

Application Note 007

Preparing and introducing standards using thermal desorption tubes

Introduction

Calibration and quality control are integral to any quantitative analytical method, and it is important that the loading and analysis of calibration standards replicates, as closely as possible, those of the samples themselves. For this reason, tube-based thermal desorption-gas chromatography (TD-GC) systems should be calibrated by loading standards onto sample tubes and desorbing them through the complete two-stage TD process.

There are two types of standards for tube-based TD:

- **Calibration standards** are used to calibrate the instrument across a concentration range and allow you to calculate what mass a particular peak area represents.
- **Internal standards** (ISs) allow you to account for instrument variability over time, such as changes in detector response, giving improved precision and accuracy.

This application note explores the use of both types of standards.

Calibration standards

The calibration standard used can either be in the liquid or gas phase – each has its advantages.

Liquid-phase standards are used for volatile and semi-volatile compounds and are prepared *via* serial dilutions. The same injection volume should be used for all injections in a multi-level calibration series so that each tube is subjected to the same purging to remove the solvent before analysis. Typically, 0.5–1 μL of a liquid standard is injected, with 1 μL being the recommended maximum injection volume. This method is usually cost-effective, but preparation and loading can be time-consuming.

Gas-phase standards are typically used for very volatile compounds, which cannot be loaded in the liquid phase due to their high vapour pressure at standard temperature and pressure. Loading standards in the liquid phase requires selective purging of the solvent without loss of analytes, which relies on the solvent being less retained on the sorbent than the target analytes. This is often not possible when working with very volatile compounds, so gas-phase standards are required. These standards can be more expensive to purchase but speed up laboratory workflows, as they often do not require dilution and require less purging during loading onto the sorbent tube.

Introducing standards to sorbent tubes

Loading standards in the vapour phase is considered optimal for TD applications as it replicates real-world samples as closely as possible.

Markes' Calibration Solution Loading Rig (CSLR™) (Figure 1) has been designed specifically for loading sorbent tubes with gas- or liquid-phase standards, and complies with key TD standard methods such as ISO 16017, US EPA Method TO-17 and ASTM D6196.



Figure 1: The Calibration Solution Loading Rig (CSLR™).

Checklist for calibration

- How volatile are the analytes?
 - Very volatile – consider using gas-phase standards.
 - Volatile – consider using liquid-phase standards.
- What are the breakthrough volumes of the analytes on the sorbent?
 - Higher volume = better retention.
- What is the breakthrough volume of the solvent on the sorbent?
 - Lower volume = easier to remove.
- The maximum volume of the syringe should match the volume of the sample being injected, to ensure increased precision and accuracy.
- Any solvents used should be of chromatographic grade.
- Carrier gas can be nitrogen or helium, and must be 5.0 grade or higher.

See Application Note 020 for a list of breakthrough volumes.

The device consists of a flow path constructed of stainless steel and an unheated injector port with a controllable carrier gas supply. The sampling end of a packed sorbent tube is connected to the CSLR by a ¼" brass nut and PTFE ferrule (Figure 2).

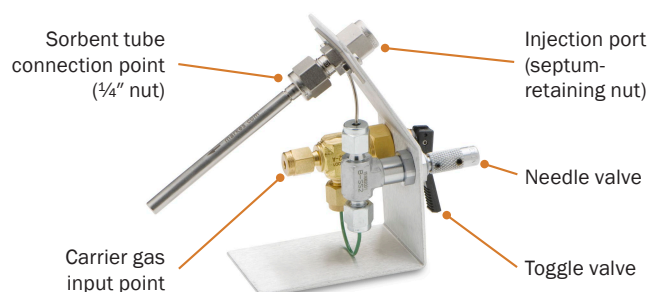


Figure 2: CSLR connections.

A carrier gas of choice, typically nitrogen, sweeps the injector port and passes through the sorbent tube to vent. The carrier gas flow is adjusted with an in-built needle valve and is normally set between 50 and 100 mL/min.

Then the calibration standard (gas or liquid phase) is drawn into a syringe and injected through the septum in the injector port into the stream of carrier gas and onto the sampling end of the attached tube. Liquid standards of volatile organic compounds (VOCs) vaporise in the flow of gas, enabling the solvent and analytes to reach the sorbent bed in the vapour phase. A sufficient volume of carrier gas is then passed through the tube, such that most of the solvent (if applicable) passes through the sorbent bed and is eliminated, whilst the compounds of interest are quantitatively retained.

After the required purge time, the gas flow is turned off using the toggle valve, and the tube is removed for analysis.

