Master TD

Thermal Desorber

Operating Manual

Edition

Operating manual - Master TD and Master Air Sampler - cod. 0310 380 006
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Warnings

The information contained in this document can be updated by DANI Instruments Spa at any time without prior warning.
DANI Instruments Spa shall not be held liable for any errors in this manual or improper use of the information contained in it or of the instrument.
It is advisable for users to carefully read all the information contained in this manual before using the instrument.

Safety Information

The sequential thermal desorber MasterTD and MasterAir Sampler are in compliance with Safety standards EN 61010-1 and CSA C22.2 EN 61010-1-04.
The instruments are in compliance with electromagnetic compatibility standard EN 61326.
The products have been designed and tested in accordance with safety standards for use in closed environments (Indoor use, Pollution degree 2, Installation category 2).
If the instruments are used in a manner not indicated by the manufacturer, the protection devices on the equipments could be damaged. If this occurs, disconnect the units from the electrical power supply and make sure they cannot be started up by accident.
The machines should only be serviced by professionally trained personnel. Do not replace parts or make modifications on the instruments unless authorized too do so.
Always disconnect the power supply cord before lifting the lid.
Users cannot replace the internal fuses.

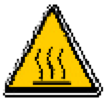
Safety symbols

The warnings in the manual and on the instrument must be observed both during operating phases and when servicing the instrument. Failure to observe these rules violates the design and instrument use safety standards.
DANI Instruments Spa bears no liability for user failure to observe these rules.

Attention!!! Warns of a condition or possible situation which could cause damage or harm the user.

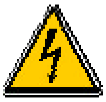
Warning Warns of a condition or possible situation which could damage or destroy the product or the operator's work

Indicates a grounded terminal.



Indicates a hot surface.

Attention! Refer to attached documentation.



Indicates hazardous voltages

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Technical Specifications

Master TD is a thermal desorber for standard dimension tube analysis able to automatically sample up to 50 samples.
The system uses the principle of two-stage thermal desorption with an electrically cooled trap, it is compatible with all the more commonly found gas chromatographs and with all types of columns, both packed and capillary.

Hardware configuration	Stand alone
Capacity	50 place electrically driven carousel
Samples	standard dimension stainless steel tubes with sealed caps and teflon coated silicone rubber septa compatible with radial symmetry diffusive samplers compatible with glass or glass-lined tubes set-up for on-line or canister sampling
Methods	methods stored with sequence option parameters setup through remote control from a Windows dedicated software.
Operating modes	Master TD • 1) Analysis • 2) Conditioning • 3) Multiple Desorption • 4) Trap Routine Master TD + Air Sampler • 1)Direct sampling • 2)Trap routine
Primary desorption	temperature: from +40 to +400 °C, increment 1°C time: from 3 to 999.9 min, increment 0.1 min Dry-step: from 0 to 30 min, from 30 to 100°C, before desorption automatic leak test every sampling memorization of the leak tube number possibility of splitting before trap inlet number of desorptions per tube: from 1 to 100

Focusing trap	adsorption temperature: -40 / +30°C, increment 1°C
	desorption temperature: +30 / +450°C, increment 1°C
	desorption time: 0 / 999.9 min, increment 0.1 min
	instant heating
	material: quartz
Transfer line	stainless steel internally coated with inert material, inside diameter 0.80 mm
	temperature: +50 / +290°C, increment 1°C
Pneumatic line in contact with sample	stainless steel entirely coated with inert material
Sampling valve	6 ports, electrically actuated temperature: +50 / +300°C, increment 1°C
Pressure controls	*Carrier gas*
	digital pressure control
	safety control on carrier gas
	max. inlet pressure: 4 bar
	optional regulation with flow rate regulator or pressure reducer
	Auxiliary gas
	electronic regulation and digital pressure reading
	digital reading of primary desorption and split flow rate
	automatic calculation and display reading of split ratio
	maximum inlet pressure : 4 bar.
Options	device for on-line sampling
Outputs	RS232 serial output for software control
	BCD output for sample identification
	remote control outputs (Start out, Ready in)
Power supply	voltage from 100 to 240 VAC (automatic selection)
	frequency from 50 to 60 Hz
	power 550 VA
Dimensions	width 450 mm, depth 490 mm, height 560 mm
Weight	30 Kg

Description

Master TD is an automatic sampler for thermal desorption of volatile and semi-volatile compounds concentrated in a sorbent material or directly present in solid or liquid samples. The sample, or sorbent, is contained in a tube closed with caps on each end.
Before desorption, the instrument performs a leak test on the tube. If this is positive, the tube is heated under a flow of inert gas to a preset temperature and for a preset time.

The volatile and semi-volatile compounds desorbed from the tube are collected in an electrically cooled trap. Then the trap is quickly heaten to a high preset temperature in order to transfer the compounds to the chromatographic column in a narrow band and a reduced volume of gas.

Master TD is able to automatically sample up to 50 samples.
It can be easily connected to any gas chromatograph and synchronized to it for an automatic and reliable management of the entire analysis system.

Figure 2-1 - Master TD

Sample Carousel

The sample carousel can hold up to 50 sample tubes.
Open the instrument lid to gain access to the carousel to load and unload tubes. Carousel positions are numbered in intervals of five.

The carousel can be moved in both directions using the "*Carousel Movement*" option in the *Manual Operation* page of the TD Manager (see "Operation - TD Manager" chapter).

The tubes inserted in the carousel must be closed at both ends.
If the tubes contain sorbent, the filling side must face up because the desorption gas flows from the bottom of the tube; this way the desorption takes place counter current to the sampling.

When the sequence starts, the carousel turns until the first tube of the method is lined up with the heating device.
A perforated piston equipped with a needle at the end, pushes the tube up until it reaches a stationary upper needle. The desorption gas from the lower needle flows along the tube and goes out of the upper needle.

When desorption is completed, the tube is returned to its original place in the carousel.

Sampling tubes and closing system

The sampling tubes can be made of steel, glass or glass-lined steel or other inert material.

The dimensions are 90 mm (3.5") in length and 6.3 mm (1/4") outer diameter. Any type of commercial tube with these dimensions can be used as long as it is equipped with closing devices specific for Master TD.

The tube closing system, which is the same for both ends, is composed of a silicone rubber septum and an aluminum cap. The surface of the septum facing the inside of the tube is coated with Teflon. 5 and 4 mm diameter septa are available for steel and glass tubes, respectively.
The aluminum cap has a rubber ring providing seal on the tube and a tapering at the hole to guide needle introduction.

The tubes can be filled with a sorbent and thus used for active or passive sampling of volatile components in a gaseous phase (for example monitoring of environmental pollution or in work sites).
In other cases the tubes are filled directly with the sample, primarily solid, which contains volatile or semi-volatile substances (for example, polymers, packing material etc.). Even fairly viscous liquids like resins, greases etc. can be directly desorbed in the tube. It is important to keep the end of the tube perfectly clean from any type of residual material.
In addition, the use of labels or other types of identification systems should not be placed directly on the tubes.

Tube heating device

The tube heating device consists of a quartz cylinder with a heating element wrapped around it.
When the sequence starts, the tube is lifted into the heating device. After the gas seal test on the

tube (*Leak Test*), the water is eliminated (*Dry Step*), the cylinder is heated to the set temperature, the tube is heated by radiation and the volatile compounds are desorbed from the matrix (primary desorption).
The desorption temperature can be set between 40 and 400 °C.

