These should be identical to those used for sampling, *i.e.* from the same batch, with a similar history of use and prepared in the same way and at the same time as those used for sampling. Other blank tubes should be prepared as above, but kept in the laboratory for use as analytical blanks.

At the end of sampling, tubes should be resealed with long-term storage caps using the CapLok tool or appropriate spanners to ensure correct tightening of the caps. The time and date must be noted together with tube identification numbers and any obvious anomalies. Sealed sampled tubes, replicates and blanks should be removed from the shelters and wrapped individually, or in small batches, in clean uncoated aluminium foil and placed in a clean, non-emitting airtight container (*e.g.* uncoated paint can or Tupperware®-type box) for storage and transport.

Ambient or refrigerated storage (~4°C) conditions are suitable. Tubes should be analysed within 14 days whenever possible. If refrigerated conditions are used for storage/transport, tube sealing caps should be retightened once they have reached minimum storage temperatures. Equally, refrigerated tubes must be allowed to re-equilibrate at ambient temperature before the seals are opened for laboratory analysis. If the tubes are opened when cold, condensation may occur inside the sampler, compromising the analysis.

Transport and analysis

Samplers sealed with long-term storage caps, as described above, may be transported by conventional overland postal services if the laboratory is far from the sampling location. Extra care should be taken for air transport. Shipment in standard (unpressurised and unheated) cargo holds should be avoided wherever possible. However, even this should not adversely affect tube integrity, provided appropriate care is taken regarding cap tightening and tube storage. Samplers should be analysed within 14 days of the end of the sampling period using TD–GC, and the analysis method should allow discrimination between the different compounds to be monitored.

Analysis is by TD–GC(MS) following procedures given in ASTM D6196-07, US EPA Method TO-17 or ISO 16017. Markes' ULTRA-UNITY™ automated thermal desorber is a suitable analytical TD system, offering full compliance with standard methods, *i.e.* industry-standard diffusion tubes, two-stage cryogen-free operation, backflush desorption of the focusing trap, stringent leak testing of every sample prior to analysis and sealing of tubes on the autosampler before and after analysis. Markes' TD systems are also the only ones to offer SecureTD-Q™ technology (quantitative re-collection for repeat analysis) and method validation according to ASTM D6196 Section 13.4.2. This overcomes the one-shot limitation of conventional TD technology.

Whichever thermal desorption technology is selected, useful options to consider include:

- Automated dry-purge – used to selectively purge water from tubes containing less hydrophobic sorbents such as carbon molecular sieves. Dry-purging must be carried out in the sampling direction immediately prior to desorption
- Internal standard addition – used to automatically introduce gas-phase internal standard (for example deuterated toluene) onto the sampling end of sampled or blank tubes immediately after leak testing
- Back-pressure-regulated electronic mass flow control of the carrier gas to stabilise retention times – independent of sorbent or split flow
- Electronic mass flow control of split flow for improved method/system resettability.

Analytical conditions will vary depending on target analytes and the sorbent selected, but backflush desorption means it is possible to use a single multi-sorbent focusing trap for TD analysis, even if a range of sorbents/samplers were used to cover the analyte range. Optimum trapping temperatures in the focusing trap will also vary depending on factors such as the target compound range, the sorbents selected and atmospheric humidity.

Focusing trap sorbents and trapping temperatures can be chosen for selective elimination of water and permanent gases with simultaneous quantitative retention of target analytes for all but the most volatile species (such as C_2 hydrocarbons) (for more information, see Application Note TDTS 26 on water management).

Specifications regarding acceptable blank levels are given in thermal desorption standard methods for ambient air monitoring (ISO 16017, ASTM D6196, *etc.*), but are generally in the order of 20 ng total organics on-tube (100 ng for porous polymer sorbents such as Chromosorb 106) and less than 10% of the lowest measured value for each of the compounds of interest.

Many GC capillary columns will be suitable for this application, and should provide sufficient resolution between the compounds of interest. Critical separations include ethylbenzene and *m*-xylene, and also between benzene and cyclohexane. FID or MS detectors are most commonly used.

The analytical system should be capable of detecting less than 1 ng of all species and quantifying less than 3 ng. This equates to <0.2 ppb for all species over a 2-week sampling period (see below).

Ideally, the method for introduction of a calibration standard into the analytical system should be as similar to the sampling method as possible. Therefore, the calibration standards should be introduced onto a standard thermal desorption tube, either from a standard atmosphere or by injection of a liquid standard onto the tube in a flow of carrier gas (see Application Note TDTS 7 on calibration of thermal desorption systems).

Calculation and interpretation of data

Detailed advice regarding the calculation of atmospheric concentrations from the mass of analyte collected on a diffusively sampled sorbent tube is presented in Application Note TDTS 25. Some relevant uptake rates (*U*) are provided in Table A1 (see Appendix A), and a full listing can be found in Application Note TDTS 1.