After loading, each calibration tube should be capped with brass storage caps (or with DiffLok™ caps if using an automated system), and analysed within a few days.

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 therefore assumed:

- Good laboratory practice is followed with respect to solvent purity (if solvent is required) and syringe use/cleanliness.
- The tubes onto which the standard is to be loaded have been thoroughly conditioned and their blanks verified.
- The carrier gas is of high purity – 5.0 grade (i.e. 99.999% purity) or higher – and contains negligible levels of VOCs.

Other factors to take into account when using the CSLR are:

- **Choosing the appropriate sorbent tube** – Select the correct sorbent for the analytes of interest, and ideally use this tube for both the calibration and sampling. Advice on sorbent selection can be found in Application Notes 005 and 020.

- **Selecting the solvent (liquid standards only)** – Where possible, select a solvent that will be unretained by the sorbent in the tube (or at the very least, one that has a very low breakthrough volume), so that it can be swept to vent in the flow of carrier gas while target components are quantitatively retained. Examples include methanol or acetone with Tenax®. See the Appendix for further information.
- **Setting the purge flow rate** – The carrier gas flow rate through the CSLR should be set between 20–100 mL/min (100 mL/min is often used to save time). Remember to check the breakthrough volume of the target analytes when selecting purge flow rates.
- **Selecting the purge time** – The purge time required will depend on the solvent used as well as the sorbent-analyte combination. Typical purge times are 3–5 minutes. As a rule, gas-phase standards generally require less purging than liquid standards, because the analytes are already in the gas phase and there is no need to remove solvent. However, as with the purge flow rate, it is important to consider breakthrough volumes of target analytes when setting the purge time.

Example: Using parameters of 100 mL/min for 3 minutes means that 300 mL will be purged through the tube. Therefore, the breakthrough volume for each analyte must be higher than 0.3 L, whilst the breakthrough volume for the solvent should, ideally, be lower than this value.

- **Confirming correct parameters** – Check for breakthrough when setting up the CSLR by connecting a second sorbent tube in series using a stainless-steel union (C-UNS10). Analyse the breakthrough tube and check for the analytes. If breakthrough has occurred during spiking, reduce the purge time and flow rate.

Tips for successful standard loading

- Gas standards are preferred for very volatile compounds to avoid solvent interferences.
- To inject an accurate volume, it is important to equilibrate gas syringes to atmospheric pressure.
- If the analytes of interest are very volatile and not available as a gas standard, try to find a solvent more volatile than the target analytes, otherwise it may not be possible to remove the solvent.
- If the tube is packed with two or more sorbents of increasing strength, consider the breakthrough volumes on all sorbent beds (see Application Note 020 for breakthrough volumes).
- Whenever liquid standards are used and it is not possible to selectively purge the solvent (for example when using strong sorbents), low injection volumes ($\leq 0.5 \mu\text{L}$) should be used.
- If adding multiple standards to a single tube, load the liquid standards containing the highest-boiling compounds first, and the gas standards and/or lightest components last.
- When performing a multi-level calibration series using liquid standards, the same injection volume should be used for all injections.

Choosing a concentration range for the calibration

A typical multi-level calibration procedure requires at least three concentrations (and preferably five or more). The mid-concentration standard should contain an amount that is as close as possible to the expected mass of analytes found in real samples. At least one standard should be at a lower level (e.g. $0.25 \times$ the expected level) and one at a higher level (e.g. $2.5 \times$ the expected level).

It is therefore necessary to calculate the approximate mass of the analyte expected in a typical sample. Once this is known, the concentration of the calibration solutions can be calculated, and the standards prepared.

If the expected atmospheric concentration is unknown, assume analytes will be present at one-tenth of the specified limit level. For example, if working to a method with an exposure limit of 0.5 ppb, you should assume analytes could be present at 0.05 ppb.

Once the required analyte mass is known, the concentrations 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:

$$U = \frac{\text{Mass adsorbed onto tube (ng)}}{CT}$$

$$\begin{aligned} \therefore \text{Mass adsorbed onto tube (ng)} &= UCT \\ &= 1.67 \times 1 \times 480 \\ &= 801.6 \text{ ng} \end{aligned}$$

In this case, the mid-range standard concentration should be set so that 800 ng of toluene is introduced in a single (e.g. 1 μ L) liquid injection. The lower-level standard would typically be set to introduce ($800 \times 0.25 =$) 200 ng and the higher standard set to introduce ($800 \times 2.5 =$) 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 (0.1 μ g/g)

$V = 10$ L

$M = 100$ g/mol

Calculation:

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

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

\therefore 24 L of air with 100 ppb n-heptane contains $0.1 \mu\text{g/g} \times 100 \text{ g} = 10 \mu\text{g}$ of analyte

\therefore 10 L of air with 100 ppb n-heptane contains $(10 \text{ L}/24 \text{ L}) \times 10 \mu\text{g} = 4.17 \mu\text{g}$ of analyte

In this case, the mid-range standard concentration should be set so that 4 μ g of toluene are introduced in a single liquid injection. The lower-level standard would typically be set to introduce ($4 \times 0.25 =$) 1 μ g and the higher standard set to introduce ($4 \times 2.5 =$) 10 μ g.

