

Use of Thermal Desorption Tubes for Monitoring of VOCs – An investigation of Diffusive Uptake Rates and Other Sampler Characteristics

#### **PERTEC 2015**

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Mention of company names or products does not constitute endorsement by HSL/E

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#### Contents



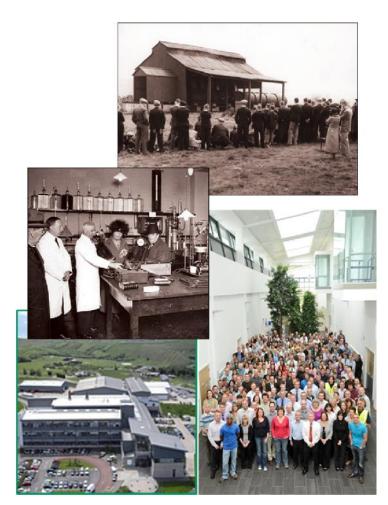
- Thermal Desorption
- Sorbent types
- Standard Atmospheres
  - Development
  - Uses
- Sorbent Testing
- The future
- Q & A



## **HSL** Overview

HEALTH & SAFETY LABORATORY

- The UK's Health & Safety Laboratory
- Established in 1911
- Science Division of the UK Health and Safety Executive (HSE)
- To support the HSE mission and directly help organisations become healthier, safer, and therefore more productive places in which to work
- Over 350 staff covering some
   50+ disciplines on 550 acres





## Principal of Thermal Desorption



- Analytes (VOCs) collected onto thermal desorption (TD) sorbent tube
- Sorbent tube heated releasing collected analytes
- Released analytes recollected on a cold trap
- Cold trap rapidly heated and analytes transferred to a gas chromatograph (GC) via a heated transfer line







## Advantages of Thermal Desorption

- Reusable samplers
- Improved sensitivity
  - Allows reduced sample loadings
  - Better for diffusive sampling
- Automated analysis
  - Lower cost
  - Improved reliability
- Compatible with wide volatility range
- No solvent related interferences





## Sorbent Types



- Porous polymers
  - Tenax TA<sup>™</sup>; Chromosorb-106<sup>™</sup>
- Graphitised carbon blacks
  - Carbograph 5TD<sup>™</sup>; Carbopack X<sup>™</sup>
- Carbonised molecular sieves
  - Sulphicarb<sup>™</sup>; Carboxen 1000<sup>™</sup>
- Traditional molecular sieves
  - 5Å; 13X
- Dual and three bed tubes
  - Tenax-Unicarb<sup>™</sup>; Air-Toxics<sup>™</sup>





## Limitations of Thermal Desorption



TD is not suitable for...

- Some very volatile compounds or permanent gases
- Compounds less volatile than C<sub>40</sub>
- Some very reactive compounds, e.g. formaldehyde
- Compounds not compatible with GC analysis



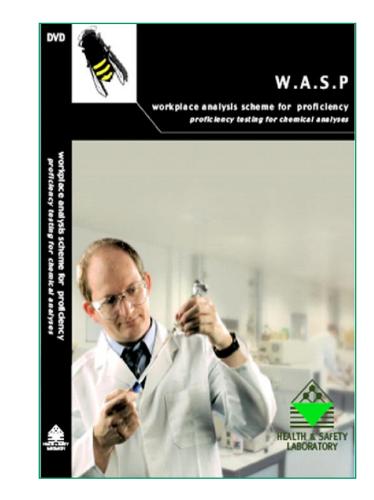






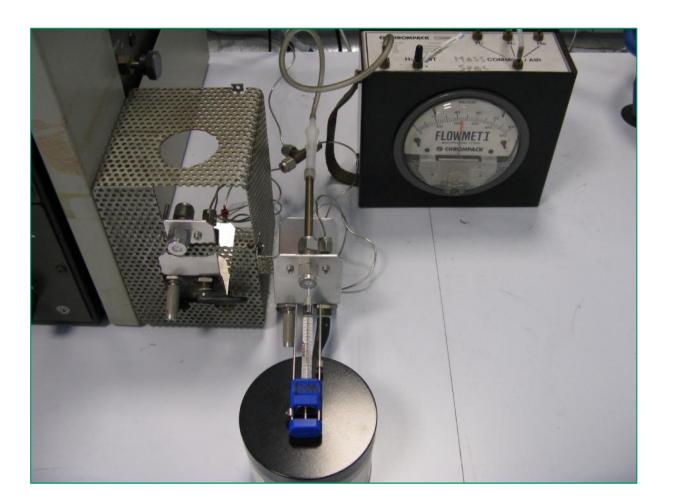




















#### **Standard Atmospheres**



A "standard test atmosphere" is a test chamber containing a gas of known composition (usually air containing small amounts of gaseous contaminants), and may be either static (sealed) or dynamic (with a flow through the chamber) in nature