As an example, the following calculations would apply to a sampler packed with Carbograph 1TD that was found to have collected 100 ng of benzene over 2 weeks:

$$\begin{aligned}\text{Concentration (ppb)} &= \frac{\text{Mass (ng)}}{10 \times U\ (\text{pg ppb}^{-1}\ \text{min}^{-1}) \times \text{Time (weeks)}}\\ &= \frac{100}{10 \times 2.02 \times 2}\\ &= 2.5\ \text{ppb}\end{aligned}$$

A quantitation limit of 3 ng can therefore be seen to equate to <0.1 ppb concentration for benzene over a 2-week monitoring period.

Concentration data can be compared across all sampling points – including background (upwind) locations – to estimate the contribution of the source to ambient/background levels and to compare all data points against regulated limit levels. This will allow an assessment of any potential risk to health for those living in the vicinity.

For detailed advice on using perimeter concentrations and wind speed/direction measurements to determine the actual level and compound distribution of refinery emissions, please refer to the UK Energy Institute/Environment Agency protocol[3].

For a description of how to input urban/ambient air monitoring data to suitable software programs for providing pollution isopleths (*i.e.* for illustrating the distribution of pollution across an area), see ref. 7.

References

1. prEN 14662: Ambient air quality – standard method for the measurement of benzene concentrations. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
2. EN ISO 16017: Air quality – sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling.
3. *Protocol for the determination of the speciation of hydrocarbon emissions from oil refineries*, UK Energy Institute/Environment Agency, May 2004.
4. UK HSL MDHS Method 63/2: 1,3-Butadiene in air – Laboratory method using molecular sieve diffusion samplers, thermal desorption and gas chromatography.
5. EN 13528: Ambient air quality – diffusive samplers for the determination of concentrations of gases and vapours. Requirements and test methods. Part 1: General requirements. Part 2: Specific requirements and test methods. Part 3: Guide to selection, use and maintenance.
6. N.T. Plant, M.D. Wright and R.H. Brown, European diffusive sampling initiative: Final project report. 1999, HSL Publications Report No. OMS/99/08.
7. N. Gonzalez-Flesca, M.S. Bates, V. Delmas and V. Cocheo, Benzene exposure assessment at indoor, outdoor and personal levels. The French contribution to the Life MACBETH Programme, *Environmental Monitoring and Assessment*, 2003, 65: 59–67.
8. ASTM D6196-03: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.
9. US EPA Method TO-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes.
10. N.A. Martin, P. Duckworth, M.H. Henderson, D.J. Marlow and B.A. Goody, Determination of 7- and 14-day 1,3-butadiene diffusive uptake rates for the sorbent Carbopack X in axial samplers, *The Diffusive Monitor*, 2003, 14: 4–6.
11. T. Hafkenscheid, F. Langelaan and A. Baldan, Uptake rates for 4-week diffusive sampling of chlorinated butadienes in indoor air, *Proceedings of Measuring Air Pollutants by Diffusive Sampling*, Montpellier, France, September 2002.

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Appendix A – Uptake rates

Compound	Sorbent	Exposure time (weeks)	Uptake rate ($\text{pg ppb}^{-1}\ \text{min}^{-1}$)	Comments
Benzene	Carbograph 1TD [a]	1	2.14	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		2	2.02	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		4	1.85	Fully validated: preEN 14662-4 & ISO/EN 16017-2
	Chromosorb 106	2	1.47	Fully validated: preEN 14662-4 & ISO/EN 16017-2
	Carbopack X	2	1.99	Fully validated: preEN 14662-4 & ISO/EN 16017-2
Toluene	Carbograph 1TD [a]	1	2.16	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		2	2.13	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		4	2.07	Fully validated: preEN 14662-4 & ISO/EN 16017-2
	Chromosorb 106	2	1.91	Fully validated: preEN 14662-4 & ISO/EN 16017-2
Xylene	Carbograph 1TD [a]	1	2.37	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		2	2.07	Fully validated: preEN 14662-4 & ISO/EN 16017-2
		4	1.94	Fully validated: preEN 14662-4 & ISO/EN 16017-2
	Chromosorb 106	2	2.09	Fully validated: preEN 14662-4 & ISO/EN 16017-2
Ethylbenzene	Carbopack B [a]	2	2.19	Partially validated: ISO/EN 16017-2
		4	2.30	Partially validated: ISO/EN 16017-2
Trimethylbenzene	Carbopack B [a]	2	2.20	Partially validated: ISO/EN 16017-2
		4	2.30	Partially validated: ISO/EN 16017-2
Decane	Tenax TA	4	2.93	Partially validated: ISO/EN 16017-2
Undecane	Tenax TA	4	3.34	Partially validated: ISO/EN 16017-2
Buta-1,3-diene	Carbopack X	1	1.19	Partially validated: MDHS63-2 [4]
		2	1.02	Partially validated: NPL [10]
n-Nonane	Tenax TA	1–2	2.00	RV > 1000 L; $U_{\text{long-term}}$ extrapolated from $U_{8\text{ h}}$
n-Dodecane	Tenax TA	4	3.75	RV >1000 L; $U_{\text{long-term}}$ predicted from that for undecane
Tetrachlorobutadiene	Tenax TA	4	3.00	Partially validated: NMI [11]
Pentachlorobutadiene	Tenax TA	4	3.40	Partially validated: NMI [11]
Hexachlorobutadiene	Tenax TA	4	3.50	Partially validated: NMI [11]

Table A1: Long-term uptake rates for axial diffusive sampling of ambient air (data kindly supplied by Dr Theo Hafkenscheid).

