TDTS 7

Calibration: Preparing and introducing thermal desorption standards using sorbent tubes

Introduction

When calibrating any piece of analytical equipment, it is important that the loading and analysis of standards replicates, as closely as possible, that of the samples themselves. For this reason a thermal desorption–gas chromatography (TD–GC) system should be calibrated by loading the standard onto a sample tube and desorbing it through the system, so that it is subjected to the complete two-stage thermal desorption process.

Internal standard (IS) addition to tubes is also possible, giving greater precision. The IS can be added either manually or, for automated TD, using the internal standard dry purge (ISDP) accessory.

Introducing standards to sorbent tubes in the vapour phase

This method is considered to be optimum for air monitoring applications where analytes are sampled in the vapour phase. Markes' Calibration Solution Loading Rig (CSLR™) was specifically designed for this purpose (Figure 1).

The CSLR consists of an injection port with a controlled carrier gas supply and a sorbent tube connection. The sampling (typically grooved) end of a packed sorbent tube is connected into the port with a ¼″ brass nut and PTFE ferrule.

The carrier gas flow is set, with a needle valve, to 50–100 mL/min, and this sweeps the injection port and passes down through the sorbent tube to vent. The calibration solution or gas standard is introduced through the injector septum in the normal fashion. Liquid standards vaporise in the flow of gas, and analytes reach the sorbent bed in the vapour phase.

A sufficient volume of carrier gas is then allowed to pass through the tube such that most of the carrier solvent (if applicable) passes through the sorbent bed and is eliminated, whilst the compounds of interest are quantitatively retained.

Criteria for using the CSLR

When using the CSLR, it is important to bear in mind that the analytical system is being calibrated for *trace* amounts of the compounds of interest. The following points are assumed:

- Good laboratory practice is followed with respect to solvent purity (if required) and syringe use/cleanliness
- The tubes onto which the solution is to be loaded have been thoroughly conditioned and their blanks verified
- The carrier gas is of high purity and contains negligible levels of VOCs.

It is recommended that the gas line is constructed of solvent-rinsed ⅛″ refrigeration-grade copper tubing, connected using approved swage-type fittings. The gas supply should be positioned close to the CSLR, so that the gas line is as short as possible. A high-quality, stainless-steel-diaphragm cylinder head regulator should be used, which is capable of delivering gas pressures between about 10 and 60 psi (higher pressures are not recommended).

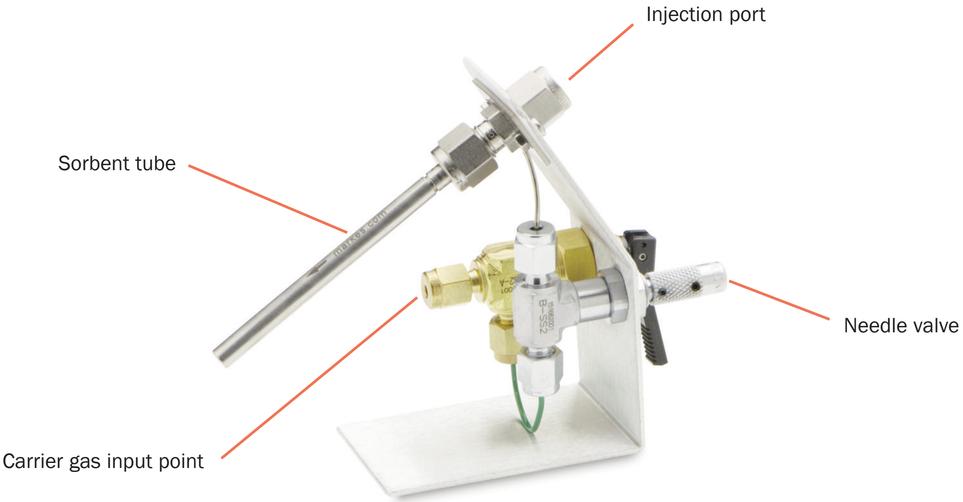

Figure 1: Markes' Calibration Solution Loading Rig (CSLR).

The carrier gas for the CSLR can be nitrogen or helium; 5.0 grade (*i.e.* 99.999% purity) or higher is recommended in each case. A high-capacity hydrocarbon filter in the carrier gas line is also recommended.

If liquid standards are being prepared, the solvent used must be at least of chromatographic grade, with negligible VOC impurities. As a check of solvent purity, it is recommended that the operational procedure is initially carried out using an injection of pure solvent. Any VOC impurities that could interfere with the calibration will be thus be retained on the sorbent tube.

Where possible, select a solvent for liquid standards that will be unretained by the sorbent in the tube, so that it can be swept to vent in the flow of carrier gas while target analytes are quantitatively retained. Examples include methanol or acetone with Tenax®. See the Appendix for further information.

Select the correct sorbent for the components of interest and pack the tube with the same mass of sorbent as used for routine monitoring, *e.g.* 200 mg Tenax TA for aromatics such as benzene, toluene and xylene (see Application Notes TDTS 5 and TDTS 20 for more information on sorbent selection).

