Calibration Solution Loading Rig

INSTRUCTION MANUAL

VERSION 2.2 December 2011

QUI0005

1. Introduction

When using the calibration solution loading rig 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 air, 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 be constructed of 1/8-inch 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 calibration loading rig so that the gas line is as short as possible. Use a high quality, stainless-steel-diaphragm cylinder head regulator which is capable of delivering gas pressures between about 10 and 60 psi (higher pressures are not recommended).

2.2. Gas Purity

Air, nitrogen or helium may be used as the carrier gas for the calibration loading rig and 5.0 grade (*i.e.* 99.999%) or higher purity gas is recommended in either case. **Note that pure air cannot be used as a carrier gas through heated inlets.**

2.3. Solvent

The solvent used must be at least of chromatographic grade, with negligible VOC impurities. It is recommended that the operational procedure is followed with an injection of pure solvent initially, as this will show up any VOC impurities which are retained on the sorbent tube and which may interfere with the calibration.

Where possible, select a solvent which will be unretained by the sorbent in the tube such 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 section 6 for further information.

2.4. Sorbent Tube

Select the correct sorbent for the components of interest and pack the tube with the same mass of sorbent as used for routine monitoring.

3. Installation

Connect the 1/8-inch copper tubing to the 1/8-inch swage-type nut (carrier gas input point) fitted on the back of the of the calibration loading rig (Figure 1). Ensure that the connection is leak tight.

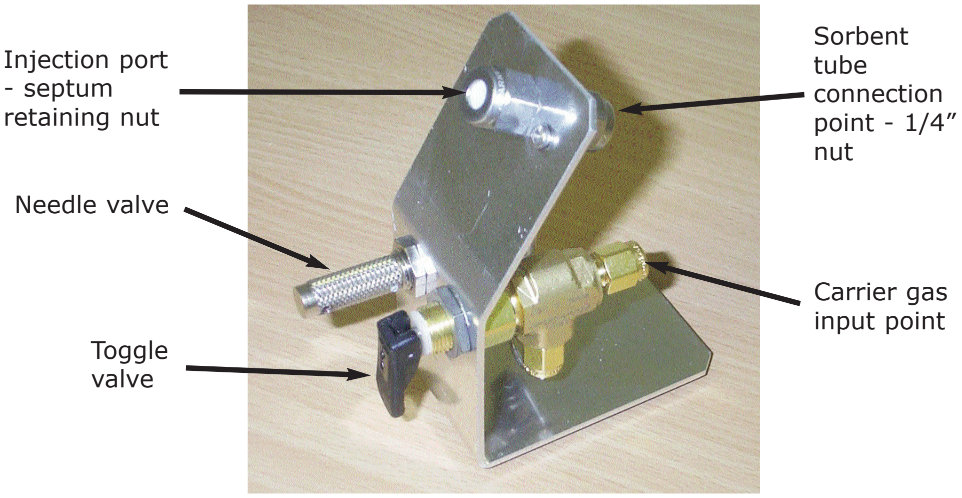

Figure 1: Photo of a Calibration Solution Loading Rig

4. Operation

A clean, conditioned tube is inserted into the CSLR with the sampling (typically grooved) end going into the 1/4-inch 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 between 50 and 100 mL/min through the tube.

For gas standards: Select an appropriately sized gas syringe such 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 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 minutes.

When injecting liquid standards: Prepare the standard solution such that the mass of analyte(s) introduced in the injection of 1–5 µL matches the expected masses that will be collected 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 vapourises 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 adsorbent bed whilst the compounds of interest are still quantitatively retained.

Remove and analyse the loaded tube as you would a normal sample.

Notes

1) Gas standards are preferred for volatile compounds

2) If the compounds of interest are volatile and if they are not available as a gas standard, the solvent selected for standard preparation may not be readily separated from the target compounds, after introduction of the standard solution. It may also be difficult to selectively purge the solvent if the tube is packed with 2 or more sorbents of increasing strength. Whenever liquid standards are used and it is NOT possible to selectively purge the solvent, low (<1 µL) injection volumes 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.

5. Calibration Solution Preparation and Calculations

5.1. Introduction

A typical multilevel calibration procedure requires 3 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 and one at a higher 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** that is 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. [**Note**: with atmospheric monitoring - if the expected atmospheric concentration is unknown, then assume it will be at 1/10 of the recommended limit level.]

5.2. Calculating 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 hours (480 minutes)

U = 1.67 ng.ppm^{-1}.min^{-1}

Calculation:

$$\text{Uptake rate} = \frac{\text{ng adsorbed onto tube}}{\text{Atmospheric conc (ppm) x mins exposure}}$$

Therefore, mass adsorbed on tube = 1.67 x 1 x 480 ng

= 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)

Example: C = 100 ppb

V = 10 L

M = 100

Calculation: 24 L of n-heptane vapour at 20°C and atmospheric pressure would weigh 100 g.

(1mole of vapour at 20°C & atmospheric pressure occupies ~24 L)

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

10 L at 100ppb contains 10/24 x 10 µg = 4.17 µg

In this case, the mid-range standard concentration should be set such that 4 µg of n-heptane are introduced in one, 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 w/w (C)
	Typical mass sampled (M)
Example:	C = 1% weight per weight
	M = 20 mg
Calculation:	1% of 20 mg = 0.2 mg

Therefore expected mass is 200 µg

In this case, the mid-range standard concentration should be set such that 200 µg of toluene are introduced in one, 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 which will be used to inject the calibration standards. A 1, 5 or 10 µl syringe may be used depending on the range of analtyes 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 5 µl syringe for a 5 µl injection.

5.3.1. Example calculation

Assume that the mass of analyte required to be injected onto the tube is 4 µg
Assume that the syringe volume used is 5 µl
The solution should be prepared containing 4 µg per 5 µl *i.e.* 0.8 µg/µl
Prepare a volumetric solution at this concentration *i.e.* 0.08% (*e.g.* 8 µl analyte in 10 ml solvent).

5.4. Calculation of the precise mass of analyte

Calculate the precise mass of analyte present using the formula:

Density = mass per unit volume

Assume density is 0.927

1ml of solvent as prepared above will contain 0.8 µl analyte. Therefore the analyte mass in 1 ml will be:

0.927 x 0.8 = 0.742 mg

Thus, 1 µl solvent will contain 0.74 µg analyte and 5 µl solvent will contain 3.71 µg

5.5. 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 5.2. above.

6. General notes and 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.

Where possible select a solvent which is not well retained by the sorbent in use. The most common selection is methanol when using Tenax, Carbopack/Trap or Chromosorb 106.

If the solvent is unretained, 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 litre 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.* 1 µl.

Component	Breakthrough volume (L) on 200 mg Tenax	Component	Breakthrough volume (L) on 200 mg Tenax
1,1,1-Trichloroethane	2.2	Ethoxyethylacetate	30
1,1,2-Trichloroethane	68	Ethylacetate	7.2
1,1-Dichloroethylene	0.84	Ethylbenzene	280
1,2-Dichloroethane	10.8	Ethyoxyethanol	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	Tetrachloroethylene	96
Carbon tetrachloride	12.4	Toluene	76
Chloroform	3.8	Trichloroethylene	11.2
Dichloromethane	0.9	Trimethylbenzene	3600
Ethanol	0.36	Xylene	600

Table 1: Breakthrough volumes of some typical VOCs