Sampling valve

The sampling system is composed of an electrically activated 6 port valve housed in a heated block. The entire unit is protected by a thermally insulated aluminum box.
During the *Leak Test* and *Dry Step* phases, the gas flows directly from the tube to the outlet *Vent* without passing through the trap.
At the beginning of the primary desorption phase, the valve is activated and the gas, before flowing through the outlet *Vent,* passes through the trap.
At the end of this phase the valve returns to the initial position to let the carrier gas pass through the trap.
The pneumatic lines in contact with the sample are made of steel entirely coated with fused silica.
The sampling valve temperature can be set between 50 and 300°C.

Trap

The trap consists of a 200 mm long quartz tube with a 4 mm outside diameter. The ends are connected to special fittings with PTFE seals.
The trap equipped with the instrument is filled with Tenax GR 60-80 mesh for approximately 4 cm.
It is possible to purchase empty traps to fill according to the instructions described in the *Maintenance* chapter.
The pneumatic configuration is made in order to desorb the trap in counter current to the collection.
This condition facilitates desorption of compounds at a high boiling point and is compatible with use of a multi-layer trap.

Trap heating and cooling device

The trap heating and cooling devices are placed in a single block aligned with the center line of the trap.
The block moves from one end to the other of the trap. In one position the filling is under the cooling device, in the other under the heating device.
Cooling is obtained using a Peltier cell electric system. The minimum temperature reached is - 40 °C.
Heating occurs through a spiral heating element and the maximum desorption temperature is +450 °C (according to the sorbent material).
During tube heating the block is positioned so that the section of the trap containing the sorbent is lined up with the cooling element, which is constantly maintained at the set temperature. Three minutes before the end of this phase, the heating element is activated and stabilizes at the set trap desorption temperature. At the end, the block moves to the hot area when the temperature is correct. Thus the trap is instantaneously heated, without any limit of temperature gradient, which guarantees a quick transfer and in a narrow band of the compounds to the gas chromatograph.

Transfer line

The transfer line connects the desorber to the gas chromatograph.
It is a 0.80 mm stainless steel tube internally coated with inert material.

It can be heated from 50 up to 290°C.
A needle is screwed at the end of the transfer line to introduce into the gas chromatograph injector (see *Installation* chapter).
For special applications, it is possible to connect the transfer line directly to the column using a dead volume reduced coupling (see *Installation* chapter).

Split at trap inlet

Master TD is equipped with a split outlet between the tube and the trap: part of the sample contained in the tube is eliminated through the split before reaching the trap. The split can be used to eliminate water if a high quantity is present, or when the sample is very concentrated.
The gas flow rate at the split outlet can be regulated using a needle valve located on the backside of the instrument. The outlet is on the back of the instrument (SPLIT) too.
The digital flow rate control mounted on the line, reads the value of the split flow rate which is shown directly on the Status (see *Operation* chapter).

TD Manager

TD Manager is the driver that controls Master TD. In its four windows the operator can set and display all the operating parameters.
The TD Manager window constantly displays the instrument status and any warning or alarm messages.

External connections

Master TD has the following external connections:

- power supply
- RS232 serial output
- remote control output
- BCD output for sample identification

The connections are located on the back of the instrument (see *Installation* chapter).

Pneumatic

The instrument is equipped with two separate inlets on the back for carrier gas (CARRIER IN) and auxiliary gas (AUX IN).

Normally, the carrier gas is supplied and regulated by the gas chromatograph.
However, inside the sampler there is a digital pressure control which detects the presence of gas (PM). If there is no carrier gas, the instrument signals an error condition and automatically disables all heating devices, interrupting the sampling sequence in progress.
The carrier gas flows to the injector through the transfer line.

The auxiliary gas is used to desorb the sampling tube.
It is possible to use a different gas rather than the carrier gas (usually Nitrogen).
The auxiliary gas is regulated by a digital pressure control (DPC).
The pressure is set using the keyboard and appears on the display (see *Operation* chapter). A

digital flow meter (FM) in the *Vent* line reads the desorption gas flow rate; the flow rate appears directly on the display.
The auxiliary gas line has a solenoid valve (SV2) which automatically closes during the leak test.
A solenoid valve (SV3) is also mounted on the split line to control the opening of the split (see *Operation* chapter). In addition to the split flow rate value, it is also possible to display the split ratio (desorption gas flow rate : split flow rate).

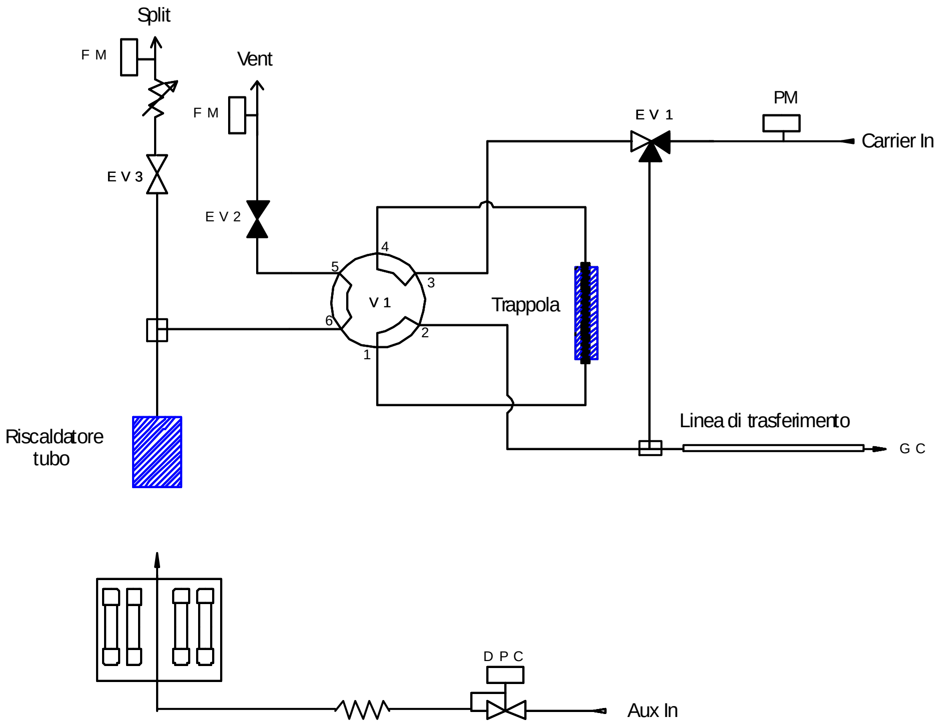


Figure 2-2 - Pneumatic scheme

Installation

Environmental Conditions

The Master TD Thermal Desorber must be installed in an environment with suitable temperature and humidity conditions for best operation and long life.

The MasterTD Thermal Desorber can operate in a temperature range from 0 to 40 °C and in a relative humidity range from 5 to 95%. Maximum altitude is 2000 meters.

However, the instrument performs best at 20-25°C room temperature and relative humidity of 40-50%.

Exposure to corrosive, gaseous, liquid or solid substances can damage the material used in Master TD and therefore must be avoided.

Positioning

A normal laboratory bench is suitable for installing Master TD with a free surface space approximately 75 cm deep and 55 cm wide which is able to support at least 35 kg. It is also important to leave a space of at least 20 cm behind the instrument to allow the electronic parts to cool properly.

The instrument is approximately 55 cm high; the area above must be free from shelves or other obstacles which would limit the access to the upper part of the instrument and suitable air circulation.

The instrument is normally installed on the left side of the gas chromatograph.

The maximum distance from the gas chromatograph must consider the length of the transfer line which is approximately 80 cm.

Electrical Power Supply

Power voltage

DANI Master TD is equipped with a variable power supply with automatic voltage selection. It can operate with a power supply voltage between 100-240 VAC and a frequency between 50 and 60 Hz. Mains supply voltage fluctuations have not to exceed +/-10% of the nominal supply voltage.

