Thermal Desorption Technical Support

Note 9: Monitoring Materials and Processes for VOCs at High and Trace Levels

Keywords:

Materials Emissions, Food, Flavour & Fragrance, Purge & Trap, On-line, Process Gas

Thermal desorption has long had a place as a high sensitivity alternative to solvent extraction for the determination of volatile organic compounds (VOCs) in environmental health and safety applications. Recent developments have extended its application to routine quality assurance and quality control testing. Whatever the nature of the product or raw material containing the VOCs – solid, liquid, gas, emulsion, resin, *etc.* – thermal desorption can provide an efficient, readily-validated and cost-effective alternative to conventional laboratory sample preparation methods.

What is thermal desorption?

Strictly speaking, thermal desorption (TD) is the process of extraction/desorption of volatile and semi-volatile organic analytes from a sorbent or sample matrix using heat and a flow of inert gas rather than solvent. In practice it is invariably a multi-step procedure, automating much more than the extraction process. The latest technology now combines versatile on- or off-line sampling with solvent-free extraction, analyte concentration and automatic transfer of analytes to the measurement system in a concentrated vapour 'slug'. It can be used to ease measurement of VOCs in almost any sample that, for one reason or another, cannot be introduced directly to a standard laboratory gas chromatograph (GC)
Thermal desorption offers many advantages over conventional solvent-based sample preparation methods - liquid extraction, solvent exchange, steam distillation, *etc*.

Key benefits include

- 10^3 - 10^4 fold improvement in sensitivity (no extraction solvent to dilute compounds of interest)
- Automation – labour and cost saving
- Selective focusing/concentration of compounds of interest with elimination of matrix interferences
- No laboratory contamination or solvent disposal issues
- Reduced errors
- Reusable sorbent tubes (where applicable)
- Compatibility with process/on-plant measurement as well as laboratory work

Thermal desorption is still most commonly combined with laboratory GC or GC-Mass Spectrometry (MS) technology to provide detailed quantitative and qualitative information on each individual (speciated) organic present in a sample. However, modern thermal desorption systems, such as UltrA-UNITY from Markes International (Figure 1), are also compatible with alternative direct read-out analysers, such as E-nose sensors, which minimise cycle times, enhance throughput and provide a more factory-friendly process monitoring package.

Figure 1: UltrA-UNITY automated thermal desorber

Application range

Thermal desorption can automate or drastically reduce the number and complexity of sample preparation steps required for a wide range of quality assurance/quality control applications. Depending on the nature of the material tested, solid or liquid samples may either be weighed into empty thermal desorption tubes/tube liners for **direct desorption**, or purged (on- or off-line) into sorbent tubes/traps. This is known as **purge and trap**. Gas phase samples can be collected on sorbent tubes for subsequent off-line analysis or monitored in real-time using discontinuous on-stream analysers. The range of sample types is illustrated in Figure 2.

On- or off-line purge and trap of volatile emissions

Natural, typically non-homogeneous and high humidity samples, such as fresh/prepared food, composite materials and biological samples, are best suited to on- or off-line purge and trap type sampling. The approach facilitates sampling entire or representative portions of samples as diverse as canned meat, hot coffee, bacterial cultures, insects and, with specialist apparatus, multi-layer construction materials. Example apparatus is shown in Figures 3 and 4. Samples can either be purged into ambient temperature sorbent tubes for subsequent off-line analysis or purged/pumped directly into the focusing trap of an on-line desorber for semi real-time measurement. The combination of purge and trap with thermal desorption not only improves productivity, but also facilitates selectivity. Tube and focusing trap sorbents may be used which selectively retain specific analytes while allowing bulk ingredients – water and/or ethanol for example - to break through.

