HEALTH & SAFETY LABORATORY

# 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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# Disclaimer

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

The findings and conclusions in this presentation are those of the author and do not necessarily represent the views of HSL/E

# Contents

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

# HSL Overview

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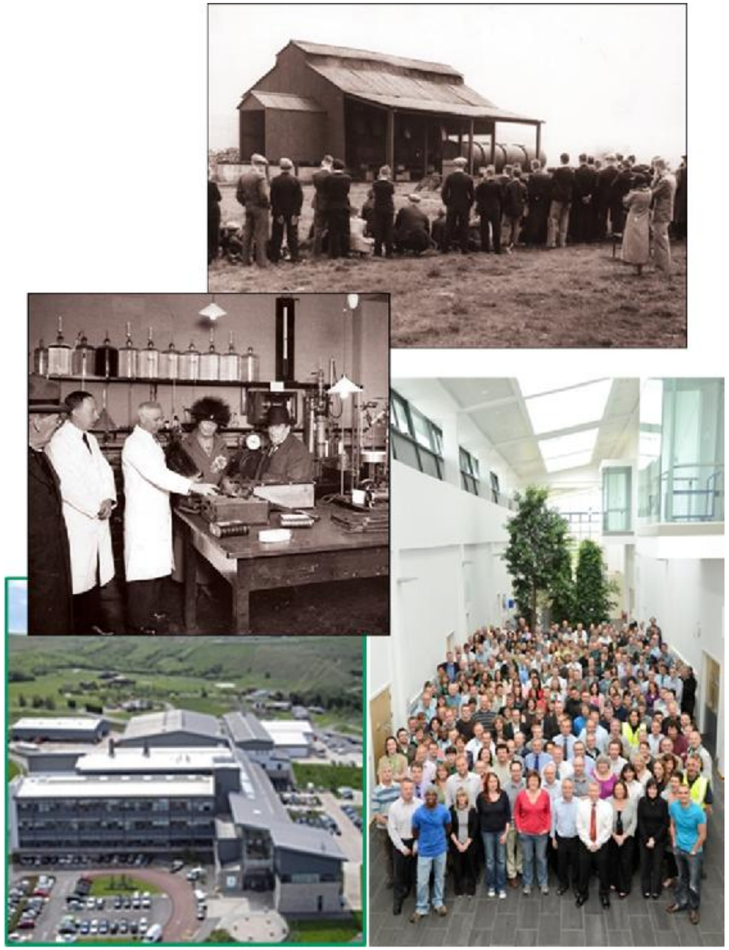
- The UK's Health & Safety Laboratory
- Established in 1911
- Science Division of the UK Health and Safety Executive (HSE)
- To support the HSE mission and directly help organisations become healthier, safer, and therefore more productive places in which to work
- Over 350 staff covering some 50+ disciplines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



# Principal of Thermal Desorption

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- 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

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

# Limitations of Thermal Desorption

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TD is not suitable for…

- Some very volatile compounds or permanent gases
- Compounds less volatile than $C_{40}$
- Some very reactive compounds, e.g. formaldehyde
- Compounds not compatible with GC analysis

# Tube Loading – The Old Way!

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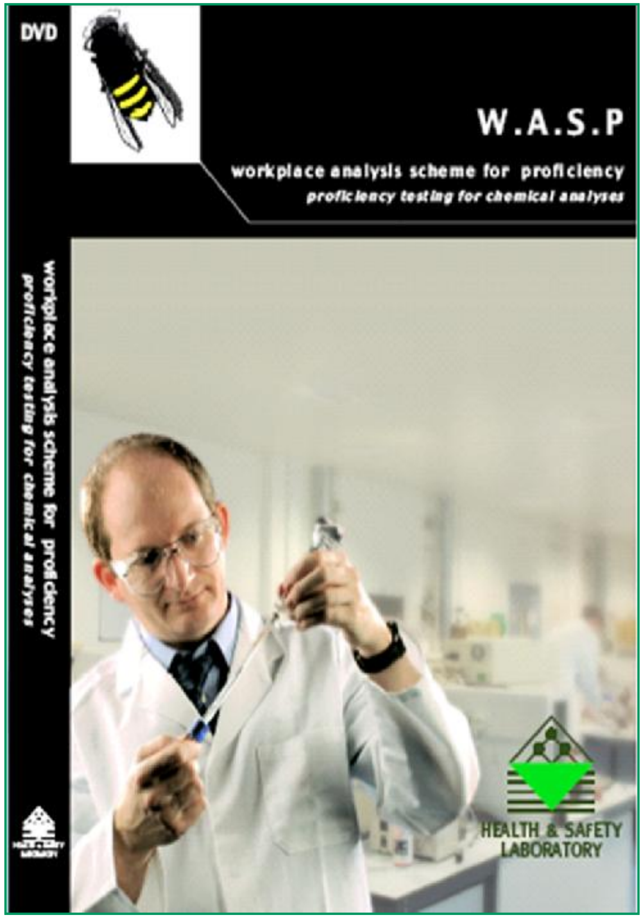

