

# Calibration Solution Loading Rig (CSLR™)



## Instruction for use

**PRODUCT REFERENCE:**

Calibration Solution Loading Rig    C-CSLR



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## 1. Introduction

Markes International's Calibration Solution Loading Rig (CSLR) (part no. C-CSLR) has been specifically designed for loading sorbent tubes with gas- or liquid-phase standards. With an unheated injector port, it also complies with key TD standard methods such as ISO 16017, US EPA Method TO-17 and ASTM D6196.

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. It is assumed therefore that good laboratory practice is followed with respect to solvent purity and syringe use/cleanliness. It is assumed that the tubes onto which the solution is to be loaded have been thoroughly conditioned and their blanks verified. Finally, it is also assumed that the carrier gas being used (whether nitrogen or helium), is of high purity and contains negligible levels of volatile organic compounds (VOCs).

## 2. Requirements

### 2.1 Gas supply lines

It is recommended that the gas line is constructed of  $\frac{1}{8}$ " refrigeration-grade copper tubing connected using approved swage-fittings. Laboratory gas line joints and connections must never be brazed. Position the gas supply as close as possible to the CSLR so that the gas line is as short as possible. Use a high-quality, stainless-steel-pneumatics regulator (U-GAS03) that is capable of delivering gas pressures between about 10 and 60 psi (higher pressures are not recommended).

### 2.2 Gas purity

Nitrogen or helium may be used as the carrier gas for the CSLR, and 5.0 grade (*i.e.* 99.999%) or higher-purity gas is recommended.

### 2.3 Gas regulation

A single regulator pneumatics accessory (part no. U-GAS03) is required for delivery of gas to the loading rig at a suitable pressure to enable further precision control of flow. This is achieved using the in-built needle valve on the loading rig.

## 2.4 Standard

The CSLR can be used to introduce either liquid or gas phase standards, as outlined in section 4. Gas standards should be of a suitable concentration to allow loading directly onto the TD tube. Equipment required in each case is outlined in the table below:

Liquid standard	Gas standard
<ul style="list-style-type: none"> <li>■ Glassware and solvent to prepare dilutions</li> <li>■ High purity analytes of interest</li> <li>■ Dilution solvent (see below)</li> <li>■ Liquid syringes (e.g. 1 µL)</li> </ul>	<ul style="list-style-type: none"> <li>■ Cylinder of gas standard at suitable concentration</li> <li>■ Gas cylinder regulator (dual-stage stainless steel)</li> <li>■ ¼" stainless steel Swagelok type nut</li> <li>■ 9.5 mm septa</li> <li>■ Gas-tight syringes (e.g. 100 µL, 1 mL, 50 mL)</li> </ul>

## 2.5 Solvent

For liquid standards, 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 retained on the sorbent tube and can be assessed.

Where possible, select a solvent that will be un-retained by the sorbent in the tube, so that it can be purged from the tube in the flow of carrier gas, while target analytes are quantitatively retained. Example solvents include methanol or acetone with Tenax® TA. See Section 6 for further information.

## 2.6 Sorbent tubes

Select the correct sorbent for the analytes of interest. Ideally this type of tube should be used for both the calibration and sampling. Advice on sorbent selection can be found in Application Notes 005 and 020.

### NOTES

For sorbent advice or any related queries please contact one of our technical experts.

## 2.7 Flowmeter

A flowmeter is required to check the flow rate of carrier gas through the tube for the loading of standard.

## 2.8 Syringe

A suitable syringe (liquid or gas-tight) will be required for introduction of standard. For liquid standards, the same volume should be used from each prepared concentration, therefore 1 liquid syringe is required.

For gas standards, a single standard (mix) is used to prepare all tubes, with increasing volumes being loaded onto individual tubes.

It is recommended that the gas-tight syringe used matches that of the volume being injected for increased accuracy. Therefore a 5-point calibration may require 5 gas-tight syringes of increasing volume.

## 3. Installation

Connect the  $\frac{1}{8}$ " copper tubing to the  $\frac{1}{8}$ " swage-type nut (carrier gas input point) fitted on the back of the CSLR (Figure 1). Ensure that the connection is leak-tight.

