CAMSCO's CALIBRATION SOLUTION LOADING RIG INSTRUCTION MANUAL

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1. Introduction

Congratulations on purchasing the CAMSCO's Calibration Loading Rig (CCLR) from CAMSCO! Unlike other company's products, CCLR is made of all stainless steel parts (except some consumables, see section 6 for further information) and high-precision machining. When used correctly this device should offer many years of reliable service.

When using the CCLR it is important to make sure that the analytical system is being calibrated for trace amounts of the compounds of interest. It is assumed therefore that good laboratory practice (GLP) 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 amounts 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 Swagelok fittings. Laboratory gas line joints and connections must never be brazed. Short gas line is preferred and can be achieved by positioning the gas supply as close as possible to the CCLR. Use a high quality, stainless-steel-diaphragm cylinder head regulator which is capable of delivering gas pressures between 10 and 60 psi **(pressures higher than 100 psi are not recommended)**.

2.2. Gas Purity

Air, nitrogen or helium may be used as the carrier gas for the CCLR and 5.0 grade (*i.e.* 99.999%) or higher purity gas is recommended in all cases. **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. As a control experiment, it is recommended that the operational procedure is followed with an injection of pure solvent first, as this will detect any VOC impurities which are retained on the sorbent tube and which may interfere with the calibration.

Where possible, select a solvent which will not be retained 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 7 for further information.

2.4. Sorbent Tube

Quality sorbent tubes, such as the ones professionally manufactured at CAMSCO, is key to the success of any thermal desorption system.

2.4.1. Sorbent Selection

It is very important to select the correct sorbent(s) for the components of interest, please refer to CAMSCO's Sorbent Selection Chart or contact CAMSCO professionals for sorbent selection and tube design.

2.4.2. Consistency

Use tubes with the same mass of sorbent as used for routine monitoring, and if possible, use sorbent from the same lot number. At CAMSCO, we take great care to ensure consistency; it is highly recommended that you use CAMSCO's quality tubes on the CCLR.

2.4.3. Cleanliness

Thoroughly condition the tube before loading the calibration solutions, please note that some carbon based sorbents may need multiple conditioning cycles to clean.

Again, we at CAMSCO take quite a few extra steps to clean the sorbent, the tube itself, and any accessory that goes into a tube during the manufacturing process. To recondition your tube, please follow CAMSCO's Sorbent Selection Chart and Certificate of Compliance (COC) for instructions.

2.4.3. Complete vaporization

Calibration tubes should have a small (approximately 8-10 mm) plug of clean, silanised glass wool placed at the front (grooved) end of the sampling tube. This ensures that the syringe needle is wiped clean of all solution before being removed from the loading rig and thus optimizes precision.

The plug of glass wool should be removed prior to analysis.