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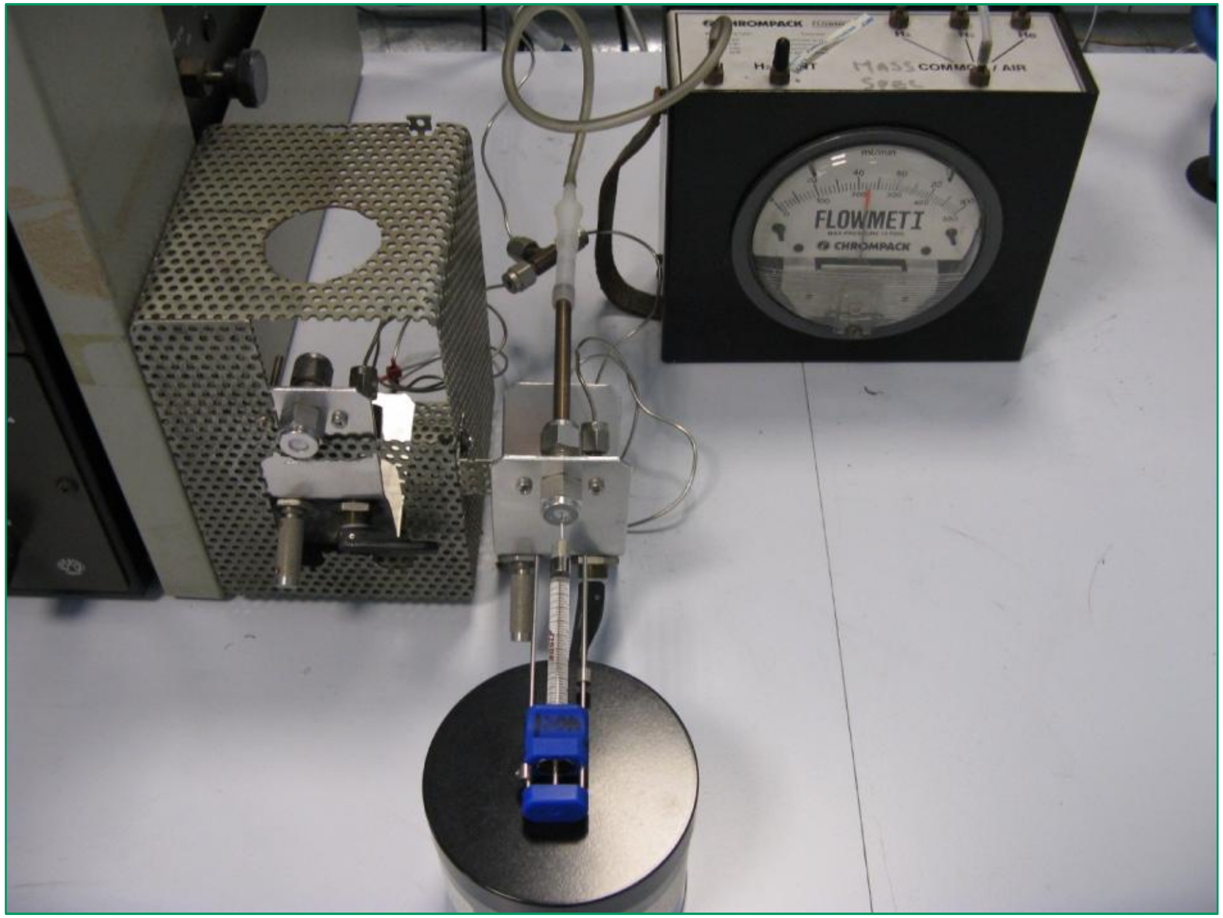

# Tube Loading – The Old Way!

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# Standard Atmospheres

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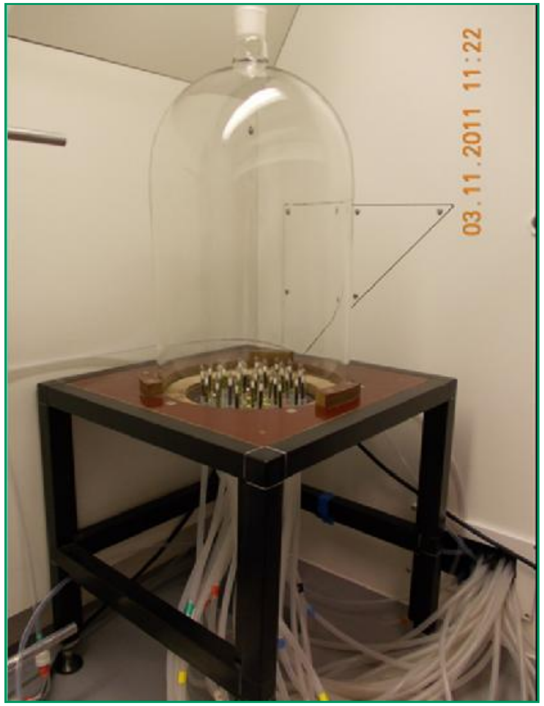
A "standard test atmosphere" is a test chamber containing a gas of known composition (usually air containing small amounts of gaseous contaminants), and may be either static (sealed) or dynamic (with a flow through the chamber) in nature

# Dynamic Test Atmospheres

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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

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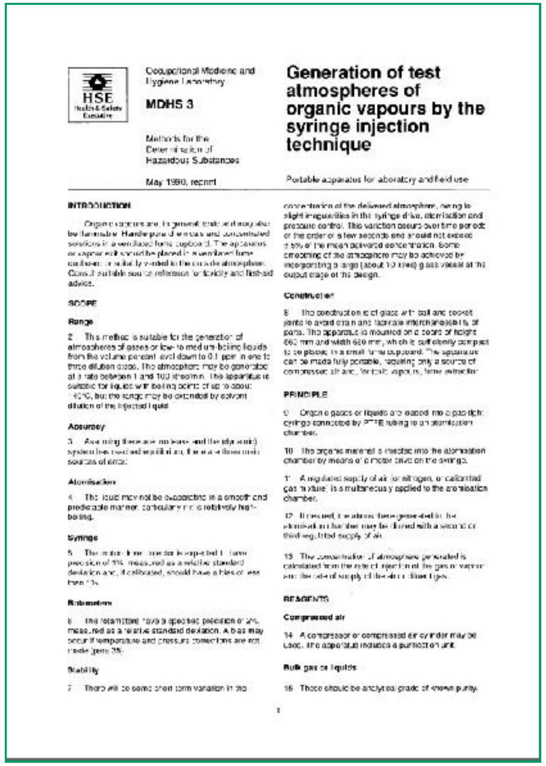
HSL has been developing standard atmosphere equipment for almost 30 years