A dynamic test atmosphere system typically incorporates some, or all, of the following elements:-

- A means of delivering a known volume and/or flow of air to the chamber
- A means of introducing a known mass and/or volume of contaminant into the system
- A means of verifying the composition of the atmosphere inside the chamber
- A means of controlling temperature and/or relative humidity inside the chamber

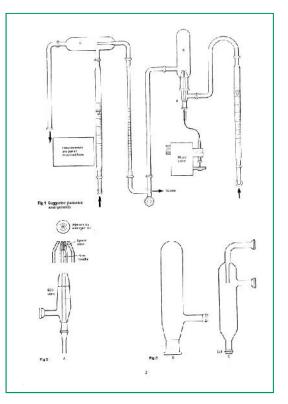


## Test Atmospheres – The Beginnings



#### HSL has been developing standard atmosphere equipment for almost 30 years

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Stability		Bulk gas or liquids





## Test Atmospheres – The Beginnings



We started off with valves, switches, rotameters, weird and wonderful chambers...



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## Test Atmospheres – The Beginnings

...and some very impressive examples of glass-blowing!



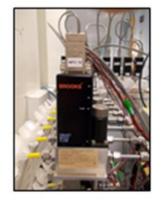


## Test Atmospheres – The Big Change



# Then came the PC, the mass flow controller and someone clever enough to get the two to talk to each other!



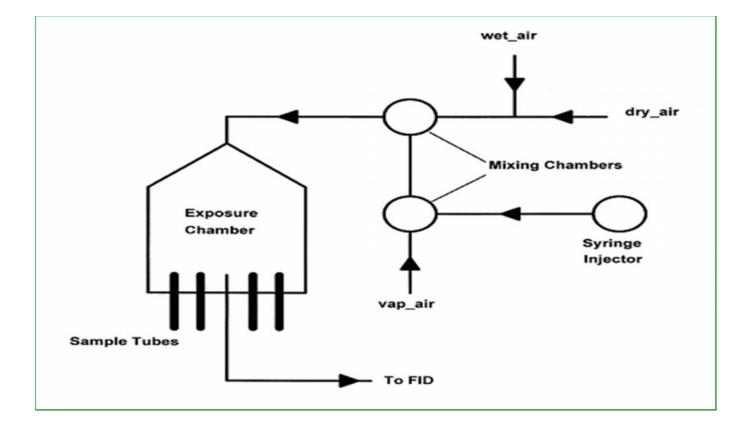






## HSL Test Facility - Schematic







## HSL Test Facility - Hardware

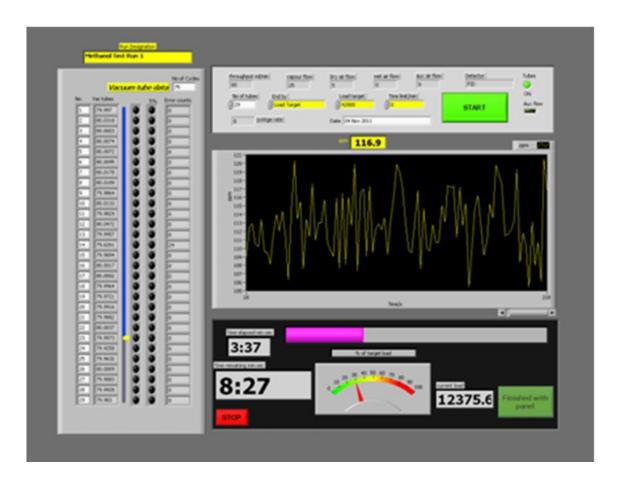






## HSL Test Facility - Software







## Tube Loading – The New Way!

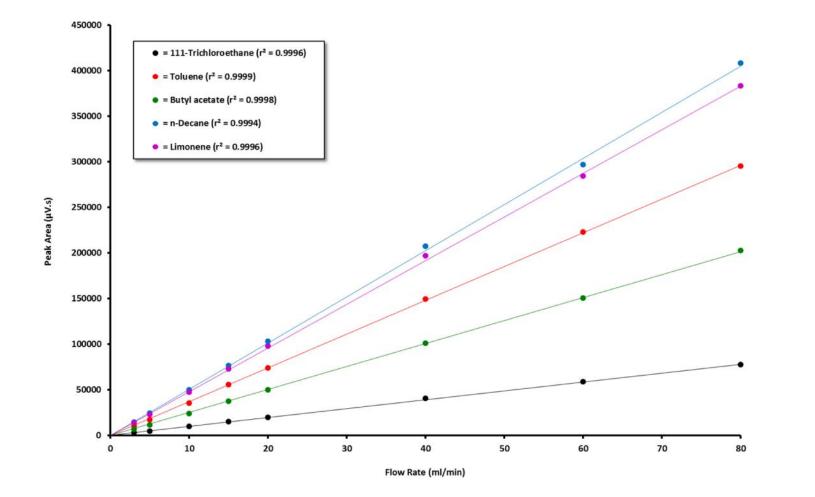




#### Test Equipment



## HSL Test Facility – Linearity Check



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## Use of Standard Atmospheres



As well as loading PT and check tubes, HSL uses standard atmospheres to test the following aspects of tube performance

- Desorption efficiency
- Storage stability
- Breakthrough volumes
- Effect of sampling flow rate
- Diffusive uptake rates





## Sorbents Tested



- Tenax TA<sup>™</sup>
- Chromosorb-106<sup>™</sup>
- Carbopack X<sup>™</sup>
- Carbograph 1TD<sup>™</sup>
- Carbograph 5TD<sup>™</sup>
- Carboxen 1000<sup>™</sup>



## Analytes Tested

Sevoflurane

Sorbent Testing

