# *TDTS 6*

# Common problems with thermal desorption and how to solve them

## Introduction

Thermal desorption–gas chromatography (TD–GC) is now a well-validated and widely used technology. However, in common with most analytical techniques, troubleshooting is still important, especially during method development.

This document describes some of the most commonly encountered concerns, relating to systems employing any UNITY™ instrument (with or without an ULTRA™ autosampler) or a TD-100™ automated system, and advises on how best to address them.

The following issues are covered:

## 1. Poor peak shape

### Tailing/broadening of *early* peaks

| Cause | Remedy |
|---|---|
| Tailing or broadening of early peaks may be an indication that the cold trap packing has deteriorated. | On UNITY the cold trap should be replaced after 1000 desorptions or 12 months, whichever comes first. |

### General poor peak shape

| Cause | Remedy |
|---|---|
| A poor connection between the transfer line and the analytical column may also distort peak shapes. | The connecting ends of both the column and the transfer line should be cut cleanly using a fused silica column-cutting tool. The union or connector assembly should be an inert, zero-dead-volume fitting recommended for connecting capillary tubing. |
| Normal aging (or the desorption of tubes containing highly reactive compounds) can produce activity in the transfer line or in the analytical column. This results in peak broadening or tailing, particularly of more dynamic or polar compounds. | Check the connection between the column and transfer line. |
| If the problem persists, the transfer line 'insert' may have deteriorated. | Check that the transfer line is installed correctly on the thermal desorber. Replace the deactivated fused silica insert inside the transfer line. |
| If there is still no improvement, the analytical column may have deteriorated. | Consider replacing the analytical column. |

### Broad peaks

| Cause | Remedy |
|---|---|
| Cold trap sorbent being too strong. | Replace cold trap with one packed with weaker sorbents (if in doubt, contact Markes for advice). |
| Low desorption flow. | The desorption flow (*i.e.* the sum of the outlet split and column flows) should exceed 2 mL/min for a UNITY cold trap for optimum peak widths. Note that non-Markes systems may require a much higher trap desorption flow. |
| Loading a cold trap with relatively large quantities (>1 mg) of water/solvent and heating at maximum rates (>60°C/s) can cause flash-vaporisation, resulting in peak broadening, splitting or discrimination, as seen with conventional GC injectors. | Either reduce the mass of water or solvent reaching the cold trap (*e.g.* by careful adjustment of the cold trap temperature or use of an inlet split) or reduce the trap heating rate, *e.g.* to 40°C/s. |
| Overloading of the GC analytical column will cause band broadening. (High-resolution capillary columns work optimally with analyte masses less than 200 ng per component. | Use one or both split options, if necessary, to ensure that the analytical column is not overloaded. |

## 2. Contamination – Chromatogram artefacts

Most thermal desorption applications require sorbent, either in the cold trap or in both the tube and the cold trap. Whenever sorbent is used, there will always be a small but distinct background signal from the sorbent itself. The minimum level of inherent artefacts varies from one sorbent to another, from below 10 pg for graphitised carbons to 5–10 ng for a tube fully packed with Chromosorb® or PoraPak™ porous polymer sorbents.

Running a test sequence is highly recommended to refine the search for the identity of the artefact source. This is done as described below:

***Test sequence***

**A** **Run a blank GC analysis** (Press the "Start" button on the GC)

**B** **Desorb the cold trap** (Use normal method parameters)

**C** **Purge and desorb the cold trap** (Purge for 10 min using the "Set gas flows" option)

**D** **Desorb an empty tube at 50°C**

**E** **Desorb an empty sample tube** (under normal analytical conditions)

**F** **Desorb a clean sample tube** (under normal analytical conditions)

**G** **Desorb an actual sample tube** (under normal analytical conditions)

*N.B.* It is important to include both laboratory and field blanks (as in US EPA Method TO-17) in any monitoring project. Both laboratory and field blanks should have been packed using the same batch of sorbent and conditioned and sealed at the same time as tubes to be used for sample collection. Laboratory blanks should be kept in the laboratory in a replicate of the container used to transport field blanks and sampling tubes. Field blanks should be subjected to all the same operations as a sample tube except for the actual process of either pumping air through the tubes or exposing them diffusively.

