# Application of Thermal Desorption to Occupational Exposure Monitoring

## Introduction to occupational exposure monitoring

Occupational hygiene, in its broadest sense, is the recognition, evaluation and control of health hazards arising from work – a trained hygienist needs to understand a range of subjects from health and safety legislation through to toxicology, hazardous substances, physical agents, exposure assessment and exposure control strategies. To some extent, occupational hygiene is relevant in all workplaces although, in practice, it is most applicable to environments in which significant health risks exist. These can range from call centers with noise hazards to chemical sites handling bulk quantities of very toxic substances. The legislation and practical measures for managing human exposure to chemicals will vary from one national jurisdiction to another but, in the United Kingdom, they are implemented in the Control of Substances Hazardous to Health (COSHH) Regulations (*http://www.hse.gov.uk/coshh/*) produced by the Health and Safety Executive (HSE), which recommend using valid and suitable occupational hygiene techniques to estimate the amount of employee exposure to substances hazardous to health. Exposure monitoring has played a major role in the development and evolution of UK occupational hygiene and is a key element in the 'evaluation' stage of the recognition, evaluation and control philosophy. Monitoring is often invaluable when making an initial assessment of a work environment, providing quantitative evidence to allow development of robust exposure control strategies. Subsequent repeat monitoring may be required to demonstrate that adequate exposure control is being achieved and maintained over time.

**Authors**

N. Plant and C. Keen
Health & Safety Laboratory
Analytical Sciences
Buxton, Derbyshire, SK17 9JN, UK

A. Tipler
PerkinElmer Life and
Analytical Sciences
710 Bridgeport Avenue
Shelton, CT 06484 USA

HEALTH & SAFETY LABORATORY

PerkinElmer®
precisely.

In practice, exposure monitoring most commonly refers to personal sampling where the sampling device is mounted in the workers' breathing zone, providing an estimate of the inhalation exposure averaged over the measurement period. Sampling for gases and vapors may be carried out using active (pumped) or passive (diffusive) sampling. Techniques other than personal sampling using direct-reading hand-held instruments or colorimetric tubes do not provide a direct measure of inhalation exposure and must be used with caution. Such techniques are frequently misused by the inexperienced, and can lead to gross errors being made when estimating exposures. In straightforward situations, an experienced occupational hygienist may be able to evaluate exposure and assess risk without monitoring. Often, however, worker exposure is dependent on a complex interplay of processes, exposure controls and human factors. Monitoring demonstrates the adequacy of controls required for compliance with exposure limits. Monitoring also has a role to play in exposure modeling and epidemiology.

In the UK, the use of intuitive assessment rather than monitoring has led to an apparent decline in the amount of exposure monitoring carried out in workplaces. A combination of factors accounts for this and may include the perception that monitoring is complex, costly and time consuming. An experienced occupational hygienist should judge whether the benefits of monitoring outweigh these factors. The introduction and evolution of the COSHH Essentials "control banding" approach in the UK provides generic control solutions dependent upon substance and process. The exposure controls described by COSHH Essentials, if correctly used and understood, should result in adequate exposure control. It may appear that implementing the recommended controls removes the need for monitoring but the complex interaction of workers with processes means that frequently this is untrue. Any exposure controls should be validated once installed, and exposure monitoring provides the best basis for this.

The UK occupational exposure limit framework was comprehensively reviewed during 2004-2005 by a panel of experts in order to establish the evidence base of every numerical limit value and to assess the probability that the existing limit was truly protective of health. This resulted in an overall reduction by about 100 in the number of substances with a designated workplace exposure limit. A large proportion was substances inherited from the U.S. Threshold Limit Value (TLV) list with either limited or no known UK application. There are no immediate plans to replace these deleted limits,

although new evidence may restore limits at the same or a different value in the future. Any new European limit values recommended by the EU Scientific Committee on Occupational Exposure Limits (SCOEL) are normally adopted unchanged by EU member states. When comparing the numerical limits of different jurisdictions, it is essential to be aware of the philosophy and documentation behind them. Some are health based, while some are derived from good practice controls. In a recent revision of the UK COSHH regulations, the existing requirements to follow good practice are being clarified and brought together by the introduction of eight principles, which will apply regardless of whether a substance has an Occupational Exposure Limit:

- Design and operate processes and activities to minimize emission, release and spread of substances hazardous to health
- Take into account all relevant routes of exposure – inhalation, skin absorption and ingestion – when developing control measures
- Control exposure by measures that are proportionate to the health risk
- Choose the most effective and reliable control options which minimize the escape and spread of substances hazardous to one's health
- Where adequate control of exposure cannot be achieved by other means, provide, in combination with other control measures, suitable personal protective equipment
- Check and review regularly all elements of control measures for their continuing effectiveness
- Inform and train all employees on the hazards and risks from the substances with which they work and the use of control measures developed to minimize the risks
- Ensure that the introduction of control measures does not increase the overall risk to health and safety

In the UK, the enforcement body is the Health and Safety Executive (*http://www.hse.gov.uk/*) supported by the laboratory services of the Health and Safety Laboratory (HSL) (*http://www.hsl.gov.uk/*) which provides exposure monitoring and other services such as risk assessment tools, accident investigation and general safety research. HSL has a history of developing monitoring methodologies for a wide range of workplace contaminants and is experienced in generating, collating and interpreting high-quality data on occupational exposures across a range of industries. Most relevant is the long association of HSL expertise with the methodology

of thermal desorption and its application to monitoring chemical vapors in the workplace. This method continues to generate exposure information for HSE/HSL by a simple non-intrusive sampling procedure followed by automated analysis. The recent advances in technology, now commercially available, have greatly increased the confidence in producing reliable and accurate quantitation of complex mixtures of volatile substances in air.

