Calibration and standards

Calibration is one of the most important considerations for any quantitative analysis, and Markes provides a wide range of standards and accessories to make TD calibration as easy as possible for busy labs. We supply everything from stand-alone tube loading rigs and internal standard addition accessories to audit and check-standards pre-loaded onto sorbent tubes.

Markes’ Application Notes TDTS 7 and TDTS 75pS present detailed technical advice on preparing sorbent tube standards and calibrating your thermal desorption system. Markes’ team of TD specialists is also always on hand to help you succeed.

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Standards and accessories for reliable and quantitative thermal desorption
Calibration Solution Loading Rig (CSLR™)

Key TD standard methods (e.g. ISO 16017 and US EPA Method TO-17) recommend that liquid- and gas-phase standards are loaded onto the sampling end of clean sorbent tubes in a stream of carrier gas using unheated apparatus.

Markes’ Calibration Solution Loading Rig (CSLR) has been specifically designed for loading sorbent tubes with gas- or liquid-phase standards. It has a flow-path constructed of stainless steel and consists of an unheated injector port with a controlled carrier gas supply. The sampling end of a packed sorbent tube is connected to the CSLR by a ¼" brass nut and PTFE ferrule.

The carrier gas flow is adjusted using a needle valve, and is normally set between 50 and 100 mL/min, according to standard methods. This sweeps the injection port and carries the standard into the sorbent tube. The calibration standard (gas or liquid phase) is introduced through the injector septum using an appropriate precision syringe. The compounds of interest are swept onto the sampling end of the attached tube in the stream of carrier gas, and reach the sorbent bed in the vapour phase.

Advice on routine calibration of TD methods is given in Markes’ Application Notes TDTS 7 and TDTS 75p 92.

Hints and tips

► Wherever possible, to simplify the analytical procedure, a sufficient volume of carrier gas is allowed to pass through the sorbent bed to remove the bulk of solvent (for liquid standards), while quantitatively retaining compounds of interest.

<table>
<thead>
<tr>
<th>Description</th>
<th>Part number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration Solution Loading Rig</td>
<td>C-CSLR</td>
</tr>
<tr>
<td>Septum, 9.5 mm (for CSLR), pk 10</td>
<td>C-SPTA</td>
</tr>
</tbody>
</table>

Liquid-phase external calibration

It is not always possible or convenient to introduce liquid standards in a stream of carrier gas as described above. In these cases, liquid standards can be injected directly onto the back of specially packed sorbent tubes (glass is recommended) containing a 1 cm bed of Tenax TA held in place by a 1 cm bed of quartz wool. See Application Note TDTS 7p 92 for more details.

Check-standards

Check-standards contain a range of routine and challenging analytes, and are useful when setting up instrumentation or troubleshooting. Markes supplies two types of check-standard, both prepared on conditioned Tenax TA sorbent tubes.

Instrumentation check-standards contain benzene, toluene, o-xylene, isobornyl methacrylate (IBMA) and dioctyl phthalate at a nominal concentration of 90 ng/µL for each component. A single check-standard is supplied with all Markes’ systems. Replacement check-standards are available in packs of 10.
Material emissions check-standards enhance validation and quality control for service and manufacturing labs using TD–GC(MS) to test chemical emissions from products and materials. The Tenax TA sorbent tubes are pre-loaded in the gas phase with a range of polar and non-polar VOCs ranging in volatility from C₆ (n-hexane) to C₁₆ (n-hexadecane), at a nominal loading of 100 ± 10 ng per compound. The standard complies with the ISO 17025 method for loading tubes (also in accordance with ISO 9001).

The material emissions check-standard contains:
- n-Hexane
- 4-Methylpentan-2-one
- Toluene
- n-Butyl acetate
- Cyclohexanone
- Phenol
- 1,2,3-Trimethylbenzene
- 4-Phenylcyclohexene
- n-Hexadecane

Note that all these compounds are included in the ‘Indoor air and material emissions’ proficiency testing scheme described below.

<table>
<thead>
<tr>
<th>Description</th>
<th>Part number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check-standard (BTX, isobutyl methacrylate (IBMA) and dioctyl phthalate), 90 ng/µL (nominal), Tenax TA, pk 10</td>
<td>C-CHK10</td>
</tr>
<tr>
<td>Check-standard (material emissions), 100 ng per tube (nominal), Tenax TA, pk 10</td>
<td>C-CHK10-ME</td>
</tr>
</tbody>
</table>

Do you participate in a Proficiency Testing scheme for TD?

