MARKES international

TDTS

Thermal Desorption Technical Support

Note 75: Liquid standard injection, tube impedance and other factors which may cause discrimination during the calibration of thermal desorption methods

Keywords

TD Operation; Calibration; Impedance; Discrimination

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Introduction

It is not uncommon for calibration standards, used during thermal desorption (TD) analysis of vapours trapped on sorbent tubes, to be different from field samples. The ideal TD standard is prepared by introducing a fixed volume of an accurate gas standard of the compounds of interest onto an identical sorbent tube to those used for field sampling of vapours. However, accurate gas standards are notoriously difficult and expensive to generate; particularly in the case of labile, polar or less volatile analytes and at low concentrations. For this reason, and as specified in most TD standard methods, routine thermal desorption calibration is normally carried out by introducing liquid standard solutions to the sampling end of sorbent tubes in a stream of carrier gas. The bulk of solvent is then generally purged from the sorbent tube during the standard loading process (See TDTS 7 - *Calibration: preparing and introducing standards using sorbent tubes*).

However, it is not always possible to completely purge the solvent from the tube – for example when dealing with volatile compounds or with strong sorbents. In this case, standard tubes containing relatively large masses of solvent (possibly several milligrams) will be used to calibrate sample tubes which are solvent-free. Conversely, whether loaded from the liquid or gas phase, standard tubes are generally dry. However, tubes used for field sampling may contain several milligrams of water, depending on the sorbent used and the prevailing atmospheric conditions.

Similarly, it is often convenient to use different tube sorbents for calibration to those used for field monitoring. For example, Certified Reference Standards on TD tubes and tubes provided for quality assurance/proficiency schemes are most commonly packed with 200 mg Tenax TA™, whereas tubes used for field sampling may be packed with 500 mg carbon black or two or three different sorbents depending on the application (see TDTS# 5 *Advice on sorbent selection, tube conditioning, tube storage and air sampling*, and TDTS# 20 *Confirming sorbent tube retention volumes and checking for analyte breakthrough*). Different TD sorbents have very different densities and are available in a range of particle sizes from 20-40 to 60-80 mesh. Some sorbents are also more prone than others to the formation of 'fines'. (Fines are small, dust-like particles of sorbent that fill the voids in the sorbent bed and cause blockages. They are most commonly caused by rough handling *e.g.* dropping the tubes or repeated insertion of syringe needles to introduce standard.) All of these factors can affect the back pressure of a tube and its impedance to gas flow.

This technical note describes the issues which may arise as a result of differences between samples and calibrants for thermal desorption and the operating conditions under which the effects may be significant. Guidance for minimising the impact of such differences and for validating that a given method is not subject to these effects is also presented together with advice on routine monitoring of tube impedance.

Potential analytical impact of varying tube impedances

Tube impedance – normal range

Tubes manufactured by Markes International are all prepared using weighed masses of sorbents and each individual tube is flow tested under a fixed supply pressure (~0.5 psig) to ensure it exceeds a minimum threshold flow of 200 ml/min. Tubes which fail this test are rejected and repacked.

However, not all tube manufacturers use this level of care and the variation in impedance of different brands of sorbent tube can be very significant. The back pressure of a range of commercial pre-packed and self-packed standard sorbent tubes [3.5-inch long x 6.4 mm O.D. x ~5 mm I.D. (stainless steel) or ~4 mm I.D. (glass)] was evaluated by UK Health and Safety Laboratory with a flow of 50 ml/min N_2 as described in their report OMS/2002/15 – See Table 1.

Sorbent type	psi	kPa
Tenax TA 35-60 (Chrompack)	0.145±0.04	1.00±0.3
Chromosorb 106 (Chrompack)	0.160±0.03	1.10±0.2
Carbograph 1 TD (Alltech)	0.087±0.01	0.60±0.1
Carbograph 5 TD (Markes)	0.029±0.01	0.20±0.1
Carbopack B (glass) (Supelco)	0.493±0.04	3.40±0.3
Carbopack X (Supelco)	0.131±0.03	0.90±0.2
Carboxen 1000 (glass) (Supelco)	0.377±0.04	2.60±0.3
Carbopack B / Carboxen 1003 (glass) (Supelco)	0.232±0.03	1.60±0.2
Carbopack B / Tenax GR (glass) (Supelco)	0.305±0.03	2.10±0.2
Carbotrap 300 (glass) (Supelco)	1.306±0.58	9.00±4.0
Molecular Sieve 5Å (Chrompack)	0.145±0.06	1.00±0.4

Table 1: Back-pressure of a range of industry standard stainless steel and glass tubes - N_2 at 50 mL/min

Preliminary observations from this data are that standard glass tubes containing carbon black or carbon molecular sieve sorbents, particularly tubes packed with multiple beds of these sorbents, are prone to high impedance even at moderate (50 mL/min) flow rates. Such sample tubes are therefore most at risk of discrimination due to impedance variation if tubes with more normal back-pressure are used for calibration or quality assurance.

The potential impact of high impedance tubes/traps during sampling

In reality, the biggest practical issues caused by high impedance sorbent tubes (or focusing traps) are likely to be observed during sampling. Both on- and off-line monitoring methods involving active sampling (pumped or pressure controlled) are subject to error if tubes or traps become 'blocked' *i.e.* if the back-pressure increases to such an extent that the sampling pumps or delivery mechanism cannot reach the required sampling flow and either cut-out completely or deliver lower sampling flows/volumes than those expected.

Pumped tube sampling

All personal monitoring pumps have a tube impedance/flow limit and will struggle to deliver the required sampling rate if tube impedance increases above a given level. This level varies from pump to pump depending on make and model. However, standard methods for air/vapour monitoring with pumped sorbent tubes invariably require calibration of each sample train (*i.e.* each specific pump and tube combination) before field monitoring. This means that pump/tube combinations which struggle to reach the desired flow can be eliminated before field monitoring begins. Furthermore, routine checks of tube impedance should be carried out by users, say every 20 or so uses. In either case it means tubes with high back pressure can be excluded from field monitoring exercises so that no samples are compromised.