Operation

A clean, conditioned tube is inserted into the CSLR with the sampling (typically grooved) end going into the ¼″ brass nut and PTFE ferrule, which is tightened.

The carrier gas supply to the sorbent tube is switched on and adjusted to give a flow of 50–100 mL/min through the tube.

For gas standards: Select an appropriately sized gas syringe so that the mass of analytes introduced in the standard match the approximate masses that will be collected during field monitoring. For example, 1 mL of a 1 ppm standard can be used to calibrate 1 L air samples at ~1 ppb. Simply withdraw the volume of gas standard required into the gas syringe and inject through the septum of the CSLR into the stream of carrier gas. Leave the sorbent tube attached to the CSLR for ~5 min.

For liquid standards: Prepare the standard solution so that the mass of analyte(s) introduced in the injection matches the masses expected during field monitoring (see below for more information). Having loaded the syringe with the required volume of solution (typically 1–5 µL), push it gently through the septum until it touches the retaining gauze in the tube. The syringe is then retracted by ~1 mm and the calibration standard is injected. The syringe is then pushed in again gently to touch the gauze, before removal. The solution vaporises in the carrier gas flow and is passed onto the sorbent tube in the vapour phase.

A sufficient volume of carrier gas is allowed to pass through the tube so that most of the carrier solvent (*e.g.* methanol) passes through the sorbent bed, while the compounds of interest are quantitatively retained (see Appendix).

Remove and analyse the loaded tube as for a normal sample.

Notes

1. Gas standards are preferred for volatile compounds.
2. If the compounds of interest are volatile and not available as a gas standard, the solvent may not be readily separated from them. It may also be difficult to selectively purge the solvent if the tube is packed with two or more sorbents of increasing strength. Whenever liquid standards are used and it is NOT possible to selectively purge the solvent, low injection volumes (<1 µL) should be used.
3. If using only Tenax TA in the sorbent tubes, injection volumes up to 5 µL can be used, provided the solvent is purged from the tube prior to analysis.

Calculating the expected sample mass

A typical multilevel calibration procedure requires at least three (and preferably five) standard solutions, with the mid-concentration standard being selected so that the masses of analytes introduced to a tube are comparable to those found in real samples. At least one standard at a lower level (*e.g.* $^1/_{10}$ of the expected level) and one at a higher level (*e.g.* twice the expected level) are also required. It is therefore necessary to calculate approximately what mass of analyte is expected in a typical sample (if the expected atmospheric concentration is unknown, then assume it will be $^1/_{10}$ of the recommended limit level).

Once the required analyte mass is known, the concentration of the standard solutions can be calculated. This is best illustrated by the following examples:

Example 1: Diffusive air monitoring for toluene

Information required:

Expected atmospheric concentration: C
Sampling time: T
Diffusive uptake rate: U

Example:
$C = 1$ ppm
$T = 8$ h (480 min)
$U = 1.67$ ng ppm^{-1} min^{-1}

Calculation: U = ng adsorbed onto tube/CT

$$\therefore \text{ ng adsorbed onto tube} = UCT = 1.67 \times 1 \times 480 = 801.6$$

In this case, the mid-range standard concentration should be set so that 800 ng of toluene are introduced in a single 1–5 µL injection. The lower-level standard would typically be set to introduce 200 ng and the higher standard set to introduce 2000 ng.

Example 2: Pumped air monitoring for n-heptane

Information required:

Expected atmospheric concentration: C
Volume of air to be collected: V
Molecular weight of component: M

Example:
$C = 100$ ppb
$V = 10$ L
$M = 100$ g/mol

Calculation:

1 mole of vapour at 20°C and atmospheric pressure occupies ~24 L.

∴ 24 L of n-heptane vapour at 20°C and atmospheric pressure would weigh ~100 g

∴ 24 L of air with 100 ppb n-heptane contains 10 µg of analyte

∴ 10 L of air with 100 ppb heptane contains $^{10}/_{24}$ × 10 µg = 4.17 µg of analyte

In this case, the mid-range standard concentration should be set so that 4 µg of toluene are introduced in a single 1–5 µL injection. The lower-level standard would typically be set to introduce 1 µg and the higher standard set to introduce 10 µg.

Example 3: Solid sampling for residual acetone

Information required:

Expected concentration (w/w):	*C*
Typical mass sampled:	*M*

Example: *C* = 1% (w/w)
M = 20 mg

Calculation:

1% of 20 mg = 0.2 mg = 200 µg

In this case, the mid-range standard concentration should be set so that 200 µg of toluene are introduced in a single 1–5 µL injection. The lower-level standard would typically be set to introduce 50 µg and the higher standard set to introduce 500 µg.

More information on calibration can be found in various national and international standard methods (see Application Note TDTS 3).

Internal standard (IS) addition

External standards allow you to calculate what mass a particular peak area represents. Internal standards allow you to account for any variability from sample to sample, giving improved precision.