3. Installation

Figure* 1a: *Front view of a CCLR

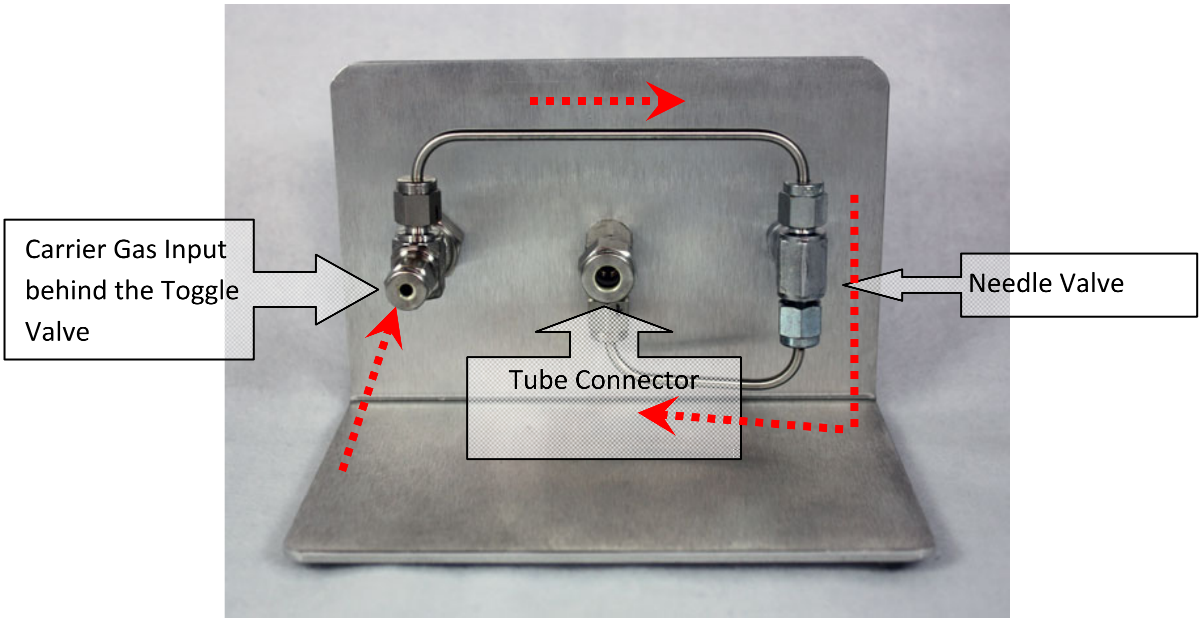


Figure 1b*: *Back view of a CCLR: dotted red line indicates the direction of carrier gas flow