HSE Health & Safety Executive

Occupational Medicine and Hygiene Laboratory

MDHS 3

Methods for the Determination of Hazardous Substances

May 1990, reprint

## Generation of test atmospheres of organic vapours by the syringe injection technique

Portable apparatus for laboratory and field use

INTRODUCTION

SCOPE

Range

Accuracy

Atomisation

Syringe

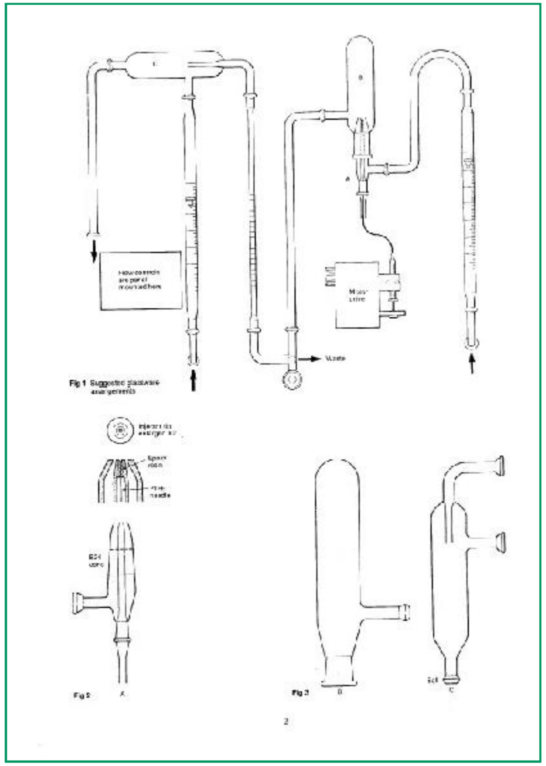
Stability

Construction

PRINCIPLE

REAGENTS

Compressed air



# Test Atmospheres – The Beginnings

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


# Test Atmospheres – The Beginnings

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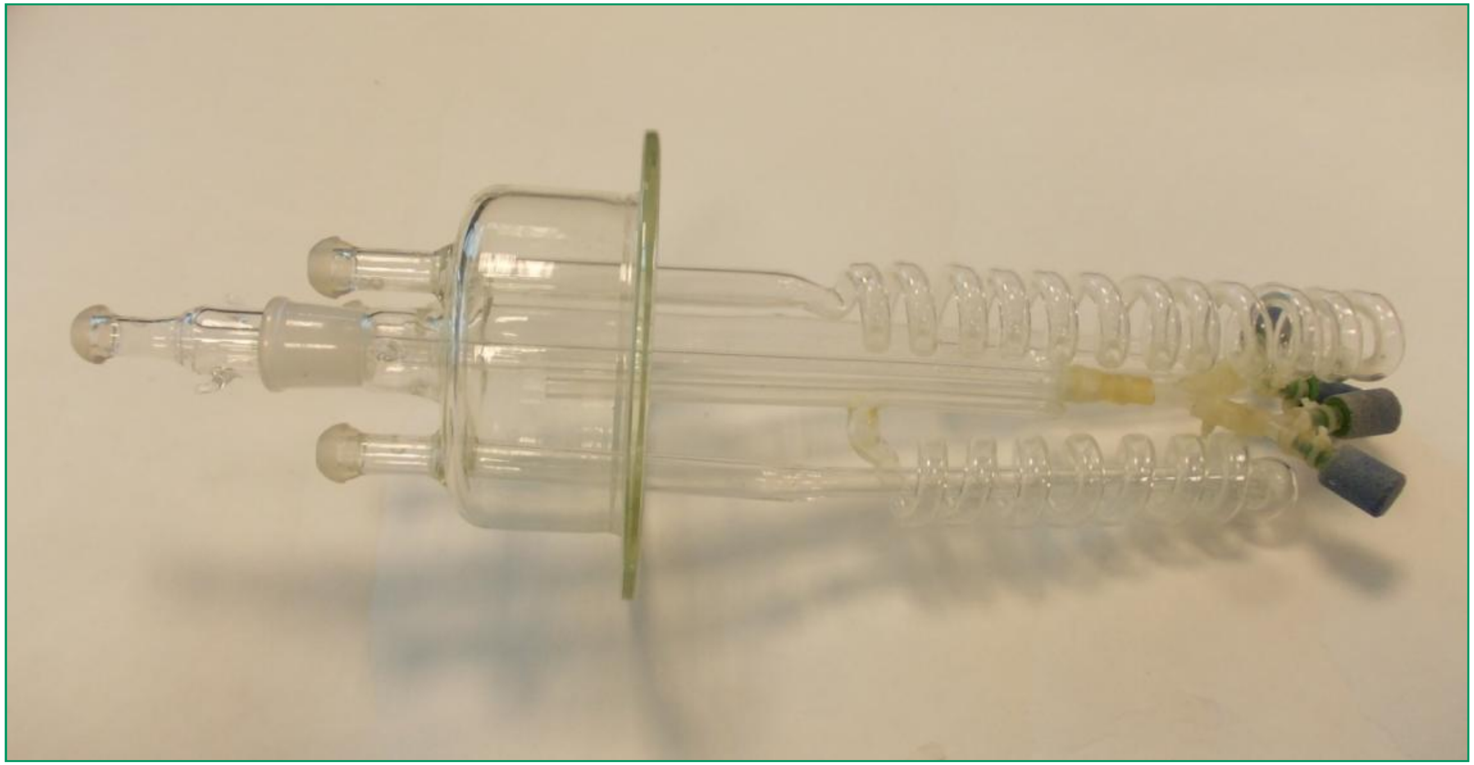
…and some very impressive examples of glass-blowing!



# 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

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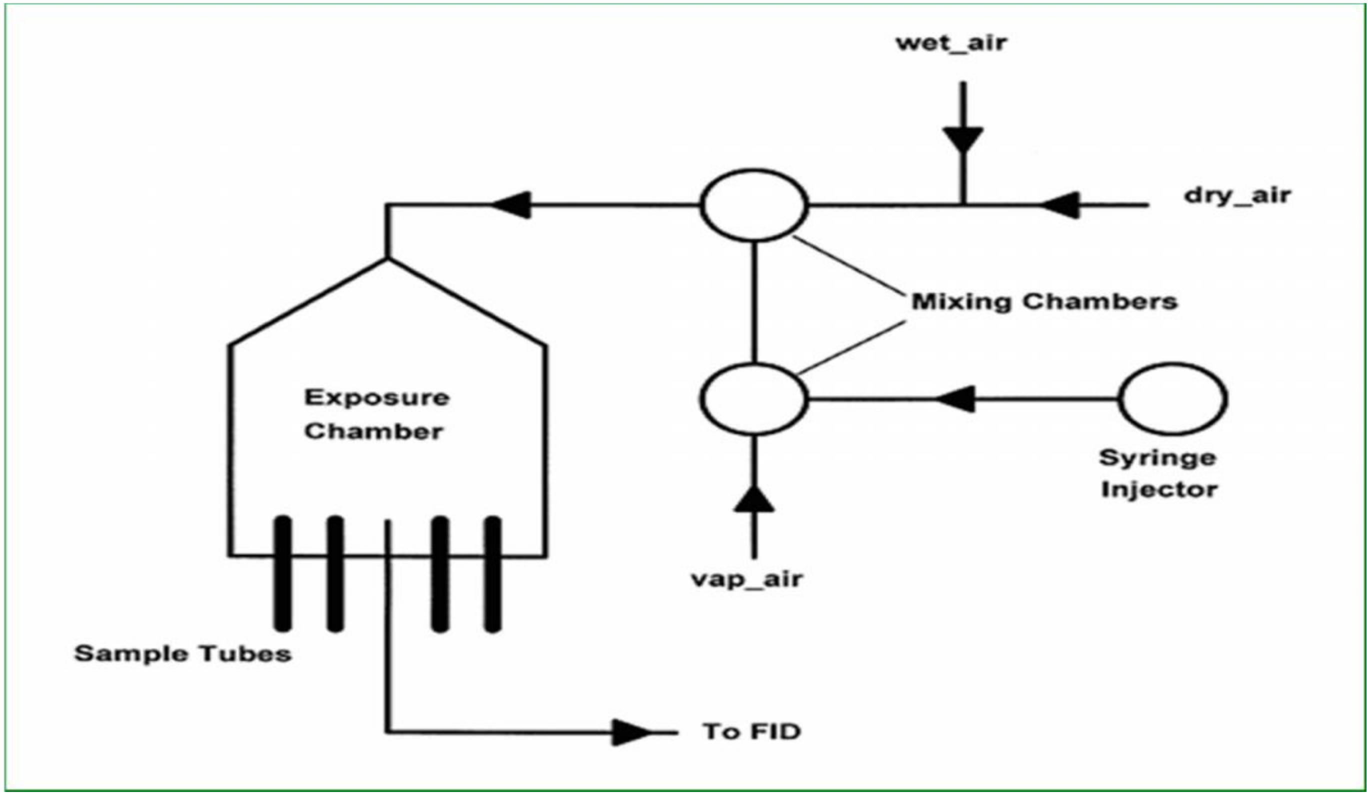

