Thermal Desorption: A Practical Applications Guide

I. Environmental Monitoring & Exposure to Chemicals at Work

2nd Edition

MARKES international

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Introduction to Markes International Ltd

Formed in 1997, Markes International is world leader in the development and manufacture of analytical thermal desorption (TD) instrumentation and associated sampling equipment for measuring VOCs and semi-volatiles in air & materials.

Markes has pioneered major TD innovations such as quantitative re-collection for repeat analysis (**SecureTD-Q™**), **TubeTAG™** RFID tube labels, **DiffLok™** enabling technology for robust tube automation and cryogen-free analysis of multiple canister air samples. All these innovations feature in Markes' well known modular range of TD instruments: **UNITY™**, **ULTRA™**, **Air Server™** and the most recent addition, the **TD-100™**. Other ground-breaking TD products from Markes International include the twin-trap **TT24-7™** for continuous, online air monitoring, and unique sampling accessories such as the **Micro-chamber/Thermal Extractor™** and **HS5-TD™** for liquid and solid samples.

Markes' TD units can be seamlessly combined with all major brands of GC and GC/MS to provide trace or high level monitoring solutions.

What is analytical TD?

Analytical thermal desorption is a sample introduction technique for GC and GC/MS, which uses heat and a flow of inert gas, rather than an organic solvent, to extract/desorb analytes from the sample media, delivering them directly to the gas chromatograph. Since the early 1980s, TD has provided the ultimate versatile sample introduction technology for GC, by combining selective concentration enhancement with direct extraction into the carrier gas and efficient transfer/injection, all in one fully automated and labour-saving package.

Markes International Ltd, UK headquarters

Applications

Thermal desorption is now recognised as the technique of choice for environmental and workplace air monitoring. Relevant standard methods include: EN ISO 16017, EN 14662 (parts 1 & 4), prEN 13649, ASTM D6196, US EPA TO-17 and NIOSH 2549. Related applications include monitoring chemical warfare agents (CWA) in demilitarisation/destruction facilities & civilian locations (counter-terrorism).

TD is also routinely used for monitoring volatile and semi-volatile organic compounds [(S)VOCs] in products and materials. Examples include residual solvents in packaging & pharmaceuticals, material emissions testing and food, flavour & fragrance profiling.

This publication presents several real world applications in environmental air monitoring and occupational health & safety. Accompanying publications cover the application areas of:

- Food, flavour, fragrance & odour profiling
- Defence & forensic
- Chemical emissions from products & materials

Environmental monitoring

- Atmospheric research
- Ambient/urban air monitoring
- Industrial (stack) emissions testing
- Odour monitoring
- Indoor air quality
- Soil gas & vapour intrusion assessment
- Trace volatiles and odours in water
- Workplace air monitoring/industrial hygiene
- Personal exposure monitoring (inhalation)
- Biological exposure assessment (breath testing)



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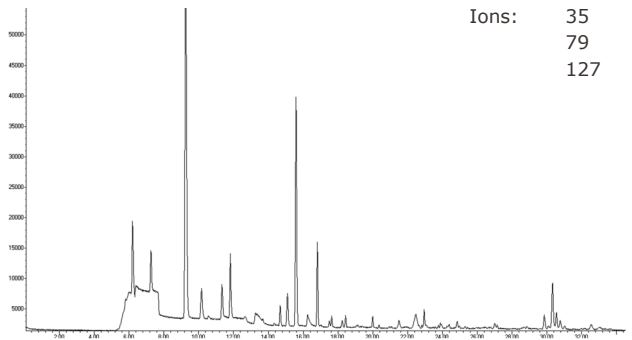
Atmospheric research



30 ml of air from bubbles in the ice core collected in canisters. Analysis by TD-GC/MS in NCI mode. Low ppt detection limits

Background:

Markes thermal desorption instrumentation is used extensively in atmospheric research for monitoring trace organic vapours. For example:

- Global migration of pollution
- Research into stratospheric chemistry
- Marine research: Studying the oceans as a potential 'sink' or reservoir for air pollutants
- Historical pollution data *e.g.* levels of freons in air bubbles trapped in polar ice

Markes TD systems offer best available desorption efficiency allowing splitless operation & optimum sensitivity without liquid cryogen

Std. methods: EN ISO 16017-1, ASTM D 6196, US EPA TO-17, (tubes) or US EPA TO-15 (canisters)

Typical analytical conditions:

Sampling: Pumped multi-sorbent tube or canister

TD: Series 2 (UltrA-)UNITY or TD-100 for tubes, UNITY-CIA 8 (+ dryer) for canisters

Dry purge if no dryer used during sampling

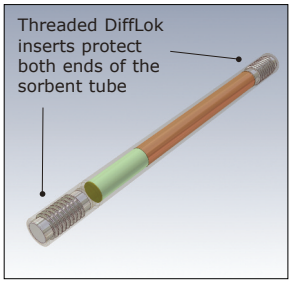
Splitless desorption

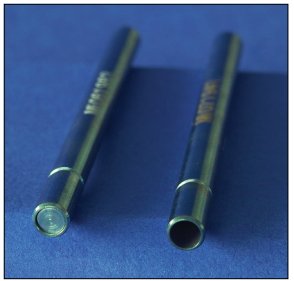
Trap: U-T16GHG-2S or U-T15ATA-2S

Analysis by GC/MS using SIM, NCI or TOF MS

References: TDTS 81 (TO-15), 86 (TO-17) & 87 (ultra-volatile freons & other greenhouse gases)

SafeLok™ – Specialist sample tubes for trace detection

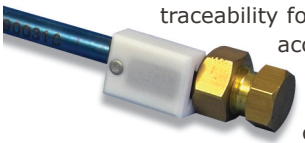




SafeLok samplers incorporate Markes patented DiffLok technology to prevent artifact ingress. This aids trace level monitoring

TubeTAG

All Markes tubes, including SafeLok tubes, are now available with or without TubeTAG electronic (RFID) tube labels. TubeTAG offers fail-safe tracking of tubes in transit for field monitoring. It also enhances tube traceability for GLP and laboratory accreditation. Recorded information includes: sorbent details, number of thermal cycles, date of packing, *etc.*



* *GB 2337513*
US 6,564,656 B1

Background:

SafeLok samplers have the same sorbent capacity as standard tubes but incorporate Markes patented* diffusion-locking (DiffLok) technology at both ends of the tube to prevent artefact ingress.

With the same external dimensions as standard TD tubes, SafeLok tubes are uniquely suited to monitoring ultra-low concentration environments *e.g.* at the North Pole or mid-Pacific. Samples are protected from contamination during storage/transport & during subsequent TD-GC/MS analysis in a conventional laboratory.

Implementation of TubeTAG with SafeLok tubes significantly enhances the traceability of key samples.

Std methods: EN ISO 16017-1, US EPA TO-17, ASTM D 6196

Typical analytical conditions:

Sampling: Pumped multi-sorbent SafeLok tube

TD: Series 2 (UltrA-)UNITY or TD-100

Dry purge

Splitless desorption

Trap: Select according to target analyte range

Analysis by GC/MS

References: TDTS 61 (diffusion locking technology) & Markes TD accessories & consumables catalogue

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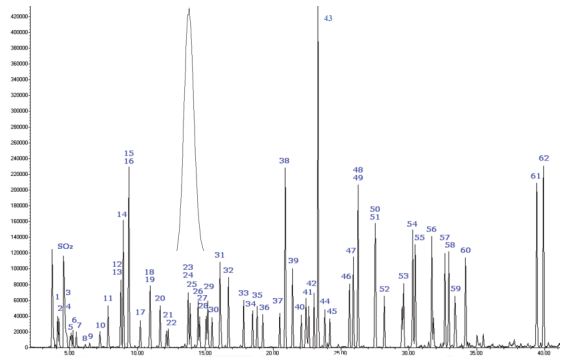
TO-17: 'Air toxics' in urban air using pumped sampling onto sorbent tubes



1	Propylene	21	Vinyl acetate	42	Tetrachloroethylene
2	Dichlorodifluoromethane	22	Cis-1,2-Dichloroethylene	43	Methyl *n*-butyl ketone
3	1,2–Dichlorotetrafluoroethane	23	Methyl ethyl ketone	44	Dibromochloromethane
4	Methyl chloride	24	Ethyl acetate	45	1,2–Dibromoethane
5	1,2-Dichloroethane	25	Tetrahydrofuran	46	Chlorobenzene
6	1,3-Butadiene	26	Chloroform	47	Xylene
7	Vinyl chloride	27	1,1,1-Trichloroethane	48	Xylene
8	Methyl bromide (bromomethane)	28	Cyclohexane	49	Xylene
9	Chloroethane	29	Carbon tetrachloride	50	Styrene
10	Trichlorotrifluoroethane (Freon 113)	30	Benzene	51	Tribromomethane
11	Ethanol	31	*n*-Heptane	52	1,1,2,2-Tetrachloroethane
12	1,2-Dichloroethylene	32	Trichloroethylene	53	1,2,4-Trimethylbenzene
13	1,1,2-Trichlorotrifluoroethane	33	1,2–Dichloropropane	54	1,3,5-Trimethylbenzene
14	Acetone	34	1,4-Dioxane	55	1-Ethyl-4-methyl benzene
15	Carbon disulfide	35	Bromodichloromethane	56	Ethylbenzene
16	Isopropyl alcohol	36	Trans-1,3-dichloropropene	57	1,2-Dichlorobenzene
17	Methylene chloride	37	Methyl isobutyl ketone	58	1,3-Dichlorobenzene
18	*Tert*-butyl methyl ether	38	Toluene	59	alpha-Chloromethylbenzene
19	*n*-Hexane	39	Cis-1,3-Dichloropropene	60	1,4-Dichlorobenzene
20	1,1-Dichloroethane	40	Trans-1,2-Dichloroethylene	61	1,2,4-Trichlorobenzene
		41	1,1,2-Trichloroethane	62	Hexachloro-1,3-butadiene

Pumped sampling of 1 L of 1 ppb air toxics standard analysed splitless using ATA tubes. Inset shows close-up of extracted mass ion 45 for IPA, demonstrating excellent peak shape

Background:

US Clean Air Act regulations have identified specific 'Hazardous Air Pollutants' (HAPs) also known as 'air toxics'. These analytes cover a wide range of polarities & volatilities & are most effectively monitored using pumped sampling onto multi-sorbent tubes with automated TD-GC/MS (scan) analysis.

