

UNITY

Thermal Desorber

USER MANUAL

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QUI-0002

VERSION 5.2



MARKES
international
L I M I T E D

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1 Warnings and disclaimers

1.1 Electricity

Ensure that the mains cord is correctly wired and that the ground leads of all electrical units are connected together via the circuit ground to earth.

Any work undertaken on the incoming AC line components should be performed by a qualified electrician.

UNITY™ must be unplugged from the mains before any panels are removed.

1.2 Compressed gases

Handle cylinders of compressed gas with care. Avoid knocking valves and ensure that correct valves and gauges are used. If possible, store and site gas cylinders outside the laboratory, firmly clamped in position.

1.3 Hydrogen gas

Although hydrogen may be used as a carrier gas for standard GC and thermal desorption care must be taken in case the high temperatures involved in thermal desorption cause hydrogenation of reactive and/or unsaturated species.

2 UNITY Preinstallation Check List

2.1 Minimum computer specification for UNITY control

In general a PC with sufficient resources to run 32 bit Windows (95, 98, ME, 2000, XP, NT4(series 4)) will have adequate performance for controlling UNITY. As such the minimum PC requirement recommended is a 400MHz Pentium with 64MB RAM and a minimum of 20MB of free disc space (for the UNITY software installation). A Windows compatible mouse is also required.

The user interface requires a minimum SVGA (800x600 pixel) screen resolution and ideally an XGA (1024x768 pixel) screen resolution 256 colour in both cases.

The PC requires a free serial comms port for communication with UNITY. An additional serial comms port is required for each of the following accessories: Air Server™, ULTRA™, SecureTD™, Headspace unit. UniSense™ (UNITY plus sensor) requires two free serial comms ports.

UNITY communicates at 57600 baud. Whilst lower baud rates can be programmed, this is not recommended as it will result in degradation of system performance (most modern PCs will support communication at this speed).

A 9 way Null modem cable is supplied for connecting UNITY to the PC comms port.

The PC will also require an internet connection if the browser facility, included in UNITY's user interface, is to be used. The browser is not required for system operation.

2.2 GC equipment requirements

UNITY is usually connected to a gas chromatograph configured with appropriate conventional or mass spectrometer (MS) detectors. No conventional GC injector is required for UNITY operation. Ready and external start connections are required on the GC.

2.3 Access into the GC oven

The UNITY heated transfer line is lined with 0.25 mm I.D., 0.35 mm O.D. uncoated deactivated fused silica which butt connects with the capillary analytical column inside your GC oven. It is important that the heated and insulated portion of the transfer line extends as far as the skin of the GC oven such that the GC oven heating begins at the point where heating of the transfer line ends. A 25 mm diameter access hole is thus required into the GC, with a 6.5 mm hole in the GC inner oven wall. Further information is provided in Section 4.3.1.

2.4 GC configuration/parameter selection

From a GC perspective, UNITY may simply be regarded as a multipurpose, stand alone GC injector for

capillary or 1/8 -inch packed columns. No conventional GC injector is required for UNITY operation. The rest of the GC system - column, oven, data handling, detector, etc. - should be configured and used, as per normal chromatographic practice for the analytes of interest.

If multiple applications are to be carried out or if samples are uncharacterised; for example when monitoring unknown atmospheres, a good general purpose GC configuration comprises 25-30 m, 0.25mm or 0.32 mm ID, 1 or 2 µm phase thickness bonded methyl silicone capillary column with a FID or mass spectrometer detector.

2.5 Laboratory location

2.5.1 Space requirements

UNITY occupies minimal bench space, being only 12 cm wide, and can sit either side of the gas chromatograph.

2.5.2 Recommendations relating to the quality of the laboratory air

UNITY is a powerful concentration device and is often used to determine trace levels of organic analytes. It is advisable to store and operate UNITY in a clean laboratory environment with minimal atmospheric concentrations of organic vapours.

2.5.3 Recommendations relating to the quality of the laboratory gas lines

As UNITY is a concentrator, even trace level contaminant's in laboratory gas lines can become significant interferents in the chromatograms produced. It is recommended that gas lines be constructed of refrigeration-grade copper tubing connected using approved swage-fittings. Laboratory gas line joints and connections must never be brazed. Position the gas supplies as close as possible to the analytical system i.e. such that the gas lines are as short as possible. Use a high quality, stainless steel diaphragm cylinder head regulator for the carrier gas supply.

2.6 Services

2.6.1 Power

UNITY is automatically compatible with all conventional mains power supplies ranging from 90 to 255 V and 50 or 60 Hz. It is not necessary to manually select or switch voltages. The maximum power consumption of UNITY is 400 W.

2.6.2 Pressure controlled supply of dry air or nitrogen

2.6.2.1 Functions

UNITY requires a pressure-regulated supply of dry air or nitrogen at between 55 and 70 psi both to actuate the main valve and to purge the cold trap box.

Note: The dry air / nitrogen supply is critical and UNITY must never be switched or left on without this gas supply.

For UNITY prior to serial number U-10235 the dry air/Nitrogen the UNITY should never be switched on without the supply of dry air / Nitrogen.

UNITYs with serial number greater than U-10235 has a built in sensor to prevent damage to the Peltier cell, in the event that UNITY is run without the dry air / Nitrogen supply being switched on. The UNITY status bar will read "Equilibrating" and the Trap temperature will not reach the temperature set.

It is recommended that a secondary pressure regulator be used to control the supply of dry gas to UNITY in addition to that controlling the general laboratory line pressure. Any conventional pressure regulator should suffice for this and suitable pneumatic control may already be available on your GC. Alternatively, Markes International Ltd. supply a pneumatic control accessory (P/N U-GAS01) for both air and carrier gas - see section 2.6.3.3. It is recommended that the pressure in the laboratory air line be 10 psi higher than that supplied to UNITY.

2.6.2.2 Specification required (dryness / purity)

The compressed air or nitrogen must be dry (dewpoint lower than -35°C.) Conventional air compressors / nitrogen generators may be used provided the gas produced is adequately dried.

2.6.2.3 Consumption

Dry air or nitrogen flows at <200 ml/min into the cold trap box creating a slight positive pressure and minimising ingress of water from the laboratory atmosphere. If the cold trap box was not purged, ice would quickly build up around the Peltier cell which is maintained at -25°C throughout UNITY operation.

Gas consumption for valve actuation is minimal.

2.6.3 Pressure controlled carrier gas supply

2.6.3.1 Gas selection - type / purity

Helium is invariably used as the carrier gas for capillary chromatography and nitrogen for packed column or sensor work. 5.0 grade (i.e. 99.999%) or higher purity gas is recommended in either case. Although Hydrogen may be used as a carrier gas for standard GC and thermal desorption applications, care must be taken in case the high temperatures involved in thermal desorption cause hydrogenation of reactive and / or unsaturated species.

2.6.3.2 Line pressures and recommended pneumatic control

UNITY requires a regulated supply of carrier gas at a pressure to suit the analytical column / system selected. The UNITY gas flow path has minimum (<2 psi) impact on total system impedance. Suitable pneumatic control for the carrier gas may already be available on your GC. The performance of most common capillary columns is optimised at between 1 and 2 ml/min typically requiring between 10 and 30 psi head pressure. High quality pressure regulators incorporating a stainless steel diaphragm are recommended for carrier gas control. The pressure in the laboratory carrier gas line should be at least 10 psi higher than that supplied to UNITY.

2.6.3.3 UNITY and Electronic Pneumatic Control (EPC)

(Only relevant for installations on Agilent 6890GCs - see Appendix Five)

For optimum performance the carrier gas pressure to the EPC module should be regulated to approximately 15 to 20 psi above the column head pressure.

Note: As EPC only controls the carrier gas, suitable pneumatic control of the dry gas will still be required. A U-GAS01 from Markes International includes a carrier gas regulator to step down the carrier pressure and a separate regulator and gauge for control of the dry air or nitrogen, and is therefore recommended in this case.

Note: When installing onto an existing 6890GC the firmware on the GC must be A.03.08 or later (for A-series) or N.04.09 (for N-series). To check the firmware version, use the keyboard on the GC press: Options > Diagnostics > Instrument Status and then scroll down to 'Version' where you will see the version of the firmware running on the instrument.

2.6.3.4 Filters

Deoxo and organic filters should be included in the carrier gas line just upstream of connection to the UNITY-GC analytical system.

3 System description and summary of operation

(For more detailed information, see Section 22.)

3.1 Parameters and ranges

See Table 1 below

Parameter	Range
Mode	Standard 2(3) Stage Thermal Desorption
	Tube Conditioning
	Direct Sampling (only applicable if UNITY is used in conjunction with multi-purpose Direct Inlet Accessory)
	On Line Air (only available if UNITY is used in conjunction with Air Server)
Split on in standby	Yes/No
Ambient temperature carrier gas purge	Time settable between 0.0 and 99.9 minutes in 0.1 minute increments.
Split on during tube purge	Yes/No N.B. At least one of these
Trap in-line during tube purge	Yes/No options must be selected
Elevated temperature purge or stage 1 of primary (tube) desorption (optional)	35.0 to 350.0°C (settable in 1° increments) for 0 to 999.9 minutes (settable in 0.1 minute increments)
Trap in-line during elevated tube purge	Yes/No N.B. At least one of these
Split on during elevated tube purge	Yes/No options must be selected
Primary tube desorption (stage 2 if optional elevated temp. purge employed)	50 to 380°C (settable in 1° increments) for 0 to 999 minutes (settable in 0.1 minute increments.)
Split on during primary (tube) desorption	Yes/No
Cold trap focusing temperature	-15 to +50°C (settable in 1° increments.)
Cold trap (secondary) desorption temperature minutes.	50 to 400°C (settable in 1° increments) for 0 to 99.9 (settable in 1 minute increments.)
Cold trap heating rate	Max (ballistic heating reaching 100°C/sec during first critical stages of trap heat) or options between 1° and 40°C/sec
Split on during secondary (trap) desorption	Yes/No
Flow Path Temperature	50 to 210°C
GC Cycle Time	0 to 999.9 minute
Minimum Carrier Gas Pressure	0.0 to 99.0 psi

Table 1. Parameters and Ranges for UNITY thermal desorber

3.2 Sample flow path and key system components

A detailed schematic of the UNITY flow path in Standby Mode is shown in Figure 2. Key components include the heated valve (material: PTFE), cold trap (material: quartz), transfer line (material: uncoated, deactivated fused silica) and connecting tubing (Silcosteel.)

3.3 Operational sequence for 2(3) stage desorption mode

(For more detailed information, see Section 22.)

When a tube is placed and sealed into the flow path of UNITY for conventional 2(3) stage desorption, it undergoes the following sequence of operations:

Standby (Figures 1 and 2)

Options: - Split flow on or off

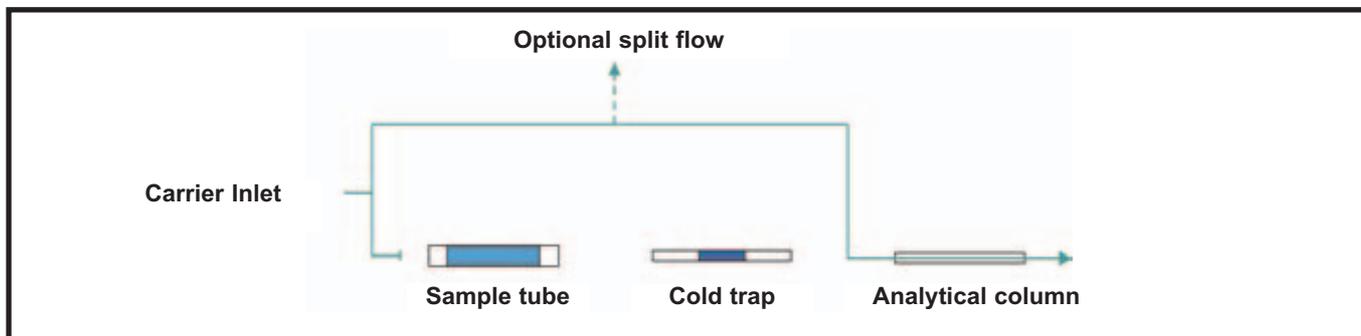


Figure 1. Simplified schematic of the UNITY flowpath in standby mode

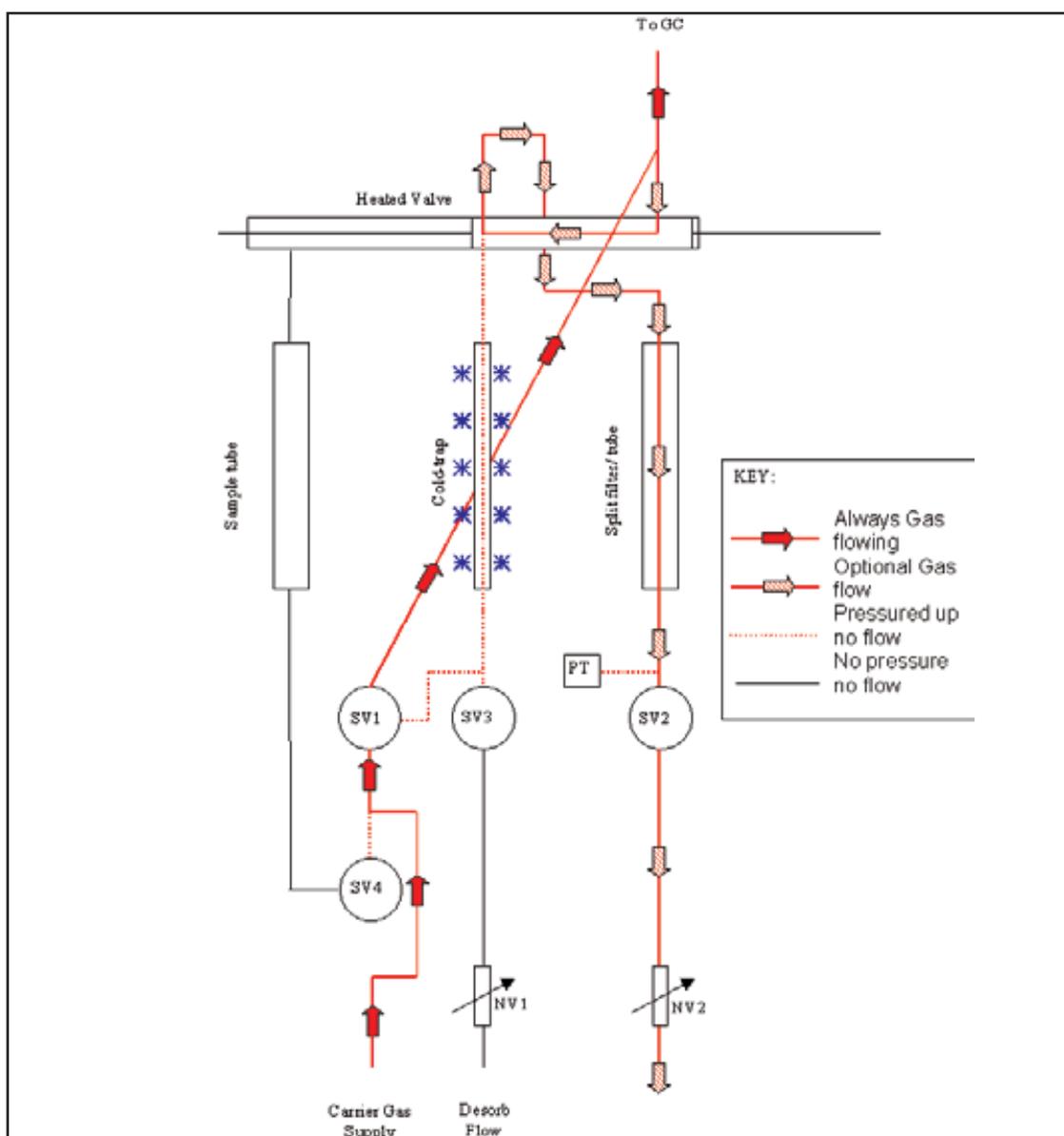


Figure 2. Detailed Schematic of UNITY flowpath in Standby Mode (split off)

Ambient temperature purge (Figures 5a, 5b and 6)

Options: - Split flow on or off

Cold trap: - in or out of line

Note: Either the split flow or the desorb (trap) flow or both must be open during the purge.

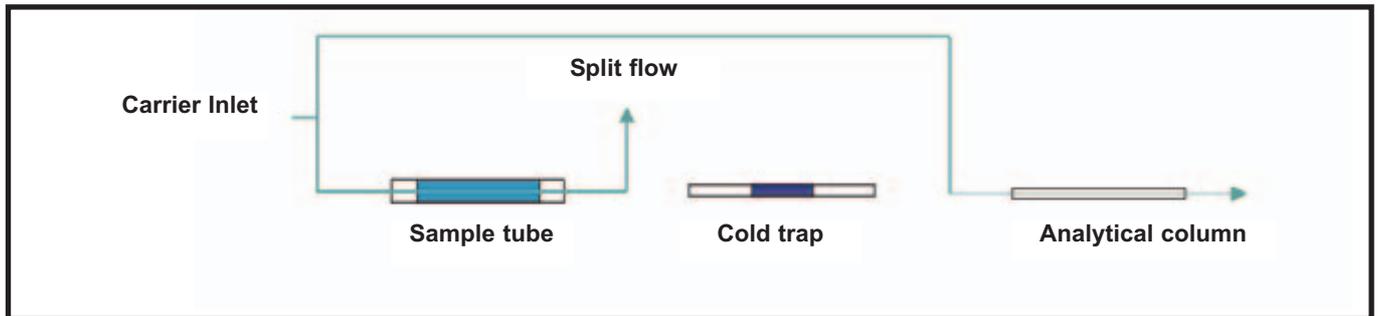


Figure 5a. Simplified schematic of the UNITY flowpath in ambient temperature purge mode - cold trap off line

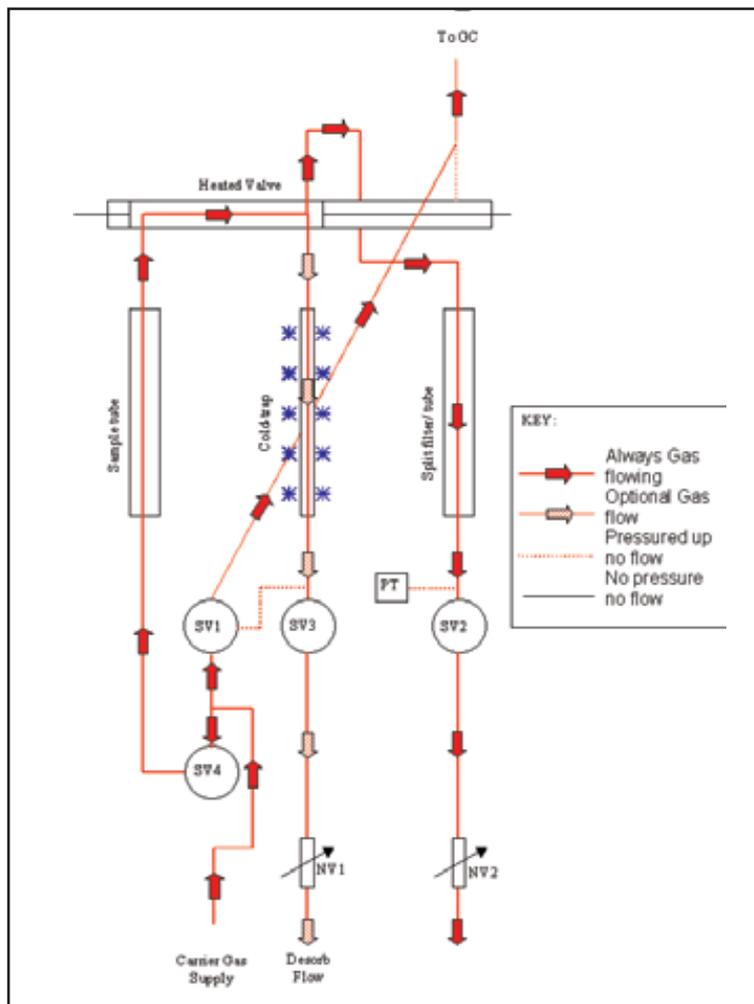


Figure 5b. Detailed schematic of UNITY flowpath in ambient temperature purge mode - cold trap off /on line

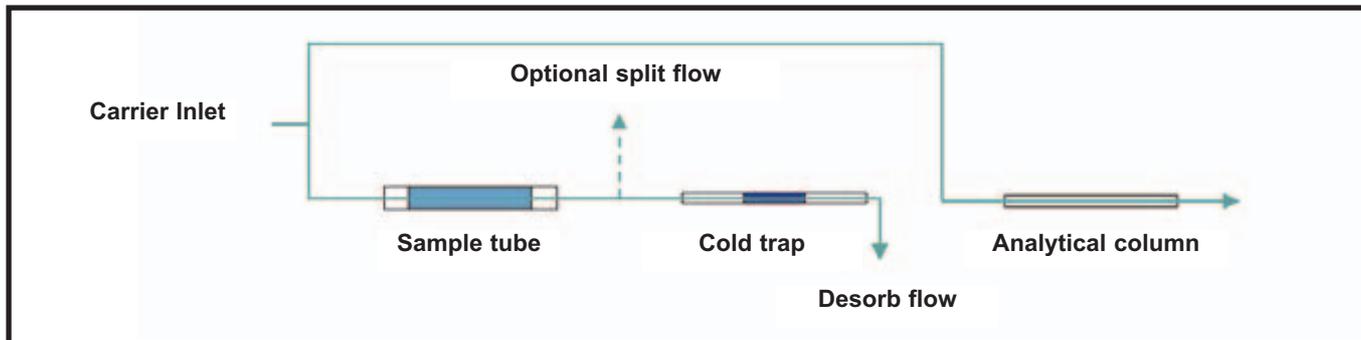


Figure 6. Simplified schematic of UNITY flowpath in ambient temperature purge mode - cold trap on line

Elevated temperature purge (optional) (Figures 7a and 7b)

Options: - Split flow on or off

Cold trap: - in or out of line

Note: Either the split flow or the desorb (trap) flow or both must be open during the purge

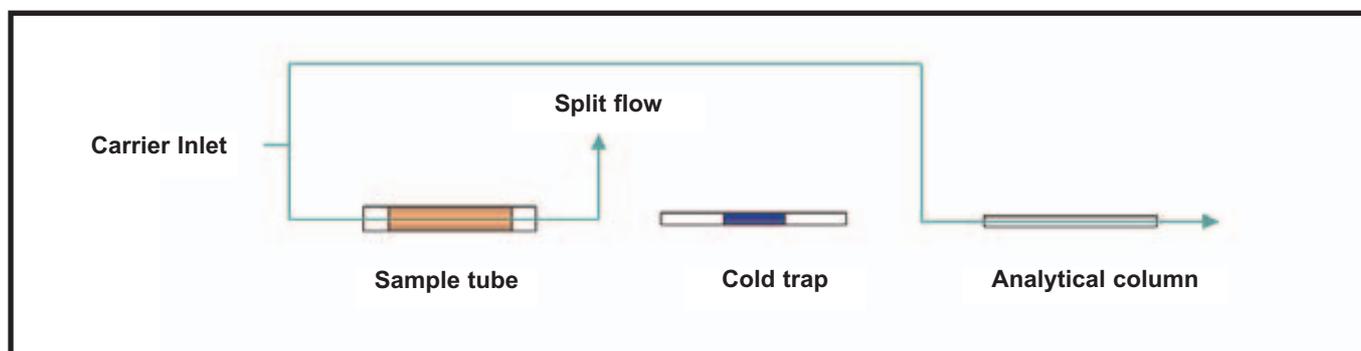


Figure 7a. Simplified schematic of UNITY flowpath in elevated temperature purge mode - cold trap off line

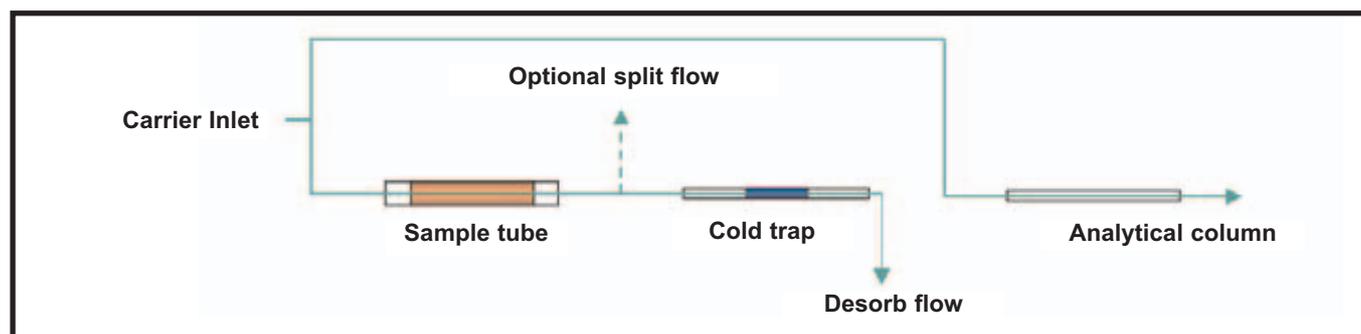


Figure 7b. Simplified schematic of UNITY flowpath in elevated temperature purge mode - cold trap on line

Primary (tube) desorption (Figures 8a and 8b)

At the start of primary (tube) desorption the tube oven begins to heat (either from ambient or from the temperature of the optional elevated temperature purge if selected). **Note that the tube desorption time is measured from the beginning of tube oven heating and not from the time at which the sample tube reaches its desorption temperature.**

Options: - Split flow on or off



Figure 8a. Tube Desorption - Series of simplified schematics showing analytes being desorbed from the sample tube to the cold trap

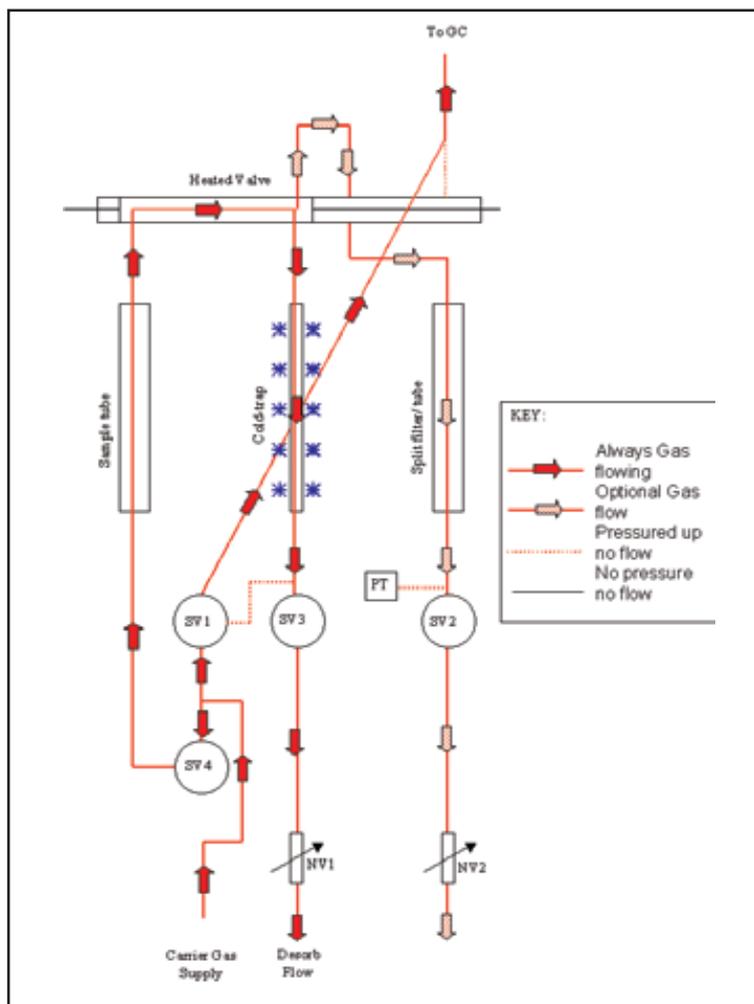


Figure 8b. Detailed schematic of UNITY flowpath in primary (tube) desorption mode

Pre-Trap Fire Purge (Figure 9)

Following primary desorption, the heated valve is moved and carrier gas is flushed through the split tube and the trap to remove any residual air and water prior to trap injection. It may also be used to dry purge the cold trap prior to injection when direct desorbing solid or humid samples.

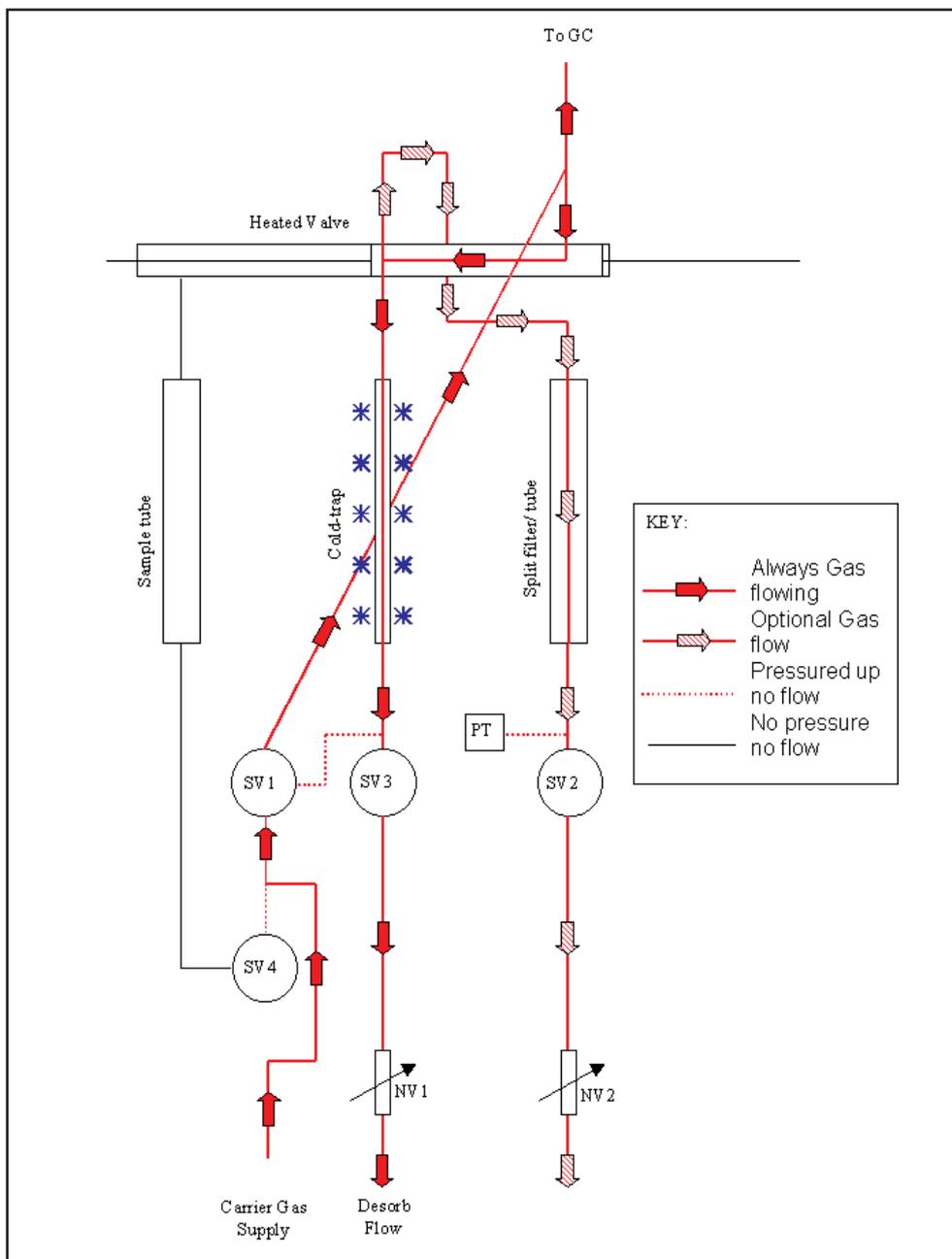


Figure 9. Detailed schematic of UNITY flowpath in pre-trap fire purge mode

This purge step is pre-set to run for 18 seconds. If the user requires a different purge time this can be set in View > Options > Sequence section of the UNITY software (Section 16.4)

Secondary (trap) desorption (Figure 10a & b)

Options: - Split flow on or off

Note that the flow path of UNITY remains in the trap desorption configuration until the trap has cooled back down below 50°C.

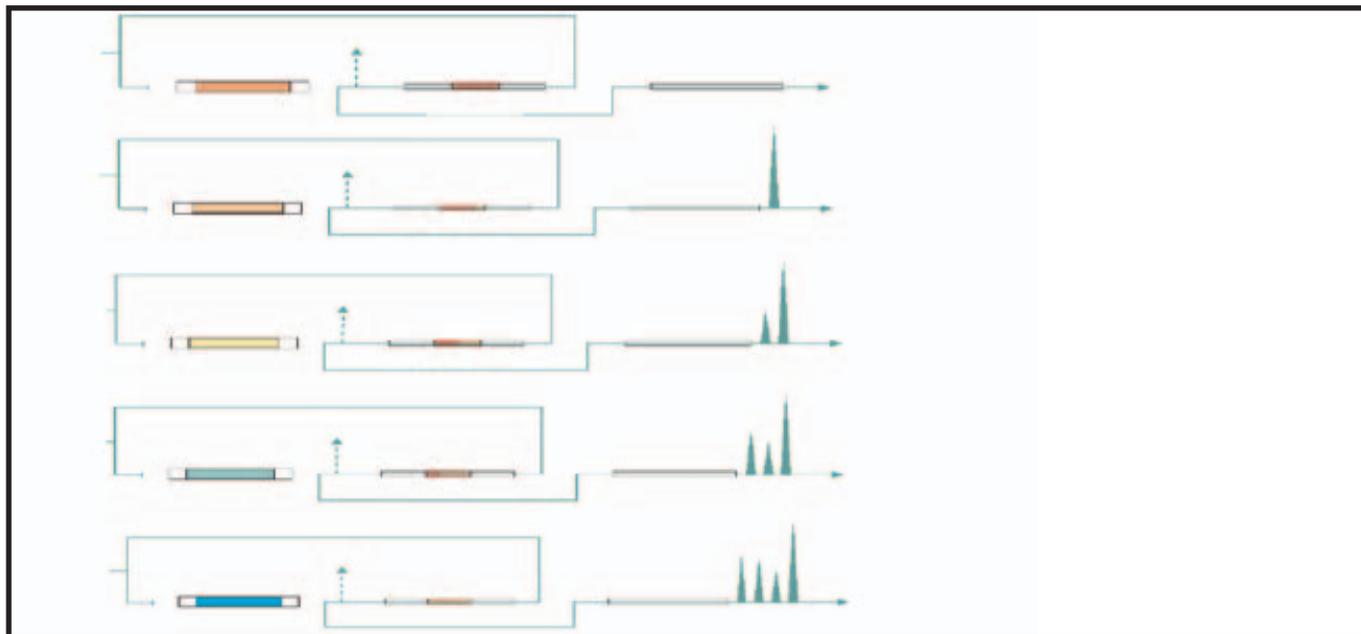


Figure 10a. Trap Desorption - Series of simplified schematics showing analytes being desorbed from the cold trap to the analytical column and the sorbent tube cooling to ambient

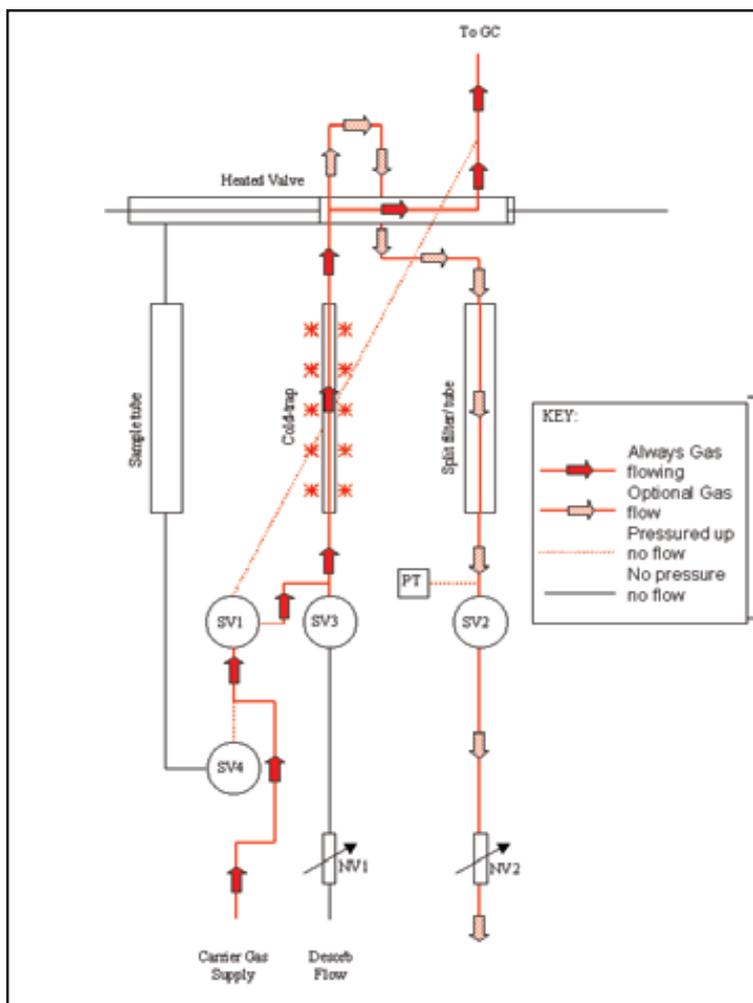


Figure 10b. Detailed schematic of UNITY flowpath in Secondary (trap) desorption mode.

3.4 Operational sequence for tube conditioning mode

(See Section 22.1 for further details)

The first four stages of operation in tube conditioning mode; - standby, pressurise, leak test and ambient purge are identical to those described above for 2(3) stage desorption (Figures 2 to 6.)

Stage five of tube conditioning is primary (tube) desorption with the split flow on and the cold trap off-line (Figure 7.)

3.5 Sample tubes

UNITY is compatible with industry standard sample tubes - 3.5-inches (89 mm) long by 1/4-inch (6.4 mm) O.D with 5 mm (stainless steel and coated steel) or 4 mm (glass) I.D.. Sorbent is retained in stainless steel (or coated steel) tubes using stainless steel (or coated steel) gauzes and a gauze retaining spring. Quartz or glass wool is recommended for retaining the sorbent in glass tubes.

3.6 Tube desorption oven

The UNITY tube desorption oven heats up rapidly (~150°C/min) at the start of elevated temperature purge or tube desorption. It begins to cool at the end of primary (tube) desorption and reaches 50°C from 300°C within 10 minutes.

3.7 Tube filters and seals

When ready for analysis, sample tubes are placed into the cool desorption oven with the sampling (grooved) end pointing to the rear of the instrument. Operation of the lever mechanism seals the sample tube into the UNITY flow path. Temperature resistant Viton O-rings seal onto the outer wall of the sample tube, ~2 mm from either end. Each O-ring should last for >1000 tube-sealing operations. In the event of failure, O-rings at both ends of the sample tube are readily replaced by the user. (See Section 35.4.)

A porous PTFE filter sits just behind the O-ring in both sample tube seals. These prevent UNITY flow path contamination in the event that sorbent particles or high boiling sample materials migrate out of the tube. The filters are readily accessed for user replacement. (See Section 35.5.)

3.8 The cold trap

The cold trap contains a 2 mm diameter x 60 mm long bed of sorbent (30 to 100 mg depending on sorbent density) supported by quartz or glass wool. **Note that the length of the first plug of glass wool is included in the total 60 mm sorbent bed.**

3.9 Cold trap cooling and heating

UNITY contains a 2-stage peltier cell, which uniformly cools the entire 60-mm sorbent bed to a minimum of -10°C in ambient temperatures as high as +30°C. N.B. The minimum is reset at -15°C for ozone precursor systems. At -10°C, a cold trap packed with an appropriate series of sorbents including carbonised molecular sieve, allows quantitative retention of compounds as volatile as ethene and freons from over 500 ml of gas/air. No liquid cryogen is required. With the trap at -15°C quantitative recovery of ethyne can be demonstrated from over 200 ml of gas/air.

Note: C₂ hydrocarbons (ethyne, ethene, ethane) and the most volatile freons cannot be sampled using sorbent tubes at ambient temperatures - Breakthrough volumes are too small for practical use even with the strongest tube sorbents. These compounds must be collected in bags or canisters or sampled on line. These whole air/gas samples are then introduced to the UNITY cold trap using an Air Server Accessory.

Once all the target analytes have been collected and focused in the cold trap, the trap oven heats ballistically reaching rates in excess of 60°C/sec for the first critical stages of trap desorption. Uncompromised capillary chromatography is produced without on-column focusing and with desorption flows as low as 2 ml/min. This facilitates splitless operation with high-resolution capillary GC.

3.10 Gas flow through the cold trap

The UNITY cold trap operates in backflush mode - the sample gas stream enters and leaves the cold trap through the narrow-bore/restricted end which points to the rear of the instrument. Backflush desorption allows use of a series of 2 or 3 sorbents of increasing strength in the cold trap - For example; Tenax TA™

(weak) backed up by Carbograph 1TD™ (medium), backed up by UniCarb™ (strong). This facilitates the analysis of wide volatility range samples. (High boiling compounds are retained by and quantitatively desorbed from the first weak sorbent, without ever coming into contact with the stronger sorbents behind.)

3.11 Trap filters and seals

As with the sample tube, the cold trap is sealed into the gas flow path of UNITY via O-rings, which seal on the outer wall of the trap tube. At the cool non-valve end of the trap, the O-ring is backed up with a porous PTFE filter to prevent contamination of the pneumatics in the event of sorbent particles migrating out of the trap. The user has access to this O-ring seal and filter in the brass trap connector (Section 4.2), but a Service visit is required to access and change the trap O-ring seal in the heated valve.

As the cold trap is only changed infrequently, the seals will rarely, if ever, need to be replaced. It is recommended that UNITY is professionally serviced once per year and that the valve-end seal be changed as part of this annual maintenance operation.

3.12 Split filters

There is a split filter tube packed with charcoal (P/N UTD-5065) on the split line upstream of the on/off solenoid and needle valves. This prevents contamination from the sample reaching the valves or laboratory air. The flow path up to the charcoal filter is heated and constructed of inert, Silcosteel® tubing. The filter itself is the same size as a standard sample tube and may be readily replaced by a clean sorbent tube if the split effluent is to be re-collected for repeat analysis, see Section 34. The split filter (or re-collection tube) is sealed into the split flow line using easy-connect, Viton O-ring seals and by operating a lever in the same manner as the sample tube. The sampling end/grooved end of the re-collection tube should point to the rear of the instrument.

Conventional charcoal split filters will become contaminated over time and should be reconditioned or repacked when required (Section 35.10.)

3.13 User interface

UNITY is controlled from an IBM or compatible PC via software operating in a 32 bit Windows™ environment (Windows 98, ME, 2000 or NT4). Everyone familiar with Microsoft® Office and related Windows products should readily understand the interface.