Online monitoring

In the case of TD-based on-line air monitoring systems, where air or gas is drawn directly into the focusing trap of the thermal desorber under electronic mass flow control; 'blocked' or high-

impedance focusing-traps can impact the flow rate and volume of gas sampled. However, as the same trap is used for collecting each sample in the sequence, back-pressure typically increases only gradually – for example; due to the collection of fine particles from the sample stream or fragmentation of the trap sorbent over extended periods (months). This is, therefore, unlikely to cause run-to-run variation. Markes on-line TD monitoring equipment incorporates filters in the sample stream (to prevent the ingress of fine particles) and uses flow sensors to log actual flows/volumes during sampling. This ensures that quantitative monitoring data can continue to be obtained and alerts the user whenever the trap needs changing.

The potential impact of variable tube impedance during TD analysis

Older thermal desorption technology, with forward flow desorption and no valve to isolate the primary sorbent tube from the GC column during analysis (see Figure 1) is/was inherently subject to significant error due to tube impedance variation.

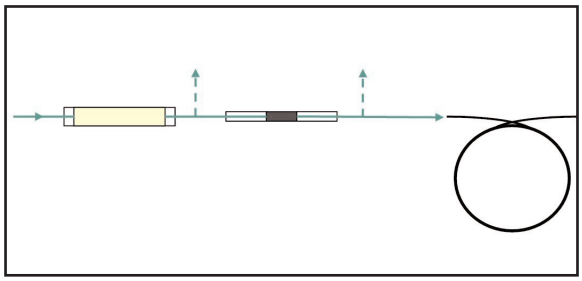

Figure 1: Flow schematic showing forward flow TD system with no valve

In this type of flow path configuration, any significant change in tube impedance causes the carrier gas pressure downstream of the sorbent tube to vary; thus affecting both split flow (if applicable) and chromatographic retention time. This effect is observed whether the supply of carrier gas to the thermal desorber is manually or electronically controlled and impacts both quantitative and qualitative analysis.

Modern configurations of two-stage TD are much less susceptible to issues related to tube impedance because the primary sorbent tube is isolated from the focusing trap and GC(/MS) during secondary (trap) desorption/initiation of the GC run (figure 2b).

Note that the impedance of the primary sample tube cannot impact the column head pressure or split flow during secondary (trap) desorption & initiation of the GC(/MS) analysis, because the tube is not in the carrier gas flow path at this time (Figure 2a).

However, if the TD method requires an 'inlet' split *i.e.* a split during primary (tube) desorption (figure 2a), variation in tube impedance can have an effect on the split ratio, particularly if the system is being operated at low carrier gas pressures. Any variation in selected desorption temperatures can also exacerbate this effect. An example of the discrimination that can be caused by variation in tube impedance, under extreme inlet split conditions (high (140 mL/min) inlet split flow and low (8 psi) column head pressure) is shown by UK HSL in their report OMS/2002/15 – see Table 2.

Under these high flow/low pressure conditions, sorbent tubes with high back-pressure simply cause so much impedance that the pressure of gas immediately downstream of the sample tube is not sufficient to drive the gas through the focusing trap or split vent at the rates programmed. This remains true whether the split and desorb flows are manually or electronically controlled.

In this situation, where the pressure downstream of the sample tube is too low to supply the flows required, gas tends to take the path of least resistance, *i.e.* it passes preferentially through the split vent with proportionally less of the sample stream passing through the comparatively high impedance focusing trap. The discrimination observed is thus a result of the split ratio being effectively increased for high impedance tubes (relative to those of lower impedance) thus causing lower apparent recovery from the high impedance tubes. At higher operating pressures and more moderate gas flow rates, tube impedance is unlikely to cause discrimination, even when operating with inlet split – see Table 3 overleaf. (Reproduced from Report OMS/2002/15 with the kind permission of UK HSL).