Power supply cable

For the safety of the operator the instrument is grounded through a three-conductor power line cord, according to International Electrotechnical Commission (IEC) regulations. The cord must be inserted in a socket equipped with a correctly connected earth ground contact.

Make sure the socket is grounded. Before connecting the instrument to the power supply, make sure that the switch on the back of the instrument is in the "OFF" position. Insert the cable into the socket and then flip the switch to "ON".

Pneumatic supply

Choosing the gas type

Master TD is equipped with two distinct inlets for carrier and auxiliary gas (Figure 3-1).
The maximum inlet pressure allowed is 4 bar (58 psig). It's better to use a two stage pressure regulator upstream from the lines and a single stage regulator near the instrument.
The gas must have a high level of purity because volatile organic compounds in the gas could contaminate the trap and be released during desorption.
The trap is isolated from the carrier gas during the desorption process to minimize contamination.
In any case it is important to use extremely pure gases (99.995% or better).
It is better to install filters on the gas lines to eliminate hydrocarbons, oxygen and humidity and to obtain the best performance.
The choice of carrier gas is primarily based on the analysis and the type of detector installed on the gas chromatograph.
The auxiliary gas can be different from the carrier gas because the inlets are separate. Normally Nitrogen is used because of its density and low cost.

Attention !!!

When using Hydrogen as carrier gas, be very careful to avoid letting explosive Air/Hydrogen mixtures form. Carefully check the seal on the lines which supply the Hydrogen.
Hydrogen must not be used as auxiliary gas !!

Figure 3-1 - Gas inlets on the back of the instrument

Connection to the gas supply

Connect the instrument to the supply line using preconditioned steel or copper tubing with the minimum number of connections possible. Do not use plastic tubing as it is permeable to Oxygen and other substances and could contaminate the column or detector.
Do not ever clean the tubing with organic solvents as any remaining solvent could build up in the trap. The tubing diameter is based on the distance between the instrument and the gas supply source and the total gas flow rate required.
A 1/8" tubing, like the one supplied with the instrument, is suitable for most cases.
The gas inlets, located on the back of the instrument (figure 3-1), consist of 1/8SW male bulkhead connectors.
To connect the pipes proceed as follows:

- Cut the tubing to the desired length. Always leave it slightly longer for minor movements of the instrument.
- Fit a 1/8SW ss nut (cod. 2300 460 040) on the tubing and a brass seal (cod. 2306 360 140) with the conical part facing outwards. Both pieces are equipped with the instrument.
- Insert the tubing to the bottom of the gas inlet connector and finger-tighten the nut.
- With a 7/16" wrench tighten the nut 1 and 1/4 turns.
- Check the seal on the pneumatic line.

Discharge outlet

During operations using the split between the tube and trap, a part of the desorbed sample is eliminated to the outside environment through an outlet on the back of the instrument (SPLIT). If the sample contains toxic or harmful substances, it is a good idea to convey this gas towards a suction hood and connect the pipe directly to the discharge.

Connection to Gas Chromatograph

Connecting the transfer line

Connect the desorber to the gas chromatograph by inserting the end of the transfer line in the gas chromatograph injector.
The needle has dimensions of 0.7 mm outer dia. x 0.4 mm inner dia. (cod. 2322 590 003) and can be used on injectors for packed and capillary columns.

To prevent the transfer line needle from blocking when inserting it, unscrew the injector septum holder and insert the needle in the templated septum. Then screw the septum holder again with the needle inserted.
In addition, to prevent the needle from bending, replace the capillary injector flat septum holder with the high septum holder supplied with the instrument.

Connecting carrier gas

Adjusting the gas chromatograph

In the standard configuration, the instrument is set-up for using the gas chromatograph carrier gas regulation system and thus the standard configuration is not equipped with any pressure or flow rate regulator.
Effect the connection as described below:

- Intercept the gas chromatograph carrier gas line near the injector.
- Connect the carrier gas supply tubing to the CARRIER inlet on the back of the instrument using an adapter to 1/8SW.
- Close the line towards the injector (for example with a union and a nut). If the gas chromatograph is DANI, unscrew the 6 MB nut at the inlet of the bulkhead union located under the upper part of the gas chromatograph and replace it with a 6 MB cap nut.
- Regulate the pressure or gas flow rate directly from the gas chromatograph.

Note: adding an external circuit on the carrier gas line causes additional pressure drop which cannot be calculated. Thus it is possible that the carrier gas flow rate calculated by the gas chromatograph (where available) is much higher than that actually present in the column.

External connections

Remote control

DANI Master TD communicates with the gas chromatograph via two remote controls:

- A connection for receiving the signal from the gas chromatograph when it is in a Ready condition (*Ready in*).

Note: in standard conditions, the instrument is configured to receive the Ready IN command as a closing contact, as this mode is used by DANI gas chromatograph. If the instrument is to be connected to a gas chromatograph which produces an opening contact, modify the configuration in the Setup page of the TD Manager (see "Operation-TD Manager" chapter).

- A connection to send the gas chromatograph the start signal (*Start out*); the signal is a closed contact, without voltage, produced when trap desorption starts.

To connect the remote controls, insert the remote connection cable (Cod.5103 509 008) in the RMT connector on the back of the instrument. Connect the wires as follows:

- Master TD Start OUT (orange/brown wires) - GC Start IN
- Master TD Ready IN (gray/green wires) - GC Ready OUT

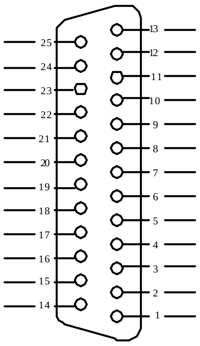
If connecting to other gas chromatographs, refer to the instructions provided for each one.

Serial connection

The desorber communicates with the PC via a RS232C serial output. Use the serial cable supplied with the instrument to connect the instrument to the computer (Cod. 5103 009 004).

BCD connection

The instrument has a BCD signal output connector for identifying the tube undergoing analysis. The signal is produced by a closed contact among a combination of pins which identifies the number of the tube according to the binary code and a common pin (GND). A diagram of the connections is shown in figure 3-2.



PIN 1 --> BCD1
PIN 2 --> BCD2
PIN 3 --> BCD4
PIN 4 --> BCD8
PIN 5 --> BCD10
PIN 6 --> BCD20
PIN 7 --> BCD40
PIN 9 --> GND

Figure 3-2 - BCD connections

Leak test

After the desorber has been assembled and connected to the gas chromatograph, it is advisable to effect a leak test on the entire pneumatic circuit, from the carrier gas inlet to column outlet. This procedure should be repeated each time the system is worked on, for example if the column or transfer line is replaced.
Proceed as follows:

- Disassemble the detector head and close the main body with the specific cap or disconnect the column from the detector and insert the end is a silicone rubber septum, if capillary, or close it with a cup nut if packed.
- Leave the desorber in stand-by conditions, and regulate the carrier gas pressure to approximately 2 bar (30psig). Wait a few minutes for the pressure to stabilize in the entire system and check the value of the current pressure.
- Turn off the pressure supply and check the value reading. After a minimum decrease, the pressure value must remain constant. If, after approximately 5 minutes, the pressure drop is less than 0.04 bar, the system is sealed.
- If the pressure decrease is less than 0.04 bar, it means that there is a leak in the system. Repressurize the system and find the leak by using a soapy solution. Check all fittings, particularly those made most recently.
- Find the leak, tighten the fitting until it is eliminated and repeat the leak test.
- Replace the detector or remount the column.