## Techniques for occupational exposure monitoring

### Simple techniques

The use of air samplers, such as filters and sorbent tubes, is a universal approach to air monitoring. The collection mechanisms may employ deposition, adsorption or even derivatization on the sampler. Sampler type and analytical technique are entirely dependent on the analytes under examination. In its most basic form, analysis might be as simple as fiber counting for asbestos, gravimetry (for monitoring wood dust), or a reagent color change.

### Sophisticated techniques

For the identification and quantification of complex mixtures or for biological monitoring (e.g. of breath samples) more sophisticated techniques may need to be employed. In the case of airborne volatile hydrocarbons, sampling of complex mixtures on sorbent tubes is the preferred approach, followed by thermal-desorption analysis. Key to this method is a cryofocusing stage in which analytes released during the primary desorption step are re-collected on a second sorbent bed held at a very low temperature. This enables analytes, which may have been widely distributed over the sorbent bed of the sampling tube, to be held in a tight band on the cold trap, at which point a second thermal desorption "injects" the analyte on the capillary gas chromatography (GC) column. Separation depends on the physical properties of the analytes and the type of column used. Detection methods normally include mass spectrometry (MS), flame ionization (FID) or electron capture (ECD), although other methods are possible. The benefits of MS are that co-eluting substances can be resolved and quantified with high sensitivity using ion fragments. However, in the workplace, unlike ambient monitoring, it is often the case that the substance of interest is either at a greater concentration than other contaminants, or there are no significant co-elutions. In these cases, MS may not be required and the preferred

approach is the use of FID, which gives a good linear and stable response over a wide dynamic range and consequently is simple to calibrate and maintain.

Recovery from thermal desorption methods is generally > 95%, assuming the analyte is not thermally labile and the correct analytical conditions have been used. This is a positive advantage over solvent desorption, particularly for polar compounds on charcoal, where recovery cannot be assumed to be complete and is allowed in performance standards to be as low as 75%. A further disadvantage of solvent desorption is that compliance with the 75% criterion is allowed to be established in laboratory tests that do not necessarily account for all the ways that humidity and concentration might affect the desorption efficiency. In addition, thermal desorption does not require the use of noxious solvents which can mask early-eluting analytes. With minimal preparation required, handling error is significantly reduced and a high sample throughput maintained.

## Application of thermal desorption

### Scope and field of application

Thermal desorption affords the opportunity of a rapid and reliable indication of airborne vapor concentrations in the workplace. The technique is applicable to passive (diffusive) and active (pumped) sampling. Thermal desorption may also be used for direct analysis of solids, particles or swabs and also spiked liquids.

This approach recommends a number of sorbents intended for different ranges of volatile organic compounds (VOCs). For example, Tenax® is appropriate for aliphatic hydrocarbons from heptane to decane and aromatic compounds from toluene to trimethylbenzene. It is also suitable for esters, ketones, chlorinated hydrocarbons, alcohols and ethers of similar volatilities, as well as some higher-boiling compounds. Very volatile substances must be sampled on stronger sorbents such as Chromosorb® 106, Carboxens or other forms of activated carbon. Sorbents other than those specified may be used if their diffusive uptake rates are known and their thermal blank is small.

The upper limit of the useful concentration range is set by the sorptive capacity of the sorbent and by the linear dynamic range of the gas chromatograph's column and detector. In this instance, the sorptive capacity of the tube must be viewed in terms of the total number of

analytes and the ability of the sampler to retain them all simultaneously. In active sampling, the ability of the sample tube to retain an analyte is expressed as the retention volume or safe sampling volume at which point analyte will break through and be lost. The lower limit of the useful range depends on detector noise and the analyte blank. The method also requires that there is minimal water retained on the sampler prior to desorption and therefore operators must be cautious when using hydrophilic sorbents in high-humidity environments.

The long-term stability of volatile organic compounds on Tenax® is good and may be acceptable up to several years in the case of non-polar hydrocarbons. The stability of VOCs on Chromosorb® 106 or other sorbents is not as well documented but is generally acceptable on the basis of storage tests of up to a few weeks.

## Methods

### Introduction

This section will outline both the required sampling approach and also the general instrument conditions such as flow rates and temperatures. The UK Health and Safety Laboratory has prepared methods in the series *Methods for the Determination of Hazardous Substances* (MDHS). Of particular relevance to thermal desorption is MDHS 80, *Volatile Organic Compounds in Air – Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography.* Other publications in the MDHS series are also relevant. These are MDHS 53, 63, 72, 88, 89 and 96 and are available on the HSE website at *http://www.hsl.gov.uk/publications/mdhs_list.htm*. The COSHH Regulations require that people who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. They also include a requirement to assess the health risk created by work involving substances hazardous to health and to prevent or control exposure to such substances. Employers (in the UK) must therefore ensure that the requirements of the COSHH Regulations are fully satisfied before allowing employees to undertake any procedure described in this method.

### Principle

An appropriate sorbent is selected for the compound or mixture to be sampled (more than one tube may be necessary). For diffusive sampling, the rate of sampling must have been validated, normally by prior calibration in a standard atmosphere. Values for sampling rates (effective uptake rate) on diffusive tubes of the PerkinElmer type are available in the standards

ISO 16017-2, ASTM D6196-03, the method MDHS 80 (UK HSE) and in the newsletter *The Diffusive Monitor,* 8 (1996). The data in these four publications overlap to a large extent because they have a common source. For ambient-benzene validation data, the best source is EN 14662-4.