4 UNITY Installation

4.1 Packing list

The following items are contained in your UNITY shipment. Please inform your distributor immediately if there are any shortages. Items marked with a * are consumable items and may require replacing at intervals. These items are available in various pack sizes and the commercial part numbers required to re-order them are given in the 'Focusing on Volatiles' brochure included at the back of this manual. Alternatively further information may be found on our web site www.markes.com

Part No.	Description	Qty
<i>General Parts</i>		
U-UNITY(e)	UNITY(e) instrument	1
UTD-5003	Transfer line	1
UTD-1165	Perspex cover	1
U-SW001	Software CD	1
U-T2GPH*	General Purpose Cold Trap (packed with sorbent) + Trap Certificate	1
Z-0024	Mains cable (suitable for your geographic location)	1

Part No.	Description	Qty
<i>Documentation</i>		
UTD-9001	User Manual and Brochure Pack	1
QUI-1014	UNITY Quick Reference Guide	1
<i>UNITY common parts - shipping kit</i>		
UTD-5105*	Sampling tube packed with Tenax TA. Conditioned and capped with ¼-inch brass SwageLok type caps fitted with combined PTFE ferrules. Etched with a unique serial number	1
UTD-1050*	Disc Sintered PTFE 5.1mm	2
UTD-1074*	Disc Sintered PTFE 6.5mm	2
UTD-1125	Autosystem Clamp	1
UTD-5062	Tube Extractor	1
UTD-5063	Tool Kit (standard)	1
UTD-5064	Trap Alignment Tool	1
UTD-5065	Split Filter Tube Packed with Charcoal (unetched)	1
UTD-5093*	Fused Silica Transfer Line Insert 1.5m & PTFE Sleeve	1
Z-0026	Union 1/8 "x 1/8" Brass SwageLok	1
Z-0050	Union Reducer 4 mm x 1/8" Brass	1
Z-0055	Tubing Plastic 4mm	1m
Z-0087*	O-ring Size 006 Viton	2
Z-0089*	O-ring Size 010 Viton	4
Z-0092*	O-ring 3mm ID, 1mm Section	2
Z-0097*	Quick Seal Connector and Instructions	2
Z-0145	Tube Copper 1/8" - 3M	1
Z-0157	Nut 1/16 St St Swagelok	1
Z-0189	Cable PC	1
Z-0283*	Ferrule 1/16 Graph. Vesp. 0.4mm	2
Z-0285	O-ring Insertion Tool	1
Z-0351	O-Ring Extraction Tool	1
Z-0372	Washer 1/4" x 1 1/2"	2
Z-0371	Washer 1/4" x 1"	2
Z-0449	Washer 1/4" x 2"	1
Z-FS6A3	Fuse 5mm x 20mm 6.3anp Antisurge	1
Z-NM4FSS	Nut M4 St St	4
<i>For UNITY</i>		
UTD-5095	PCB GC Interface for UNITY + GC	1

Part No.	Description	Qty
<i>For EPC ready UNITYe</i>		
UTD-5098	PCB GC Interface for UNITYe	1
	<i>EPC parts for installation on 6890/6850GC</i>	
Z-0026	Union Brass 1/8" - 1/8"	2
Z-0040	Ferrule 1/8" x 1/16" Graph Vesp	5
Z-0108	Tube PEEK 1/16" OD x 0.03" bore	3m
Z-0402	Ferrule 1/8" x 2mm Graph Vesp	1

Table 2. Packing List for UNITY thermal desorber

4.2 Installing the cold trap

4.2.1 Trap sorbent selection

As a general rule, because it is maintained at sub ambient temperatures, sorbent selection is less critical for the trap than the sample tube.

For most applications involving VOCs ranging from C₅ - C₃₂, a trap containing ~ 30mm bed of Tenax TA backed up by ~ 30mm Carbograph 1TD™ separated and supported at each end by unsilanised glass wool plugs, will suffice. (P/N U-T2GPH)

Traps containing the three sorbents Tenax TA backed by Carbograph 1TD™ backed by Carboxen 1000™ each separated and supported by unsilanised glass wool plugs would be ideal for focusing compounds ranging from C₂ - C₂₄. (P/N U-T4WMT).

Note: This type of trap will retain a small % of water and therefore requires very careful selection of analytical conditioning parameters. (See Section 13.3)

4.2.2 Packing the cold trap

Note that ready-packed traps are available from Markes International Ltd. Please see Table 3 for details. Empty trap tubes (P/N U-T7EMP) are also available for the user to pack as required. The UNITY cold trap is constructed of quartz and has an O.D. of 2.9 mm, and an I.D. of 1 mm at the inlet / outlet end and an I.D. of 2 mm at the other end. It is fragile and should be packed with care.

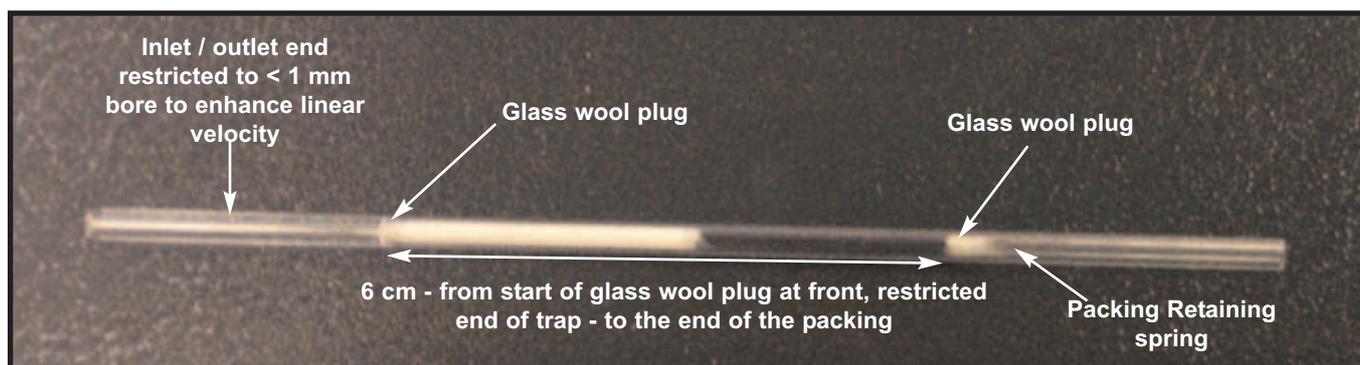


Figure 11. A packed UNITY cold trap

Empty cold traps should be packed from the wider (2 mm) bore end using the following procedure. First insert a 2-5 mm plug of quartz or glass wool using a suitable flexible tool such as a 15 cm length of 1/16-inch, narrow bore plastic tubing (PTFE or PEEK tubing is ideal.) Pour in the required amount of sorbent.

Note: A 6 cm length of the wider bore section of the trap tube, measured from the point of the bore restriction, is subjected to full cooling and heating power.

The trap packing, including all but the back glass / quartz wool plug, should be within this 6 cm length

of the trap (Figure 11.) Note that analytes enter and desorb from the trap through the restricted end. Multibed traps must therefore be packed with the sorbents arranged in order of increasing strength from the narrow end. (See notes on sorbents in Section 8.1.) 1 to 3 mm plugs of quartz wool must separate different sorbents. Plug the end of the trap with another glass wool plug, backed with a packing retaining spring. If unsilanised glass (rather than quartz) wool is used in the cold trap, it may cause degradation and / or tailing of polar and labile compounds. Silanised glass wool does not suffer from these limitations but must not be taken above 275 °C or breakdown products from the silylating reagent will coat the sample flow path of the desorber, reducing recovery of high boiling compounds.

Note: Do not over-compress the cold trap packing as this will cause high impedance, which may limit trap desorption flows. If high trap desorption flows will be required, for example when using a high split ratio, use 40-60 rather than 60-80 mesh sorbent.

Part Number	Name	Application
U-T1HBL	High Boilers Trap	Suitable for VOCs from n-C ₆ to n-C ₄₀
U-T2GPH	General Purpose Hydrophobic Trap	Suitable for VOCs from n-C _{4/5} to n-C _{30/32}
U-T3ATX	Air Toxics / TO-14 Trap	Suitable for VOCs from n-C ₂ to n-C ₁₂
U-T4WMT	Water Management Trap	Suitable for VOCs from ethane to n-C ₂₀ - allows selective elimination of some water but is less hydrophobic than the 'General Purpose Hydrophobic' trap
U-T503F	Ozone Precursor / Freons Trap	Suitable for Ozone Precursors from acetylene to trimethyl benzene and Freons
U-T6SUL	Sulphur Trap	Suitable for volatile, reactive species such as sulphur containing compounds
U-T7EMP	Empty Cold Trap	
U-T8CUS	Custom packed Cold Trap	
U-T9TNX	Tenax Cold Trap	For selective elimination of volatiles and for other general TD applications with target analytes ranging in volatility from n-C ₆ to n-C ₃₂
U-T10CW	Chemical Agents Trap	For high boiling compounds such as Chemical Warfare agents and phosphorus pesticides
U-T11GPC	General Purpose Graphitised Carbon Trap	Recommended for EPC operation, suitable for VOCs from n-C _{4/5} to n-C _{30/32} (NB not suitable for thermally labile compounds)

Table 3. List of UNITY Cold Traps available from Markes International

4.2.3 Cold trap installation

Once UNITY and its accessories have been taken out of the main packing box, lift off the black perspex cover. **N.B.** The perspex cover is supplied with a modification for optional addition of automated sampling. Tilt the front upper panel of the instrument forwards and away from the rest of the instrument on its hinge (Figure 12.) Find the Pozidriv™ screwdriver supplied as part of the standard tool kit within the shipping kit.

Hook the screwdriver under the far side of the hinge as shown in Figure 12 and push firmly upwards and towards the back of the instrument. This separates the hinged cover from the rest of the instrument. Put the cover to one side.

Note: The carrier gas supply to the instrument and the instrument itself must be turned off before using

the following procedure to install or replace a packed cold trap.

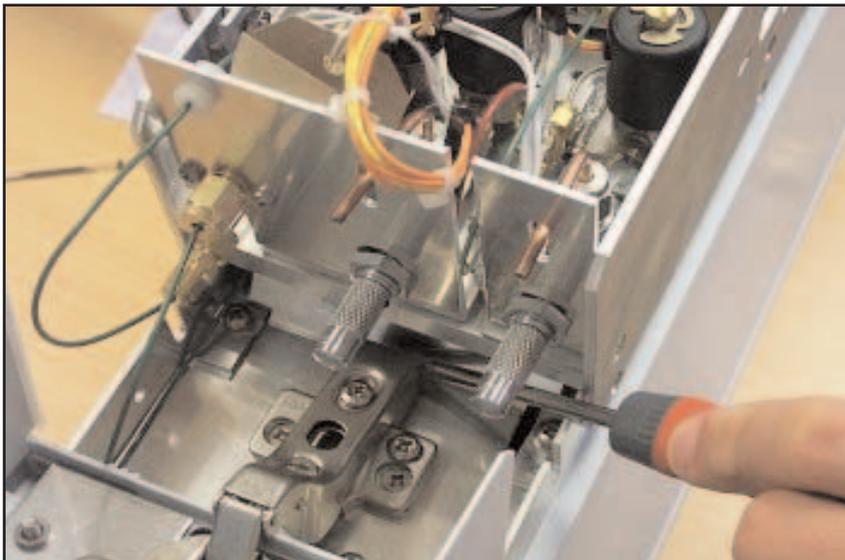


Figure 12. Removal of the front hinged panel

Using the 7/16 x 1/2" AF wrenches (spanners) provided in the tool kit, undo the 1/8-inch brass nut connecting the 1/16 -inch peek tubing to the front of the desorb pneumatics panel. (Figure 12) Undo the nut (labeled as nut B in figure 13) furthest from the solenoid valve on the 1/16 x 1/16-inch union connecting the desorb pneumatics assembly to the carrier bypass line (Figure 13). Pull the wire harness out of its retaining clip and uncouple the black plug in the middle of the harness.

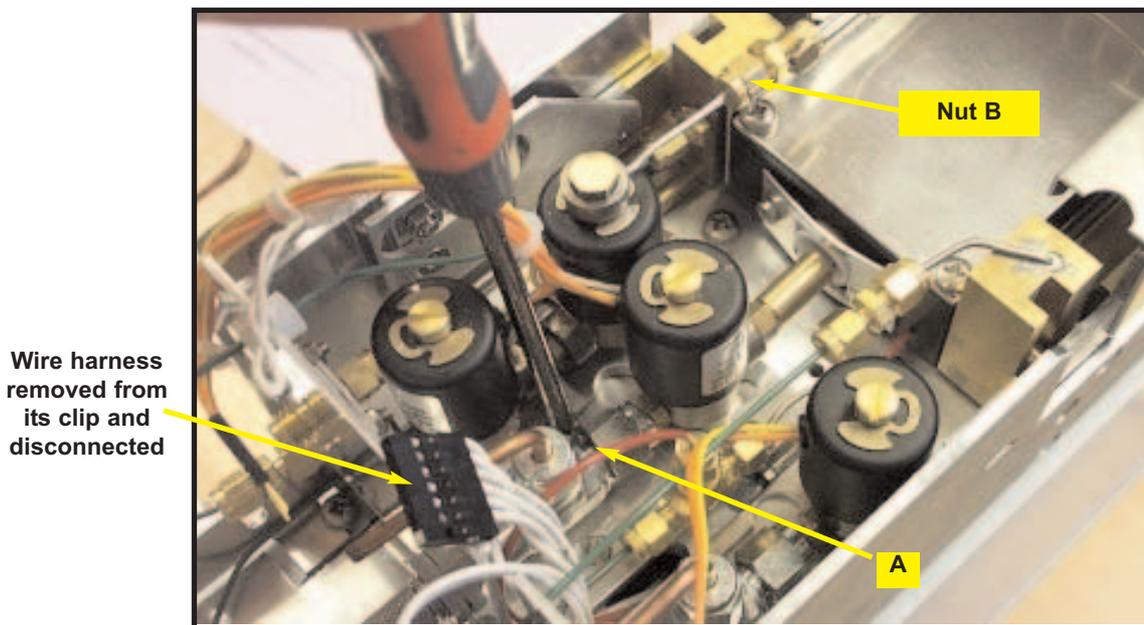


Figure 13. Loosening the pneumatic assembly for cold trap insertion

Using the Pozidriv screwdriver supplied in the tool kit, loosen the screw at the bottom of the desorb pneumatics assembly - marked A in Figure 13 - Loosen screw A by ~4 turns. Do not remove the screw completely. Gently pull the desorb pneumatic assembly towards the front of the instrument being careful to keep it in the horizontal plane by keeping screw A inside the slot in the pneumatic assembly base plate. The swivelling brass trap connector will usually be left attached to the pneumatics as they are withdrawn (Figure 14.) Once clear of screw A, pull the pneumatics forward and rotate to the left thus providing sufficient space to insert the cold trap.

The sample enters and leaves the cold trap from the narrow bore end via the heated valve. The cold trap should be positioned in the cold trap box such that the narrow bore end is nearest the heated valve - i.e. pointing to the rear of the instrument.

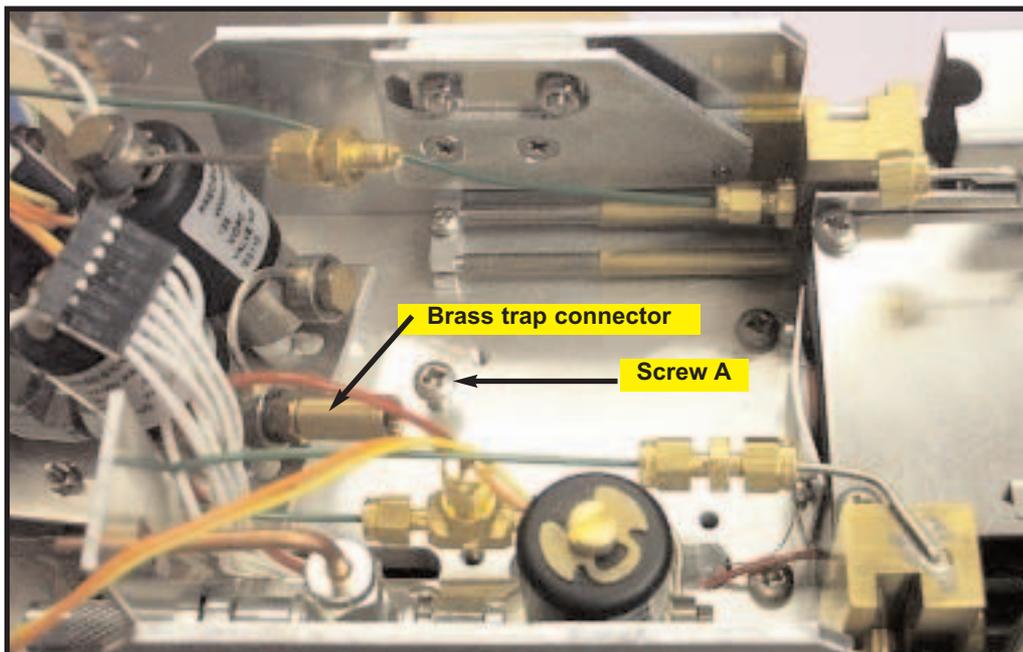


Figure 14. Pneumatics assembly withdrawn

Remove the packed cold trap from its packaging along with the two small Viton spacer O-rings (Z-0092) from the shipping kit. Place the two O-rings within 20 mm of the wide bore end of the trap (Figure 15.)

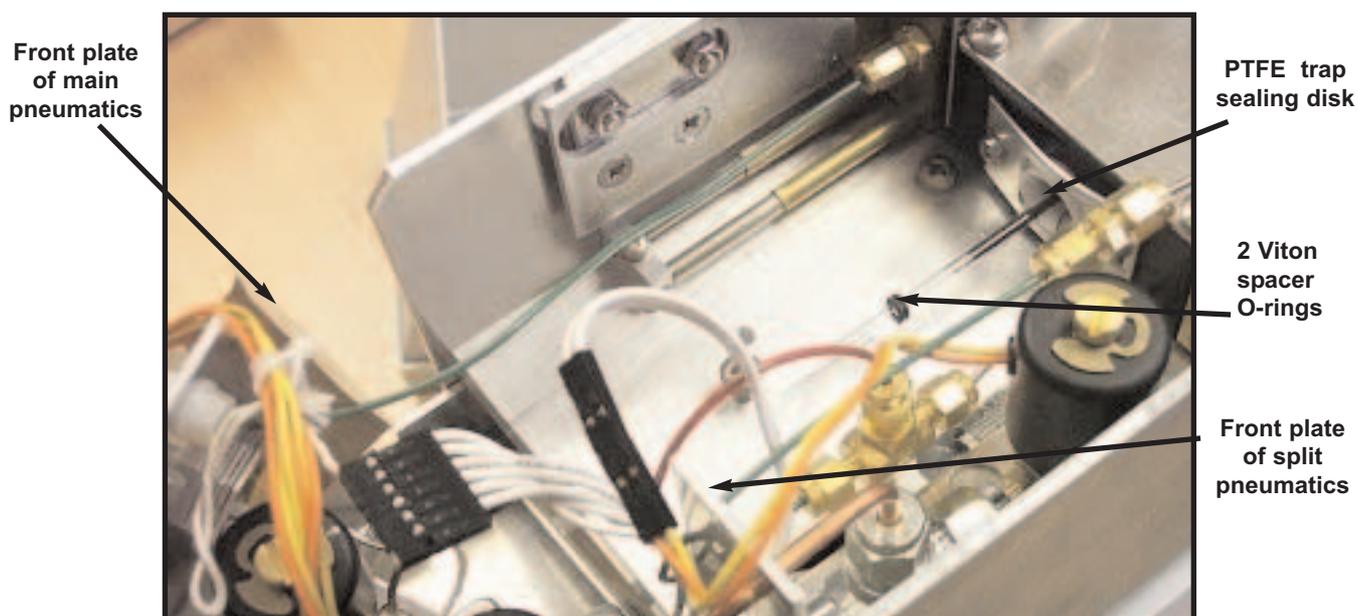


Figure 15. Inserting the quartz cold trap tube

Gently push the restricted / narrow-bore end of the trap tube into the cold trap box. You will feel increased resistance as the cold trap pushes into the seal at the valve end. **DO NOT APPLY EXCESSIVE FORCE TO THE QUARTZ COLD TRAP TUBE** - swizzling (turning) the cold trap slowly with your fingers as it is pushed into the cold trap box can make installation easier. Before installing a cold trap tube for the first time or whenever in doubt about how much force to apply or the locations of the various system components practice once or twice using the trap alignment tool supplied with the shipping kit.

Note: NEVER SWITCH UNITY ON WITH THE TRAP ALIGNMENT TOOL INSTALLED.

The trap seals are already aligned and gentle, steady pressure should be sufficient to push the tube into the valve seal. Approximately 11 mm of quartz tube should be protruding beyond the face of the white PTFE sealing disk once the trap tube is properly located. Bring the pneumatic assembly back and relocate screw A in the slot on the pneumatic assembly base plate. Take care here that the brass trap

connector does not hit the end of the quartz cold trap. Push the assembly gently back in the horizontal plane guided by screw A. Apply gentle steady pressure to push the trap into the sealing O-ring located inside the brass trap connector.

Note: When the trap tube and connector are correctly positioned, the front plate of the main pneumatic assembly should align closely with that of the split pneumatic assembly. Retighten screw A firmly and reconnect the unions and gas connections. Reconnect the plug in the electrical harness and replace it in the clip on the pneumatics front plate.

4.3 Installing the transfer line

UNITY is supplied with a universal transfer line to convey desorbed analytes from UNITY to a gas chromatograph or other analytical system. The sample path utilises a deactivated fused silica line (0.25mm I.D. and 0.35mm O.D.) heated over its entire length by means of a distributed heater and at the GC end by heat conduction from the GC oven.

The line is 1m long, which is sufficient to reach most gas chromatographs even when a mass spectrometer is attached.

4.3.1 Connecting the transfer line to the gas chromatograph

Most GCs have built in access to the oven region by means of holes in the side, top or back of the oven, with "knock out" sections in the outer casing.

If all such access points are already in use it is possible to gain entry via an unused injector or detector port with or without a heated zone.

The general approach is illustrated in the three diagrams, figures 16, 17 and 18, and the simplest entry is shown in Figure 16.

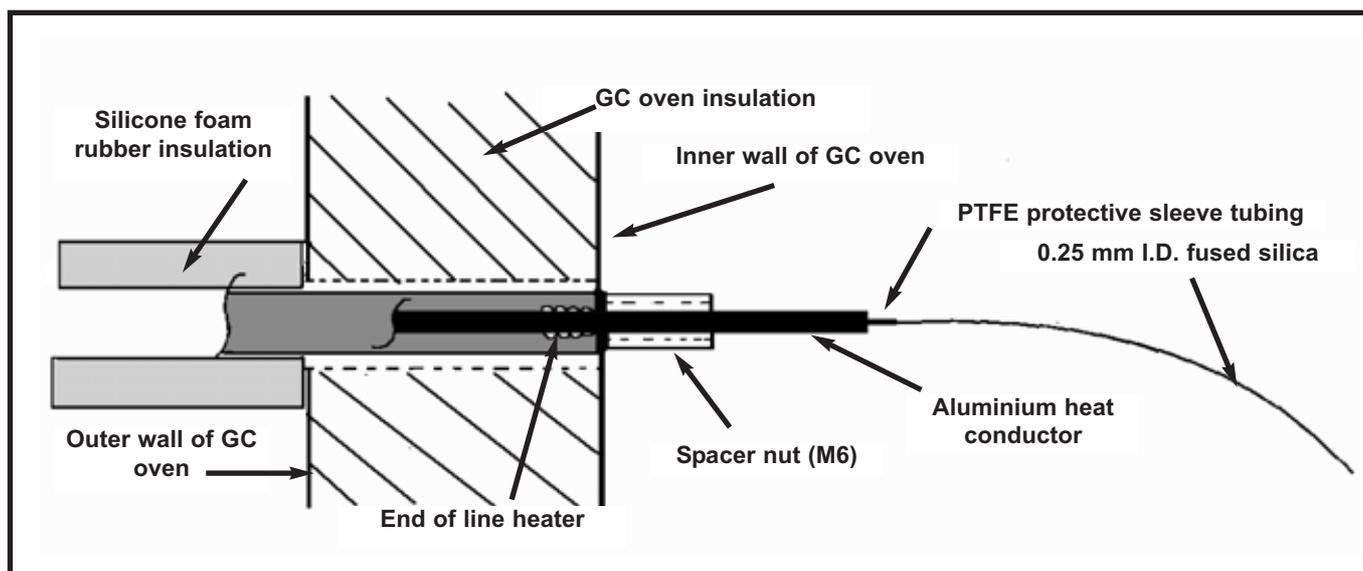


Figure 16. Connecting the transfer line through the outer casing of the gas chromatograph

Note: In all cases, the fused silica line and PTFE sleeve tubing are fitted as the final operation.

Locate a hole in the inner oven wall with a corresponding hole leading to the outside of the instrument. It is usually necessary to displace the oven insulation material to enable the flexible metal line to be pushed against the outside of the inner oven wall.

If the GC oven wall insulation is particularly thick it may be necessary to shorten the silicone foam rubber insulation sleeve, which is intended to rest against the outer wall of the GC oven.

The M6 spacer nut (attached to a 1/4-inch spacer tube on the transfer line) secures the line casing to the oven wall allowing the 1/8-inch aluminium sleeve to protrude into the oven. If the hole in the inner oven wall is larger than the end of the line, fit one of the large metal washers from the shipping kit at this point.

In figure 17 the entry to the GC oven is through the fan protection grill. In this situation the 1/4-inch spacer tube attached to the transfer line prior to the spacer nut is used to extend the line and a special U-shaped metal support bracket is pushed through adjacent holes in the grill to press against the oven inner wall.

Note: The line **must not** be secured with a nut against the fan grill as this could be distorted causing it to hit the fan.

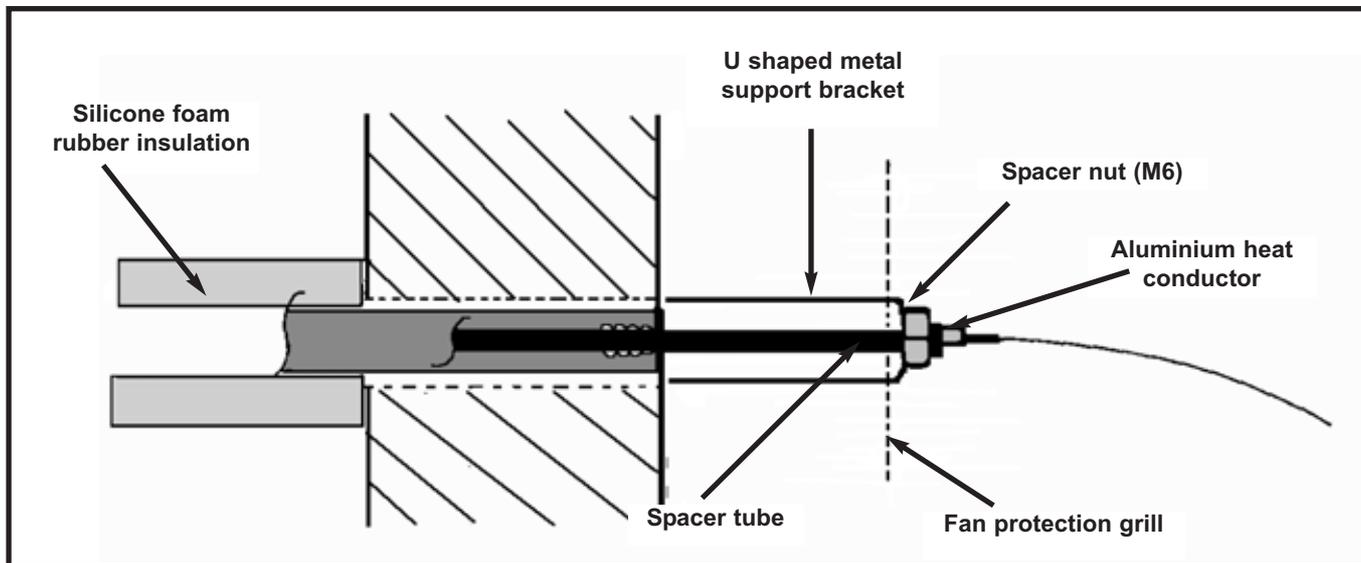


Figure 17. Entry through the fan protection grill

Engineers with detailed knowledge of the GC may wish to remove the fan grill and secure the line as in Figure 18 which shows installation via a heated zone block. As the entry hole will generally be larger than the diameter of the metal line sleeve, one or more of the large washers supplied will be needed. If the heated zone block is particularly deep both the M6 spacer nut and spacer tube will be needed as shown.

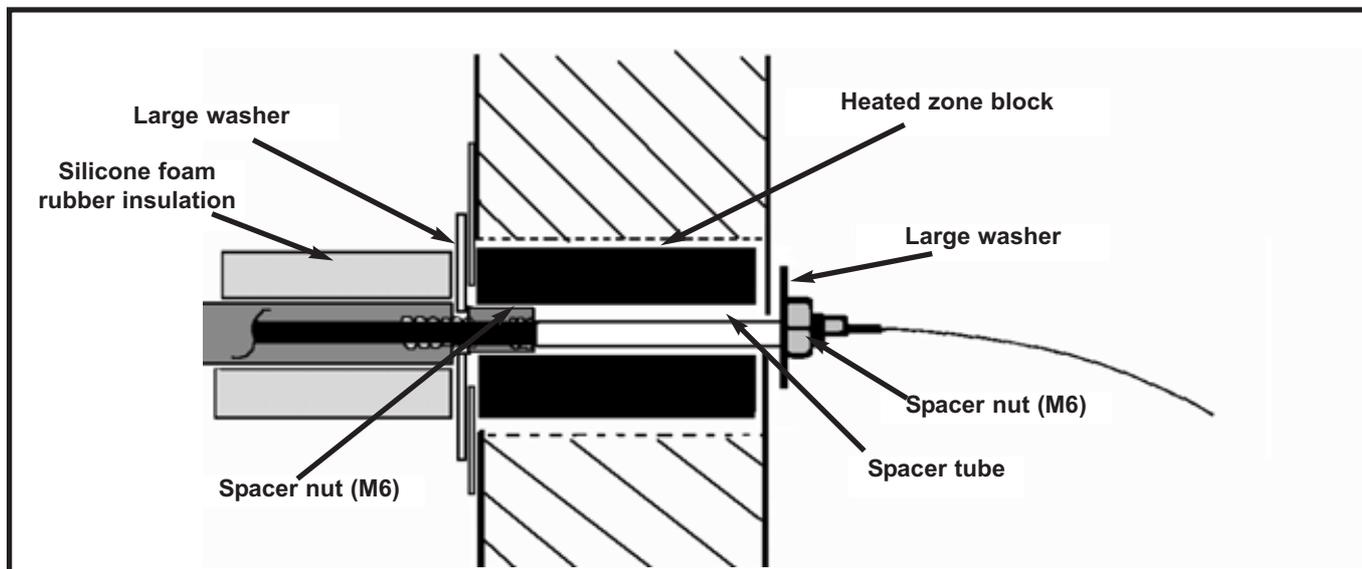


Figure 18. Installation via a heated zone

This part of the line derives its heat from the heated zone block which should be set to run at a conveniently high temperature, preferably 50°C above the line setting but **not above 250°C** as the silicone foam rubber insulation will be damaged.

The parts supplied can be used in other combinations to suit particular instrument configurations.

4.3.2 Installing the fused silica transfer line insert

Once the heated line has been fitted to the GC, the fused silica plus associated PTFE sleeving (see shipping kit) are pushed from the GC end, along the 1/8-inch aluminium tube until they protrude from the other (UNITY) end of the transfer line.

4.3.3 Connecting the transfer line to UNITY

Place UNITY on the bench on the most convenient side of your gas chromatograph. Ensure that the transfer line will reach from the top of UNITY to the selected entry point into the GC oven.

Ensure that UNITY is switched off and cool. Remove the rear top cover on UNITY by unscrewing and removing the black knob on the rear outer cover (Figure 19). The rear cover is then free to slide backwards and away from the instrument. If the air inlet pipe is in place this must be removed.

(This is a push fit coupling, to release the tube press on the outer ring and at the same time pull the tube). The top of the heated valve is now exposed, as shown in figure 20.



Figure 19. Photograph showing black knob fixing rear top cover to UNITY

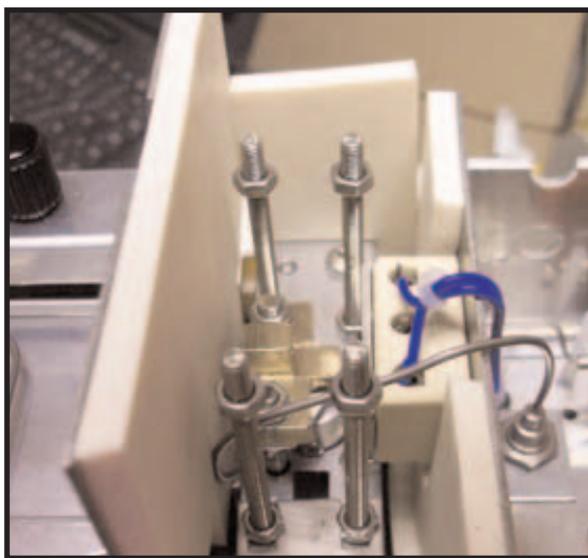


Figure 20. Photograph of the heated valve

Figure 21 shows a partly sectioned view of the completed assembly while figure 22 gives detail of the position of the end of the fused silica tube inside the drilled out end of the Silcosteelled tube from the heated valve.

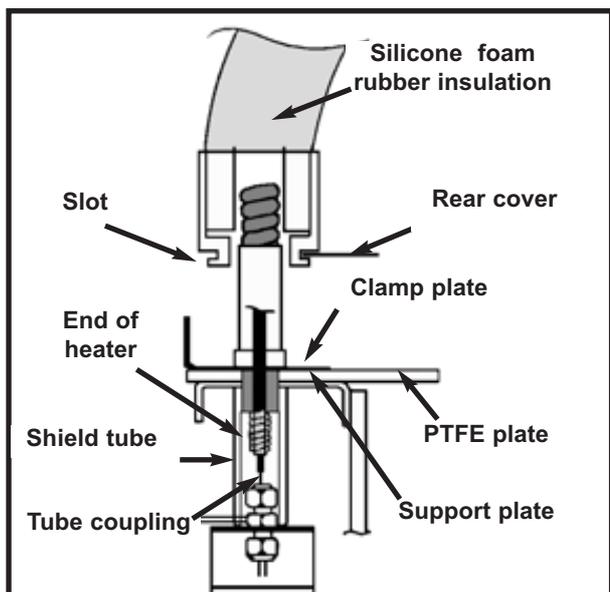


Figure 21. Partly sectioned view of the transfer line connection to UNITY

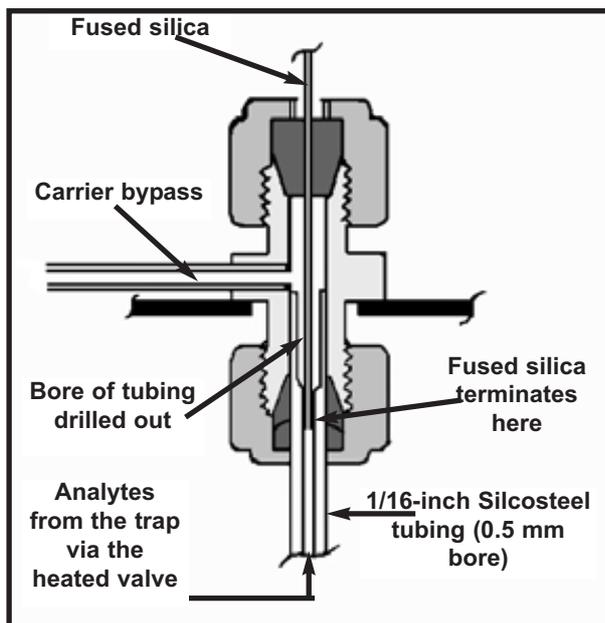


Figure 22. Tube coupling detail

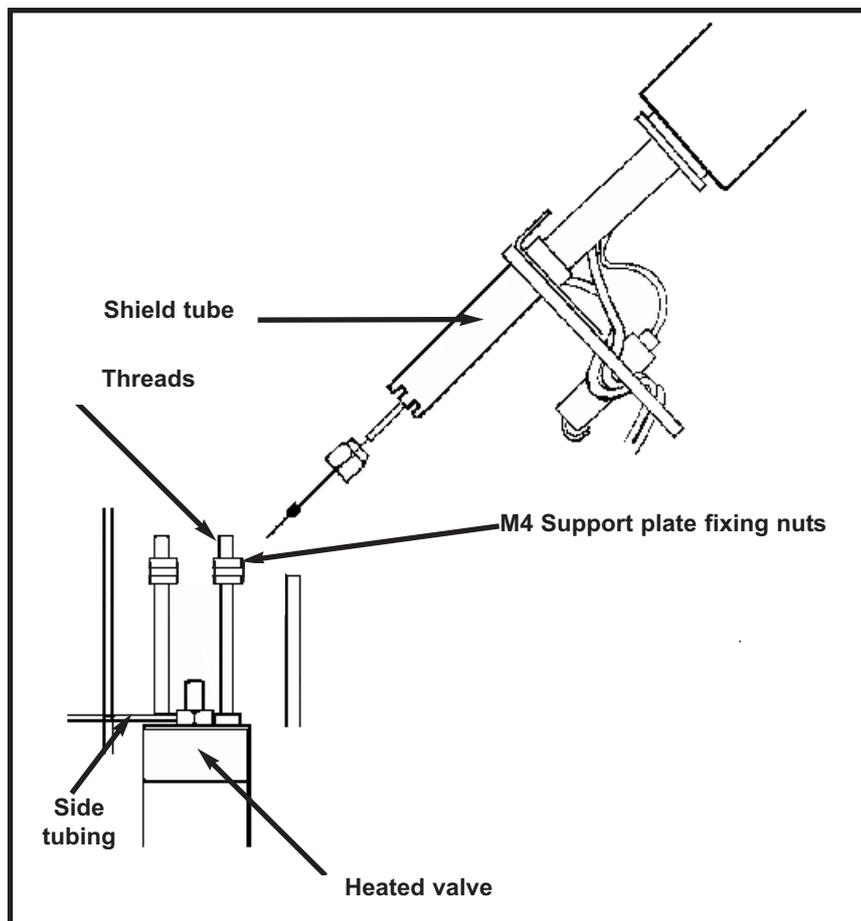


Figure 23. Transfer line support plate

If the fused silica terminates in the space above the end of the Silcosteeted tube some analytes can diffuse into the side arm causing measurable peak tailing. The 0.25 mm I.D. fused silica transfer line must be installed through the union and on into the narrow bore part of the Silcosteeted tubing. Four nuts (M4) for fixing the PTFE plate of the transfer line to the support plate are included in the shipping kit. (Figure 23). Pull about 20 cm of fused silica from the PTFE line casing. Cut off the first few mm of fused silica using an approved capillary cutting tool to remove dirt etc.. Make a mark 25 - 30 mm from the end of the fused silica using typing white-out fluid or an alternative marker. (These operations are easier if an assistant can hold the end of the line and make the mark etc.). Slide the 1/16-inch stainless steel Swagelok type nut and a 1/16 x 0.4 mm ferrule onto the end of the fused silica. The mark must be behind the ferrule to avoid contamination.

Note: If a 0.32 mm I.D. / 0.45 mm O.D. piece of fused silica is used then the mark should be placed approximately 16 mm from the end, and a 1/16-inch x 0.5 mm ferrule will be required.

Feed the fused silica into the top of the tube union and slide the ferrule into position. Screw the nut onto the union and, with the fused silica still loose, position it so that the mark is level with the top of the ferrule. Tighten the nut to trap the fused silica and then tighten a further 1/2 turn using one of the 8 mm wrenches (spanners) provided in the shipping kit. **Do not** over tighten or the ferrule will become distorted.

Carefully bring the clamp plate, PTFE plate and shield tube down into the position shown in figure 21 with the shield tube covering the union nut. The shield tube should be positioned such that the 1/16th side tubing projects through one of the cutouts.

Push the clamp plate and PTFE plate down on to the four exposed threads.

Use the 4 x M4 nuts to tighten the PTFE plate onto the four exposed threads.

Plug the orange 8-way connector into the socket in the base plate by the heated valve (see figure 20). This connector is polarised and fits with the row of wires to the right when viewed from the front of UNITY. The 2 blue heater wires are positioned nearer the front of the instrument, in the connector.

From the back of UNITY slide the rear top cover towards the front of the instrument. When the leading edge reaches the foam insulation of the transfer line, pull up the white plastic end sleeve on the foam insulation so that the slot in the base of the end sleeve is level with the U-cut out in the cover. Push the cover until the back cover moulding is level with the lower case. Replace and tighten the black knob on the back cover which was originally removed.

4.3.4 Coupling the fused silica transfer line to the GC analytical column

Return to the GC and connect the column to the end of the transfer line using the quick seal column connectors provided (P/N Z-0097). Instructions are included in the UNITY shipping kit.

4.4 Cabling.

4.4.1 Power

UNITY operates on any voltage in the range 95 to 255V and from 50 to 60 Hz. It is not necessary to manually select or switch voltages. The system adjusts automatically. The power lead connects to the power input socket on UNITY's back panel (Figure 24). A 2 m power lead is provided (P/N Z-0024).