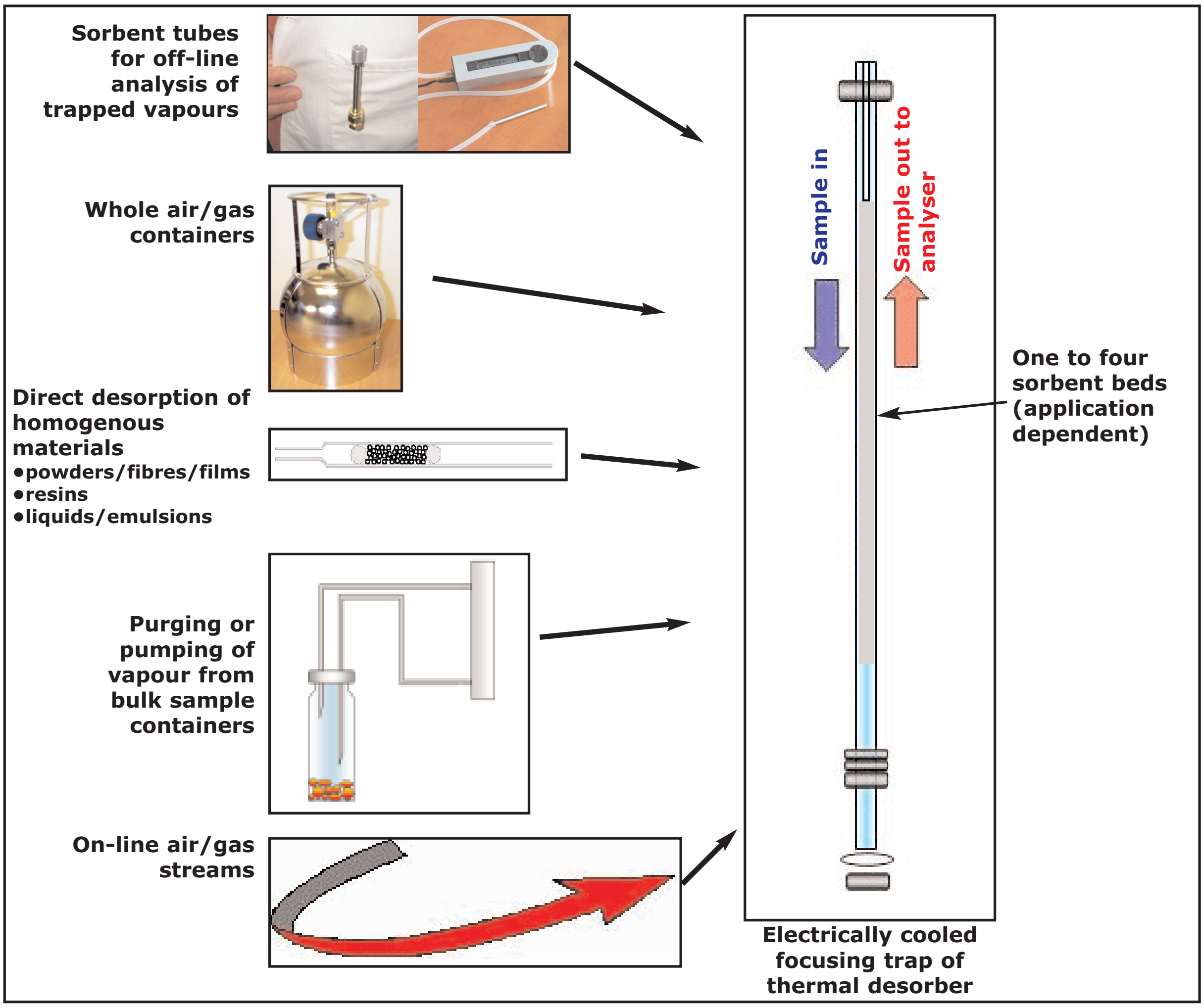

Figure 2: Range of sample types suitable for thermal desorption analysis

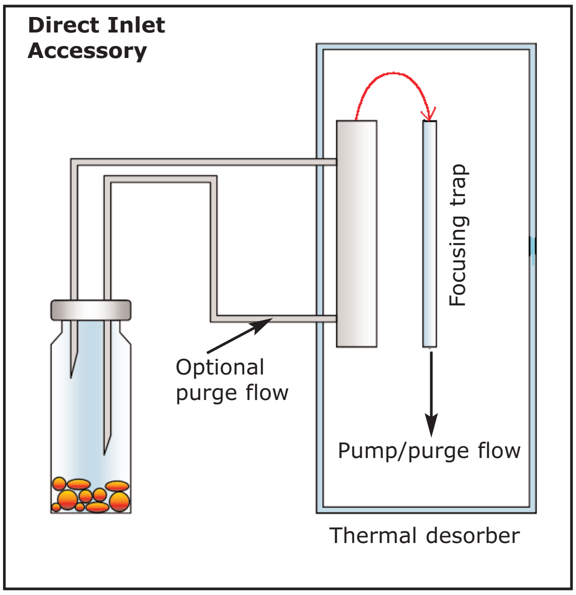

Figure 3: Direct pump/purge sampling of vapours from non-homogeneous materials

Figure 4: FLEC cell for sampling gaseous emissions from construction materials

Example applications

1. Determination of emissions from construction products using the Field and Laboratory Emission Cell (FLEC®)

Emissions from floor coverings, wall coatings and other building materials can contribute to atmospheric VOC concentrations in the indoor environment. Under guidelines given in the new standard prENV 13419, manufacturers of construction materials are advised to test new products at various times after manufacture using emission chambers or portable emission cells like the FLEC (figure 4). The FLEC is ideal for planar materials such as dried paints/coatings, flooring materials or wood products and is simply placed onto a test material sample. Pure humidified air is then passed over the material inside the FLEC cell to simulate real-world environmental conditions. Exhaust gases are collected either onto sorbent tubes for off-line analysis (Figure 5) or pumped directly into the focusing trap of an on-line thermal desorber for monitoring rapid changes in the emission profile.

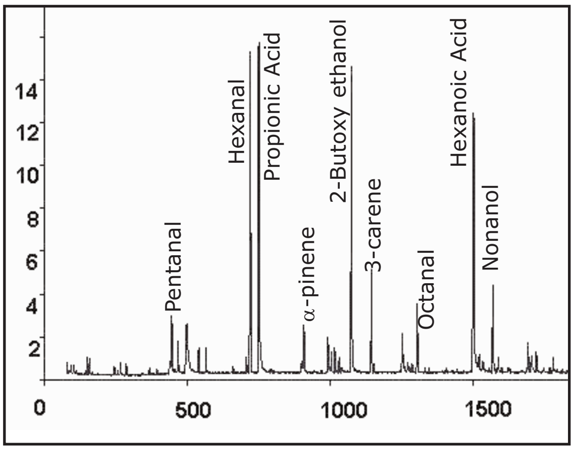

Figure 5: Chromatogram of key organic compounds emitted by linoleum floor coverings

2. *Shelf-life of fresh or prepared foods*

As foods age, oxidation or decomposition generate indicative and often malodorous organic volatiles. The presence of these compounds in the headspace vapour immediately above a food sample is one of the first indications that a product has past its sell-by date. A simple thermal desorption-based laboratory procedure can be developed for objectively evaluating the freshness of natural ingredients or products:

Fresh or prepared food samples - pizza, canned meat, breaded fish, *etc.* - are simply placed in a suitable glass vessel and incubated at ambient or elevated storage temperatures under a flow of pure air. Samples of effluent air from the purge vessel are either collected intermittently onto conditioned tubes packed with one or more sorbents, or can be passed directly into the cold trap of the UNITY thermal desorber on a semi-continuous basis using a Direct Inlet accessory in pumped mode (see Figure 3 and brochure Mi BINLET, available from Markes International). Tube and focusing trap sorbents are selected to retain target analytes while allowing water, ethanol and other interferences to purge to vent. One or a combination of hydrophobic sorbents *e.g.* Tenax TA™ or graphitised carbon, may be used for quantitative retention of organics ranging in volatility from pentane while allowing the bulk of water/ethanol to pass through unretained. Complete flavour profiles are more typically collected using two or even three sorbents in series.