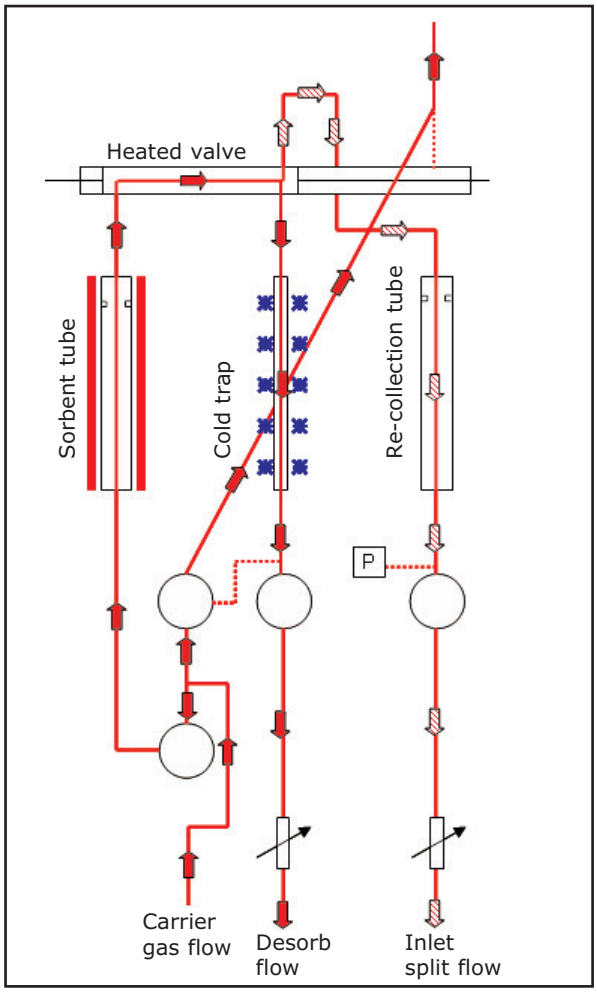

Figure 2a: Markes UNITY TD flow path during primary (tube) desorption

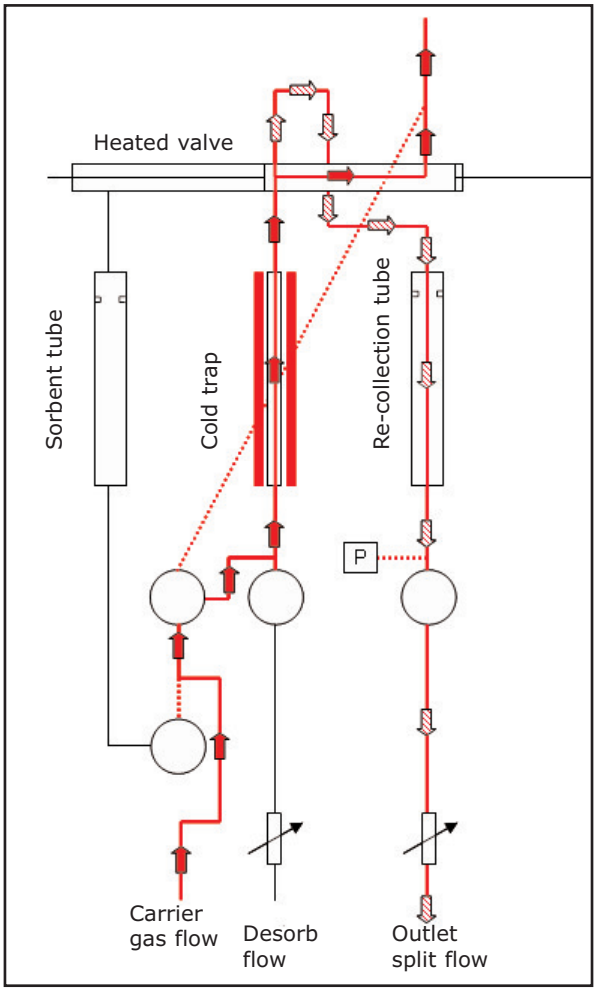

Figure 2b: Markes UNITY TD flow path during secondary (trap) desorption

Tube	C 106 mass (mg)	Back-pressure (psi)			Flow during conditioning (mL/min)	TD split flows (mL/min)			Toluene peak area $\mu V.s^{-1}$ (TIC)
		Before conditioning	2 h conditioning	17 h conditioning		Inlet	Desorb	Outlet	
A	100	0.06	0.07	0.06	98	143	10.2	57.8	72657
B	100	0.03	0.04	0.03	110	144	10.6	56.9	69882
C	104	0.06	0.06	0.04	95	144	10.6	~57	65221
D	101	0.04	0.06	0.03	92	145	11.5	~57	68305
E	103	0.09	0.09	0.07	94	145	10.5	~57	64394
F	100	0.03	0.04	0.03	105	146	10.7	~57	56383
									66140 ±5660 (mean±s.d.)
G	531	0.25	0.26	0.25	30	136	9.9	57.0	61566
H	528	0.22	0.25	0.23	31	137	9.7	~57	50546
I	529	0.22	0.25	0.23	31	137	10.4	~57	54540
J	526	0.22	0.25	0.23	31	137	9.7	~57	54033
K	527	0.23	0.25	0.23	30	137	10.1	~57	61140
L	527	0.23	0.25	0.23	30	138	10.2	~57	57576
									56567 ±4327 (mean±s.d.)

Table 2: Recovery of ~17 µg toluene from TD-GC system, operating with high inlet split and at 8 psi pressure. 14% lower recovery is observed with high impedance tubes (Toluene loaded from gas phase)

Minimising the impact of impedance variation during desorption

Sorbent tubes

As described above, the impact of varying tube impedance in an automatic desorption sequence, is unlikely to be significant except when using a very high inlet split flow with relatively low carrier gas pressure – a rare and usually ill-advised combination. Nevertheless, Markes TD systems facilitate monitoring of tube and trap impedance, during the thermal desorption process, to detect and minimise any risk of discrimination.

At one extreme there is the issue of completely blocked tubes. Blocked tubes are detected during the ambient temperature leak test at the beginning of the run and are not analysed. After completion of a sequence, the error log reports any such failures and allows the user to investigate samples which have failed the leak test for this reason.

More moderate variation in tube impedance is detected on Markes thermal desorbers by continuous monitoring of carrier gas pressure downstream of the sorbent tube/trap at all stages of system operation, *e.g.* standby, pre-purge, primary (tube) desorption and secondary (trap) desorption.

Tube	C 106 mass (mg)	Back-pressure (psi)			Flow during conditioning (mL/min)	TD split flows (mL/min)			Toluene peak area $\mu V.s \times 10^{-3}$ (FID)
		Before conditioning	2 h conditioning	17 h conditioning		Inlet	Desorb	Outlet	
A	100	0.06	0.07	0.06	98	63.0	21.4	80.3	104.6
B	100	0.03	0.04	0.03	110	62.8	21.3	81.0	85.2
C	104	0.06	0.06	0.04	95	62.9	21.4	80.6	107.7
D	101	0.04	0.06	0.03	92	62.8	21.7	82.0	99.6
E	103	0.09	0.09	0.07	94	62.6	21.4	81.9	108.7
F	100	0.03	0.04	0.03	105	62.3	21.4	81.8	101.8
									101.3 ± 9 (mean±s.d.)
G	531	0.25	0.26	0.25	30	62.5	21.3	80.7	93
H	528	0.22	0.25	0.23	31	62.7	21.6	80.8	102.6
I	529	0.22	0.25	0.23	31	62.4	21.3	81.4	99.6
J	526	0.22	0.25	0.23	31	62.2	21.3	81.9	90.2
K	527	0.23	0.25	0.23	30	62.2	21.3	82.2	104.9
L	527	0.23	0.25	0.23	30	62.6	21.3	81.9	94.5
									97.5 ± 6 (mean±s.d.)