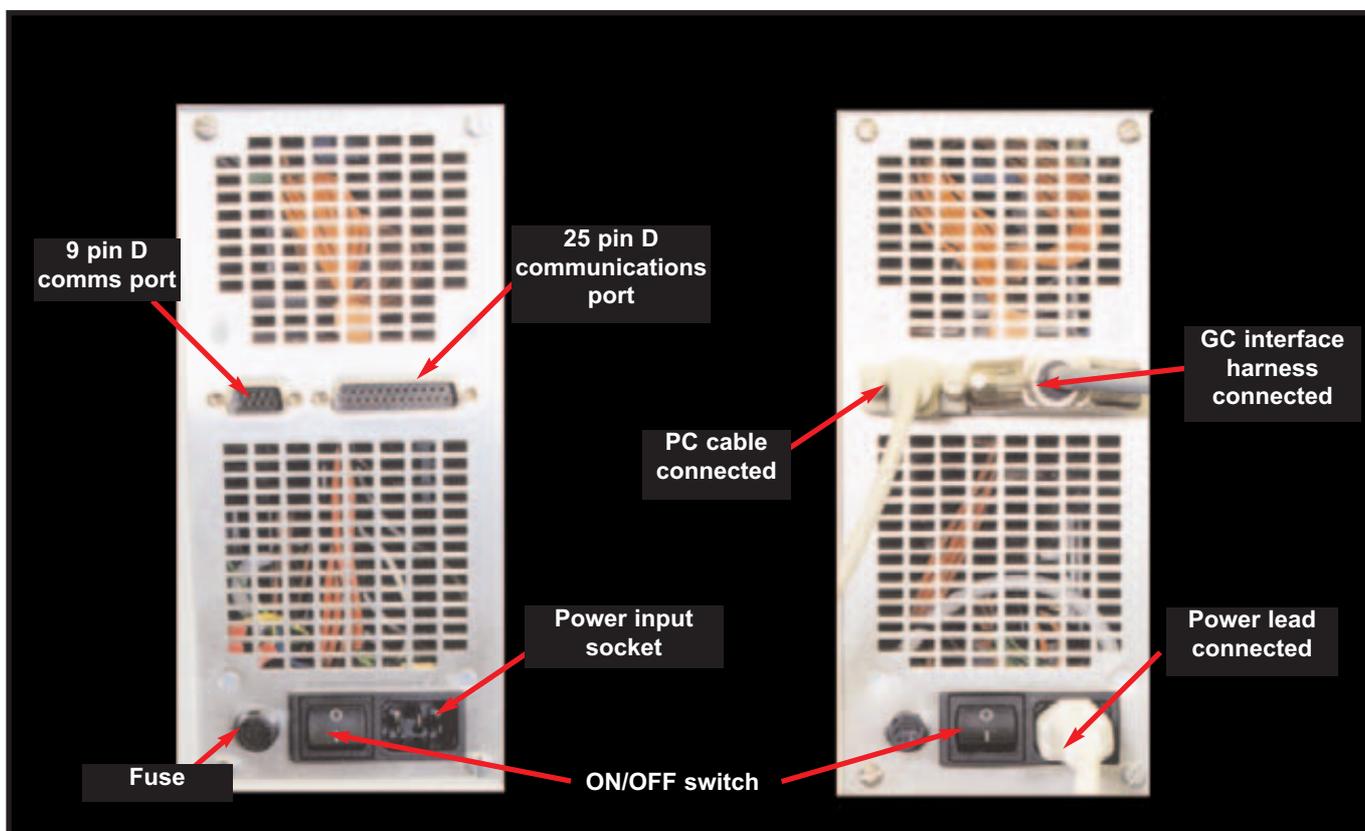


Figure 24. UNITY back panel

4.4.2 Connecting UNITY to the rest of the analytical system

For additional information regarding connection of EPC Ready UNITYe - see Appendix Five

Find the GC Interface harness (P/N UTD-5095) provided in the shipping kit. This cable connects UNITY with the external start and ready connections on the GC. The cable consists of a 25 pin D connector, which is plugged into the 25 pin D communications port on the back panel of UNITY, with 8 free coloured wires at the other end of the cable.

Note: This is a special interface supplied with UNITY and not interchangeable with 'off the shelf' 25 pin D cables.

The **white and red** wires are the most commonly used **UNITY Ready In** connections and the **yellow and green** wires are the **UNITY Start Out** connections. The brown, black and purple wires are only used under certain circumstances and should normally be left free and unconnected.

The UNITY Ready In connections must be connected to the Ready Out connections of the GC.

The UNITY Start Out connections must be connected to the Start In (or External Start) connections of the GC.

These connections are contact closure connections, which are either normally open (and close to cause an event) or normally closed (and open to cause an event). The GC interface logic (Normally Open / Normally Closed) is selected under the UNITY software Options, for further information see Section 16.6.

Further information regarding connecting UNITY to a number of GCs from a variety of manufacturers is provided in Appendix Two.

4.4.3 Connecting UNITY to the PC

Use the cable provided (P/N Z-0189) to connect the 9-pin 'D' communications port on UNITY's back panel (Figure 24) to the serial comms port of the PC.

4.5 Connecting the gas supplies

See Section 2.6 for details of the gas supplies required.

4.5.1 Carrier gas

Locate the 1/8-inch brass union at the end of the plastic tubing at the rear of UNITY. Use this and a length of the 1/8-inch, refrigeration-grade copper tubing provided in the shipping kit (P/N Z-0145) to connect UNITY to the carrier gas pressure regulator. For installation of EPC regulated carrier gas refer to Appendix 5

4.5.2 Air / Nitrogen - dry gas supply

Locate the 4 mm plastic tubing (P/N Z-0055) and the associated 4mm to 1/8-inch union (P/NZ-0050) (see shipping kit.) Push one end of the plastic tubing into the push fit coupling at the rear of UNITY. Use standard laboratory 1/8-inch nylon or copper tubing to connect the air pressure regulator to the union at the other end of the 4 mm tubing.

Note: If the UNITY pneumatic accessory, U-GAS01, is purchased with UNITY, this is provided with a mm push-fit connector. The 1/8-inch to 4 mm union will not be required in this case.

4.6 Disconnecting / Connecting the auxilliary heater

To operate UNITY at flow path temperatures lower than ~ 130 °C the auxilliary heater must be unplugged from the socket at the back of UNITY (see figure 25). To access the plug and socket first remove the UNITY rear top cover by unscrewing the black retaining knob (Figure 19). The rear cover is then free to slide backwards and away from the instrument. (**Note:** If the air inlet pipe / carrier gas and / or septum purge pressure monitoring lines are already connected then these must be removed before the cover can be taken off). Once the plug has been disconnected from the socket the rear cover should be replaced and pneumatic connections remade.

Note: It is not possible to run with U-INLET and the additional heated valve heater concurrently.

For further information regarding flow path temperatures please see Section 27

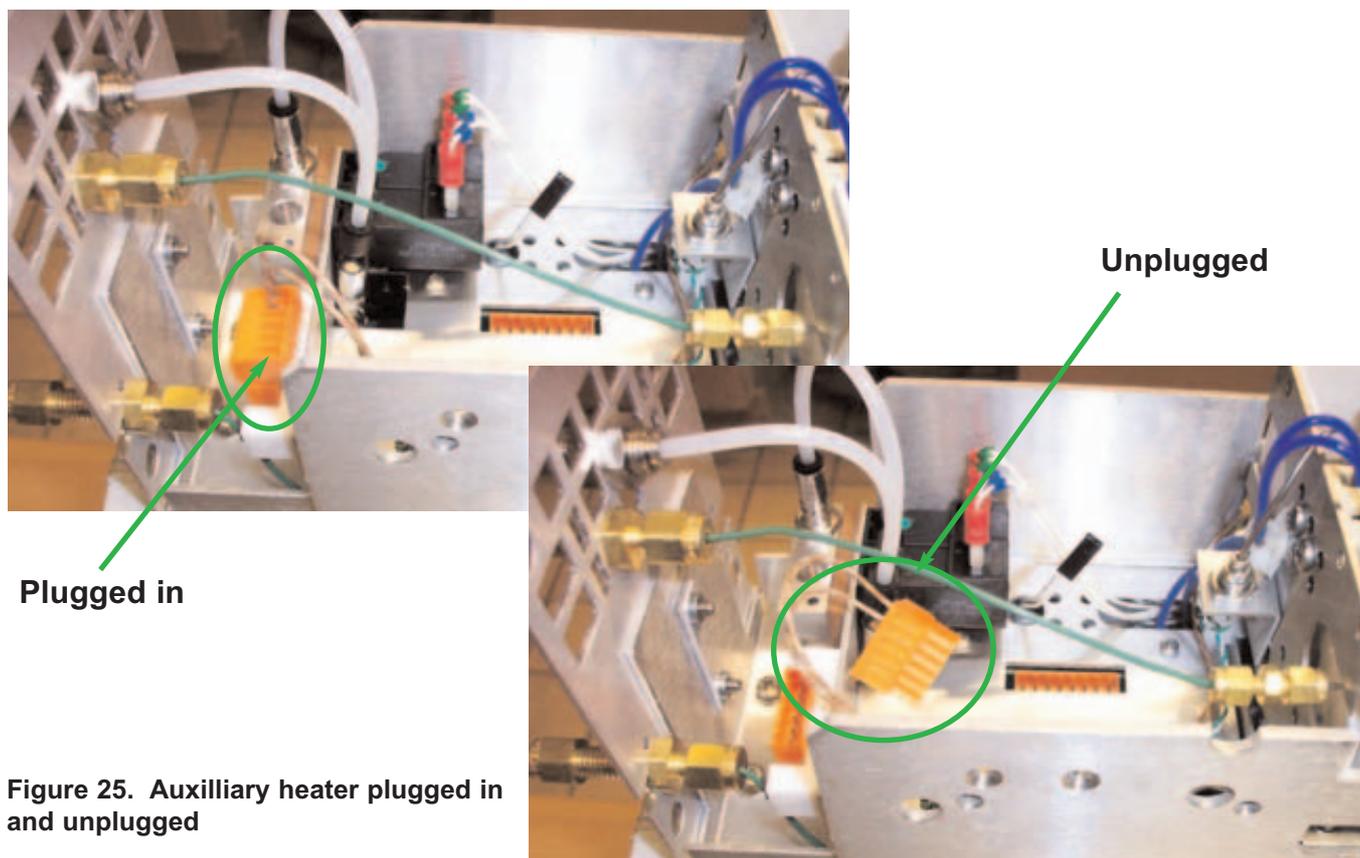


Figure 25. Auxilliary heater plugged in and unplugged

5 Switching on.

Check that the cold trap has been installed (Section 4.2), that the transfer line, gas supplies and all necessary cables are connected and that UNITY operating software has been installed on the PC (Section 6) before switching UNITY on.

The UNITY power (on/off) switch is located at the back of UNITY (Figure 24).

Whenever UNITY is switched on, the electrical (Peltier) coolers begin to function immediately, but all of the instrument's heaters (including those of the heated valve and transfer line) remain off until the software is loaded.

Note the power to UNITY must never be switched on without the supply of dry air or nitrogen also being on unless UNITY has been fitted with a pressure switch (See section 2.6.2).

6 Loading the UNITY software

6.1 Loading UNITY software onto your PC

Ensure that your PC is configured with one or other of the 32-bit versions of Windows and meets all other specifications presented in Section 2 of this manual. It is advised to close down other applications on your PC while loading UNITY software.

Unpack the UNITY software CD supplied in the shipping kit. Insert the CD into the appropriate compartment of the PC and follow instructions on the screen. Alternatively, open **Windows Explorer** (located under Start > Programs) and access the CD drive. Open the UNITY folder and scroll down the content list to **Setup.exe**. Selecting this option will initiate installation of the software. Proceed as directed.

6.2 Downloading UNITY control software from the PC to UNITY to initialise the system

Ensure that all the electrical connections between UNITY, the PC and the rest of the analytical system are in place (Section 4.4.) UNITY should be switched on (Section 5) and the LED on UNITY's front panel should be red.

Once UNITY software has been loaded onto your PC, access the program - usually under **Start > Programs**. This causes the PC to try to start downloading the software to UNITY.

Note: UNITY must be switched on in order for software to be downloaded to it.

If communications between the PC and UNITY are established successfully, a **Downloading UNITY Firmware** message and countdown box appears on the computer screen and the UNITY LED turns amber.

If for some reason, communication is not established an **Instrument not Detected** box appears with a number of options, **Cycle Power and retry? Run simulation? Select options? and Exit?** . Choose **Select options**. This will take you to Ports tab of Options under the View menu (see section 16). Ensure that the correct PC comms port is selected. Change the default comms port if necessary by clicking on the down arrow and then clicking on the correct comms port in the list. Close down UNITY software, switch the power to UNITY off, wait ten seconds and then switch UNITY back on again. Re-access the UNITY program on the PC as described in the paragraph above.

Once the PC has successfully downloaded the software to UNITY, the LED on the front panel turns green and UNITY begins to operate using the active controlling method (see 17.1). The controlling method will contain default parameters when UNITY software is first downloaded.

Information about removing UNITY software from your PC is given in Appendix One.

6.3 The UNITY LED

Note: The UNITY LED **does not** indicate system status with regard to sample analysis. Instead, the LED is an indicator of whether or not the instrument is under the control of the PC.

When the UNITY LED is red, this indicates that the instrument is switched on and that no controlling parameters have yet been downloaded to it from the PC.

An amber LED indicates that the PC is downloading parameters to UNITY.

A green LED indicates that UNITY has received all the parameters from the PC and is now controlled by the PC.

7 Introduction to the principles of two-stage thermal desorption

Thermal desorption is a simple extension of the technique of gas chromatography (GC) and is most commonly used in combination with a GC analyser. In the process of thermal desorption, heat and a flow of inert gas are used to extract volatile and semi-volatile organics retained in a sample matrix or on a sorbent bed. The analytes desorb into the gas stream and are transferred into an analytical system in a small, concentrated volume of vapour.

In its most simple single-stage form, thermal desorption is of limited application. Typical sample tubes are required to be at least 1/4-inch O.D. both for representative sampling of solids and for optimum diffusive or pumped collection of usable air samples. The transfer of analytes from a 1/4-inch or larger sample tube is simply too slow to produce good quality analytical data. The peaks produced are broad, often unresolved and lead to inaccurate or impossible integration.

For this reason most commercial thermal desorbers offer some form of "two-stage" operation - i.e. they contain a focusing mechanism for concentrating analytes desorbed from the sample tube before releasing them into the analytical system in as small a volume of vapour as possible. Two basic refocusing mechanisms are used:

- > Capillary cryofocusing
- > Cold trapping

7.1 Capillary cryofocusing

Capillary cryofocusing does produce excellent, capillary-compatible chromatography, but it can be extremely costly in terms of liquid cryogen consumption. More importantly, such systems are prone to sblocking with ice during the desorption of humid samples. This is an analytical disaster. Thermal desorption is, by definition, a dynamic process and any blockage or restriction of the desorption gas flow has a significant impact on the efficiency of the process.

7.2 Cold trapping

Refocusing on a small, electrically-cooled sorbent trap, which can then be rapidly heated to desorb 99% of analytes within a few seconds, is invariably the technique of choice for thermal desorption. Such systems have been shown to quantitatively retain analytes as volatile as C₂ hydrocarbons, while at the same time being able to desorb fast enough to produce uncompromised, high resolution capillary chromatography with low, or even zero split ratio. There is the obvious benefit of eliminating costly liquid cryogen and there is little risk of blocking a typical 2 mm internal diameter secondary cold trap with ice.

8 Guidance on air sampling

8.1 Sorbent selection

The choice of sorbent principally depends upon the volatility (specifically the vapour pressure) of the analyte concerned. In short, the sorbent or series of sorbents selected must quantitatively retain the compounds of interest from the volume of air / gas sampled and must then release those compounds as efficiently as possible when heat is applied and the flow of (desorption) gas reversed. As vapour pressure data is not always readily available, a useful "Rule of Thumb" is to use the boiling point of the component as a guide to its volatility. In general;

.....the more volatile the analyte to be trapped - the stronger the sorbent must be.

Although many different sorbents are now commercially available, a selection of eleven covers the usual

working range:

8.1.1 Carbotrap C (20-40 mesh) / Carbopack C (60-80 mesh) / Carbograph 2TD (range of mesh sizes)

Sorbent Strength:	Very weak
Specific Surface Area (m ² /g):	» 12
Approximate analyte volatility range:	n-C ₈ to n-C ₂₀
Example Analytes:	Alkyl benzenes, hydrocarbons to n-C ₂₀
Sorbent Maximum Temperature:	>400°C
Recommended Conditioning Temperature:	350°C to 400°C
Recommended Desorption Temperature:	300°C to 350°C
Notes:	Hydrophobic, minimal (<0.1 ng) artifacts, some activity with labile compounds, friable

8.1.2 Tenax TA or GR (range of mesh sizes available)

Sorbent Strength:	Weak
Specific Surface Area (m ² /g):	»35
Approximate analyte volatility range:	n-C ₇ to n-C ₃₀ Bpt. 100°C to 450°C
Example Analytes:	Aromatic compounds (except benzene), apolar components boiling point >100°C, polar components boiling point >150°C, PAHs and PCBs.
Sorbent Maximum Temperature:	350°C
Recommended Conditioning Temperature:	325°C
Recommended Desorption Temperature:	Up to 300°C
Notes:	Hydrophobic, low inherent artifacts (< 1ng), inert, graphitised form best for PAHs and PCBs, efficient desorption, use 35-60 mesh to minimise fines and eliminate "leakage" through conventional sorbent retaining gauzes

8.1.3 Carbotrap (20-40 mesh) / Carbopack B (60-80 mesh) / GCB1 (range of mesh sizes available) / Carbograph 1TD (range of mesh size)

Sorbent Strength:	Medium / Weak
Specific Surface Area (m ² /g):	»100
Approximate analyte volatility range:	n-C ₅ to n-C ₁₄
Example Analytes:	Ketones, alcohols, aldehydes and apolar components within the above volatility range. Perfluorocarbon tracer gases
Sorbent Maximum Temperature:	>400°C
Recommended Conditioning Temperature:	350°C to 400°C
Recommended Desorption Temperature:	300°C to 350°C
Notes:	Hydrophobic, low artifacts (<0.1 ng), some activity with labile compounds, friable

8.1.4 Chromosorb 102 (range of mesh sizes available)

Sorbent Strength:	Medium
Specific Surface Area (m ² /g):	»350

Approximate analyte volatility range	Boiling point 50°C to 200°C
Example Analytes:	Alcohols, oxygenated compounds, haloforms less volatile than methylene chloride
Sorbent Maximum Temperature:	250°C
Recommended Conditioning Temperature:	225°C (250°C for short (<15 mins) periods only)
Recommended Desorption Temperature:	No higher than 220°C
Notes:	High artifacts (=10ng), for trace level analysis condition at 225°C and desorb sample tubes no higher than 200°C to reduce background, hydrophobic, inert

8.1.5 Chromosorb 106 (range of mesh sizes available)

Sorbent Strength:	Medium
Specific Surface Area (m ² /g):	»750
Approximate analyte volatility range:	n-C ₅ to n-C ₁₂ . Boiling point 50°C to 200°C
Example Analytes:	Hydrocarbons, benzene, volatile oxygenated compounds
Sorbent Maximum Temperature:	225°C to 250°C
Recommended Conditioning Temperature:	225°C (250° C for short (<15 mins) periods only)
Recommended Desorption Temperature:	No higher than 200°C
Notes:	High artifacts (=10 ng), for trace level analysis condition at 225°C and desorb sample tubes no higher than 200°C to reduce background, hydrophobic, inert

8.1.6 Porapak N (range of mesh sizes available)

Sorbent Strength:	Medium
Specific Surface Area (m ² /g):	»300
Approximate analyte volatility range:	n-C ₅ to n-C ₈ . Bpt. 50°C to 150°C
Example Analytes:	Volatile nitriles, e.g. acrylonitrile, acetonitrile, propionitrile. Pyridine, volatile alcohols, ethanol, methyl ethyl ketone
Sorbent Maximum Temperature:	190°C
Recommended Conditioning Temperature:	180°C to 190°C
Recommended Desorption Temperature:	No higher than 180°C
Notes:	Hydrophobic, high artifacts (=10 ng), for trace level analysis condition at 180°C and desorb sample tubes no higher than 160°C to reduce background levels, low maximum temperature - repack tubes after 50 thermal cycles, inert

8.1.7 Porapak Q (range of mesh sizes available)

Sorbent Strength:	Medium
Specific Surface Area (m ² /g):	»550
Approximate analyte volatility rang:	n-C ₅ to n-C ₁₂ . Boiling point 50°C to 200°C
Example Analytes:	VOCs within volatility range above, oxygenated compounds

Sorbent Maximum Temperature:	250°C
Recommended Conditioning Temperature:	225°C (250°C for short (<15 mins) periods only)
Recommended Desorption Temperature:	No higher than 225°C
Notes:	High artifacts (=10 ng), for trace level analysis condition at 225°C and desorb sample tubes no higher than 200°C to reduce background levels

8.1.8 Spherocarb / UniCarb (60 - 80 mesh only)

Sorbent Strength:	Strong
Specific Surface Area (m ² /g):	»1200
Approximate analyte volatility range:	C ₃ to n-C ₈ . Boiling point -30°C to 100°C
Example Analytes:	Very volatile compounds e.g. VCM, ethylene oxide, carbon disulphide, dichloromethane, chloromethane. Volatile polar compounds e.g. methanol, ethanol, acetone
Sorbent Maximum Temperature:	>400°C
Recommended Conditioning Temperature:	350°C to 400°C N.B. Increase temp from 250°C stepwise and slowly
Recommended Desorption Temperature:	300°C to 350°C
Notes:	Some hydrophilicity, low artifacts (<0.1 ng), inert, excellent batch-to-batch reproducibility, non-friable

8.1.9 Carbosieve SIII (60 - 80 mesh only)

Sorbent Strength:	Very Strong
Specific Surface Area (m ² /g):	~800, but primarily operates on molecular sieve principal with 15/40Å pores
Approximate analyte volatility range:	Primarily for C ₂ hydrocarbons and smaller molecules. Boiling point -60°C to 80°C
Example Analytes:	Ultra volatile hydrocarbons
Sorbent Maximum Temperature:	>400°C
Recommended Conditioning Temperature:	350°C N.B. Slow conditioning required as for Spherocarb
Recommended Desorption Temperature:	300°C
Notes:	Some hydrophilicity, low artifacts (<0.1 ng), easily and irreversibly contaminated by higher boiling components - protect with front bed of weaker sorbent

8.1.10 Carboxen 1000 (Range of mesh sizes available)

Sorbent Strength:	Very strong for small molecules
Specific Surface Area (m ² /g):	>1200,
Approximate analyte volatility range:	permanent gases and light hydrocarbons (C ₂ , C ₃). Boiling point -60°C to 80°C
Example Analytes:	Ultra volatile hydrocarbons
Sorbent Maximum Temperature:	>400°C
Recommended Conditioning Temperature:	350°C N.B. Slow conditioning required as for

	Spherocarb
Recommended Desorption Temperature:	To suit analyte
Notes:	Some hydrophilicity, low artifacts (<0.1 ng), easily and irreversibly contaminated by higher boiling components - protect with front bed of weaker sorbent

8.1.11 Molecular Sieve (Range of mesh sizes available)

Sorbent Strength:	Very strong for small molecules
Approximate analyte volatility range:	Boiling point -60°C to 80°C
Example Analytes:	1,3 butadiene (13X), nitrous oxide (5Å)
Sorbent Maximum Temperature:	350°C
Recommended Conditioning Temperature:	300°C (increase temperature gradually)
Recommended Desorption Temperature:	To suit analyte
Notes:	Significantly hydrophilic - do not use in humid conditions, high artifacts (>10 ng), easily & irreversibly contaminated by higher boiling components

8.2 Packing Tubes

A range of prepacked sorbent tubes is available from Markes International Ltd. All tubes are etched with a unique serial number (e.g. Mi 017625) and are available in the following formats.

- >stainless steel industry standard thermal desorption tubes, suitable for diffusive (passive) or pumped.
- >glass industry standard thermal desorption tubes, suitable for pumped sampling.
- >Silcosteel[®] industry standard thermal desorption tubes, suitable for diffusive or pumped sampling. (These tubes have been coated with a very thin (a few Ångströms) inert layer which makes them suitable for the sampling and analysis of very labile components).

All tubes may be supplied in the following formats:

- >empty - (Empty steel or coated steel tubes are supplied) with the front sorbent retaining gauze fitted and the second gauze and gauze-retaining springs supplied separately.
- >packed with a known mass of any specified sorbent (or known masses of two or three sorbent beds), and supplied with a packing report detailing the mass of packing in each tube.
- >packed, conditioned and capped with long term (1/4-inch brass) storage caps, supplied with background chromatogram showing artifact levels.

For advice on sorbent choice, packing of empty tubes or for prices for any of the above please contact Markes International Ltd. by email: enquiries@markes.com or by telephone: +44 1443 230935 or fax: +44 1443 231531

8.3 Diffusive Monitoring

8.3.1 Principles and Theory

Diffusive monitoring is widely used in all conventional air monitoring scenarios, i.e. occupational hygiene plus indoor and ambient air monitoring. By eliminating the requirement for a sampling pump, diffusive monitoring provides a simple and cost effective method of collecting the large number of samples required in many air monitoring programmes.

Diffusive monitors must be capable of maintaining the following conditions during sampling:

- >ambient concentration of the analyte at the surface of the monitor.
- >zero concentration of the analyte at the surface of the sorbent.

>a linear concentration gradient between the two.

When these conditions apply, Fick's 1st Law of Diffusion applies and analytes will migrate to the surface of the sorbent at a rate that is dependent on:

- >the distance between the sorbent surface and the monitor surface.
- >the cross-sectional area of the sampler.
- >the time of exposure.
- >the diffusion coefficient of the analyte through air.
- >the ambient concentration of the components.

This is expressed by the following formula:

$$U_m = \frac{60 \times D_1 A}{Z}$$

Where: U_m is the ideal uptake rate; mL/min.

D_1 is the diffusion coefficient through air of the vapour under study; cm^2/sec .

A is the cross sectional area of the sampling tube; cm^2 .

Z is the path length of the air gap; cm.

8.3.2 Tube-type Axial Diffusive Samplers

Early diffusive samplers were badge type designs, with large cross sectional areas and short path lengths and they suffered from severe restrictions because of air speed effects at the surface of the badge. The stable conditions required for diffusion according to Fick's Law could never effectively be established. Badges are also unsuitable for analysis by thermal desorption / gas chromatography.

Early in 1979 Working Group 5 of the UK Health and Safety Executive specified a 3.5-inch x 1/4-inch O.D. tube-type diffusive monitor, compatible with thermal desorption, that has now been accepted as an 'Industry Standard'. The first keynote publication detailing the design was published in 1981¹. The tube has a cross sectional area of 0.191 cm^2 and a sorbent retaining gauze positioned 14.3 mm from the sampling end of the tube (Figure 26). This typically gives a diffusive path length (air gap) of $\sim 1.5 \text{ cm}$.

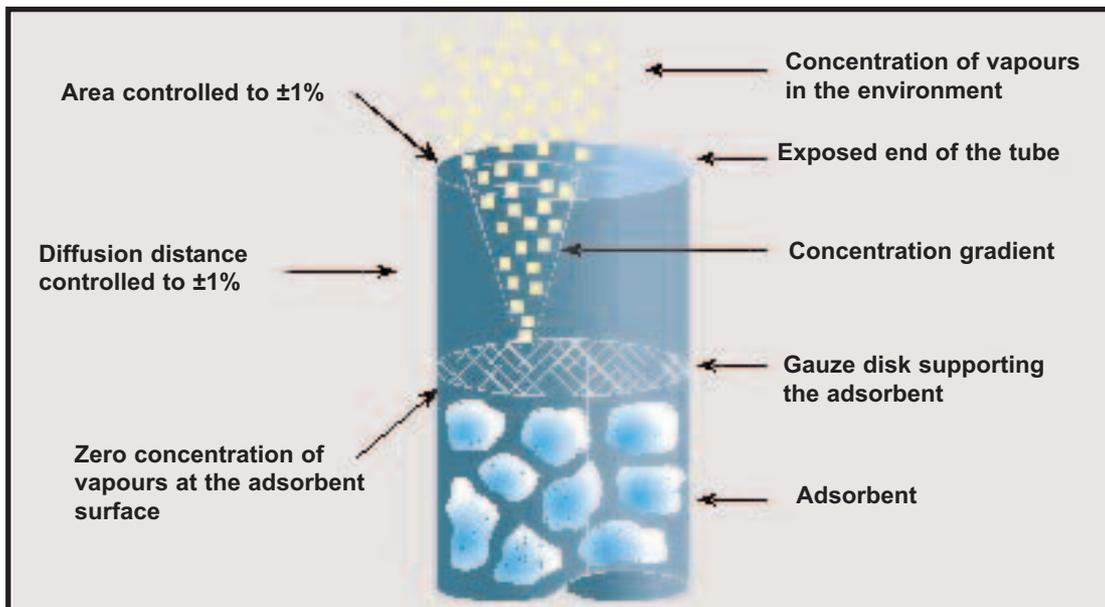


Figure 26. Axial diffusive sampling on a sorbent tube

Using this diffusive tube the atmospheric concentration of a compound is determined using the following equation:

$$\text{ppm} = \frac{\text{Weight of sample on monitoring tube (ng)}}{U_p \times \text{sampling time (min)}}$$

Where U_p = ideal uptake rate in ng/ppm/min

The actual uptake rate, which applies to a particular analyte being sorbed onto a particular sorbent under a set of monitoring conditions, may differ significantly from the ideal uptake rate and will depend on the strength of the analyte / sorbent interaction.

However, as the actual uptake rates of many analytes on a range of sorbents have now been published, little, if any, experimental work is required on the part of a user. Markes International Ltd. Thermal Desorption Technical Support Note 1: Uptake Rates on Standard Tubes presents a current listing of uptake rates, reproduced from Issue 8 of The Diffusive Monitor with the kind permission of the editor².

If an uptake rate is not available for a given analyte there are several options:

1. Calculate an ideal value from Fick's equation and diffusion coefficients published in the literature.
2. Determine the uptake rate experimentally using one of the following internationally recognised protocols:
 - > Protocol for assessing the performance of a diffusive sampler; UK Health & Safety Executive, Methods for the Determination of Hazardous Substances No. 27
 - > EN 838: Workplace atmospheres - requirements and test methods for diffusive samplers for the determination of gases and vapours; CEN/TC 137/N55 (1991)
 - > prEN 13528: Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods (Parts 1 and 2)
 - > Protocol for the evaluation of passive monitors; Kennedy ET et al, US National Institute for Occupational Safety and Health (NIOSH). Published in "Diffusive sampling; An alternative approach to workplace air monitoring" CEC Pub. No. 10555EN (1986)
 - > American National Standard for Air Sampling Devices - Diffusive Type for Gases and Vapours in Working Environments; ANSI/ISEA 104-1998
 - > Standard Practice for Evaluating the Performance of Diffusive Samplers-ASTM D6246-98

These protocols recommend a series of laboratory and field experiments to determine and validate effective uptake rates, and can be time consuming.

3. Predict the uptake rate by using a combination of simple short experiments and a computer software programme. Further information is given in Markes International Ltd. Thermal Desorption Technical Support Note 2: Prediction of Uptake Rates for Diffusive Tubes.

8.3.3 Diffusive sampling in practice

Much of the early work done with tube type diffusive samplers focused on occupational hygiene monitoring and hence 8 hour exposure of the tubes (a typical working shift), to atmospheric concentrations of several ppm. However, it has since been shown that diffusive monitoring is suitable for sampling over much longer periods of time (up to six weeks), and for much lower atmospheric concentrations (sub ppb)^{3,4,5}, providing the correct sorbent is used.

However in very low atmospheric concentrations (~1 ppb) and when a result is required within a few hours, tube-type (axial) diffusive sampling does not provide a sufficient mass of analyte on the tube.

8.3.4 Radial Diffusive Samplers (Figure 27)

Tube-type (axial) diffusive samplers have a typical sampling rate equivalent to 0.5 to 1 ml/min and are widely used both for 8-hour occupational hygiene exposure (typically at the ppm level) and long term (two to four week exposure) ambient diffusive monitoring (typically at the ppb / high ppt level). For short-term exposure these tubes have a minimum detection limit of 10 - 50 ppb depending on the nature of the analytical system. Although much environmental monitoring takes place over a 2 to 4 week period there are often occasions where a much shorter sampling period (30 mins to 6 hours) would be preferable - perhaps to monitor the effects of industrial processes, changes in traffic volumes or short term climate effects. In these cases the tube-type diffusive samplers are hampered by their slow uptake rate and are unsuitable for monitoring ambient concentrations.

The novelty of radial diffusive samplers is the orientation of their diffusion path that is parallel to the

radius of the tube. They have a cylindrical diffusive surface area equal to 23.6 cm^2 . (Over 100 X greater than tube-type samplers). Due to the high adsorbent surface area combined with short diffusive path they have an effective sampling rate typically 50 - 100 times that of normal axial tubes. Therefore radial diffusive samplers may be used for short duration, low concentration exposure - a scenario previously unsuitable for passive devices. For this short term exposure (up to 6 hours) these tubes have a minimum detection limit of about 50-100ppt. The diffusion barrier is provided by a porous polymer body - See figure 27.

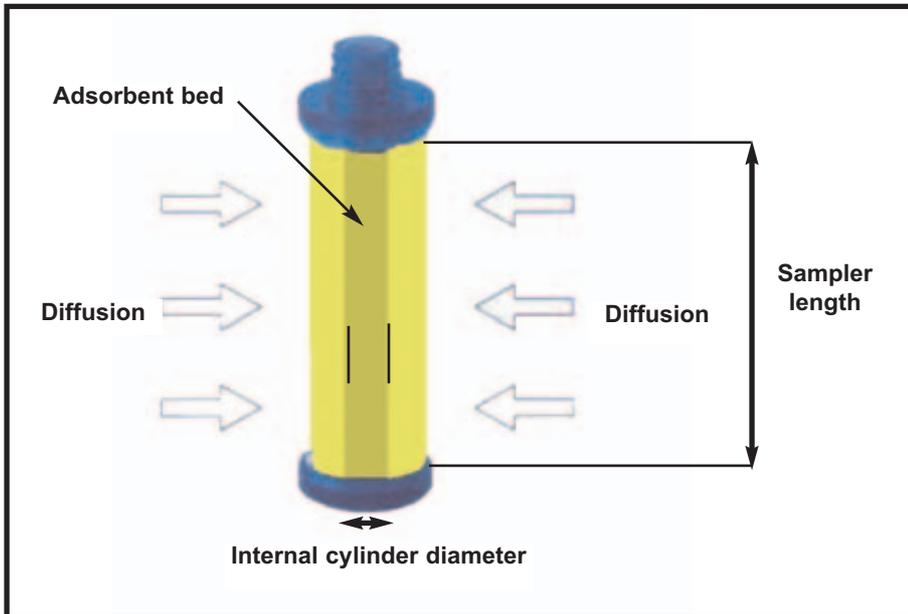


Figure 27. Radial diffusive sampling

Due to the much higher sampling rate, care must be taken not to saturate the sorbent with the components of interest.

Once exposed the sorbent containing cartridge is emptied out of the radial diffusive sampler into an empty thermal desorption carrier tube, and sealed with standard 1/4-inch long term storage caps. The tube may then be analysed by thermal desorption in the normal fashion.

Note: The adsorption of analytes along the whole length of the sampler may mean that more stringent desorption conditions may be required for complete desorption relative to axial counterparts.

8.3.5 When diffusive sampling is not applicable

Diffusive sampling is not suitable for all monitoring applications.

Diffusive sampling is normally carried out using sorbent tubes packed with a single bed of sorbent. If several analytes of differing volatilities are to be monitored, requiring two or more different sorbents (xylene on Tenax and methanol on Spherocarb for example), then two different diffusive monitors have to be used in parallel.

Diffusive sampling cannot generally be used with glass or conventional glass lined tubes (GLT) as the cross sectional area (A) is different to that of the standard stainless steel or Silcosteel[®] tubes, due to increased wall thickness. The length of the air gap is also hard to define accurately when glass or quartz wool plugs are used to retain the sorbent.

If uptake rate data is not available and if there is no time to measure or calculate an up take rate, then diffusion sampling cannot be used.

8.4 Pumped Air Monitoring

When diffusive sampling is not appropriate (see above), pumped sampling is used. During pumped sampling, air is drawn through the front (grooved) end of an uncapped tube at a suitable flow rate. Flow rates should be between 10 and 200 ml/min, although 500 ml/min can be used for short sampling times. Flows below 10 ml/min are subject to high percentage errors due to diffusion and some sort of diffusion limiting cap must be used. (Contact Markes International for further information). 50 ml/min is optimum.

Constant flow type pumps should be used with sorbent tubes as they maintain a constant flow over a range of pressures and therefore compensate for any impedance variations between tubes.

A constant flow pump (FLEC pump), suitable for use with sorbent tubes with a wide variety of impedances is available from Markes International Ltd. The FLEC Pump operates at flow rates from 1 to 999.9 ml/min. QUI-0002 vs 5.2 September 2006

The oil-free rotary pump ensures a pulseless operation over the flow range. Feedback from the built in mass-flow sensor secures a reproducible, precise and constant flow even under dramatic changes in the air restriction. This means that the pump is suitable for sampling a wide range of sorbent tubes - all with a varying back pressure.

For further details please contact Markes International Ltd. by telephone: +44 1443 230935, fax: +44 1443 231531 or email: enquiries@markes.com

Pumped sampling is compatible with tubes packed with two or more sorbents to facilitate the retention of analytes with a range of volatilities. (N.B. the weakest sorbent is always at the sampling (grooved) end of the tube).

Pumped sampling is also compatible with glass and glass lined tubes.

When monitoring analytes using pumped sampling it is essential to select the correct sorbent or series of sorbents for the target analytes and to take note of the safe sampling volume (SSV) for those compounds - i.e. the total volume of a particular analyte that can be drawn through a sorbent tube with no risk of analyte breakthrough. A comprehensive listing of SSVs is given in Volatile Organic Compounds in Air; UK Health and Safety Executive, Methods for the Determination of Hazardous Substances No. 72. Markes International Ltd. Thermal Desorption Technical Support Note 20:- Determining Validating Safe Sampling Volumes also contains a listing of SSVs.

¹Dr RH Brown, J Charlton, KJ Saunder; *Am.Ind.Hyg.J.*;(42)12/81pp 865-869 *The development of an Improved Diffusive Sampler*

²Dr M D Wright , Editor, *The Diffusive Monitor*, Health & Safety Laboratory, Broad Lane, Sheffield, S3 7HQ, UK, Fax: +44 114 289 2362

³*Long Term Diffusive Sampling of Volatile Organic Compounds in Indoor Air*; VM Brown, DR Crump, D Gardiner and CWF Yu, *Environmental Technology*, Vol 14, pp 771-777, 1993

⁴pr EN14662 *Ambient air quality - standard method for the measurement of benzene concentrations. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.*

⁵ASTM D6196-03 *Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.*

9 Guidance on Materials Testing

Thermal desorption can be used for materials testing as well as air monitoring, and is used to measure volatile organic compounds in products as varied as pharmaceuticals, packaging film, foodstuffs, beverages, paints, polymers and ointments.

There are two methods of sampling for materials testing:

- > Direct desorption of material from tubes.
- > Off-line purge and trap into sorbent tubes.

Samples most suited for off-line purge and trap include natural, typically non-homogeneous and high-humidity samples such as fresh or prepared food. Dry or more homogeneous materials, such as therapeutic drugs, packaging materials, resins, spices, ointments and creams, polymers and water based paints can be weighed into empty tubes and desorbed directly.

9.1 Direct Desorption of material from tubes

Direct thermal desorption of volatile or semivolatile organics from samples weighed straight into empty desorption tubes or appropriate tube liners is probably the most straightforward and cost-effective

sampling procedure for otherwise difficult materials. The method facilitates the analysis of the most challenging materials combining sample cleanup, analyte extraction, sample concentration and analyte injection / introduction into one fully automated operation.

Direct TD is appropriate only if the desired extraction takes place at a temperature below the decomposition point of other materials in the sample matrix, and if the relatively small sample size that

can be measured into a TD tube is representative of the sample as a whole.

Most samples are best weighed into a tube insert or liner (P/N C-PI010 (pk10) or C-PI100 (pk100)), rather than directly into a glass or steel desorption tube. (Liners are typically constructed of heat shrink PTFE tubing with a reduced diameter at one end, (see figure 28), a small plug of glass wool is usually inserted at the restricted end.) The liner is not always necessary, for example with film samples, but saves clean-up of expensive sample tubes and eliminates the risk of the degradation from samples coming into contact with metal tube surfaces.

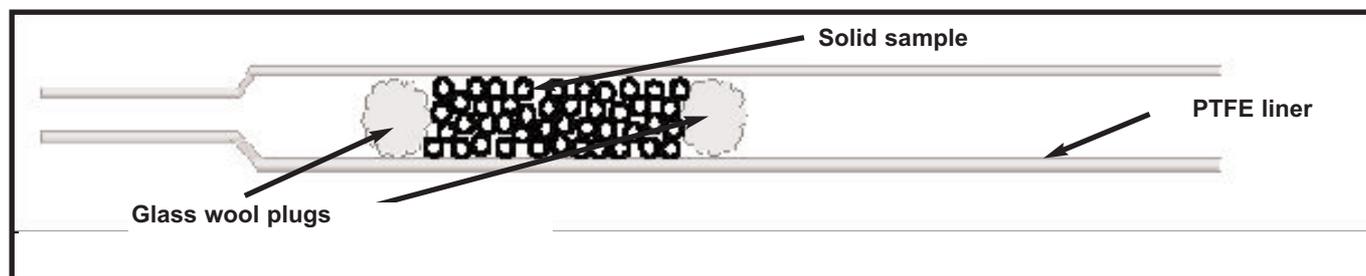


Figure 28. PTFE liner with solid sample

Note: PTFE tube inserts have an O.D. of 4.9 mm and can only be used with stainless steel, silcosteel or sulfosteel tubes, not glass tubes.

Direct TD is compatible with a wide range of material types. These fall into two broad categories: Solid samples and semi-liquid products.

9.1.1 Solid samples

The critical issue with solid samples is that they should have a high surface area e.g. powders, granules (particle size $<1 \text{ mm}^3$), fibres or films. Bulk solids should be ground with a coolant such as solid carbon dioxide to increase surface area before the material is weighed into sample tubes. For packaging films, a standard sized section (typically 5 cm x 10 cm) should be cut and rolled into a tube before insertion into the sample tube.

The sample material should not be packed so tightly that the tube is blocked. It is essential that the gas flow path should not be blocked with sample. TD is a dynamic process and the gas must be allowed to pass through the sample tube unrestricted.

The solid must be placed inside the sample tube such that it is well within the heated zone of the thermal desorber. For UNITY, the heated zone is the central 60 mm section of the 89 mm tube, approximately 15 mm at either end is outside the desorption oven.

Direct thermal desorption is particularly useful for the analysis of organic volatile impurities in drugs. Conventional solvent extraction is complicated in this case by the insolubility of many drugs in common and safe solvents. Some residual solvents in drugs actually form part of the crystal structure. Complete dissolution or breakdown of the crystal structure is therefore required before an accurate determination of organic volatile impurities can be made. Provided the drug melts at a temperature below its decomposition point TD thus provides a quick and simple alternative to solvent extraction. Complete extraction can typically be achieved within 5 minutes. PTFE liners are recommended to minimise risk of drug degradation.

9.1.2 Liquids, emulsions, resins and other semi-liquid products

Samples such as epoxy resins, edible fats, ointments / therapeutic creams, water based paints and a host of other semi-liquid homogeneous products may also be analysed by direct desorption. A PTFE liner is invariably recommended in these cases to prevent tube contamination. Sometimes a short bed of Tenax is also recommended at the front of the metal sample tube. The PTFE insert is then pushed into the tube behind this. The Tenax works as a precolumn holding up high boilers from the sample matrix and preventing these compounds from contaminating the system flow path. The Tenax, if required, can alternatively be placed at the restricted end of the PTFE liner held in place by glass wool plugs. Note that PTFE inserts have a maximum temperature of 250°C.