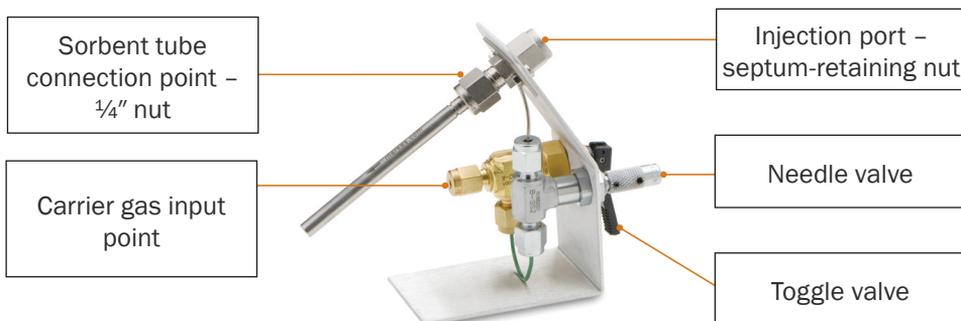


Figure 1: The CSLR.

## 4. Operation

Ensure the sorbent tube is conditioned prior to use.

Attach the flowmeter to the non-sampling end of the sorbent tube and connect the tube to the CSLR with the sampling end (grooved end) inserted into the ¼" brass nut and PTFE ferrule on the back of the port. (It is important that standard is introduced onto the tube in the sampling direction.) Tighten the fitting to finger-tight and then secure using a spanner or CapLok tool.

Turn on the regulators to introduce the flow to the sorbent tube. Monitor the flow rate through the tube and adjust the carrier gas supply using the needle valve on the front of the CSLR so that the total flow is between 50-100 mL/min (optimum purge flow may need to be determined based on the breakthrough volumes for the analytes of interest on the sorbent used - see Application Note O20.

Once the flow is correct the flowmeter can be removed. You are now ready to inject your standard.

### 4.1 Gas standards

Select the size of gas syringe that is most applicable to the volume that you would like to take from your cylinder. The mass of analytes introduced in the standard should 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.

The mid-point of the calibration should be close to the expected target sample concentration. The following guidelines should be followed when preparing gas standards for injection:

- Attach a ¼" stainless steel Swagelok-type nut, fitted with 9.5 mm septa, onto the standard cylinder regulator (using stainless steel adaptors if required).
- Turn on the regulator and set to ~10 psi, then close the valve on the cylinder and confirm that the pressure holds. If pressure drops, there is a leak present that needs to be addressed.
- Once the system is leak-tight, open the cylinder.
- Use the gas tight syringe to pierce the septa. The residual gas pressure within the regulator should be used to fill the syringe.

**NOTES** Take care to hold the plunger in case the syringe fills too quickly.

- With smaller volume syringes, it may be necessary to slowly pull the syringe plunger during loading. Do not pull too fast as this may create a vacuum in the regulator that can lead to compound discrimination.
- After removing the needle from the septum, allow it to equilibrate at atmospheric pressure for consistency of injection volume. This can be checked by placing the tip of the syringe in clean, distilled water and looking for bubbles.
- Inject to the tube using the calibration loading rig immediately
  - Insert the syringe into the injection port of the CSLR through the septum;
  - Resistance will be felt when the syringe meets the gauze within the tube, pull back slightly.
  - Inject into the stream of carrier gas. Inject slowly over 2–10 seconds to avoid excessive flow through the tube
- Leave the sorbent tube attached to the CSLR for approx. 3 minutes (depending on breakthrough volumes) to ensure complete transfer of the gas standard and adsorption of the target analytes on the sorbents in the tube.
- Turn off the gas flow and detach the sorbent tube.
- Tubes should be capped with DiffLok caps if using an automated system, then placed in the tray. If using a manual system the tube can be placed directly in the tube oven or capped with brass caps for later analysis.

Setup required for loading of gas standards, including:



(i) Connection union & septum



(ii) dual-stage regulator



(iii) gas-tight syringe

## 4.2 Liquid standards

Ensure the syringe is clean. It can be cleaned with the solvent used to create the standards.

Prepare the standard solution so that the mass of analyte(s) introduced in the injection volume matches the expected masses that will be collected during field monitoring (see below for more information).