Table 3: Recovery of ~17 µg toluene from TD-GC system, operating with inlet split and at 46.1 psi pressure. No significant difference in recovery is observed between low and high impedance tubes. (Toluene loaded from gas phase)

It is normal for the carrier gas pressure down stream of the sorbent tube or focusing trap to vary slightly during the various stages of TD operation and as the temperature of the tube or trap increases during the desorption process. However, exceptional changes of carrier pressure downstream of the tube during primary desorption, is a clear indication that a particular tube has a different impedance to the others in a sequence. Markes thermal desorbers incorporate a user-settable 'minimum pressure' parameter which will prevent analysis of any tube exhibiting unusually high back pressure.

Focusing trap

While focusing trap impedance is unlikely to change dramatically from run-to-run under normal operating conditions, a step change in focusing-trap impedance could be expected when a trap is replaced or if a different secondary desorption temperature is selected. In either case, back-pressure regulated electronic carrier gas control (ECC) of the carrier gas stabilises the carrier gas pressure at the head of the analytical column/outlet split point, ensuring that column and outlet split flows remain constant independent of trap parameters – impedance, split flow, trap desorption temperature, *etc.* (see Figures 3a and 3b).

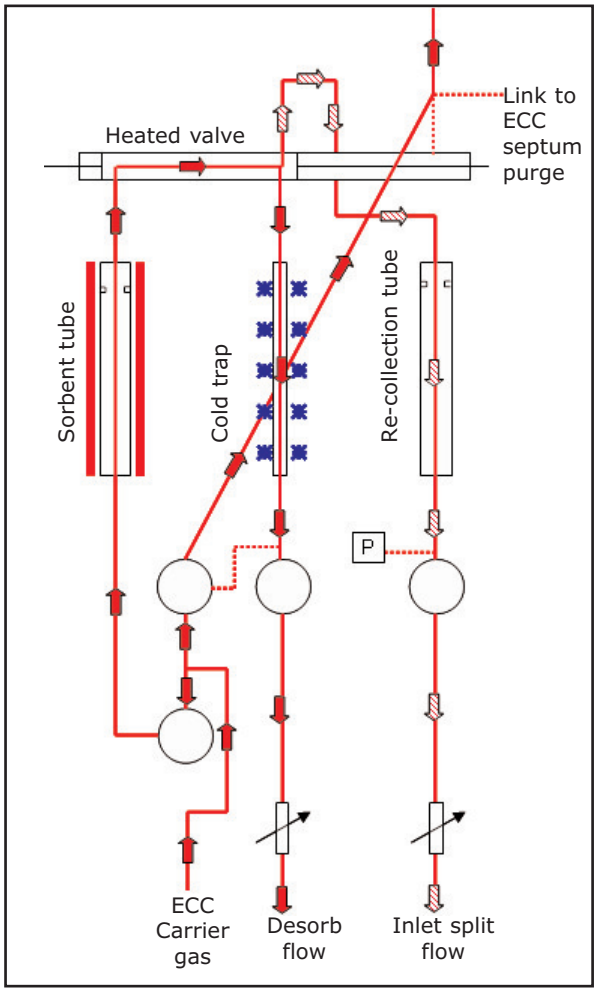

Figure 3a: UNITY TD system with ECC control, flow path during primary (tube) desorption

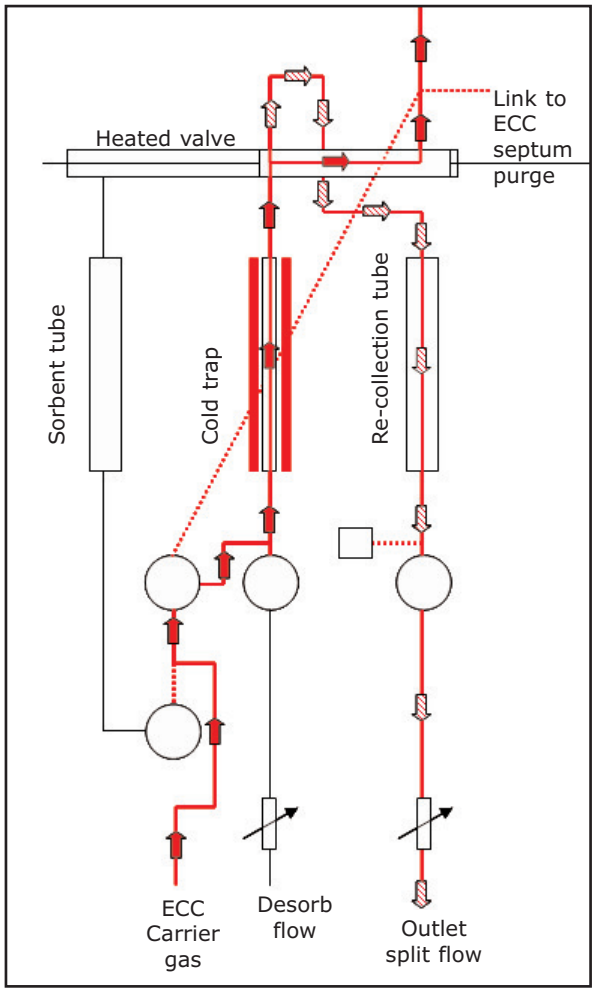

Figure 3b: UNITY TD system with ECC control, flow path during secondary (trap) desorption

Back-pressure regulated ECC (Figure 3) is the recommended carrier gas control configuration for Markes thermal desorbers and has the added advantage of being integrated with the GC/MS software. This allows access to the full range of ECC-based software enhancements available from leading GC/MS suppliers. (See TDTS 47 *The Analysis of Landfill Gas Compounds using Thermal Desorption GC/MS and a Retention Time Locked Database* and TDTS 66 *Improving the identification and measurement of trace odorous and toxic components during materials emissions testing.*)

Potential analytical impact of varying tube humidity/solvent levels

Residual solvent or exceptionally high humidity, in standard or sample tubes respectively, is much more likely to cause significant analytical discrimination than impedance variation. It is one of the most common causes of quantitative errors during measurement with thermal desorption – GC(/MS).