Excessive quantities of decomposition/oxidation compounds or deviations from the normal odour/flavour profile can then be quantitatively assessed from the subsequent thermal desorption -GC/MS analysis and used as reliable, objective indicators of product quality and stability. Semi-continuous, direct sampling into the UNITY thermal desorber using the Direct Inlet accessory allows changes in odour/flavour profile to be monitored in real time.

3. *Potable spirits*

C_4 to C_6 ethyl esters make excellent markers for the maturity of potable spirits such as whisky. Pumping or purging a given volume of whisky headspace vapour into a conditioned Tenax tube or focusing trap allows selective concentration of higher boiling flavour components, including ethyl esters, while water and more volatile alcohols, aldehydes, *etc.*, pass through the tube unretained. This procedure simplifies the subsequent GC analysis facilitating detection of ethyl esters and other higher boiling indicators of spirit maturity whilst simultaneously eliminating water and the large ethanol peak which would otherwise mask most of the chromatogram. The method is ideal for quality control of spirits to be used as ingredients in products such as cream liqueurs.

4. Identification and life-cycle *studies on natural species*

Biologists use another variant of purge-and-trap/thermal desorption technology to identify plant, animal or microbial species, map life-cycle changes and characterise the origins of hybrids and cultivars of scented plants[1]. Specimens are placed in glass containers or special nylon bags in a sampling method derived from that used by forensic scientists to analyze fire debris for residual accelerants in cases of suspected arson. Samples are incubated or purged, as required, before pumping an aliquot of the headspace vapour into a sorbent tube or online TD system. The fragrance profile obtained from subsequent TD-GC/MS analysis acts as a fingerprint helping to characterise the sample under the test conditions and allows it to be compared to other related or control samples.

Direct desorption

Dry or homogeneous materials, for example, therapeutic drugs, packaging materials, resins, spices, ointments/creams, polymers, water-based paints, edible fats, *etc.*, can be weighed into empty tubes or tube liners and desorbed directly (Figures 6 and 7).

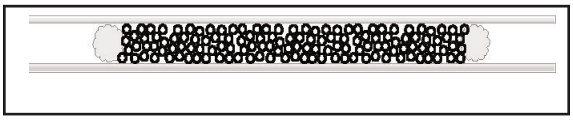

Figure 6: Dry, homogeneous material weighed directly into an empty tube for direct desorption

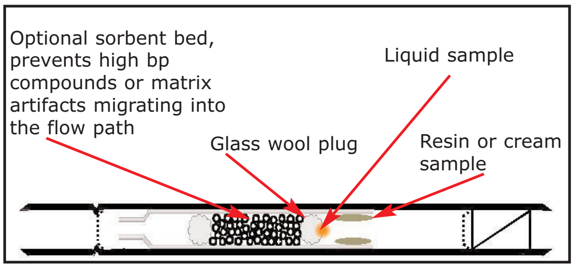

Figure 7: Liquid or resinous materials measured into a PTFE liner, and placed inside an empty tube for direct desorption

In this case, sample preparation is essentially reduced to zero and the associated risk of error introduction is eliminated. This has to be one of the most straightforward and cost effective sampling procedures for otherwise difficult materials. As above, with the combination of purge and trap and thermal desorption, the actual thermal desorption procedure can be tailored to meet analytical requirements. Either a characteristic 'odour profile' or complete, quantitative extraction of specific target analytes can be achieved. The method facilitates analysis of the most challenging materials – combining sample cleanup, analyte extraction and sample injection/introduction into one simple, automated operation.