Typically, 0.5 – 1  $\mu\text{L}$  of a liquid standard is injected, with 1  $\mu\text{L}$  being the recommended maximum injection volume for standard practice. If only using Tenax<sup>®</sup>, injection volumes of up to 5  $\mu\text{L}$  can be used provided the solvent can be completely purged prior to analysis whilst the analytes of interest are still retained.

Loading should be carried out according to the guidelines below:

- Connect the sample loading rig to a supply of suitable inert, VOC free carrier gas at  $\sim 10$  psi
- Activate flow toggle switch to allow gas to flow
- Attach sorbent tube to the loading rig at the sampling (grooved) end, ensuring the tube is secured by the PTFE ferrule and hand-tighten the nut
- Attach flow meter to rear of tube
- Adjust flow of carrier gas using the needle valve to between 50 - 100 mL/min. 100 mL/min is the flow rate typically used
- Prepare syringe with standard and slowly insert needle through the septum in the injection port.
- Once you feel the needle touch the gauze at the front of the tube, retract the syringe by  $\sim 2$  mm

- Inject quickly then go forward and touch the gauze, wait about 10 seconds to allow all liquid to transfer from the tip of the syringe before removing the needle. The solution vaporises in the carrier gas flow and is passed onto the sorbent tube in the vapour phase
- Leave tube to purge for 3 minutes (A sufficient volume of carrier gas is required to pass through the tube so that most of the carrier solvent (e.g. methanol) passes through the sorbent and away to vent whilst the compounds of interest are still quantitatively retained.)
- Replace the tube caps and turn off the carrier gas flow. Tubes should be capped with DiffLok caps if using an automated system, then placed in the tray. If using a manual system the tube can be placed directly in the tube oven or capped with brass caps for later analysis



(i) Connection of sorbent tube into Swagelok fitting



(ii) use of flowmeter to check carrier gas flow through tube



(iii) Insertion of standard through injection port

## Tips

- [1] Gas standards are preferred for very volatile compounds because of the difficulty of finding suitable solvents that purge off before the analytes of interest reach breakthrough.
- [2] If the analytes of interest are volatile and not available as a gas standard, it may not be possible to selectively purge the solvent without loss of analytes.
- [3] It may also be difficult to selectively purge the solvent if the tube is packed with two or more sorbents of increasing strength.
- [4] Whenever liquid standards are used and it is NOT possible to selectively purge the solvent, low (<0.5  $\mu\text{L}$ ) injection volumes should be used.
- [5] If multiple standards are to be added to a single tube, load the liquid standards containing the highest-boiling compounds first, and the lightest components and/or gas standards last, to avoid loss of more volatile compounds during purging.
- [6] If using a liquid standard, the same injection volume should be used for all injections in a multi-level calibration series.

## 5. Calibration solution preparation and calculations

### 5.1 Introduction

A typical multi-level calibration procedure requires at least three (and preferably five) standard solutions, with the mid-concentration standard being such 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.  $\frac{1}{4}$  of the expected level) and one at a higher level (e.g.  $2\frac{1}{2}$  times the expected level) are also required.

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

Note: It is easier to prepare the standards to an approximate concentration volumetrically, and then calculate the exact mass of analyte present in the solution.

This is best illustrated by the following examples.

**NOTES** For atmospheric monitoring, if the expected atmospheric concentration is unknown, then assume it will be at 1/10 of the recommended limit level.

## 5.2 Calculation of the expected sample mass

### 5.2.1 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<sup>-1</sup> min<sup>-1</sup>

Calculation: Mass on tube = C × T × U  
 = 1 × 480 × 1.67  
 = **801.6 ng**

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

### 5.2.2 Pumped air monitoring for n-heptane

Information required: Expected atmospheric concentration (C)  
 Volume of air to be collected (V)  
 Molecular weight of component (M<sub>w</sub>)

Example: C = 100 ppb (100 parts in 10<sup>9</sup>)  
 V = 10 L  
 MW = 100 g mol<sup>-1</sup>  
 Molar volume at 20°C & atmospheric pressure (V<sub>M</sub>) = ~24 L mol<sup>-1</sup>

Calculation: Mass on tube = (V/V<sub>M</sub>) × M × C  
 = (10/24) × 100 × (100/10<sup>9</sup>)  
 = 4.17 × 10<sup>-6</sup> g  
 = **4.17 µg**

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

### 5.2.3 Solid sampling for residual acetone

Information required: Expected concentration (weight %) (C)  
Typical mass sampled (M)

Example: C = 1%  
M = 20 mg

Calculation: Mass on tube =  $(C/100) \times M$   
=  $(1/100) \times 20$   
= 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 one 500 µg.