The issue can arise during inlet, outlet or double split methods. Even splitless desorption methods, though immune to split discrimination, can suffer from adverse chromatographic effects due to high solvent or water content, which can affect quantitation.

Tube	C 106 mass (mg)	Back-pressure (psi)			Flow during conditioning (mL/min)	TD split flows (mL/min)			Toluene peak area $\mu V.s^{-1}$ (TIC)
		Before conditioning	2 h conditioning	17 h conditioning		Inlet	Desorb	Outlet	
A	100	0.06	0.07	0.06	98	63.0	21.4	80.3	1086
B	100	0.03	0.04	0.03	110	62.8	21.3	81.0	1081
C	104	0.06	0.06	0.04	95	62.9	21.4	80.6	1084
D	101	0.04	0.06	0.03	92	62.8	21.7	82.0	1090
E	103	0.09	0.09	0.07	94	62.6	21.4	81.9	1087
F	100	0.03	0.04	0.03	105	62.3	21.4	81.8	1090
									1086 ± 4 mean±s.d.
G	531	0.25	0.26	0.25	30	62.5	21.3	80.7	822
H	528	0.22	0.25	0.23	31	62.7	21.6	80.8	842
I	529	0.22	0.25	0.23	31	62.4	21.3	81.4	792
J	526	0.22	0.25	0.23	31	62.2	21.3	81.9	792
K	527	0.23	0.25	0.23	30	62.2	21.3	82.2	784
L	527	0.23	0.25	0.23	30	62.6	21.3	81.9	770
									801 ± 27 mean±s.d.

Table 4: Recovery of ~20 µg toluene from TD-GC system, operating with inlet split and at 46.1 psi pressure. 26% lower recovery is observed for the higher impedance tubes due to solvent retention. (Toluene loaded from the liquid phase)

An example of discrimination due to variable solvent content is shown in Table 4 (reproduced from Report OMS/2002/15 with the kind permission of UK HSL.)

In this case, 5.0 µL of toluene solution in methanol (3.4 mg/mL) was introduced to tubes packed with two different masses (100 mg and 530 mg) of Chromosorb 106 sorbent, in a stream of carrier gas (50 mL/min). The analytical conditions used were the same as those used for analysis of the gas standard (see Table 3) in which no discrimination due to impedance variation was observed. The 26% reduction in data between tubes packed with 100 mg and those packed with 530 mg of Chromosorb 106 was thus purely due to the excess solvent retained by the tubes with the larger mass of sorbent. The difference in the two measurements is due to split discrimination caused by flash vaporisation of the retained solvent during desorption. As the solvent vaporises and expands this raises the gas pressure inside the TD flow path, temporarily increasing the split flow relative to the desorb and/or column flow. Analytes desorbing/eluting from the sorbent at the same time as the solvent will thus be subjected to a higher split flow/ratio than later eluting compounds.

Split discrimination of this kind has been extensively reported for all forms of flash vaporising GC injection. The optimum solutions are to programme or slow down the heating rate of the sorbent tube/trap (such that the solvent or water vaporises more slowly and without causing a pressure surge) and to minimise the mass of solvent/water retained. Markes thermal desorption systems are uniquely designed to minimise split discrimination due to differences in humidity/ solvent content between standards and sample tubes. Relevant features include:

- Automated on-and off-line options for dry purging of sample tubes, in the sampling direction. This helps reduce any differences in humidity content between the sorbent tubes in a sequence.
- The primary tube desorption oven, heats from ambient at ~3°C/sec at the start of tube desorption, to ensure gradual solvent /water vaporisation and to eliminate any risk of a pressure surge which might change the inlet split ratio. Note that the data shown in Table 4 was generated using a pre-heated tube desorption oven which is more prone to discrimination due to flash vaporisation.
- The option of inlet splitting, with quantitative re-collection for validation. In cases where analyte concentrations are sufficiently high to allow a moderate to high split (>20:1), the mass of water or solvent reaching the focusing trap can be significantly reduced by introducing a split on the inlet to the cold trap *i.e.* during primary (tube) desorption.
- The internal focusing trap of Markes thermal desorbers has been optimised for selective elimination of water/solvent to minimise risk of discrimination. Relative to older TD technology, the Markes trap contains an extended (60 mm) sorbent bed ensuring quantitative retention of target analytes without sub-ambient cooling. The 60 mm bed length of sorbent used in every Markes thermal desorber matches the maximum sorbent bed length used in industry standard sample tubes and allows the type and bed length of sorbents used in the focusing trap to replicate those used for air monitoring.

  While the I.D. of the focusing trap is much smaller than that of a sample tube (to ensure optimum desorption efficiency during capillary GC analysis) the volume of gas passing from the sample tube to the focusing trap during primary (tube) desorption (typically <500 mL) is invariably lower than that used for tube sampling (typically >5L). Therefore, any compound which can be quantitatively retained by the sample tube during air monitoring at ambient temperatures, can also be quantitatively retained by the focusing trap at ambient temperature. The advantage of this is that most volatile solvents and water can be selectively, but not completely, purged from sorbent tubes/traps at ambient temperature. In effect the extended sorbent bed of the Markes focusing trap thus introduces a second automated dry purge/solvent purge step allowing the mass of water/ solvent retained by the system to be reduced, typically by another order of magnitude.