[a] Carbograph 1TD and Carbopack B are equivalent graphitised carbon black sorbents with identical surface areas (100 m^2/g).

Appendix B – Ozone precursors

European list

Ethane
Ethene
Ethyne
Propane
Propene
n-Butane
Isobutane
1-Butene
trans-2-Butene
cis-2-Butene
1,3-Butadiene
Isopentane
1-Pentene
2-Pentene
Isoprene
n-Hexane
Isohexane
n-Heptane
n-Octane
Isooctane
Benzene
Toluene
Ethylbenzene
m- + *p*-Xylene
o-Xylene
1,2,4-Trimethylbenzene
1,2,3-Trimethylbenzene
1,3,5-Trimethylbenzene
Formaldehyde
Non-methane hydrocarbons (NMHCs)

US list

Ethane
Ethene
Propane
Propene
Isobutane
n-Butane
Acetylene
trans-2-Butene
But-1-ene
cis-2-Butene
Cyclopentane
Isopentane
n-Pentane
trans-2-Pentene
1-Pentene
cis-2-Pentene
2,2-Dimethylbutane
2,3-Dimethylbutane
2-Methylpentane
3-Methylpentane
Isoprene
2-Methyl-1-pentene
Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
Cyclohexane
2-Methylhexane
2,3-Dimethylpentane
3-Methylhexane
2,2,4-Trimethylpentane
n-Heptane
Methylcyclohexane
2,3,4-Trimethylpentane
Toluene
2-Methylheptane
3-Methylheptane
n-Octane
Ethylbenzene
m- + *p*-Xylene
Styrene
o-Xylene
n-Nonane
Isopropylbenzene
n-Propylbenzene
m-Ethyltoluene
p-Ethyltoluene
1,3,5-Trimethylbenzene
o-Ethyltoluene
1,2,4-Trimethylbenzene
n-Decane
1,2,3-Trimethylbenzene
m-Diethylbenzene
p-Diethylbenzene
n-Undecane
n-Dodecane

Appendix C – Hazardous Air Pollutants (HAPs)

As defined by the HON rule under US Clean Air Act Amendment and in US EPA Method TO-17 (* = Compounds cited in US EPA Method TO-14).

* Methyl chloride
* Vinyl chloride
Diazomethane
1,3-Butadiene
* Methyl bromide
Phosgene
Vinyl bromide
Ethylene oxide
* Ethyl chloride
Acetaldehyde
* Vinylidene chloride
Propylene oxide
Methyl iodide
* Dichloromethane
* 3-Chloropropene
Carbon disulfide
Methyl *tert*-butyl ether
Propanal
* 1,1-Dichloroethane
2-Chloro-1,3-butadiene
Chloromethyl methyl ether
Acrolein
1,2-Butylene oxide
* Chloroform
Ethyleneimine
Hexane
* Acrylonitrile
* 1,1,1-Trichloroethane
Methanol
* Carbon tetrachloride
Vinyl acetate
Methyl ethyl ketone (MEK)
* Benzene
Acetonitrile
* 1,2-Dichloroethane
Triethylamine
* 1,2-Dichloropropane
2,2,4-Trimethylpentane
Bis(chloromethyl) ether
* 1,3-Dichloropropene
* Toluene
* Trichloroethene
1,1,2-Trichloroethane
* Tetrachloroethene
Epichlorhydrin
* 1,2-Dibromoethane
Bromoform
* Chlorobenzene
* Ethylbenzene
* Xylenes
* Styrene
Methyl isobutyl ketone (MIBK)
* 1,1,2,2-Tetrachloroethane
Cumene
Acrylic acid
N,*N*-Dimethylformamide
Acetophenone
Dimethyl sulfate
* Benzyl chloride
1,2-Dibromo-3-chloropropane

Bis(2-chloroethyl)ether
Chloroacetic acid
Aniline
* 1,4-Dichlorobenzene
Acrylamide
N,*N*-Dimethylaniline
Hexachloroethane
* Hexachlorobutadiene
Isophorone
N-Nitrosomorpholine
Cresylic acid
o-Cresol
o-Hydroxyphenol
Phenol
* 1,2,4-Trichlorobenzene
Nitrobenzene
Ethyl acrylate
Methyl methacrylate

Appendix D – Compounds of interest listed in the UK Energy Institute/Environment Agency protocol for monitoring refinery parameters

Total unsaturates and total saturates broken down by carbon number (C_2 to C_{12}) (to sum to 100% by weight).

Benzene
Toluene
Xylene (all isomers)
Ethylbenzene
Total aromatics
1,3-Butadiene
Ethane
Propene
Butenes (all isomers)
Pentenes (all isomers)
1,2-Dichloroethane
1,1,2,2-Tetrachloroethane

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