- Methanol
- Ethanol
- Acetone
- Isopropanol
- Pentane
- Dichloromethane
- 2-Butanone
- Ethyl acetate
- Ethanethiol
- n-Hexane
- Dimethylsulphide
- Vinyl acetate

- Propylbromide
- Methylcyclopentane
- Tetrahydrofuran
- 111-Trichloroethane
- n-Butanol
- Cyclohexane
- n-Methylpyrrolidine
- 1,4-Dioxane
- Trichloroethylene
- Methyl isobutyl ketone
- Toluene
- n-Butyl acetate

- Tetrachloroethylene
- m-Xylene
- Styrene
- Butoxyethanol
- -Pinene
- n-Decane
- 1,2-Dichlorobenzene
- Limonene
- Butoxyethyl acetate
- Naphthalene
- Ethyl disulphide
- n-Tridecane





## **Desorption Conditions**



- In order to obtain reliable results it is essential to establish optimum desorption conditions
- The following variables were investigated using sets of air loaded replicate samples
  - Desorption volumes (time and flow)
  - Desorption temperature
  - Split flows
- Clear differences were found in the optimum desorption conditions for different sorbents
- Shows the importance of identifying optimum desorption conditions for each sorbent type





## Recovery & Retention Volume (1)



- For effective sampling it is essential to select a sorbent able of capturing and retaining the components of interest
- The amount of analyte that can be retained also depends on the mass and condition of the sorbent
- Retention Volume (RV) is the volume of gas required such that 5% of analyte passes through the tube.
- Information on RVs available in EN ISO 16017 or HSE Method MDHS 72
- Information is limited and usually obtained from tests on single analytes rather than mixtures





## Recovery & Retention Volume (2)



- Tubes loaded with 1-litre of air loaded with ~ 5 ppm of each analyte at a flow rate of 100 ml/min
- Tube then purged with dry air at 100 ml/min over a range of time periods to give sample volumes of 1, 6, 31, 145 and 289-litres
- Secondary tube fitted in series to capture any analytes passing through the primary tube
- Air loaded tubes also compared with liquid spiked tubes purged with 0.05 and 1-litre volumes of dry nitrogen