The same criteria apply here as with solid samples, the sample must be placed within the heated zone of the thermal desorber, and the material should not block the tube. In order to ensure a clear gas flow

path through the middle of the liner, viscous samples such as resins and ointments should be smeared around the inner wall of a PTFE liner plugged with glass wool.

9.2 Off-line purge and trap into sorbent tubes

Natural and high humidity samples such as fresh or prepared food, soils etc. are more suited to off-line purge and trap or headspace - type sampling because of their non-homogeneous nature. A sample size small enough to fit inside a thermal desorption tube would not be representative.

A large sample (the whole product if applicable) should be placed inside a large non-emitting (e.g. glass) container which is purged with high purity air or gas e.g. nitrogen and the exhaust gas stream collected onto a clean sorbent tube or directly into the UNITY cold trap. The rules regarding sorbent selection are the same as for air sampling. (see Section 8.1)

10 Guidance on TD / GC analytical conditions

Note: These conditions are for guidance only. If other vapour phase components are present in the atmosphere or product they will also be collected on the tube and trap and desorption conditions may have to be modified to ensure that they are fully desorbed - even if their measurement is not important. Similarly GC conditions may have to be modified to ensure that all components have eluted from the column. (for further information, see TDTS21)

10.1 Occupational Hygiene

Example: Diffusive monitoring of a paint shop for trichlorethane and o-xylene vapours.

Typical sampling conditions:

Diffusive monitoring for 8 hours using a Tenax TA tube. (In a 100 ppm atmosphere, the mass of each component collected will be ~100 µg)

Typical UNITY conditions:

Desorption temp:	275°C
Desorption time:	5 minutes
Cold trap packing:	Tenax TA
Cold trap focusing temp:	-10°C
Cold trap (secondary) desorption temp:	300°C
Secondary desorption time:	3 minutes
Flow path temp:	120°C
Desorb flow:	~ 4 ml/min
Inlet split:	~ 52 ml/min
Outlet split:	~ 50 ml/min

Typical GC conditions:

Column:	Non-polar, 0.32 mm I.D. x 1 µm film capillary column e.g. BP1, DB1, CPSil 5CB etc.. 30-50 m
Column flow:	~ 2 ml/min
Carrier Gas:	Helium
Isothermal temp (1):	50°C
Isothermal time (1):	5 minutes
Ramp rate (1):	10°C/min
Isothermal temp (2):	200°C
Detector:	FID

Detector temp: 250°C

The gas flows in this example represent a total split ratio of ~ 360:1, therefore giving a column loading of ~ 280ng.

10.2 Ambient / Indoor air

The levels of VOC pollutants found in ambient and indoor air are very similar (low ppb), although in any given location the concentration of VOC pollutants in indoor air is approximately three times that found in the local ambient air.

Example: Diffusive monitoring of ambient air for benzene.

Typical sampling conditions: Diffusive monitoring of benzene in an atmosphere for 4 weeks using a Chrom. 106 tube. (1 ppb concentration will lead to the adsorption of ~ 50 ng benzene)

Typical UNITY conditions:

Desorption temp: 200°C

Desorption time: 10 minutes

Cold trap packing: Tenax

Cold trap focusing temp: -10°C

Cold trap (secondary) desorption temp: 250°C

Secondary desorption time: 5 minutes

Flow path temp: 120°C

Desorb flow: ~ 30 ml/min

Inlet split: OFF

Outlet split: Up to 20 ml/min if required for re-collection

Typical GC conditions:

Column: Non-polar, 0.32 mm I.D. x 1 µm film capillary column e.g. BP1, DB1, CPSil 5CB etc.. 30-50 m

Column flow: ~ 3 ml/min

Carrier Gas: Helium

Isothermal temp (1): 50°C

Isothermal time (1): 5 minutes

Ramp rate (1): 10°C/min

Detector temp: 250°C

The gas flows in this example represent splitless or low split options, giving column loadings of between 50 ng (splitless) and 6.5 ng (outlet split flow set at 20 ml/min).

10.3 Materials testing - residual solvents in consumer products

Example: Measurement of ppm-level residual solvents in pharmaceuticals.

Typical sampling conditions: 10 mg of pharmaceutical weighed into a PTFE liner and held in place by glass wool plugs

Typical UNITY conditions:

Desorption temp: 220°C

(This temperature is very dependent upon the nature of the matrix, see Section 9)

Desorption time: 3 minutes

Cold trap packing:	Tenax/CarbopackB/(Spherocarb) depending on solvents concerned
Cold trap focusing temp:	-10°C
Cold trap (secondary) desorption temp:	230°C
Secondary desorption time:	3 minutes
Flow path temp:	120°C
Desorb flow:	~ 4 ml/min
Inlet split:	OFF
Outlet split:	~ 40 ml/min
<u>Typical GC conditions:</u>	
Column:	Non-polar, 0.2 - 0.32 mm I.D., thick film (1 - 5 mm) capillary column e.g. BP1, DB1, CPSil 5CB etc..
Column flow:	~ 1 ml/min
Carrier Gas:	Helium
Isothermal temp (1):	40°C
Isothermal time (1):	5 minutes
Detector:	FID
Detector temp:	250°C

The gas flows in this example represent a total split ratio of ~ 40:1

10.4 High boiling components

Example: Analysis of C₁₀ to C₂₆ hydrocarbons.

<u>Typical sampling conditions:</u>	Pumped sampling of 10 litres of air onto a Tenax tube. (In a 1 ppb atmosphere, the mass of each component collected on the tube will be ~100-200 ng)
-------------------------------------	--

Typical UNITY conditions:

Desorption temp:	310°C
Desorption time:	20 minutes
Cold trap packing:	Quartz wool plus Tenax TA
Cold trap focusing temp:	-10°C
Cold trap (secondary) desorption temp:	325°C
Secondary desorption time:	20 minutes
Flow path temp:	120°C
Desorb flow:	~ 50 ml/min
Inlet split:	~ 50 ml/min
Outlet split:	~ 48 ml/min

Typical GC conditions:

Column:	Non-polar, 0.32mm I.D., thin film capillary column e.g. 0.25 mm BP1, DB1, CPSil 5CB etc..
Column flow:	~ 5 ml/min
Carrier Gas:	Helium
Isothermal temp (1):	100°C

Isothermal time (1):	2 minutes
Ramp rate (1):	10°C/min
Isothermal temp (2):	320°C
Isothermal time (2):	10 minutes
Detector:	FID
Detector temp:	350°C

The gas flows in this example represent a total split ratio of ~ 20:1 giving a column loading of between ~5 - 10 ng.

11 Calibration and preparing and introducing standards

When calibrating any piece of analytical equipment it is important that the loading and analysis of the standards replicates as closely as possible that of the samples themselves. For this reason a thermal desorption - gas chromatograph (TD/GC) system should be calibrated by loading the standard onto a sample tube and desorbing it through the system so that it is subjected to the complete two-stage thermal desorption process.

Due to the nature of the samples analysed by TD/GC it can be difficult to introduce an internal standard except by a gas sampling valve at some time during the desorption process. External standard methods of calibration are therefore more common.

There are two procedures that are commonly used to introduce calibration standards into sample tubes, each with its own set of essential criteria. Whichever method you choose it is vital to comply with the requirements for that method alone.

Calibration Method 1 involves introducing standards onto tubes via an injector such that analytes reach the sorbent bed in the vapour phase.

Calibration Method 2 involves introducing measured volumes of liquid standards directly into tubes.

11.1 Calibration Method 1. - Introducing standards in the vapour phase using the Calibration Solution Loading Rig

This method is considered to be optimum for air monitoring applications where analytes are sampled in the vapour phase. The Markes International Calibration Solution Loading Rig (CSLR)(P/N C-CSLR) was specifically designed for this purpose. (Figure 29)

The CSLR consists of an injector port with a controlled carrier gas supply and a sorbent tube connection point. The sampling (grooved) end of a packed sorbent tube is connected to the CSLR via a 1/4-inch brass nut and combined PTFE ferrule. The carrier gas flow is set, via a needle valve, to between 80 and 100 ml/min. It sweeps the injection port and passes down through the sorbent tube to vent. The calibration solution is introduced through the injector septum using a standard GC syringe in the normal fashion. The solution vaporises in the flow of gas and reaches the sorbent bed in the vapour phase.

Where possible, sufficient volume of carrier gas is allowed to pass through the tube such that most of the solvent passes through the adsorbent bed whilst compounds of interest are still quantitatively retained.

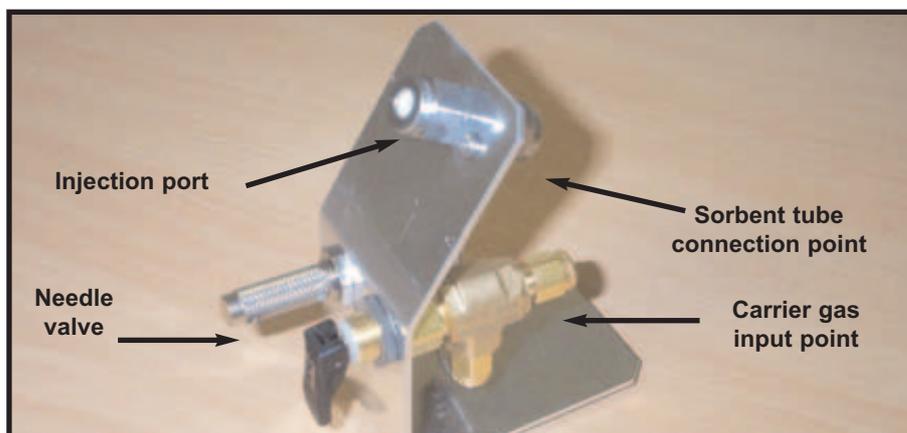


Figure 29. Photo showing a CSLR as used in calibration method 1

11.1.1 Criteria for Method 1

When using the CSLR, it is important that good laboratory practice is followed with respect to solvent purity and syringe use / cleanliness. The tubes onto which the solution is to be loaded should have been thoroughly conditioned and their blanks verified. Finally, air, nitrogen or helium may be used as the carrier gas. It should be of high purity (99.999% or higher) and contain negligible levels of volatile organic compounds (VOCs). Note that pure air cannot be used as a carrier gas through heated inlets.

Select the correct sorbent for the components of interest e.g. Tenax for aromatic compounds.

If possible, select a pure (chromatographic grade) solvent that is not well retained by the sorbent selected e.g. methanol when using Tenax tubes.

The carrier gas flow rate through the injector and sample tube should be set at 80 - 100 ml/min.

Insert the syringe needle through the septum such that the tip of the needle is in the gas flow. Except for high boiling analytes (b.p. > 150°C) do not touch the sorbent retaining gauze with the syringe needle. Depending on the nature of the the compounds of interest, it may help analytical precision if a small plug of heat-treated glass wool is placed into the CSLR just behind the septum to ensure the syringe needle is wiped clean before removal.

If the solvent in use is unretained by the sorbent, leave the tube connected to the injector with carrier gas flowing until >95% of the solvent has broken through. (Typically 5 mins for methanol on Tenax TA under a 100 ml/min flow of carrier gas.) Check that there are no analyte losses under these conditions.

Note: As a 5 µl injection volume can usually be introduced more accurately than a 1 µl one 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 5µl syringe for a 5µl injection. Do not inject >1 µl volume of standard if it is not possible to purge the solvent to vent.

Method 1. is best suited for dilute solutions i.e. less than 0.1% and for components which boil between 60 and 250°C.

11.2 Calibration Method 2. -Introducing standards directly as liquids

This is the simpler method of loading calibration standards and involves no additional equipment other than a syringe. A sample tube is packed with a 1 cm sorbent bed, backed up by quartz or glass wool. The sample is introduced to the rear of the tube, through the quartz wool and deposited as a liquid droplet on the sorbent bed. (Figure 30)

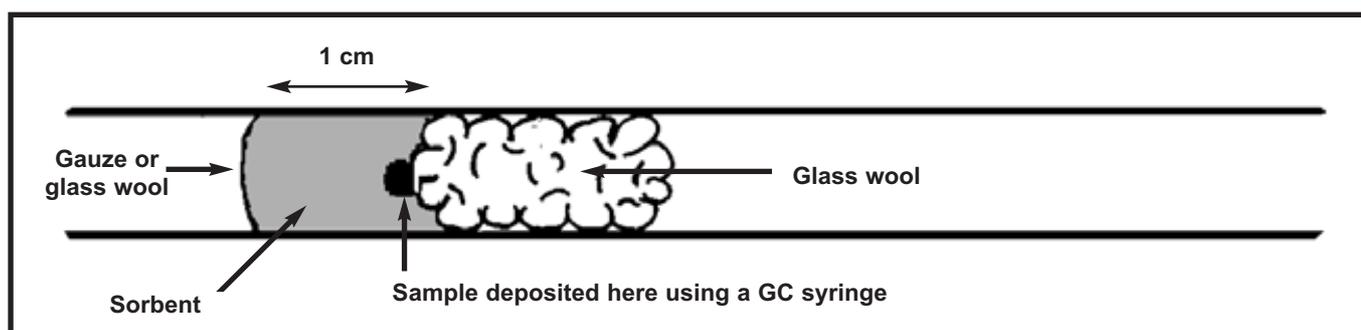


Figure 30. Calibration Method 2

11.2.1 Criteria for Method 2

Select the correct sorbent for the components of interest e.g. Tenax for aromatic compounds.

Select a pure (chromatographic grade) solvent that is at least partially retained by the tube and cold trap sorbents. This is essential to avoid the components of interest being carried through the short sorbent bed as the unretained solvent migrates through the tube in liquid form (ie analytes may be lost through what is, in effect, a liquid chromatographic process through the tube). Examples of solvents that are compatible with Tenax sorbent include ethyl acetate and n-octane. Methanol and acetone are not suitable.

Ensure that the solvent of choice does not coelute or interfere chromatographically with any of the components of interest.

As some solvent will appear in the chromatogram it is preferable to use smaller injection volumes i.e. <1 µl. As the standard is introduced at ambient temperatures syringe dead-volume effects are negligible.

The standard must be introduced onto the rear of the sample tube, through the glass wool, to ensure that no volatile components are lost during the initial pressurisation and purge stages of desorption.

11.3 Calculating the expected sample mass

A typical multilevel calibration procedure requires at least 3 (typically 5) 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 is expected in a typical sample. This is best illustrated by the following examples. [N.B.: if the expected atmospheric concentration is unknown, then assume it will be at 1/10th of the recommended limit level.] Once the required analyte mass is known the concentration of the standard solutions can be calculated.

11.3.1 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 = $\frac{\text{ng adsorbed onto tube}}{\text{Atmospheric conc. (ppm) x minutes exposure}}$

Therefore mass adsorbed on tube = 1.67 x 1 x 480
= 801.6ng

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.

11.3.2 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 would contain 10 µg of analyte
10 L at 100 ppb 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 toluene 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.

11.3.3 Solid sampling for residual acetone

Information required: Expected concentration w/w C

Example: Typical mass sampled M
 C = 1% weight for 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. More information on calibration can be found in various national and international standard methods as listed in table 4.

Method	Description
US EPA Method TO-17	Determination of VOCs in ambient air using active sampling onto sorbent tubes
ASTM D6196-03	Standard practice for selection of sorbents and pumped sampling / thermal desorption analysis procedures for volatile organic compounds in air.
NIOSH Method 2549	VOCs - (screening) using multibed sorbent tubes, thermal desorption, GC-MS
ISO 16017	Air quality - sampling and analysis of VOCs in ambient, indoor and workplace air by sorbent tube / thermal desorption / GC.
UK HSE MDHS 72	VOCs in air. Lab method using pumped solid sorbent tubes, thermal desorption and GC.
USK HSE MSDHS 80	VOCs in air. Lab method using diffusive solid sorbent tubes, thermal desorption and GC.

Table 4. National and international standard methods relating to calibration

11.4 Quality assurance and calibration

Maintaining the analytical quality of the results obtained from your complete analytical system, (UNITY - GC/GCMS - Data Handling System) requires systems of Internal Quality Control (IQC) and External Quality Assessment (EQA). EQA is also known as Proficiency Testing (PT).

IQC monitors the day-to-day consistency of the analytical system and routine calibration procedures using quality control samples within the laboratory.

EQA/PT is a system for objectively assessing lab. results by using an external agency.

The analysis of Certified Reference Standard tubes for thermal desorption - gas chromatography provides a measure of both IQC and EQA. In general however, participation in an external Proficiency Testing / EQA scheme is also recommended.

11.4.1 Certified Reference Standard (CRS) tubes

CRS tubes for thermal desorption 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 the international standards tabulated above.

Three routine CRS tubes are available from Markes International Ltd.:

- > Benzene, toluene and o-xylene at 1 µg each component (occupational hygiene levels).
- > Benzene, toluene and o-xylene at 25 ng each component (ambient air / environmental levels).
- > TO-17 Standard containing 25 ng each of 10 compounds with a wide range of polarity and volatility (ambient air / US EPA TO-17).

Custom CRS tubes can also be prepared to your specification containing up to six VOCs at levels from 10 ng to 100 mg.

All analyte masses are traceable to primary standards and each package includes a certification document, shipping blank and user instructions.

Further information can be obtained from Markes International Ltd., Unit D3, Llantrisant Business Park, Pontyclun, CF72 8YW, UK. Tel: (44) 1443 230935, Fax: (44) 1443 231531, email: enquiries@markes.com

11.4.2 External Quality Assessment Schemes

Participation in an external quality assessment scheme will provide information over a period of time, as to how the laboratory performs in relation to its peers. Many schemes also offer access to technical advice, which may help if the laboratory experiences problems with a particular analytical method.

The most widely used international EQA scheme for thermal desorption - gas chromatography is the Workplace Analysis Scheme for Proficiency (WASP), coordinated by the UK Health and Safety Executive. Standard 1/4 -inch OD thermal desorption tubes are packed with Tenax and loaded with benzene, toluene and m-xylene ready for thermal desorption analysis. Samples are sent out quarterly.

Further information can be obtained from:

Mr Peter Stacey
Secretary, WASP Steering Group
Health and Safety Laboratory
Broad Lane
Sheffield
S3 7HQ
UK

Tel: +44 (0) 1142 892000

Fax: +44 (0) 1142 892850

One thermal desorption related standard is also available from the European standards agency BCR. It is Certified Reference Material (CRM) 112 (Benzene, toluene and m-xylene on Tenax TA) available in UK through:

LGC: Laboratory of the Government Chemist
The Office of Reference Materials
Queens Road
Teddington
Middlesex
TW11 0IY
Tel: +44 20 8943 7000

E-mail: orm@lgc.co.uk

12 Insertion and removal of a sample tube in UNITY

12.1 Insertion

Tubes are inserted using the left-hand lever mechanism. Orientate the tube such that the sampling (grooved) end is pointing to the rear of the instrument. Before inserting a sample ensure that the tube oven is relatively cool, note that the oven temperature is displayed on the UNITY software status bar (see Section 14.3).

Place the tube horizontally in the tube oven, such that it is clear of the seals at both ends. Operate the lever towards the rear of the instrument to seal the tube into UNITY's flow path.

The instrument is then ready to run.

12.2 Removal

As soon as a tube has been desorbed (i.e. after primary desorption) it can be removed from the desorption oven. If the oven and tube are still hot (you can check this by looking at the software status bar (Section 14.3), it is strongly recommended that the tube extractor tool, included in the shipping kit, is used to remove the tube. Use the tool to grasp the tube at the end released from the tube seal and pull steadily.

13 Preparing for analysis

13.1 Sample tube orientation for quantitative desorption

Industry standard stainless steel or Silco/Sulfosteel sample tubes from Markes International have one groove 14.3 mm from the sampling end of the tube. This is used to position the front sorbent retaining gauze. When using a tube packed with sorbent for air sampling, different analytes will migrate through the sorbent bed to a greater or lesser extent, depending on the analyte affinity for the sorbent in use.

During desorption all analytes must be removed from the sorbent tube to ensure quantitative analysis and to leave the tube clean and ready for reuse. This is best achieved in backflush mode - i.e. analytes are desorbed back out of the sampling end of the tube using a reverse gas flow. The sorbent tube should therefore be oriented such that the sampling end of the tube is pointing towards the rear of the instrument.

13.2 Tube conditioning

Freshly packed sorbent tubes, including the Tenax tube shipped with UNITY, will require conditioning prior to use. There are several points to note when conditioning sample tubes using UNITY as opposed to an external Tube Conditioning / Dry-Purge Rig (P/N R-TC20).

- > Always use the dedicated Tube Conditioning Mode so that contaminants from the tube are vented to the charcoal filter and are not passed onto the cold trap.
- > Set the split flow to at least 50 ml/min (preferably 100 ml/min) to assist efficient conditioning.
- > Carefully double-check the maximum isothermal temperature for the sorbent in use and never condition at more than 10°C below this.
- > Set the flow path temp to at least 190°C while conditioning tubes. This prevents contaminants from condensing inside the UNITY flow path and helps to condition the system.

13.2.1 Typical parameter settings for conditioning various sorbent tubes

NOTE that the MAXIMUM temperature used to condition a multi-bed sorbent tube must be below the maximum temperature of the LEAST THERMALLY STABLE sorbent in the tube.

13.2.1.1 Tenax TA / Tenax GR

Carrier flow rate = 100 ml/min

2 hours at 320°C followed by 30 minutes at 335°C

If possible restrict subsequent analytical desorption temperatures to <300°C. This will reduce background noise and increase tube lifetime.

Tenax tubes should show artifact levels of less than 1 ng benzene equivalent for each artifact.

13.2.1.2 Chromosorb 106 / Chromosorb 102

Note: Chromosorb 106 / 102 should be bulk preconditioned at 190°C for 16 hours prior to packing into thermal desorption tubes to eliminate shrinkage.

Carrier flow rate = 100 ml/min

2 hours at 220°C followed by 30 minutes at 230°C

If possible restrict subsequent analytical desorption temperatures to <200°C. This will reduce background noise and increase tube lifetime.

Chromosorb tubes should show artifact levels of <10 ng benzene equivalent for each artifact.

13.2.1.3 Carbopack B / Carbotrap / GCB1 / Carbopack C / Carbotrap C

Carrier flow rate = 100 ml/min

2 hours at 350°C followed by 30 minutes at 400°C

If possible restrict subsequent analytical desorption temperatures to <350°C. This will reduce background noise and increase tube lifetime.

Graphitised carbon black tubes should show artifact levels of less than 0.1 ng benzene equivalent for each artifact.

13.2.1.4 Sphero carb / Unicarb / Carbosieve SIII / Carboxen 1000 / Carboxen 569

Carrier flow rate = 100 ml/min

1 hour at 100° followed by 1 hour at 200°C followed by 1 hour at 300°C followed by 30 mins at 380°C (N.B. The tubes do not need to cool down between each temperature increase)

If possible restrict subsequent analytical desorption temperatures to <350°C. This will reduce background noise and increase tube lifetime.

These tubes should show artifact levels of less than 1 ng benzene equivalent for each artifact.

13.2.1.5 Molecular Sieve 13X, Molecular Sieve 5Å

Carrier flow rate = 100 ml/min

1 hour at 100° followed by 1 hour at 200°C followed by 1 hour at 300°C followed by 1 hour at 350°C (N.B. The tubes do not need to cool down between each temperature increase)

If possible restrict subsequent analytical desorption temperatures to <320°C. This will reduce background noise and increase tube lifetime.

Molecular Sieve tubes should show artifact levels of less than 1 ng benzene equivalent for each artifact.

13.3 Cold Trap conditioning

Once the sample tubes have been conditioned, the cold trap must also be cleaned. If the cold trap contains no molecular sieve or carbonised molecular sieve type sorbents, trap conditioning is most easily achieved using the Trap Heat function on UNITY - see Section 26. As with tube conditioning it is essential to check the maximum isothermal temperature of the sorbent in the trap and never to set the trap temperature more than 10°C below this. In addition use a split flow of at least 50 ml/min to ensure efficient conditioning of the trap and to reduce the mass of contamination allowed to reach the analytical column.

Cold traps packed with molecular sieve or carbonised molecular sieve type sorbents should be conditioned in several steps with increasing temperatures using tube desorption mode to give an extended purge of carrier gas. The following instructions for "Water Management Traps" may be generally applied to all cold traps containing carbonised molecular sieves:

Recommended conditioning parameters

- > 2/3 stage desorption mode with 10 min tube desorb.
- > Trapping temperature: +30°C.
- > Flow through the cold trap during focusing: 20 to 40 ml/min.
- > Minimum prepurge time (on-line mode) or prepurge time + tube desorb time (tube desorb mode) must be set to ensure complete elimination of oxygen and should exceed 10 mins if possible.
- > Flow through the hot trap during desorption: 50 ml/min - almost all sent to the split.
- > Step 1: trap desorption at 275°C for 10 mins.
- > Step 2: trap desorption at 300°C for 10 mins.
- > Step 3: trap desorption at 325°C for 10 mins.
- > If analytical desorption temperatures need to exceed 325°C, a 4th conditioning step should be used with the trap desorption at 340°C for 10mins.

Recommended optimum analytical conditions for traps containing carbonised molecular sieves are:

- > Trapping temperature: either -10°C or +25 to +30°C.
- > Flow through the cold trap during focusing: 5 to 20 ml/min.
- > Dependent on the selected flow (above), the minimum prepurge time (on-line mode) or the sum of the prepurge time + tube desorb time (tube desorb mode) must be set to ensure complete elimination of oxygen - See warning above.
- > Desorption temperature: 300°C for 3 minutes.

> Flow through the hot trap during desorption: 2 to 50 ml/min.

14 'About' the UNITY user interface

14.1 Windows platform

UNITY's flexibility is reflected in its control software, which runs on 32 bit versions of Windows, namely Windows 98, Windows 2000 and Windows NT 4.0. It will NOT run on Windows 3.1. The status with NT 3.51 is unknown i.e. it should work theoretically but has not yet been tested. The software should be intuitive to anyone familiar with Microsoft Office products.

Other Windows software may be active on the PC at the same time as UNITY software, for example data handling software, word processing and spreadsheet functions.

14.2 Operating languages

Currently UNITY software is in English.

14.3 Status bar

The UNITY status bar (figure 31) displays all key UNITY parameters and is always visible and on top of the desktop while the software is open, whether maximised or iconised. The parameters shown on the status bar are as follows. The level of information presented for each category may be selected by a right click of the mouse on the appropriate section of the status bar.

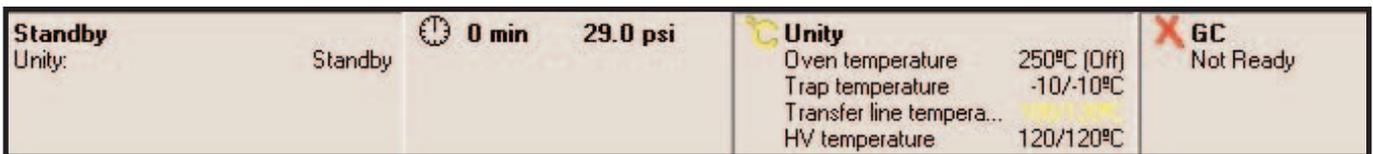


Figure 31. UNITY software status bar

Status	Shows the overall status of Unity as it progresses through the various stages of the sequence i.e. Standby, Leak Test, Trap Heat etc Status will also report tube failures i.e. Tube Leaked
Elapsed Time:	Shows the time elapsed since the start of the function currently operating on UNITY and should be read in conjunction with the Status parameter. For example if the Status is reading Prepurge and the Elapsed Time is reading 0.3 this tells us that UNITY is 0.3 minutes (i.e. 18 seconds) into the ambient purge. If the Status is reading Primary Desorb and the Elapsed Time is 4.9 - then it is 4.9 minutes since the start of tube desorption and so on.
Pressure	Shows the pressure of the carrier gas within the Unity flow path.
°C Unity	Displays the status of the Unity heated zones. The set point and the status for each heated zone Oven, Trap, Transfer Line and Heated valve can be displayed by clicking over the temperature zone and choosing the zone or select all. The status of each zone selected will be displayed
"GC"	Indicates whether the GC status is ready (tick) or not ready (X)

15 UNITY Operation: System 'Ready' status

15.1 Internal system checks

UNITY continually monitors the actual temperature of its internal heated / cooled zones (cold trap, sample flow path, etc.) and the actual carrier gas pressure and compares them to the set values. When first switched on UNITY status changes to Standby and the display for UNITY temperature will be highlighted until all zones reach the relevant set point.

Note: A run may be started when UNITY is **Not Ready** and the run will then pause, waiting for the appropriate zone to reach temperature before desorbing the tube. The status will read **Equilibrating** at this stage.

Note: The actual temperature of the tube oven has no effect on the ready status as heat is not applied to the oven until tube desorption starts.

15.2 Checks on external components of the analytical system

UNITY is connected to the GC via the GC Interface Harness (see Section 4.4.2. and Appendix Two).

The analytical system should be configured such that all components "downline" of the GC (e.g. mass spectrometer, data handling system etc.) must be ready before the GC will become ready. This ensures that no sample is injected from UNITY onto the GC when the analytical system is not able to analyse the sample and collect the data.

When the GC comes ready it will provide a signal to UNITY via the Interface Harness and the GC indicator on the status bar will change from a cross to a tick

UNITY checks this signal, to ascertain whether the GC is ready, twice during its operation sequence;

- > Before going to tube desorb, and
- > Before going to trap heat.

If UNITY finds that the GC not ready, it will indicate as such and display **Equilibrating** on the status bar.

UNITY will continue to wait until it receives an external ready signal from the GC system before proceeding to either of these two stages.

16 UNITY Options

The Options page is accessed in the UNITY software via **View > Options** (figure 32).

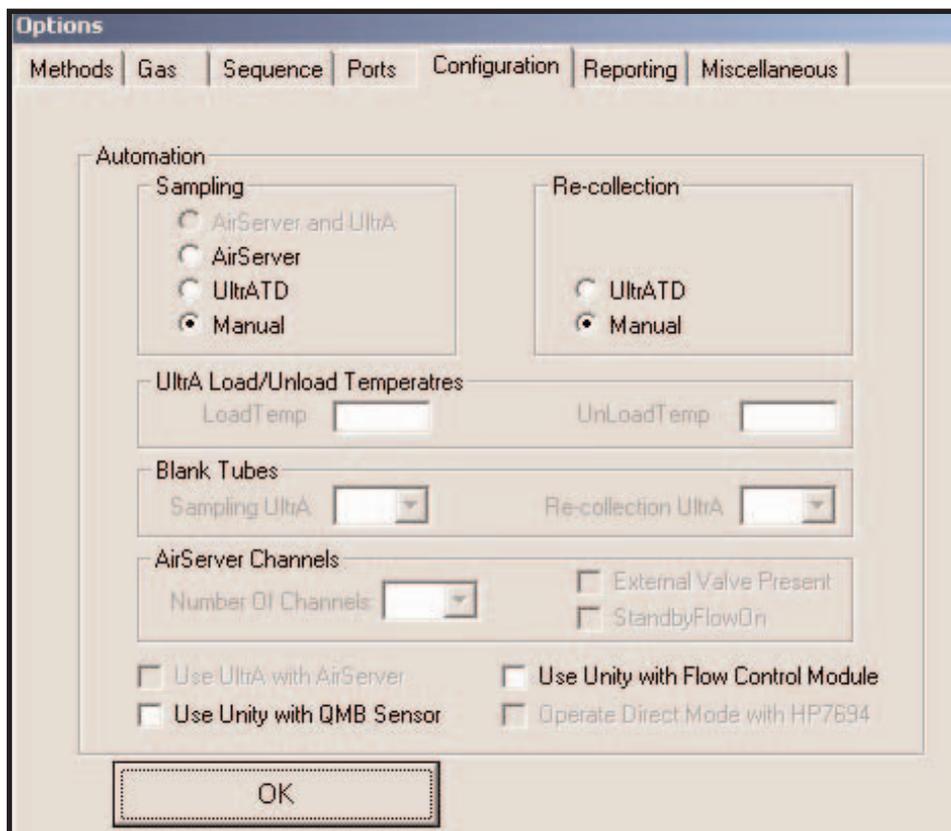


Figure 32. Options page

16.1 Methods options

Accessed by selecting **View > Options > Methods**. There are two method functions which can be changed; the Method Directory used and the information given in the active window bar.

The **Method Directory** will be set by default to the directory where UNITY was installed.

To change this directory double click on the current path and select the new path from the directory.

If **Show Full Path** is selected then the active window bar will show the full path and file name of the method in the active window bar, if it is not selected then the active window bar will only display the file name for that method.

If **Show Method Name** is selected then the active window bar will show the text entered in the Method Name section of the properties dialogue box (see Section 17.3).

If **Show Method Path** is selected then the active window bar will show the file name of the method in use, with or without the full path depending on whether Show Full Path is selected.

16.2 Gas option

Found under Gas. The user has a choice of which units to use for carrier gas pressure display. These are psi or kPa and they are selected by clicking beside the unit of choice. **Note:** if a flow control module is being used, the user is also able to select the type of carrier gas being used.

16.3 Sequence option

This option provides the user with the option to indicate whether dry purge accessory is fitted and of changing the default times for certain stages of the sequence and.

Unity Dry Purge

Check this box if the Unity Dry Purge option is fitted

Pre Trap fire Purge

Allows an entry for the time taken to purge the trap prior to desorption. Default is 0.3 min

Air Server post leak test Pressure release This requires an Air Server (see Air Server User Manual)

Post tube desorb pressure release.

Allows entry for the time taken to release the carrier gas pressure in the tube at the end of tube desorption. This avoids loss of adsorbent from a pressurised tube, particularly if the tube has no gauze fitted to restrain the adsorbent, as it is removed from UNITY flow path. The default is 0.3 min.

A number of other options are greyed out which are available only when accessory modules are configured

16.4 Port options

Used to instruct UNITY which communications port on the PC is being used, to set the Baud rate for the PC / UNITY communications and to set the GC Interface logic.

The communications port is selected via a drop down menu.

The GC Interface logic is set to reflect whether the GC sense is Open or Closed for both GC Start (Out) and GC Ready (In). i.e. for the particular GC being used is the contact Open or Closed to reflect a Start signal, and Open or Closed to reflect a Ready signal. This information is usually provided in the GC Users Manual. Further information can be found in Appendix Two.

16.5 Configuration options

This option is only required if UNITY is to be used in conjunction with an Air Server, ULTRA, QMB Sensor, HP7694 or MFC Flow Control Module from Markes International. When selected, the software displayed on the PC is specific for the accessory selected and is different from the standard screen. For further details, see the appropriate accessory user manual.

16.6 Report option

This option influences the information recorded in the 'sequence reporter' page of method linking (see

Section 33). Recording parameters are selected by clicking on the appropriate box(es). **N.B.** the reporting options available will change if an accessory is being used in conjunction with UNITY.

16.7 Miscellaneous option

User: Used to input details of user name and company, which will automatically appear in the properties dialogue of each saved method.

Trap Heat: UNITY can use two sets of parameters when undertaking **Trap Heat**. Either those used in the existing **Controlling Method** (Section 17.1) or a special set of parameters used in the **Trap Heat Method** (Section 26).

The default set of Trap Heat parameters is set in the UNITY Options section. Select **View, Options** and then **Trap Heat**. A choice between **Use Controlling Method Parameters** and **Use Dedicated Trap Heat Method** is given. Select your preferred option.

Print: Found under the **Print** section of the Options page, this gives the user the option between printing UNITY methods out as a text string, or printing them out as displayed on the screen. Select the preferred option.

17 UNITY Methods

17.1 Controlling method

At all times one method is identified by UNITY as that controlling the system - i.e. the method dictating the set parameters. This method is called the **Controlling Method** and cannot be deleted or closed until another method is loaded as the controlling method. To load a method - i.e. to make it the controlling method - use either the **Load icon (✓)** or select **File** and then **Load** from the menu. As soon as a method is loaded, this displaces the method previously identified as that controlling UNITY and UNITY immediately starts to set the new parameters. The instrument status changes accordingly. Only one method is identified as the controlling method at any one time.

Note: An active method is not necessarily the controlling method. The active method is simply that last modified or accessed by the operator. The controlling method is always identified as such in the bar at the top of its window, whether active or not.

17.2 Generating a new method

New methods are generated by either selecting **File > New**, by clicking the **New File Icon** - the blank sheet of paper - at the top left-hand side of the toolbar, or by pressing **CTRL and N**.

A new method screen will be brought up containing a set of default parameters ready for you to modify. Once the method has been generated it can be named and saved - see 17.3 below.

17.3 Saving a new method

New methods can be saved by -

1. Pressing the **floppy disk icon** at the left of the tool bar or
2. Selecting **Save** under the **File** menu or
3. Pressing **CTRL and S** or
4. Selecting **Save As** under the **File** menu

Using the first three routes brings up the **Properties** dialogue box (Figure 33). Using route 4 brings up the **Method File Directory** and allows a file name to be entered for the method. The Properties dialogue box then automatically appears with the file name in the appropriate field.

The Method **Author** and **Company** names will appear in the Method Properties dialogue box, as set up under **Options** (Section 16.7). If nothing has been entered for these fields under Options the blanks may be filled in at this stage. The **Method Name** and **Notes** sections can be used to provide additional information on the method if required.

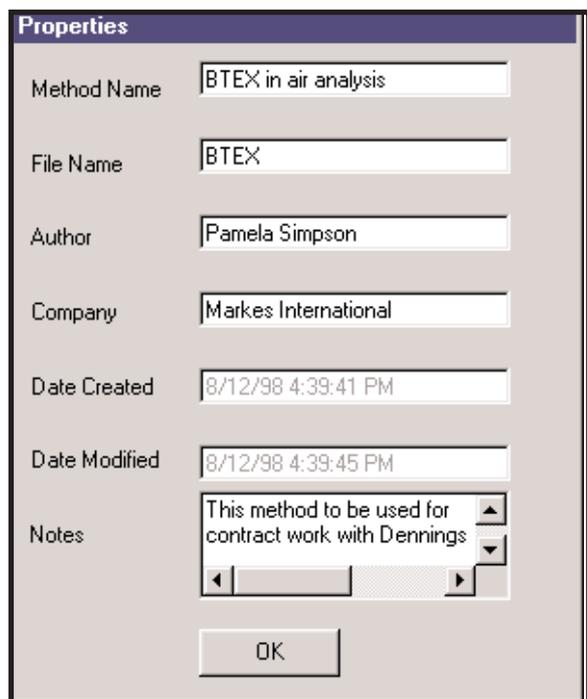


Figure33. Properties Dialogue Box

17.4 Opening a stored method

Methods are opened by using the standard Windows protocol i.e. by either selecting **File** and then **Open** or by clicking the **open file icon** - the open folder - at the top left-hand side of the toolbar. This brings up the directory - nominated under **Options** (Section 16.1) - containing UNITY method files. Select the required file name and click **OK** or double-click on the required file name to access it.

17.5 General method file functions

These functions operate as in all Windows software packages.

17.5.1 Copy method parameters

Ensure that the UNITY method you wish to copy is the active method. Clicking on it with the left hand mouse button will make it active if necessary. Select **Edit** and then **Copy**, or click the **copy icon** - the two identical, overlapping pages - on the toolbar. (The shortcut **CTRL and C** can also be used.)

Copy will put a "text copy" of the active method onto the Windows Clipboard (in English Only), thus allowing you to **Paste** the text string into another application such as a word processor.

Copy is used to transfer a method as a text string into third party word processing packages.

Note: It is possible to open UNITY methods directly into word processing / spreadsheet packages such as WORD and EXCEL. (N.B. When opening UNITY methods directly into EXCEL treat the data type as delimited and use the '=' character as the delimiter).

17.5.2 Paste

Paste is activated after **Copy** has been used and allows for a copy of the active method to be pasted to another method (after THAT method has been made Active).

Note: UNITY does not support pasting from the Windows clipboard i.e. you cannot paste from the Word processor to UNITY.

17.5.3 Print method

Select **File** and then **Print** or click on the **print icon** - the image of a printer, fifth icon from the left on the tool bar - to print the method. This function will either print the entire method, including properties and gas flows (if entered), as a text string or will simply print the main method page as it appears on the computer screen. Method print format is selected under **Options** - Section 16. **Print Preview** under the **File** menu will display the print format on the screen if needed. It is the active method that is printed.

17.5.4 Saving existing methods

An existing method can be modified and saved by selecting **File** and then **Save** or by clicking the **save icon** - the floppy disk - on the left-hand side of the toolbar. Selecting **File** and then **Save As** brings up the **method file directory** and invites the operator to rename the method file. Once a method file name is entered, the **properties** dialogue box appears. There is no application for the "Save All" function under the **File** menu at the present time.

18 Schematic display of UNITY status

A simple schematic illustrating the status of UNITY can be displayed on the screen at all times during system operation. This is accessed using the **status icon**, third from the right on the tool bar - or by selecting **View** and then **Status Show**.

For example, figure 34 shows the system in **Primary Desorb mode with split**.

The schematic display of UNITY status is linked directly to operation of the instrument. The display is thus not just cosmetic, but is a representation of the actual status of the instrument.

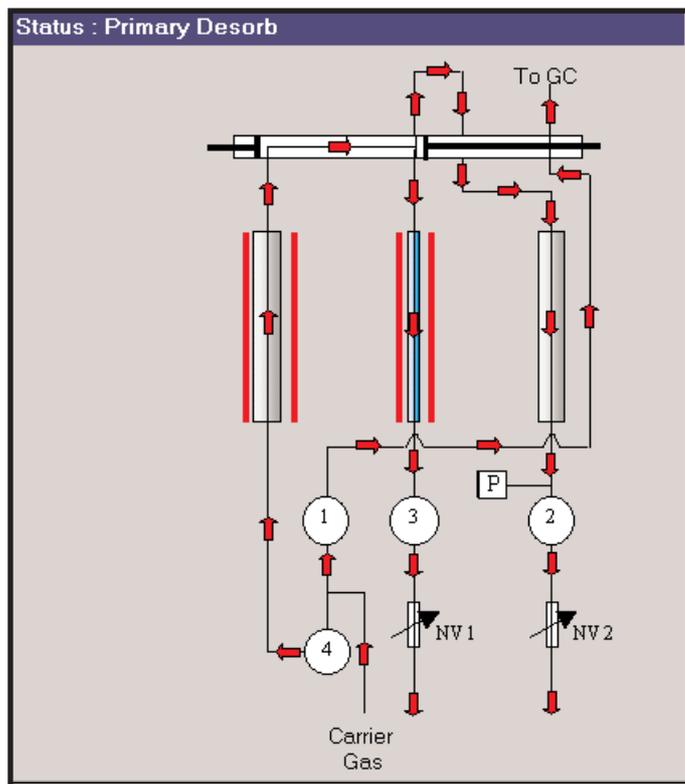


Figure 34. Status schematic displaying UNITY in Primary Desorb Mode

19 Split on or off in standby

When UNITY is in standby state, i.e. not being used overnight or at weekends etc., it is usual to have the split turned off in order to save expensive carrier gas. (8 hours overnight at 50 ml/min would use ~24 litres of carrier gas). However if UNITY is being operated with a mass spectrometer (MS) or an electron capture detector (ECD) on the gas chromatograph it is strongly recommended that the split be left on in standby. This is because, in common with all split capillary injectors, if there is no positive gas flow passing through the split vent for long periods of time, air will ingress into the system through the split vent and cause an undesirable increase in background signal.