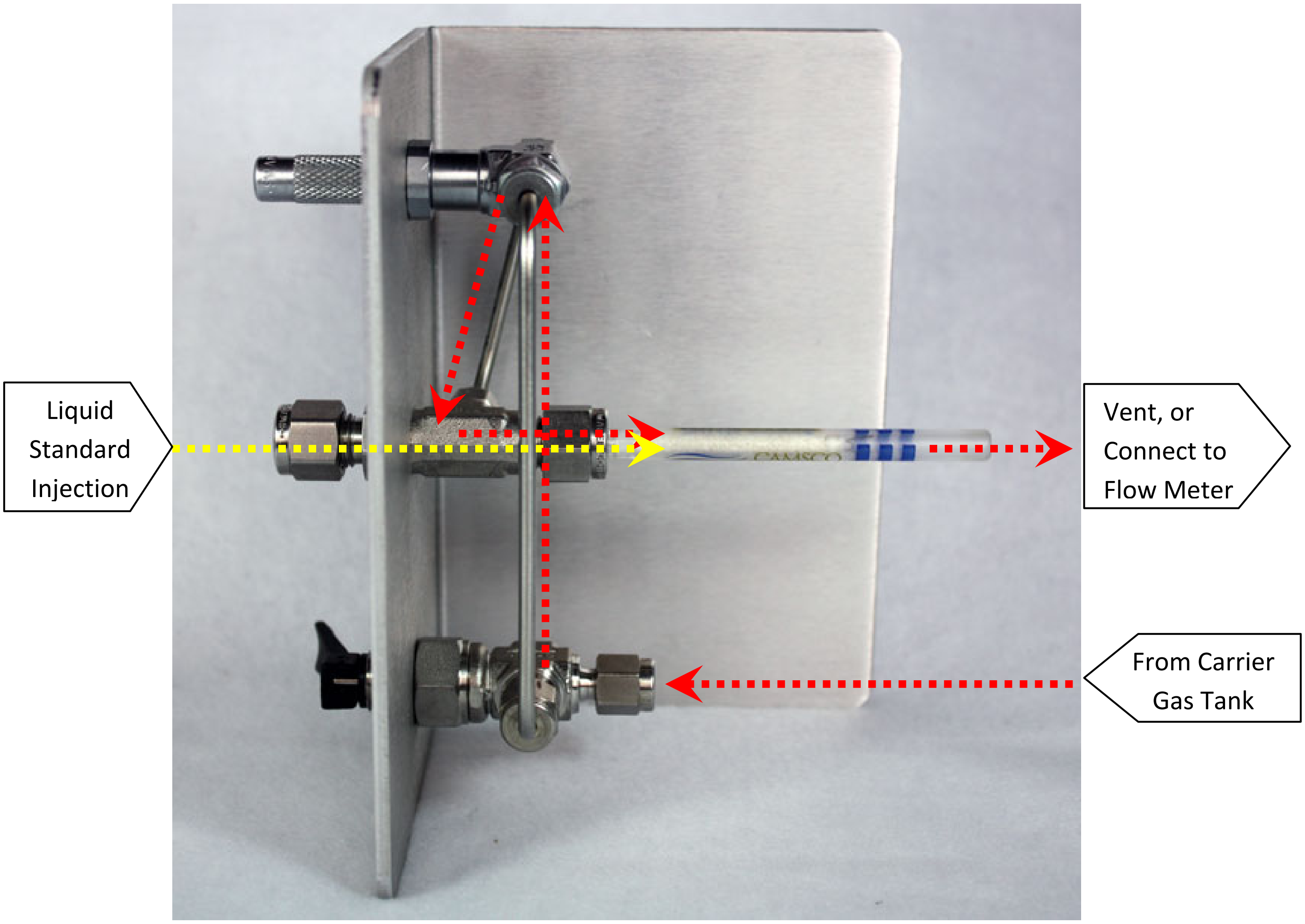


***Figure 1C*: Top view of a CCLR with a glass tube connected: dotted red line indicates the direction of carrier gas flow, dotted Yellow line indicates the injection of liquid standard**

CCLR comes pre-assembled and ready to use. Connect the 1/8-inch copper tubing to the 1/8-inch stainless steel nut (carrier gas input point) fitted on the back of the of the toggle valve (Figure 1A/1B/1C). Ensure that the connection is leak tight.

4. Operation

Insert a clean, conditioned tube with the sampling (corseted) end into the 1/4 " stainless steel nut (Figure 1C) on the back and finger tighten the nut. Tighten the nut a further quarter turn using a wrench and ensure that the connection is leak free.

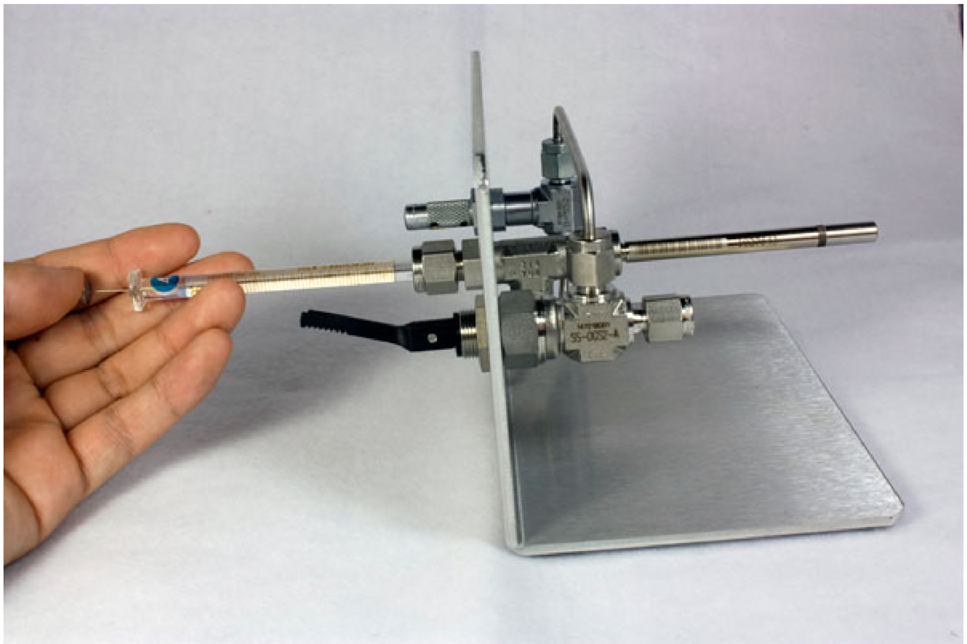
Turn on the carrier gas supply to the sorbent tube using the toggle valve on the front of the unit, and adjust the flow through the tube to between 80-100 ml/min using the needle valve on the front of the unit. **Note:** The toggle valve is off when the handle points down, and on when the handle is lifted up. The flow rate may be monitored by an in-line flow meter, which is not included in the CCLR but widely available elsewhere.