## Recovery & Retention Volume (3)



- Sorbents such as Tenax TA and Carbograph 1TD show low recovery of sorbents with boiling points of < 100°C due to breakthrough</li>
- Some stronger sorbents, particularly Carbon Molecular sieves, gave low recovery of some components due to incomplete desorption
- Chromosorb 106 and Carbograph 5TD showed good performance with the selected analytes
- Dual bed tubes such as Tenax-Unicarb and Tenax-Carboxen 1003 perform better with the selected analytes than Tenax alone





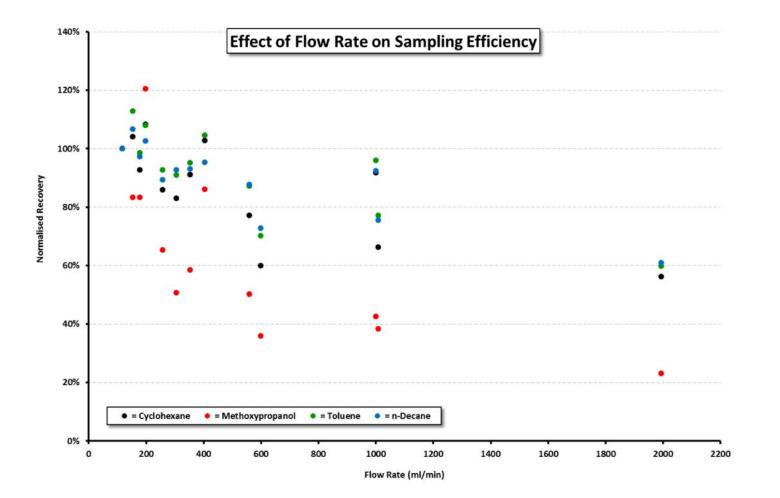


- Typical recommended flow rate for this type of sample is 50 150 ml/min
- Tubes spiked with ~20 µg each of cyclohexane, methoxypropanol, toluene and n-decane
- Purged with 3-litres of dry nitrogen using increasing flow rates and decreasing time periods
- Results indicate flow rates up to 200 ml/min can be used, but above this sampling efficiency begins to become very variable



## Flow Rate and Sampling Efficiency







## Storage Trials

- Storage trials carried out on sample tubes loaded in humidified air (~30% RH)
- Mass of each analyte was approximately 1 µg; loading volume was 1-litre; samples analysed over a 3-month time period
- Tenax and Chromosorb show good storage stability for most components over 3 months
- Carbograph 5 TD and Carbopack X show storage stability for most components for 1 month
- Stronger sorbents and dual-bed tubes can show 'losses' due to ineffective recovery









#### **Diffusive Uptake Rates**



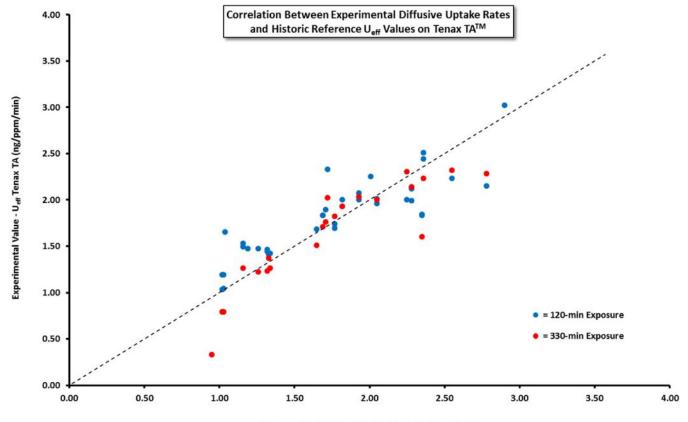
- Tubes exposed to ~5 ppm at ~20°C and ~30% RH with exposure times of 120 and 330 min
- Compared with active samples (5 ml/min for 120 min)
- Combination of 37 analytes and 7 sorbents generated over 4,700 analytical results
- A comparison of the results with reference values for Tenax TA and Chromosorb 106 showed generally good correlation
- Large amount of data allows uptake rates for different sorbents to be compared
- Possibility of predicting uptakes for common analytes on new sorbents or new analytes on existing sorbents