The split flow may be reduced to 10 ml/min to minimise carrier gas consumption if required.

Checking the box on the top line of the method page selects **Split On in Standby**. An unchecked box will turn the **Split Off in Standby**.

20 The Leak Test

Once in position in the desorber flow path, each tube is pressure tested, without heat or carrier gas flow, to ensure there are no leaks. The test is deliberately stringent. If sample tubes fail to seal properly or if a leak develops in any other part of the system flow path, data obtained from that analysis would not be valid. Every part of the UNITY flow path, including the main valve, is tested for leaks during the pressure test (the only exception is the point where the transfer line is connected to UNITY). For this reason, following installation of the transfer line it is recommended that a leak detector is used to detect any leaks at this point in the flow path. Many competitive thermal desorption systems do not offer such a comprehensive leak test. Without this, there is always risk of an undetected leak and data integrity cannot be guaranteed.

The 'no-heat, no-flow' specification ensures that sample integrity is maintained while the UNITY leak test is in progress. If the tube fails the leak test, it will not be analysed and UNITY displays a **Tube leaked** error message in the status box on the main status bar. The user must clear this message by pressing the **Stop sequence** icon - the black square - on the tool bar, before proceeding.

A leak test may be carried out manually via the leak test icon furthest on the right on the tool bar. Clicking

on this icon opens a dialogue box with a button to pressurise the flow path and to perform a leak test. The Leak Test function should be used in conjunction with a He leak detector

The Leak Test dialogue box also allows the valves controlling the flow path to be operated independently for assistance with diagnosis of leaks.

20.1 Description of leak test

From the **Standby** position, (Figure 1), the UNITY Status changes to **Leak test** (Figure 35). Solenoid valve SV4 and the heated valve activate to allow carrier gas through the tube and into the cold trap and split filter, but with the exits from both these devices closed so that the whole sample flow path is pressurised to capillary column head pressure. Carrier gas continues to be supplied to the capillary analytical column throughout the leak test (as it is through every other stage of UNITY operation).

After 5 seconds the solenoid valve SV4 turns off and a pressure transducer, positioned between the split filter and SV2, monitors the pressure in the sample flow path. If the measured pressure drops by more than 5% in 30 seconds this is classified as a leak in the sample flow path and UNITY status changes to **Tube Leaked**. UNITY will continue to display this message until it is acknowledged and cleared by the user clicking the **Stop sequence** icon - the black square on the toolbar.

If the system maintains pressure, no leak is detected and UNITY passes on to the second part of the leak test. For this SV2 is activated briefly, to depressurise the sample flow path, and then switches off again. The sample flow path pressure is again monitored to see if it increases by 5% over 30 seconds. This would indicate an internal leak across the heated valve.

If UNITY fails this part of the leak test, the status again changes to **Tube Leaked** and the user must stop the sequence by clicking the **Stop sequence** button. Failure of this part of the leak test requires the attention of a trained service engineer.

20.2 Main causes of Leak Test Failure

20.2.1 Wearing of the O-rings which seal the tube

Two size 010 Viton O-rings are used to seal the sample tube into the UNITY flow path. These seal on the outer wall, not the chamfered bezel, of the tube, ~2 mm from each end. This O-ring position minimises wear, but it is possible that O-rings will start to leak after ~1000 sealing operations. O-ring lifespan will be reduced if UNITY is stored or operated in an aggressive environment - e.g. one with high levels of atmospheric pollutants, particularly chlorinated solvents or ozone - or if UNITY is used with sample tubes with damaged ends.

Details of how to change tube-sealing O-rings are given in the Routine Maintenance Section 35.4.

20.2.2 Interference with the tube seal by fibres and particles

If glass / quartz wool is used to retain sorbents or samples inside a tube and stray fibres protrude from the end, these are likely to cause leak test failures. Similarly if sorbent or sample particles are allowed to migrate from the tube and reach the O-ring seals these too will cause leak test failures.

It is advisable to visually inspect each tube and both tube seals on UNITY before placing a tube into the system. Use a low-pressure air jet to remove contamination from the tube seals if necessary. In some

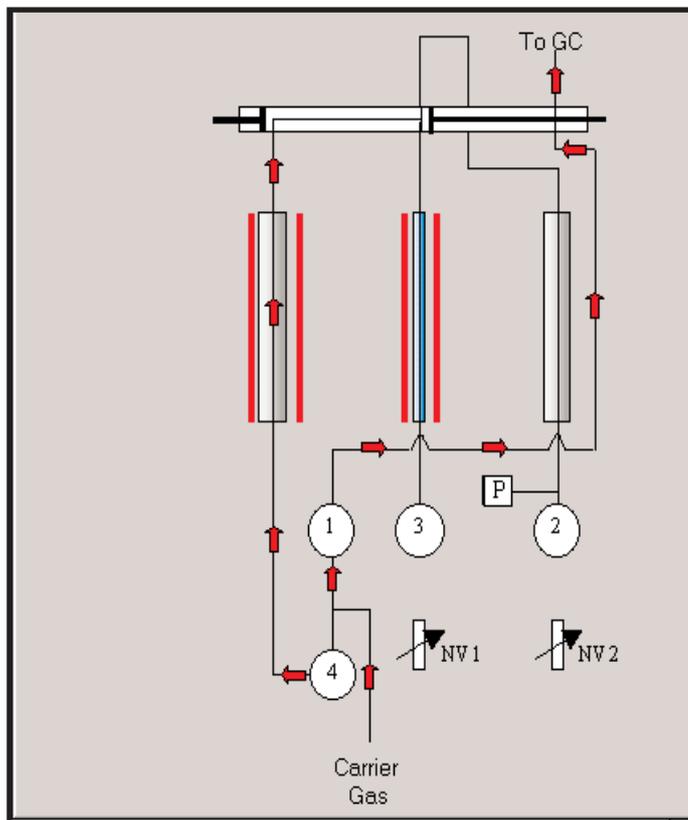


Figure 35. UNITY Schematic showing Pressurise Status

cases it may be necessary to remove and clean or replace contaminated O-rings. See Section 35.4. spare O-ring seals are provided in the shipping kit (Section 4.1).

20.2.3 Damaged O-rings

The most likely cause of damaged O-rings is damaged or out of specification sample tubes, for example chipped glass tubes or burred and / or unchamfered stainless steel tubes. If such tubes are identified they should be disposed of immediately.

Damaged O-rings must always be replaced, see Section 35.4.

20.2.4 Leaking split filter tube seal

The split filter tube, on the right hand side of UNITY, is the same size as a sample tube and is sealed into the instrument flow path in the same way - i.e. with two size 010 Viton O-rings. The above paragraphs on sample tube leaks are equally applicable to the split filter tube.

20.2.5 Wearing of the cold trap seals

The cold trap tube is sealed into the UNITY flow path using two small, size 006, Viton O-rings. The O-ring at the non-valve end of the trap tube (i.e. the end nearest the front of the instrument), is located in the brass trap connector and is user accessible (Section 4.2). The seal at the heated valve end (i.e. that pointing to the rear of the instrument) is not user accessible.

The cold trap O-ring seals seal on the outer wall of the trap tube and should thus, as with the sample tube, remain effective for over 1000 trap sealing operations. It is, therefore, extremely unlikely that these seals will wear out over the lifetime of the instrument, unless a damaged cold trap is used. It is, however, a sensible precaution to get both trap seals changed during annual service maintenance of the instrument.

20.2.6 Other causes of leak failures

If none of the above are found to rectify a persistent tube leak test failure, an internal leak has developed, for example in the main heated valve. This can only be rectified by a qualified service engineer.

21 Sample tube purge at ambient temperature

21.1 Functions / objectives

Each tube must be purged thoroughly with carrier gas to remove air before heat is applied. Even the smallest trace of oxygen could result in sorbent and possible analyte oxidation, generating artifacts and compromising data quality. With normal porous polymer or graphitised carbon sorbents, a volume of carrier gas, ~ 10 times the capacity of the sample tube, is required to completely eliminate air. This equates to 20 ml purge volume for glass tubes (capacity ~2 ml) and 30 ml purge volume for stainless steel tubes (capacity ~ 3 ml). A more stringent purge (~50 times the tube volume) is required to completely eliminate air from tubes packed with conventional or carbonised molecular sieve-type sorbents.

21.2 Control of the carrier gas flows during ambient purge

The ambient purge carrier gas flow can either pass through the cold trap to the 'desorb flow' vent or through the split filter to the 'split flow' vent or both as it comes out of the sample tube.

21.2.1 Trap in or out of line

The cold trap is user selectable to be in or out of line during the ambient temperature purge. It is generally recommended for the cold trap to be off line at this stage, to ensure that any water purged from the tube is not retrapped on the cold trap. Applications involving the direct desorption of volatile components from materials such as pharmaceuticals, plastics etc. are an exception to this rule. In these cases, and especially if the material contains ultra volatile target analytes such as acetaldehyde, it is advisable to have the trap in line.

21.2.2 Split on or off

If the trap is selected to be off line during tube purge (the most usual configuration), by default the split flow is always turned on to give a flow through the tube.

If the trap is selected to be in line the user has a choice of whether the split vent is on or off. The split should be selected to be the same as during the tube desorb process and is therefore determined by the sensitivity of the analysis. Further information on selecting and setting split flows is given in Section 25.

21.2.3 Determining the prepurge time

The flow through the sample tube during the ambient temperature purge is controlled as follows:

- > Trap in line, split off: purge flow controlled via the needle valve on the desorb flow vent (left-hand needle valve)
- > Trap off line, split on: purge flow controlled via the needle valve on the split vent (right-hand needle valve)
- > Trap in line, split on: total purge flow = flow through cold trap (controlled via the needle valve on the desorb flow vent (left-hand needle valve)) + flow through split vent (controlled by the needle valve on the split vent (right-hand needle valve))

The Prepurge time should be set such that, with the given purge flow, the necessary purge volume (Section 21.1) is passed through the sample tube before the end of ambient purge and the beginning of tube heat. Typical prepurge times are 1-3 minutes for normal sorbents and materials samples and 10 minutes for molecular sieves and carbonised molecular sieves.

22 Desorption modes

Two modes are available:

- > Tube Conditioning
- > Standard 2(3) Stage Desorption

Select between the modes by using the up and down arrows.

22.1 Tube conditioning mode

This mode is used to condition sorbent tubes prior to sampling. See Section 13.2 for further information on conditioning tubes. The method screen is the simplest of the three modes and is shown in figure 36.

In tube conditioning mode, the cold trap is off line all the time so that desorbed materials cannot contaminate this or the GC analytical column. Only a few of the usual thermal desorption parameters are relevant in a Tube Conditioning Method:

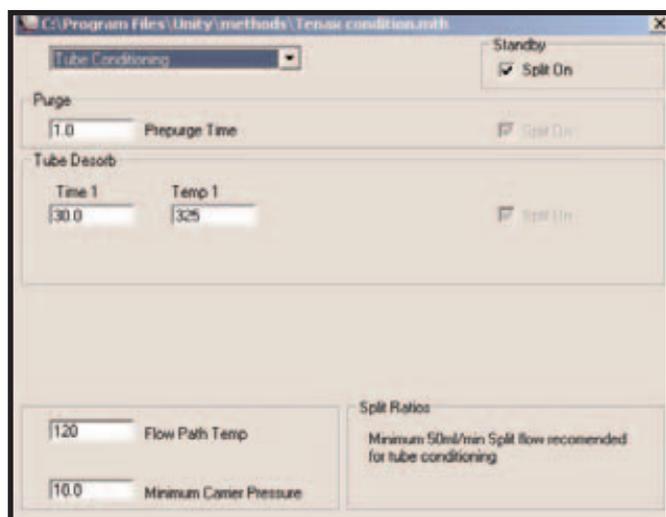


Figure 36. Tube Conditioning Mode Screen

22.1.1 Parameters

- Mode:** Set to **Tube Conditioning**.
- Split on in Standby:** See Section 19 - click on the box to enter a check if **Split On** in Standby is required.
- Purge:** Set **Prepurge** time by clicking in box and typing the required time. 1 minute at 30 ml/min is enough to purge oxygen from most sorbent tubes. However, this should be extended to 5 or 10 mins at 30 ml/min for molecular sieve and carbonised molecular sieve type sorbents.
- Note:** The cold trap is, by default, off line during ambient purge in tube conditioning mode. The split flow is therefore switched on by default.
- Tube Desorb:** The desorb time - **Time 1** - and desorption temperature - **Temp 1** - are set by clicking in the relevant boxes and typing in the required values. The split flow is automatically switched on during tube desorption in this mode. The gas flow through the sample tube is controlled by the (right-hand) needle valve on the split flow vent. It is recommended that a split flow of at least 50 ml/min be used during tube conditioning.
- Flow Path Temp:** Set the temperature required for the sample flow path by clicking in the box and typing in the required value. High temperatures (180 to 210°C) are recommended during tube conditioning. (See also section 27)
- Min Carrier Pressure:** Set a minimum carrier gas pressure just below that at which you normally operate UNITY and the GC analytical column. If the carrier gas pressure drops below this minimum pressure, UNITY status will change to **Low Carrier Pressure** and UNITY will become Not Ready. This prevents tubes being heated with a low carrier gas supply which could damage the sorbents in the tube.

Note: Method parameters may either be entered by clicking on each box in turn, typing in the parameter and then pressing **Enter** or by entering in the first parameter and then using the tab key to automatically enter the parameter and move the cursor to the next active box. **The last parameter change should always be completed by pressing Enter.**

22.2 Standard 2(3) stage desorption

Standard 2(3) stage desorption is the mode used for most routine thermal desorption work.

22.2.1 Parameters

- Mode:** Set to **Standard 2(3) stage desorption**.
- Split on in Standby:** See Section 19 - click on the box to enter a check if **Split On in Standby** is required.
- Purge:** Set the ambient **Prepurge Time** by clicking in the relevant box and typing the required time (See Section 22.1.1 for advice on prepurge times).
- If required (see Section 21), select **Trap In Line** during the prepurge by clicking on the box to enter a check. Similarly, click on the **Split On** box to enter a check if a split is required during the prepurge. Remember one or other or both of these flows must be selected during the prepurge (Section 21).
- Tube desorb / elevated temp. purge:** Set the **Time 1** - desorb time - and the **Temp 1** - desorption purge temperature - by clicking in the relevant boxes and typing in the required values.
- Tube desorption may be carried out split or splitless i.e. all the sample from the sample tube can be transferred to the trap or part of it sent to the split vent. If a split is required during tube desorption (a so-called inlet split),

(see Section 25), check the relevant box. If the split is selected to be off during tube desorption, all the analytes will be transferred from the tube to the cold trap.

If an elevated temperature purge is required (see Section 23), then **Time 1** and **Temp 1** should be set to reflect the required elevated Prepurge time and temperature. In this case, **Time 2** and **Temp 2** become the actual analytical tube desorb time and temperature and time values should be entered appropriately.

Typical elevated temperature purge settings are 10-15 minutes at 50-100°C.

Note: It is the entry of the second tube desorb time - **Time 2** - in the appropriate box which indicates to the system that an elevated temperature purge is required. When a value is entered for **Time 2** an extra **Trap In Line** check box appears in the line referring to stage 1 of tube desorb. As stage 1 of tube desorb is now, effectively, an elevated temperature purge, it becomes appropriate, as in ambient temperature purge, to deselect the cold trap. The cold trap is invariably selected off-line and the split flow on during elevated temperature purge because the purpose of elevated temperature purge is generally to eliminate volatiles from the tube and system before analysis of higher boiling target analytes.

Gas flows during elevated temperature purge are controlled as described in Section 21 for the ambient temperature purge. Section 23 gives additional details about tube purge at elevated temperature.

When using 2 stages of tube desorption, remember to place a check in the second split on box if an inlet split is required for the analysis.

The gas flow through the hot tube during its analytical desorption = the flow through the cold trap (the so-called desorb flow - controlled via the left hand needle valve) + the inlet split flow, i.e. the flow through the split vent (controlled via the right hand needle valve), if any.

Trap Desorb:

Set the **Trap Low** temperature by clicking in the box and typing in the required value. Most applications work well with a **Trap Low** of -10°C. Obvious exceptions to this include the analysis of samples containing high levels of water or standards containing unwanted solvent. In these cases it may be useful to maintain a **Trap Low** temperature at or near ambient (25-30°C). This allows water and volatile solvents such as methanol and methylene chloride to breakthrough the trap (depending on which sorbents are in the trap) and be eliminated from the system before trap desorption and the beginning of the chromatographic analysis.

Set the **Trap High** temperature and the **Trap Hold** time as appropriate for the trap sorbent and target analytes.

Trap desorption can be carried out split or splitless - i.e. If a split is required during trap desorption (a so-called outlet split), (see Section 25), check the relevant box. If the split is selected to be off during trap desorption, all the analytes will be transferred from the trap to the GC analytical column during desorption. The flow through the trap when it is hot = the flow through the GC column plus that through the split vent (controlled via the right hand needle valve), if any.

Flow path Temp:

Set the temperature required for the heated valve and sample flow path by clicking in the box and typing in the required value. The following general guidelines may be applied:

- > All analytes, volatile enough to be present in the air in the vapour phase at ambient temperature, will pass comfortably through the

system with the flow path between 120°C and 150°C. For ease of use, extended system lifetime and trace level operation a lower temperature (e.g. system default temperature of 140°C) is often preferred.

> Whenever analysing labile compounds use a low (<100°C) flow path temperature and, where possible, increase gas flow rates (linear gas velocities) inside the system. (See Section 4.6 for instructions on how to disconnect the auxilliary heater to achieve a lower flow path temperature)

> Use the highest possible flow path temperature (200°C-210°C) for analysing semivolatile organics.

GC Cycle Time:

The **GC Cycle Time** = GC Run Time + GC Cool Down Time + Equilibration (if appropriate). If a **GC Cycle Time** is entered, UNITY will calculate the time at which it can begin the next tube desorption stage such that at the end of that tube desorption and at the time the trap is ready to heat, the GC will have just come ready from the previous analysis. To enter a **GC Cycle Time** click in the relevant box and type in the required value. See Section 29 for further information.

Min Carrier Pressure:

Set a minimum carrier gas pressure below that at which UNITY is normally operated. If the carrier gas pressure drops below this minimum pressure, UNITY status will change to **Low Carrier Pressure** and UNITY will not come Ready. If the carrier gas pressure drops below the minimum pressure during a run, UNITY will enter **Low Carrier Gas** status and the tube oven (if heating) and trap heater (if heating) will start to cool down.

Note: Method parameters may either be entered by clicking on each box in turn, typing in the parameter and then pressing **Enter** or by entering in the first parameter - e.g. **Split On In Standby** and then using the tab key to automatically enter the parameter and move the cursor to the next active box. The last parameter should be completed by pressing **Enter**.

Split Ratios:

The inlet, outlet and total split ratios can be viewed, when applicable, in the box at the bottom right hand corner of the method page once the measured flows have been entered into the method. Flows may be entered by clicking on the **Confirm/Enter Flows** button to bring up the relevant dialogue box, see Figure 38.

For measurement of gas flows see Section 25. Once the values have been entered and confirmed by pressing **OK**, the split ratios are automatically calculated and displayed.

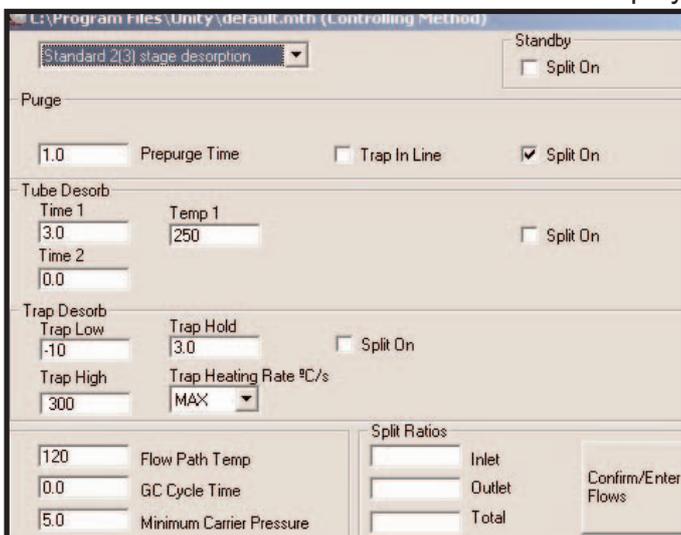


Figure 37. Standard 2(3) Stage Desorption Method Screen

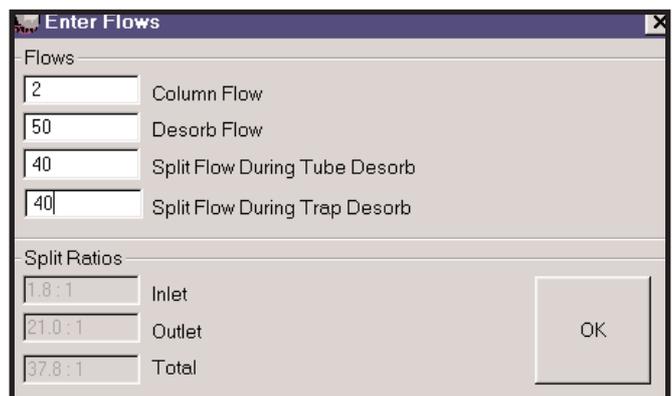


Figure 38. Confirm/Enter Flows Dialogue Box

22.3 Other operating modes

Other mode options are available for UNITYs configured with special accessories. These are the MFC Flow Control Module, ULTRA Accessory, Air Server Accessory and QMB Sensor Accessory respectively. For more information on these operating modes or accessories please see the relevant operating instructions. Alternatively, contact Markes International Ltd. directly on Tel: +44 (0)1443 230 935, Fax: +44 (0) 1443 231 531 or email: enquiries@markes.com .

23 Sample tube purge at elevated temperature

The elevated purge option is used for selectively eliminating water and / or high levels of unwanted volatile components. The trap is, by definition, almost always out of line during elevated temperature purge, which means that the split flow must be on. The elevated temperature purge immediately follows, and does not replace, the ambient temperature purge.

Example applications are:

- > Eliminating high levels of water collected on sorbent tubes when monitoring humid atmospheres.
- > Eliminating high levels of ethanol from a sample of the flavour profile of potable spirits when the components of interest are higher boiling esters and ketones.
- > Eliminating high levels of volatile solvent from higher boiling (e.g. aromatic) standards introduced onto sorbent tubes as droplets of liquid solution.

The elevated purge temperature and time are set under the **Tube Desorb** section of a **Standard 2(3) Stage Desorption** Method, as explained in Section 22.2.1.

24 Practical considerations for sample tube desorption

24.1 Sorbent maximum temperatures

It is essential that sorbents are never heated above their maximum recommended temperature. If the sorbent maximum temperature is exceeded, this will result in sorbent decomposition, significant artifact formation and possible irreversible contamination of the UNITY valve and flow path.

The 'natural' background or minimum artifact level of any given sorbent will also increase with temperature, even below the sorbent maximum. Therefore, in order to increase sorbent lifespan and minimise artifact levels, we recommend that sorbents are never taken above a temperature 10°C below the sorbent maximum, even during the conditioning procedure and that analytical tube desorption temperatures are set typically 20 - 50°C below this.

24.2 Importance of desorption flow

Thermal desorption is a dynamic process. It relies not just on heat, but on a flow of carrier gas to extract the volatile components from the sorbent or sample matrix. The 4-5 mm ID of standard sample tubes mean that efficient desorption requires a flow of carrier gas in excess of 10 ml/min. This flow is the sum of the flow through the trap (controlled by the desorb flow (left-hand) needle valve) plus the inlet split flow (controlled by the split flow (right-hand) needle valve), if any. The upper limit of the tube desorption flow is determined by the carrier gas head pressure, cold trap impedance and maximum needle valve flows. As a rule of thumb, the higher the column head pressure the faster the possible split and tube desorption flows. Further information can be found in Section 25.

24.3 Testing for complete desorption

The most simple test for complete desorption is to repeat the desorption process and check for carryover of components of interest i.e. the appearance of a significant percentage of analytes (say >5%) in the second analysis. It is important to note that with certain samples, particularly large pieces of polymeric materials, it is advisable to leave an interval of several hours before re-desorbing the sample. This is because some volatiles (e.g. residual monomers) take time to migrate within the sample structure.

Note: Direct thermal desorption of volatiles from materials works best for samples with a high surface

area to mass ratio - i.e. powders, small (<1 mm³) granules, fibres and thin films (See Section 9).

Certain samples e.g. Vinyl chloride monomer (VCM) in PVC, will not desorb to completion. There is, in effect, an equilibrium between VCM and PVC at any given temperature and thermal desorption cannot reduce VCM levels to below this equilibrium level. In these cases, the best approach is to develop desorption conditions which successfully extract a high (>90) and reproducible percentage of target volatile during the first desorption.

Note also that some applications do not require complete desorption - for example flavour profiling of dried foods. In these cases, it is simply necessary to find the conditions under which a representative and reproducible chromatographic profile of the flavour is obtained.

24.4 Verifying desorption efficiency

International standard methods which use thermal desorption usually require that the desorption efficiency be verified in some way. Comparing the results from UNITY with those obtained by direct injection of a series of three standard solutions via a conventional split/splitless GC injector is used to confirm desorption efficiency. It is difficult to duplicate the UNITY split ratio on a split/splitless injector and it is therefore recommended to include a stable, readily analysed compound (e.g. toluene or deuterated toluene) in the standard to allow calculation of split ratio differences.

Example: Consider a GC system with a split ratio of 57:1

Mass of analyte	Mass of analyte, corrected for split ratio (ng)	Area Counts	Response Factor (area counts / corrected mass)
1ng	0.0175	105	5985
5ng	0.0877	498	5677
10ng	0.1754	1013	5774

Consider a UNITY - GC system with a split ratio of 119:1

Mass of analyte	Mass of analyte, corrected for split ratio (ng)	Area Counts	Response Factor (area counts / corrected mass)
1ng	0.0084	46	5474
5ng	0.0420	255	6069
10ng	0.0840	511	6081

The average response factors are 5812 - GC system and 5875 - TD system. It is therefore clear that there is complete desorption of the analytes through the TD system and desorption efficiency has been verified.

25 Setting desorb and split flows

25.1 When should desorb / split flows be measured?

- > Whenever a needle valve adjustment knob has been moved (deliberately or accidentally).
- > Whenever the GC column has been changed.
- > Whenever the carrier gas pressure to UNITY has been changed.

In practice this often occurs at the start of a sequence of analyses to confirm/ensure that no system changes have taken place.

25.2 The Set Gas Flow function

The **Set Gas Flow** function is accessed by selecting **Instrument** and then **Set Gas Flow** from the drop
 QUI-0002 vs 5.2 September 2006

down menu. Alternatively, click on the **Set Gas Flows** icon - the needle valve symbol - on the toolbar.

25.2.1 What does the system do when I select Set Gas Flows?

On selecting **Set Gas Flows** a dialogue box as shown in Figure 40 is displayed. If your analysis method is to include a split (single or double) then answer Yes to the question in the box. The UNITY flow path will then set itself up as shown in figure 40 and both the desorb flow (left-hand copper outlet tube and needle valve) and the split flow (right-hand copper outlet tube and needle valve) can be adjusted and measured.

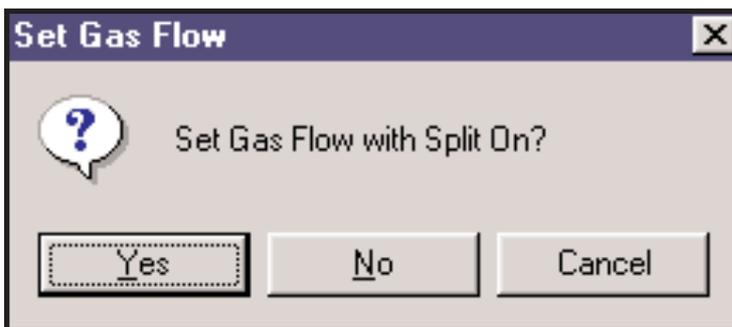


Figure 40. Set Gas Flow Dialogue box

If your analysis method is completely splitless, then answer No to the question in the box. The UNITY flow path will then set itself up as shown in figure 41 but with SV2 switched OFF so that there is no split flow, only the desorb flow, to be adjusted and measured.

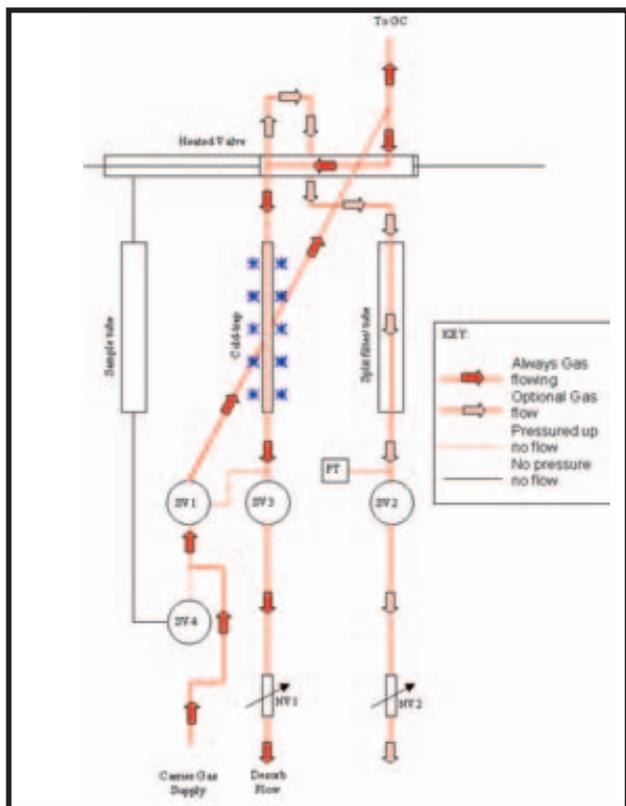


Figure 41. Sample flow path during Set Gas Flow with split on

25.2.2 Measuring and adjusting flows during Set Gas Flow

A flow meter is essential to measure the gas flows on UNITY. A simple one made from a graduated burette and some rubber tubing with a reservoir of soap solution will suffice, however a digital one is more convenient and is available from Markes International Ltd

Most applications will require a flow meter with a minimum working range of 1 and 100 ml/min.

If a manual bubble flow meter is being used, then a stopwatch will also be required, unless the GC being used has a stop watch function built into its software.

Note: It only makes sense to adjust and measure flows for the current controlling method.

To measure the flow, push the flow meter tubing over the relevant copper outlet pipe. Flows are adjusted by turning the adjustment knob clockwise to close the needle valve and reduce the flow and anticlockwise to open and increase the flow.

Note: The flows measured using **Set Gas Flows** are approximate. Approximate flows and split ratios

are sufficient for most methods, as there will be minimal run to run flow / split ratio variability. If it is necessary to know absolute flow rates for some reason, remeasure the actual flows by desorbing a blank tube before the start of sample analysis. Measure the desorb and split flow (if applicable) during tube desorption and the split flow again (if applicable) during trap desorption. The split flow may be slightly lower during trap desorption than during tube desorption because of the relatively higher impedance of the narrow cold trap tube.

The column flow should be measured at the detector end using procedures recommended for the GC in question.

Once adjusted and measured as required, all the flows should be entered into the **Confirm/Enter Flows** dialog box on the controlling method (Figure 37). The relevant flows should be measured as described above, and entered or simply confirmed by clicking **OK**.

25.2.3 To Exit the Set Gas Flows Function

After the measurement of gas flows is complete the user must press the **Stop sequence** - black square - icon to exit the **Set Gas Flows** function and return UNITY to **Standby** status.

25.3 Gas flow constraints - Minimum settings, maximum settings

The system must be set up with at least 10 ml/min flow through the tube - and at least 2 ml/min desorb flow through the cold trap during tube desorption to provide efficient desorption of the tube and efficient transfer of analytes to the cold trap. Use much faster flows through the hot tube (>50 ml/min) and at least 10 ml/min through the cold trap when analysing high boilers (>n-C₂₀).

At least 2 ml/min must be used to desorb the trap. All of this flow can be directed to the GC analytical column or to a combination of column and split vent.

The flow through the cold trap should not normally be allowed to exceed 100 ml/min during either tube desorption or trap heat.

When calculating split ratios (see Section 25.4.4), be aware that at carrier gas pressures lower than 10 psi it is not possible to set the needle valves to above 100 ml/min with any degree of accuracy.

Some variation in flow will be observed through a needle valve if used at less than 2 ml/min.

Flow through tube during tube desorption = desorb flow + split flow (if selected)

Flow through trap during tube desorption = desorb flow

Flow through trap during trap heat = column flow + split flow (if selected)

25.4 Sample splitting

UNITY may be set up to offer sample splitting between zero (splitless) and 10,000:1 (double split). The split that is required for a particular analysis will be dependent on the analyte mass in the sample tube, the analytical column capacity and the sensitivity of the GC detector selected.

25.4.1 Calculating analyte masses in the sample tube

In order to determine the required split it is necessary to have an approximate idea of the mass of analyte is expected to be retained / collected in the sample tube.

For direct desorption of volatiles from materials, the mass of analyte is most easily determined experimentally from control or real-life samples. It can also be calculated from relevant material specifications where appropriate e.g. if the specification for residual chloroform in cough medicine is 1% w/w a 20 mg sample will contain 200 µg or less of chloroform.

For air monitoring applications the calculations are a little more complex as they depend on variables such as diffusive uptake rate, pumped volume and molecular weight. Figures 42 and 43 show calculated masses that can be used as a quick reference guide.

Uptake Rate ng/ppm/min	1.3	1.5	1.7	2.0	2.5
Atmospheric concentration					
100ppm	0.624mg	0.72mg	0.816mg	0.96mg	1.2mg
10ppm	6.24µg	7.2µg	8.16µg	9.6µg	12µg
1ppm	0.624µg	0.72µg	0.816µg	0.96µg	1.2µg
100ppb	62.4ng	72ng	81.6ng	96ng	120ng
10ppb	6.24ng	7.2ng	8.16ng	9.6ng	12ng
1ppb	0.624ng	0.72ng	0.816ng	0.96ng	1.2ng

Figure 42. Mass of component collected during **8 hours** diffusive monitoring

Molecular Weight	50	75	100	150	200
Atmospheric concentration					
1000ppm	20mg	30mg	40mg	60mg	80mg
10ppm	200µg	300µg	400µg	600µg	800µg
1ppm	20µg	30µg	40µg	60µg	80µg
10ppb	200ng	300ng	400ng	600ng	800ng
1ppb	20ng	30ng	40ng	60ng	80ng
100ppt	2ng	3ng	4ng	6ng	8ng

Figure 43. Mass of component collected when **10 litres** of air is pumped onto a sorbent tube

25.4.2 Analytical column capacity

The capacity of an analytical column will depend on its diameter and the thickness of the film of stationary phase. As a general rule a 0.25 mm i.d. column with a 0.25 µm film has an approximate sample capacity of 100 ng / component. Wider bore and thicker film columns will have a higher sample capacity - up to low micrograms in the case of thick film (5 mm), 0.53 mm i.d. columns. Narrower bore and thinner film columns will have a lower sample capacity - below 10 ng / component in some cases.

25.4.3 GC system detection limits

The specification of GC detectors varies from type to type and manufacturer to manufacturer and it is advisable to consult the relevant manufacturer regarding detection limits. However, the following general guidelines may be useful:

- > Mass Spec., full scan mode: Modern systems should comfortably be able to detect and quantify a single compound at 10-100 pg.
- > Mass Spec., single ion mode: Modern systems should comfortably be able to detect and quantify a single compound at 1 pg.
- > Flame Ionisation Detector (FID): Typical detection limits 10-100 pg for individual hydrocarbons.

> Electron Capture Detector (ECD): Highly selective detector. Used for halogenated solvents. Detection limits well below 1 pg for compounds such as carbon tetrachloride and some heavily halogenated pesticides.

> Thermal Conductivity Detector (TCD): General purpose, low sensitivity detector. Typical detection limits in the order of 10 ng.

25.4.4 Calculating Splits

Once the mass of analyte expected, the detection limits of the system and the analytical capacity of the column are all known, then an overall ideal split can be calculated.

For example if the expected mass of analyte on the sample tube is 50 µg and the analytical column capacity is 100 ng then a total split of at least 1/500 is required to prevent column overload - i.e. only 0.2% of the sample must be transferred to the column.

One of three different split modes can be utilised:

Zero split or splitless operation

Single split operation

Double split operation

25.4.4.1 Zero split - splitless operation

Unusually among thermal desorbers, UNITY can operate in splitless mode in conjunction with narrow bore (0.32 mm ID) columns and MS detectors as the minimum flow required through the cold trap during trap heat is 2 ml/min.

Notes for splitless operation:

During tube desorption the desorb flow must be set to at least 10 ml/min to provide enough flow through the sample tube for efficient thermal desorption.

During tube desorption the desorb flow should not far exceed 50 ml/min or there may be a risk of breakthrough from the cold trap.

During splitless operation:

Flow through tube during tube desorption = Desorb Flow

Flow through trap during tube desorption = Desorb Flow

Flow through trap during trap heat = Column Flow

25.4.4.2 Single split operation

During single split operation the split may either be open during tube or trap desorption. The advantages of having the split open on the way into the trap (inlet split) are:

1. That a relatively fast flow can be used through the tube to facilitate desorption while, at the same time, the flow passing through the cold trap is kept low to aid retention and focusing of analytes.
2. That the cold trap is not overloaded with solvent or analytes - The UNITY cold trap is designed for optimum desorption speed / efficiency and is deliberately small and fast-heating. Split discrimination and / or peak splitting may be observed if the trap is allowed to become overloaded with volatile solvent or water.

Notes for single split operation:

During tube desorption the desorb flow must be set to at least 10 ml/min to provide enough flow through the sample tube for efficient thermal desorption.

During tube desorption the desorb flow should not exceed 50 ml/min or there may be a risk of breakthrough from the cold trap.

During tube desorption the desorb flow should not be less than 2 ml/min to ensure efficient sweeping of analytes onto the trap sorbent.

The flow through the trap during trap heat should not exceed 100 ml/min.

During single split operation:

Flow through tube during tube desorption = Desorb Flow + Split Flow (if selected)

Flow through trap during tube desorption = Desorb Flow

Flow through trap during trap heat = Column Flow + Split Flow (if selected)

Split = either $\frac{\text{Desorb Flow}}{\text{Split Flow} + \text{Desorb Flow}}$ or $\frac{\text{Column Flow}}{\text{Column Flow} + \text{Split Flow}}$

25.4.4.3 Double split operation

During double split operation the split is open both during tube desorption and trap heat.

Notes for double split operation:

As above for single split operation.

During double split operation:

Flow through tube during tube desorption = Split Flow + Desorb Flow

Flow through trap during tube desorption = Desorb Flow

Flow through trap during trap heat = Split Flow + Column Flow

Split = Inlet Split x Outlet Split
= $\frac{\text{Desorb Flow}}{\text{Desorb Flow} + \text{Split Flow}}$ x $\frac{\text{Column Flow}}{\text{Column Flow} + \text{Split Flow}}$

25.5 Gas flow through the analytical column

Gas flow through the analytical column (Column Flow), should always be optimised for chromatographic separation of the analytes of interest and not for thermal desorption. Typical capillary column flows range from 0.5 ml/min for 100 µm ID columns to 10 ml/min and above for 530 µm columns. UNITY offers maximum split ratio versatility with columns that operate most effectively at >10 psi and flows between 0.5 to 2 ml/min.

25.6 UNITY systems with the carrier gas supply to the GC analytical column controlled by electronic pneumatic control (EPC)

When combined with certain models of commercial GC(-MS), UNITY systems can be configured with EPC control of the carrier gas as it leaves the cold trap and enters the fused silica (or length of analytical capillary column) inside the transfer line. In this case, manual adjustment of the desorb and split flows, as described above, is still required.

Key benefits of EPC's control of the carrier gas through the column include retention time stability (even when split flows are changed significantly) and pressure programming for enhanced chromatographic performance with higher boiling compounds. More information is given in the associated appendix to the main UNITY Operators manual.

25.7 UNITY systems configured with the accessory for electronic mass flow control of the split flow

The Mass Flow Control Accessory (U-MFC) is available for both stand-alone UNITY and ULTRA-UNITY but not for UNITY-Air Server systems. It offers automatic adjustment and closed loop control of the split flow during standby, purge, tube desorption and trap desorption which means that different split flows can be set for each of these different phases of operation. The accessory also offers electronic flow readout during manual adjustment of the desorb flow. More information is given in the associated appendix 8 of this UNITY Operators Manual.

26 The Trap Heat Function

26.1 When should Trap Heat be used?

The **Trap Heat** function should be used to condition a freshly packed trap or to clean a contaminated trap provided it contains no molecular sieve or carbonised molecular sieve type sorbents. Please note that traps containing these sorbents must **NEVER** be desorbed using Trap Heat Mode. These traps must be conditioned using tube desorption to ensure that enough carrier gas passes through the cold trap to completely eliminate oxygen before heat is applied (see Section 13.3). When Trap Heat is used to condition traps, a large outlet split ratio (>30:1) should be used on the outlet to the trap to minimise the percentage of contaminants desorbed from the trap reaching the analytical column. During the first two or three desorptions of a freshly packed trap it is also advisable to set the analytical column at a high temperature to ensure all contaminants are swept through the system.

Note: It may be useful to use the Trap Heat function while operating the GC under standard analytical conditions to obtain a blank profile of the system once the trap has been well conditioned.

It is also advisable to undertake a Trap Heat clean up run before a series of samples, especially if the system has been idle for some time, e.g. overnight.

26.2 The Trap Heat Method

UNITY can use two sets of parameters when undertaking **Trap Heat**. Either those used in the existing **Controlling Method** or a special set of parameters identified as the **Trap Heat Method**. The choice between these two is made under **Options** (see Section 16). The selected option will then appear as the default **Trap Heat** conditions whenever this function is accessed.

The **Trap Heat Method** is accessed by selecting **View** and then **Trap Heat Method**, then the following dialogue box appears (Figure 44).

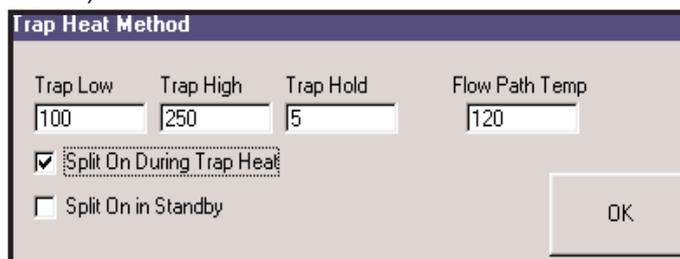


Figure 44. Trap Heat Method Dialogue Box

The required parameters are entered in the boxes. Checking the relevant boxes will activate the split on during trap heat / standby.

26.3 What does the system do when I select Trap Heat?

Trap Heat is selected either by selecting **Instrument** and then selecting **Trap Heat**, or by selecting the **Trap Heat icon** - the red icon - on the toolbar.