Draw the required volume of calibration solution into a well rinsed syringe. (See section 5 for details of preparing the calibration solution).

Quickly wipe the needle with a clean, dry, lint-free cloth to remove any excess solution from the outside. **Note:** If the needle is wiped too slowly, solution can be drawn out of the needle onto the cloth *via* capillary action.

Loosen the septum retaining nut slightly and then pierce the septum with the needle and insert the needle 3 to 3.5 cm. This will place the needle in the middle of the glass wool plug and ensure that all the solution is transferred from the syringe to the tube, without the needle touching the front-end adsorbent retaining gauze **(Note:** if the needle is pushed in too far then the front-end gauze may be displaced and adsorbent may leak from the tube.)

Depress the plunger in a swift movement to eject all the calibration solution from the syringe and then wait a short time (~20 seconds) before withdrawing the needle from the septum to allow full evaporation of the sample. See illustration below:



Note: As a 5 µl injection volume can usually be introduced more accurately that a 1 µl injection, and as the solvent is being purged from the tube prior to analysis, a larger injection volume is generally recommended. For optimum precision, the injection volume should be the maximum volume of the syringe used *i.e.* use a 5 µl syringe for a 5 µl injection. **Do not inject >1 µl volume of standard if it is not possible to purge the solvent to vent.**

Allow a sufficient volume of carrier gas to pass through the tube that is being loaded to so that most of the carrier solvent (e.g. methanol) passes through adsorbent bed whilst still quantitatively retaining the compounds of interest *(e.g.* BTX). This step can be fine-tuned by the operator where necessary. (See section 7 for further information).

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

Repeat the procedure for the range of calibration standards being used, to produce a calibration curve (theoretically a straight line, provided that no breakthrough is happening) which may be plotted as shown in figure 2.

N.B. This plot should give you a straight-line of the type $y = mx+c$, where: m is the gradient and represents the response factor (number of area counts per ng of compound injected); c is the y-intercept, which should be near zero as it represents the number of area counts when no sample is injected.

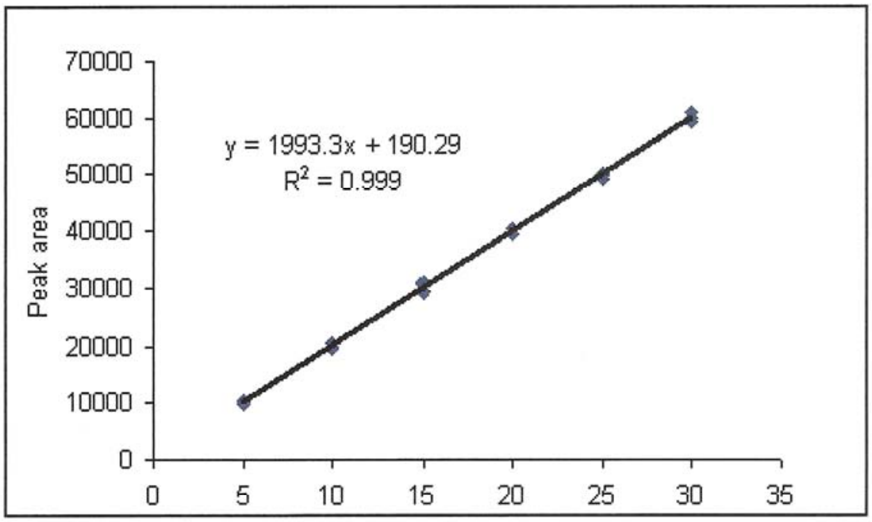


Figure 2: An example calibration curve

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 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. [**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: 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 µg 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 vapor at 20°C and atmospheric pressure would weigh 100 g.
(1 mole of vapor 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 the 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 analytes being injected and the chosen solvent (see section 7). 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. Accessories and consumables