The diffusive sampler is exposed to air for a measured time period. The organic compound vapors migrate down the tube by diffusion and are collected on the sorbent. Alternatively, active pumping may be used. The collected vapors are desorbed by heat and are transferred under inert carrier gas into a gas chromatograph equipped with a suitable capillary column and a flame ionization detector.

### Sorbents

A wide variety of sorbents is available such as porous polymers, graphitized carbons and carbon molecular sieves. Two of the more commonly used sorbents are listed below.

- **Tenax®:** Tenax® porous polymer sorbent (particle size 0.18-0.25 mm; 60-80 mesh) preconditioned by heating in an inert atmosphere at 250 ˚C before use. Tenax® is available in a number of forms, including Tenax® TA and Tenax® GR (graphitized).

- **Chromosorb®:** Chromosorb® porous polymer sorbent (particle size 0.18-0.25 mm; 60-80 mesh) preconditioned by heating in an inert atmosphere at 190 ˚C before use. Chromosorb® is available in a number of forms, including Chromosorb® 102 and 106. Chromosorb® 106 may be conditioned at 250 ˚C.

### Collection of samples

Select and expose an appropriate sorbent tube by replacing the sealing cap on the sampling end with the diffusion cap, which must be properly seated to ensure the correct air gap and consequently the correct sampling rate. The sealing cap on the non-sampling end is not removed. When used for personal sampling, the tube should be mounted in the worker's breathing zone, for example on a lapel. The orientation of the tube is not critical. When used for fixed location sampling, a suitable sampling site is chosen. If the sample is likely to be exposed to rain, fix the tube with the closed end uppermost to avoid collection of rainwater. At the end of the sampling period, replace the sealing cap. Sample blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes, except for the actual period of sampling.

## Standards for calibration

Standards are normally prepared in methanol at a suitable concentration and injected onto an appropriate sorbent tube under a flow of nitrogen to purge off the excess methanol, retaining the calibration analytes. The purge volume will vary depending on sorbent type due to differences in the retention volume of methanol. In some cases, residual methanol can cause variations in the response recorded at the detector so it is essential that 99.9% is removed. An alternative approach is the use of standards prepared by standard atmosphere method. These are commercially available, if required. The main advantage in this case is that the calibration tube is loaded in the same manner as the sample tube.

## Analysis

The sorbent tube is placed in a compatible thermal desorption apparatus. Air is purged from the tube to avoid chromatographic artifacts arising from the thermal oxidation of the sorbent or gas chromatographic packing. The tube is then heated to displace the organic vapors which are passed to the gas chromatograph. The desorbed sample occupies a volume of several milliliters of gas, which is concentrated by using a secondary sorbent and a cold trap.

Desorption conditions should be chosen such that desorption from the sample tube is complete, and no sample loss occurs from the secondary trap. Typical parameters used with the PerkinElmer® TurboMatrix™ 650 ATD Thermal Desorber for the determination of toluene from Tenax® TA are shown in Table 1.

A variety of capillary columns may be used for the analysis of hydrocarbons and the choice will depend largely on which compounds, if any, are present that might interfere in the chromatographic analysis. Tests reported here use a 50 m x 0.22 mm fused-silica column with thick-film (1 μm) BP-1 stationary phase. The GC oven conditions utilize a controlled-temperature program from 50 ˚C to 250 ˚C at 5 ˚C/min. A common alternative is the 60 m x 0.32 mm Vocol column with typical operating conditions of 100 ˚C (0.5 min); 5 ˚C/min 180 ˚C (3.5 min); 2 ˚C/min 200 ˚C (2.5 min); 4 ˚C/min 220 ˚C (2.5 min).

## Quantification

Recovered mass determined by reference to calibration standards prepared in methanol or by standard atmosphere can be expressed either as mass or volume concentration. For active samples, the mass value is expressed as concentration by dividing by the sample volume. For diffusive samples, a sampling-rate constant is required.

- Mass concentration of analyte for Diffusive Air Sample

  Calculate the weight (μg) of organic vapor in the sample by using the calibration graph prepared for spiked tube standards. Also calculate the weights of organic vapor in the blank tubes. Then:

$$\text{Concentration of organic vapor in air (mg m}^{-3}) = \frac{1000\,(m - m_{blank})}{U' \times t} \quad \text{where}$$

$m$ = weight (μg) of organic vapor on sample tube
$m_{blank}$ = weight (μg) of organic vapor on blank tube
$U'$ = uptake rate (ml min$^{-1}$)
$t$ = exposure time (min)

| Table 1. Instrument Parameters. | | | | | |
|---|---|---|---|---|---|
| **Temperature Settings** | **(˚C)** | **Time Settings** | **(min)** | **Split Flow Rates** | **(ml/min)** |
| Valve | 225 | Purge | 1 | Inlet Split | 71 |
| Transfer Line | 225 | Primary Desorption | 7 | Outlet Split | 30 |
| Primary Desorption | 250 | Trap Hold | 2 | Desorption Flow | 21 |
| Cold Trap | -30 | Cycle Time | 35 | Column Flow | 1.2 |
| Secondary Desorption | 300 | | | | |
| Heating Rate (˚C/second) | 99 | | | | |
| **Other Parameters** | | | | | |
| Mode: 2-Stage Desorption | | | | | |
| Injections: 1 | | | | | |
| Constant Flow Method | | | | | |

To express concentrations reduced to specified temperature and pressure conditions, then:

$$C_{corr} = C \times \frac{101}{P} \times \frac{T}{298} \quad \text{where:}$$

P is the actual pressure of the air sampled, in kPa;
T is the actual temperature of the air sampled, in Kelvin.