Markes cryogen-free TD technology meets all the requirements of TO-17 compliant air toxics analysis

Std. method: US EPA Method TO-17

Typical analytical conditions:

Sampling: Pumped sorbent tube (20-50 ml/min)

Sorbent: 'Air Toxics' (ATA) or 'Universal' tubes

TD system: Series 2 (UltrA-)UNITY or TD-100

On or offline dry purge before desorption

Desorption: 10 mins at 320ºC

Trap: U-T15ATA-2S (Air toxics/soil gas): +25 to 330ºC

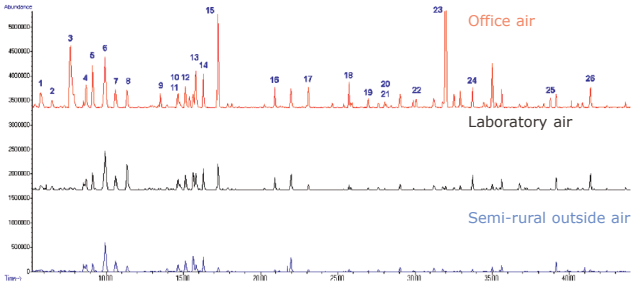
Split: Splitless or low split during trap desorption only

Column: 60 m x 0.32 mm x >1 µm for 'volatiles'

Analysis: GC/MS (scan)

References: Markes Technical Support Document for TO-17, TDTS 86 (using sorbent tubes to monitor air toxics in air as per TO-17)

MTS-32™ Sequential tube sampler



1	Methanol	11	Cyclohexane	21	Cyclohexanone
2	2-methyl butane	12	3-methyl hexane	22	Alpha-myrcene
3	Ethanol	13	Heptane	23	D-limonene
4	Acetone	14	Acetic acid	24	Phenol
5	Isopropyl alcohol	15	1-methyl-2-propanol	25	Menthol
6	2-methyl pentane	16	Toluene	26	2-phenoxy ethanol
7	3-methyl pentane	17	Hexanal		
8	Hexane	18	Xylene		
9	Ethyl acetate	19	Xylene		
10	2-methyl hexane	20	Alpha-pinene		

Three 1 L real air samples collected using 'Universal' sorbent tubes and desorbed splitless using TO-17 conditions as above

Applying TO-17:

TO-17-type methods, based on pumped air monitoring with multi-sorbent tubes, can be applied to ambient indoor and outdoor air samples. They facilitate simultaneous analysis of a wide range of apolar & polar organic vapours including very-volatile, volatile & semi-volatile components.

Markes TD systems uniquely feature quantitative re-collection of any split flow (primary or secondary) for repeat analysis and simple validation of recovery per standard methods, such as ASTM D6196 (SecureTD-Q).

Example analytical conditions are listed above

TO-17 performance data using Markes TD technology with GC/MS (scan):

Retention volumes for lightest components (propene, methyl chloride):

- >2 L on 'Air Toxic' (ATA) tubes at 25ºC
- >1 L on 'Universal' tubes at 25ºC

Detection limits: <0.1 ppb for all compounds in scan

Linearity: Typical R^2 values of 0.99 at low ppb

Precision: Typical % RSDs <6

Carryover: <0.1%

SecureTD-Q confirms quantitative recovery across the volatility range

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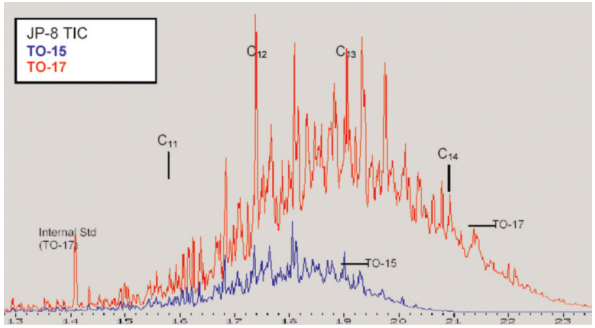
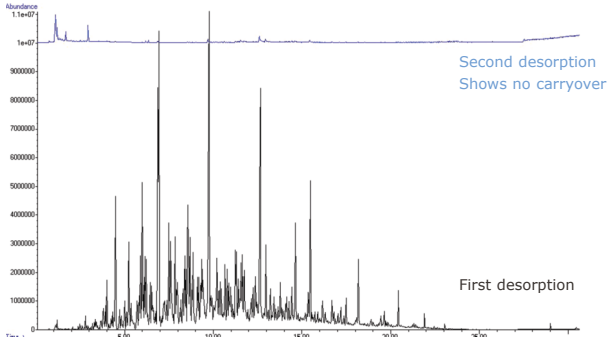
Soil gas and vapour intrusion assessment



Profiles of soil gas contaminated with kerosene (JP-8) sampled using sorbent tubes (red) and canisters (blue). Data presented courtesy of Air Toxics Inc., CA, USA



First and second desorptions of a Soil Gas tube used to sample diesel vapour in contaminated soil

Background:

Soil gas measurements are used to assess the potential risk to human health from vapour intrusion into nearby buildings & to identify sources for mitigation & liability management. Key target analytes include gasoline & middle distillate fuels plus solvents *e.g. dry cleaning or degreasing agents.* Canister, bag and sorbent tube sampling methodologies are used.

Markes Soil Gas tubes allow quantitative recovery of the widest range of potential target analytes, without water interference. Markes' TD systems also benefit this application by accommodating tube & canister samples on the same analytical platform & by offering re-collection for repeat analysis of tube samples.

Standard methods: US EPA Methods TO-17 or TO-15

Typical analytical conditions:

Pumped sampling onto Soil Gas tubes

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 300ºC for 5 mins

Trap: U-T15ATA-2S (Air toxics/soil gas):+25 to 330ºC

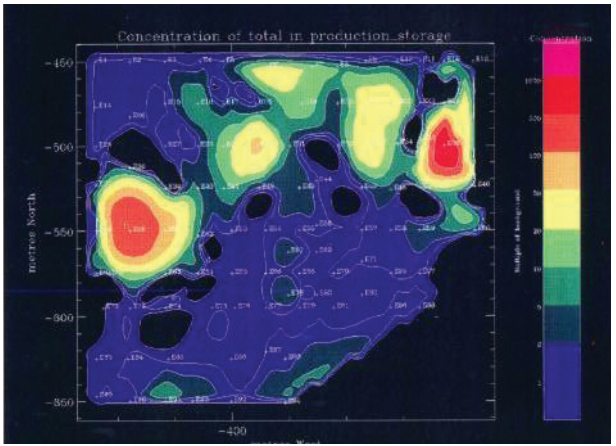
Splitless to 5,000:1 (double) split depending on contamination level

Apolar analytical capillary column

Analysis: GC/MS (scan)

References: TDTS 80 (Soil gas) & Hayes, H. C., *et al.* (2007), Evaluation of sorbent methodology for petroleum impacted site investigations, *Proc. Air & Waste Man. Assoc. conf. on vapor intrusion*

In situ monitoring of underground contamination



Soil probes arranged in a grid pattern around an industrial site allow low-cost mapping of contaminated ground

VOC-Mole soil probe fitted with a sorbent tube configured for diffusive (passive) sampling

Background:

Underground fuel or chemical leaks present a grave environmental risk. Markes VOC-Mole™ soil probes containing standard diffusive or pumped tube samplers allow cost-effective, *in situ* screening of large areas of land including active production sites. They can also be placed along the length of fuel pipelines to provide early warning of a leak. VOC-Moles configured with diffusive (passive) samplers are easy to deploy & allow rapid (*e.g.* 15 minute) or longer term (24 to 48 hour) exposure. The soil probes themselves can be left *in situ* if regular monitoring is required. Subsequent automated TD-GC/MS analysis allows identification of the nature, source & spread of ground contamination.

Typical analytical conditions:

Sampling: Sorbent tubes used diffusively inside soil probes

Sorbent: Tenax® TA or Soil Gas tubes

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 280ºC

Trap: Tenax TA or U-T15ATA-2S: +25ºC to 320ºC

Splitless to 5000:1 double split, depending on the contamination level

Analysis: GC/MS (scan) or GC-FID

References: TDTS 29 (monitoring soil pollution using soil probes) & TDTS 80 (Soil gas analysis)

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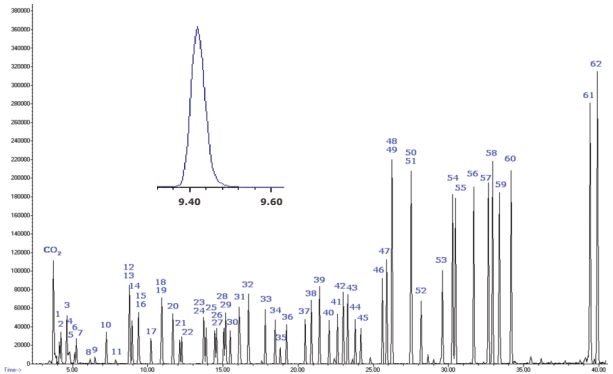
TO-15 'air toxics' in urban air using canisters



1	Propylene	20	n-Hexane	43	Methyl n-butyl ketone
2	Dichlorodifluoromethane	21	1,1-Dichloroethane	44	Dibromochloromethane
3	1,2-Dichlorotetrafluoroethane	22	Vinyl acetate	45	1,2-Dibromoethane
4	Methyl chloride	23	Trans-1,2-dichloroethylene	46	Chlorobenzene
5	Chloroethane	24	Methyl ethyl ketone	47)	
6	1,3-Butadiene	25	Ethyl acetate	48)	Xylene
7	Vinyl chloride	26	Tetrahydrofuran	49)	
8	Methyl bromide (bromomethane)	27	Chloroform	50)	
9	1,2-Dichloroethane	28	1,1,1-Trichloroethane	51	Styrene
10	Trichlorotrifluoroethane (Freon® 113)	29	Cyclohexane	52	Tribromomethane
11	Ethanol	30	Carbon tetrachloride	53	1,1,2,2-Tetrachloroethane
12	1,1-Dichloroethylene	31	Benzene	54	Trimethylbenzene
13	1,1,2-Trichlorotrifluoroethane	32	n-Heptane	55	Trimethylbenzene
14	Acetone	33	Trichloroethylene	56	1-Ethyl-4-methyl benzene
15	Carbon disulfide	34	1,2-Dichloropropane	57	Dichlorobenzene
16	Isopropyl alcohol	35	1,4-Dioxane	58	Dichlorobenzene
17	Methylene chloride	36	Bromodichloromethane	59	Chloromethylbenzene (alpha)
18	*Tert*-butyl methyl ether	37	Cis-1,3-dichloropropene	60	Dichlorobenzene
19	Cis-1,2-dichloroethylene	38	Methyl isobutyl ketone	61	1,2,4-Trichlorobenzene
		39	Toluene	62	Hexachloro-1,3-butadiene
		40	Trans-1,3-Dichloropropene		
		41	1,1,2-Trichloroethane		
		42	Tetrachloroethylene		

Splitless analysis of 1 L x 1 ppb air toxics standard in a canister. Inset shows close-up of extracted mass ion 45 for IPA, demonstrating excellent peak shape.