Operating principle

Sequential tube desorber Master TD has 5 operating modes:

- Analysis
- Conditioning
- Multiple desorption
- Direct sampling
- Trap routine

Each operating mode has a different sequence of events. Standby condition, instead, is separate from the selected operating mode. It is shown in the pneumatic diagram in Figure 4-1.
In the standby condition, the carrier gas flows directly in the column without passing through the cold trap. This reduces the risk of any contaminants in the gas building up in the trap and then being desorbed with the sample. The auxiliary gas line, instead, is closed. The VENT line is open (SV2) while the split line is only open if the SPLIT option has been activated in the method. Tube heating is disabled while the electric cooling device is activated if the method provides a focusing temperature lower than the room temperature.

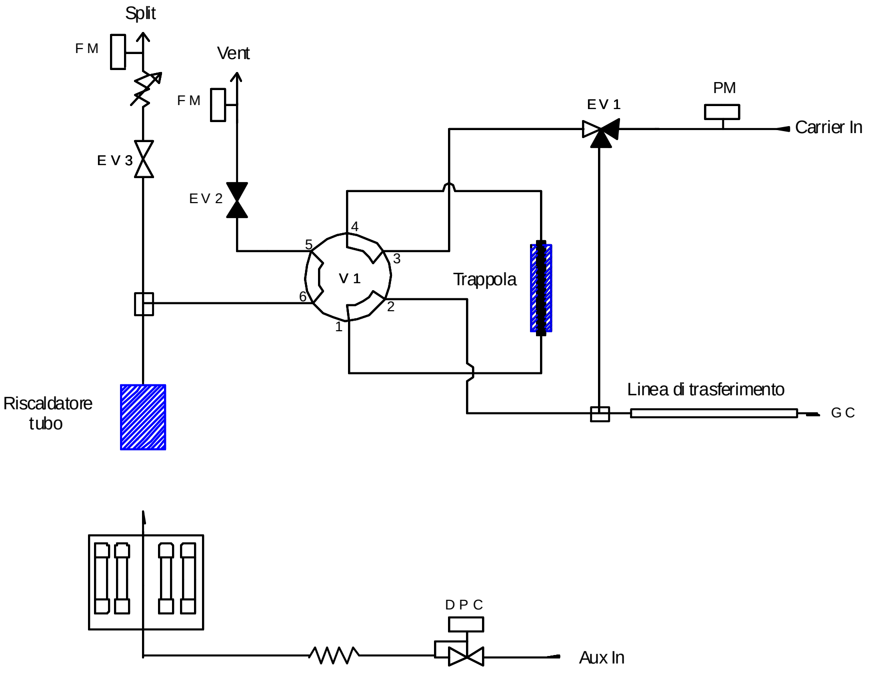


Figure 4-1 - Standby

Analysis

The *Analysis* operating mode produces the complete cycle of two-stage desorption and is thus the most used mode.

After a cold leak test, the tube is heated to a preset temperature (primary desorption). At the same time, a flow of inert gas transfers the desorbed compounds into the trap, kept at a low temperature, where they are concentrated again. In the next phase the trap is instantaneously heated and the compounds are transferred by carrier gas into the chromatographic column.

At the beginning of the operating cycle, the carousel rotates lining the tube up with the heater. The tube is lifted and the pressure regulator of the auxiliary gas (DPC) opens and brings the pressure to the preset value. Auxiliary gas flows for 20 seconds to eliminate the air present in the tube and refills the line (figure 4-2). Then valve SV2 closes. The pressure stabilizes at a value which is memorized as a reference. The auxiliary gas supply closes, and for 20 seconds the instruments verifies that the current pressure is not different from the memorized pressure. If the difference is less than or equal to 0.04 bar, the tube is considered sealed and the sequence of operations continues. If the difference in pressure is greater, a leak in the tube is diagnosed. In this case, the tube is returned to the carousel and the sequence continues for the next tubes. The event is memorized in the *Log File* (see *Operation* chapter).

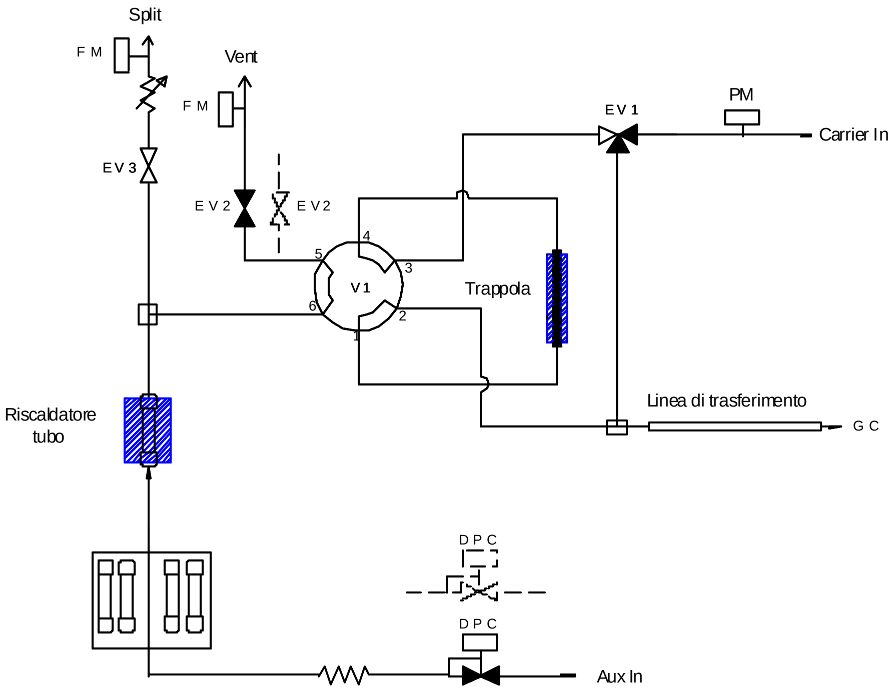


Figure 4-2 - Pressurization and Leak test

If the method includes the *Dry Step*, the heater brings the temperature to the value set for this phase, the valve of VENT SV2 opens and the auxiliary gas flow for the set time to eliminate any humidity in the sample.

The tube desorption phase takes place as follows. If the split is going to be used, valve SV3 opens. Switching valve V1 rotates to enable the trap on the auxiliary gas line, Solenoid valve SV2 opens. Regulator DPC reaches the pressure set for auxiliary gas.
The heater reaches the temperature set for tube desorption. The cooling device, kept at the lower temperature setting, is positioned where the trap fills.
These conditions are maintained for the amount of time established by the method for tube desorption (Figure 4-3).

Three minutes before the end of this phase, the trap heating device is activated: during this time it stabilizes at the upper temperature set for desorption.