- Volume concentration of analyte for Diffusive Air Sample

  Alternatively, the concentration of organic vapor in the sampled air may be expressed in ppm.

$$\text{Concentration of organic vapor in air (ppm)} = \frac{1000\,(m - m_{blank})}{U \times t} \quad \text{where}$$

U = uptake rate (ng ppm$^{-1}$ min$^{-1}$)

Uptake rates in ml min$^{-1}$ and ng ppm$^{-1}$ min$^{-1}$ are related by

$$U'\,(\text{ml min}^{-1}) = U\,(\text{ng ppm}^{-1}\,\text{min}^{-1})\,\frac{24.5}{MW} \times \frac{T}{298} \times \frac{101}{P}$$

where

24.5 = molar volume (liters) at 298 K and 101 kPa
MW = molecular weight of volatile organic compound
T = temperature of sampled air in Kelvin
P = pressure of sampled air in kPa.

## Data quality

### Quality control

An appropriate level of quality control should be employed when using this method. Typically, a full quality-control procedure is part of the validation for a new method and would involve analysis of a set of 6 or more quality-control tubes. Desorption efficiency should be verified as 100% and the calibration rigorously checked to ensure accuracy. The deviation of the quality-control tubes from the expected result can be determined and should be no worse than 4% – otherwise, corrective actions should be undertaken. (Note that other pass/fail criteria may be adopted for practical purposes, depending on whether a particular result is considered fit for purpose.) One or more known reference-control tubes should be analyzed with all the subsequent analytical sequences and, if possible, trends in instrument performance monitored.

### WASP proficiency testing scheme

It is strongly advised that analysts participate in an external quality-assurance scheme such as, for example, the Workplace Analytical Scheme for Proficiency (WASP) administered by HSL. Information about the full range of analytes covered by this scheme is available at *http://www.hsl.gov.uk/proficiency-testing/index.htm* or by contacting the following Email address: *Proficiency.Testing@hsl.gov.uk*. This scheme, which is recognized by ISO 17025 accreditation bodies, includes an analysis of aromatic hydrocarbons on thermal desorption tubes at occupational loadings. Participants are ranked according to a performance index described in the scheme protocol. Thermal desorption tubes loaded in the environmental (ng) range are also available under the WASP subsidiary scheme, EnACT (Environmental Analytical Chemical Testing).

### Diffusive uptake rates

Approximate values for substances not listed in the sources previously mentioned may be obtained by using an empirical relationship between $U_{ratio}$ and $V_g$. $U_{ratio}$ is the effective uptake rate $U_{eff}$ divided by the theoretical uptake rate $U_{th}$, and $V_g$ is the dynamic specific retention volume. The uptake rates of VOCs on the PerkinElmer type sampler are not significantly affected by ambient-air movement, provided a minimum of about 0.01 m s$^{-1}$ is maintained. There is a slight reduction in the uptake rate for benzene with increasing ambient temperature, amounting to about 0.0008 ml min$^{-1}$ (°C)$^{-1}$ or 0.2% (°C)$^{-1}$. A similar change in uptake rate with temperature is expected for other compounds. The sampling rate on porous polymers is generally unaffected by humidity up to 95% RH at 20 °C. The sampling rate of toluene on porous polymers at around the Workplace Exposure Limit is not significantly affected by the simultaneous presence of hexane, heptane, decane and xylene at similar concentrations.

## Thermal-desorption instrumentation

The first automated thermal-desorption instrument, the PerkinElmer ATD50, was introduced in 1982 specifically to support industrial-hygiene applications. Over the last 25 years, although significant enhancements have been made to the technology, the fundamental principles remain the same as they were then. Technical enhancements have been made mainly to allow thermal-desorption instrumentation to be used for a much wider range of applications such as environmental monitoring, materials testing, forensic work and building testing. Industrial hygiene still remains one of the most important application areas for thermal desorption and the technique continues to have significant advantages over others.

The term "thermal desorption" usually refers to the technique of two-stage thermal desorption. Step 1 involves heating the sample tube and applying a flow of carrier gas to carry the vaporized analytes into a small
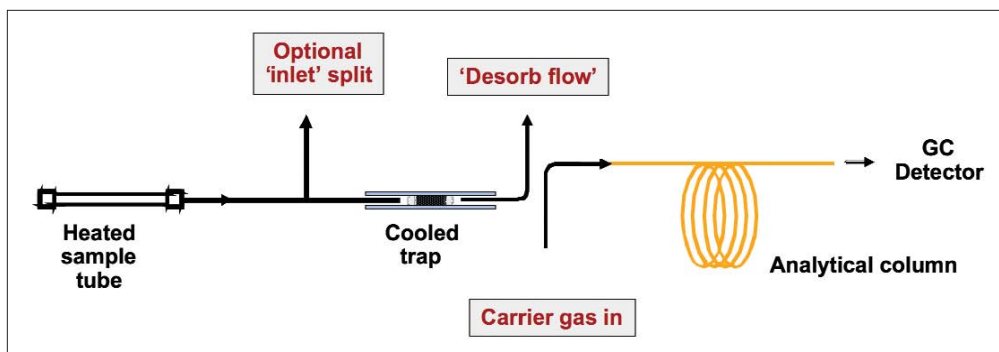
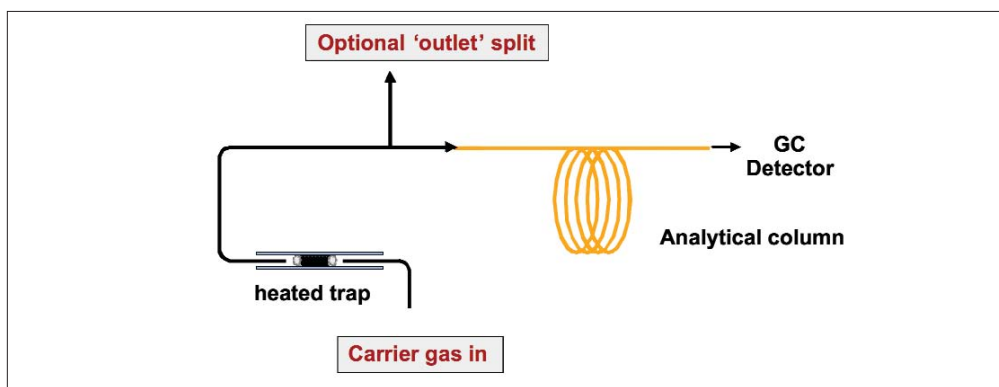*Figure 1.* First step in a 2-stage thermal-desorption analysis.