# HSL Test Facility - Hardware

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# HSL Test Facility - Software

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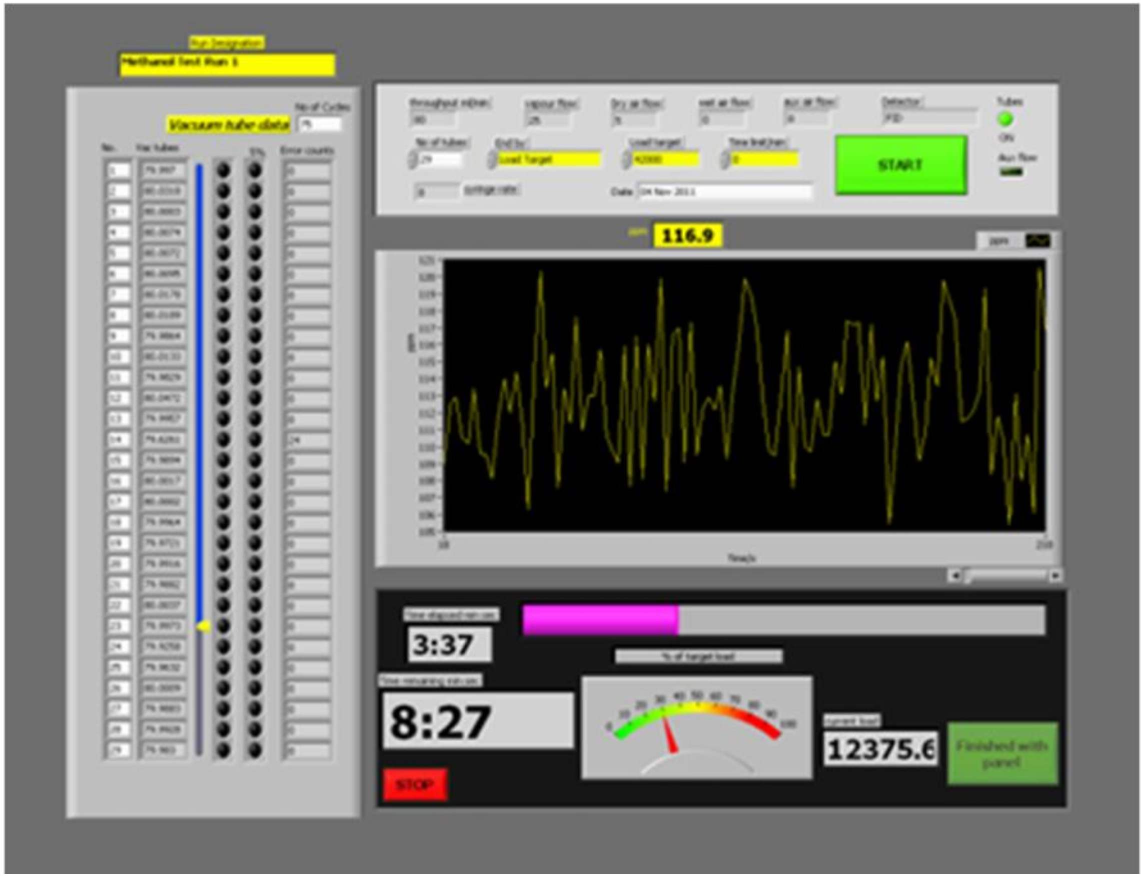