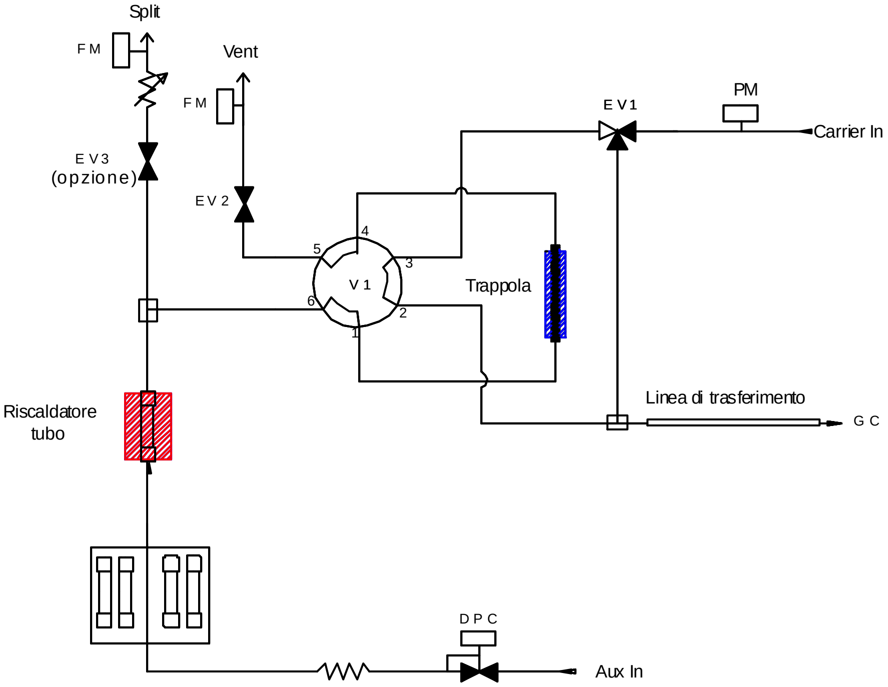


Figure 4-3 - Tube desortpion

At the end of the primary desorption phase, switching valve V1 rotates to its initial position and the trap is disabled from the auxiliary gas circuit.
Solenoid valve SV1 activates to allow passage of carrier gas through the trap. Immediately after, the heating block, which has reached set temperature, moves to the part of the filled trap.

At this point, the trap desorption phase starts and continues for the time established by the method (Figure 4-4).

At the same time, the sampler sends a start signal to the gas chromatograph to start the chromatographic analysis.
Simultaneously, the auxiliary gas regulator closes, the tube is put back in the carousel and tube heating is disabled.

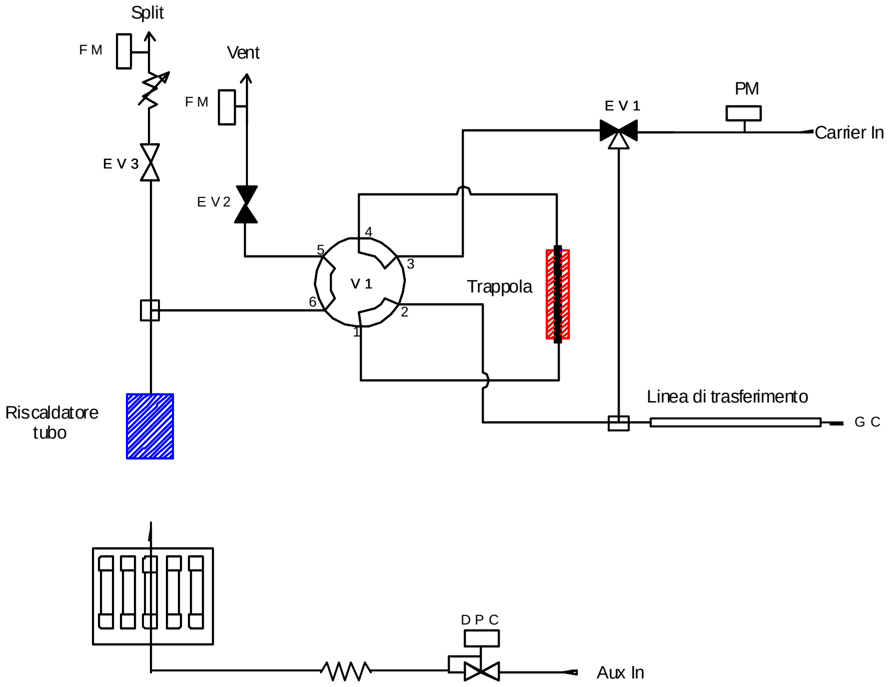


Figure 4-4 - Trap desorption

At the end of this phase, the heating device is disabled. After approximately 3 minutes, the block moves back to its initial position. One minute after the desorption phase, solenoid valve SV1 returns to its previous status.
The instrument returns to its initial conditions and is ready to process the next tube.

Conditioning

In the *Conditioning* operating mode, the tubes filled with sorbent are heated to a preset temperature for a preset time in the presence of an auxiliary gas flow. The purpose of this operation is the eliminate any volatile impurities from the tube before it is used for sampling.
Before being heated each tube undergoes a leak test. The sequence of operations in this phase is the same as those described for the *Analysis* mode (Figure 4-2).

At the end of the *Leak Test*, the tube is heated to a temperature and for a time established by the method. The auxiliary gas flow is eliminated directly at the SPLIT outlet (Figure 4-5). The gas flow rate, regulated by a needle valve located on the backside of the instrument, is shown directly on the display (see *Operation* chapter).

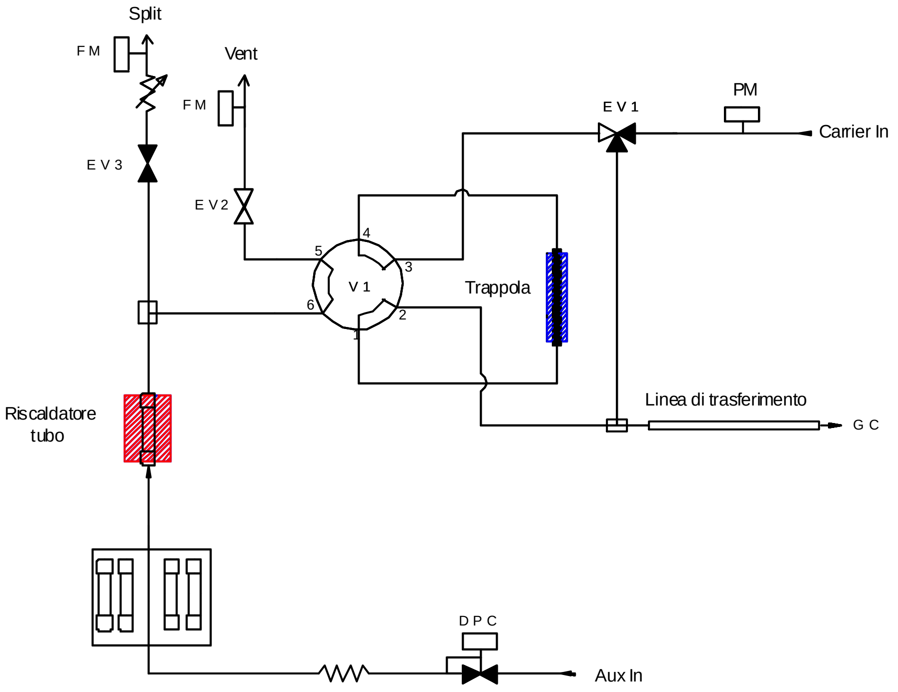


Figure 4-5 - Conditioning

Multiple Desorption

The *Multiple Desorption* mode is used when it is not possible to extract the volatile compounds from the matrix in a single desorption sequence.
This is the case when there are solid samples where volatile compounds are strongly bound to the matrix (for example polymer material) or samples which deteriorate when heated to a high temperature.

Each tube, before being heated, undergoes a leak test. The sequence of operations is the same as that described for the *Analysis* mode (Figure 4-2).

If the seal is positive, the tube is heated to the temperature and for the time established by the method without the passage of gas. In this phase, the auxiliary gas pressure regulator is closed, solenoid valve SV2 is open to allow the gas to expand and rotating valve V1 is switched (Figure 4-6).