As part of our service to customers, Markes likes to make thermal desorption users aware of complementary third-party services that could be of interest and benefit. Proficiency testing (PT) schemes are a case in point.

PT schemes for thermal desorption work by providing participating laboratories with spiked tubes for analysis. The tubes are analysed by these laboratories, preferably as part of their routine operation, and the results reported to the scheme organisers. The laboratories involved are then provided with a report showing how closely their results agree with the accepted values.

Regular participation in a proficiency-testing scheme:
- Provides a laboratory with an important independent insight into their performance
- Benchmarks laboratory performance against other scheme participants
- Allows laboratories to demonstrate commitment to measurement quality to regulatory agencies, accreditation bodies and laboratory customers.

The Workplace Analysis Scheme for Proficiency

One of the most popular PT schemes for thermal desorption is the Workplace Analysis Scheme for Proficiency (WASP). This tests the performance of laboratories measuring exposure to hazardous chemical substances in the ambient, indoor and workplace air environments using TD methods. The scheme was established in 1988, and currently has more than 200 laboratory participants worldwide. The WASP scheme is operated by the UK Health & Safety Laboratory, which oversees management, registration and membership, together with preparation and distribution of the spiked tubes, processing the participant data and providing reports.

WASP can offer the following useful PT analyte/sample combinations:

### Ambient air
- Testing environment: ISO 16017-1 & 2 and US EPA TO-17
- Analytes: BTEX
- Loading: 15–300 ng †

### Indoor air and material emissions
- Testing environment: ISO 16000-6
- Analytes: A range of 13 indoor-relevant (S)VOCs
- Loading: 50–300 ng

### Workplace air
- Testing environment: ISO 16017-1 & 2
- Analytes: BTEX
- Loading: 0.5–200 µg †

- Testing environment: ISO 16000-3
- Analyte: Formaldehyde
- Loading: 3–60 µg ‡

† Analytes provided together on a TD sorbent tube packed with Tenax TA. Test samples dynamically loaded from a standard atmosphere based upon procedures set out in ISO 6145-4.

‡ Glass fibre filter spiked with DNPH derivative. Note this requires HPLC, and is not compatible with TD–GC(MS) methods.

If you are interested in WASP, please contact the UK Health & Safety Laboratory on +44 (0)1298 218553 or proficiency.testing@hsl.gov.uk

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**T:** +44 (0)1443 230935 **T:** 886-483-5684 (USA toll-free)
### Certified reference standard (CRS) tubes

All analytical methodology is subject to performance criteria and quality assurance tests. Reference standards should be used at regular intervals for analytical quality assurance and to confirm routine calibration procedures.

CRS tubes offered by Markes International are prepared by an expert national standards laboratory following approved methodology (ISO 6145 parts 4 or 8, accredited to ISO 17025). They are certified traceable to primary standards. CRS tubes are prepared by introducing known concentrations of compounds into individually labeled sorbent tubes. Analyte masses are accurate to ±3% at levels above 100 ng, and at ±5% for masses from 10–100 ng.

Typically, CRS tubes are loaded with a small number of analytes that are representative of the method being undertaken. They provide a convenient tool for in-house quality assurance of the complete TD–GC(MS) analytical process and associated calibration protocols. Routine use of CRS tubes complies with guidance given in international standard methods and provides continual assurance of system and procedure reliability, thus contributing to staff confidence. In these respects, in-house use of CRS tubes complements participation in external proficiency testing schemes such as WASP p 45.

All CRS tubes are supplied in packs of 10 standards with an additional shipping blank. Standards are wrapped in aluminum foil and sealed into air-tight boxes prior to shipment. A chromatogram of the shipping blank is supplied, together with a certificate of standard traceability. BTX and TO-17 standards are supplied with an example chromatogram and full user instructions.

### BTX standards

BTX CRS tubes loaded with benzene, toluene and o-xylene are available either at 100 ng per component (suitable for the majority of environmental applications) or at 1 µg per component (suitable for many industrial air and material emissions applications). These standards are prepared using conditioned Tenax TA tubes and have a certified shelf-life of 6–12 months.

### TO-17 standard

A TO-17 CRS is available loaded with nine components of varying volatilities and polarities that are typical of the compounds found during air toxics monitoring. (N.B. This standard is prepared to order and typically has a longer lead time than the BTX standards.)