# Tube Loading – The New Way!

# HSL Test Facility – Linearity Check

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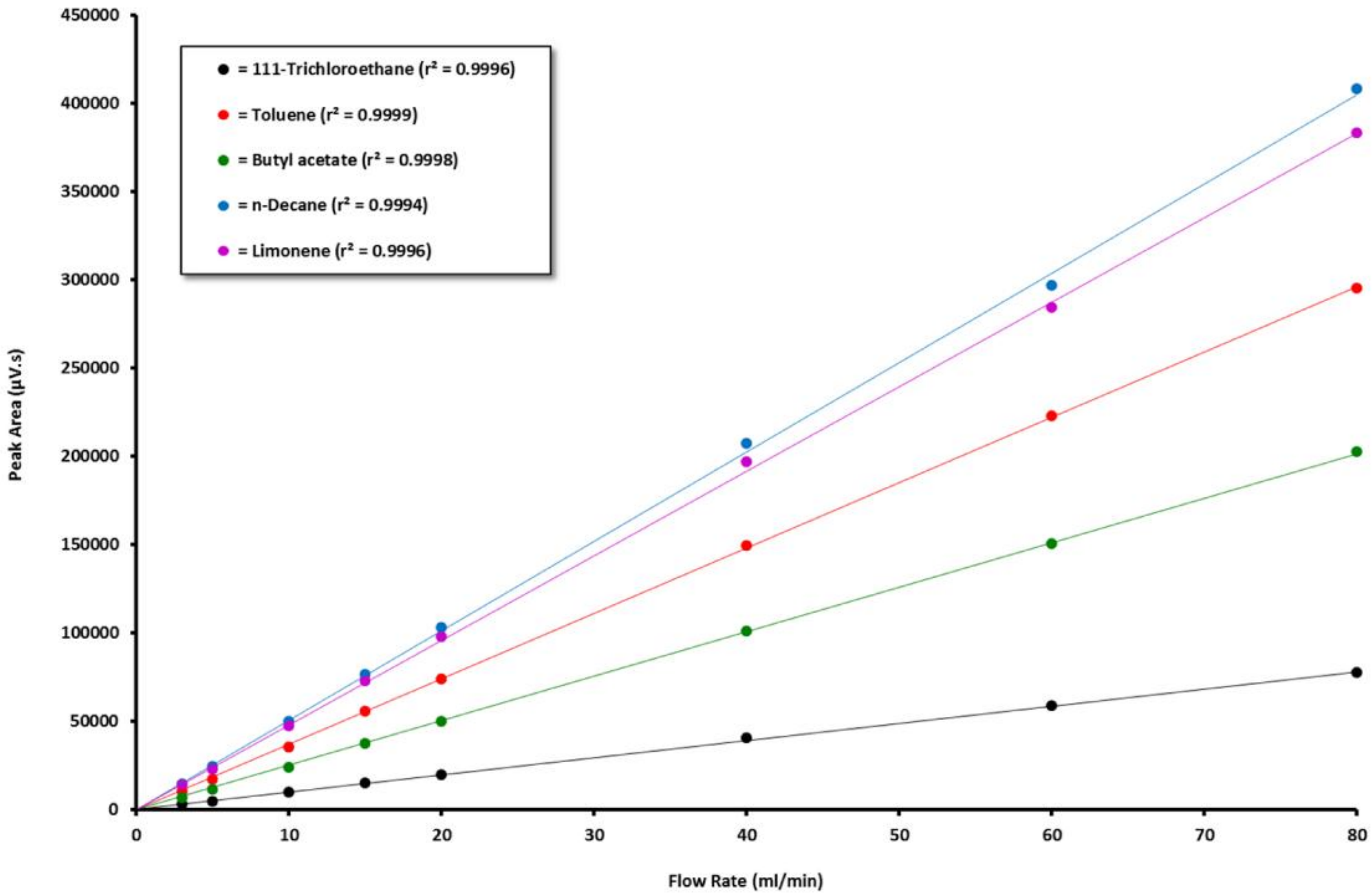

# Use of Standard Atmospheres

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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™
- Chromosorb-106™
- Carbopack X™
- Carbograph 1TD™
- Carbograph 5TD™
- Carboxen 1000™

# Analytes Tested

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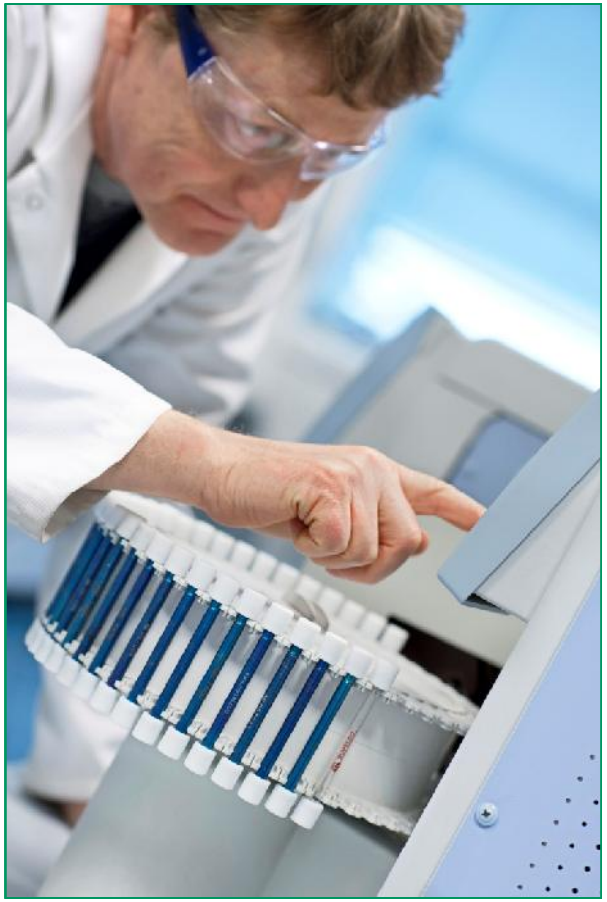
- Sevoflurane
- Methanol
- Ethanol
- Acetone
- Isopropanol
- Pentane
- Dichloromethane
- 2-Butanone
- Ethyl acetate
- Ethanethiol
- n-Hexane
- Dimethylsulphide
- Vinyl acetate
- Propylbromide
- Methylcyclopentane
- Tetrahydrofuran
- 111-Trichloroethane
- n-Butanol
- Cyclohexane
- n-Methylpyrrolidine
- 1,4-Dioxane
- Trichloroethylene
- Methyl isobutyl ketone
- Toluene
- n-Butyl acetate
- Tetrachloroethylene
- m-Xylene
- Styrene
- Butoxyethanol
- α-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)

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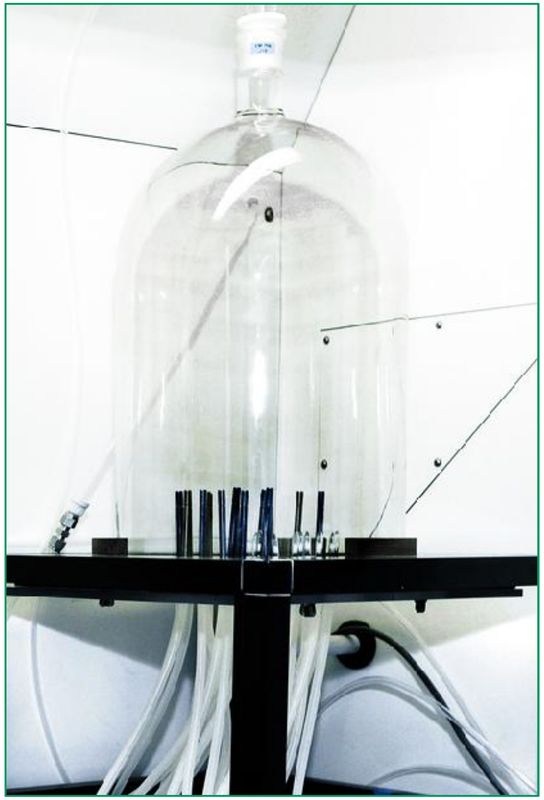
- For effective sampling it is essential to select a sorbent able of capturing and retaining the components of interest
- The amount of analyte that can be retained also depends on the mass and condition of the sorbent
- Retention Volume (RV) is the volume of gas required such that 5% of analyte passes 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)

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- 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)

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- Sorbents such as Tenax TA and Carbograph 1TD show low recovery of sorbents with boiling points of < 100°C due to breakthrough
- 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