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 μ g

In this case, the mid-range standard concentration should be set so that 200 μ g of acetone are introduced in a single liquid injection. The lower-level standard would typically be set to introduce ($200 \times 0.25 =$) 50 μ g and the higher standard set to introduce ($200 \times 2.5 =$) 500 μ g.

More information on calibration can be found in various national and international standard methods (see Application Note 003).

Having calculated the masses required for each of the calibration points, the next step is to prepare a stock standard via serial dilution. A guide to calculating the required amount of analyte needed to create the stock solution can be found in the CSLR user manual.

Typically, 1 μ L of each solution is then injected onto individual tubes and run using the same analytical method. The responses from these points are used to create the calibration curve on the data handling system, from which the sample concentration can be determined. More detailed information on calculating atmospheric concentrations can be found in Application Note 025.

Preparing calibrations with gas standards

The majority of commercially available gas standards are supplied as 1 ppm or 100 ppb, so often do not require dilution. A calibration series is prepared by injecting different volumes of the standard; for example, to calibrate for 1 L samples between 0.5 and 25 ppb, it is possible to simply load between 5 mL (0.5 ppb equivalent) and 250 mL (25 ppb equivalent) of a 100-ppb standard.

Full step-by-step instructions for setting up and using the CSLR can be found in the user manual, and instructional videos can be found at the following locations:

- [How to introduce standards to sorbent tubes](#)
- [How to introduce gas standards to complement liquid standards](#)

Internal standard (IS) addition

Internal standards allow you to account for any variability from one sample injection to another, giving improved precision. An example of the benefits of IS addition during analysis would be accounting for varying detector responses (e.g. as the mass spectrometer 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.

Choosing the IS

The IS should ideally be in the 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. Deuterated versions of target analytes are usually the best choice as IS compounds.

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.

If the standard is not available in the gas phase, liquid standards can be used, which are manually loaded onto a sorbent tube using the CSLR as described previously. This method will also be required if you are using a manual TD instrument.

Automated IS addition

IS addition can also be an automated process. Markes' addition accessory features a 1 mL loop, which automatically introduces a gas-phase IS in one of three ways (Figure 3):

1. Onto a sampled tube prior to analysis for QC purposes.
2. Onto the focusing trap – ideal for direct desorption applications.
3. Onto blank tubes prior to shipping, which can then be used to monitor sample tube integrity during transport/handling and storage.

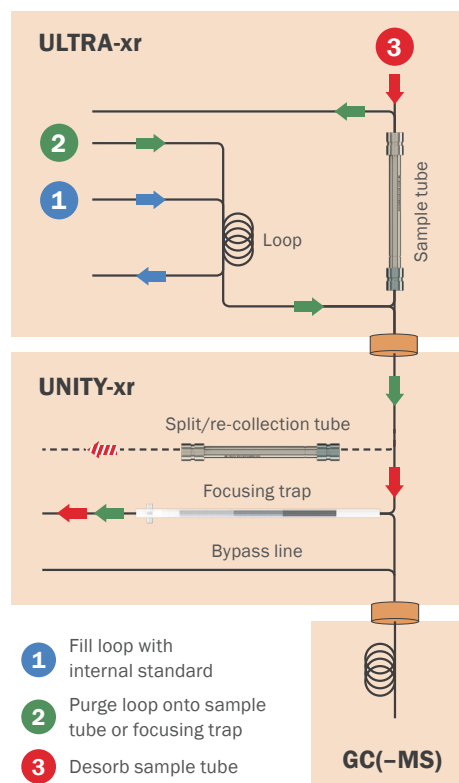


Figure 3: A 1 mL loop automatically introduces a gas-phase internal standard onto the sampling end of a sorbent tube prior to desorption (pictured are schematics of the inner workings of Markes' UNITY-xr™ thermal desorber and the ULTRA-xr™ high-throughput autosampler).

The standards used during analysis (points 1 and 2) and those used for checking the integrity of the sampling tube (point 3) should be different, so that you can quickly and easily identify where issues have arisen (if any).