Background:

For the ultimate in air sampling flexibility (canisters, bags & sorbent tubes), Markes TD systems offer full compliance with US EPA Methods TO-15 and TO-17.

Systems offer automated sequencing for up to 8 canisters/bags together with manual or automated tube desorption. Electrically-cooled focusing (no liquid cryogen required), versatile water management & uniquely efficient trap desorption all combine to minimize running costs, optimize uptime and ensure uncompromised analytical performance (sensitivity, repeatability, *etc.*).

Standard method: US EPA TO-15 (supersedes TO-14)

Typical analytical conditions:

TD system: Series 2 UNITY-CIA 8

Volume sampled from canister: 100 ml to 1 L

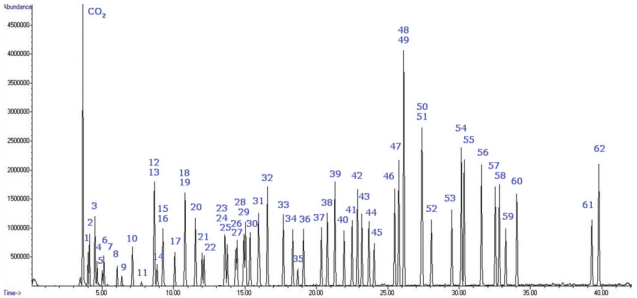
Trap: U-T15ATA-2S or U-T16GHG-2S: 25ºC. 40ºC/s to 320ºC (3 mins)

Split: Splitless or low split during trap desorption only

60 m x 0.32 mm ID x 1.80 µm thick film capillary column for 'volatiles'

Analysis: GC/MS (scan)

Reference: TDTS 81 (Analysis of canister air samples using cryogen-free thermal desorption in compliance with US EPA method TO-15)



1	Propylene	20	n-Hexane	43	Methyl n-butyl ketone
2	Dichlorodifluoromethane	21	1,1-Dichloroethane	44	Dibromochloromethane
3	1,2-Dichlorotetrafluoroethane	22	Vinyl acetate	45	1,2-Dibromoethane
4	Methyl chloride	23	Trans-1,2-dichloroethylene	46	Chlorobenzene
5	Chloroethane	24	Methyl ethyl ketone	47)	
6	1,3-Butadiene	25	Ethyl acetate	48)	Xylene
7	Vinyl chloride	26	Tetrahydrofuran	49)	
8	Methyl bromide (bromomethane)	27	Chloroform	50)	
9	1,2-Dichloroethane	28	1,1,1-Trichloroethane	51	Styrene
10	Trichlorotrifluoroethane (Freon® 113)	29	Cyclohexane	52	Tribromomethane
11	Ethanol	30	Carbon tetrachloride	53	1,1,2,2-Tetrachloroethane
12	1,1-Dichloroethylene	31	Benzene	54	Trimethylbenzene
13	1,1,2-Trichlorotrifluoroethane	32	n-Heptane	55	Trimethylbenzene
14	Acetone	33	Trichloroethylene	56	1-Ethyl-4-methyl benzene
15	Carbon disulfide	34	1,2-Dichloropropane	57	Dichlorobenzene
16	Isopropyl alcohol	35	1,4-Dioxane	58	Dichlorobenzene
17	Methylene chloride	36	Bromodichloromethane	59	Chloromethylbenzene (alpha)
18	*Tert*-butyl methyl ether	37	Cis-1,3-dichloropropene	60	Dichlorobenzene
19	Cis-1,2-dichloroethylene	38	Methyl isobutyl ketone	61	1,2,4-Trichlorobenzene
		39	Toluene	62	Hexachloro-1,3-butadiene
		40	Trans-1,3-dichloropropene		
		41	1,1,2-Trichloroethane		
		42	Tetrachloroethylene		

Splitless analysis of 1 L x 1 ppb air toxics standard in a canister using a series 2 UNITY-CIA 8 system configured for analysis of trace ultra-volatile greenhouse gases

Applying TO-15:

Canisters are ideally suited to ultra-volatile organics such as freons & C_2 hydrocarbons which are difficult to trap on sorbent tubes at ambient temperature. They also offer convenient grab sampling.

Markes TD systems are uniquely suited to split or splitless analysis of volatiles in canisters and operate cryogen-free.

TO-15 performance data using series 2 UNITY-CIA 8 with GC/MS (scan):

Retention volumes for lightest components (propene, methylchloride):

- >2 L on focusing trap U-T16GHG-2S at 25ºC
- >1 L on focusing trap U-T15ATA-2S at 25ºC

Detection limits: <0.1 ppb for all compounds in scan mode

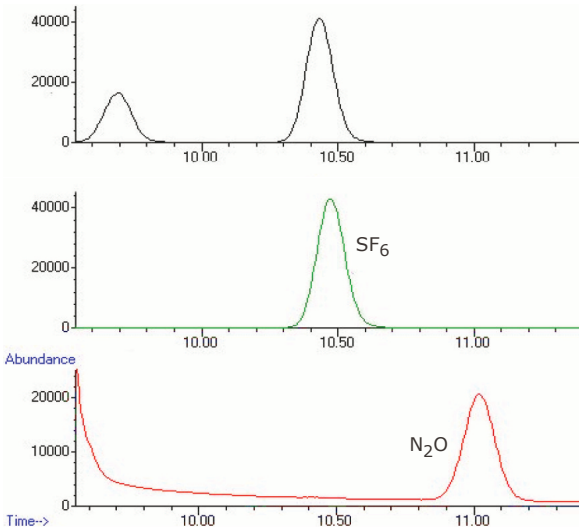
Linearity: Typical R^2 values of 0.99 at low ppb

Precision: Typical % RSDs <6

Carryover: <0.1%*

** N.B. Canisters themselves are prone to incomplete recovery of polar sepcies and components boiling above n-$C_{8/10}$, such as naphthalene. They may also be difficult to clean.*

Monitoring trace ultra-volatiles with high global warming/ozone depletion potential



Extracted ions 69 (black), 172 (green) and 30 (red) from a full scan analysis of 25 ml of a 100 ppb standard of CF_4, C_2F_6, SF_6 and N_2O

Background:

Some of the regulations developed in response to the Kyoto protocol require the monitoring of trace level ultra-volatile compounds with high global warming & ozone depletion potential such as perfluorinated hydrocarbons (CF_4, C_2F_6, *etc*), the tracer gas SF_6 and N_2O. These compounds boil from -128°C and are extremely difficult to trap/concentrate and measure at low levels.

Markes online or canister-based TD systems feature cryogen-free operation and efficient splitless desorption and are uniquely suited to monitoring these compounds on- or offline. Detection limits range down to 0.05 - 0.2 ppt for SF_6 and C_2F_6 respectively, using TD-GC/MS (quadrupole, SIM)

Typical analytical conditions:

Sample volume: 25 ml (CF_4), 150 ml (N_2O) to 1 L (SF_6, C_2F_6)

System: Series 2 UNITY-CIA 8

Trap: U-T16GHG-2S: -30ºC. 40ºC/s to 320ºC (3 mins)

Splitless desorption

50 m x 0.53 mm ID alumina PLOT column + 5 m x 0.18 mm restrictor

Analysis: GC/MS (SIM), or ECD or TOF MS

Reference: TDTS 87 (A cryogen-free method for measuring trace greenhouse gases in air)

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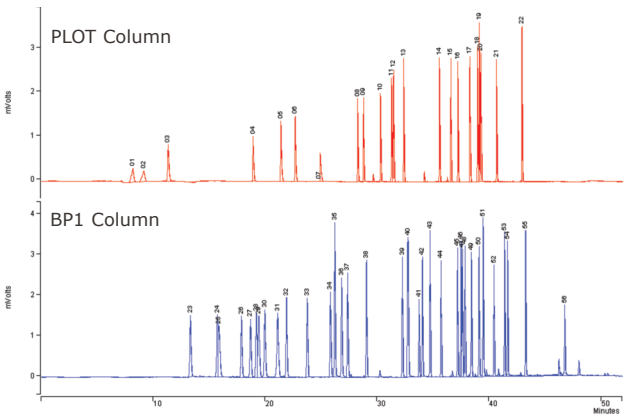
'Ozone precursors' (C_2 to C_{10} hydrocarbons) in ambient air