**If a consistent pattern of artefacts is found in all sample, field and laboratory-blank chromatograms, the source of the contamination should be investigated as follows:**

**Contamination at Step A**

| Possible cause | Remedy |
|---|---|
| Contamination in the GC/detector. | Check/replace column; clean the MS detector. |

**Contamination at Step B**

| Possible cause | Remedy |
|---|---|
| Cold trap sorbent(s)/charcoal filter. | After cleaning the sample tubes, desorb the cold trap to a temperature just below the maximum of the least stable sorbent in the trap. Use an outlet split flow of at least 50 mL/min and keep the instrument flowpath as hot as possible (>190°C). Heat the trap for at least 10 min and allow the GC to run through a full temperature program run, with a hold time of at least 30 min at a top temperature just below the maximum recommended for the analytical column in question. If many high-boiling contaminants elute from the column after the trap desorption, repeat the procedure. |
| The charcoal filter on the split flow vent can become a source of contamination in extreme cases. | Either replace the old packing with well-conditioned charcoal or thoroughly condition the filter in a GC oven using temperatures of 400°C with over 100 mL/min flow of pure nitrogen or helium for at least an hour.<br>When monitoring for trace-level analytes, select a sorbent with the lowest possible inherent artefact levels, and set the chromatographic conditions so that individual artefacts do not interfere with the target compounds. |

**Contamination at Step B, increased after Step C**

| Possible cause | Remedy |
|---|---|
| Gas-line contamination of the gas supply. | Carrier gas lines, regulators, gauges, filters and even the gas itself are common sources of contamination in thermal desorption. Initial investigations should include:<br>• Ensuring that the gas itself is minimum 5.0 grade (99.999% pure) helium or nitrogen<br>• Ensuring that the regulator is fitted with a stainless steel diaphragm<br>• Ensuring that the cylinder is connected to the UNITY using the shortest possible length of acetone-washed refrigeration-grade copper tubing with no brazed joints; only brass or stainless steel, ungreased Swagelok-type unions should be used for tubing connections<br>• Installing new filters/traps for oxygen and organics in the carrier gas supply line next to the UNITY. |

**Contamination at Steps C or D**

| Possible cause | Remedy |
|---|---|
| Flowpath contamination of the gas supply. | To establish whether or not the gas supply is at fault, repeatedly desorb a clean, empty tube using identical conditions except with steadily increasing primary desorption times. Use the normal cold trap low temperature. If artefact levels rise proportionally with the primary (tube) desorption times, then the contamination is either linked to the carrier gas supply, or there is a consistent source of contamination somewhere between the tube and the inlet to the cold trap. Check all the components of the gas supply system. |
| Silanised glass wool has been inadvertently desorbed at temperatures above 250°C. | The analytical flowpath will need to be cleaned for at least 48 h by repeatedly desorbing a blank tube at high temperatures, with maximum flowpath temperatures and with desorb and split flows of at least 50 mL/min.<br>*N.B.* Unsilanised glass or quartz wool should be used as standard in the cold trap and sample tubes, and should be conditioned at high temperatures before use. Silanised glass wool can be used, but is only recommended for the analysis of labile compounds, and must never exceed 250°C, even during conditioning. |

**Contamination at Steps E, F or G**

| Possible cause | Remedy |
|---|---|
| Contamination of the PTFE frit in the sample flowpath just downstream of the sample tube, or an O-ring. | A visual inspection of the frit or O-ring is usually sufficient to determine whether or not it is clean. See the Technical Support Manual for further details. |

**Contamination at Step G**

| Possible cause | Remedy |
|---|---|
| The sample tubes have become contaminated. | A badly contaminated or suspect batch of sample tubes should be conditioned for ~2 h at a temperature close to, but below, the maximum temperature of the sorbent packing. See the Appendix for details of tube conditioning. |