*Figure 2.* Second step in a 2-stage thermal-desorption analysis.

each tube and the plumbing system are automatically leak tested at the start of every analysis. Only when the system has determined that there are no leaks will the analysis continue. In this way, valuable and unique samples will not be analyzed unless the system is completely leak-free.

## Programmable pneumatic controls (PPC)

The advent of electronically-controlled pneumatic supplies has not only simplified the way instruments are set up and used, but has also added the ability to monitor pressures and flow rates at all times. Thus, if there is any leak or blockage or any other pneumatic failure in the system, it will be immediately detected and the remaining samples will be preserved.

adsorbent trap which is usually cooled. This trap collects and focuses the analytes. In step 2, the trap is rapidly heated and carrier gas carries the desorbed analytes as a narrow band into a gas chromatograph for separation, identification and quantification. Figures 1 and 2 illustrate the main steps involved in a typical two-stage thermal-desorption analysis.

One issue that is of major concern to industrial hygienists is that the sample tubes can only deliver a single result. If there are any issues with the instrumentation, then the result is completely lost.

For this reason, modern instruments have adopted a number of features to improve reliability and to provide the user with more information regarding the integrity of the analysis. The PerkinElmer TurboMatrix 650 ATD is a good example of how instruments have progressed over the years to assist laboratories in getting better and more reliable data. The following sections describe some of these features and their potential benefit to the industrial hygienist.

## Comprehensive leak testing

Any gas leaks in the system represent a potential loss of sample with a commensurate effect on the analytical results. To ensure that there are no leaks in the system,

## Sample re-collection

Technology has been developed to enable a fraction of the original sample to be returned to the initial or a fresh sample tube. This addresses one of the major concerns of the industrial hygienist in that now it becomes possible to get a second (or further) analysis from the same tube sample.

## Tube impedance testing

The packing integrity of every tube and the trap can be automatically determined at the time of analysis by measuring the pressure drop across the adsorbent bed. Any movement, crumbling, compression or loss of the packing may be detected by a change in the pressure drop for a given carrier-gas flow rate. This capability allows users to QC check the condition of the tubes as part of the normal analytical regime and make assessments as to their suitability for continued use.

Further information on these and other features may be found on the following technical notes at *www.perkinelmer.com/gclibrary*:

- Sample Re-Collection on the TurboMatrix 650 ATD Thermal Desorber
- Tube and Trap Impedance Testing on the TurboMatrix 650 ATD Thermal Desorber

## Validation of the TurboMatrix 650 ATD Thermal Desorber

### Introduction

HSL was approached by the instrument manufacturer PerkinElmer and asked to carry out beta and customer acceptance testing of the new TurboMatrix 650 ATD. The unit, together with a Clarus® Gas Chromatograph (GC) fitted with a flame ionization detector (FID) plus computing and software accessories, were supplied by PerkinElmer. The testing protocol was agreed between HSL and PerkinElmer and explored the new features of the instrumentation. The most relevant areas are outlined under the following headings. In brief, the general features include effluent split recapture, tube impedance monitoring, split-flow control, constant column flow and many other time-saving features such as dead-time conditioning. Testing was by both real-time usage for general sample analysis and by specific testing exercises. A valuable and interactive relationship between HSL and PerkinElmer evolved in which improvements and recommendations were continually being made, facilitating the development of an efficient and effective thermal-desorption system. This unit is now HSL's primary system for general hydrocarbon analysis by thermal desorption. The facility to re-collect sample effluent also exists in other thermal-desorption systems. The main difference lies in that the TurboMatrix 650 ATD only recaptures secondary desorbtion effluent flow rather than both primary and secondary desorption effluent flow, and that the TurboMatrix 650 ATD can also measure tube and trap impedance which has already been identified as an important consideration in HSL report OMS-2002-15.

### Repeatability during 2-stage desorption

The repeatability of analysis was tested by preparation of identical loaded tubes using a standard atmosphere system. In this example from WASP Round 72, sets of pre-cleaned Tenax® TA sorbent tubes were loaded with BTmX at nanogram levels and with BTo/m/pX at microgram levels and analyzed in single-split and double-split modes, respectively, with no sample recapture. Results are presented in Tables 2 and 3 (determined by flame ionization detection).

