TDTS 21

Developing and optimising TD methods

It is recommended that this Application Note is read in conjunction with Application Notes TDTS 5 (Advice on sorbent selection, tube conditioning, tube storage and air sampling) and TDTS 19 (Minimising artefacts – Considerations for storage and transport of sorbent tubes).

Summary of the analytical sequence

Pre-desorption system checks

Markes' TD systems carry out stringent sample and system integrity checks before thermal desorption of each sample. These include:

- **Tube leak testing**. Tubes are stringently leak-tested at the GC carrier gas pressure, without heat or gas flow applied, before analysis. Tubes which fail the leak test, are not analysed but retained intact. When a tube fails on an automatic system, the system continues to leak-test and analyse subsequent tubes. Details of failed tubes are stored in system memory. These measures prevent sample losses and help ensure data quality.
- **Leak testing of the sample flow path**. Critical parts of the sample flow path, such as the focusing trap and main valve, are also leak-tested prior to desorption of each tube. The sequence is halted if any leak is detected in the main sample flow path.
- **A stringent, ambient-temperature carrier gas purge of air (and water) from the tube and sample flow path**. This prevents analyte and sorbent oxidation, thus minimising artefact formation, ensuring data quality and extending tube lifetimes. The focusing ('cold') trap should be in-line throughout the carrier gas purge to retain any ultra-volatile analytes 'desorbed' from the tube prematurely. Tubes containing carbonised molecular sieves should ideally be purged for 15 min with a carrier gas flow of 30–50 mL/min to complete eliminate oxygen before heat is applied.
- **System 'ready' status**. The 'ready' status of the GC, detector(s), data processor and all parts of the analytical system are automatically checked by the TD device before tube desorption and trap desorption. It is not possible to desorb a sample into the analytical system if it is not ready to accept and analyse samples. Note that the check of 'ready' status before tube desorption can be overridden in the interest of optimising sample throughput.

Analytical sequence

The complete TD analytical procedure is:

1. **Predesorption system checks**
2. **Desorption of the sorbent tube and refocusing of the target analytes on the focusing trap**. Desorption typically takes place at 200–300°C for 5–15 min with a carrier gas flow of 20–100 mL/min – see Application Note TDTS 5 for more details). The focusing trap (or cold trap) is typically held at ambient or sub-ambient temperatures. Note that gas flow through the focusing trap during tube desorption should not exceed 50 mL/min.
3. **Splitting the sample as it is transferred from the tube to the focusing trap (optional)[2]**. Note that if method sensitivity will allow an input split, this is one way of allowing optimum (high) tube desorption gas flow to be used with optimum (slow) trap desorption flows.
4. **Rapid desorption of the focusing trap in backflush mode[1] and transfer of the analytes into the analytical column**. Desorption takes place at ~100°C/s in the initial stages of trap heating, reaching a top temperature of 250–350°C, with a 'hold' time of 1–15 min, and an inert/carrier gas flow of 2–50 mL/min.
5. **Splitting the sample as VOCs are transferred from the focusing trap to the analytical column (optional)[2]**. Desorbing the focusing trap automatically initiates the GC run.

All volatiles should be stripped from the sorbent tubes during the TD process, leaving them clean and ready for immediate reuse. However, particularly for trace-level monitoring, it is sometimes advisable to routinely condition tubes at higher temperatures than are used for sample analysis. In these cases, high-temperature tube conditioning methods can be linked automatically to run on the same set of tubes at the end of an analytical sequence.

Note that Markes' thermal desorbers facilitate collection of the split effluent for sample archiving or repeat desorption.

Selecting and validating optimum TD conditions

Typical desorption conditions for a range of common sorbent tubes are presented in Application Note TDTS 5.

The determination and validation of suitable TD conditions for new analyte–sorbent combinations may be carried out as follows:

- Check the maximum temperature of the sorbent(s) and upper temperature limit of stability for the compound(s) of interest. Ensure that at no time during method development are these temperatures exceeded.
- Start with the list of recommended desorption conditions given in TDTS 5 – unless target analytes are relatively labile. For relatively labile analytes, keep the sample flow path as cool as possible, lower the desorption temperature to just below the boiling point of the least volatile analyte and increase the flow through the tube to at least 40 mL/min.
- Focusing traps packed with the following sorbents will handle almost every air monitoring application:
  - Tenax® and Carbopack™ B (for n-C_4 and heavier)
  - Tenax, Carbopack B and a carbonised molecular sieve (e.g. Carboxen™ 1000) (for compounds ranging in volatility from n-C_3 to n-C_{30})