## 3. Component carryover

### Carryover in the sample tube

| Cause | Remedy |
|---|---|
| Invariably caused by incomplete desorption. | Best addressed either by using more stringent desorption conditions or by selecting a weaker sorbent for collecting the samples. The gas flow rate is particularly important. The flow through the sample tube during desorption is the sum of the desorb flow and the inlet split flow, and should normally total at least 30 mL/min. The flow through the tube during desorption should never be less than 10 mL/min.<br><br>When thermally desorbing volatiles directly from resinous or solid samples, desorption can be enhanced by increasing the surface area of the sample, *e.g.* by smearing a resinous sample in a thin layer around the inside of a PTFE tube liner or by grinding solid material. (A cooling agent such as solid $CO_2$ can be added to the sample during the grinding process to minimise the loss of volatiles). It is also important to ensure that solid or resinous samples do not block the carrier gas flow path. Thermal desorption is a dynamic process and if the flow path becomes blocked, this stops the passage prematurely, causing carryover.<br><br>When desorbing volatiles direct from a material substrate, it is important to make sure that the entire sample is located within the central 6 cm portion of the sample tube. The desorption ovens of most thermal desorbers, including UNITY, only cover and directly heat the central 6 cm portion of each tube. |

### Carryover in the cold trap

| Cause | Remedy |
|---|---|
| In a multi-bed trap, carryover can occur if higher-boiling target analytes are allowed to reach the stronger sorbent materials. | Check that the sorbents are arranged in order of increasing sorbent strength from the sampling end. Try reducing the cold trap temperature and flow during primary (tube) desorption, and increasing the trap temperature and flow during secondary (trap) desorption. If neither of these steps are successful, increase the length of the front (weaker) bed of sorbent. |

### Carryover in other parts of the sample flowpath

| Cause | Remedy |
|---|---|
| Particles and fibres are one of the most common causes of leak test failure, and can cause unpredictable adsorption of analytes (resulting in carryover and artefacts) in the tube seal area. | Check that sorbent material, or sample matrix, is not migrating from the tube and into the seal assembly to which the tube connects during desorption. |
| If the sample or sorbent in the tube or trap has been overheated, very high boiling point material is likely to have been vapourised inside the tube or trap, only to recondense in the cooler parts of the sample flow path, *i.e.* the tube seal assembly, the internal tubing, the transfer line and the main valve. This will result in adsorption of analytes, carryover and peak ghosting. | The only option in this case is to get the entire sample flow path replaced by a qualified service engineer. |
| If silanised glass wool has been used in either the sample tube or trap and has been heated to temperatures above 250°C, this will have eluted residues which will contaminate the sample flow path and may cause carryover. | To recondition, cycle the system for 48 hours with an empty tube, maximum flow path temperatures and high (>50 mL/min) flows. |
| Contaminated frits can cause carryover and/or artefacts (see Section 2 (steps **E–G**), where this is also considered). | Visually inspect the PTFE filter disks/frits in the tube seal. |

## 4. Poor peak precision

| Cause | Remedy |
|---|---|
| Incorrect introduction of standards onto sample tubes. | Standards, whether gas-phase or liquid, are best introduced onto the sampling end of blank sorbent tubes using Markes' Calibration Solution Loading Rig (CSLR™). Detailed information on this is given in Application Note TDTS 7.<br><br>In summary, the calibration standard is introduced through the injector septum using a standard GC syringe. Carrier gas, at 80–100 mL/min, sweeps through the injector port, vaporising liquid solutions and ensuring that analytes reach the sorbent bed in the gas phase.<br><br>Liquid standards should ideally be prepared in a solvent that is unretained by the sorbent(s) in the tube (methanol is a common choice). If the carrier gas is allowed to flow through the tube for 3–5 min, the mass of solvent on the tube will be significantly reduced (or even completely eliminated), thus simplifying subsequent analysis.<br><br>*N.B.* Liquid standards can also be introduced by direct loading. This is best done to the rear of a tube prepared with a short (~10 mm) bed of sorbent, backed up by conditioned, unsilanised glass or quartz wool. Note, though, that this may result in poor precision if the solvent is totally unretained by the sorbent (*e.g.* methanol on Tenax), due to the droplet of solvent carrying through some of the analytes during the initial carrier gas purge. Higher-boiling analytes may also require more stringent desorption conditions than real-life air monitoring samples, where all the 'higher-boilers' are retained on the first few millimetres of sorbent. [Note that if liquid standards are loaded directly onto the front of the sample tube, much of the standard will remain in the form of a liquid droplet, and will be effectively unretained by the sorbent. An unpredictable percentage of the most volatile compounds in the sample are then prone to loss by diffusion into the headspace inside the tube, thus giving poor precision.] |
| Low carrier gas pressure/flow settings. | The standard fine-metering needle valves used on UNITY and on other leading automated thermal desorbers to control desorb and split flows are subject to variation (drift) at flow rates below 5 mL/min., particularly at low pressures (<10 psig). This can result in poor precision. If this is an issue when trying to achieve low split ratios, UNITY allows you to turn the split off altogether and desorb the cold trap splitless, just using the capillary column flow. High-resolution capillary chromatography will be produced with trap desorption flows down to 2 mL/min.<br><br>Instability may also be introduced by the electronic carrier control (ECC) during trap desorption. To prevent this, ensure the carrier supply pressure is 5 psi above the maximum electronic pneumatic control (EPC) during the run (see ECC installation manual). |