This combination of TD features minimizes the risk of analytical discrimination due to variable masses of water/solvent in sample/standard tubes. Moreover this aspect of system design is complemented by the SecureTD-Q facility offered by Markes thermal desorbers. SecureTD-Q allows quantitative re-collection of both inlet and outlet split (manual or automated (100-tube) configurations available) allowing users to repeat analyses and validate the analytical data. Application of SecureTD-Q for thermal desorption method and data validation is described below.

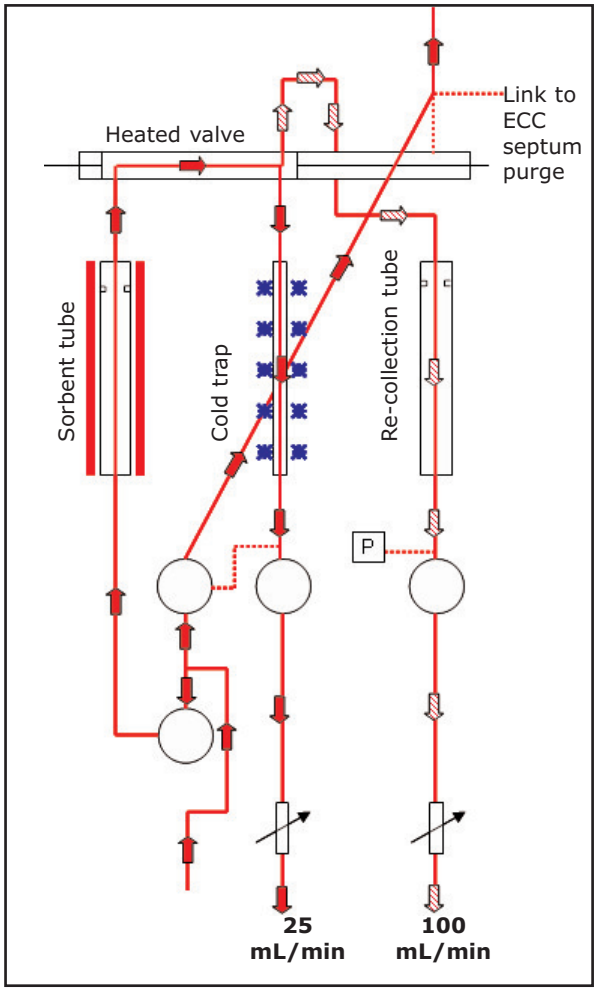

Figure 4a: Primary (tube) desorption showing gas flows for example 1

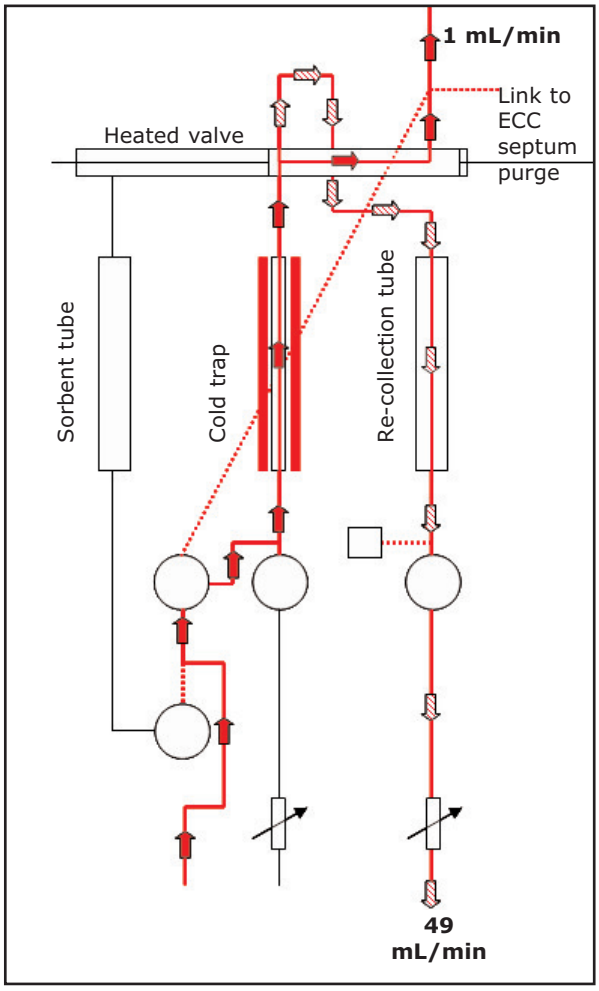

Figure 4b: Secondary (trap) desorption showing gas flows for example 1

Using SecureTD-Q to validate thermal desorption data

Pioneered by Markes International in 1998, quantitative re-collection of TD samples (SecureTD-Q) has set a new benchmark for analytical thermal desorption technology. SecureTD-Q is available on all Markes thermal desorption systems and allows repeat analysis and validation of TD methods/data (*e.g.* as referenced in international standard methods such as ASTM D6196-03). By facilitating quantitative re-collection of both inlet and outlet split flow, SecureTD-Q is ideal for evaluating thermal desorption analytical data for possible discrimination due to varying impedance or solvent/water levels. [Application of SecureTD-Q for TD method/data validation is explained in the associated Markes brochure.]

Quantitative re-collection of inlet split is essential as a test for discrimination due to tube impedance variation as this can only be an issue for inlet split methods (see above). Inlet split methods are also most susceptible to discrimination due to variable solvent/water levels. Application of SecureTD-Q as a validation tool in both cases is illustrated below with examples:

Example 1:

Using low impedance Certified Reference Standard (CRS) tubes packed with 200 mg Tenax for quality assurance of various types of field monitoring tube under the following TD analytical conditions:

Carrier pressure: 8 psi

Inlet split flow: Set to 100 mL/min

Desorb flow (trap flow during primary (tube) desorption): Set to 25 mL/min

Outlet split flow: Set to 49 mL/min

Column flow: 1 mL/min

Re-collection tube: 200 mg of conditioned Tenax

The desorption process is illustrated in Figure 4.