The compounds included are benzene, toluene, o-xylene, 1,2,4-trimethylbenzene, dichloromethane, 1,1,1-trichloroethane, methyl tert-butyl ether, methyl ethyl ketone and ethyl acetate. The required concentration of the standard can be specified. These standards are prepared on conditioned Tenax TA tubes and have a certified shelf-life of 6 months.

### Custom standards

If you require a special combination of components pre-loaded onto conditioned sorbent tubes, Markes also offers a custom CRS tube service. Up to eight components can be specified, with the sorbent typically being Tenax TA (although others are available). However, data must be available to demonstrate the stability of the compound/sorbent combination requested. If you require custom-specified CRS tubes, please discuss your requirements with a Markes specialist prior to ordering (enquiries@markes.com).

### Description of CRS tubes

<table>
<thead>
<tr>
<th>Description</th>
<th>Part number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRS (BTX), 100 ng, pk 10</td>
<td>C-BTX100-10</td>
</tr>
<tr>
<td>CRS (BTX), 1 µg, pk 10</td>
<td>C-BTX1UG-10</td>
</tr>
<tr>
<td>CRS (TO-17), specify concentration, pk 10</td>
<td>C-TO17XX-10</td>
</tr>
<tr>
<td>CRS (custom), pk 10</td>
<td>C-CUST-10</td>
</tr>
<tr>
<td>CRS (custom), pk 20</td>
<td>C-CUST-20</td>
</tr>
<tr>
<td>CRS (custom), pk 40</td>
<td>C-CUST-40</td>
</tr>
</tbody>
</table>

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1. Prior to March 2008, TO-17 CRS standards included butan-1-ol. New data shows that this component is not stable over the shelf-life of the CRS, and therefore it is no longer included in the standard.
Internal standards

Many TD air monitoring methods (tube- or canister-based) benefit from the addition of a gas-phase internal standard (IS). Markes provides the option of IS addition capability on all automated TD configurations, whether tube- or canister-based – see the relevant sections on ULTRA autosamplers, TD-100 systems and CIA Advantage systems for more details.

Hints and tips

► Selection of the optimum IS gas depends on the application. Typical internal standard compounds include deuterated hydrocarbons (e.g. toluene-d8) and halogenated compounds (such as bromofluorobenzene).
► The internal standard gas should be supplied in a pressurised cylinder fitted with a high-purity regulator capable of supplying standard to the TD system at pressures up to 50 psig.
► The concentration of internal standard required depends on the expected concentration of the analytes. As a general rule-of-thumb:
  • If the expected mass of analyte on the tube is about a nanogram, then a 1 ppmv internal standard is suggested
  • If the expected mass of analyte on the tube is about a picogram, then a 1 ppbv internal standard is suggested.

Markes offers a 1 ppm IS gas containing four halogenated/deuterated compounds (in bulk nitrogen), suitable for use with US EPA Methods TO-14/TO-15/TO-17 and other TD–GC/MS applications:

<table>
<thead>
<tr>
<th>Compounds (in N2)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromochloromethane</td>
<td>1-Bromo-4-fluorobenzene</td>
</tr>
<tr>
<td>Chlorobenzene-d5</td>
<td>1,4-Difluorobenzene</td>
</tr>
<tr>
<td>Cylinder</td>
<td>Aluminium construction (8.3 cm × 29.5 cm) Pl-marked for compliance with EU regulations and US DOT specifications 3AL2216 2.2 lb/1 kg</td>
</tr>
<tr>
<td>Pressure/regulation</td>
<td>110 L of gas at 1800 psig CGA-180 outlet fitting</td>
</tr>
</tbody>
</table>

1. Fill loop with internal standard
2. Purge loop onto sample tube
3. Desorb sample

Schematic of internal standard/dry-purge (ISDP) accessory for ULTRA

Gas standards for external calibration of environmental methods

Markes also offers a selection of gas standards suitable for a variety of canister-based air monitoring methods. All cylinders are of aluminium construction (8.3 cm × 29.5 cm) and PI-marked for compliance with EU transport regulations and US DOT specification 3AL2216.

Sulfur component mix – 1 ppm

Supplied in nitrogen at 1800 psig, this standard has a 6-month stability and an accuracy of ±10%. 1 mL of this standard contains approximately 2–7 ng of the following components:

- Carbonyl sulfide
- Dimethyl sulfide
- Ethane thiol
- Hydrogen sulfide
- Methane thiol

Volatile (Japan) component mix – 1 ppm

Supplied in nitrogen at 1800 psig, this mixture of volatile organics contains some compounds that are traditionally difficult to prepare as calibration standards. 1 mL of this standard contains approximately 2–7 ng of the following components:

- Acrylonitrile
- Benzene
- Buta-1,3-diene
- Chloroform
- Dichloromethane
- Tetrachloroethene
- Trichloroethene
- Vinyl chloride

1. These items may be unavailable in some territories – please contact Markes International for further information.
2. Pressurised cylinders of gas standards are subject to ‘hazardous materials’ shipping supplements by most freight carriers.