## 5. Poor analyte recovery

| Cause | Remedy |
|---|---|
| Reactive compounds are poorly recovered. | The recovery of reactive compounds can often be improved by increasing the desorption time and gas flow rate while reducing the desorption and flow path temperatures. Many volatile, labile analytes will pass successfully through UNITY with flowpath temperatures as low as 50°C. |
| Desorption and/or column flow rates are insufficient. | Desorption flow rates of at least 30–50 mL/min. should be used for both the tube and cold trap to increase the linear velocity of sample vapours inside the instrument. For semi-volatile compounds the column flow rate should be increased to 4–5 mL/min if possible, by using wider-bore (0.32–0.53 mm) capillary columns. For the analysis of extremely labile, relatively involatile components (>n-$C_{12}$), a 10–20 mm plug of silanised glass or quartz wool should be used before the cold trap packing. |
| Incomplete desorption or adsorption onto contaminants in the analytical system. | Redesorb the sample and monitor any apparent carryover. If carryover is found, follow the guidance given above. |
| Sorbent packing is not optimal. | If a multibed sorbent tube is being used to monitor/collect vapour-phase analytes, ensure that the different sorbents are kept in discrete beds separated by unsilanised glass or quartz wool plugs, and that they are arranged in order of increasing sorbent strength, *i.e.* weak to strong from the sampling end. It is also particularly important that multibed tubes are desorbed in backflush mode. This approach to sample collection and desorption ensures that higher-boiling compounds only come into contact with the weaker sorbents, and can thus be readily and quantitatively desorbed. |

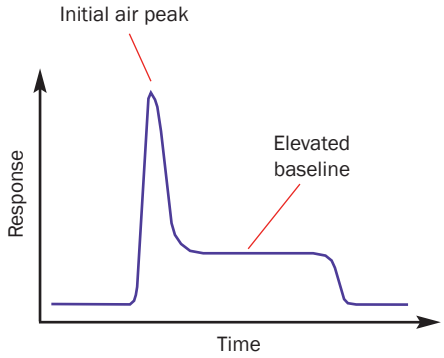
## 6. Cold trap cooling problems

| Cause | Remedy |
|---|---|
| The Peltier cooling unit will not function unless the dry gas supply is switched on, with a pressure of 50 psi. The supply of air or nitrogen to UNITY must have a dew point below –50°C, as this gas stream is used to purge the cold trap box. The two-stage Peltier cell reaches a temperature below –30°C, and this is maintained whatever the selected temperature of the cold trap. If moist gas is used to purge the cold trap box, ice will build-up on top of the Peltier cell and around the cold trap, ultimately restricting its ability both to maintain low temperature and to heat up rapidly during secondary desorption. | If a build-up of ice has occurred, switch off the instrument, open the cold trap box and remove as much of the ice as possible. Carefully use a hair dryer or hot air gun to gently dry up any remaining water in the cold trap box. |
| If desorb flows in excess of 100 mL/min are used and if tube desorption temperatures are above 300°C, the cold trap may struggle to maintain low temperatures during a long (>15 min) primary desorption. | Check that the fan at the rear of the instrument is not blocked and there is sufficient space (at least 10 cm) around the instrument. Check also that helium is not being used to purge the cold trap box and the ambient temperature is less than, or equal to, 30°C. |

## 7. High air/water background

| Cause | Remedy |
|---|---|
| Back-diffusion of air through the O-rings in the system. | O-Rings are used to create a strong seal around the sample tubes and cold trap on UNITY. These are relatively impervious to air, and the air/water background on a UNITY–GC/ECD or UNITY–GC/MS system should be similar to that observed using conventional GC injectors. However, in common with other split GC injectors, it is recommended that the split flow is on 'standby' when using UNITY with a GC/MS system. This maintains a positive flow of at least 10 mL/min of helium through the split vent, preventing back-diffusion. |