1	Ethane	20	3-Methylpentane	40	*m/p*-Xylene
2	Ethylene	21	Isoprene	41	Styrene
3	Propane	22	2-Methyl-1-Pentene	42	*o*-Xylene
4	Propylene	23	Methylcyclopentane	43	n-Nonane
5	Isobutane	25	2,4-Dimethylpentane	44	Isopropylbenzene
6	n-Butane	26	Benzene	45	n-Propylbenzene
7	Acetylene	27	Cyclohexane	46	*m*-Ethyltoluene
8	trans-2-Butene	28	2-Methylhexane	47	*p*-Ethyltoluene
9	1-Butene	29	2,3-Dimethylpentane	48	1,3,5-Trimethylbenzene
10	*cis*-2-Butene	30	3-Methylhexane	49	*o*-Ethyltoluene
11	Cyclopentane	31	2,2,4-Trimethylpentane	50	1,2,4-Trimethylbenzene
12	Isopentane	32	n-Heptane	51	n-Decane
13	n-Pentane	33	Methylcyclohexane	52	1,2,3-Trimethylbenzene
14	*trans*-2-Pentene	34	2,3,4-Trimethylpentane	53	*m*-Diethylbenzene
15	1-Pentene	35	Toluene	54	*p*-Diethylbenzene
16	*cis*-2-pentene	36	2-Methylheptane	55	n-Undecane
17	2,2-Dimethylbutane	37	3-Methylheptane	56	n-Dodecane
18	2,3-Dimethylbutane	38	n-Octane		
19	2-Methylpentane	39	Ethylbenzene		

Splitless desorption of 56-compound US EPA mix of ozone precursors using series 2 UNITY-Air Server with dual column/dual FID GC and Deans switch

Background:

C_2 to C_{10} hydrocarbons, originating from car exhausts, have been identified as precursors to the formation of street level ozone and urban smog. US, European and other regulators require round-the-clock monitoring of these compounds in major urban centres during the summer months. Series 2 UNITY-Air Server allows continuous, unattended and cryogen-free monitoring at low to sub-ppb levels and automatic sequencing between a minimum of 3 channels (sample, standard & blank). Markes series 2 TD systems offer splitless desorption & uniquely high cryogen-free retention volumes for ultra-volatiles such as acetylene & ethane. Systems are operated in remote, unattended monitoring stations, with data accessed *via* telemetry and processed/validated at remote network control centres.

Official guidance: US EPA Tech. Assist. Document for sampling and analysis of ozone precursors

Typical analytical conditions:

Sampling: Online from manifold at 25 ml/min

Sampling volume: 400 - 1000 ml

TD system: Series 2 UNITY-Air Server with dryer

Trap: U-T17O3P-2S: -30 to 320ºC at 40ºC/sec

Splitless desorption

GC configuration: Either GC, dual column, dual FID & Deans switch, or single FID with "PoraPLOT" type column

Reference: TDTS 16

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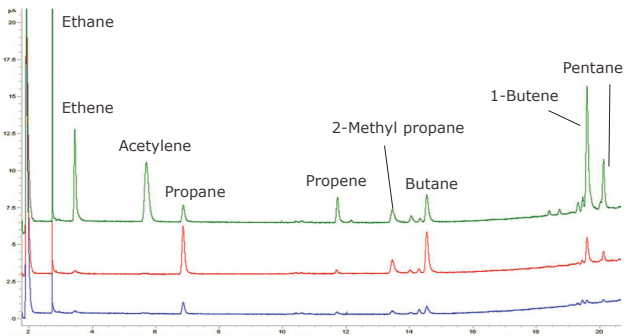
Online monitoring of diurnal variation of pollutants in ambient air

Key:
Blue (3 am),
Red (12 noon),
Green (5:30 pm)



Online monitoring of semi-rural/semi-industrial ambient air using series 2 UNITY-Air Server GC/FID and GS-GasPro-type 'PoraPLOT' column showing how the VOC profile varies with time

Background:

Markes series 2 UNITY-Air Server systems offer cryogen-free, online monitoring of trace volatiles in ambient air, using GC/FID or GC/MS. The optimised focusing trap contains an extended (60 mm) bed of multiple sorbents which is held at -30ºC and desorbed in backflush mode at rates up to 100ºC/s. This enables ultra-volatile hydrocarbons/freons to be quantitatively retained and efficiently released at the same time as much higher boiling components, such as naphthalene, trimethyl benzene & hexachloro butadiene.

A wide range of vapour-phase components (ozone precursors, hazardous air pollutants and odour components) can all be monitored simultaneously.

Typical analytical conditions:

Sample: A 200 to 1000 ml volume of air sampled at 10-25 ml/min (optional dryer)

System: Series 2 UNITY-Air Server (with Nafion® dryer)

Trap: U-T17O3P-2S: -30ºC to +25ºC. 40ºC/s to 320ºC (3 mins)

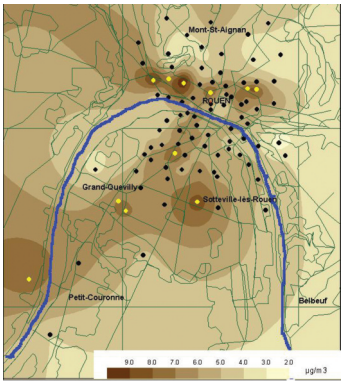
Splitless desorption

GS-GasPro™ 30 m x 0.32 mm capillary column for 'volatiles'

Analysis: GC/FID

References: TDTS 16 (online round-the-clock air monitoring), 32 (analysis of sulphur compounds), 81 (analysis of canister air samples with US EPA method TO-15) & 87 (monitoring trace greenhouse gases in air)

Mapping criteria pollutants in ambient air by diffusive sampling



Rouen (Northern France).

Interpolated benzene isoconcentration plot.

Measurements performed from 19-23/01/98

RFID tagged sorbent tube (TubeTAG)

References: TDTS 10 (diffusive monitoring of ambient air), TDTS 01 (uptake rates), TDTS 42 (radial diffusion for TD) & TubeTAG brochure

Background:

Accurate mapping of pollution levels across a major urban centre requires hundreds of sampling points.

Diffusive (passive) samplers are low-cost and easy to deploy facilitating large-scale and/or detailed environmental surveys. Markes unique TubeTAG electronic tube labelling system benefits large scale field monitoring studies, by eliminating transcription errors & enhancing traceability.

Series 2 (UltrA-)UNITY and TD-100 systems feature the option of onboard read/write of tagged tubes for complete, error-free automation

Std. methods: EN 14662-4, EN ISO 16017-2, ASTM D 6196

Typical analytical conditions:

Sampling: Diffusive (passive)

Sorbent: Carbograph™ 1TD (benzene), Carbopack™ X (1,3-butadiene)

Monitoring time: 7-14 days (axial), 4-6 hours (radial)

TD system: Series 2 (UltrA-)UNITY or TD-100 with onboard TubeTAG read/write

Desorption: 5-10 minutes at 320ºC

Trap: Carbograph 1TD/Carbopack X from +30 to 320ºC

Split: ~20:1 during trap desorption only

Analysis by GC-FID or GC/MS

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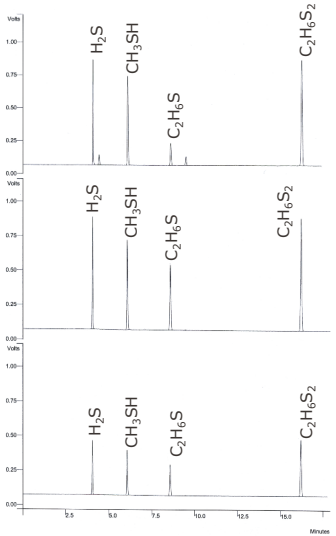
Odorous industrial emissions



Compound	Detection limit (ppb)	Linearity (at ppb levels)	Reproducibility (% RSD at 20 ppb)	Recovery (% at 80% relative humidity)
H_2S	0.15	0.9973	4.1	93
CH_3SH	0.15	0.9983	1.8	108
C_2H_6S	0.15	0.9999	0.8	107
$C_2H_6S_2$	0.10	0.9993	0.8	108

Background:

Highly odorous sulphur compounds in industrial or landfill emissions must be controlled to sub or low-ppb levels. These very volatile & highly reactive compounds are usually sampled online or in canisters/bags & analysed using TD-GC/PFPD.

Markes series 2 UNITY is a uniquely versatile TD platform. The standard system allows selection of low flow path temperatures without installation of special valving. This facilitates analysis of thermally labile components such as mercaptans & other odorous species. Markes online TD systems have also demonstrated exceptional analytical performance and reliability in unattended field operation

Std. method: Korean Government Guidance Method - Standard Method for Off-Odour Analysis (2005)

Typical analytical conditions:

Sample volume: 100-500 ml

TD system: Series 2 UNITY-Air Server with dryer

TD flowpath: 80ºC

Trap: U-T14H2S-2S (H_2S): -30 to 250ºC

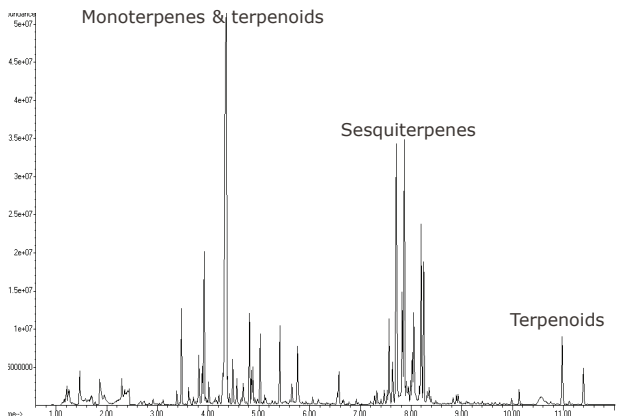
Split: 12:1 during trap desorption only

Column: 60 m x 0.32 mm x 5.0 µm, apolar

Analysis: GC/PFPD

References: TDTS 32 (analysis of sulphur compounds), Ki-Pong Song, *et al.*, (2007), *Korean Journal of Odour search and Engineering, Vol 6 (1), 33-39*

Biogenic emissions: Vapour-phase organic chemicals from moulds, plants, *etc.*



ppb-Level terpenes in air above leaf litter

Background:

Plants, moulds, animals & other life forms emit VOCs & contribute to the 'cocktail' of organic vapours in ambient air. Monoterpenes are emitted by pine trees on sunny days, possibly as a defence against potential photochemical damage. These reactive hydrocarbons are monitored using pumped sampling onto inert tubes packed with Tenax TA followed by TD-GC/MS analysis. Similarly, the detection of methyl benzoate in indoor air can indicate mould growth & geosmin in water indicates the presence of certain algae (see also page 20). The profile of vapour-phase organics can also sometimes be used to identify the precise species of plant, mould, *etc* and/or the phase of growth.