Split ratios:

Inlet split:	25/125 = 1/5
Outlet split:	1/50
Total split:	1/250

Primary and *repeat* analyses *of a* ***low impedance (Tenax) tube*** *containing 10 µg each of toluene and n-C_{12}*

Primary analysis:

Amount of toluene & n-C12 reaching focusing trap	**2 µg** (1/5 inlet split)
Amount of toluene & n-C12 re-collected during tube desorption	**8 µg**
Amount of toluene & n-C12 reaching analytical column & detector	**40 ng** (1/50 outlet split)
Amount of toluene & n-C12 re-collected during trap desorption	**1.96 µg**
Total amount of each compound re-collected	**9.96 µg**

Repeat analysis (i.e. analysis of the re-collected sample):

Amount of toluene & n-C12 reaching focusing trap	**1.99 µg** (1/5 inlet split)
Amount of toluene & n-C12 re-collected during tube desorption	**7.97 µg**
Amount of toluene & n-C12 reaching analytical column & detector	**39.8 ng** (1/50 outlet split)
Amount of toluene & n-C12 re-collected during trap desorption	**1.95 µg**
Total amount of each compound re-collected	**9.92 µg**

Note that analytical data from the re-collected sample is almost identical (99.6%) to data from the primary analysis for both compounds reflecting the expected split ratios and indicating no discrimination/loss.

However, if the analysis of **high impedance,** multi-sorbent tubes, using these analytical conditions, gave an effective inlet split ratio of **1/5.5** rather than the expected **1/5**, the results of the primary (original sample) and secondary (re-collected sample) analysis, would be as follows:

Primary and repeat analyses of a ***high impedance tube*** *containing 10 µg each of toluene and n-C_{12}*

Primary analysis:

Amount of toluene & n-C12 reaching focusing trap	**1.82 µg** (1/5.5 inlet split)
Amount of toluene & n-C12 re-collected during tube desorption	**8.18 µg**
Amount of toluene & n-C12 reaching analytical column & detector	**36.4 ng** (1/50 outlet split)
Amount of toluene & n-C12 re-collected during trap desorption	**1.78 µg**
Total amount of each compound re-collected	**9.96 µg**

Repeat analysis (using a low impedance Tenax re-collection tube):

Amount of toluene & n-C12 reaching focusing trap	**1.99 µg** (1/5 inlet split)
Amount of toluene & n-C12 re-collected during tube desorption	**7.97 µg**
Amount of toluene & n-C12 reaching analytical column & detector	**39.9 ng** (1/50 outlet split)
Amount of toluene & n-C12 re-collected during trap desorption	**1.95 µg**
Total amount of each compound re-collected	**9.92 µg**

Note that, in this case, results from the primary analysis (with 36.4 ng of each compound reaching the column and detector) are lower than those from the repeat analysis (with 39.9 ng of each compound reaching the column and detector), thus clearly indicating that discrimination had occured in the primary analysis. Moreover, the uniformity of the discrimination across the volatility range points to impedance rather than flash vaporisation of water/solvent as the primary cause.