Direct thermal desorption is compatible with a wide range of different material types - salt/sugar solutions, suspensions, resins, creams and plain solids. The only rules for success are as follows:

- Ensure solid materials have a high surface area – powders, granules (particle size <1 mm^3), fibers or films. Bulk solids should be ground with a coolant such as solid carbon dioxide before the material is weighed into sample tubes.
- The gas flow path must not be blocked with sample. Thermal desorption is a dynamic process and gas must be allowed to pass through the sample tube unrestricted.
- Ensure that the sample is placed inside the sample tube such that it is well within the heated zone of the thermal desorber used.

Direct thermal desorption is only appropriate provided the desired extraction takes place at a temperature below the decomposition point of other materials in the sample matrix, and the relatively small sample size that can be measured into a thermal desorption tube is representative of the whole sample. Most samples are best weighed into a tube insert or liner, rather than being weighed directly into a glass or steel desorption tube. This eliminates any risk of degradation from samples coming into contact with metal tube surfaces (Liners are typically constructed of heat shrink PTFE tubing with a reduced diameter at one end – see Figure 7).

Within these limitations thermal desorption provides automatic on-line extraction/preparation system for everything from water based paints to dried soups, from drugs to printed packaging film and from to toothpaste to epoxy resin.

Example applications

1. *'Off-odour' or 'taint'*

By eliminating most or all of the sample preparation steps typically involved in troubleshooting, something as subjective as taint in soap flakes or off-odour in edible fat, thermal desorption can speed up and simplify identification of impurities and hence pinpoint the source of many quality problems.

Both these materials have been real-world success stories for thermal desorption……

(1) In the case of the edible fat, samples of control and 'problem' material were weighed into PTFE sample liners packed with clean glass wool and inserted behind a short bed of conditioned Tenax sorbent. After a 10 minute desorption at moderate temperatures, the profile of volatiles obtained from the tainted sample could be compared with that from the control. Fat constituents and other solids were retained by the glass wool and Tenax and did not interfere with the analysis. Used liners were disposed of.

(2) After a week of trying various extraction solvents in combination with GC and high resolution MS technology, the cause of malodour/taint in a batch of soap flakes had not been successfully identified. Once received by the thermal desorption laboratory, a small sample of soap flakes (~100 mg) was weighed into a PTFE liner and held in position with clean glass wool plugs. The liner was inserted into an empty desorption tube and a TD-capillary GC/MS method was established using moderate desorption conditions (~100°C for 10 minutes). Using TD/GC and bench top MS technology, one analysis of the tainted soap and one of a control (less than 2 hours work in total) was enough to demonstrate that a homologous series of pyrazoles was causing the taint problem.

[Note: there is no need for complete extraction of volatiles during a qualitative investigation. Obtaining a representative odour profile is more important. Moderate desorption temperatures are therefore generally recommended when monitoring for unknowns]

2. *Organic Volatile Impurities in Drugs*

The analysis of drug volatiles is complicated both by the fact that many are difficult to dissolve in common/safe solvents and because many of the residual solvents in question form part of the crystal structure. Complete dissolution or breakdown of the crystal structure is therefore required before an accurate determination of organic volatile impurities.

Thermal desorption provides a quick and simple alternative to solvent extraction provided a drug melts at a temperature below its decomposition point. Complete extraction can typically be achieved in 2-3 minutes. PTFE liners are recommended to minimize risk of drug degradation (see TDTS 41 for more information).

3. *Residual epichlorohydrin in epoxy resin*

Epichlorohydrin, the toxic volatile monomer used in epoxy resin production, is typically present at low ppm concentrations in samples of epoxy-based adhesives. Around 40 mg of resin is simply smeared around the inner wall of a PTFE tube liner plugged with glass wool as described above. Provided care is taken to maintain a clear gas flow path through the middle of the liner, and that the sample of resin is positioned well within the heated zone of the desorber, approximately 95% extraction efficiency is achieved in a single 10 minute desorption at a temperature (typically ~175°C) well below that of polymer degradation. Savings achieved using this method versus conventional solvent extraction procedures are such that the production facility responsible for method development recouped the cost of their automated thermal desorption equipment within one month of operation.