# Flow Rate and Sampling Efficiency

- 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

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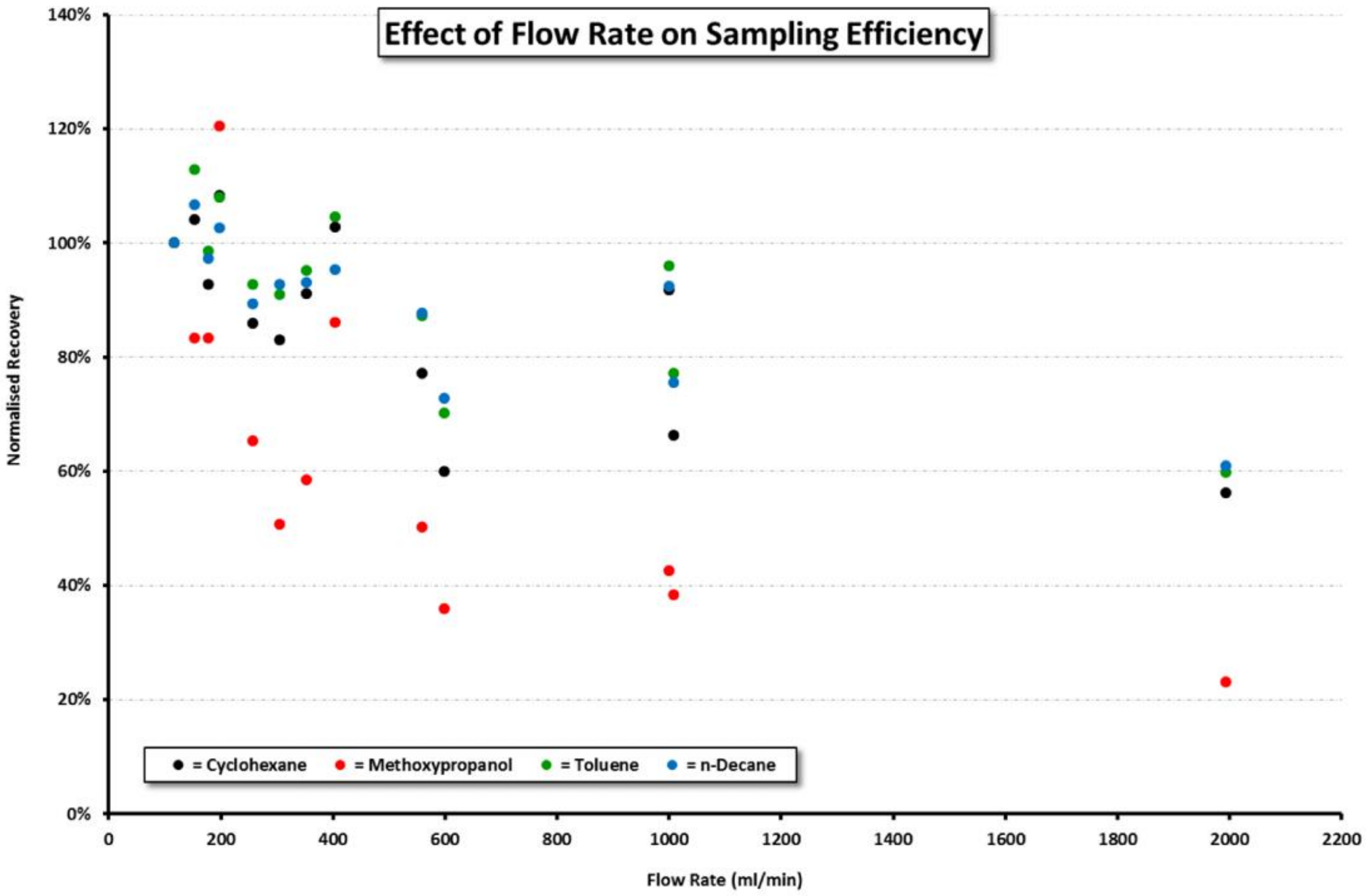

# Storage Trials

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- 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