  The focusing trap can alternatively be packed with the same sorbent or ratio of sorbents as used in the sample tube. [Note that a focusing trap can be packed with up to three sorbents plus an initial plug of glass or quartz wool]. Once the focusing trap has been selected and installed, set it to a suitable temperature for quantitative retention of the most volatile target analytes.
- Load a tube with the same masses of the compound(s) of interest as are likely to be collected from the highest real-life air concentrations, and include an analyte that is already validated under these or similar conditions to an internal standard. Do not add water.
- Ensure that at least 20 mL/min of carrier gas is passing through the tube during desorption, and set up the split ratios, if appropriate, such that the mass of each analyte reaching the analytical system will be readily detected, but will not overload the GC column or detector[3].
- Set the sample flow path temperature high enough to prevent analyte condensation but not so high as to cause degradation. Analytes sufficiently volatile to be present in the vapour phase in the air at ambient temperature do not usually require flow path temperatures above 100°C.
- Set the focusing trap desorption temperature to slightly above the tube desorption temperature, provided this doesn't exceed that allowed for the sorbent or analytes in question. Set a trap desorption flow for efficient transfer (typically 2 mL/min or above) and a trap desorb ('hold') time of 2 min.
- Desorb the tube three times under these conditions using appropriate GC conditions. If any of the analytes are observed during chromatographic analysis of the second or third desorption of the sample tubes, increase desorption temperature, flow or time until all of the analytes are desorbed in one heating cycle.

  Notes:
  - For the sake of minimising artefact formation, it is best to use the lowest possible temperature demonstrated, to give complete thermal desorption of all analytes
  - UNITY™ allows this method development process to be automated
  - In some cases, for example direct desorption of materials, the analytical objective is not to get complete extraction of volatiles, but simply desorption of a reproducible 'profile'. This is typically best achieved using lower temperatures and longer desorption times
- Once the correct conditions have been established, run three replicates each with three desorptions to confirm the result. Check that the precision of the data from the three first desorptions is better than 10% RSD, and if complete desorption is required, that there is no (<1%) carryover of the analyte(s) on the second or third desorptions of the tubes.
- Calculate the mean response factors for each of the analyte(s) and normalise them to the internal standard compound to create relative response factors (RRFs). Compare the RRFs produced by the TD system to those obtained using the same analytical column and detector when the sample is injected *via* a conventional GC inlet set up with similar carrier gas flows and split ratios as appropriate[4].

  If the RRFs agree within 10%, the following factors have been demonstrated:
  - Quantitative desorption from the tube (primary desorption)
  - Quantitative retention on the trap during primary desorption
  - Quantitative desorption from the trap (secondary desorption)
  - Quantitative transfer from the thermal desorber to the analytical column

  The analytical method can therefore be considered valid in these respects.
- If there is a risk of high humidity (>65%) in the atmosphere to be tested and if the following analytical conditions apply:
  - Split ratio <10:1
  - A less hydrophobic sorbent is in use in the sample tube

Cold trap parameters should be selected to allow selective elimination of water. Test this by comparing results from dry tubes desorbed:

- With the trap low temperature set at –10°C
- With the trap temperature set for selective elimination of water (typically 25–30°C). Comparing the results should confirm no breakthrough of target analytes at the higher focusing temperature. Confirm this using a humid standard

- Three replicates of a low-level standard, representative of the lower limits of detection required, should then be analysed under the analytical conditions selected. The signal-to-noise ratio for the analyte(s) under these conditions should be at least 10:1, and individual artefacts should be at 10%, or less, of the peak area of the analyte(s).
- A triplicate multi-level calibration and precision test should then be carried out, and the results shown to comply with acceptable performance criteria.

Method performance criteria

The relative standard deviation of a sequence of standards analysed by a TD–capillary GC system should be of the order of 1–5%, depending on the stability of the analytes, the split ratio, the signal-to-noise ratio and the presence of interfering artefacts. A series of six laboratory-prepared or commercially obtained standard tubes should demonstrate better than 10% RSD for all analytes unless the signal-to-noise ratio is worse than 10:1 or artefact levels are higher than 10% of a given analyte peak area. RSD levels for the analytical system must be better than 20% for all compounds to be analysed using that method.

The reproducibility of sorbent tube monitoring methods (*i.e.* sample collection and analysis) is typically in the order of 10% for microgram-level samples and <20% for nanogram-level samples. The figures quoted represent the total error for the entire sample collection and analytical procedure. These results are well within typical environmental monitoring method performance criteria of 25–30%.

Notes

1. The employment of 'backflush' mode *(i.e.* with the gas flow in the reverse direction to that of the air flow during sampling) is particularly important for multibed tubes. A rare exception is the analysis of nitrous oxide (see Application Note TDTS 18 for more details).
2. This is only required to prevent column or detector overload during the analysis of high-concentration or large-volume samples, or when using ultra-sensitive detectors such as the ECD.
3. ECD detectors may be overloaded by as little as 1 ng of some highly halogenated species such as carbon tetrachloride.
4. Do not attempt to develop a TD procedure for any compound which is known or suspected to degrade using conventional flash-vaporising GC injectors.

Trademarks

Version 3
July 2012