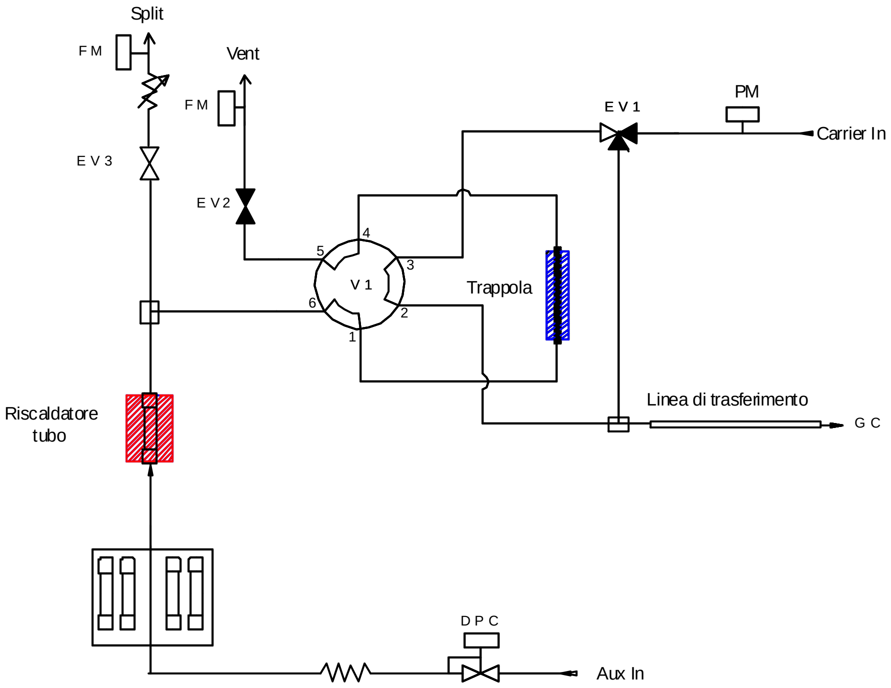


Figure 4-6 - Tube heating

One minute before heating ends, the auxiliary gas flow rate regulator opens to the pressure value set in the method solenoid valve SV3 is open if the SPLIT option is selected for the method and the volatile compounds in an equilibrated state during the gaseous phase are transferred to the trap kept at a low temperature (Figure 4-7).

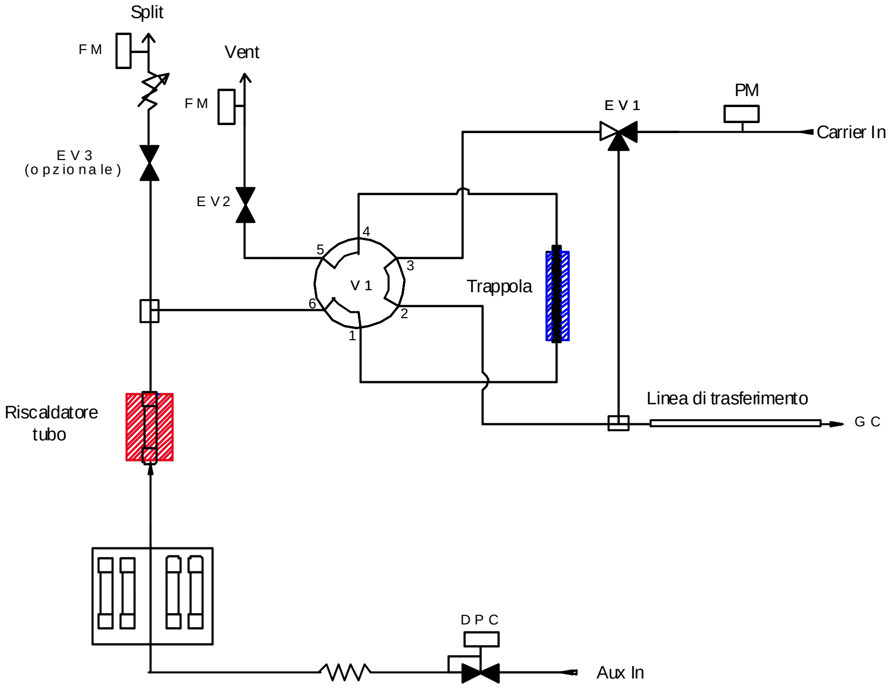


Figure 4-7 - Transfer to trap

Next, the switching valve returns to its initial position, solenoid valve SV1 activates and the carrier gas transfers the compounds from the heated trap to the gas chromatograph for the amount of time established by the method (Figure 4-8).

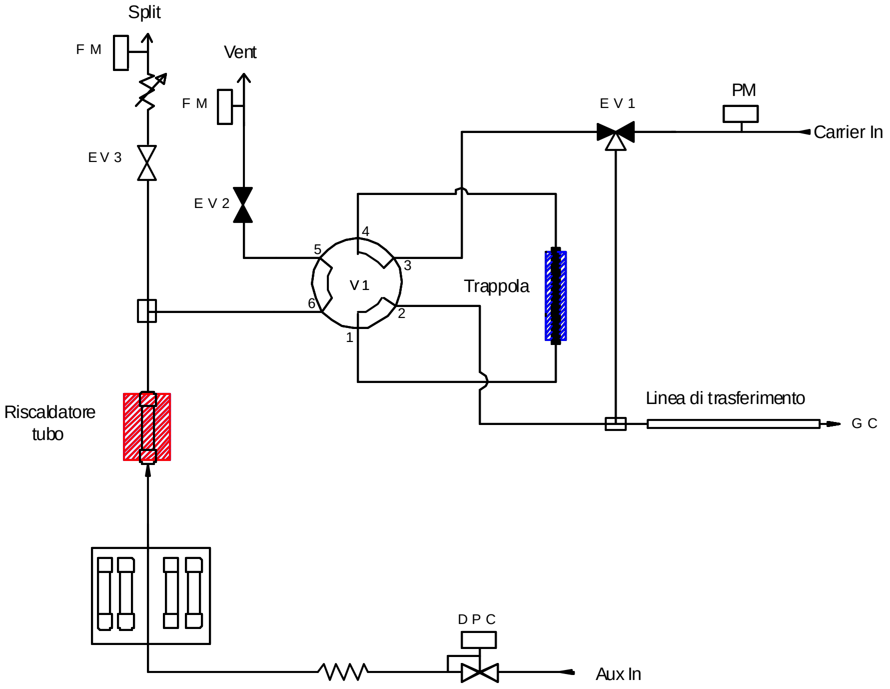


Figure 4-8 - Trap desorption and next tube heating

At the same time, the auxiliary gas closes again and the tube undergoes another heating. Once the trap desorption time has finished, solenoid valve SV1 deactivates and switching valve V1 goes back into position to bring the trap in line with the tube (Figure 4-6).
One minute before the end of the second heating, the volatile compounds are transferred to the trap and then to the gas chromatograph as described for the first heating.
The sequence of events is repeated for each tube for the number of repetitions established in the method. Once the last heating is finished, the tube is returned to the carousel.
In this way, because the heating time is constant, the sample undergoes an exponential extraction of volatile compounds. After a certain number or repetitions, all the volatile compounds are extracted from the sample, so it is possible to calculate total contents.
Because the heating time cannot be less than the analysis cycle, these two times must match: the time set for the analysis cycle is also the heating time.
The analysis cycle must include the duration of the analysis itself and the gas chromatograph cooling time up to Ready conditions.

Direct Sampling

The *Direct Sampling* operating mode sets up the instrument for direct sampling from the environment, bag or canister using the AIR SAMPLER (the optional external suction device) and then transferring the sample to the gas chromatograph.
A known volume of gaseous sample is concentrated directly in the trap. Then the volatile compounds are thermally desorbed from the trap and directly introduced into the column.
The operating cycle includes a first phase where the vacuumed sample flows through the trap, kept at a low temperature. The flow rate and sampling time determine the total sample volume.
Volatile and semi-volatile compounds present in the gaseous sample are kept in the trap (Figure 4-9).