Table 2. Repeatability at Low Loadings.

| WASP Round 72 – ENVIRONMENTAL LOADINGS | | | |
|---|---|---|---|
| (n = 10) | Benzene (ng) | Toluene (ng) | m-Xylene (ng) |
| SET 1 Mean | 225.03 | 120.07 | 153.54 |
| % RSD | 1.29 | 1.11 | 1.32 |
| SET 2 Mean | 113.04 | 141.34 | 110.40 |
| % RSD | 4.18 | 2.12 | 1.92 |
| SET 3 Mean | 116.41 | 73.49 | 45.06 |
| % RSD | 1.29 | 1.14 | 1.11 |
| SET 4 Mean | 149.99 | 95.18 | 58.33 |
| % RSD | 1.94 | 2.69 | 1.60 |

Table 3. Repeatability at High Loadings.

| WASP Round 72 – OCCUPATIONAL LOADINGS | | | |
|---|---|---|---|
| (n = 10) | Benzene (µg) | Toluene (µg) | o/m/p-Xylene (µg) |
| SET 1 Mean | 1.51 | 12.53 | 20.80 |
| % RSD | 1.46 | 1.42 | 1.53 |
| SET 2 Mean | 22.51 | 77.44 | 145.54 |
| % RSD | 3.10 | 1.47 | 1.18 |
| SET 3 Mean | 7.99 | 61.53 | 49.14 |
| % RSD | 1.03 | 1.74 | 2.62 |
| SET 4 Mean | 1.77 | 38.93 | 34.72 |
| % RSD | 0.95 | 1.53 | 1.81 |

Results show that, generally, the repeatability is between 1 to 2% RSD at both loading levels although benzene has results that fall outside this range. It should be remembered, however, that this repeatability is not just an expression of the analytical uncertainty, but of the sample-loading step as well, and therefore the uncertainty due to the instrumentation alone is smaller.

### Repeatability of desorption and of recapture

The TurboMatrix 650 ATD has the option to recover the sample onto the same tube as the original sample. This is particularly useful as it reduces the number of tubes required (and consequent cost and maintenance), but also reduces the possibility of introduction of artifacts or contamination from a new tube. This last consideration is of great significance in the context of enforcement work. The repeatability of the new recapture facility was tested using 16 Tenax® sorbent tubes loaded with BTX by standard atmosphere in the low-microgram range. The results presented in Table 4 (Page 9) show the repeatability of the primary analysis data when the TurboMatrix 650 ATD is set in *Desorb-Recollect-Same* mode followed by

the repeatability of subsequent desorption of the re-collected tube. In total, the sample was re-collected 3 times giving a total of 4 data sets per analyte. According to theoretical calculations, the split recapture was expected to be 97.6% with 2.4% going onto the column. To achieve this, the inlet split is set to zero such that the entire sample is retained on the cold trap, followed by outlet splitting to column and sample tube.

The precision of recovery from the first desorption ranges from 3.1 to 3.5%, depending on analyte. Normally, a repeatability of 1 to 2% is achieved when using the TurboMatrix 650 ATD in *2StageDesorb* mode and this slight reduction in quality is assumed to be due to using the recapture facility, but it is not clear exactly why this might be.

Relative to the initial desorption, the re-analysis of the first collected tube shows a recovery of 96.3 to 97.1%, which is consistent with the expected amount. This is more or less maintained through the two following desorptions, demonstrating good consistency.

The repeatability of the first re-analysis is comparable to the initial desorption run but thereafter begins to decline in quality. This is most noticeable for benzene, where it falls from an initial 3.1% to 8.9% at the fourth desorption. This is believed to be due to the fact that benzene during this test was being recaptured onto a still warm tube and possibly not being efficiently retained. This potential problem has now been addressed by the instrument manufacturer in increasing the cool-down period to up to 5 minutes prior to firing the trap and beginning re-collection. This significantly improved the recapture of benzene.

## Recovery tests

In this test, the recovery of a re-collected sample was compared when using the same tube and a new tube to receive the sample. Loading levels are in the 100-µg range and expected recovery is 97.6%. The TurboMatrix 650 ATD has the option to recover the sample onto the same tube as the original sample, as discussed above, and also onto a completely fresh new tube loaded onto a specified location on its carousel. By the nature of the physical plumbing and valve operations within the instrument, these two processes are slightly different and may lead to slight differences in performance. In addition, the new tube is definitely cold rather than cooled. Clearly, the ability to recapture onto a new tube presupposes that the tube is new and has been correctly selected, since it is now possible to use a different sorbent type for re-collection. It might be that, in some circumstances, a strong or weak sorbent may be selected to assist in the removal of unwanted analyte.

Table 5 shows re-collection data for the desorption and analysis of BTX loaded onto Tenax® TA and retained onto the same tube, a new Tenax® tube, and onto an Air Toxics tube. In each case, the repeatability of the initial desorption is similar, as expected. However, when examining the repeatability of the re-run, re-collected tube, there is considerable improvement in the quality of the data for benzene for re-collection onto a new tube. This is because, at the time of the test, the cool-down period was still set short and the tube was too hot for effective re-collection in the *Desorb-Recollect-Same* mode.