Once **Trap Heat** has been selected, UNITY will ask you to confirm that the default method is that which you wish to use. For example, if the default method was set to Use Controlling Method Parameters then the box message will read **Heat Trap with the Controlling Method Parameters - Yes, No, Cancel**. If **Yes** is selected, UNITY proceeds with trap heat. If **No** is selected the instrument software immediately takes you to the relevant section under **Options** to change your selection (see Section 16.3). Also, a **wait for GC Ready, before Heating** option is made available. Depending on the response to this option, UNITY will either wait for an External Ready signal from the GC equipment before proceeding, or continue the trap heat regardless of the GC status.

26.4 Parameters for cold trap conditioning

Ensure that the dedicated **Trap Heat Method** or the **Controlling Method**, if being used, are compatible with the maximum temperature of the least stable sorbent in the cold trap.

26.5 Selection of the Trap Low Temperature in Trap Heat Method

When using **Trap Heat** several times to clean a freshly packed trap, it is advisable to use a dedicated

Trap Heat Method and set the **Trap Low Temperature** to its maximum + 50°C, in order to save the time taken for the system to equilibrate.

26.6 Selection of the Trap Hold time

This is typically set to 3 minutes to ensure all analytes are desorbed from the trap and that the trap is again clean and ready to use for the next sample. If very high boiling components are being analysed then longer hold times - e.g. 20-30 minutes - are recommended.

Note: Carrier gas continues to flow through the cold trap for a further 3 minutes after the end of the trap hold time to ensure that carrier gas continues to sweep through the cold trap sorbent while it is hot.

27 Sample flow path - valve and transfer line - temperatures

27.1 Construction materials

Heated valve	= PTFE
Cold Trap	= Quartz
Transfer Line	= Fused Silica - inside a PTFE sleeve
Connecting tubing	= Short lengths of 0.5 mm bore Sulfinert™ tubing

27.2 Temperature ranges

Maximum temperature 210°C, minimum temperature 50°C.

Note: To operate UNITY at flow path temperatures lower than 130°C the auxilliary heater must be disconnected (see section 4.6)

Note that 200°C is sufficient to allow quantitative recovery of compounds having boiling points as high as n-C₃₂, although it is also recommended that high gas flows are used for these applications to maintain a high linear gas velocity and optimise analyte recoveries.

Also note that any compound of sufficient volatility to be present in air in the vapour phase in significant concentrations at ambient temperature will pass quantitatively through the flow path at temperatures of 120°C to 150°C. The default flow path temperature is 140°C

27.3 Transfer line to GC column connection

Details of the transfer line to capillary column coupling are given in Section 4.3. Unlike many competitive thermal desorbers, which couple to the GC via a standard liquid injector, this direct connection minimises risk of leaks, peak broadening and cold spots.

28 Minimum Carrier Gas Pressure Setting

This parameter is used to provide a minimum carrier gas pressure below which UNITY becomes **Not Ready**. If the carrier gas pressure falls below the set value, UNITY will stop operating and show a status of **Low Carrier Pressure**. This helps prevent sample losses.

The carrier gas pressure units may be set in psi (default) or kPa. To change the default gas pressure units, select **View** then **Options** and then select the **Gas** page - check the required units and then click OK.

29 GC Cycle Time

The **GC Cycle Time** is used to optimise sample throughput on UNITY by overriding the external ready check before tube desorption. Use of **GC Cycle Time** means that the tube can be redesorbed under the next set of desorption conditions while the GC is still analysing the previous sample.

To use this function, add up the GC run, cool down and equilibration times and enter the sum as the **GC Cycle Time** in the desorption method. UNITY then calculates when it can start the desorption of a second

sample such that at the point of trap Heat, the GC will have finished analysing the previous sample and be ready and waiting for the next. Note that the GC Cycle Time will not override the final GC ready check prior to the trap heating and the sample being injected - In other words the trap will not desorb if, due to miscalculation or some system error, the GC is not ready at the end of tube desorption.

If the GC cycle time parameter in the UNITY method is left at zero, the UNITY will leak test and purge a subsequent tube, but will not proceed to primary (tube) desorption until the GC status is 'READY'.

30 Start Run key

Start Run is used to start a desorption sequence and is accessed by selecting **Instrument** and then **Run**, or by clicking the **Start Run icon** - the black triangular symbol - on the toolbar.

31 Stop sequence key

The **Stop sequence** function is used to **stop a run** or **sequence of runs**, exit the **Set Gas Flows** mode, **Exchange split tube** mode and **Trap Heat** procedure. **Stop** is accessed by the **Stop sequence icon** - the black square - on the toolbar.

When the Stop key is pressed during a single desorption run, a dialogiue box appears, asking the user if they are sure they want to stop. The user then selects either OK - to stop the run, or cancel to continue running.

When **Stop sequence** is pressed during a sampling sequence a dialogue box appears and the user is given a number of options:

continue running, stop after next injection of this sample, stop after all injections of this sample, stop at the end of this cycle, and stop immediately. **Note:** the '**stop after end of this set**' option is only available if UNITY is used in conjunction with ULTRA. Select the appropriate option by clicking on it followed by OK.

Note: If you stop a run at any point after the tube desorption process has started then some components will have already passed onto the trap which will therefore need cleaning - along with the GC column - prior to analysing a new sample.

32 Method development

32.1 Guidelines for parameter selection

There are four parameters that can be manipulated to optimise a thermal desorption method. They are the same four parameters used in conventional gas chromatography, i.e.

Temperature

Time

Gas Flow

Sorbent (stationary phase in conventional GC)

Each parameter must be set to facilitate the analytical objectives at each stage of the process.

32.1.1 Tube Desorption

During tube desorption the objectives are as follows:

Tube - 100% desorption of the components of interest

Trap - retention of that percentage of the target components selected to reach the trap (plus selective elimination of unwanted volatiles, e.g. water)

Therefore, within the constraint of not exceeding the maximum temperature of the tube sorbent or the sample matrix, the tube desorption conditions should be as high a temperature as possible, with as fast

a gas flow as possible and long enough for complete desorption of target analytes.

Meanwhile the trap conditions at that time - i.e. during tube desorption - should be as low a temperature as possible, with as low a gas flow as possible and for a short enough time to prevent breakthrough (loss) of target analytes.

Notes:

The time selected for tube desorption will be, by definition, the same as that during which the trap must retain all components. Primary desorption time is therefore a compromise between complete tube desorption and complete trap retention. In practice, the sub-ambient trap temperature and facility to independently adjust tube and trap flow rates using the inlet split, means that a satisfactory compromise is never difficult to achieve.

There should be a gas flow of at least 10 ml/min through the tube for efficient desorption.

There should be a gas flow of at least 2 ml/min through the trap during primary (tube) desorption to ensure that analytes are swept safely onto the cold trap sorbent.

The cold trap temperature should be set to a temperature suitable for retaining all the analytes of interest during primary desorb. A typical temperature of -10°C is suitable for retaining analytes as volatile as ethane. If the user wishes to deliberately purge unwanted volatiles from the cold trap during tube desorption a higher temperature may be chosen. One example of this is the analysis of water based paint where a Tenax-packed trap is set at 20-30°C to allow the water to purge through prior to injecting onto the GC.

32.1.2 Trap Desorption

During trap desorption the objectives are as follows:

Tube - no longer applicable

Trap - 100% desorption of all compounds retained by the trap and efficient transfer into the column

Therefore, within the constraints of not exceeding the sorbent maximum temperatures, the trap desorption conditions should be as high a temperature as possible, with as fast a gas flow as possible and long enough to allow complete desorption, but without extending the overall cycle time - i.e. the trap should be cool and ready to collect the next sample before the end of the GC run.

Note:

There should be a gas flow of at least 2 ml/min through the trap during trap desorption. Trap desorption flows should not exceed 100 ml/min.

32.2 Method validation

There are now several International Standards covering thermal desorption methodology for a wide range of applications including ambient air, indoor air and workplace environment monitoring, materials emissions monitoring etc. A comprehensive listing is given in Markes International Ltd. Thermal Desorption Technical Support Note 3: Relevant International Standards.

Quality assurance (QA) guidelines given in these standards should be followed wherever applicable.

33 Method linking

Methods can be linked together to perform consecutively on a given tube. This is most useful where an analytical method is to be followed by a tube conditioning method or to automate the process of thermal desorption method development.

Method linking is accessed by clicking the **Link icon** - linked chain symbol - on the toolbar, or by selecting link on the main menu bar.

Method linking is implemented by making successive methods the controlling method. Once selected, Method linking asks the user to add the relevant methods to the **Link table** (Figure 45) and to indicate how many injections (repetitions) of each method are to be carried out. After a method has been run the

next method in the sequence is downloaded to UNITY and run.

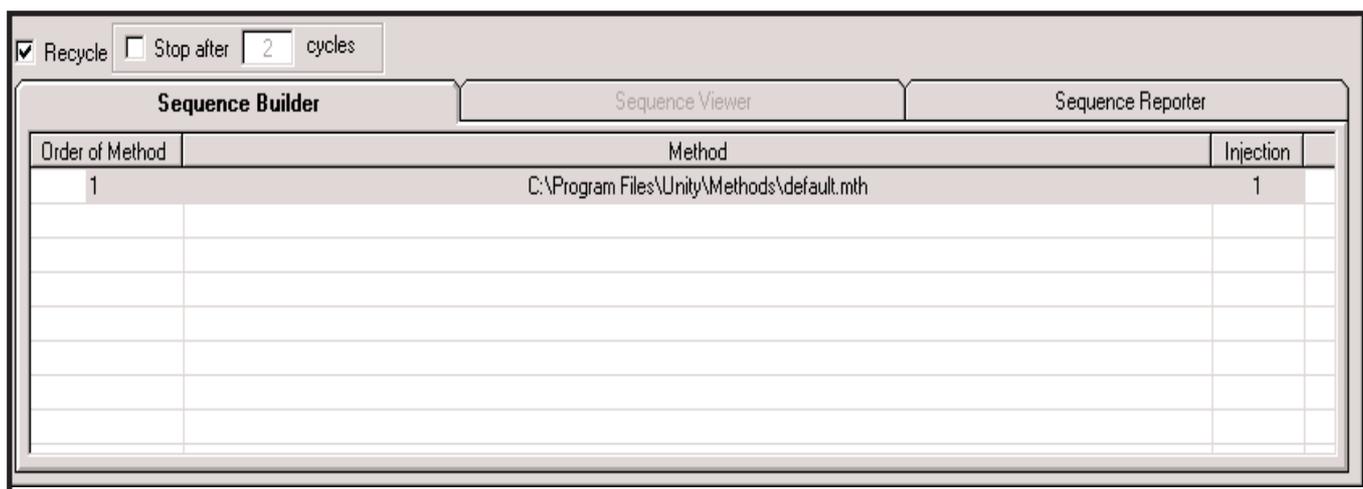


Figure 45. Method linking table

To add an existing method to the link table, right click anywhere in the method columns and select 'Add Item' from the list of options. The appropriate method can then be selected for the directory.

The 'Delete Item' option allows the user to delete a highlighted method from the link table, although the delete key on the keyboard will also work.

Selection of 'New Sequence' will open a new method linking table.

'Open Sequence' will enable the user to open a previously saved method linking table.

'Add Sequence' allows the user to introduce a series of run previously stored as a sequence file to the current sequence.

To change the number of injections, double click on the existing number and select the appropriate figure from the drop down method. The software allows 1 - 100 injections of a particular method. The user is also given the option of 'recycling' the linked methods by checking the 'recycle' box at the top left corner of the method linking table. This will recycle the process until stopped by the user. However, a set number or recycles can be selected by checking the 'stop after' box, and entering the appropriate number of repeats in the 'cycles' box.

Link also provides a simple mechanism for repeat analysis of a single tube with one desorption method by selecting one method and recycling it.

Note: Should the stop sequence button be pressed during a linking sequence, a dialogue box containing a number of options appears. This enables the user to either continue running, or stop the sequence at one of the stages listed (see Section 31).

Note: GC cycle time will operate in the same manner as a single tube desorption.

34 SecureTD™ - Re-collection for repeat analysis

UNITY facilitates the quantitative re-collection of the split portion of a sample onto a clean sorbent tube thus facilitating repeat analysis. This is of real benefit in situations where it is not possible or prohibitively expensive to collect replicate samples.

To re-collect the split effluent, the normal charcoal-packed split filter tube (P/N UTD-5065) supplied with UNITY must be replaced with a conditioned sorbent tube - the SecureTD tube. Note that this procedure should only be carried out with the system in standby mode. In order to access the tube on the split side (charcoal or SecureTD), the exchange split tube icon (fifth from the right) must be selected. This will isolate the split tube from the carrier gas supply without disrupting the flow to the analytical column. This allows chromatography to continue uninterrupted as the SecureTD and charcoal tubes are exchanged (see Figure 46).

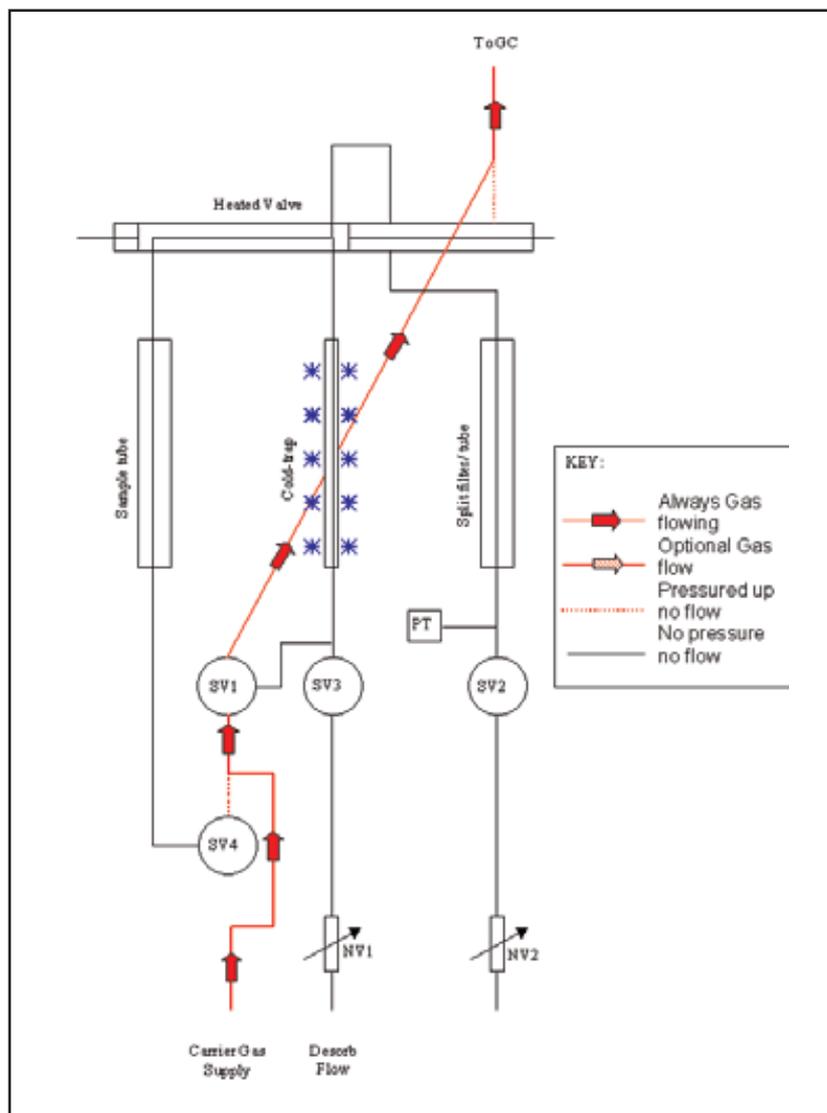


Figure 46. Schematic showing flowpath during exchange of split tube mode

Once 'exchange split tube' has been selected, lift the right-hand levered tube cover to release the charcoal split tube from one of its seals. Use your fingers or the tube extractor tool to gently pull the tube free from the other seal. Once the charcoal tube has been removed, the clean (SecureTD) sorbent tube should be inserted with its sampling (grooved) end pointing to the rear of the instrument. Lower the right-hand levered tube cover to seal it into position then press the stop icon (black square) to return the carrier gas flow path to normal standby status.

If the sample is being re-collected during an analysis, re-activate the 'exchange split tube' icon as soon as the desorber returns to standby mode after trap desorption. Remove the re-collected sample using the above procedure and cap it immediately. Insert another clean (SecureTD) sorbent tube or the charcoal split tube as required and press the STOP icon to return to normal standby mode.

Note: SecureTD will not work for methods that are operated entirely splitless. Either an inlet or outlet split or both are required.

As well as repeat analysis, SecureTD simplifies method development, provides a convenient method validation tool and allows critical samples to be archived when required.

For further information on split re-collection for repeat analysis see TDS 24 and Markes brochure "Validation of Thermal Desorption featuring Secure TD-Q"

35 Routine maintenance

35.1 Packing tubes

35.1.1 How to pack tubes

Ensure that empty tubes are fitted with a sorbent retaining gauze in the correct position at the front of the tube - the position of this gauze is critical for diffusive sampling. (Factory supplied empty tubes arrive with the gauze pre-fitted).

Tubes should be gravity filled with sorbent (not filled under pressure). For compliance with International Standards and accreditation schemes the mass of sorbent packed into the tube should be measured and recorded.

Once the appropriate mass of sorbent has been poured into the tube a few taps on a hard surface will be sufficient to settle the packing. A second sorbent retaining gauze should be inserted using a TubeMate (C-TBMTE) or other suitable tool, until the gauze sits firmly on top of the sorbent (without compressing the packing). A gauze retaining spring is then inserted using the TubeMate to hold the

gauze in place.

35.1.2 Lifespan of tubes

The lifespan of a freshly packed tube will depend upon the following:

- > The sorbent type
- > The maximum temperature the tube has been desorbed at
- > The temperature the tube has routinely been desorbed at
- > The number of desorption cycles (analytical and tube conditioning) it has undertaken

Assuming the sorbents have not been taken over their maximum temperatures, Tenax TA tubes and tubes packed with carbon based sorbents are good for over 100 cycles, a Chromosorb 106 tube is good for up to 100 cycles.

35.2 Conditioning tubes

Tubes will require conditioning when freshly packed and when they have been stored for longer than 24 hours (for trace level analysis) or 7 days (for ppm level analysis), without being fitted with 1/4-inch brass storage caps. Tubes should be cleaned using the dedicated tube conditioning mode on UNITY or using the TC-20 Multi tube conditioning rig.

See Section 13.2 or TDTS 5 for further information.

35.3 Long term storage of clean and sampled tubes

Conditioned or sampled tubes should always be stored using 1/4-inch brass Swagelok-type screw caps fitted with combined PTFE ferrules (P/N C-CFO20 (pk20) or C-CF200 (pk200)). It is recommended that these be tightened by hand plus a further quarter turn using conventional spanners or ideally a Markes International Ltd. Cap-Lok tool (C-CPLOCK).

It is not necessary to store capped tubes in refrigerated conditions unless they are sampled, multibed tubes in which case refrigeration may be required to prevent analyte migration to the stronger sorbents. In fact in most cases differential contraction of the tubes and seals at fridge or freezer temperatures can cause the caps to come loose. If refrigeration is to be used, caps must be retightened (a quarter turn) once they have reached their storage temperature.

Note: A tube should be allowed to warm up and equilibrate properly at ambient temperature before the beginning of sampling. If this is not done, a significant mass of water from the atmosphere will be retained in the tube via simple condensation.

Note: If tubes are to be transported in such a way as to be exposed to very cold temperatures, it is advisable to follow the above retightening procedure by cooling the tubes prior to shipment.

When monitoring trace level atmospheric components, conditioned and sampled tubes can be wrapped in uncoated aluminum foil and / or placed in a sealed, non-outgassing container, such as an uncoated tin, during transportation and storage. See TDTS 19 for more information.

35.4 Changing tube seals

The tube O-Ring seals are found at either end of the tube sealing mechanism.

UNITY should be switched off before O-rings are removed or replaced.

If they are required to be changed they should be hooked out with the O-Ring extraction tool from the shipping kits.

New seals should be pushed into position using the O-Ring insertion tool supplied in the shipping kit to nudge them evenly into the seating. Also use the O-Ring insertion tool to smooth around the inner diameter of the O-Ring as it is being pushed into place to avoid distortion.

35.5 Changing tube filters

Tube filters (P/N UTD-1050) should always be changed at the same time as the O-Rings. Once the O-Rings are removed, the same pointed implement can be used to hook out the tube filters. The clean filters should be pushed in with the O-Ring insertion tool or with any clean, flat-ended metal rod of suitable diameter.

35.6 Removing the cold trap

******* Ensure UNITY is switched off before removing the cold trap.*******

Remove the desorb pneumatics as described in Section 4.2.3. As the pneumatics are pulled forward, the horizontal movement will pull the cold trap out of its seal at the pneumatics/non valve end. It will be left sealed at the valve and projecting from the cold trap box. If the brass connector and the cold trap are pulled forward with the pneumatics assembly, hold the cold trap in position with the finger and thumb of one hand and continue to pull the pneumatics forward (towards the front of the instrument) in a **horizontal plane** until the trap is released. If the brass connector becomes detached from the pneumatics but remains attached to the cold trap, it should be carefully removed from the end of the cold trap once the trap has been completely removed from the cold trap box. Ensure that the pneumatics assembly is completely clear of the cold trap before lifting it out of the horizontal plane via the keyhole in the slot. Once the pneumatics have been moved completely out of the way, enough room is left to withdraw the cold trap from the cold trap box without obstruction.

Note: If the removal of the cold trap is met with resistance, the use of a rubber laboratory glove will provide a better grip of the quartz cold trap. Use a gentle twisting motion to withdraw the trap. If the cold trap is still difficult to remove in a completely cold system, it may be necessary to switch the unit back on temporarily to warm up the valve O-Ring, before switching the unit back off again and reattempting to withdraw the trap.

35.7 Packing the cold trap

See Section 4.2.2

35.8 Changing the cold trap seals

******* Do not attempt to change the cold trap seal at the heated valve end - this is a service only function.*******

The user may change the cold trap seal at the other end although it is highly unlikely to be necessary unless a cracked or broken cold trap has damaged the seal.

To change the seal access the cold trap as if it were to be changed (see Section 35.6) but only withdraw it partially from the cold trap box.

On the end of the cold trap will be 2 small O-Rings (P/N Z-0092). A single fat O-Ring (P/N Z-0087) is also located within the brass connector and can be removed with a pointed implement.

35.9 Changing the cold trap filters

The user may change the cold trap filter at the pneumatics end.

To change the filter (P/N UTD-1074) access the cold trap as if it were to be changed (see Section 35.6) but only withdraw it partially from the cold trap box.

The cold trap filter is positioned in the back of the brass connector. Sometimes it may be attached to the cold trap itself in which case it is easy to remove, and sometimes it will be at the back of the brass collar and can be hooked out with a pointed implement as described above.

A new filter can be easily pushed into the brass connector.

35.10 Changing the charcoal filters

If you are not recollecting the split effluent for subsequent analysis, the charcoal filters will trap the split effluent to prevent it being vented to the atmosphere. Therefore the filters will require changing at routine intervals.

It is suggested that the filters are repacked with conditioned charcoal every three months.

Charcoal filters are loaded in the same manner as tubes, with the grooved end facing the back of UNITY.

See Section 34 for an explanation of the "Change Split Tube icon" and associated procedure.

Once the split tube has been isolated from the carrier gas flow by selecting the 'Change Split Tube' icon, remove the charcoal tube by lifting the black knob of the sealing mechanism and using the Tube Extractor tool to grip the charcoal tube and remove it from the seal.

35.11 Replacing the fuse

If it appears that no power is reaching UNITY when it is switched on, either the fuse inside the instrument or the fuse located in the plug of the power lead (Z-0024) may require replacement. First switch off the power and disconnect the power lead at the socket. To replace the fuse inside UNITY, locate the fuse access point as shown in figure 24, and using the appropriate screwdriver, undo the black screw until the fuse holder is released. Replace the existing fuse with the spare from the shipping kit. Re-insert the fuse holder into the hole, and retighten the screw thereby securing the fuse in place. If both the UNITY fuse and the power lead fuse have been replaced, but the instrument still appears not to have power, please contact your local dealer.

36 Trouble shooting

36.1 Contamination - The presence of artifacts in the chromatogram

Artifacts are usually the result of either insufficient conditioning of the tube/cold trap or contamination from the carrier gas or carrier gas supply equipment.

36.1.1 The carrier gas supply

The carrier gas supply is a common source of contamination in thermal desorption. Contaminants may derive from the gas itself, cylinder head regulators, gas lines or carrier gas filters. To establish whether the gas supply is at fault use the following procedure: - Desorb a clean, empty tube for two minutes and monitor the resultant chromatogram. Extend the primary desorption time to 5 minutes and repeat the experiment. Continue to extend the desorption time steadily in this way and check to see whether the contamination increases with the length of time that the cold trap is exposed to the gas flow.

If the level of background contamination does increase with time of exposure to the gas, then the carrier gas supply may be contaminated and the various components of the supply system should be checked. Ideally, each thermal desorption system should have its own independent carrier gas supply, separate from any other conventional chromatographs in the laboratory.

Note: UNITY is such a good concentrator of VOCs that normal laboratory gas lines, which perform perfectly well for conventional GC analyses, can produce artifacts on the system. It is recommended that the gas itself and gas line components meet the following requirements:

Minimum 5.0 grade (99.999% pure) helium or nitrogen should be used.

The carrier gas cylinder head regulator should have a **stainless steel diaphragm**.

The cylinder should be connected to UNITY using as short a length of acetone-washed refrigeration grade copper tubing with no brazed joints as possible - Only brass or stainless steel, ungreased Swagelok-type unions should be used for tubing connections.

New filters/traps for oxygen and organics should be installed in the carrier gas supply line next to UNITY.

36.1.2 Contamination from the sample tubes or cold trap

If the contamination is shown, from the experiment described above, not to be coming from the carrier gas, the next most likely candidates are the sample tube(s) and/or cold trap. The following conditioning procedures are recommended:

Sample tubes should be thoroughly conditioned for approximately 2 hours at a temperature close to but below the maximum temperature of the sorbent packing. The fully automatic TC-20 sorbent tube conditioner from Markes International Ltd. (part number R-TC20) is a cost effective and time saving tool for cleaning up to 20 tube simultaneously. However, UNITY does offer a dedicated tube conditioning mode such that contamination from the tube is directed to vent, not to the cold trap or other critical flow path components, during the conditioning process. The conditioning temperatures recommended for various sorbents are detailed in Section 8. The flow through the tube during tube conditioning (equivalent to the flow out of the split vent) should be at least 50 ml/min. It is almost never necessary to repack contaminated tubes with fresh sorbent. The lifetime of a tube is at least 50 (porous polymer sorbents) or 200 (carbon-based sorbents) thermal cycles - and they can nearly always be cleaned by thorough conditioning until this point. Once tubes are conditioned, they should all be capped with

ungreased, brass screw caps configured with combined PTFE ferrules (cap assembly part numbers C-CF020 (pk 20) or C-CF200 (pk 200)) and stored in a clean, sealed container such as a glass jar or uncoated tin can. It is not necessary to refrigerate or freeze cleaned tubes nor do they need to be stored under nitrogen, but it is recommended that a permeable container of 1-2 g conditioned charcoal be placed inside the jar or tin with the tubes to adsorb traces of vapor phase organics.

After conditioning the sample tubes as described, clean the cold trap using the conditions given in Section 13.3.

Once the tubes and trap have been conditioned reset the TD-GC(-MS) system to the required analytical parameters and analyze one of the conditioned tubes. **In terms of toluene equivalents, individual artifacts should be in the order of 1 ng or less for carbon-based sorbents or Tenax TA and below 10 ng for other porous polymer sorbents.**

36.1.3 Other potential sources of contamination

The PTFE frit in the sample flow path just down stream of the sample tube can become contaminated over time. A visual inspection of the frit is usually sufficient to determine whether or not it is clean.

The charcoal filter on the split flow vent can become a source of contamination in extreme cases. Either replace the old packing with well conditioned charcoal or thoroughly condition the filter in a GC oven using temperatures of 400°C with over 100 ml/min flow of pure nitrogen or helium for at least an hour.

Unsilanized glass or quartz wool should be used as standard in the cold trap and sample tubes and should be conditioned at high temperatures before use. Silanized glass wool can be used but is only recommended for the analysis of labile compounds and must never be taken above 250°C, even during system conditioning. If silanized glass wool has been inadvertently desorbed at temperatures much above 250°C, the system will need to be cycled using a blank tube at high temperatures with the split vent open (>50 ml/min) for at least 48 hours to clean the sample flow path.

Sub-ng level artifacts can be generated from the system itself if the flow path is taken above 180°C. To minimise these artifacts for high temperature work, condition the system frequently at 200°C using 2-stage desorption and double split operation. Note that if samples were collected in the vapour-phase at ambient temperature, flow path temperatures above 120°C are rarely required.

36.2 Poor Peak Shape / Peak Splitting

Peak broadening, particularly of early eluting components, is often an early indication that the cold trap packing needs changing. The trap sorbent is subjected to rapid heating during the analysis of every sample and should therefore be replaced regularly - after 1000 desorptions or 6 months (whichever comes first).

Normal aging or the desorption of tubes containing aggressive compounds can produce activity in the transfer line or in the analytical column itself. This results in peak broadening or tailing. If this occurs, the capillary column or the fused silica insert inside the transfer line should be replaced.

A poor connection between the transfer line and the analytical column will also distort peak shapes. To avoid this, the connecting ends of both the column and the transfer line should be cut cleanly using a fused silica column cutting tool. The union or connector assembly should be an inert, zero dead volume fitting recommended for butt connecting capillary tubing.

Broad peaks can also result from the selection of too strong an adsorbent in the cold trap or from low carrier gas flows through the trap during desorption. The gas flow through the cold trap during secondary desorption (i.e. the sum of the outlet split flow and the column flow) should exceed 2 ml/min for a UNITY cold trap for optimum peak widths.

If a cold trap is loaded with relatively large quantities (>1 mg) of water or solvent and if it is heated at maximum rates (>60°C/sec), flash vapourisation of the solvent or water may result in a temporary pressure surge causing peak splitting or discrimination as seen on conventional GC injectors. In these cases, either reduce the amount of water or solvent retained by the cold trap (e.g by raising the cold trap temperature or by use of an inlet split) or slow down the trap heating rate.

If the GC analytical column is overloaded this will cause band broadening. High resolution capillary columns work at optimum with analyte masses in the order of 20-200 ng. Use the outlet splitter or both the inlet and outlet splitters if necessary, to ensure that the analytical column is not overloaded.

36.3 Carryover of components of interest

36.3.1 Carryover in the Sample Tube

In the case of vapour phase sampling onto sorbent tubes, carryover is usually caused by incomplete desorption and is usually addressed either by using more stringent desorption conditions or by selecting a weaker sorbent for collecting the samples. The gas flow rate is particularly critical. The flow through the sample tube during desorption is the sum of the desorb flow and the inlet split. This total flow must exceed 10 ml/min and should normally be at or above 30 ml/min.

When thermally desorbing volatiles directly from solid samples, desorption may be enhanced by increasing the surface area of the sample - for example, by grinding the solid material. (Solid CO₂ can be added to the sample during the grinding process to minimise the loss of volatiles).

When analysing solid or resinous materials, it is important to ensure that the sample is not completely blocking the carrier gas flow path. Thermal desorption is, by definition, a dynamic process and if the flow path becomes blocked, the thermal desorption process will be incomplete resulting in carryover. It is also essential to ensure that the entire sample is located within the central 6 cm portion of the sample tube and does not extend into the last 1.5 cm at either end of the tube. This is because the desorption oven only covers and directly heats the central 6 cm portion of the tube.

36.3.2 Carryover in the cold trap

As with the sample tube, more stringent desorption conditions or a weaker trap sorbent should be used to eliminate carryover in the trap.

36.3.3 Carryover in other parts of the sample flow path

Check that 'fines' - small particles of sorbent material - or sample matrix are not "escaping" from the tube and migrating into the seal assembly to which the tube connects during desorption. The presence of sorbent particles in the seal will cause unpredictable adsorption of analytes and peak 'ghosting'.

If the sample or the sorbent in the tube or trap is over-heated in error, this may have caused high boiling materials to deposit in the internal flow-path of UNITY. In most cases, such contamination is easily dealt with by temporarily operating the system with a blank tube at high temperatures and high carrier gas flow rates. Service intervention to replace parts of the flow path may be required in extreme cases.

If silanised glass wool has been used in either the sample tube or trap and has been heated to temperatures above 275°C, this too can elute residues which will temporarily contaminate the sample flow path. To recondition: cycle the system for 48 hours as described above.

Visually inspect the PTFE filter disks / frits in the tube seal. Highly contaminated frits can cause carryover.

36.4 Poor precision

Poor precision is generally either the result of incorrect introduction of standards onto sample tubes or use of very low carrier gas pressure/flow settings.

36.4.1 Introduction of standards

Information on calibration and standard introduction can be found in Section 11 or in a separate Technical Note from Markes International (TDS No.7), but to summarise, it is recommended that standards be introduced onto the sampling end of blank sorbent tubes in the vapour phase. With pressurised gas phase standards, this is most readily achieved using a calibrated gas loop and rotary valve. The standard should be swept from the loop onto the tube using at least 200 ml of carrier gas. Liquid standards should ideally be prepared in a solvent that is unretained by the sorbent(s) in the tube (methanol is a common choice) and should be introduced via an unheated conventional GC injector or the Loading Rig available from Markes International Ltd. (as described in Section 11). If the carrier gas is allowed to flow through the tube for 5-10 minutes, the solvent will be eliminated prior to analysis thus simplifying the subsequent chromatography.

If liquid standards are loaded directly onto the front of the sample tube, much of the standard will remain in the form of a liquid droplet - effectively unretained by the sorbent. An unpredictable percentage of the most volatile compounds in the sample are then prone to loss via diffusion into the headspace inside a tube thus giving poor precision. Droplets of liquid standard introduced into the rear of a sorbent tube

may also result in poor precision:

- > If the standard is prepared in a solvent that is totally unretained by the sorbent in the tube, for example methanol on Tenax, analytes may be lost via a liquid chromatographic type process as the droplet of solvent, carrying some of the analytes, passes through the sorbent during the initial carrier gas purge.
- > Higher boiling analytes introduced to the back of a fully packed sorbent tube may require more stringent desorption conditions than real life air monitoring samples where all the higher boilers are retained on the first few millimeters of sorbent. This will result in carryover and poor precision for these analytes.

36.4.2 Low carrier gas pressures/flows

The standard fine-metering needle valves used on UNITY and on leading automated thermal desorbers to control the desorb and split flows are subject to variation ('wanderation') at flows below 5 ml/min, particularly at low pressures (<10 psi) and this can result in poor precision. If this is an issue when trying to achieve low split ratios, turn the split off altogether and desorb the cold trap splitless, using just the column flow. High resolution capillary chromatography will be produced with trap desorption flows down to 2 ml/min. Alternatively select a longer and / or narrower GC analytical column such that higher column head pressures can be selected.

36.5 Poor recovery/loss of sample

Recovery of labile components may often be improved by increasing the desorption time and **gas flow rate** while reducing the desorption and flow path temperatures. Many volatile labile analytes will pass successfully through UNITY with valve and transfer line temperatures as low as 50°C. Desorption flow rates of at least 30-50 ml/min should be used for both the tube and cold trap to increase the linear velocity of sample vapours inside the instrument. Even the column flow rate should be increased to 4-5 ml/min if possible by adopting wider bore (320-530 mm) capillary columns or by using hydrogen as the carrier gas. For the analysis of extremely labile, relatively involatile components (bp > n-C₁₂), silanized glass or quartz wool alone should be used as the cold trap packing material where possible.

Low recovery may also result from incomplete desorption or adsorption onto contamination within the system. To check for this, redesorb the sample and monitor any apparent carryover.

Check that at least 10, preferably 30 ml/min gas flow is passing through the tube during primary desorption in the reverse direction to that used during sampling - i.e. in backflush mode.

If a multibed sorbent tube is being used to monitor / collect vapour-phase analytes ensure that the different sorbents are kept in discrete beds separated by unsilanised glass wool plugs or steel gauzes and arranged in order of increasing sorbent strength - i.e. weak to strong from the sampling end. It is also particularly important that multibed tubes are desorbed in backflush mode. This approach to sample collection and desorption ensures that higher boiling compounds only come into contact with the weaker sorbents and can thus be readily and quantitatively desorbed. N.B. it is sometimes necessary to store samples collected on multibed-tubes under refrigerated conditions to prevent the migration of intermediate volatility compounds onto the stronger sorbent thus resulting in incomplete desorption of these species.

36.6 Cold trap cannot attain its low temperature

Check that the supply of gas to the system pneumatics (air or nitrogen) is dry (dew point < -35°C) as it is this gas stream that is used to purge the cold trap box. UNITY's two-stage Peltier cell reaches a temperature of around -25°C. This temperature is maintained whatever the selected temperature of the cold trap. If moist gas is used to purge the cold trap box or if UNITY is left switched on without a dry gas supply, ice will build-up on top of the Peltier cell and around the cold trap, ultimately restricting its ability both to maintain low temperature and to heat up rapidly during secondary desorption. If such a build up of ice has occurred, switch off the instrument, open the cold trap box and remove as much as possible of the ice. Carefully use a hair dryer or hot air gun to gently dry up any remaining water in the cold trap box.

If desorb flows in excess of 150 ml/min are used with helium or hydrogen carrier gas and if the selected tube desorption temperatures are above 250°C, the cold trap may not be able to maintain a temperature of -10°C during primary desorption.

Inability to attain the selected cold trap low temperature can also be caused by insufficient air flow across

the Peltier cooler. Check that the fan at the rear of the instrument is not blocked and that there is sufficient space (at least 10 cm) to the rear of the instrument. If there is no apparent cause of poor air flow, switch UNITY off and contact Service.

36.7 High Air / Water background when using MS detectors

Viton O-rings are used to create a strong seal around the sample tubes and cold trap on UNITY. These are relatively impervious to air and the air / water background on a UNITY GC-ECD or -MS system should be similar to that observed with conventional GC injectors. However, it is recommended that the split flow be selected to be 'on in standby' when using UNITY with a GC-MS system. This maintains a positive flow of 10 ml/min or more of helium through the split vent and prevents back diffusion of air through the splitter. Another common cause of high air / water background is the capillary-capillary connector linking the transfer line to the column. Nut and ferrule type unions must use graphitised-vespel ferrules for GC-MS work. Alternatively, push fit glass connectors can be used.

36.8 Persistent leak test failures

See Section 20.

37 Diagnostics

Accessing diagnostics requires a password and is a service only function.

38 Accessing product and support information on the World Wide Web

38.1 Markes International Limited - Home Page and facilities

Markes International can be accessed at:

www.markes.com

Details of new products, applications, and technical help are available.

Registration (www.markes.com/registration) allows you to access further technical information.

38.2 Consumables and Spares

An up to date list of available consumable items is given in the brochure 'Focusing on Volatiles' which is included in Appendix Three of this manual- further details can be obtained from Markes International Ltd. direct on

Email consumables@markes.com

Fax +44 1443 231531

A routine maintenance kit (P/N RMK-0001) is also available and contains sufficient consumable spares for over 12 - months operation.

For itemised spares please refer to the shipping kit list in Section 4.1.

38.3 Applications library

Information on thermal desorption applications can be obtained from your Markes International sales office. Alternatively contact Markes International Ltd. direct on:

Email enquiries@markes.com

Fax +44 1443 231531

A current listing of technical support notes is included in the documentation package shipped with your instrument.

38.4 Technical support

In the first instance contact your local Markes International sales office.

Alternatively contact Markes International Ltd. direct on:

Email techsupport@markes.com
Fax +44 1443 231531
Tel +44 1443 230935

38.5 Downloading software upgrades

All UNITY software, including the low-level embedded system control firmware, is distributed on PC media (e.g. floppy disk, CD, email etc.). Thus software upgrades are straightforward and do not require a service engineer or the removal of any boards from UNITY.

Future upgrades will be available through the Markes International Web Site.

38.6 Automation accessories.

UNITY upgrade paths include both the ULTRA 100-tube autosampler and the Air Server Accessory for round the clock on-line air monitoring and automated sampling from canisters / airbags. Both accessories can be retrofitted to your UNITY system. For more information, please contact your local Markes International dealer or Markes International directly - see above.

39 Trademarks

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UNITY USERS MANUAL APPENDIX ONE

Uninstalling UNITY software from the computer

If UNITY software has to be reinstalled on a PC for any reason, it is vital that the PC is purged of the previous version of software **before installing / reinstalling the new software**.

In order to ensure that the PC system is correctly purged of all relevant files it is important to follow these instructions fully.

!!!SIMPLY DELETING THE FOLDER CONTAINING THE UNITY SOFTWARE IS NOT SUFFICIENT AND WILL OFTEN CAUSE THE SYSTEM TO FAIL!!!

Procedure

A1.1. Uninstalling the Unity Software

As with any Windows software the correct way to uninstall the UNITY software is to use the **Add / Remove Programs** option from the Control Panel.

1. Click on the **Start** button - choose **Settings** - and select **Control Panel**.
2. In the **Control Panel** select **Add/Remove Programs**.
3. Scroll down the list presented and select **Unity**.
4. Click on **Add/Remove** and follow the on screen prompts. The Unity software should now be uninstalled.

A1.2. Checking the Windows System Directory

Some computers fail to completely remove all the associated DLL files when software is uninstalled. It is important to check the windows system directory to ensure that all the DLLs have been removed.

The windows system directory is found:

- in W95/98 ...\\windows\\system\\ and
- in NT ...\\winnt\\system32\\

The files that must be removed (deleted) from the windows system directory are:

- OLAComm.dll**
- UnityComm.dll**

NO OTHER FILES SHOULD BE DELETED FROM THE DIRECTORY.

A1.3. Removing all traces of UNITY from the registry

!!!CARE ! Altering anything else other than the Unity entries can cause irreparable damage to the Windows operating system!!!

Again, some computers will fail to remove registry entries during uninstall and this must be checked before reinstalling the software.

1. To run the Windows Registry Editor, click on the **Start** button and select **Run**.
2. Type **regedit** into the run command line and select **OK**.
3. The registry editor will now open and you need to find the UNITY folder in the registry.
4. Press **CTRL + F** to open the Find dialogue box.
5. Type "**VB and VBA Program Settings**" into the text box and press **Enter**.
6. Open the **VB and VBA Program Settings** folder by clicking on the + sign. You should now see the **Unity** folder. **See the diagram below - the UNITY folder is ringed.**
7. Select the UNITY folder itself and press **delete**. You will be prompted - are you sure you want to

delete the folder - select **YES**.