Markes series 2 (UltrA-)UNITY or TD-100 systems offer quantitative re-collection for repeat analysis (SecureTD-Q). This is an invaluable feature for validating quantitative recovery of biogenic emission components (some of which are extremely reactive) through the analytical system.

Typical analytical conditions:

Sampling: Pumped sorbent tube

Sorbent: Tenax TA in stainless/Silcosteel® tube

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 220ºC

Trap: U-T9TNX-2S (Tenax): -10 to 250ºC

Split: Low split during trap desorption only

Analysis: GC/MS (scan)

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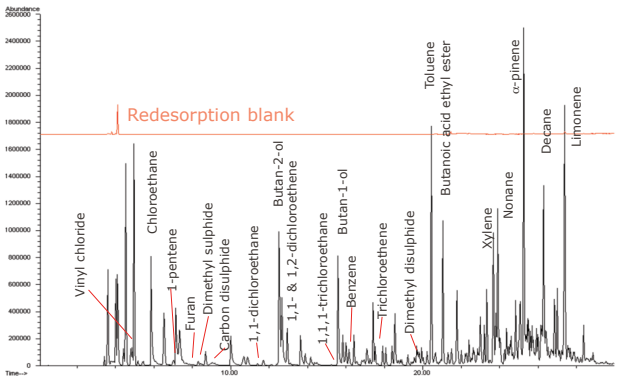
Odours & toxics in landfill gas



100 ml landfill gas with trace target analytes & many major components identified

1 Vinyl chloride (Toxic)
2 1,3-Butadiene (Toxic)
3 Methyl Mmercaptan (Odour)
4 Chloroethane (Toxic)
5 1-Pentene (Odour)
6 Furan (Toxic)
7 Ethyl mercaptan (Odour)
8 1,1- Dichloroethene (Toxic)
9 Dimethylsulphide (Odour)
10 Carbon disulphide (Odour) (Toxic)
11 1,2-Dichloroethene (Toxic)
12 1,1-Dichloroethane (Toxic)
13 Propyl mercaptan (Odour)
14 Tetrachloromethane (Toxic)
15 Benzene (Toxic)
16 Trichloroethene (Toxic)
17 Butyl mercaptan (Odour)
18 Dimethyldisulphide (Odour)
19 Ethylbutyrate (Odour)
20 2-Butoxyethanol (Toxic)

References: TDTS 32 (sulphur compounds) & TDTS 47 (analysis of landfill gas)

Background:

New regulations in Europe & several Asian countries require monitoring of trace toxic & odorous compounds in landfill gas. Such analysis is either carried out online (see page 15) or by drawing 100-200 ml samples through a special sorbent tube using a simple bellows pump or large gas syringe.

The patented inert valve within series 2 (UltrA-) UNITY and TD-100 facilitates subsequent offline analysis of the sampled tubes by allowing low flow path temperatures to be selected *e.g.* 120ºC in this example. Quantitative recovery of labile odorous analytes, such as ethanethiol, can also be validated using SecureTD-Q.

Official guidance: UK Env. Agency publication 'Monitoring trace components in landfill gas.'

Typical analytical conditions:

Sample volume: 100-500 ml

Sorbent: Silcosteel tube with Tenax TA/UniCarb™ (at same temp as gas)

TD system: Series 2 (UltrA-)UNITY or TD-100

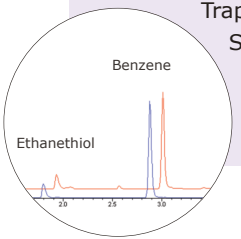
TD flowpath: 120ºC

Trap: Sulphur trap -15 to 220ºC (40º/min)

Split: From 10:1 to 50:1

Column: 60 m x 0.25 mm ID x 1.4 µm film DBVRX

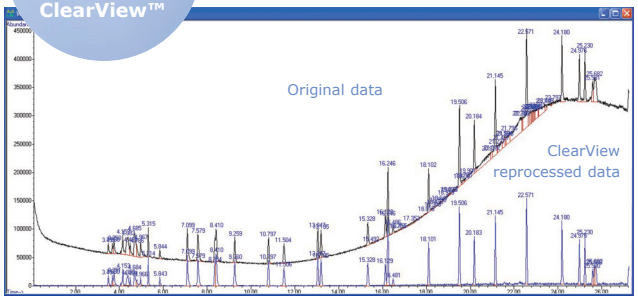
Analysis: GC/MS (scan)

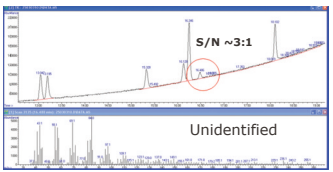


SecureTD-Q: Repeat analysis validates quantitative recovery of ethanethiol through the TD flowpath

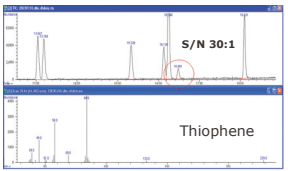
Software tools for minimising GC/MS background & enhancing trace analysis

Analysis of a trace level landfill gas standard using the thick film capillary column described above. ClearView completely eliminates interference from column bleed





Peak at 16.48 mins unidentified in original data



Peak at 16.48 mins automatically identified as thiophene in ClearView reprocessed data

Background:

ClearView™ uses a sophisticated algorithm to accurately & dynamically compensate for chromatographic background as it changes throughout a run. The process works even if the same mass ion is present in both the background and the peaks of interest. Original data files are retained intact so implementation of ClearView is risk free.

ClearView™ works with all makes of GC/MS & can be used to reprocess stored data files individually or in batches. Reprocessing takes seconds. ClearView can also be executed/implemented within the environment of several leading brands of GC/MS data processing software during an automated sequence of analyses.

Key advantages include:

- Improvement in spectral purity for enhanced automatic identification of trace components
- Reduced signal to noise for improved sensitivity/detection
- Facilitates scanning from low masses
- Productivity: Reduces/de-skills data interpretation, boosting sample throughput
- Compatible with scan, SIM/scan & SIM data (see page 20)

References: TDTS 83 & 85 (Using ClearView reprocessing to enhance trace GC/MS analysis)

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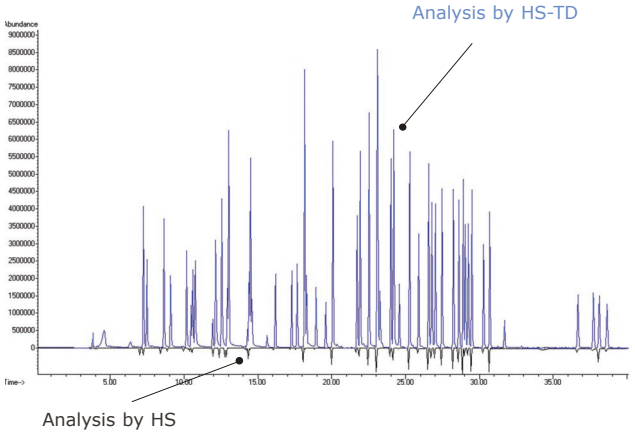
HS-TD: Simple & sensitive analysis of purgeable VOCs in water



Trace level purgeable VOCs in drinking water analysed by conventional HS (black) and HS-TD (blue)

Background:

Headspace–thermal desorption (HS-TD) brings together two of the most powerful GC introduction techniques & offers optimum sensitivity for trace-level volatiles in solid, liquid and gas-phase samples.

Pressurised headspace vapours are transferred from the sample vial & into the UNITY 2 focusing trap before being desorbed/injected into the GC(MS) in a reverse flow of carrier gas. The process of headspace vapour transfer & focusing can be done in a single stage, or repeated several times to optimise sensitivity before the trap is finally desorbed to trigger GC analysis.

Repeated pressurisation & evacuation of headspace vials also extends the compatible analyte volatility range relative to conventional equilibrium headspace. This allows lower boiling compounds to be measured at the same time as the volatiles.

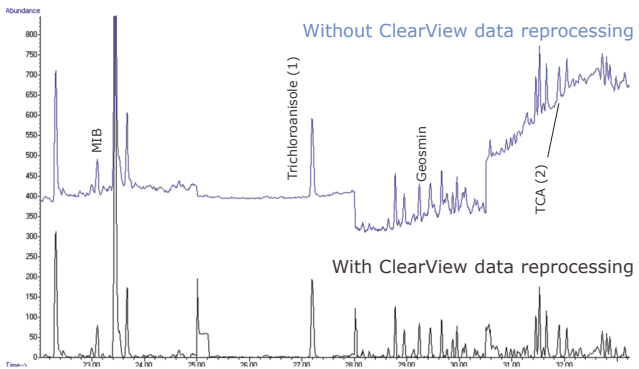
HS-TD options available for UNITY 2 include:

- The cost-effective manual HS5 module (5 vial capacity)
- A range of leading brand HS autosamplers

Typical analytical conditions are shown below

Reference: HS5-TD brochure

Trace (ppt) level odorants in drinking water using HS-TD with ClearView



5 ppt level odorants in drinking water analysed by HS-TD-GC/MS (SIM) shown with & without ClearView reprocessing

Reference: TDTS 78 (ppt-levels of odorants in drinking water using HS-TD)

Background:

Drinking water is prone to contamination by naturally-occurring odorous compounds such as geosmin, methyl-*i*-borneol & trihaloanisoles. These components produce a musty/'earthy' smell that is detectable by consumers at concentration levels down to 10 ppt.

HS-TD offers a simple, innovative & readily-automated approach to routine analysis of odorants in drinking water. Detection limits down to 1 ppt can be achieved using conventional 20 ml HS vials/caps and GC/MS (quad/SIM). ClearView reprocessing software optimises signal-to-noise (sensitivity) at the lowest levels. Further enhancements could be possible *e.g*. by employing aluminium-coated vial caps, by including a salting-out step and/or by using enhanced MS technology.

