Thermal Desorption Technical Support

Note 60: The complementary role of thermal desorption (TD) alongside other sample preparation/introduction technologies for Gas Chromatography (GC)

Keywords:
Equilibrium headspace (HS), purge & trap (P&T), solvent extraction, solid phase extraction/micro-extraction (SPE/ME)

Introduction

Thermal desorption is one of the most versatile sampling preparation/introduction technologies available for gas chromatography. It plays a wide ranging and complementary role to other GC sampling methods such as equilibrium headspace, purge and trap, *etc.* and is often combined with these other techniques during the final transfer/injection of compounds to the analyser. The following brief review of each of the main GC 'front-end' technologies summarises the advantages, limitations and applications of each.

Equilibrium headspace (HS)

Equilibrium HS is one of three gas extraction technologies used with GC. It is quantitative, provided vapour samples are taken from sealed sample vials after equilibrium has been established between volatile organic compounds (VOCs) in the gas-phase and those in the sample matrix. At this stage the concentration of VOCs in the sample can be derived from the concentration of VOCs in the headspace vapour, provided that there are no unpredicted matrix sorption effects. It is the most convenient sample introduction method for pure equilibrium-based sample systems (*e.g.* liquids or polymers) especially when targeting analytes that are more volatile than the sample matrix *e.g.* ethanol in blood, solvent in shampoo and solvents in waste water. Equilibrium HS selectively enhances the concentration of volatiles relative to higher boiling compounds or sample matrix constituents. The technique is suitable for analyte concentrations > 1 ppb (SCAN) or >0.1 ppb (SIM). In these cases there is no need to add solvent / buffer, carry out multi-step discontinuous gas extraction or worry about refocusing on the capillary column. Equilibrium headspace involves negligible sample preparation and uses disposable glass vials thus minimizing clean-up time and costs. A typical sample size is 5 ml.

The technique has limitations when looking at samples containing analytes with a wide variation in volatilities as it is difficult to establish an optimum equilibration temperature. A temperature high enough to establish a vapour phase concentration of the less volatile components may saturate the headspace with the volatile components adversely affecting quantification.

Purge and Trap (P&T)

P&T is another gas extraction-based sample introduction technology for GC. It is essentially similar to HS but with quantification based on exhaustive extraction of the target analytes into the carrier gas stream as it purges through the sample. P&T systems incorporate a sorbent trap which is ultimately **thermally desorbed** to transfer purged and trapped analytes to the GC system and begin the GC analysis. Typically P&T is 2 orders of magnitude more sensitive than equilibrium headspace. Again a typical sample size is about 5 ml.

Limitations are primarily linked to the fact that the technology is not optimised for capillary operation (*i.e.* the focusing traps are too large for rapid/efficient thermal desorption at low flows.) The technique is used almost exclusively for drinking and groundwater samples as it can result in foaming problems if used with waste water, soil or other dirty/complex samples. Sample vessels are usually not disposable so clean-up is generally required.

Headspace with thermal desorption (HS-TD)

HS can be combined with **thermal desorption** (TD) to enhance sensitivity and extend the volatility range of the headspace technique. The addition of TD to HS converts the HS technology from an equilibrium-based system to a sort-of stepwise (pulsed) purge and trap device. Vapours may be repeatedly swept onto the TD focusing trap before analysis. There are no foaming issues, because gas is not bubbled through the sample. It is possible to exhaustively extract volatiles from, for example, aqueous samples, thus allowing similar detection limits to purge and trap.

Some automated HS-TD systems, for example that from Markes International , provide the ultimate in analytical flexibility accommodating solid, liquid and gas-phase samples and allowing easy interchange between three different operating modes – equilibrium headspace, HS-TD and full-functionality thermal desorption (see below.)