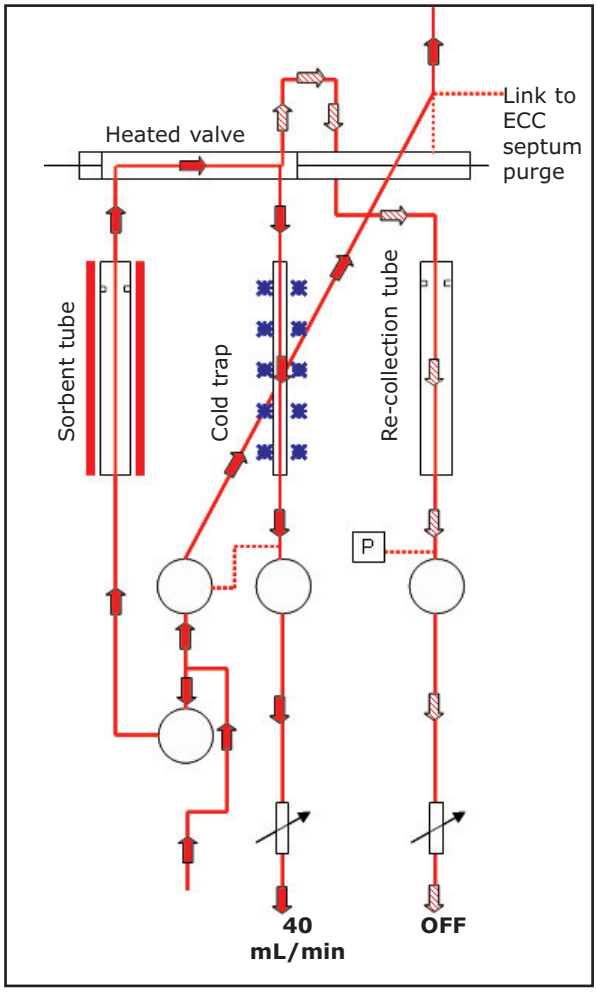

Figure 5a: Primary (tube) desorption showing gas flows for example 2

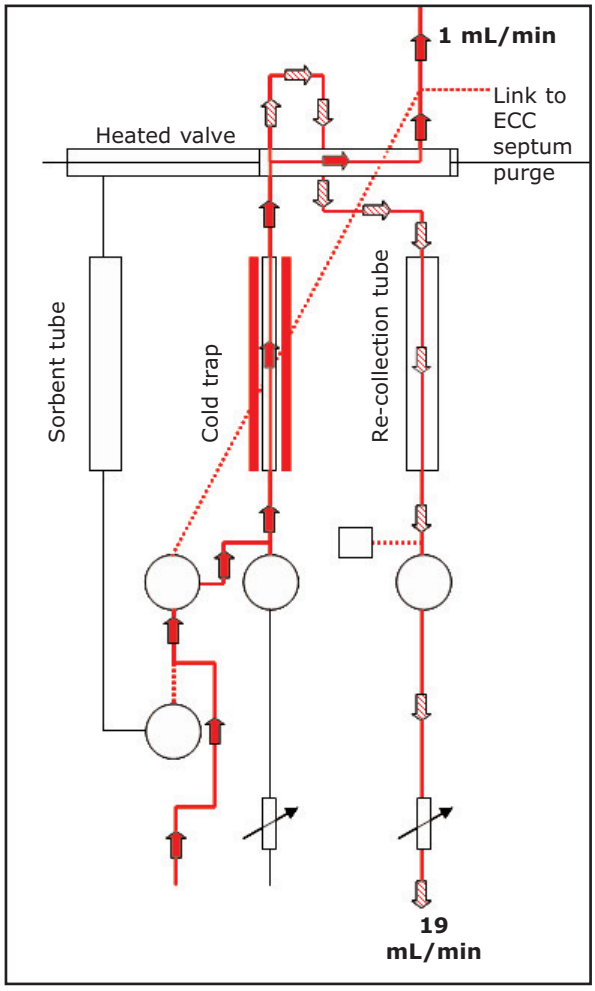

Figure 5b: Secondary (trap) desorption showing gas flows for example 2

Example 2:

Using a dry (and solvent-free) standard to calibrate a field sample tube containing 1 mg of water under the following TD analytical conditions:

Carrier pressure: 15 psi,

Inlet split: Flow off

Desorb flow (trap flow during primary (tube) desorption): Set to 40 mL/min

Focusing trap temperature: Set below 0°C

Outlet split flow: Set to 19 mL/min

Column flow: 1 mL/min

Re-collection tube: 200 mg of conditioned Tenax

The desorption process is illustrated in Figure 5.

Split ratios:

Outlet split:	1/20
Total split:	1/20

*Primary and repeat analyses of a **dry standard tube** containing 1 µg each of toluene and n-C_{12}*

Primary analysis:

Amount of toluene & n-C12 reaching focusing trap	**1 µg** (No inlet split)
Amount of toluene & n-C12 reaching analytical column & detector	**50 ng** (1/20 outlet split)
Amount of toluene & n-C12 re-collected during trap desorption	**0.95 µg**
Total amount of each compound re-collected	**950 ng**

Repeat analysis (i.e. analysis of the re-collected sample):

Amount of toluene & n-C_{12} reaching focusing trap	**950 ng** (No inlet split)
Amount of toluene & n-C_{12} reaching analytical column & detector	**47.5 ng** (1/50 outlet split)
Amount of toluene & n-C_{12} re-collected during trap desorption	**902.5 ng**
Total amount of each compound re-collected	**902.5 ng**

Note that, as expected, analytical data from the re-collected sample is 5% lower than the primary analysis for both compounds reflecting the expected split ratio and indicating no discrimination/ loss.

However, if the analysis of tubes containing 1 mg of water produced an immediate pressure surge, under these analytical conditions, giving an effective split ratio of **1/28** rather than the expected **1/20** during the early stages of secondary (focusing trap) desorption, the results of the primary (original sample) and secondary (re-collected sample) analyses, would be as follows:

*Primary and repeat analyses of a **tube containing 1 mg of water** and 1 µg each of toluene and n-C_{12}*

Primary analysis:

Amount of toluene & n-C_{12} reaching focusing trap	**1 µg** (No inlet split)
Amount of toluene reaching analytical column & detector	**35.7 ng** (1/28 outlet split)
Amount of n-C_{12} reaching analytical column & detector	**50 ng** (1/20 outlet split)
Amount of toluene re-collected during trap desorption	**964.3 ng**
Amount of n-C_{12} re-collected during trap desorption	**950 ng**

Repeat analysis (N.B. water will be purged from the re-collection tube during re-collection thus the re-collected sample will be dry):

Amount of toluene reaching focusing trap	**964.3 ng** (No inlet split)
Amount of n-C_{12} reaching focusing trap	**950 ng** (No inlet split)
Amount of toluene reaching analytical column & detector	**48.2 ng** (1/20 outlet split)
Amount of toluene re-collected during trap desorption	**916.1 ng**
Amount of n-C_{12} reaching analytical column & detector	**47.5 ng** (1/20 outlet split)
Amount of n-C_{12} re-collected during trap desorption	**902.5 ng**

Note that, in this case, results from the primary analysis of toluene (35.7 ng) were lower than the repeat (48.2 ng) indicating discrimination, but that primary and repeat analysis data for n-C_{12} (50 & 47.5 ng respectively) were as expected. This indicates that the discrimination was not uniform across the volatility range. Data showing lower than expected primary analysis results for more volatile compounds, but with expected recovery of less volatile compounds indicates discrimination caused by the pressure surge of flash vaporisation of solvent/water. This would be most simply addressed by resetting the focusing trap temperature to +30°C, allowing water to be selectively purged from the system during primary (tube) desorption.

Note that if an analysis, such as that described in example 2, was carried out with higher analyte levels (*i.e.* requiring both inlet and outlet split) and using a desorber that operated with a pre-heated oven; risk of flash vaporisation could effect BOTH the inlet and outlet split. The precautionary steps described above for minimising residual water/solvent levels should be implemented and quantitative, re-collection of both inlet and outlet split would be required to demonstrate that no discrimination had occured in either phase of TD operation.

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.