## 8. Air/water step seen when scanning to low masses with an MS detector




| Cause | Remedy |
|---|---|
| This behaviour occurs when the carrier gas supply to the GC column is through the cold trap. The initial peak of air, which is not always observed, results from the desorption of air retained on the cold trap. Traps containing carbonised molecular sieves will retain more air and water, and consequently the air peak tends to be bigger with this type of trap when compared to a general-purpose trap. | Increasing the pre-trap-fire purge time can sometimes help to reduce the size of this peak. |
| The second feature is the elevated baseline which corresponds to the time for trap desorption and cool-down. The main contribution to the step comes from water (m/z 18), nitrogen (m/z 28), oxygen (m/z 32) and carbon dioxide (m/z 44). This is not due to a leak on the cold trap, but is simply a function of the different flowpath route for the carrier gas. | If it is not necessary to scan this low, altering the scan range can reduce the effect. Successive improvements can be made by scanning from 19, 29, 33 or 45, which would eliminate some or all of the main contributors to the step. |
| If the compounds being analysed mean that changing the scan range is not an option, the important point to note is that there is no effect on the quantitation of peaks that may occur in the step. The only time there can be a problem is when a peak elutes just as the step ends. | This can be easily overcome by adjusting the cold trap desorption time by 0.2 min to alter the length of the step. |

## 9. Frequent leak test failures

| Cause | Remedy |
|---|---|
| Leaks on the thermal desorber. | Inspect the O-rings (size 010) on the split and sample tube sides with a helium leak detector. Replace as necessary (see Technical Support manual). Replacement of damaged cold trap seal O-rings should be carried out according to the Technical Support manual. In the event of solenoid valves not fully closing, check that, with the split turned off in STANDBY, there is no flow through the trap/desorb or split vent. Clean or replace the solenoid valves. |
| Leaks on the autosampler. | Damaged/worn O-rings inside DiffLok™ caps explain individual tube leak problems, not persistent leaks. Persistent leaks are often due to damaged/worn O-rings on the sealing nozzles inside UltrA. Replace O-rings according to the Technical Support Manual. |

## Appendix – Tube conditioning

The fully automatic TC-20™ off-line sorbent tube conditioner from Markes International is a cost-effective and time-saving tool for cleaning up to 20 tubes simultaneously.

Alternatively, UNITY and TD-100 also offer a dedicated tube-conditioning mode. In this mode, contamination from the tube is directed to vent, away from the cold trap. However, in common with other commercial desorbers offering tube conditioning, exhaust from the contaminated tubes still passes through some parts of the sample flow path. For this reason, it is recommended that tubes are not routinely conditioned on the analytical system.

Conditioning temperatures recommended for the most common sorbents are detailed in Application Note TDTS 5. The flow through the tube during tube conditioning should be at least 50 mL/min. The lifetime of a tube is at least 100 thermal cycles (porous polymer sorbents) or 200 thermal cycles (carbon-based sorbents). They can nearly always be cleaned by thorough conditioning until this point.

Once tubes are conditioned, they should be capped with ungreased brass caps configured with PTFE ferrules and stored in a clean, sealed container such as a glass jar or uncoated tin can. It is not necessary to refrigerate or freeze the tubes, nor do they need to be stored under nitrogen, but it is recommended that a permeable container with 1–2 g of conditioned charcoal is placed inside the jar or tin with the tubes, to adsorb traces of vapour-phase organics.

Note that refrigeration of tubes can cause long-term screw caps to become loose. Caps should be re-tightened (finger-tight plus a quarter turn with the CapLok™ tool) once the tubes have reached their minimum storage temperature. Refrigerated tubes must be allowed to equilibrate to laboratory temperature prior to analysis. Further information about storage and transport of clean and sampled sorbent tubes is given in Application Note TDTS 19.

Once the tubes and trap have been conditioned, reset the TD–GC(MS) system to the required analytical parameters and analyse one of the conditioned tubes. In terms of toluene equivalents, individual artefacts should be in the order of 1 ng or less for carbon-based sorbents or Tenax® TA, and below 10 ng for other porous polymer sorbents.

## Trademarks



Version 4
December 2012