Typical analytical conditions:

HS vials: 45-50ºC

Sample cycles:10

U-T2GPH-2S trap held at 30ºC (purgeables), & 50ºC (odorants)

60 m x 0.32 mm x 1.8 µm film 'volatiles' column for purgeables

60 m x 0.25 mm ID x 0.25µm film 1701 capillary column for odorants

Analysis: GC/MS (scan or SIM)

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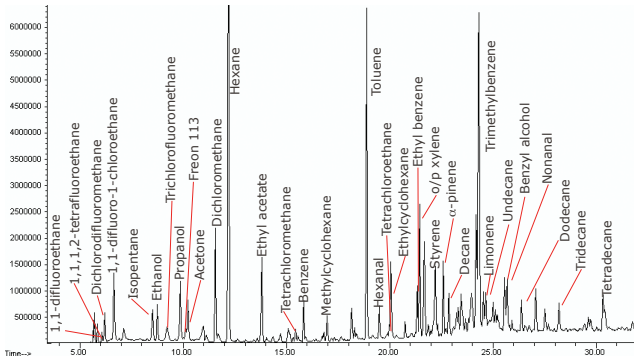
Profiling indoor air quality (IAQ)



Clean indoor air pumped onto a multi-sorbent tube & analysed by TD-GC/MS

Typical analytical conditions:

Sampling: Pumped sampling: 2-20 L

Sorbent: Tenax TA or an IAQ tube (quartz/Tenax TA/ Carbopack X)

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 280ºC (depends on sorbent)

Trap: To match tube (-30 to 300ºC)

Split: During trap desorption only ~15:1

Analysis: GC/MS (scan)

Background:

Most people in the developed world spend an estimated 70-90% of their time indoors or in vehicles. Regulators & scientists around the world are increasingly concerned about the impact of poor indoor (or in-vehicle) air quality (IAQ/IVAQ) on human health & comfort.

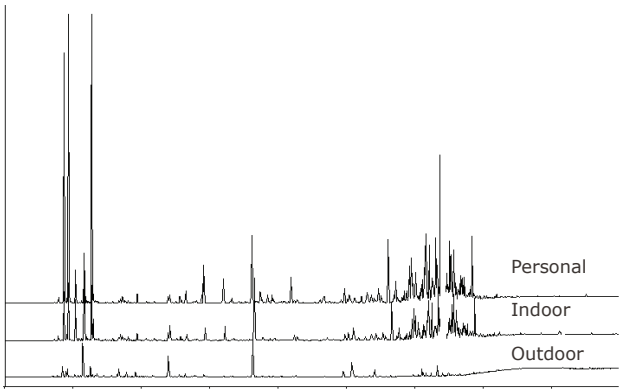
Sources of indoor pollutants include construction (or car trim) materials, furnishings, cleaning products, fuels, general consumer goods & human/animal activity (cooking, smoking, *etc.*) Recent environmental developments (*e.g.* the EC directive on Energy Performance of Buildings) are putting further pressure on IAQ by reducing building ventilation rates.

TD is used extensively for monitoring IAQ & for related applications such as materials emissions testing. In this example, pumped tube samplers were used with subsequent TD-GC/MS analysis for profiling of ppt-ppb level VOCs.

Std. methods: US EPA Method TO-17, EN ISO 16017-1, ASTM D 6196

References: TDTS 28 (monitoring indoor air), Thermal Desorption: A Practical Applications Guide. II. Residual Volatiles & Materials Emissions Testing

Personal exposure indoors



Poor indoor air quality & high personal exposure in this home were linked to a diesel car parked in a garage under the living space

Markes TubeTAG technology facilitates large scale surveys of IAQ and human exposure, by making it easier to record & check tube & sampling information without transcription errors

Background:

TD-GC/MS is used for several applications relating to poor IAQ and 'sick building syndrome'. In this case residents were complaining of poor air quality in their home. Diffusive sampling with 'axial' sorbent tubes was used to monitor indoor & outdoor air quality at the house and to monitor the personal exposure of residents.

Diffusive monitors are unobtrusive, low cost, simple to deploy (no pumps) & available with Markes unique TubeTAG technology. This makes them ideal for large-scale personal exposure studies.

Std. methods: EN 14662-4, EN ISO 16017-2, ASTM D6196

Typical analytical conditions:

Sampling: Diffusive sampling

Sorbent: Carbograph 1TD, Carbopack X or Tenax TA depending on target analyte range

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 320ºC

Trap: U-T2GPH-2S or to match tube sorbent

Split: ~10:1 during trap desorption only

Analysis: GC/MS (scan)

References: TDTS 10 (diffusive sampling in indoor air), TDTS 01 (uptake rates)

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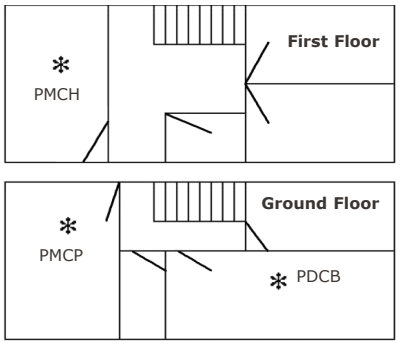
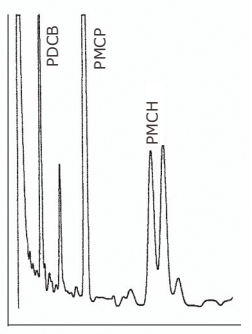
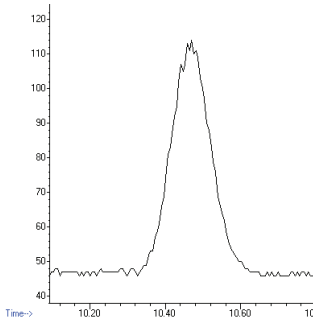
Building ventilation tests with tracer gases



Different PFCs placed in separate rooms allow the monitoring of air exchange



Perfluorocarbon tracer gases monitored using TD-GC/ECD or TD-GC/MS



0.1 ppb SF^6 monitored using online TD-GC/MS as described on page 11

Background:

SF_6 and perfluorocarbons (PFCs) are commonly used as tracer gases to determine ventilation rates & pathways in buildings & vehicles. The rise & subsequent decay of tracer gas concentrations is monitored using on- or offline TD with GC and electron capture detection (ECD) or GC/MS. SF_6 can be sampled using low volume (100-500 ml) sampling onto strong sorbent tubes but is more commonly monitored online (see page 11).

Different PFCs (*e.g.* perfluoromethyl cyclohexane (PMCH), perfluoromethyl cyclopentane (PMCP) & perfluorodimethyl cyclobutane (PDCB)) placed in different locations within a building allow the monitoring of air exchange. They are sampled diffusively or with pumps onto tubes packed with Carbograph 1TD or Carbopack B™.

Typical analytical conditions for PFCs:

Sampling: diffusive or pumped

Sorbent: 40-60 mesh Carbograph 1 TD

TD system: Series 2 (ULTRA-)UNITY or TD-100

Desorption: 5 mins at 320ºC

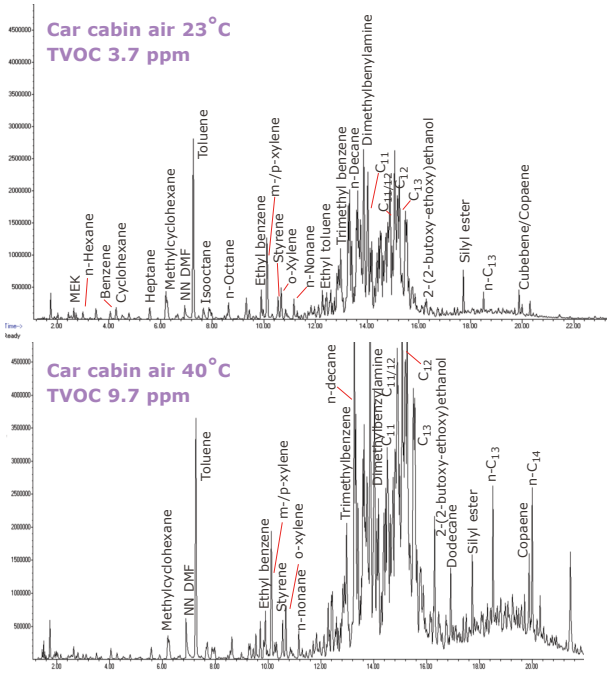
Trap: Carbograph 1 TD -30 to 300ºC

Split: Splitless or low split

Analysis: GC/MS or GC/ECD

Reference: H. Bloemen *et al*, (1992), Ventilation rate and exchange of air in dwellings, RIVM rpt, NL.

Monitoring car cabin air



Air from the cabin of a small car showing a complex range of VOCs and high total-VOC levels

Background:

Car cabins are small confined spaces. Vapour-phase (S)VOC levels can build up, especially in parked cars on a hot day. Car manufacturers & their suppliers are currently focused on improving the quality of cabin air and reducing emissions from vehicle interior trim components. IVAQ samples are typically sampled using pumped, multi-sorbent tubes and analysed by TD-GC/MS.

Markes TD systems are ideally suited to IVAQ monitoring. They offer simultaneous analysis of VOCs & SVOCs & feature a short, inert flow path that can be set at low or moderate temperatures, if required, to optimise recovery of labile odorous analytes such as amines.

Std. methods: EN ISO 16017-1, ISO 16000-6, ASTM D6196.