4. *Quality control of dried spices*

Spices and essential oils represent the high-priced 'designer' sector of the food business. Rigorous quality control is required to ensure ingredients meet the standards required and that the most expensive materials are not substituted or diluted by cheap imitations. For spices, spice mixtures, even complex dried sauce preparations, a combination of gentle desorption (for example 10 minutes at just under 100°C) with high resolution capillary gas chromatography provides an interference free and extremely reproducible flavour profile. The reproducibility is such that even slight deviations in the composition of a mixture and/or variations in product quality can be readily and objectively identified.

5. *Water-based paints*

Modern atmospheric emission regulations require control of the volatile and semi-volatile organic content of all paints and coatings. However, some of these materials present a significant monitoring and analysis challenges. In water based paints, for example, the presence of relatively large masses of water compromises capillary GC performance and the exceptionally high solid content (>80% in some cases) is guaranteed to block any syringe as soon as it is inserted into a hot GC injector.

Direct thermal desorption of small aliquots (~5 ml) of paint introduced onto a secondary glass wool plug inside a conventional PTFE tube insert overcomes both of these limitations and eliminates need for pre-analysis preparation of paint samples. During the thermal desorption process, paint solids remain safely on the glass wool plug, while volatile and semivolatile materials are purged into the instrument flow path (Note: a fresh glass wool plug should be used for each new sample). Provided a suitable two stage desorber is in use; *i.e.* one offering appropriate electronic control of a small sorbent focusing trap such as that in UNITY - see Figure 2, a combination of focusing temperatures and sorbents can be selected so all the organics of interest are retained while water passes through to vent. When the focusing trap is subsequently desorbed, an interference-free chromatogram is produced. Water and artefacts from the paint solids have all been safely eliminated prior to analysis.

6. *Therapeutic creams*

This example is a '*Pièce de résistance*' for thermal desorption. The extraction of essential oils and other organic volatiles - methyl salicilate, camphor, *etc* - from a petroleum jelly, or similar organic matrix, is extremely challenging by conventional methods. Solvents do not differentiate sufficiently between target analytes and matrix materials, and analysts resort to lengthy steam distillation techniques to prepare samples. Even then results are disappointing and a significant fraction of the petroleum jelly distills over into the sample extract precluding both capillary chromatography and automatic injection.

For thermal desorption, 20-50 mg samples of the cream are smeared inside a short PTFE tube liner containing a plug of clean glass wool in an analogous manner to the epoxy resin example detailed above. This is then pushed into a conditioned desorption tube packed with 5-10 mm Tenax TA and backed up with unsilanised glass wool. Provided the PTFE tube insert is not reused and the desorption conditions selected are the minimum required for complete extraction, the same Tenax bed may be reused many times. The Tenax tube should be repacked and reconditioned as soon as artifacts begin to appear in the chromatogram.

Trace impurities in process/industrial air and gases

Thermal desorption is also the technique of choice for on- or off-line determination of trace level volatiles in air and gas streams. Compatible sample types include:

- Pressurised gas streams
- Process vents
- Ambient/workplace air at atmospheric or sub-atmospheric pressure
- Sealed containers of gas or air *e.g.* canisters, Tedlar™ bags, cylinders

Thermal desorption systems incorporating an electrically-cooled focusing trap can be installed on-plant or in field laboratories to operate continuously with minimal operator intervention. Key functions such as sampling flows and analytical desorption parameters are typically all incorporated into one PC-controlled method and monitored continually. Even basic systems should feature automatic interchange between sample, zero and calibration gas streams at a user defined frequency. Analytes must be vapour phase and typically range in volatility from acetylene to n-$C_{14/16}$. Cycle times range from four minutes to three hours depending on application requirements and analyser choice