*Table 4.* Repeatability of Desorption and of Recapture.

| (n = 16) | Benzene | Toluene | Xylene |
|---|---|---|---|
| **1st Desorption** | | | |
| Mean Recovery | 1.000 | 1.000 | 1.000 |
| % RSD | 3.1 | 3.2 | 3.4 |
| **2nd Desorption** *(relative to 1st Desorption) Re-Collection – Same Tube* | | | |
| Mean Recovery | 0.970 | 0.971 | 0.963 |
| % RSD | 3.8 | 2.4 | 3.5 |
| **3rd Desorption** *(relative to 1st Desorption) Re-Collection – Same Tube* | | | |
| Mean Recovery | 0.983 | 0.998 | 0.995 |
| % RSD | 8.2 | 5.2 | 5.0 |
| **4th Desorption** *(relative to 1st Desorption) Re-Collection – Same Tube* | | | |
| Mean Recovery | 0.976 | 0.972 | 0.976 |
| % RSD | 8.9 | 4.5 | 4.9 |

*Table 5.* Recovery of Toluene onto New or Same Tube.

| (n = 10) | Benzene | Toluene | Xylene |
|---|---|---|---|
| **Desorb Re-Collect New Tenax®** | | | |
| RSD | 1.000 | 1.000 | 1.000 |
| | 2.4% | 0.8% | 3.4% |
| Recovery RSD | 0.991 | 0.947 | 0.980 |
| | 3.4% | 0.7% | 4.4% |
| **Desorb Re-Collect New Air Toxics** | | | |
| RSD | 1.000 | 1.000 | 1.000 |
| | 2.8% | 1.1% | 1.4% |
| Recovery RSD | 0.913 | 0.952 | 0.938 |
| | 2.3% | 3.4% | 4.0% |
| **Desorb Re-Collect Same Tenax®** | | | |
| RSD | 1.000 | 1.000 | 1.000 |
| | 2.4% | 2.5% | 2.4% |
| Recovery RSD | 0.728 | 0.977 | 0.952 |
| | 19.7% | 3.5% | 3.1% |

## Boiling-point range – recovery

The performance of the re-collection system was tested for changes in the repeatability data as a function of analyte volatility. Chromosorb® 106 tubes loaded by standard atmosphere with ~200 ng of 9 analytes (n-hexane, trichloroethylene, methylcyclohexane, n-butyl-acetate, chlorobenzene, m/p-xylene, p-ethyltoluene, 135-trimethylbenzene and limonene) were analyzed and recaptured onto the same tube and onto new Chromosorb® 106 and Tenax® tubes. The expected re-covery is 50% and, with the exception of limonene, it shows very good results. The data for limonene is believed to be confused by an interference peak. Results of these tests are shown in Table 6.

## Impedance testing

The HSL report OMS-2002-15 posed the question as to whether it was necessary to use the same sorbent for both standards and samples since, although the desorp-tion efficiency (recovery) may be 100%, a difference in the impedance of the sorbent bed may cause change in split flows at low pressure. In its report, HSL has stated the opinion that, in quantitative analysis, differences in back-pressure from tube to tube should not exceed 1% of the system pressure existing at the point of the desorp-tion phases or column inlet. Consequently, for systems run at low pressure (e.g. 8-10 psi), the report suggested that the analyst should either avoid mixing sorbent types of different flow resistance or control the system imped-ance. The TurboMatrix 650 ATD appears to offer a solution through close regulation of the pressure. Sorbent tubes

are known to change their flow characteristics with repeated use in the field and with repeated analysis. The TurboMatrix 650 ATD offers a chance to actually measure and record the impedance of all the tubes held in stock at HSL which can then be re-assessed as part of a quality-management system. An example of the variation in tube impedance is given in Figure 3 and the impact on sampling flow rates in an uncontrolled system is shown in Figure 4.
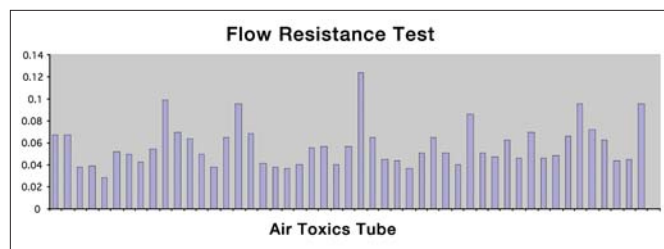


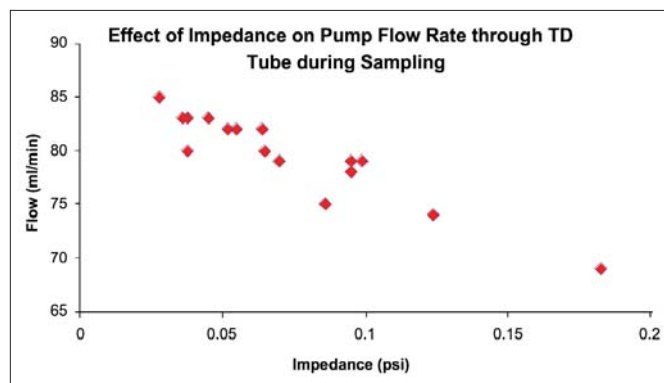Figure 3. Range of different impedances found from a selection of tubes.



Figure 4. Effect of tube impedance on active sampling flow rates.

| Table 6. Recovery of Different Volatility Analytes onto New or Same Tube. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | n-Hexane | Trichloroethylene | Methylcyclohexane | n-Butylacetate | Chlorobenzene | m/p-xylene | p-Ethyltoluene | 135-TMB | Limonene |
| **C-106 to New Tenax** | 53.2% | 47.3% | 47.5% | 55.0% | 50.9% | 51.6% | 50.3% | 51.7% | 54.3% |
| | 51.3% | 49.5% | 47.2% | 49.8% | 48.8% | 52.4% | 52.0% | 53.5% | 50.7% |
| | 51.5% | 44.6% | 45.1% | 44.1% | 47.1% | 47.8% | 48.1% | 49.7% | 51.5% |
| **C-106 to New C-106** | 51.9% | 53.0% | 44.6% | 55.9% | 49.0% | 52.5% | 52.2% | 49.6% | 55.0% |
| | 48.8% | lost | 50.0% | 43.1% | 48.2% | 49.5% | 51.9% | 49.0% | 51.0% |
| | 52.8% | 51.6% | 52.7% | 47.3% | 49.4% | 52.3% | 49.1% | 45.5% | 63.8% |
| **C-106 to Same C-106** | 46.3% | 49.4% | 47.5% | 50.5% | 50.6% | 50.6% | 50.2% | 48.9% | 50.8% |
| | 57.8% | 48.9% | 50.5% | 45.9% | 51.2% | lost | 54.4% | 50.6% | 61.1% |
| | 54.8% | 45.6% | 51.6% | 44.4% | 49.7% | 50.6% | 53.7% | 50.3% | 63.7% |
| | 52.4% | 52.9% | 48.3% | 45.0% | 48.0% | 48.8% | 49.8% | 48.0% | 61.4% |