T: +44 (0)1443 230935 T: 886-483-5684 (USA toll-free)
TO-15 ‘Air toxics’/TO-17 65-component mix – 1 ppm

Supplied in nitrogen at 1800 psig. Injecting 1 mL of this mix onto a sorbent tube or cold trap introduces 2–4 ng of each component.

Acetone
Acrolein
Benzeney
Benzyl chloride
Bromodichloromethane
Bromoform
Bromomethane
Buta-1,3-diene
Butan-2-one (methyl ethyl ketone)
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
Cyclohexane
Dibromochloromethane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane (Freon® 12)
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethylene
Dichloromethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,2-Dichlorotetrafluoroethane (Freon® 114)
1,4-Dioxane

Acetylene
Ethanol
Ethyl acetate
Ethylbenzene
4-Ethyltoluene
Heptane
Hexachlorobuta-1,3-diene
Hexane
Hexan-2-one (methyl butyl ketone)
Methyl methacrylate
4-Methylpentan-2-one (methyl isobutyl ketone)
Naphthalene
Prop-2-ol
Propene
Styrene
Tetrachloroethene
Tetrahydrofuran
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2-Chloroethene
1,2,3-Trichloroethylene
1,2,4-Trichlorobenzene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Trichloroethene
Trichlorofluoromethane (Freon® 11)
1,2,3-Trichloro-1,2,2-trifluoroethane (Freon® 113)
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene
Vinyl acetate
Vinyl chloride
m-Xylene
o-Xylene
p-Xylene

* Note that the stability of these compounds cannot be guaranteed.

Ozone precursor/PAMS 57-component mix – EPA concentrations 20–60 ppbC

Supplied in nitrogen at 1800 psig. Injecting 1 mL of this mix onto a TD cold trap introduces approximately 0.1 ng of each component (in the list below, individual concentrations in ppbC are given in parentheses).

Acetylene (40)
Benzene (30)
Butan-1-ene (30)
cis-But-2-ene (35)
trans-But-2-ene (25)
Cyclohexane
Cyclopentane (20)
n-Decane (30)
m-Diethylbenzene (40)
p-Diethylbenzene (25)
2,2-Dimethylbutane (40)
2,3-Dimethylbutane (50)
2,4-Dimethylpentane (40)
n-Dodecane (40)
Ethane (25)
Ethylbenzene (25)
Ethene (20)
m-Ethyltoluene (25)
o-Ethyltoluene (30)
p-Ethyltoluene (40)
Ethene (20)
m-ethyltoluene (25)
o-Ethyltoluene (30)
p-Ethyltoluene (40)
n-Hexane (30)
Hexan-2-one (methyl butyl ketone)
Methyl methacrylate
4-Methylpentan-2-one (methyl isobutyl ketone)
Naphthalene
Prop-2-ol
Propene
Styrene
Tetrachloroethene
Tetrahydrofuran
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,1,2-Chloroethene
1,2,3-Trichloroethylene
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene
Vinyl acetate
Vinyl chloride
m-Xylene
o-Xylene
p-Xylene

Hints and tips
► This standard contains some very volatile analytes and is not suitable for loading onto standard sorbent tubes at ambient temperature.

<table>
<thead>
<tr>
<th>Description</th>
<th>Part number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard, gas cylinder, sulfur mix, 1 ppm</td>
<td>C-GSSUL-1PPM</td>
</tr>
<tr>
<td>Standard, gas cylinder, volatiles (Japan mix), 1 ppm</td>
<td>C-GSVOL-1PPM</td>
</tr>
<tr>
<td>Standard, gas cylinder, TO-15, 65-component mix, 1 ppm</td>
<td>C-GS15-1PPM</td>
</tr>
<tr>
<td>Standard, gas cylinder, O3/PAMS, 57-component mix, EPA concentration, 20–60 ppbC</td>
<td>C-GSPAMS-EPA</td>
</tr>
<tr>
<td>Regulator, high-purity VOC, 0–100 psi outlet</td>
<td>C-GSREG-100</td>
</tr>
</tbody>
</table>

1. ppbC = parts per billion expressed as carbon.