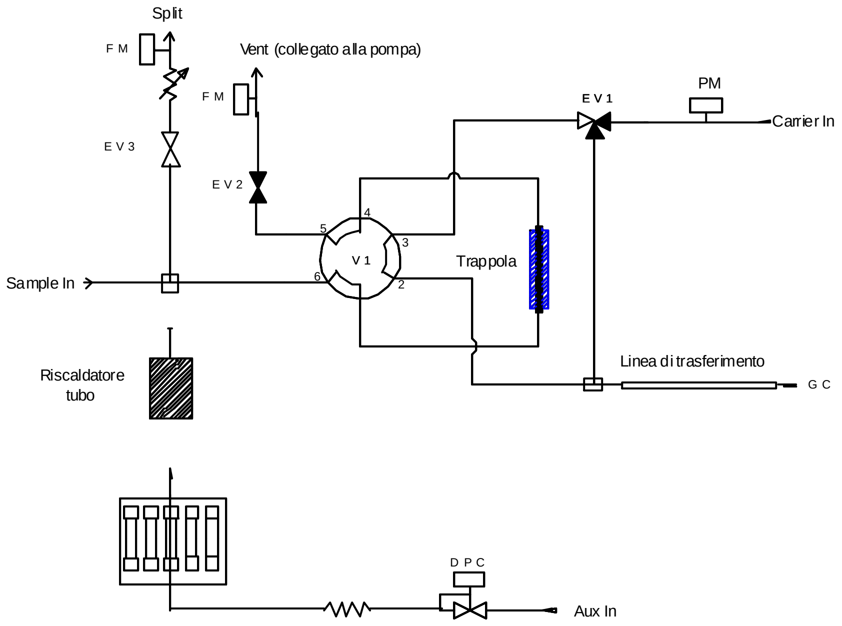


Figura 4-9 - Direct sampling

Once the sampling time is finished, desorption of the trap takes place as described in the *Analysis* operating mode. (Figure 4-4). This cycle of operations is automatically repeated for the number of times and at time intervals established in the method.

Trap Routine

In the *Trap Routine* operating mode, the trap first undergoes a leak test and then is heated to a preset temperature and for a preset time in the presence of auxiliary gas flow to eliminate any volatile impurities in the trap.

A leak test must be made every time the trap is disassembled and reassembled. Conditioning can be done after a certain period of work to restore filling performance, or when it is completely replaced with new material.

The conditioning temperature is normally 10-20 °C above the maximum temperature used for desorption, however, it should not be above the maximum use temperature specified by the manufacturer of the sorbent.

To carry out this procedure it is necessary to insert an empty, accurately closed tube in carousel position no. 1. First, a leak test is made. Unlike the *Analysis* mode, valve V1 is switched, so in addition to the tube, the trap is also enabled in the circuit. Then, the trap heating device is brought to the temperature established in the method. The trap is heated and auxiliary gas flows for the preset time.

To carry out this procedure when AIR SAMPLER option is enable, it's necessary to connect a zero grade gas to the *"BLANK"* inlet.

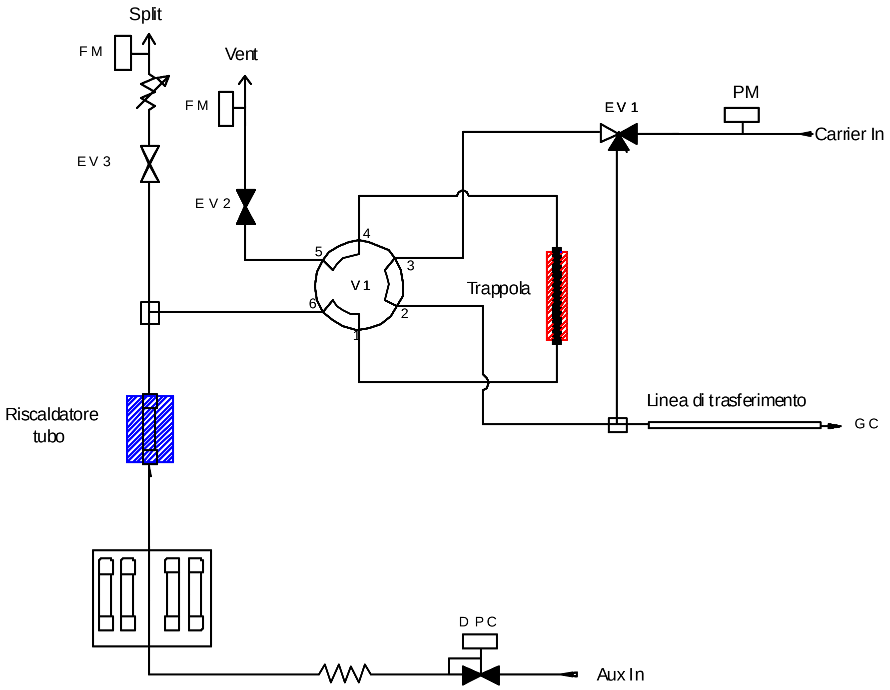


Figure 4-10 - Trap Routine

Operation - TD Manager

DANI TD Manger is a stand-alone software to be installed on your PC before starting any operation with your instrument.
It is the driver that makes it possible to control all the functions of Master TD.

PC requirements

DANI TD Manager is designed to run under any of the following operating environments: Windows 98, Windows 2000 and Windows XP.

The hardware requirements your system needs depends on the demands of the operating system employed:

- for Windows 98 and moderate speed requirements even a Pentium/200 PC with a 32MB memory shall be sufficient. For Windows 2000/XP a Pentium/450 PC MB memory shall be sufficient.
- The minimum monitor resolution is 800 x 600 pixels and 256 colours, however, we recommend a 1024 x 800 resolution and 64K colours (16 bit - High Colour).
- 20MB free capacity is required to install the program.

Program installation

- Start Windows.
- Insert the TD Manager CD in the CD-ROM drive.
- Unless installation starts automatically, locate and run the SETUP.EXE file in the *Start/Run* menu.
- Follow the on-screen instruction to complete installation.

Program start

- From the Start menu in the Task bar, select *Start/Programs/Dani Instruments/TD Manager* and click to start the program.
- At first start, the program will prompt the user to enter the User Code supplied with the program.
  Entering the right User Code enables the communication between Master TD and TD Manager.
  Entering the wrong User Code will display the message *Master TD not connected* and TD