Solvent extraction (SE)

SE is convenient for one-off samples containing volatile organics at concentrations > 1 ppm, where the nature of the target analyte(s) is known (and thus solvent selection is not an issue). The technique is also useful for extracting semi-volatiles, even at trace (<ppb) levels, as an evaporative concentration step can be used in these cases. SE requires minimal capital investment in its simplest form, but is very labour intensive, thus expensive to run. Automation is usually difficult and, if achievable at all, requires expensive complex robotics. SE is of limited utility for searching for unknowns because of solvent selection issues. It is also difficult to quantify solvent extraction for many real-world samples where partition coefficients may be difficult to define accurately. Solvent extraction efficiency is rarely better than 80% and may be as low as 10-30% depending on matrix effects – for example, sample humidity. Any variation in extraction efficiency makes quantification very difficult. SE offers limited sensitivity for volatiles.

Further information about SE may be found in TDTS46 - Comparing Thermal Desorption with Carbon Disulphide (CS_2) Extraction of Charcoal for Air Monitoring Methods

Solid phase extraction/micro-extraction (SPE/ME)

This technique is now available in a wide range of commercial forms *e.g.* SPE-tD cartridges, stir bar sorptive extraction, fibres and numerous (typically LC-compatible) pre-column cartridges. The main applications are all in the general area of measuring lower volatility organics in aqueous-based media. More volatile compounds can be observed, but are not quantitative.

In all cases the sampling device consists of some sort of probe or cartridge, typically coated with polydimethyl siloxane (PDMS) which selectively adsorbs the compounds of interest out of the matrix. Detection limits in the order of ppb to ppt are possible. There is risk of sorption of sample matrix components/contaminants, if such are present and subsequent analytical interference from the same. Care is required not to prematurely desorb any target analytes when rinsing possible contaminants from the sorbent before analysis. Analytes are subsequently extracted from the PDMS using **thermal desorption** or solvent extraction followed by GC(/MS) analysis.

The overall extraction and analysis process typically involves several manual sample preparation steps *e.g.* rinsing and drying but some of these can now be automated using simple robotics.

Quantification and sensitivity are limited by capacity (especially in the case of volatiles), matrix interferents and ultimately by the method used (SE or TD) to transfer the analytes from the sorbent to the GC

Thermal desorption (TD)

This is the third gas extraction technology commonly used for GC. It is primarily used (and is well validated) for monitoring trace (ppt to ppm) concentrations of vapour-phase organics in air or gas. Compounds are either collected in sorbent tubes (diffusive or pumped sampling) or in whole air/gas containers, prior to off-line thermal desorption-GC(-MS) analysis. TD systems can also be configured for on-line TD-GC(/MS) analysis of air/gas streams. TD-compatible sorbent tubes are re-usable. TD is readily automated and requires negligible sample preparation. It offers more concentration enhancement potential (sensitivity) than almost any other front-end GC technology. A typical sample size is 10 ml to 500 L volume of air/gas. Whatever the original air/gas sample volume, analytes are concentrated in one or more stages and are subsequently desorbed/injected into the GC analytical column in a tiny 100-200 µL volume of carrier gas. Overall concentration enhancement factors of 10^5 to 10^6 are common. Thermal desorption is also suitable for direct extraction of volatiles and semi-volatiles from sample matrices that are (a) compatible with the temperatures required and (b) sufficiently homogeneous for the mass of sample inside a tube to be representative. A typical sample size would be 5-500 mg material weighed directly into an empty tube.

TD is typically less convenient than headspace for volatile organics in liquids, but may be used in conjunction with HS (see above) to enhance detection limits. It is also the technique of choice for measuring higher boiling organics in liquid emulsions *e.g.* water based paints. Other good applications for direct TD include: resins (*e.g.* adhesives), creams/pastes (*e.g.* toothpaste, ointment) powders (*e.g.* drugs, spice, coffee), fibres (*e.g*. textiles), granules (*e.g.* polymer), and film (*e.g.* printed paper or packaging film). See TDTS 9 and others.

[*N.B.* TD applications involving the direct desorption of materials, typically fall into two categories – representative ‘fingerprinting’ of a VOC profile (incomplete extraction) and complete, quantitative extraction of the compounds of interest.]

Thermal desorption is also used as the fundamental GC introduction method in many related technologies *e.g.* Purge & trap and SPE/ME, see above.