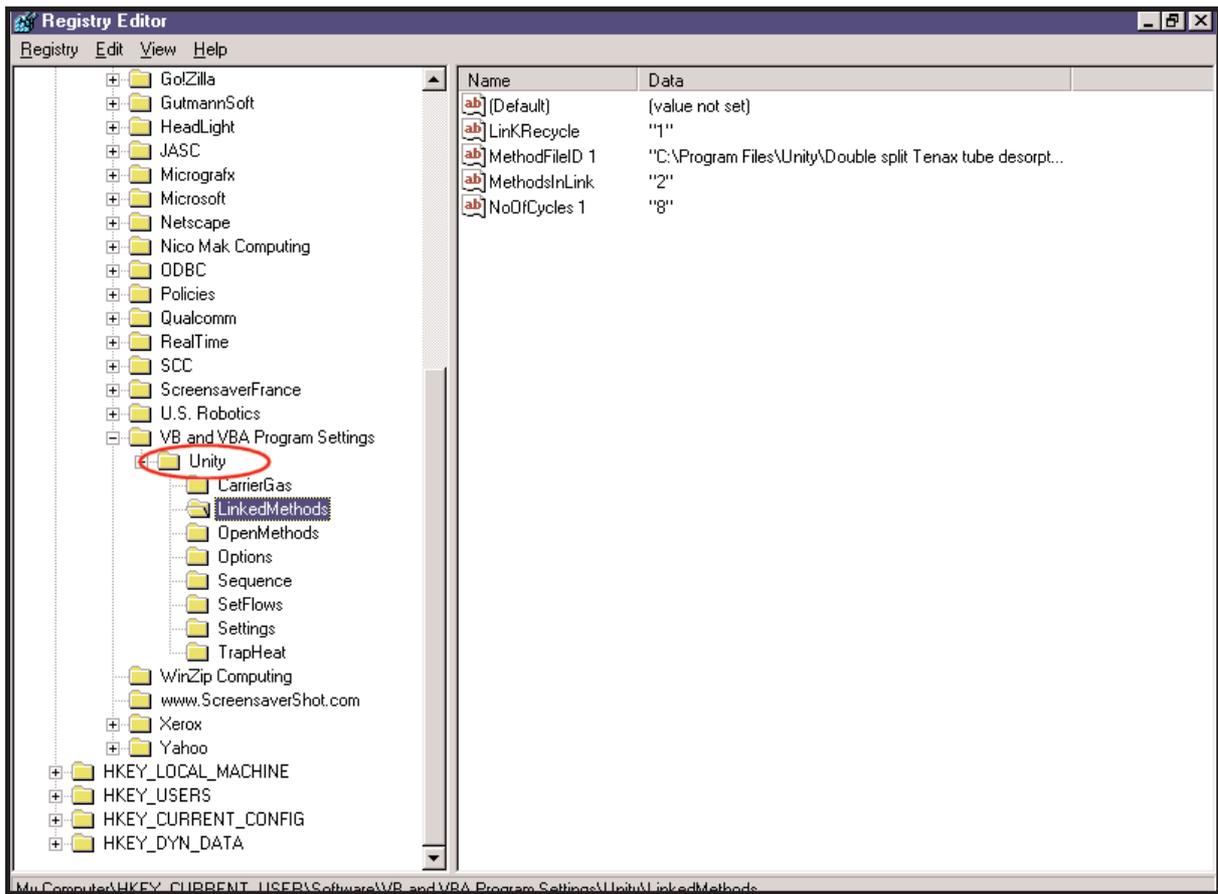


Figure 47. Windows Registry Editor

A1.4. Install / Reinstall the software

Finally install the new software from the supplied CD by launching the **setup.exe** file.

UNITY USERS MANUAL APPENDIX TWO

Connecting UNITY to a GC / GCMS System

The **READY / START** communications between UNITY and the analytical system are vital if the system is to operate correctly. Unfortunately all commercial GC / GCMS systems have slightly different connectors. This document explains the connections between UNITY and a range of analytical systems. Further information will be added to the document as it becomes available.

A2.1 UNITY General Purpose Ready / Start Cable (UTD-5095)

This cable consists of a 25pin D connector, which is plugged into UNITY, with 8 free coloured wires at the other end of the cable. The white and red wires are the most commonly used UNITY Ready In connections and the yellow and green wires are the UNITY Start Out connections. The brown, black, blue and purple wires are only used under certain circumstances and normally should be left free and unconnected.

The UNITY Ready In connections must be connected to the GC Ready Out connections.

The UNITY Start Out connections must be connected to the GC Start In (or External Start) connections.

These connections are contact closure connections, which are either normally open (and close to cause an event) or normally closed (and open to cause an event). The GC Interface logic, (Normally Open / Normally Closed) is selected under the UNITY software Options.

Usually the Ready In connections (red and white) are Normally Open, i.e. the GC is signalling that it is NOT READY. When the GC becomes Ready the connections open and send the Ready signal to UNITY.

Usually the Start connections (green and yellow) are Normally Closed, i.e. the GC does not start. When UNITY injects (fires the cold trap), the wires close and send a Start signal to the GC.

In certain circumstances the GC start connections require a voltage level rather than a contact closure and in these cases two of the other connections are used instead of the yellow and green wires. Details are given under the individual GC sections.

GC / GCMS Ready / Start connections

All modern GC / GCMS systems have the facility to receive an external start signal automatically and to provide a signal externally when they are ready.

Some GC systems are connected to a further external device such as an integrator or mass spectrometer. In this case the GC system must also be able to receive an external ready signal and to give an external start signal.

Sequence of Events

A fully configured system would therefore follow this sequence of events:

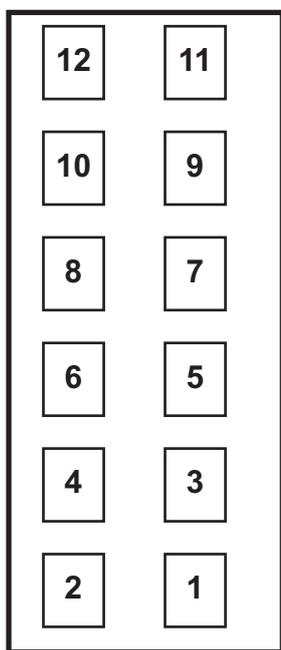
- Mass spectrometer becomes ready and sends signal to GC Ready In.
- GC therefore becomes ready and sends signal from GC Ready out to UNITY Ready In.
- UNITY fires cold trap and closes yellow and green wires thus sending a Start Out signal to the GC Start In / External Start.
- GC starts and sends a signal to the mass spectrometer Start in.

The circuit diagram for the UNITY Ready / Start cable is shown at the end of this appendix (Figure 48)

A2.2 AGILENT GAS CHROMATOGRAPHS

5890GC

The 5890 GC has a 12-pin Remote Start female connector on the top of the GC (connector nearest to the rear of the GC). A 12 pin female connector must be plugged in and connected to the UNITY Ready / Start cable as follows:



Connector viewed from the top and front of the 5890

UNITY green wire connects to pin number 1 - the remote start input

UNITY yellow wire connects to pin number 2 - the ground pin for pin 1

UNITY white wire connects to pin number 9 - the ready out

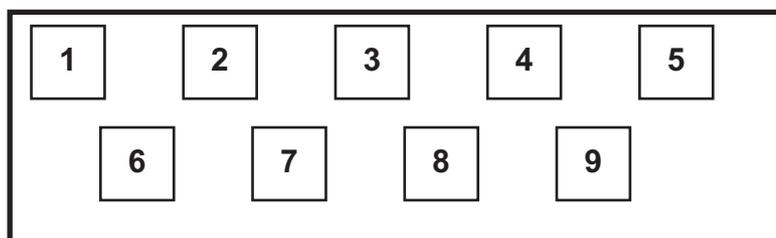
UNITY red wire connects to pin number 5 - the common output for pin 6

If pins 3 and 4 are open (unconnected) the 5890 Start initiates a run by both starting the oven temperature program and pulsing the "start out" relay - in order to start an external device i.e. mass spectrometer.

6890GC

The 6890 has a 9-pin remote start female connector on the back of the GC. A 9-pin male connector must be plugged into this and connected to the UNITY ready / start cable as follows:

Connector viewed from front



UNITY yellow wire connects to pin number 1 - GND

UNITY green wire connects to pin number 3 - Start in / Run

UNITY black wire connects to pin number 1 - GND

UNITY blue wire connects to pin number 7 - Ready

Logic:

GC Start (out): Closed

GC Ready (in): Closed

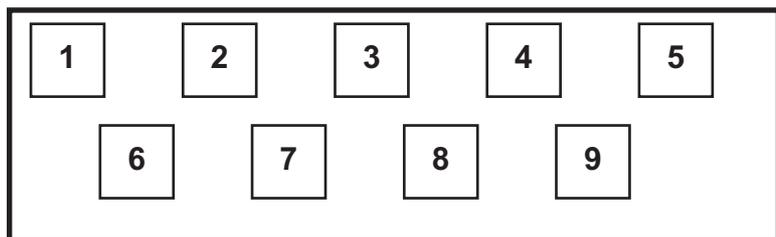
Note: If the 6890 is connected to a 5973 MSD system there will be a cable connected from a second output on the back of the GC as follows:

Ready O/P	Pin 7	(+5V high when ready) (UNITY blue wire)
	Pin 1	GND (UNITY black wire)
Start I/P	Pin 3	Start MSD system (UNITY Green wire)
	Pin 1	Start MSD system (UNITY yellow wire)

6850GC

The 6850 has a 9-pin remote start female connector on the back of the GC. A 9-pin male connector must be plugged into this and connected to the UNITY ready / start cable as follows:

Connector viewed from front



UNITY yellow wire connects to pin number 1 - GND

UNITY green wire connects to pin number 3 - Start in / Run

UNITY black wire connects to pin number 1 - GND

UNITY blue wire connects to pin number 7 - Ready

Logic:

GC Start (out): Closed

GC Ready (in): Closed

Note that the 6850 GC only has one remote / start output on the back of the GC therefore other external devices such as datahandling systems, integrators, mass spectrometers may also have to be connected to the same 9-pin connector.

Note: Markes Ready/Start cable UTD-5098 - UNITY - Agilent cable is already pre-configured with the 9-pin connector ready to plug into the Agilent 6890 / 6850 GC systems

A2.3. PERKIN ELMER GAS CHROMATOGRAPHS

AUTOSYSTEM

The input / output terminals are located under the flap on the top right hand side of the GC.

UNITY yellow wire connects to pin number 4 - marked Ex Start HI

UNITY green wire connects to pin number 3 - marked Ex Start LO

UNITY white wire connects to pin number 12 - Ready Out NC (normally closed)

UNITY red wire connects to pin number 10 - Ready Out C (common)

Logic:

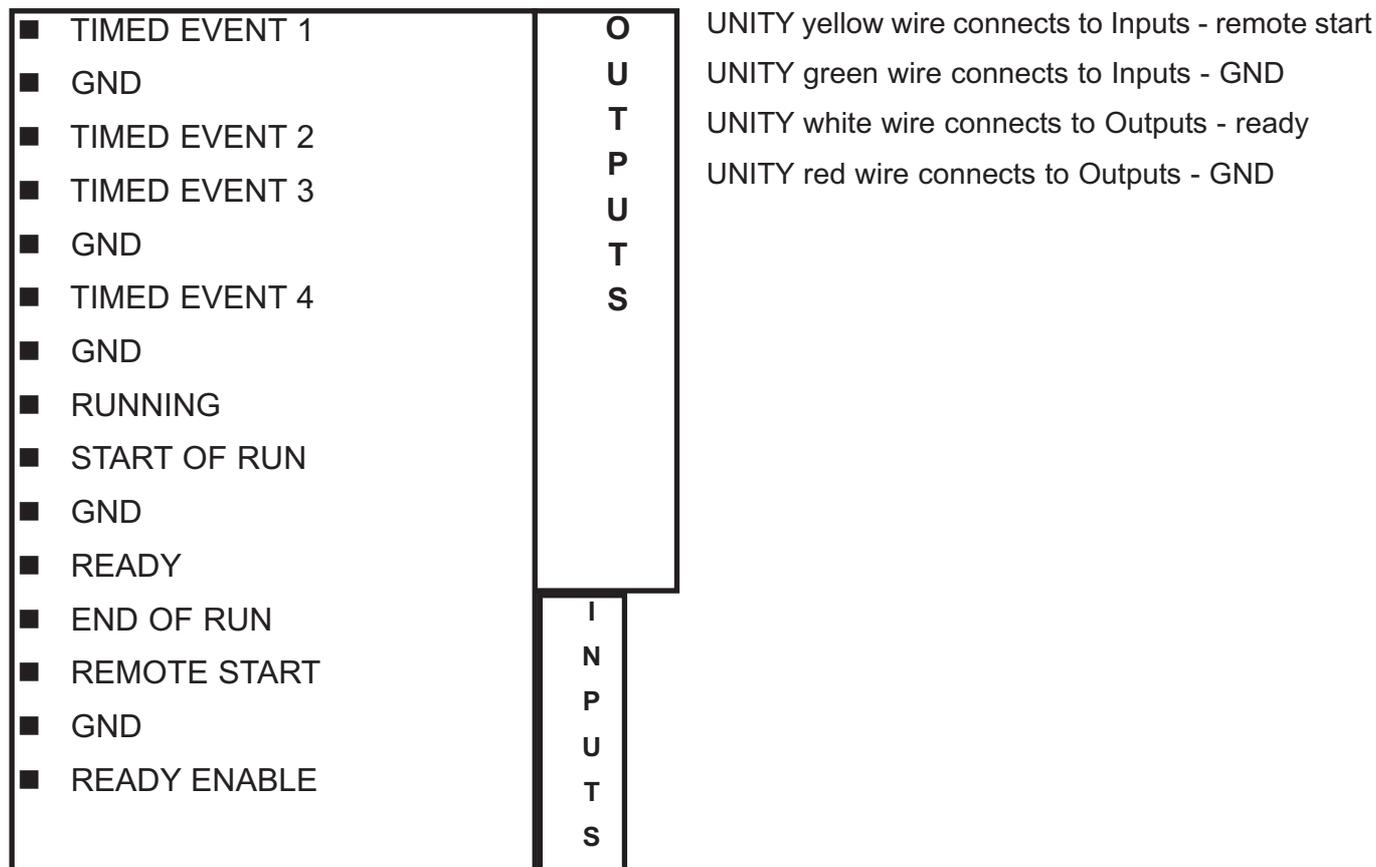
GC Start (out): Closed

GC Ready (in): Open

A2.4 THERMOQUEST GAS CHROMATOGRAPHS

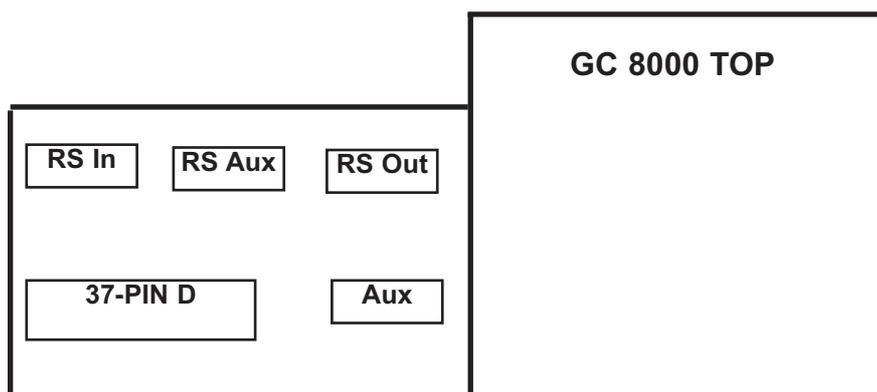
Finnegan GCQ

The input and output signal terminals on the GCQ are available from a terminal strip located under the top cover on the top deck of the GC.



Thermoquest GC 8000 Top

The input and output signals on the GC TOP are available on a female 37-pin D-socket on the back of the Mass spectrometer as shown.



- UNITY yellow wire connects to pin 1
- UNITY green wire connects to pin 24
- UNITY white wire connects to pin 20
- UNITY red wire connects to pin 2

To start, the GC must be in sampling mode and in the software in the Acquisition Control Panel you must select Inlet:

GC with contact closure autosampler



Thermoquest Trace2000

The connections to the Trace 2000 are **either** through a 6-pin round DIN connector on the interconnection cable supplied by Thermoquest **or** on an 8-pin DIN connector on the back of the system. With either connector the connection pins are the same.

UNITY green wire connects to pin 1 - GC Start

UNITY yellow wire connects to pin 3

UNITY white wire connects to pin 5 - GC Ready

UNITY red wire connects to pin 3

Note: Markes Ready/Start cable UTD-5108 - UNITY - Thermo Trace GC cable is already pre-configured with the 6-pin round DIN connector ready to plug into the Thermo Trace GC systems

A2.5 VARIAN GAS CHROMATOGRAPHS

3800

The connections to the 3800 are through either of the two (J4 and J5) 25 pin D sockets located under the detector cover.

UNITY yellow wire connects to pin 15 (+5V) - GC Start

UNITY green wire connects to pin 22 (ground)

(both 22 and 15 need to be at ground to start)

UNITY white wire connects to pin 16 - GC Ready

UNITY red wire connects to pin 17

A2.6 Connecting Unity to an external GC using the General Purpose UNITY Ready / Start Cable (UTD-5095)

Provision is made for making an electrically isolated connection from UNITY to an external device irrespective of whether that device indicates its ready state using a Voltage level (e.g. from a TTL output) or a Contact closure (e.g. using a relay).

1. Use Red and White wires if GC produces a Contact Closure.
2. Use Black and Blue wires if GC produces a Voltage Level.

NB:

As shown below (Figure 48) R2 is not normally fitted thus when using Black & Blue for "GC Ready", also connect Black to Yellow and connect this to the GC common or 0V terminal.

Similarly when using the Red and White pair of wires the Red wire and Yellow wire could be connected together and to the GC 0V or common output terminal.

Finally if for any reason (and this is most unlikely) a voltage level output is required from Unity (to signal Unity ready), then the Brown and Green wires can be connected together, via a high value resistor say 10,000 Ohm and the Yellow wire can be taken to the 0V terminal of the GC. Now ready will be signalled by the voltage on the Green wire swinging from 0->5V.

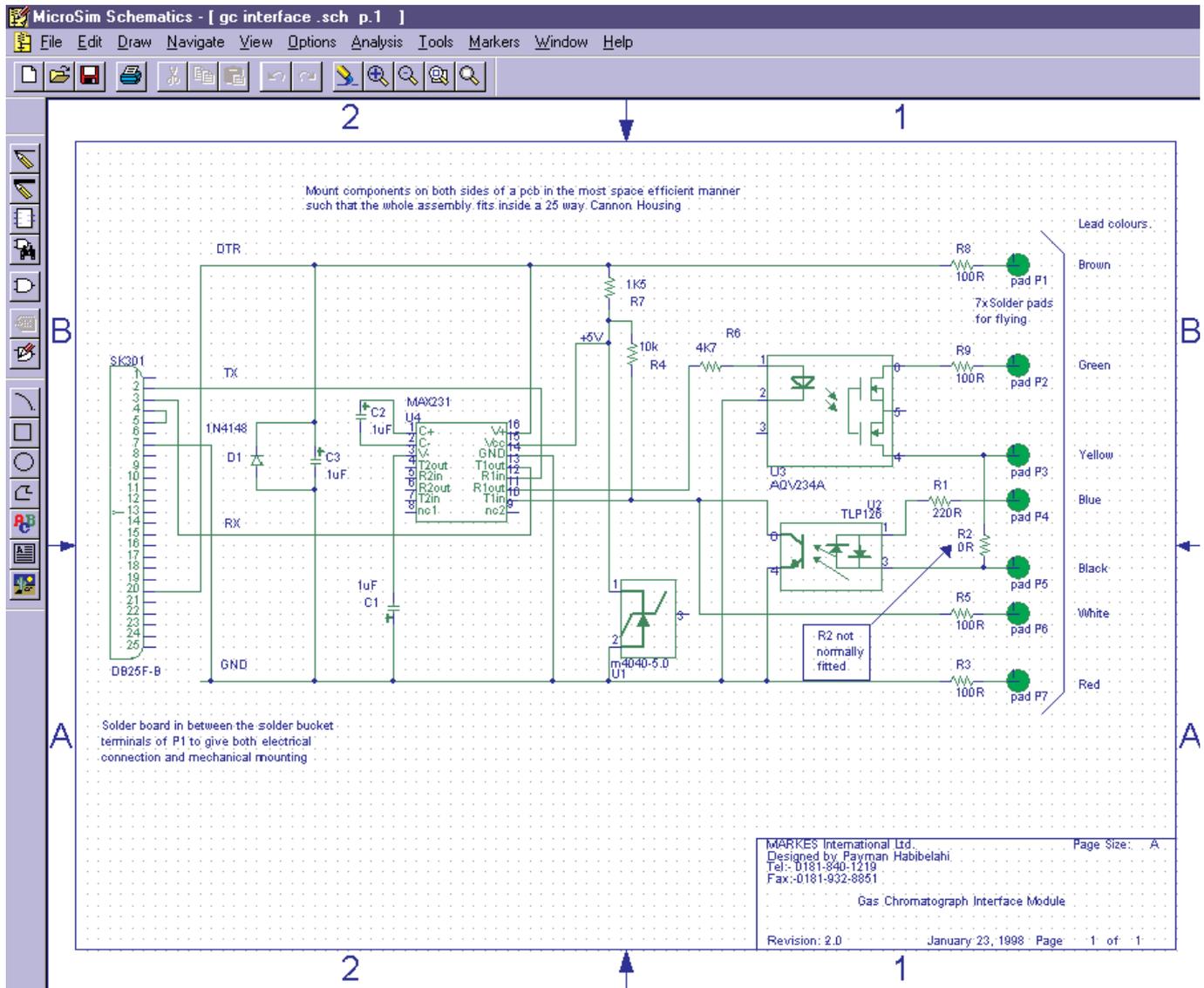


Figure 48. UNITY General Purpose Ready / Start Cable connections

UNITY USERS MANUAL APPENDIX THREE

You will find a copy of the Thermal Desorption and Air Monitoring Products catalogue & consumables enquiries form in the Literature Pack which accompanied your instrument.

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UNITY USERS MANUAL APPENDIX FOUR

Markes International Thermal Desorption Instrumentation Preinstallation Check List

Please ensure that you have all the required services in place before requesting your installation

A4.1. Minimum computer specification for UNITY control

In general a PC with sufficient resources to run 32 bit Windows (95, 98, ME, 2000, XP, NT4 (series4)) will have adequate performance for controlling UNITY. As such the minimum PC requirement recommended is a 400MHz Pentium with 64MB RAM and a minimum of 20MB of free disc space (for the UNITY software installation). A Windows compatible mouse is also required.

The user interface requires a minimum SVGA (800x600 pixel) screen resolution and ideally an XGA (1024x768 pixel) screen resolution 256 colour in both cases.

The PC requires a free serial communications port for communication with UNITY. An additional serial communications port is required to connect each of the following accessories:

- > ULTRA
- > Air Server
- > AutoSecure ULTRA
- > Mass Flow Controller (MFC)
- > MCS06/MCS08

This may be achieved through spare serial ports on the PC or through a USB hub (such as U-USBHB) which extends 1 USB port to 4 USB ports and a USB-serial port cable for each additional accessory (such as U-USBSR) which converts the USB port to a serial port.

UNITY communicates at 57600 baud. Whilst lower baud rates can be programmed, this is not recommended as it will result in degradation of system performance (most modern PCs will support communication at this speed).

A 9 way Null modem cable is supplied for connecting UNITY to the PC comms port.

The PC will also require an internet connection if the browser facility, included in UNITY's user interface, is to be used. The browser is not required for system operation.

A4.2. GC equipment requirements

UNITY is usually connected to a gas chromatograph configured with appropriate conventional or mass spectrometer (MS) detectors. No conventional GC injector is required for UNITY operation. Ready and external start connections are required on the GC.

Access into the GC oven

The UNITY heated transfer line is lined with 0.25 mm I.D., 0.35 mm O.D. uncoated deactivated fused silica which butt connects with the capillary analytical column inside your GC oven. It is important that the heated and insulated portion of the transfer line extends as far as the skin of the GC oven such that the GC oven heating begins at the point where heating of the transfer line ends. A 25 mm diameter access hole is thus required into the GC, with a 6.5 mm hole in the GC inner oven wall.

GC configuration/parameter selection

From a GC perspective, UNITY may simply be regarded as a multipurpose, stand-alone GC injector for capillary or 1/8 -inch packed columns. No conventional GC injector is required for UNITY operation. The rest of the GC system - column, oven, data handling, detector, etc. - should be configured and used, as per normal chromatographic practice for the analytes of interest.

If multiple applications are to be carried out or if samples are uncharacterised; for example when monitoring unknown atmospheres, a good general purpose GC configuration comprises 25-30 m, 0.25mm or 0.32 mm ID, 1 or 2 µm phase thickness bonded methyl silicone capillary column with a FID or mass spectrometer detector.

A4.3.Laboratory location

Space requirements

UNITY occupies minimal bench space, being only 12 cm wide, and can sit either side of the gas chromatograph. However with automated systems it is strongly recommended that the system is situated to the left of the GC (as viewed from the front). Details for each of the instruments and accessories are given below:

Recommendations relating to the quality of the laboratory air

	UNITY	ULTRA	AutoSecure UltrA	Air Server	MCS06/08	MFC
Position (as viewed from the front)		To the left of UNITY	To the right of UNITY	To the left of UNITY	To the left of UNITY	.Either side
Weight (kg)	11	23 28 when fully laden with 100 capped tubes	23 28 when fully laden with 100 capped tubes	3	5	2
Width (cm)	12	24	24	12	12	12
Height (cm)	40	53	53	26.3	26.3	26.3
Depth (cm)	50	62	62	25	50	25

UNITY is a powerful concentration device and is often used to determine trace levels of organic analytes. It is advisable to store and operate UNITY in a clean laboratory environment with minimal atmospheric concentrations of organic vapours.

Recommendations relating to the quality of the laboratory gas lines

As UNITY is a concentrator, even trace level contaminants in laboratory gas lines can become significant interferences in the chromatograms produced. It is recommended that gas lines be constructed of refrigeration-grade copper tubing connected using approved swage-fittings. Laboratory gas line joints and connections must never be brazed. Position the gas supplies as close as possible to the analytical system i.e. such that the gas lines are as short as possible. Use a high quality, stainless-steel-diaphragm cylinder head regulator for the carrier gas supply.

A4.4.Services

Power

UNITY is automatically compatible with all conventional mains power supplies ranging from 90 to 255 V and 50 or 60 Hz. It is not necessary to manually select or switch voltages.

Pressure controlled supply of dry air or nitrogen

Functions

UNITY requires a pressure-regulated supply of dry air or nitrogen at between 55 and 70 psi both to actuate the main valve and to purge the cold trap box.

Note: It is recommended that UNITY is not switched or left on without this gas supply. An inbuilt sensor / switch will ensure that the coolers remain switched off in the event of no gas supply - this will prevent the UNITY cold trap from cooling down and hence achieving 'Ready' status.

It is recommended that a secondary pressure regulator be used to control the supply of dry gas to UNITY

in addition to that controlling the general laboratory line pressure. Any conventional pressure regulator should suffice for this and suitable pneumatic control may already be available on your GC. Alternatively, Markes International Ltd. supply a pneumatic control accessory (P/N U-GAS01) for both air and carrier gas. It is recommended that the pressure in the laboratory air line be 10 psi higher than that supplied to UNITY.

Specification required (dryness / purity)

The compressed air or nitrogen must be dry (dewpoint lower than -35°C). Conventional air compressors / nitrogen generators may be used provided the gas produced is adequately dried.

Consumption

Dry air or nitrogen flows at ~100 ml/min into the cold trap box creating a slight positive pressure and minimising ingress of water from the laboratory atmosphere. If the cold trap box was not purged, ice would quickly build up around the Peltier cell, which is maintained at -25°C throughout UNITY operation. Gas consumption for valve actuation is minimal.

Pressure controlled carrier gas supply

Gas selection - type / purity

Helium is invariably used as the carrier gas for capillary chromatography and nitrogen for packed column or sensor work. 5.0 grade (i.e. 99.999%) or higher purity gas is recommended in either case. Hydrogen can also be used as the carrier gas but usual precautions, with respect to monitoring for large leaks, must be taken.

Line pressures and recommended pneumatic control

UNITY requires a regulated supply of carrier gas at a pressure to suit the analytical column / system selected. The UNITY gas flow path has minimum (<2 psi) impact on total system impedance. The performance of most common capillary columns is optimised at between 1 and 2 ml/min typically requiring between 10 and 30 psi head pressure. High quality pressure regulators incorporating a stainless steel diaphragm are recommended for carrier gas control. Suitable pneumatic control for the carrier gas may already be available on your GC. Alternatively a carrier gas control module such as U-GAS01 (see below) should be used. The pressure in the laboratory carrier gas line should be at least 10 psi higher than that supplied to UNITY.

N.B. Do not use electronic or programmable pneumatic control for the UNITY carrier gas supply unless UNITY is configured with an EPC modification suitable for use with an Agilent 6890 GC (see below).

UNITY Pneumatic Control Accessories

To ensure adequate pneumatic control, Markes International Ltd. supply a range of accessories for the control of gases to UNITY. U-GAS01 includes a high quality Porter regulator and 0-60 psi gauge for control of the carrier gas and a Norgren regulator and 1-100 psi gauge for control of the dry gas (e.g. air / nitrogen). Both gas lines are also equipped with on/off toggle valves. Contact your local Markes dealer for more information.

Alternatively, for systems to be linked to an Agilent 6890 GC or GCMS only, UNITYe can be used in conjunction with the electronic pneumatic control (EPC) module. This combination allows precise electronic control of constant, or ramped, carrier gas pressure at the split inlet to the fused silica transfer line independent of flow.

N.B. It is essential that the firmware on the Agilent 6890GC be as follows:

For 6890 A-series the firmware should be A.03.08 or later and for 6890 N-series, the firmware needs to be N.04.08

To check the firmware version, use the keyboard on the GC press: Options, Diagnostics, Instrument Status and then scroll down to 'version' where you will see the current GC firmware version.

U-GAS01 is recommended for all UNITYe EPC systems to provide pressure regulation of the carrier gas prior to the EPC module and to provide suitable pneumatic control for the dry gas.

Filters

Deoxo and organic filters should be included in the carrier gas line just upstream of connection to the UNITY-GC analytical system.

UNITY USERS MANUAL APPENDIX FIVE

Electronic Pneumatic Control Module

A5.1 Introduction

This appendix describes operation of Markes International Thermal Desorption Systems (MiTDS) in conjunction with the split/splitless (SSL) electronic pneumatic control (EPC) module on an Agilent 6890 GC. This combination allows precise electronic control of constant, or ramped, carrier gas pressure at the inlet to the fused silica transfer line within the TDS. This transfer line connects directly to the analytical column within the GC oven and thus the pressure set at this point effectively controls the flow/velocity down the analytical column.

A5.2 Operation of EPC with TDS

The standard configuration of MiTDS with a non-Agilent GC is with manual pneumatic regulation of the carrier gas supply. Under these conditions the column head pressure is monitored by the TDS but varied manually by changing the external supply pressure upstream of the system. Split flows are controlled via needle valve regulation (or optional electronic mass flow control). With manual pressure supply and regulation, changing the split flow rate leads to variation in the column head pressure and thus column flow. In turn this can affect peak shape and retention time and the proportion injected onto the column. To compensate for this calibration standards must be injected each time a change is made to the split to determine retention times and response factors.

Combining UNITY TD with EPC overcomes this limitation as it works in back pressure regulation mode with the pressure being monitored at the head of the column and any variation being compensated for at the supply. The benefits of this configuration include:

- > Creating improved reproducibility and stability of retention times.
- > Independent split flow and pressure control.
- > Ability to run in ramped pressure mode.
- > Independence of operator/lab environment.
- > Carrier gas pressure becomes part of the GC method.
- > Retention time locking.

To implement EPC with MiTDS requires that the carrier gas supply line, which normally connects the SSL EPC module to the SSL inlet, be connected to the carrier gas inlet on the TDS. Closed loop pressure control is then achieved by connecting the pressure feedback port from the TDS to the septum purge inlet on the SSL EPC module. The SSL EPC module thus monitors the pressure at the inlet to the transfer line (and hence the column) and any variation in pressure is compensated for by the upstream proportioning valve.

For optimum performance the carrier gas pressure to the EPC module should be regulated to approximately 15 to 20 psi above the column head pressure.

Note: As EPC only controls the carrier gas, suitable pneumatic control of the dry gas will still be required. A U-GAS01 from Markes International includes a carrier gas regulator to step down the carrier pressure and a separate regulator and gauge for control of the dry air or nitrogen, and is therefore recommended in this case.

The total flow measured just ahead of the proportioning valve in the EPC module is the total flow demand of the TDS and GC system (UNITY split and/or desorption flows, column flow and septum purge flow). The total flow reading displayed by the EPC module can therefore be used to independently set the desorption and split flows on the TDS system (see Section 25 of the UNITY Operator's manual).

A5.3 Known limitations of TD-EPC

> Under no circumstances can the split vent line within the SS inlet be used to control the sample splitting within the TDS because the different phases within a thermal desorption program require different degrees of split.

> The combined TD-EPC system will run in constant pressure, constant flow with ramped pressure and pulsed flow splitless modes. However if manual flow control is used on the TDS in conjunction with any inlet mode other than constant pressure then it is not possible to overlap the 1° (tube) desorption stage with GC runs and the GC cycle time parameter in the corresponding TDS method should be set to 0.0. If overlap is attempted then, due to changes in pressure during a GC run, variation will be observed in the tube desorption and split flows.

> Certain cold traps, particularly those containing a high proportion of porous polymer sorbent, exhibit high impedance when hot. This can lead to fluctuations in the pressure due to overcompensation during the secondary (trap) desorption and thus influence the column head pressure. It is possible to compensate for this effect by lowering the carrier gas pressure supplied to the inlet of the EPC module and thus limit the total flow it is able to supply.

If you have any questions regarding these points then please contact your local Markes International or Agilent technical support representative.

A5.4 Setup of EPC with TDS

Items Supplied in Shipping Kit:

Description	Quantity
1/8" - 1/8" Brass union	2
1/8" - 1/16" Graphite Vespel ferrule	5
1/8" - 2mm Vespel ferrule	1
Peek tubing	3 m

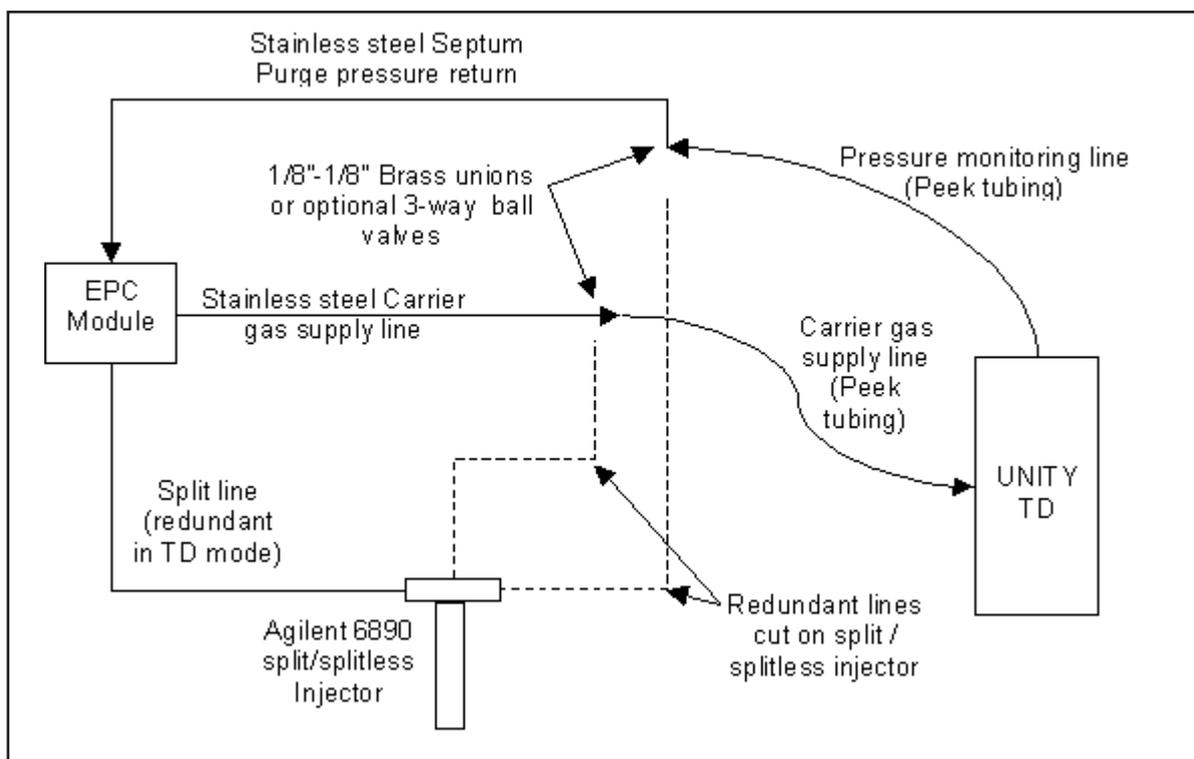


Figure 49. Schematic diagram of how the 6890 EPC module should be pneumatically connected to the TDS.

A5.5 Configuring UNITY and 6890 EPC module for use

Preparing the 6890:

- 1) Turn off the inlet EPC module on Agilent 6890
- 2) Cut septum purge and carrier gas supply lines at a suitable point for making the connections with the PEEK tubing (at least 15-20 cm from the injector). Note that an alternative solution would be to order an extra bulkhead connector (Agilent part No G2131-80500 and a screw 1390-1022). This avoids the necessity to cut the existing S/SL inlet tubing.

Connecting unions and gas lines to TDS

Important considerations:

The carrier gas supply line on the Agilent SS injector is 1/16" stainless steel tubing whereas the septum purge line is 2mm stainless steel.

Take care not to over tighten ferrules on Peek tubing as this may crimp the tubing and impede flow.

- 1) Cut the supplied 3m length of Peek tubing into two equal lengths of 1.5m.
- 2) Using one of the two supplied 1/8" brass unions, connect one of the lengths of Peek tubing to the Septum purge line using the 2mm ferrule on the stainless steel purge line and the 1/16" ferrule on the Peek tubing. This will be the pressure monitoring line and if necessary should be labelled as such for later reference.
- 3) Using the other 1/8" brass union connect the remaining length of Peek tubing to the carrier gas supply line from the EPC module using 2 of the remaining 1/16" ferrules. This will be the carrier gas supply line and can, if necessary, be labelled as such for later reference.
- 4) Connect the newly extended carrier gas supply line and the septum purge pressure monitoring line to the back of UNITY using the final 2 1/16" ferrules. (Figure 2.5 shows the UNITY connections)

Connect pressure
monitoring line here

Connect carrier gas
supply line here

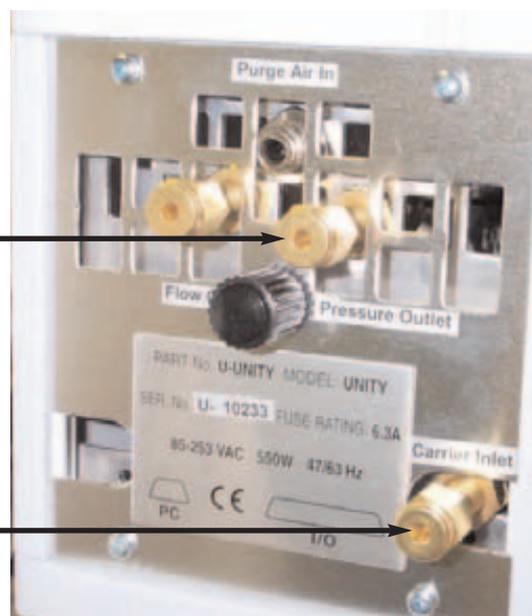


Figure 50. Carrier gas supply and pressure monitoring connections on the rear of UNITY

Setting up the EPC control in the Chemstation control software

After the analytical column has been installed in the GC oven and the fused silica transfer line from UNITY connected to it, (see section 4.3 in the UNITY Operator's manual) the EPC module may be set up.

Note that the external carrier gas supply pressure delivered to the EPC module should not exceed the maximum pressure required by more than 10-15 psi.

Setting up electronic control of the column head pressure for UNITY is very similar to that of a standard split/splitless inlet. The column dimensions may be entered in the Chemstation software which will automatically calculate the required head pressure. Or, alternatively a constant/ramped pressure or flow setting may be entered at the user's discretion

Before the column pressure value is set, the MODE of operation of the inlet has to be configured. The available choices for this injection port are split, splitless and the pulsed techniques. For correct control of UNITY the mode must be set only to SPLITLESS, and not split. In addition the splitless purge time value must be set to 999.99 minutes DIRECTLY through the keyboard of the GC (6890 firmware revision A.03.08 required). This value cannot be set using the Chemstation software as the number is rounded to 1000.0 minutes. Setting this value forces the split/splitless inlet to remain permanently in the splitless mode. The purge flow value is irrelevant.

Once the split/splitless inlet has been configured as described the column head pressure can be setup to give the desired flow rate/ velocity down the column.

UNITY OPERATOR'S MANUAL

APPENDIX 6

**This product has been discontinued.
The appendix is no longer published.**

UNITY OPERATOR'S MANUAL

APPENDIX 7

Multi-purpose Direct Inlet Accessory (U-INLET)

A7.1 Overview

The Multi-purpose Direct Inlet Accessory (U-INLET) may be added to any UNITY thermal desorption apparatus to provide a simple mechanism for direct introduction / 'on-line' sampling of bulk vapour (headspace) samples from sealed containers. It allows vapour-phase samples to be introduced directly onto the focusing trap of the desorber without first being collected on a sorbent tube.

Please note that for older UNITYs with serial numbers up to U10230 installation involves connecting a multipurpose socket and power supply leads directly to a printed circuit board in UNITY. This operation should only be undertaken at site by a Markes International trained service engineer or by return of instrument to the Markes International factory. The required power socket is preinstalled at the factory on all UNITY instruments from serial No U10230 onwards.

The accessory itself consists of a purge gas supply line and a heated, inert sampling line. Both lines are connected to an interface tube which is inserted by the user in the tube desorption oven on UNITY. Once installed, changing between direct sampling and tube desorption is as simple as changing desorption tubes and takes just a few seconds.

There are 5 sampling configurations that may be used with U-INLET, depending on the type of vessel that the sample is contained in. Please see Table 1.7 Sampling Configurations.

If sampling is to be performed from a sealed vessel, both the purge gas supply line and the heated sampling line must be connected to the sample container (see sampling configurations 1 & 2).

In all other sampling configurations (see sampling configurations 3, 4 & 5) only the heated sampling line should be attached and the purge gas supply line should be capped.

Although the method of connection will vary depending on the type of sample container involved, in all cases the seals must be leak tight.

During sampling the vapours from the sample container are swept through the heated inert sample line and into the cold trap at a flow rate controlled by the 'desorb flow' needle valve (the left hand needle valve on UNITY). The cold trap is then purged with carrier gas to remove air before being desorbed into the analytical system.