Flow resistance (impedance) challenges encountered using earlier-generation thermal-desorber models have now been overcome with the TurboMatrix 650 ATD system. This was demonstrated by a series of tubes with different impedances which were loaded with benzene at approximately 20 µg and analyzed in a continuous sequence. The results of this test are shown in Figure 5 and indicate that recovery is unaffected by changes in flow-path resistance.
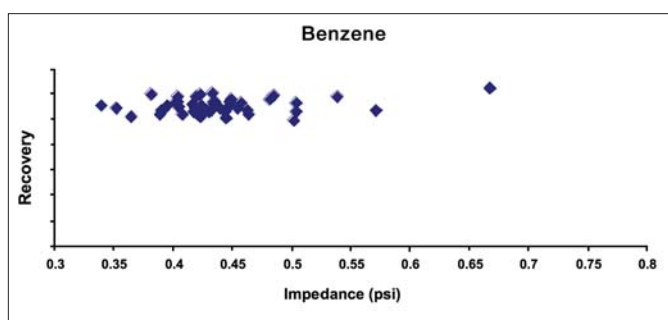


*Figure 5.* Effect of tube impedance on recovery of benzene.

#### Conditioning during GC run to save time

This time-saving mode, which allows tubes to be conditioned in the "dead time" of the GC run and therefore be ready for re-use, was tested and shown to be a worthwhile and useful function. This mode makes use of the time that the tube is waiting for the GC to run, cool down and re-equilibrate to perform the conditioning step.

#### Retention-time precision tests

Consistent retention times were confirmed over multiple runs under various system configurations and tube-loading ranges.

#### Real samples

A significant number of real customer samples were run without error over the several months of the beta-testing period. The system demonstrated itself to be far more robust and reliable than previous thermal desorber models.

## Conclusions

### Repeatability of desorption and of recapture

Repeatability of analysis is very good in the 2-stage desorption mode and is only slightly diminished during split recapture. Improvements in the recapture mechanism

suggested by HSL have increased the effectiveness and made this a very useful tool to have available.

### Recovery

Recovery from re-running the re-collected tubes is within expectation and improvements made by the supplier during the testing phase have added to the consistency and quality of the data acquired.

### Boiling-point range – recovery

The TurboMatrix 650 ATD showed good consistency in performance across a wide range of analytes.

### Impedance testing

The TurboMatrix 650 ATD can now compensate for changes in resistance in the entire flow path, resulting in better split flow and calibration reproducibility. As a consequence, in this system it is not necessary to use the same sorbent for calibration as the sample tubes.

### Overall

The TurboMatrix 650 ATD system, software and associated GC (Clarus GC) enable the analyst to rapidly load tubes and set up a multi-method TD sequence to allow the determination of widely differing sample types, running reliably without any subsequent user input to change split ratios or temperatures. The system showed great reliability with a minimum number of errors encountered and only one leak fail in over 1500 injections, plus no missed tubes. The TD sequences mostly ran as expected and methods found and loaded correctly. As with earlier models, it is user friendly with intuitive software, simple method editing and simple sequence generation. The carousel is easy to load/unload and, if required, the label clips can remain attached to the sample tubes (although HSL prefers to remove these as a precaution against possible snagging).

As with other TD systems, there is now an opportunity to re-collect analyte, on the same tube or a new tube for analysis by modified methods, with different detectors or for storage. This last aspect is very significant for the quality and traceability requirements of legal proceedings. The pressure-balanced system accounts for changes in sample or system impedance, giving greater security in the quality of the analyses. Also, using the conditioning feature, it is now possible to optimize available time.

## References

M.D. Wright, N.T. Plant and K. Gostlow, The effect of flow resistance on the recovery of volatile compounds from thermal desorption tubes, *HSL Report OMS/2002/15,* 2002.

Health and Safety Executive, Methods for the Determination of Hazardous Substances, *Analytical quality in workplace air,* MDHS 71, 1991.

Health and Safety Executive, Methods for the Determination of Hazardous Substances, *Volatile Organic Compounds in Air – Laboratory method using solid sorbent tubes, thermal desorption and gas chromatography,* MDHS 80, 1995.

COSHH Essentials: *Easy steps to control chemicals. Control of Substances Hazardous to Health Regulations,* HSG193 (Second Edition), HSE Books 2003 (http://www.coshh-essentials.org.uk).

Workplace 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, (ISO 16017-2:2003).

American Society for Testing and Materials, Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis of Volatile Organic Compounds in Air, *ASTM D6196-03,* 2003.

Air Quality – Determination of benzene in ambient air by the capillary gas chromatography method – part 4: diffusive sampling and thermal desorption, (EN 14662-4).

Diffusive uptake rates on PerkinElmer sorbent tubes, *The Diffusive Monitor*, 8, 1996.

**HEALTH & SAFETY
LABORATORY**

**PerkinElmer®**
precisely.

**For a complete listing of our global offices, visit www.perkinelmer.com/lasoffices**

007367_05