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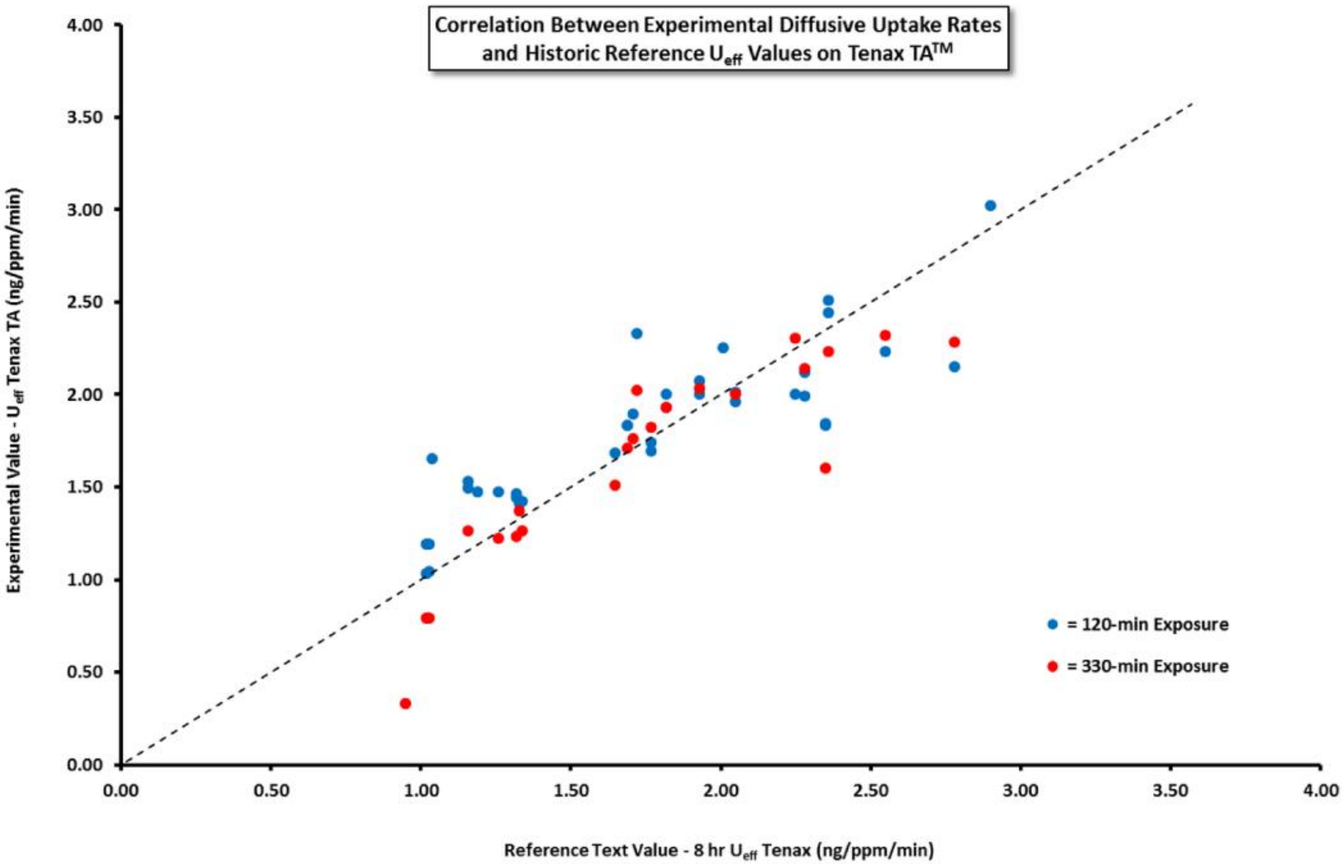
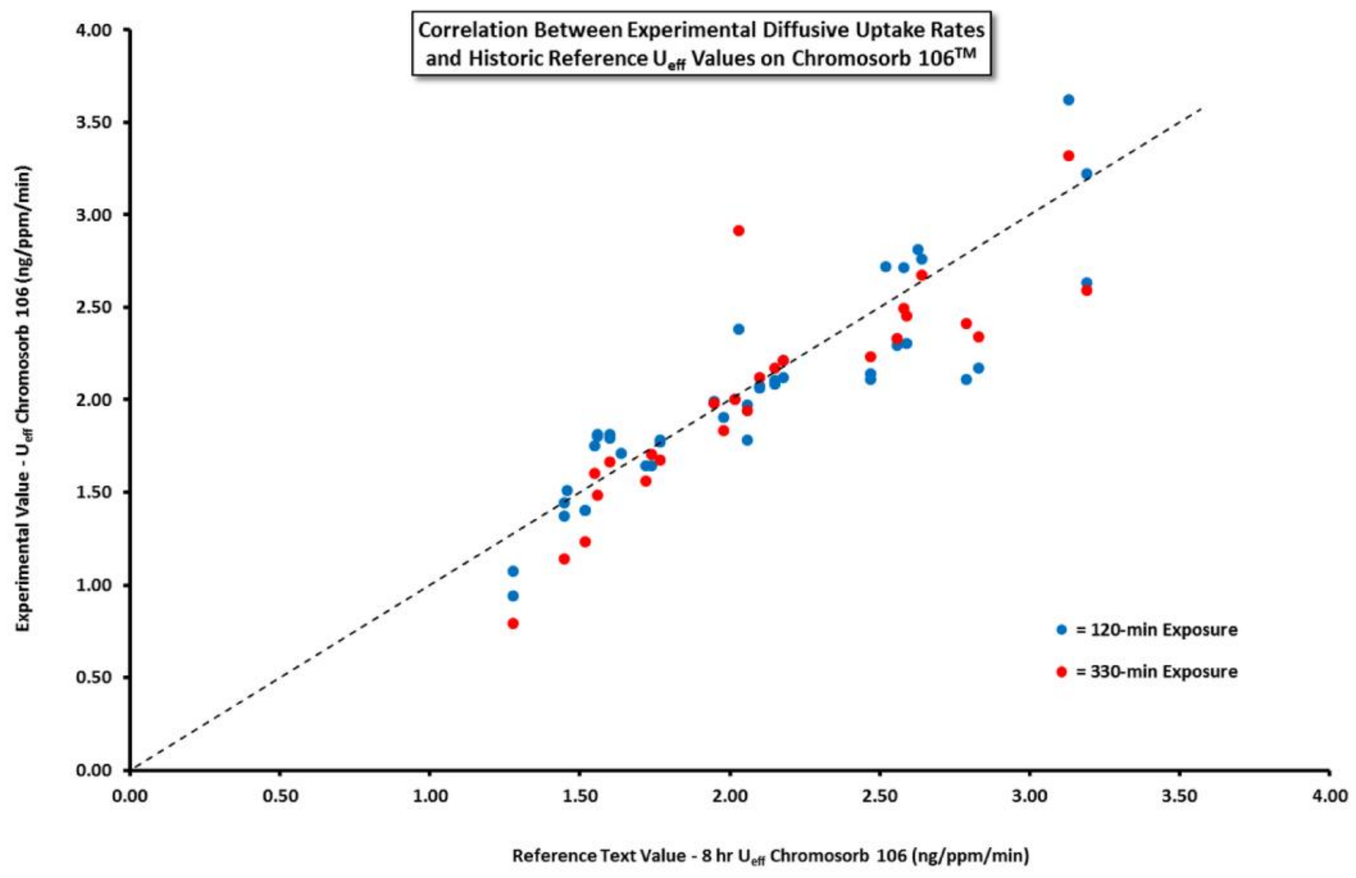
- Tubes exposed to ~5 ppm at ~20°C and ~30% RH with exposure times of 120 and 330 min
- Compared with active samples (5 ml/min for 120 min)
- Combination of 37 analytes and 7 sorbents generated over 4,700 analytical results
- A comparison of the results with reference values for Tenax TA and Chromosorb 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)