An ideal operating sequence is: User-determined volumes of gas are pumped/drawn into the electrically-cooled focusing trap at controlled flow rates ranging from 5-50 ml/minute. Only inert, non-emitting components are allowed to come into contact with the sample. Flow path is purged with carrier gas between samples to prevent carryover. After the sampling period, the focusing trap is heated rapidly in a flow of inert gas to transfer or 'inject' the retained analytes into the analyser in a concentrated vapour 'plug'. The speed of desorption from the focusing trap is such that analytes are efficiently transferred to the analytical system with flows as low as 2-2.5 ml/min. This facilitates splitless transfer and optimum sensitivity with high resolution capillary GC/GC-MS. Desorption volumes may also be adjusted to suit alternative direct-read-out measurement systems such as Enose sensors (see TDTS51 & UniSense brochure) or process MS (see TDTS15). Detection limits in the order of low parts per trillion of individual organic compounds are possible depending on sampling parameters and detector sensitivity.

Analysis is automatically initiated by the desorber when the focusing trap begins to heat. Collection of the next sample can begin within 1-5 minutes, as soon as the trap has re-equilibrated at its focusing temperature.

Example applications

Applications range from kinetic studies of organic emissions to process control of industrial gas purity (Figure 8) to continuous ambient air monitoring (Figure 9) to demilitarisation.

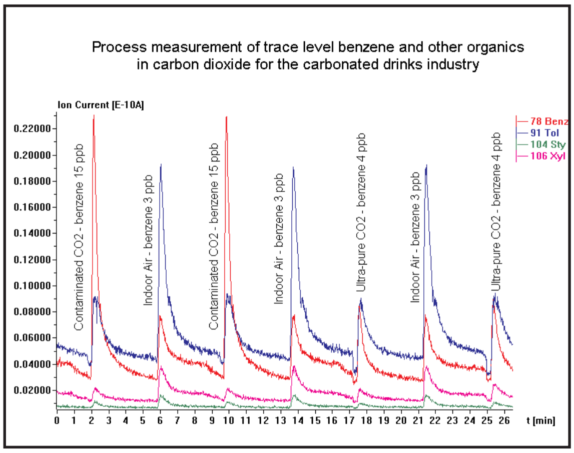

Figure 8: Process measurement of trace level benzene and other organics in carbon dioxide for the carbonated drinks industry

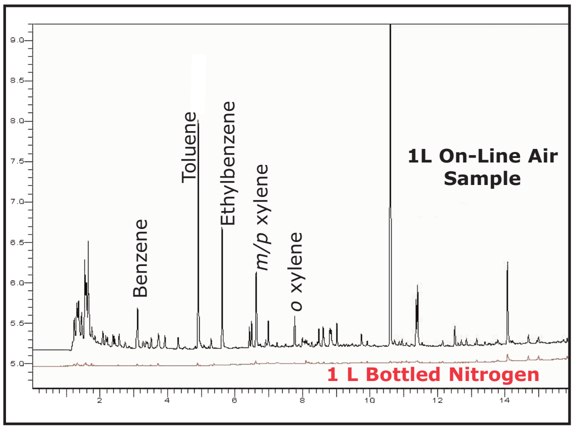

Figure 9: TD analysis of on-line air sample, compared to bottled nitrogen

Summary

The examples presented show the considerable labour-saving benefits that can be achieved using thermal desorption. The technique offers the versatility and automation to improve productivity and reduce costs for most quality control tests involving VOC measurement.Some applications could not be achieved without the sensitivity and flexibility of thermal desorption.

Could thermal desorption improve throughput and reduce costs in your lab - from polymers to foods, pharmaceuticals to paints, and regulatory to routine industrial? The answer is YES.

References

1. Chemotaxonomy of plant species using headspace sampling, thermal desorption and capillary GC. J of HRC, 14, pp 637-639, 1991.