Over time you may need to replace the septum and needle guide at the injection port (Figure 3A), and the quarter-inch PTFE ferrule at the sorbent tube connector (Figure 3B). Contact CAMSCO or our authorized distributors for assistance.

Figure* 3A: *Photo of the PTFE needle guide (white) and the septum (grey) inside the injection port

Figure 3A: Photo of the PTFE needle guide (white) and the septum (grey) inside the injection port

CAMSCO's CCLR comes standard with a quarter-inch tube connector, which can accept PerkinElmer, DANI, Shimadzu, and Markes standard tubes directly. A quarter-inch to 6mm adapter is provided should you wish to connect a Gerstel or CDS Dynatherm tube instead of the standard quarter-inch. Figure 4 shows the supplied adapter being used to accommodate a 6mm Gerstel glass tube.

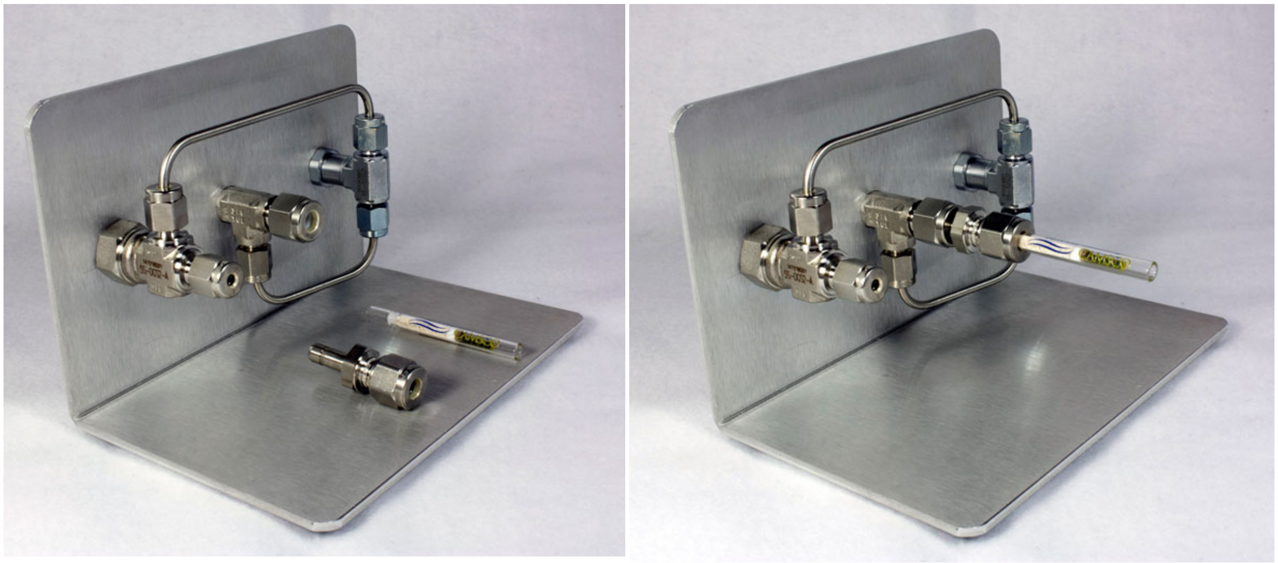


Figure 4: The supplied quarter-inch to 6 mm adapter is used to accommodate a 6mm glass tube for Gerstel

7. 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 and some carbon-based sorbents.

If the solvent is not 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 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