The outlet pressure set on the IS cylinder regulator (gas standards are supplied in pressurised cylinders) will determine the effective volume of IS gas that is added to the tube or focusing trap. For example, if the IS is regulated to 15 psig, this is two times atmospheric pressure and so 2 mL of IS will be injected, and at 30 psig (three times atmospheric pressure), 3 mL will be added. It is important to remember that IS addition should be used for normalisation rather than quantitation, so it is generally not vital to know the exact amount of standard added, so long as it remains consistent.

Typically, the ratio of the response for the IS and the analytes are calculated and used to normalise results for minor deviations in instrument response between calibrations. The IS also provides an independent measure of instrument performance; many regulated/standard methods will specify a threshold deviation in IS response, beyond which an intervention is required, e.g. 30% for US EPA Method TO-17.

Further details on using the IS accessory, including attaching the pressurised cylinder and setting flow rates, can be found in the instrument user manuals.

Quality assurance and calibration

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

- **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.
- **Proficiency testing (PT)**, also known as external quality assessment (EQA), which is a procedure 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 internal quality control and external quality assessment. Furthermore, a selection of instrument check standards is available, which can support confirmation of good instrument performance. In general, however, participation in a PT scheme is also recommended. An overview of how each of these may be used to validate analytical performance is presented below.

Internal quality control (IQC)

CRS tubes

CRS tubes for TD 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, and are prepared in accordance with approved methodology (ISO 6145) and traceable to primary standards.

CRS tubes can be used routinely to provide continual quality assurance of system performance, and validation of correct calibration. There are two varieties of CRS tubes for routine use available from Markes:

- BTX tubes, containing benzene, toluene and o-xylene, loaded with 100 ng of each component (suitable for most environmental applications).
- TO-17 tubes, containing nine analytes typical of those found during air toxics monitoring, loaded with 100 ng of each component.

Custom CRS tubes containing up to eight VOCs may also be prepared to your specification, on discussion with Markes. Each package includes a certification document, shipping blank and user instructions.

Check standards

Troubleshooting and quality assurance of instrument/application performance may be achieved through the use of check standards. These are sorbent tubes loaded with nominal amounts of both routine and more challenging analytes, which are used to validate the optimised instrument

and analytical performance, and should not be used for instrument calibration. Check standards are currently available for instrument performance (C-CHK10) and for material emissions applications (C-CHK10-ME), with the latter being prepared in compliance with ISO 17025 for testing and calibration laboratories.

For more information or advice on any of these topics, please do not hesitate to contact our technical team at enquiries@markes.com.

Proficiency testing (PT) schemes

Participation in a PT scheme will provide information, over a period of time, on 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.

One of the most popular proficiency testing schemes for TD is the 'AIR PT' scheme. This scheme tests the performance of laboratories measuring exposure to hazardous chemical substances in ambient, indoor and workplace air environments using TD methods. Standard ¼" o.d. TD tubes are packed with Tenax and loaded with benzene, toluene and m-xylene ready for TD analysis. Samples are sent out quarterly.

The scheme was originally established in 1988 as the Workplace Analysis Scheme for Proficiency (WASP), and currently has more than 300 laboratory participants worldwide. It is operated by LGC Standards (which oversees management, registration, data analysis, publishing reports, membership and distribution), working in partnership with the UK Health & Safety Laboratory (which provides technical expertise, support, and produces the dynamically loaded TD tubes and filters).

For more information on the AIR PT scheme, please email customerservices@lgcpt.com.

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 EUR12308 EN), 1989. This is summarised in S. Vandendriessche et al., *Analyst*, 1991, 116: 437–441, <http://dx.doi.org/10.1039/AN991160043>.

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>.

Trademarks

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Appendix

Component	b.p. (°C)	Breakthrough volume (L) on 200 mg				
		Carbograph™ 2TD (Carbopack C)	Tenax TA	Tenax GR	Carbograph 1TD (Carbopack B)	SulfiCarb™ (Unicarb)
Hexane	69	0.3	6.4	1.3	16	3.9 × 10 ⁶
Methanol	65	Unretained	0.07	Unretained	Unretained	264
Acetone	56	—	1.2	0.7	—	—
Dichloromethane	40	—	0.9*	0.5	0.04	395
Chloroform	61	Unretained	3.8	1.2	0.2	—
1,1,1-Trichloroethane	74	Unretained	2.2	1.8	0.6	17600

Table A1: Breakthrough volumes of typical solvents on sorbent tubes packed with 200 mg of various sorbents. * Dichloromethane should not be used with Tenax TA, as this solvent degrades the sorbent. For more breakthrough volumes, please see Application Note O20.

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