If sampling is to be performed from a non-pressurised system (e.g. ambient air, gas sampling bag - see sampling configuration 3), then a suitable pump is required to provide a means of drawing sample through the system, for example U-ASPM1 (115V) or U-ASPM2 (230V).

Control software for direct link operation is included as a dedicated mode in the UNITY operating software. The user may specify prepurge, sampling and trap purge times as required.

A7.2. Key application areas include:

- Characterisation of VOC profiles from natural products and manufactured goods - food, flavour, fragrance analysis
- Measurement of the concentration of specific residual volatiles in materials
- Monitoring emissions from living organisms - plants, microbes, fungi, insects, etc.
- Monitoring VOC pollutants in environmental water and soil samples
- VOC in industrial gas streams
- Monitoring organic vapour products from gas-phase reactions.

- Combination with existing automated headspace systems.

A7.3. Packing list

Part No.	Description
U-INLET	Multi-purpose Direct Inlet
U-MAPP7	Operating instructions - to be added as Appendix 7 of your UNITY Operator's Manual
UTD-1155	Tube Oven cover - Ultra Inlet

A7.4. Installation instructions - for UNITYs serial number U-10230 or above

Ensure that UNITY is switched off and cool before installing U-INLET.

Disconnect the carrier gas and dry gas supplies from the back of UNITY and remove the top rear cover on UNITY by unscrewing and removing the black knob (Figure 19 of main UNITY Operator's Manual.) The rear cover is then free to slide backwards and away from the instrument. Figure 1.7 shows the orange multi-purpose socket at the back of UNITY's analyser assembly into which the plug from U-INLET must be inserted, take care to ensure that the plug is fitted the correct way round as shown in figure 51.

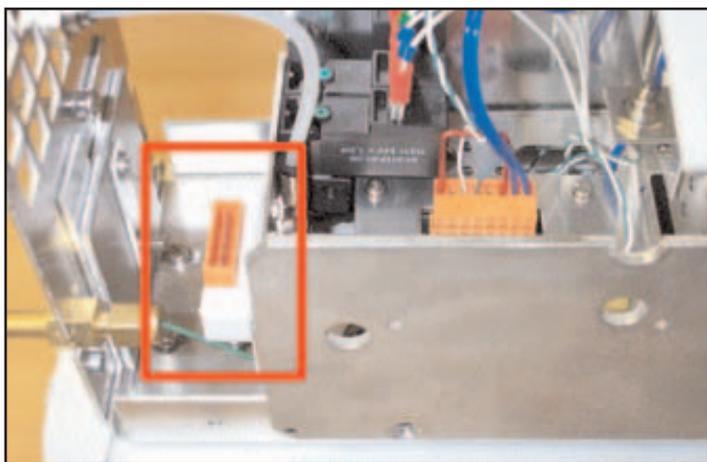


Figure 51. The multi-purpose power supply socket situated at the back on the analyser highlighted in red.

U-INLET can then be installed in the UNITY tube oven cradle as if it were a standard sorbent tube. When correctly located, the outlet and heated-inlet tubes attached to the interface tube should extend out towards the left of the instrument (figure 52).

NB. For all UNITYs with a serial number of U10230 or below the fitting of the multipurpose socket can only be carried out by a Markes International trained service engineer, or by returning to the factory.

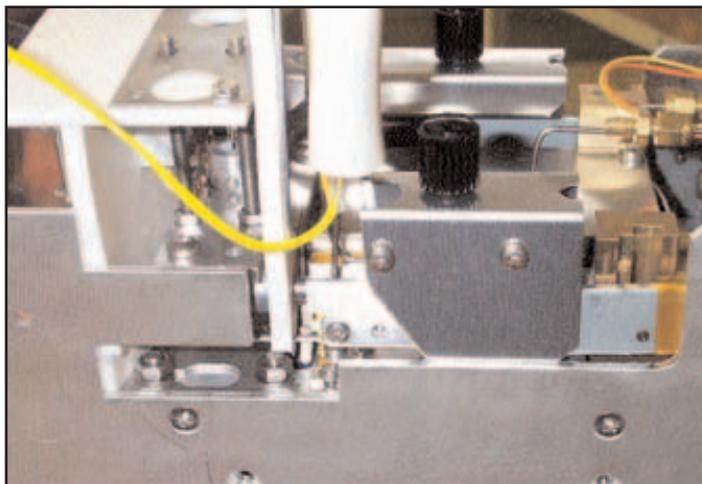


Figure 52. The installed Direct Link Tube, and modified tube oven cover.

A7.5. Connecting to the sample (vessel) - see Table 1. Sampling Configurations

Note that the carrier inlet and heated sample outlet pipes of the Direct Inlet Accessory are constructed of plain and Silcosteel 1/16th-inch stainless steel tubing respectively. These will require appropriate leak-tight fittings for connecting to the sample container. The most commonly used fittings include 1/16th-inch, stainless steel Swagelok unions or hollow syringe-type needles - suitable for piercing rubber septa, etc. Whichever type of connection is used, care must be taken that the seals into and out of the sample vessel are leak tight.

A7.6. Direct sampling modes and software control - see Table 1. Sampling Configurations

Once U-INLET is installed and connected to the sample vessel, select Direct sampling mode from the drop-down method selection box in the top left hand corner of the UNITY method window. If direct sampling mode is not available then please contact your local Markes representative for a software update.

In direct sampling mode there are five sampling configurations, depending on the type of sample vessel used, table 1 details these configurations. Four of these configurations (1, 3, 4 and 5) are dynamic direct sampling techniques, while one configuration (2) is a pulsed direct sampling technique.

IMPORTANT NOTE:

Dynamic direct sampling involves a continuous flow of carrier gas through (or from) the sample vessel sweeping the headspace vapours into the UNITY cold trap for a defined period of time and is not compatible with single needle headspace systems.

Pulsed direct sampling works by pressurising a sealed sample vessel for a set period of time and then shutting off the gas supply and allowing the carrier gas pressure to be released out through the cold trap of UNITY. This process may be repeated multiple times on a single sample to enhance the concentration of trapped analytes before desorbing the cold trap and beginning the GC(-MS) analysis. Pulsed direct sampling is thus compatible with a single inlet/outlet point and can therefore be used with single needle headspace systems

The sequence of operation in both variants of direct sampling mode is illustrated by the series of flowpath schematics shown in figures 53 - 62.

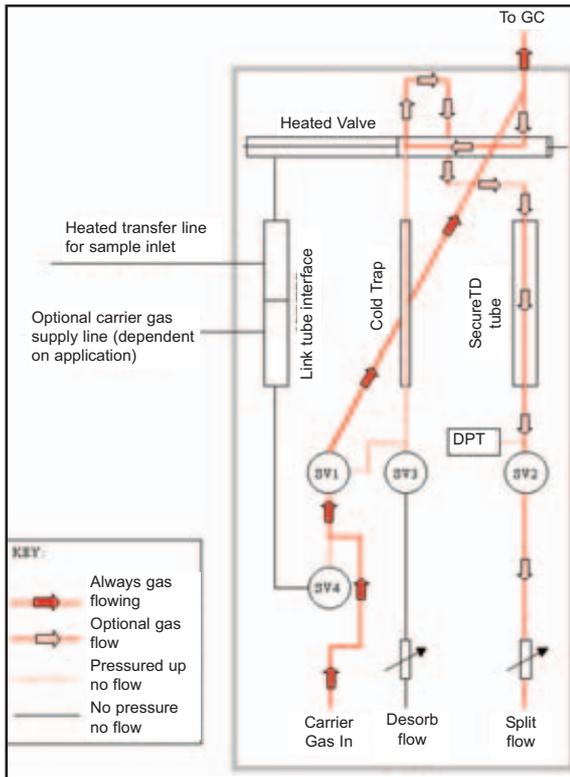


Figure 53. Standby Mode

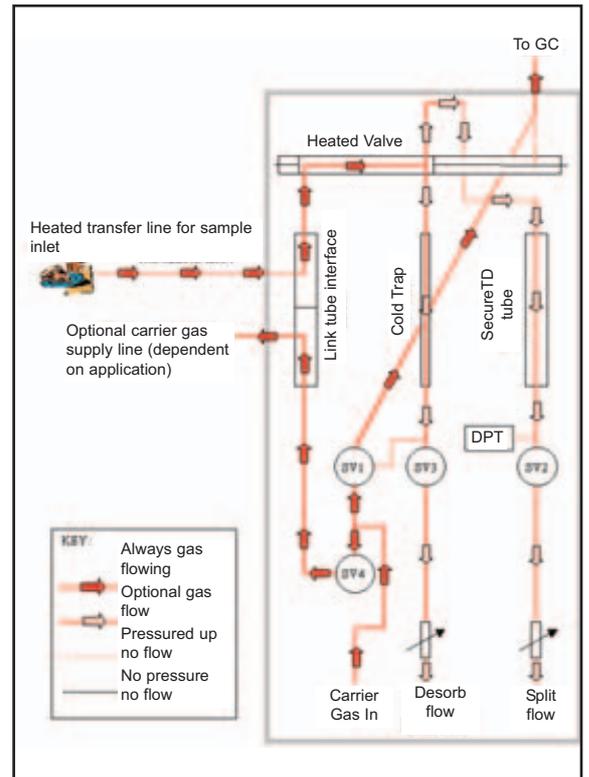


Figure 54. Prepurge

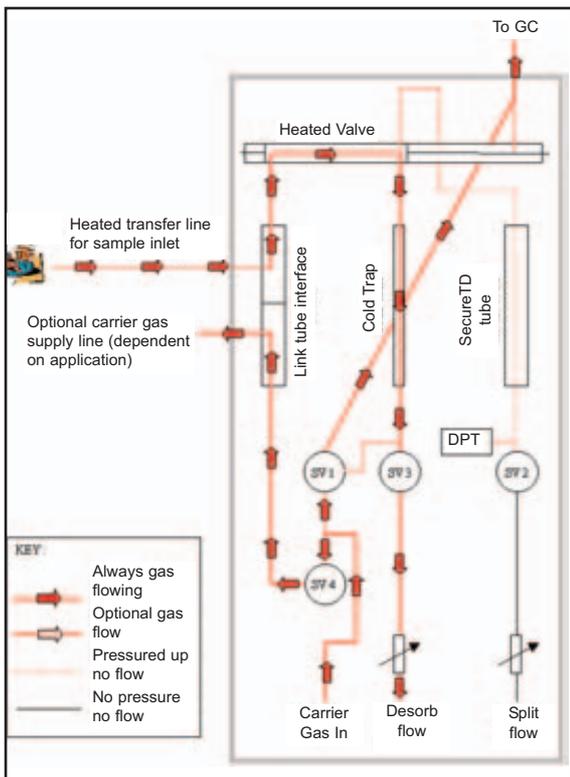


Figure 55. Dynamic Sampling

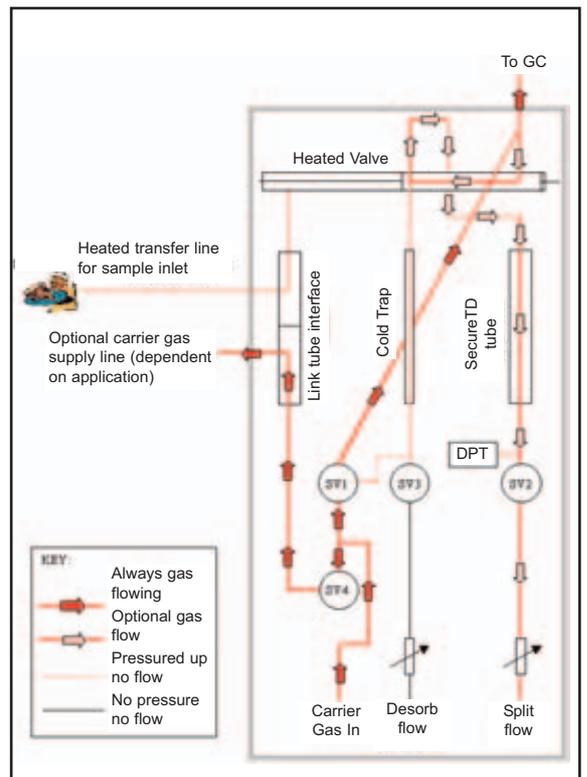


Figure 56. Pulsed Sampling - Pressurise

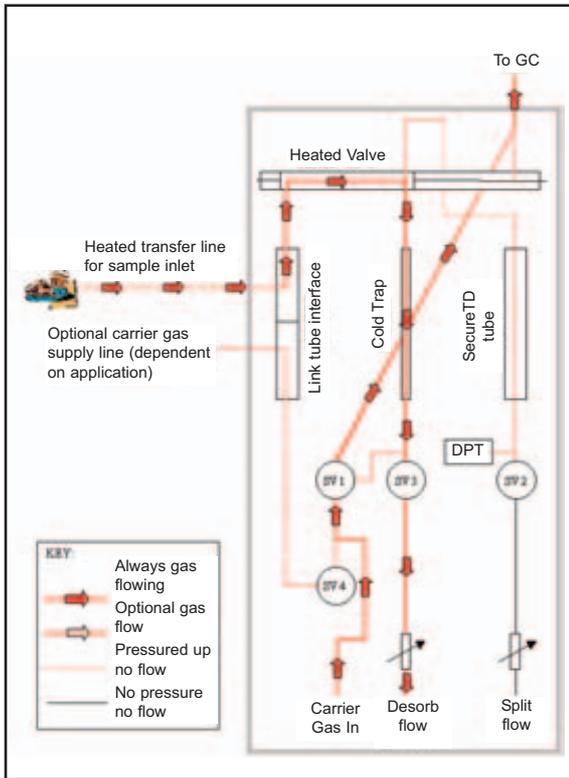


Figure 57. Pulsed Sampling - Release

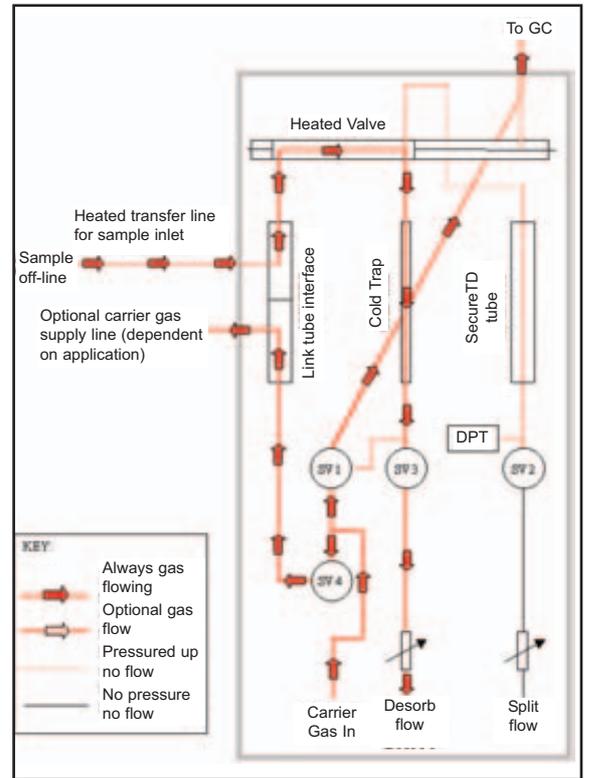


Figure 58. Pulsed Sampling - Line Purge

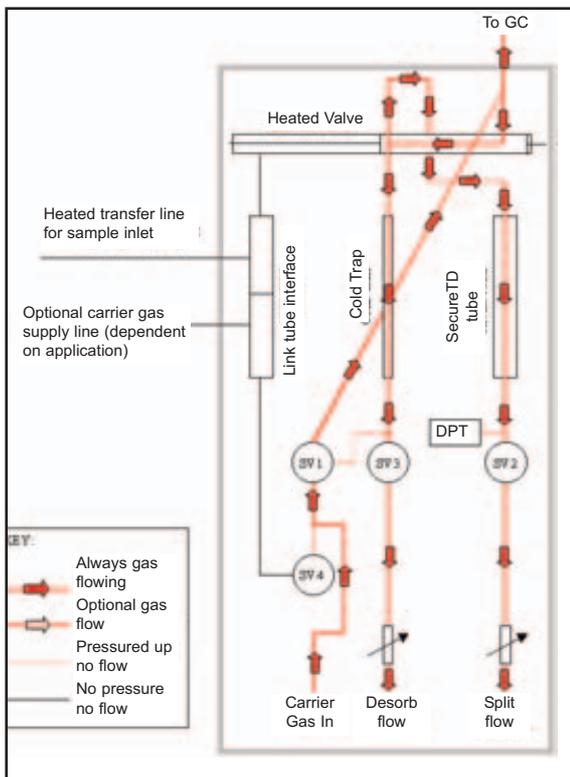


Figure 59. Trap Purge

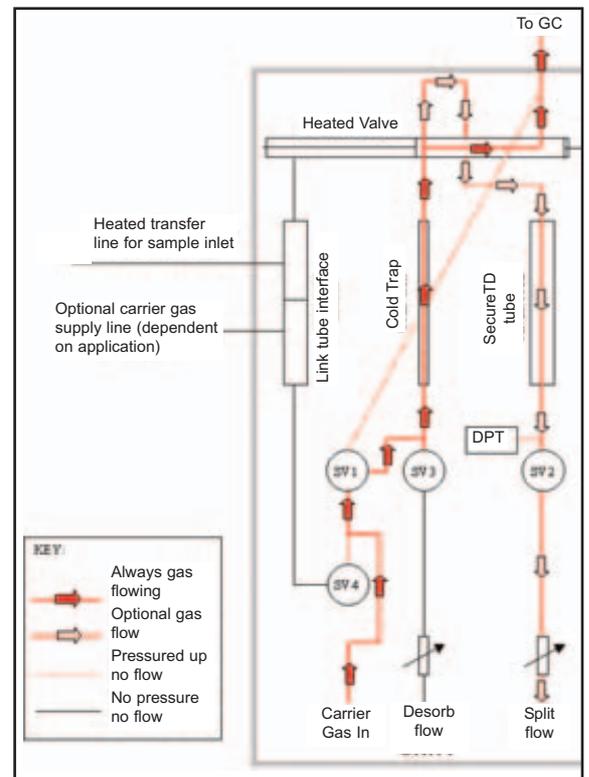


Figure 60. Trap Heat

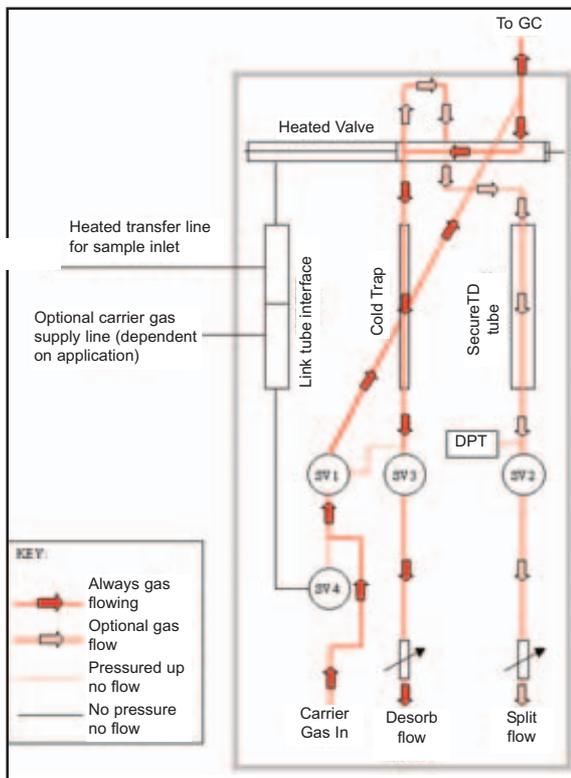


Figure 61. Set Flows

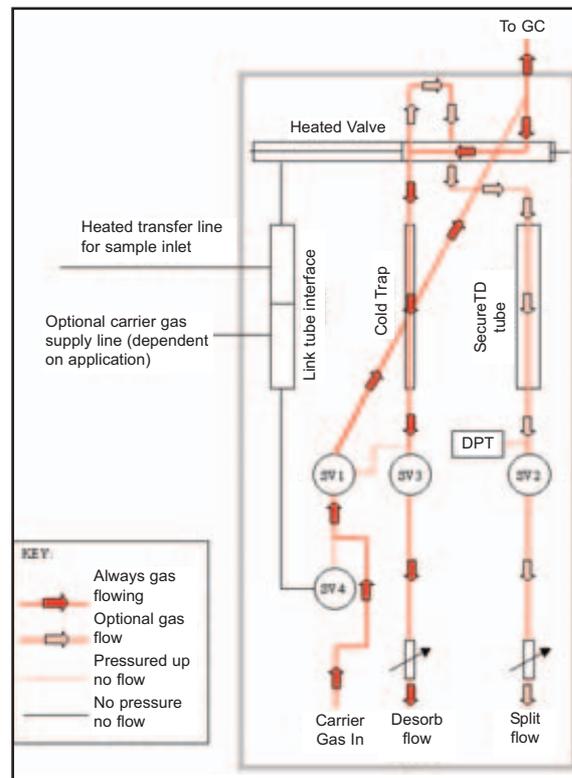


Figure 62. Exchange Split Tube

The two modes of direct sampling operation are also illustrated in the two example method screens shown in Figures 63 and 64.

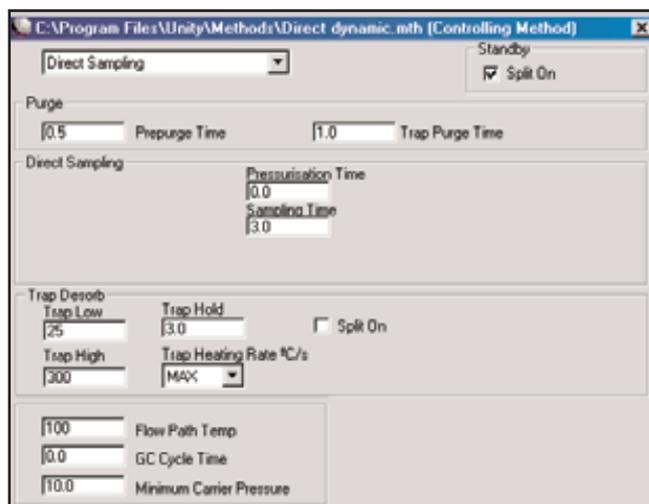


Figure 63. Direct sampling dynamic mode

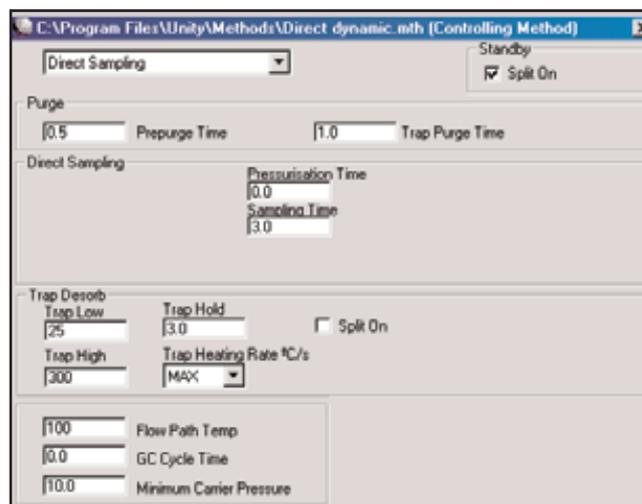


Figure 64. Direct sampling pulsed mode

Many of the method parameters used in direct sampling mode are common to those used for single tube desorption. These are described in Sections 3.3 and 22.2 of the main UNITY Operator's Manual. The method parameters exclusive to both dynamic and pulsed direct sampling mode are described below. Please refer to figures 53 to 64 as required for clarification of the notes below.

A7.6.1 Dynamic direct sampling parameters

A7.6.1.1 Pre-purge:

Pre-purge is used to sweep out the sampling lines thus eliminating carryover from previous runs. It also fills the flow path with sample gas to the point of entry into the cold trap such that accurate sampling volumes can be collected.

Note that with sampling configuration 3, (unpressurised container or whole air sample) pre-purge does NOT operate. For sampling configurations 4 & 5 the external pressure should be opened before sampling starts, e.g. in configuration 4 the external gas supply should be turned on and in configuration 5 the canister valve should be turned to open.

Pre-purge therefore defines the time for which gas sweeps through the sample lines and into UNITY through the flow-path bypassing the trap and out through the split at the flow rate set on the split (right hand) needle valve.

A7.6.1.2 Pressurisation time:

When set to zero - UNITY runs in dynamic direct sampling mode. If this is set to a number greater than zero then UNITY will function in pulsed direct sampling mode, see below.

A7.6.1.3 Sampling time:

Follows pre-purge and defines the time for which the split vent is closed and the sample from the sample vessel is purged on to the focusing trap of UNITY at a flow rate determined by the desorb (left hand) needle valve or U-MFC accessory if used.

A7.6.1.4 Trap Purge:

Follows sampling and defines the time for which carrier gas is purged through the cold-trap in the sampling direction. The carrier gas flow is determined by the desorb (left-hand) needle valve or U-MFC accessory if used. This procedure purges the trap of any oxygen prior to heating and, under certain conditions, allows selective purge of unwanted volatiles - such as water or ethanol.

A7.6.2 Pulsed direct sampling parameters

A7.6.2.1 Pre-purge:

In the case of pulsed direct sampling, prepurge pressurises the sample vessel and cleans out the sampling lines thus helping minimise carryover from previous runs and sweep any air out of the flow path. However as there is no overall flow in the sampling vessel prepurge does not flush the vessel.

Pre-purge therefore defines the time for which gas sweeps through the sample lines and into UNITY through the flow-path bypassing the trap and out through the split at the flow rate set on the split (right hand) needle valve

A7.6.2.2 Pressurisation time:

When set to any non-zero value UNITY will run in pulsed rather than dynamic direct sampling mode. When in pulsed sampling mode this defines the time for which carrier gas is supplied to the sample vessel to build up pressure prior to releasing that pressure through the cold trap.

A7.6.2.3 Sampling time:

Defines the amount of time for which the solenoid valve downstream of the cold trap is opened so that sample is transferred from the sample vessel to the cold trap. The pressure drops as soon as sampling begins until it eventually reaches atmospheric pressure.

A7.6.2.4 Equilibration time:

Governs the amount of time for which the sample in the sampling vial is allowed to re-equilibrate before it is repressurised and resampled.

A7.6.2.5 Sampling cycles:

Sets the number of times that the pressurisation, sampling and equilibration steps will be repeated for any particular sample, before desorption of the focusing trap triggers the GC(-MS) analysis.

A7.6.2.6 Flush time:

A similar step to prepurge - this stage permits carrier gas purge of the sample lines to remove any residual

sample and transfer to the trap or out of the split or both.

A7.7. Reverting from Direct Sampling Mode to Tube Desorption Mode

Changing between U-INLET and Tube Desorption Mode is a simple process.

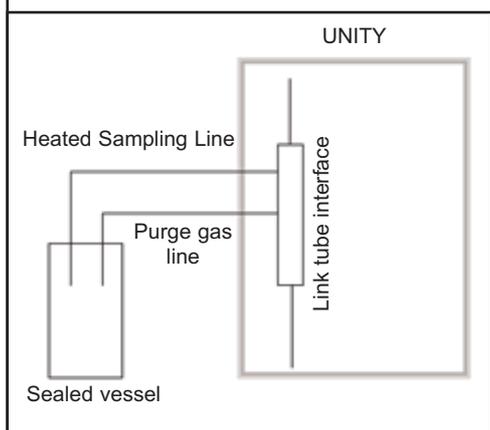
If the mode-change is to be short-term and frequent it is not necessary to unplug the accessory from the orange multi-purpose socket at the back of UNITY's analyser assembly. The U-INLET tube can be simply removed from the oven cradle and the sorbent tube placed in the oven for desorption.

NOTE: That the Direct Inlet Accessory will remain heated while it is still plugged into UNITY and care should be taken when inserting and removing sorbent tubes to avoid touching the accessory.

If the mode-change is to be longer-term and infrequent it is recommended that U-INLET is unplugged from UNITY by reversing the directions given in section 4 above.

Table 1. Sampling Configurations for Multi-purpose Direct Inlet Accessory (U-INLET)

1. Dynamic sampling from a sealed vessel

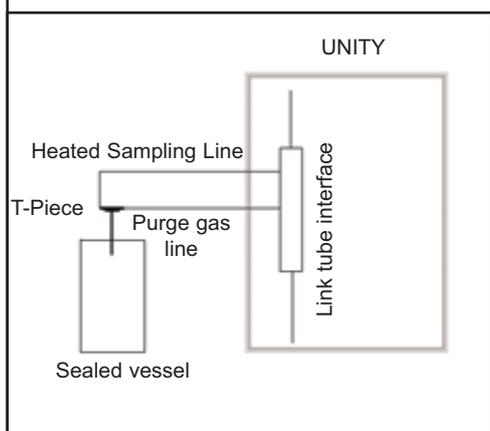


Sample in leak-tight, pressure resistant vessel with inlet and outlet line.

During pre-purge carrier gas flows from UNITY through purge line into the sample vessel and out through the heated sampling line, sweeping out the sampling lines and filling the entire flow path with sample.

During sampling, carrier gas flows from UNITY through the purge line into the sample vessel, out through the heated sampling line and into the focusing trap of UNITY. Flow rate is determined by the desorb (left hand) needle valve.

2. Pulsed sampling from a sealed vessel, e.g. headspace vial



Sample in leak-tight, pressure resistant vessel with combined inlet and outlet line.

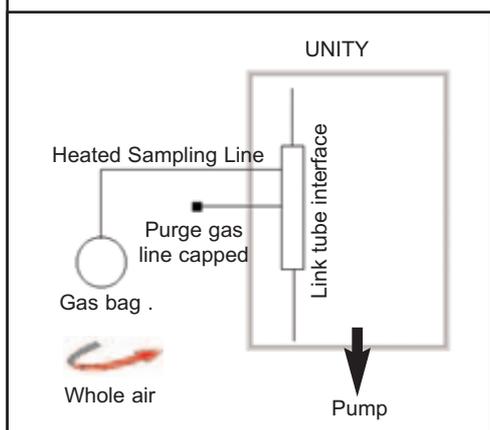
During pre-purge carrier gas pressurises the sample vessel and sweeps out the sampling lines, however as there is no overall flow in the sampling vessel prepurge does not flush the vessel.

During pressurisation carrier gas is supplied to the vessel to build up pressure prior to sampling.

During sampling, the solenoid valve downstream of the cold trap is opened so that the sample is transferred from the vessel to the trap. The pressure drops as soon as sampling begins until it reaches atmospheric pressure.

The sample can then be left to re-equilibrate before being re-pressurised and resampled. These steps can be repeated several times before desorption of the trap and analysis of the sample

3. Dynamic Sampling from a non-pressurised system, e.g. bag, whole air

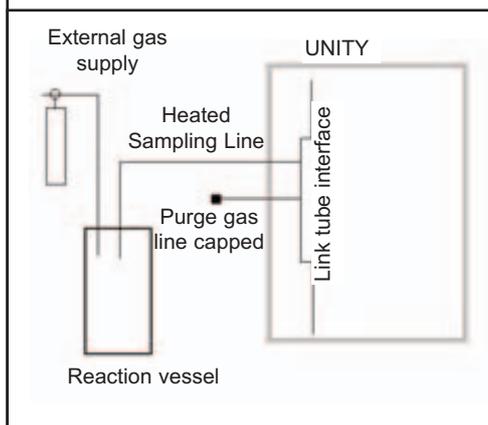


Purge gas line is capped. A pump is required to draw sample from the unpressurised container, or from whole air. The pump is attached to the desorb line.

Pre-purge does not operate in this sampling configuration mode, therefore the aliquot sampled into the focusing trap will contain the small volume of gas from the heated sampling line.

During sampling, the pump pulls sample gas from the non-pressurised vessel into the focusing trap of UNITY. Flow rate is determined by the desorb (left hand) needle valve.

4. Dynamic sampling from a reaction vessel with an external gas supply



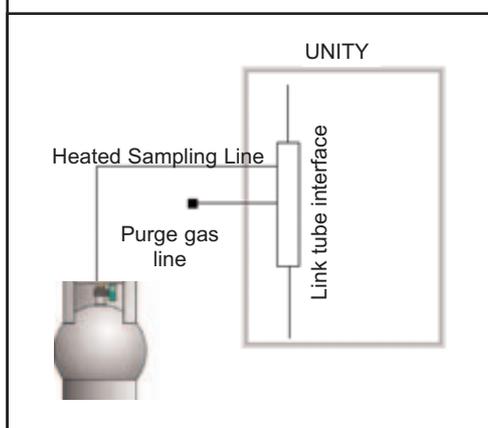
External gas supplied to leak-tight, pressure resistant reaction vessel containing sample.

Purge gas line is capped. Reaction vessel is supplied with gas from an external (pressurised) supply.

The external gas supply should be opened (no gas flows in standby). During pre-purge reaction gas flows through the sample vessel and through the heated sampling line, sweeping out the sampling lines and filling the entire flow path with sample.

During sampling, reaction gas flows from the sample vessel through the heated sampling line into the focusing trap of UNITY. Flow rate is determined by the desorb (left hand) needle valve.

5. Dynamic sampling from a pressurised container e.g. canister



Purge gas line is capped. The valve on the pressurised container should be opened (no gas flows in standby). Then during pre-purge gas flows through the sample vessel and through the heated sampling line, sweeping out the sampling lines and filling the entire flow path with sample.

During sampling, gas flows from the pressurised sample vessel through the heated sampling line into the focusing trap of UNITY. Flow rate is determined by the desorb (left hand) needle valve.

UNITY USERS MANUAL

APPENDIX EIGHT

U-MFC-Split

The Mass Flow Control Split (MFC-Split) Accessory is available for both stand-alone UNITY and ULTRA-UNITY but not for UNITY-Air Server systems. It offers automatic adjustment and closed loop control of the split flow during standby, purge, tube desorption and trap desorption which means that different split flows can be set for each of these different phases of operation.

Ordinarily the split flow is controlled by a needle valve which allows the user to adjust the flow prior to running a sample tube (see Section 25 of the main UNITY operators manual). However, this flow rate will then remain fixed throughout the run. The MFC provides the user with the option of setting varying split flow rates at different stages of the desorption process, providing greater flexibility of split ratio setting. It is particularly useful in combination with UNITY-ULTRA systems where different samples can be run with varying split ratios.

The MFC is controlled via an extended version of the UNITY thermal desorption software. Once the UNITY software has been downloaded, the user is able to interchange between the MFC system and the standard UNITY system with great ease. The MFC is connected to UNITY as shown in Figures 1 to 3.

Remove the front and rear covers of UNITY as described in section 4.23 and 4.33 of the main UNITY manual. Connect the 1/8"-1/8" union to the split output vent, attach one end of the long piece of green PEEK tubing supplied and connect it onto the union (Figure 1). Pass the green PEEK tubing along the length of the instrument using the white tubing already attached to UNITY as a guide (Figure 65). Connect the free end of the green tubing to the bulkhead union supplied with the MFC kit. This union is then attached to the back plate of UNITY using the holes provided (Figure 66). The bulkhead union is best positioned one hole across from the dry air/nitrogen supply as indicated by the label on the UNITY back cover (Figure 66).

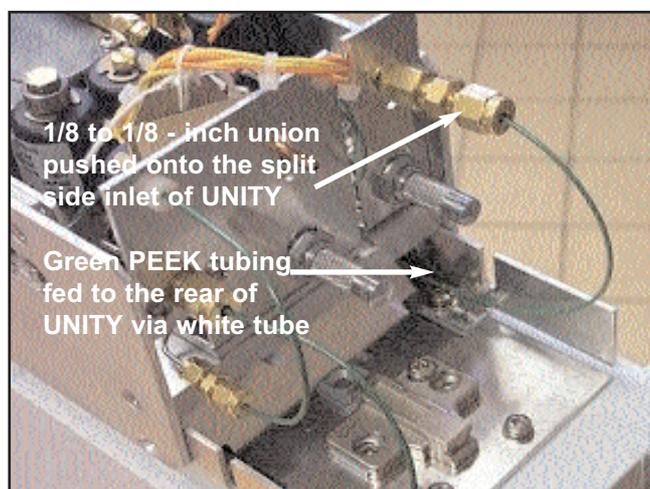


Figure 65. Connecting green PEEK tubing from the MFC shipping kit to the front of UNITY

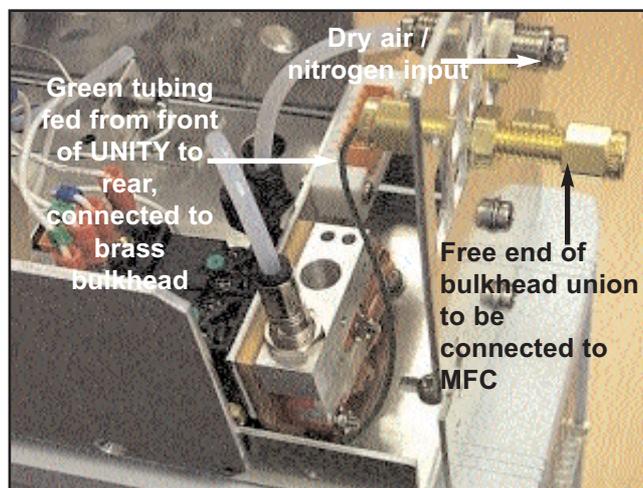


Figure 66 Connecting bulkhead union from MFC shipping kit to back plate of UNITY. Note the location of the brass bulk head - one space down and one across from the air /nitrogen supply input

Take the green PEEK tubing with the 1/8-inch nut attached to one end, and attach it to the 'flow in' position on the back of the MFC (Figure 67). Attach the free end of the tubing to the bulkhead union now secured to the back plate of UNITY. Finally, the split needle valve on UNITY needs to be opened fully. Connect MFC to the PC using the cable and serial port provided (Figure 67).

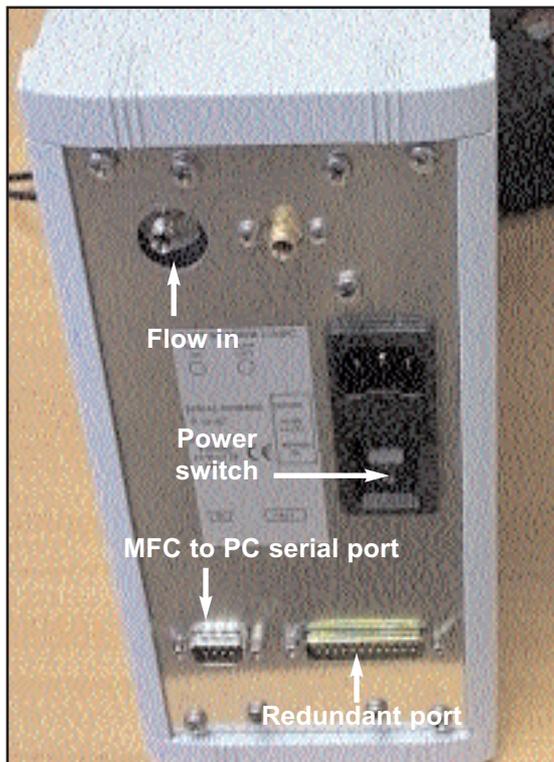


Figure 67 Rear view of the MFC showing 'flow in' connection point

Once connected, UNITY and the MFC should be switched on and the software downloaded as described in Section 6.2 of the main UNITY manual.

The PC will display the standard UNITY desorption operation page (Section 22.2 of main UNITY manual). Access the options page from the drop down list under View on the main header bar. Select the tab marked Accessories (Figure 68).

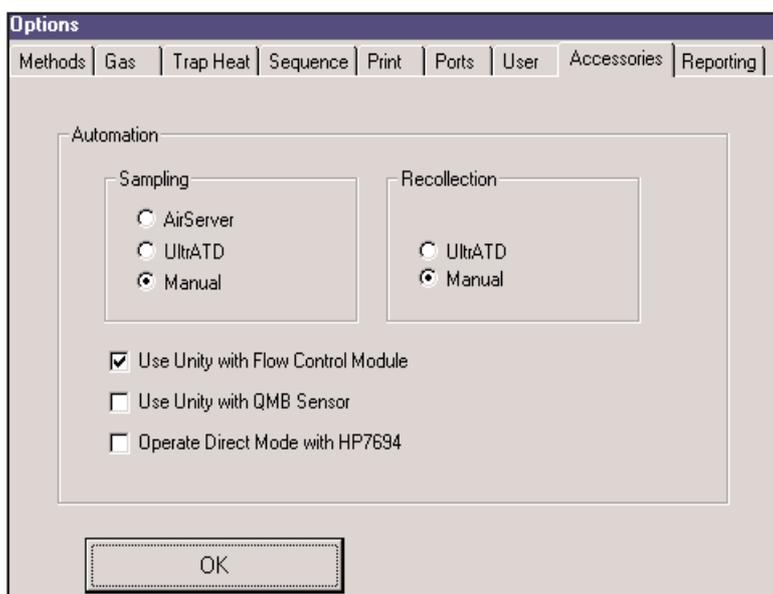


Figure 68 Options page

Select the Use UNITY with Flow Control Module option and press OK. A dialogue box will then appear which states 'the change in configuration will take effect on the next programme start up'. Click OK and close down the software by clicking on the x on the top right hand corner of the screen. Re-access the firmware again. This time a new desorption operation screen will appear. This will differ to the standard screen since the system will now recognise the addition of the MFC (Figure 69)

C:\Program Files\Unity\Methods\steve.mth [Controlling Method] (Modified)

Standard 2(3) stage desorption

Standby Flow Rate ml/min
 Split On 20.0

Purge
 1.0 Prepurge Time Trap In Line Split On Flow Rate ml/min
 20.0

Tube Desorb
 Time 1 Temp 1 Flow Rate ml/min
 10.0 280 Split On 20.0
 Time 2
 0.0

Trap Desorb
 Trap Low Trap Hold Split On
 -10 3.0
 Trap High Trap Heating Rate °C/s Split Flow ml/min
 300 MAX 20.0

200 Flow Path Temp
 15.0 GC Cycle Time
 0.0 Minimum Carrier Pressure

Split Ratios
 ??? Inlet
 ??? Outlet
 ??? Total

Confirm/Enter Flows

Figure 69 Desorption operating screen for a UNITY - MFC system

This screen is controlled in the same way as the standard UNITY. However, the user is now able to set the split flow rate for standby, purge, tube desorb and trap desorb. Selection of the 'set gas flows' icon will only give the user the option to set the desorb flow as opposed to both flows under the standard screen. Note that the desorb flow will still need to be set using the 'set gas flows' as described in Section 25.2 of the main UNITY manual.

If an ULTRA autosampler is to be added to the system then when the user enters the accessories page of the options list, they must select ULTRA TD (as described in Section B6a) of the main ULTRA manual as well as the use UNITY in conjunction with Flow Control Module item. Once the firmware is re-loaded, the main operations page will appear identical except for the addition of new flow rate boxes (Figure 69). The software is controlled as described in the main ULTRA operators manual. The only difference is the users ability to control the split flow rate at each stage of the desorption process.