Typical analytical conditions:

Sampling: Pumped sampling of 2-10 L volume

Sorbent: Tenax TA or an "IAQ" tube (*e.g.* quartz, Tenax, Carbopack X)

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 6 mins at 280ºC

Trap: U-T12ME-2S ("IAQ") Tenax TA or Tenax/Carbopack X (-30 to 300ºC)

Split: 50-200:1 (single or double split)

Analysis: GC/MS (scan)

Reference: TDTS 33 (profiling car cabin air)

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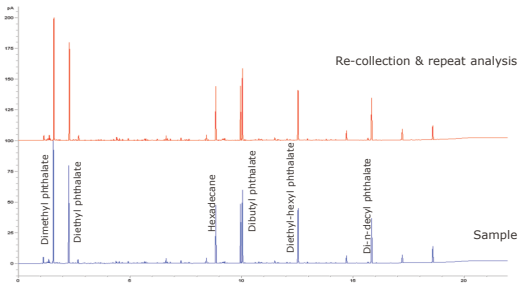
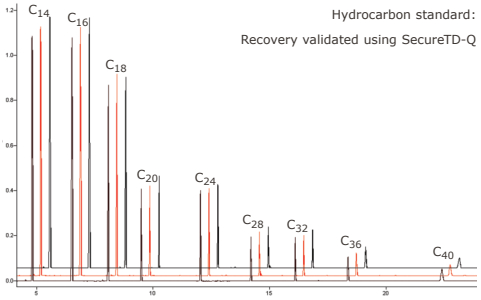
Vapour-phase semi-volatiles by thermal desorption: n-C_{40} & phthalates

Phthalate standard mixture with internal standard



Markes TD systems are compatible with the analysis of semi-volatiles such as n-C40 and didecyl phthalate. SecureTD-Q (quantitative re-collection for repeat analysis) provides a convenient means of demonstrating quantitative recovery through the system



Background:

Thermal desorption is usually associated with analysis of volatile organic chemicals. However, the short, inert, heated flow path of Markes TD systems also ensures quantitative recovery of semi-volatiles such as n-C_{40} & didecyl phthalate.

Markes SecureTD-Q technology uniquely offers quantitative re-collection of split flows from both tube & trap desorption onto a single conditioned sorbent tube. This provides a convenient means of demonstrating quantitative recovery of all analytes through the entire TD system as described in standard methods such as ASTM D6196.

Typical analytical conditions:

Sampling: Pumped sorbent tube

Sorbent: Quartz wool with 1 or 2 carbon blacks

Sample volume: Up to 100 L at up to 500 ml/min

TD system: Series 2 UltrA-UNITY

Desorption: 15 mins at 360ºC

Trap: High boilers trap (U-T1HBL-2S): -30 to 375ºC

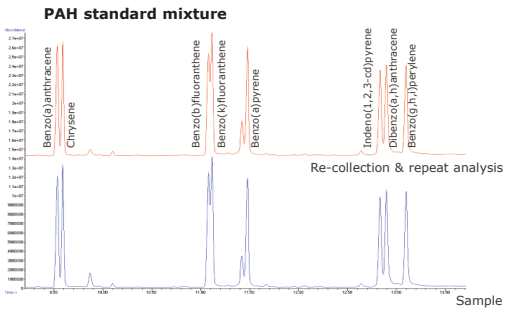
Split: Typically 50:2.5 during trap desorption only

Column: 30 m x 0.25 mm ID x 0.25 mm film apolar

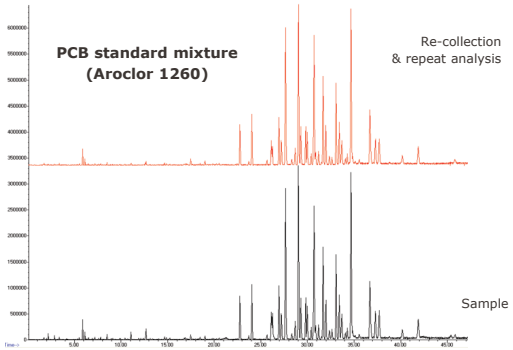
Analysis: GC/MS (SIM or scan)

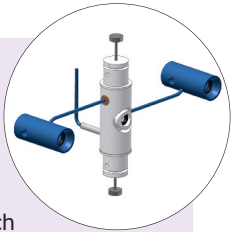
Reference: TDTS 53 (quantitative recovery of semi-volatiles)

Vapour-phase semi-volatiles by thermal desorption: PAHs & PCBs



Quantitative recovery of polychlorinated biphenyls (PCBs) and poly aromatic hydrocarbons (PAHs), including benzo-a-pyrene, through series 2 UltrA-UNITY demonstrated using SecureTD-Q





Background:

Markes' thermal desorbers owe their unsurpassed performance with semi-volatiles to the short, inert, uniformly-heated flow path & patented TD heated valve used in each (UltrA-)UNITY 2 and TD-100 system.

It is the unique valve & flow path configuration of Markes TD systems that also allows quantitative recovery of both inlet (tube desorption) & outlet (trap desorption) split flow onto the same conditioned sorbent tube for repeat analysis & validation of analyte recovery (*i.e.* SecureTD-Q).

Typical analytical conditions:

As shown on page 25.

Reference: TDTS 53 (quantitative recovery of semi-volatiles)

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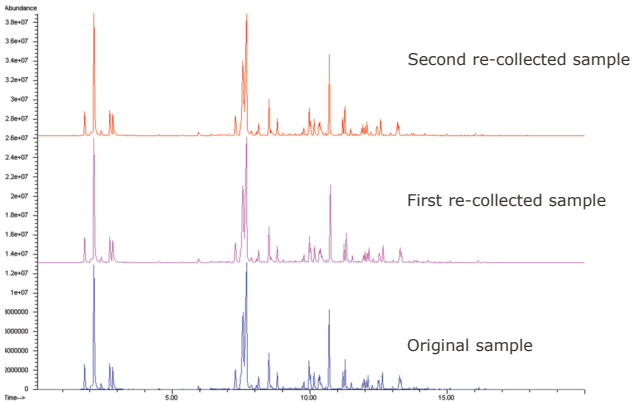
Industrial (stack) emissions – solvents



Quantitative stack analysis carried out using double splitting & an overall split ratio of 3,000:1, confirmed by SecureTD-Q

Analyte	Mass (µg) for 3 repeats using SecureTD-Q		
MEK	580	583	580
Benzene	0.14	0.18	0.18
Toluene	94	91	93
Ethyl benzene	30	30	29
PGMEA	43	43	43
Xylene	274	275	271
DMS	28	28	28
Trimethylbenzene	43	44	42

Background:

Stack gases are aggressive matrices requiring a sampling train to remove particles, acids, *etc.* The sample gas is collected onto sorbent tubes using either grab sampling (using a large gas syringe or a bellows-type pump to pull a 50-100 ml sample of stack gas through the tube) or time weighted average monitoring (using a pump with a slow flow rate of ~15/ml to pull stack gas through the tube) throughout a process.

Markes TD systems facilitate quantitative analysis of high conc. samples (>1000 ppm) by offering the option of splitting during tube & trap desorption. Vapour from ppt to high ppm can be accommodated on one analytical platform. Quantitative re-collection of both split flows facilitates simple method & data validation.

Official guidance: Revised European standard prEN 13649

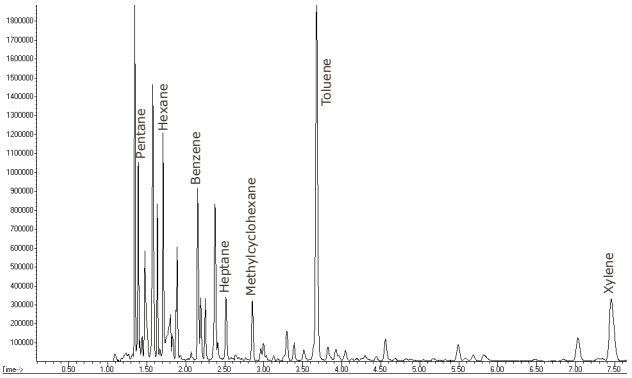
Typical analytical conditions:

Sample volume: 50-1500 ml
Sampling: Pull through tube (grab sampling or pump)
Sorbent: Tenax TA/carbon or carbon/carbon
TD system: Series 2 (UltrA-)UNITY or TD-100
Desorption: 5 mins at 330ºC or 280ºC (if TenaxTA)
Trap: Tenax TA/carbon or 2 carbons (-30 to 300ºC)
Split: 3,000:1 double split with SecureTD-Q
Analysis: GC/MS (scan) or GC/FID

Reference: TDTS 77 (stack emissions monitoring)

Industrial fence-line (perimeter) monitoring for fugitive emissions

References: TDTS 49 (fence-line monitoring), TDTS 1 (list of diffusive uptake rates for environmental monitoring) & TDTS 10 (diffusive sampling in ambient air)



2-week diffusive sampling around a refinery perimeter. VOCs detected include benzene, toluene & xylene

Background:

Is your industrial site a good neighbour? Unobtrusive diffusive (passive) samplers may be placed around a factory fence-line for extended time periods (*e.g.* 3-14 days) to monitor key 'criteria' pollutants (*e.g.* benzene & 1,3-butadiene).

Diffusive sampling provides a low cost, well-validated & quantitative monitoring method. Subsequent analysis by TD-GC(MS) offers sub-ppb detection limits. Markes' TubeTAG technology benefits fugitive emissions & industrial fence-line studies by making it easier to record & track sampling locations & other details. The onboard RFID tag read/write option available for UltrA 2 and TD-100 allows automatic entry of sample details into the sequence log.

Std. methods: EN 14662-4, EN ISO 16017-2, ASTM D 6196

Typical analytical conditions:

Sampling: Diffusive (passive) tubes

Sorbent: Carbograph 1TD, Carbopack X or other to suit target analyte

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 320ºC

Trap: Selected to suit target analyte (U-T11GPC-2S in example shown: -30 to 320ºC)

Split: Low split during trap desorption only

Analysis: GC/MS (scan) or GC/FID

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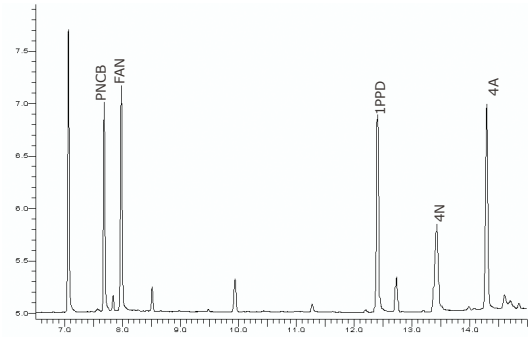
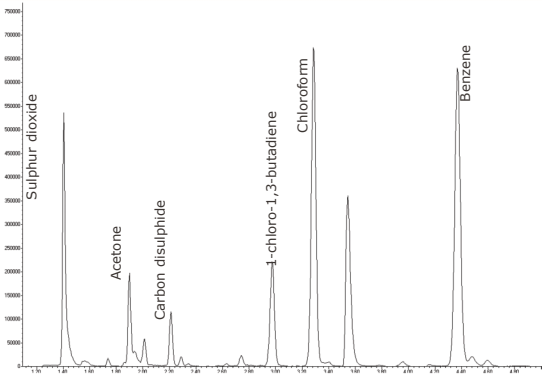
Occupational hygiene – monitoring personal exposure by inhalation



Reactive amines in workplace air



Personal exposure to solvents at work

Background:

Health & safety at work legislation requires personal exposure assessment of workers potentially exposed to toxic chemicals by inhalation. Pumped or diffusive sampling onto sorbent tubes followed by TD-GC(MS) analysis provides a solvent-free, safe analytical option with ~1000x more sensitivity than conventional charcoal tube/CS_2 extraction methods.