# Diffusive Uptake Rates (3)



# Diffusive Uptake Rates (4)

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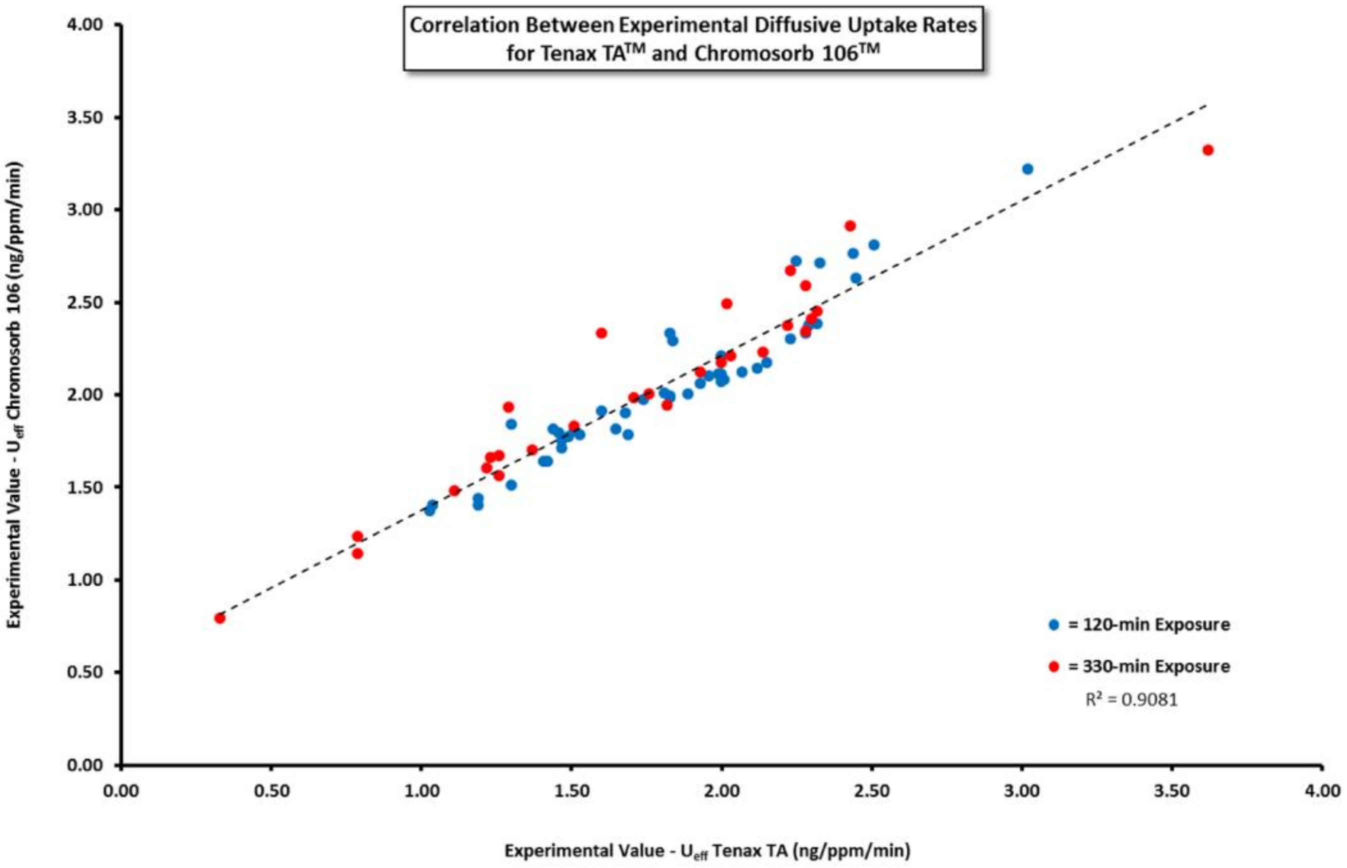
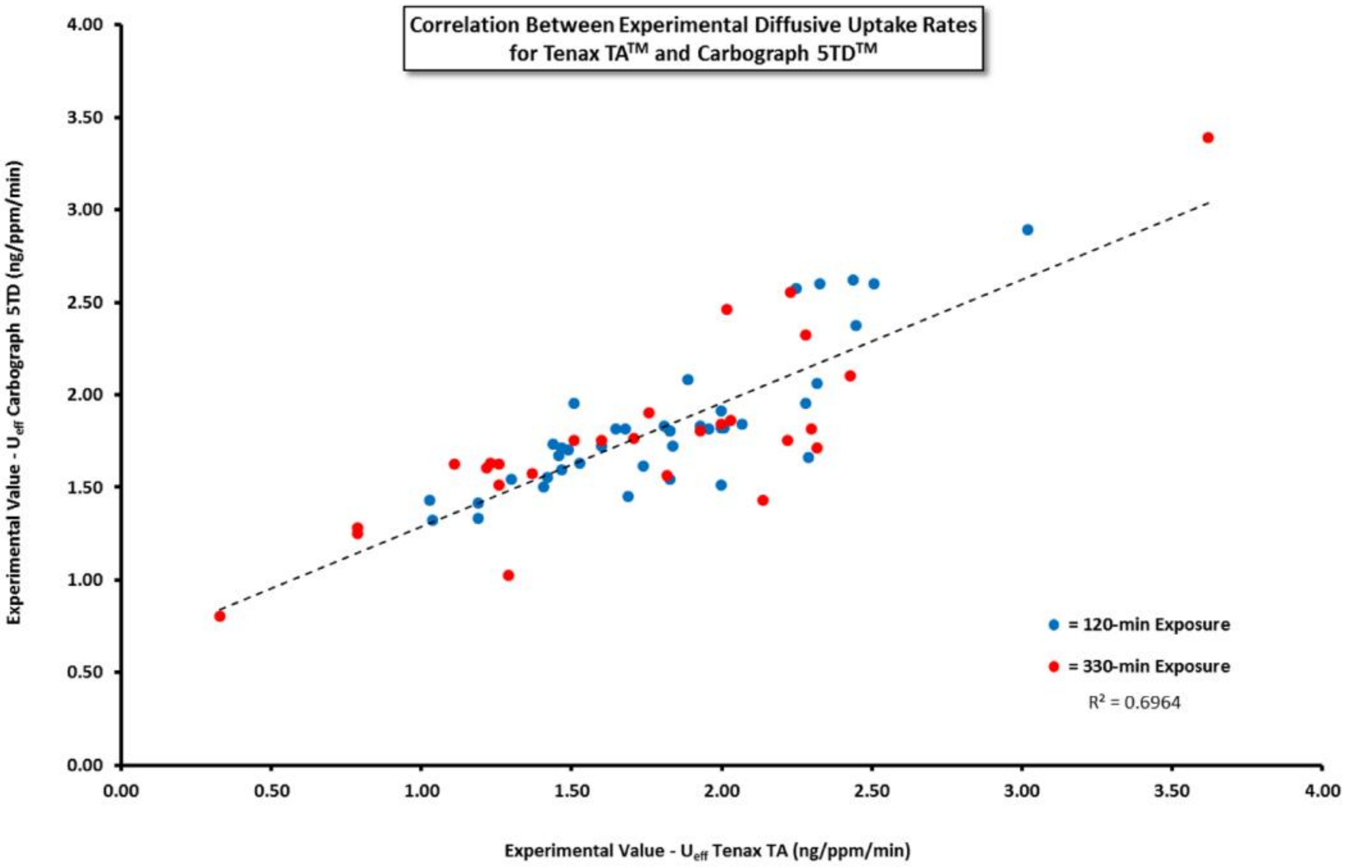


# Diffusive Uptake Rates (5)



# 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

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- 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