An example of the benefits of IS addition would be accounting for varying detector response (*e.g.* as the MS becomes dirty), which would otherwise go unnoticed, leading to lower concentrations being reported. It is also possible to load ISs onto tubes prior to transport and sampling at a remote site, which can account for any losses during transport/handling.

The IS is usually gas-phase, and can contain one or several compounds. The compound(s) chosen should be similar to the compounds of interest, but not present in the sample (*e.g.* deuterated toluene for BTX-type analysis). Ideally, they should also not co-elute with other compounds of interest.

The IS concentration should be selected so it is close to the expected real sample concentration levels, so peak area(s) can be easily integrated.

Manually loading the IS onto the tubes is achieved using the CSLR as described previously, either for liquid or gas standards. The automatic loading of ISs during an autosampler sequence requires the ISDP accessory to be fitted to either an ULTRA™ or ULTRA 50:50, and is only compatible with gas standards. Prior to desorption, the gas-phase IS is introduced through a 1 mL loop onto the sampling end of the sorbent tube, in a stream of carrier gas. Further information is available in the ULTRA (50:50) ISDP manual.

Quality assurance and calibration

Maintaining the analytical quality of the results obtained from the complete analytical system (TD–GC(MS)–software) requires:

Internal Quality Control (IQC), which monitors the day-to-day consistency of the analytical system and routine calibration procedures, using quality control samples within the laboratory.

External Quality Assessment (EQA), also known as Proficiency Testing (PT), which is a system for objectively assessing laboratory results using an external agency.

The analysis of Certified Reference Standard (CRS) tubes for TD–GC provides a measure of both IQC and EQA. In general, however, participation in an external EQA scheme is also recommended.

CRS tubes

CRS tubes for thermal desorption consist of freshly packed, stringently conditioned sorbent tubes preloaded with a certified mass of analyte(s) and capped for long-term storage. They are designed for analytical quality assurance as described in international standards.

Two CRS tubes for routine use are available from Markes:

- Benzene, toluene and *o*-xylene, containing 1 µg of each component (occupational hygiene levels)
- Benzene, toluene and *o*-xylene, containing 25 ng of each component (ambient air/environmental levels)

Custom CRS tubes containing up to six VOCs can also be prepared to your specification.

All analyte masses are traceable to primary standards, and each package includes a certification document, shipping blank and user instructions.

EQA schemes

Participation in an EQA scheme will provide information, over a period of time, as to how a laboratory performs in relation to others. Many schemes also offer access to technical advice, which may help if the laboratory experiences problems with a particular analytical method.

The most widely used international EQA scheme for TD–GC is the Workplace Analysis Scheme for Proficiency (WASP), coordinated by the UK Health & Safety Executive. Standard ¼″ o.d. thermal desorption tubes are packed with Tenax and loaded with benzene, toluene and *m*-xylene ready for thermal desorption analysis. Samples are sent out quarterly.

Further information can be obtained from the Health & Safety Laboratory: http://www.hsl.gov.uk/centres-of-excellence/proficiency-testing-schemes.aspx.

A TD-related standard is also available from the European standards agency: S. Vandendriessche and B. Griepink, The certification of benzene, toluene and *m*-xylene sorbed on Tenax in tubes: CRM 112 (Report EUR 12308 EN), 1989. This is summarised in: S. Vandendriessche *et al.*, *Analyst*, 1991, 116: 437–441 (DOI: 10.1039/AN9911600437).

Certified Reference Material (CRM) 112 (benzene, toluene and *m*-xylene on Tenax TA) is available in the UK through LGC Standards: http://www.lgcstandards.com/home/home_en.aspx.

Trademarks

CSLR™ and Ultra™ are trademarks of Markes International Ltd, UK.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

Appendix

Component	Breakthrough volume (L)	Component	Breakthrough volume (L)
Acetone	1.2	n-Hexane	6.4
Benzene	12.5	Hexan-2-one	200
Butan-1-ol	10	Methanol	0.07
Butan-2-ol	5.6	Methoxyethanol	6
Butan-2-one	6.4	Methoxypropanol	27
Butoxyethanol	70	4-Methylpentan-2-one	52
Carbon tetrachloride	12.4	Naphthalene	20000
Chloroform	3.8	Pentane	1
1,4-Dichlorobenzene	580	Styrene	300
1,2-Dichloroethane	10.8	Tetrachloroethane	220
1,1-Dichloroethene	0.84	Tetrachloroethene	96
Dichloromethane	0.9	Toluene	76
Ethanol	0.36	1,1,1-Trichloroethane	2.2
Ethoxyethanol	10	1,1,2-Trichloroethane	68
Ethoxyethyl acetate	30	Trichloroethene	11.2
Ethyl acetate	7.2	Trimethylbenzene	3600
Ethylbenzene	280	Xylene	600

Table A1: Breakthrough volumes of some typical VOCs/solvents on a sorbent tube packed with 200 mg Tenax TA.

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