## 5.3 Volumetric preparation of calibration standard

The first requirement is to know the volume of the syringe that will be used to inject the calibration standards. A 1, 5 or 10 µL syringe may be used depending on the range of analytes being injected and the chosen solvent (see Section 6).

Note that for optimum precision, the volume injected should be the maximum volume of the syringe used *i.e.* use a 1 µL syringe for a 1 µL injection.

### 5.3.1 Example calculation

To give a round figure for the volume of analyte needed, it is easiest to assume a density of 1 g mL<sup>-1</sup>.

Information required: Approximate mass to be injected onto the tube ( $M_{\text{approx}}$ )  
Assumed analyte density ( $\rho_{\text{assumed}}$ )  
Syringe volume ( $V_S$ )  
Volume to be prepared ( $V_P$ )

Example:  $M_{\text{approx}} = 4 \mu\text{g} = 0.004 \text{ mg}$   
 $\rho_{\text{assumed}} = 1 \text{ g mL}^{-1} = 1 \text{ mg } \mu\text{L}^{-1}$   
 $V_{\text{S}} = 5 \mu\text{L}$   
 $V_{\text{p}} = 10 \text{ mL} = 10000 \mu\text{L}$

Calculation:  $\text{Volume of analyte required} = (M/\rho_{\text{assumed}}) \times (V_{\text{p}}/V_{\text{S}})$   
 $= (0.004/1) \times (10000/5)$   
 $= 0.004 \times 2000$   
 $= \mathbf{8 \mu\text{L}}$

This is the amount that should be used to create the volumetric solution, this is not the volume that should be injected into the CSLR. To find the actual mass that is present, the expected mass should be corrected by the density of the analyte.

### 5.3.2 Calculating the precise mass of analyte

Information required: Approximate mass to be injected onto the tube ( $M_{\text{approx}}$ )  
 Actual analyte density ( $\rho_{\text{actual}}$ )

Example:  $M_{\text{approx}} = 4 \text{ ng}$   
 $\rho_{\text{actual}} = 0.866 \text{ g mL}^{-1} = 0.866 \text{ mg } \mu\text{L}^{-1}$  (taking the example of toluene)

Calculation:  $\text{Actual analyte mass on-tube} = M_{\text{approx}} \times \rho_{\text{actual}}$   
 $= 4 \times 0.866$   
 $= \mathbf{3.464 \mu\text{g}}$

## 5.4 Concentration calculation

Having calculated the exact mass of analyte being loaded onto the tube, you may wish to convert this into an exact atmospheric/residual solvent concentration, in order to calibrate your data handling system with the correct units. This is done by reversing the calculations in Section 5.2.

## 6. General notes and information

Select the correct sorbent for the components of interest and use this tube for the calibration and sampling.

Tubes containing 1 cm sorbent bed for calibration are intended for use with direct liquid loading onto the tube, and are NOT recommended for use with the CSLR

Where possible, select a solvent that is not well retained by the sorbent in use. When using Tenax® TA or Carbograph sorbents, the most common solvent is methanol however, please see Application Note 20 for further examples.

If the solvent is un-retained, allow a sufficient volume of carrier gas to pass through the tube to remove at least 95% of the solvent from the tube. Check that there are no analyte losses under these conditions, e.g. when using a solution of benzene in methanol on a Tenax tube, sweeping the tube with at least 1 L of gas will remove the methanol without removing any of the benzene (see Table 1).

If the solvent is retained by the sorbent in use it is advisable to keep the injection volume as low as possible, *i.e.* 0.5 µL.

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

**Table 1:** Breakthrough volumes of some typical VOCs.

## 7. Contact details

For technical support, please contact your supplier in the first instance. If they are unable to resolve your query, please contact Markes International's service department:

**E:** support@markes.com  
**T:** +44 (0)1443 230935  
**W:** www.markes.com

For an instructional product video, please visit:



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