TD tubes are also reusable indefinitely & may be RFID tagged (TubeTAG) for enhanced sample traceability.

Standard methods: UK MDHS series, EN ISO 16017, ASTM D 6196, NIOSH 2549.

Typical analytical conditions:

Sampling: Diffusive or pumped

Typical tube sorbent: Tenax or Chromosorb® 106

TD system: Series 2 (ULTRA-)UNITY or TD-100

Desorption: 5 mins at 300ºC or 200ºC (for C106)

Trap: U-T2GPH-2S (Tenax/Carbograph 1TD) :-30 to 300ºC

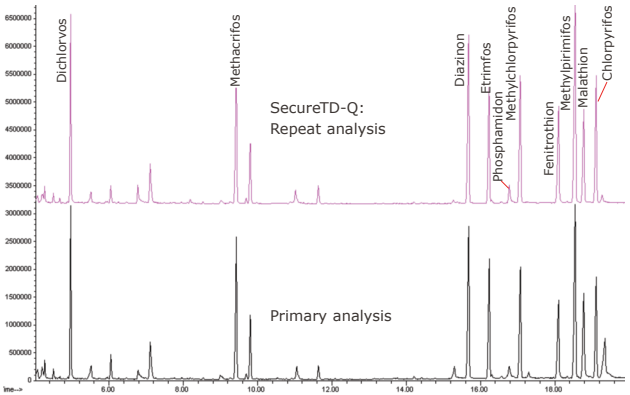
Split: 50:1 to 500:1 (typically double split)

Column: Selected to suit target analyte range

Analysis: GC/MS (scan)

References: TDTS 37 (industrial air monitoring) & TDTS 38 (occupational exposure limit levels)

Monitoring inhalation exposure to pesticides



Primary & repeat analysis of pesticides for personal exposure monitoring. Secure TD-Q confirmed quantitative recovery through the analytical system

Background:

Agricultural workers involved in pesticide application must be monitored to ensure that their exposure to these highly toxic chemicals does not exceed safe levels. Pumped monitoring using inert (glass or Silcosteel) tubes together with TD-GC/MS analysis provides a reliable & highly sensitive monitoring method.

In the example shown, Markes SecureTD-Q was used to demonstrate quantitative recovery of these difficult compounds through the system. SecureTD-Q can also benefit occupational hygiene applications by allowing samples to be archived for repeat analysis under different analytical conditions.

Standard methods: UK MDHS series, EN ISO 16017-1, ASTM D 6196, NIOSH 2549

Typical analytical conditions:

Sampling: Pumped

Sorbent: Tenax TA in glass or Silcosteel tubes

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 10 mins at 280ºC

Trap: U-T9TNX-2S (Tenax TA): -10 to 300ºC

Split: ~10:1 during trap desorption only

Analysis: GC/MS (SIM)

Reference: TDTS 39 (using TD with SecureTD-Q to monitor vapour phase pesticides)

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The advantages of TD *vs.* solvent extraction for monitoring organic vapours in air

Background:

Early methods for monitoring vapour-phase organics in air involved charcoal tubes & solvent extraction, typically with CS_2. However, with the lowering of occupational limit levels & widespread adoption of GC/MS technology, thermal desorption is rapidly superseding solvent extraction as the analytical method of choice.

Key advantages of thermal desorption *vs.* charcoal/CS_2 methods include:

- 1000 fold enhancement in sensitivity
- Reliable (>95%) desorption efficiency
- Higher degree of automation and greatly reduced running costs
- Elimination of the danger and expense associated with hazardous solvents and their disposal
- Reduced analytical interference
- Reusable sample tubes

Furthermore, Markes' introduction of SecureTD-Q now means TD is no longer a one-shot technique. Samples can be quantitatively re-collected for repeat analysis.

References: TDTS 38 (workplace limit levels) & TDTS 46 (comparing TD with CS_2 extraction of charcoal for air monitoring)

Diffusive (passive) sampling in the workplace

Standard sorbent tube fitted with a diffusion cap at the sampling (grooved) end

Background:

Unobtrusive, low-cost diffusive (passive) samplers facilitate personal exposure monitoring because they can be worn close to the breathing zone without impacting worker behaviour. Analysis by thermal desorption means tubes are reusable indefinitely. The enhanced sensitivity of TD, relative to solvent extraction, also allows compliance with new, lower threshold limit values.

Diffusive sampling tubes can be fitted with Markes TubeTAG RFID tagging technology to simplify logging & tracking of key sample-related information

Std. methods: UK MDHS series, EN ISO 16017, ASTM D 6196, NIOSH 2549

Typical analytical conditions:

Sorbent: Tenax TA, Carbograph 1TD or porous polymer sorbent (various)

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5-10 mins. Temp depends on sorbent

Trap: U-T2GPH-2S (General purpose)

Split: Between 10:1 & 500:1

Analysis: GC(MS)

References: TDTS 01 (diffusive uptake rates), TDTS 08 (principles of diffusive sampling), TDTS 38 (limit levels) & TDTS 50 (workplace air monitoring)

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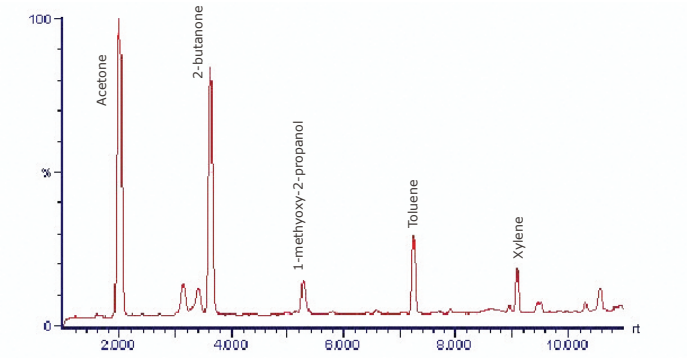
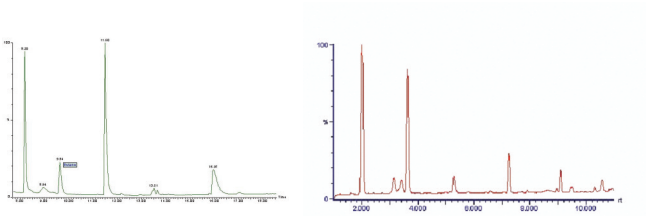
Biological monitoring *via* alveolar breath



Skin-absorbed solvents in the breath of shoe workers collected using the Bio-VOC™



Chromatogram of a clinical breath sample.
Sample collected using the Bio-VOC and analysed using TD-GC/MS (single ion monitoring at mass 43)

Reproduced by kind permission from Pyschiatric Diagnostics Ltd., Inverness, Scotland

Background:

Biological exposure monitoring allows assessment of the whole body burden of chemicals *via* all routes of exposure (skin absorption, ingestion & inhalation). Alveolar breath sampling using Markes' disposable Bio-VOC™ allows large-scale, non-invasive biological monitoring of workers using personal protective equipment (PPE) or handling skin-absorbed chemicals.

Detection of specific VOCs/VOC profiles in breath can also be used to monitor halitosis or help diagnose certain diseases (*e.g.* lung cancer & diabetes).

After breath collection, the Bio-VOC breath sample is discharged into a tube containing hydrophobic sorbents & analysed by TD-GC/MS.

Official guidance: Suite of breath sampling guidance notes available from UK HSL.

Typical analytical conditions:

Sorbent: Tenax TA or Tenax/Carbopack X

TD system: Series 2 (UltrA-)UNITY or TD-100

Desorption: 5 mins at 280ºC

Trap: Tenax TA or Tenax/Carbopack X (25-280ºC)

Splitless or low split

Analysis: GC/MS (SIM) or GCxGC/TOF MS

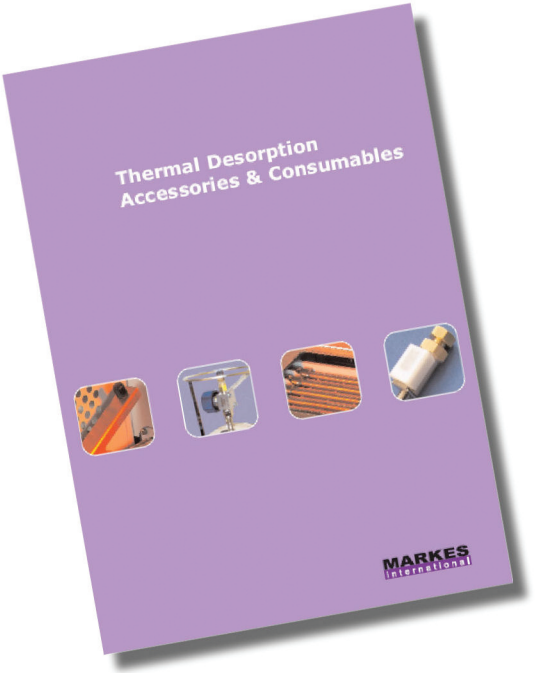
References: TDTS 13, TDTS 48 & TDTS 18

The Markes International advantage

Markes is the world leader in analytical thermal desorption and has pioneered important technical innovations such as SecureTD-Q (quantitative sample re-collection for repeat analysis), TubeTAG electronic labels for sorbent tubes and universal (multi-application) heated valve technology.

Markes leadership in TD now extends to:

- The widest available product portfolio and application range
- Product quality and reliability
- Excellence in technical and applications support



For more information on Markes comprehensive range of thermal desorption instruments and sampling accessories request your free copy of Markes TD Accessories and Consumables catalogue

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