### Diffusive Uptake Rates (2)

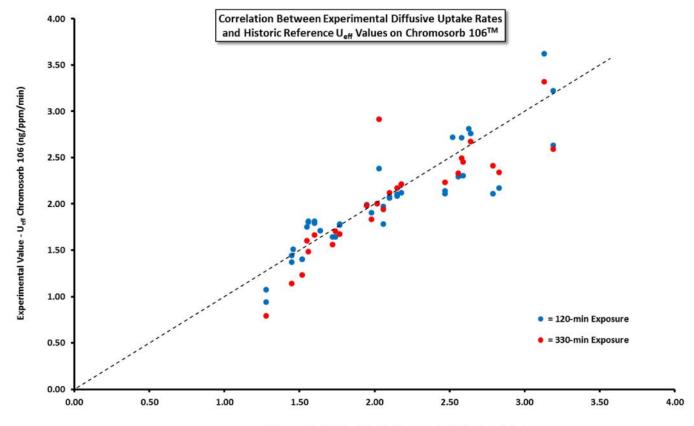


Reference Text Value - 8 hr Ueff Tenax (ng/ppm/min)





## Diffusive Uptake Rates (3)

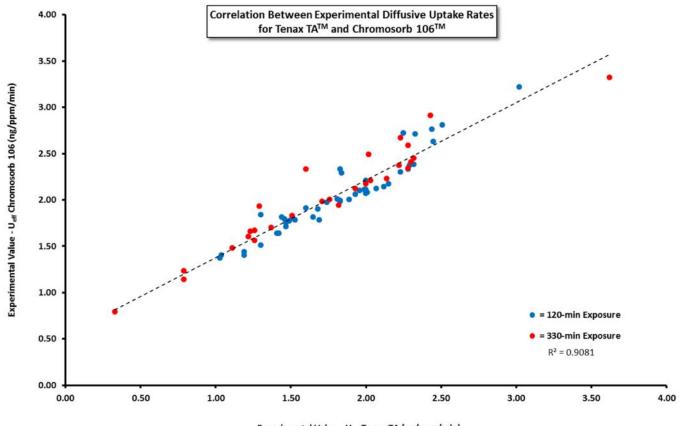


Reference Text Value - 8 hr U<sub>eff</sub> Chromosorb 106 (ng/ppm/min)



#### HEALTH & SAFETY LABORATORY

#### Diffusive Uptake Rates (4)

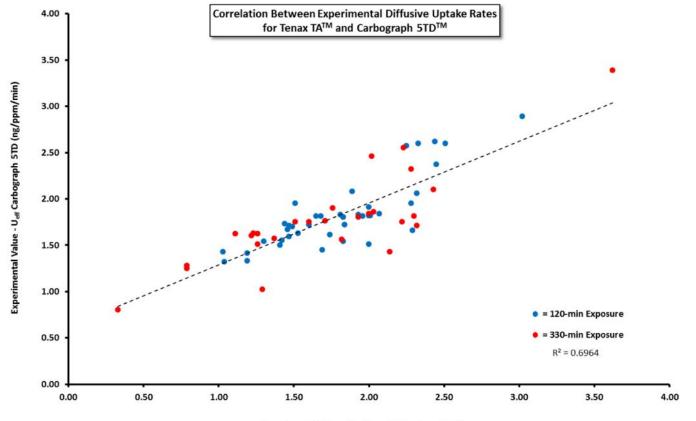


Experimental Value - Ueff Tenax TA (ng/ppm/min)





#### Diffusive Uptake Rates (5)



Experimental Value - Ueff Tenax TA (ng/ppm/min)



#### What can the information be used for?



EPA Method 325 A/B for fenceline Monitoring

- Method proposes uses benzene as the representative compound for measurement of overall emissions from refineries
- Diffusive (passive) sampling with analysis by TD-GC-MS is the measurent technique of choice



Picture Acknowledgement : Markes International



#### Future Developments



- Testing at environmental concentrations
   i.e. ppb rather than ppm
- Testing over longer time periods
   i.e. days/weeks rather than hours
- Use of alternative analyte generation systems and detectors
- Increased system capacity and functionality



 Generation of test atmospheres at variable concentrations for investigation of sampler performance to peak exposures



## Acknowledgments



- HSL: Neil Plant, Veronica Brown and Len Fuller
- PERTEC conference
- This audience for your attention