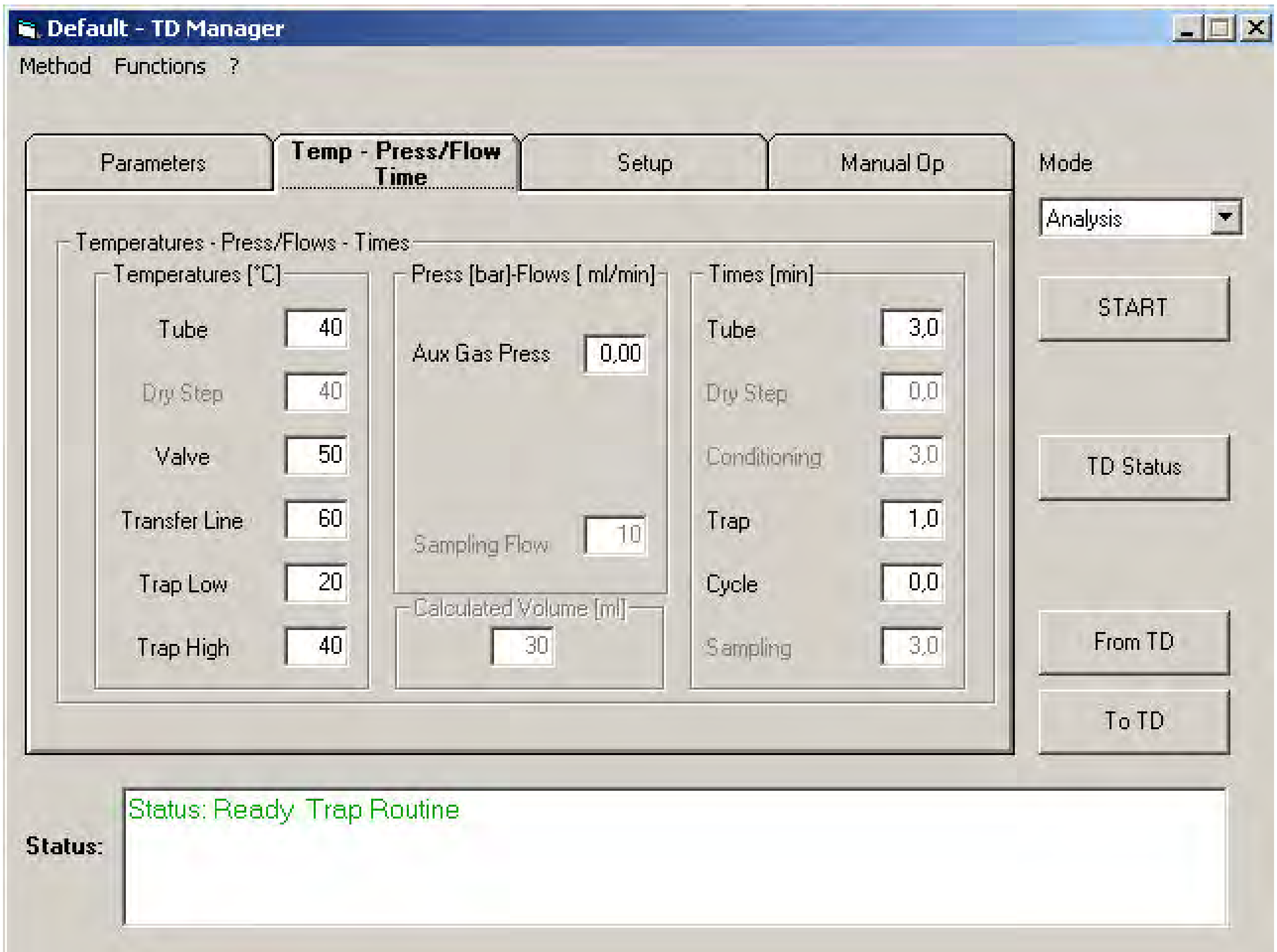
Manager won't communicate with Master TD.
It is possible to enter the right User Code anytime by selecting the question (?) menu in the Main Window and clicking *User Code*.

- Select the *COM* number to allow the communication between TD Manager and Master TD (see *Communication Setup* in the *Method* paragraph of this chapter).

Settings and operation

The Method default window in the picture below is composed of four pages (*Parameters*, *Temp-Press/Flow-Time*, *Setup* and *Manual Op*) and a column of commands on the right selectable at any time.

To know the meaning and the numerical range of each text box in the pages, read each paragraph of this chapter in the order that it is presented.



Temperatures [°C]
Tube 40
Dry Step 40
Valve 50
Transfer Line 60
Trap Low 20
Trap High 40

Press [bar]-Flows [ml/min]
Aux Gas Press 0,00
Sampling Flow 10

Calculated Volume [ml]
30

Times [min]
Tube 3,0
Dry Step 0,0
Conditioning 3,0
Trap 1,0
Cycle 0,0
Sampling 3,0

Mode
Analysis

Status: Status: Ready Trap Routine

Figure 5-1 - TD Manager

Commands

From TD

Acquires the method parameters from the Master TD. Select this command whenever you want to acquire the parameters from the instrument.

To TD

Sends the method parameters to the Master TD. Select this command whenever you want to send the modified method parameters to the instrument.

TD Status

Opens a status window (see Fig. 5-2) where it is possible to visualize all the set and actual method parameters. Four text boxes have only the actual value:

Aux Gas Flow

Visualizes the auxiliary gas flow rate which is flowing through the tube during the desorption phase.

Carrier Gas

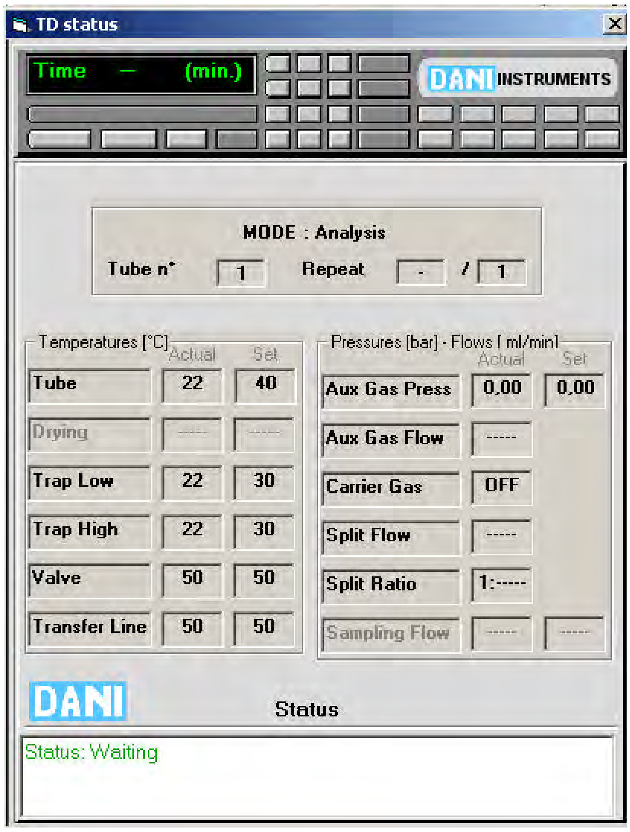
Visualizes the presence or absence of carrier gas coming from the gas chromatograph. If there's no carrier gas it is not possible to start the analytical sequence.
If the carrier gas is locally controlled by a manual pressure or flow regulator, it is possible to configure the instrument so that it reads the current pressure (see "Carrier mode" in Setup page)

Split Flow

Visualizes the gas flow rate which flows from the split during tube desorption. This value is shown only if the Split option is active.

Split Ratio

Visualizes the ratio between the gas flow rate measured at the Vent and that measured at the Split during tube desorption. This value is shown only if the Split option is active.


TD status

Time — (min.)

MODE : Analysis

Tube n° 1 Repeat - / 1

Temperatures [°C]	Actual	Set
Tube	22	40
Drying	-----	-----
Trap Low	22	30
Trap High	22	30
Valve	50	50
Transfer Line	50	50

Pressures [bar] - Flows [ml/min]	Actual	Set
Aux Gas Press	0,00	0,00
Aux Gas Flow	-----	
Carrier Gas	OFF	
Split Flow	-----	
Split Ratio	1:-----	
Sampling Flow	-----	-----

Status

Status: Waiting

Figure 5-2 - TD Status window

START

When the *START* command is selected the sampling sequence starts according to the operating parameters established by the method.
Remember to check from the TD Status window that all the parameters have been sent to the Master TD (*Set*) and that the *Actual* values correspond to the sets.

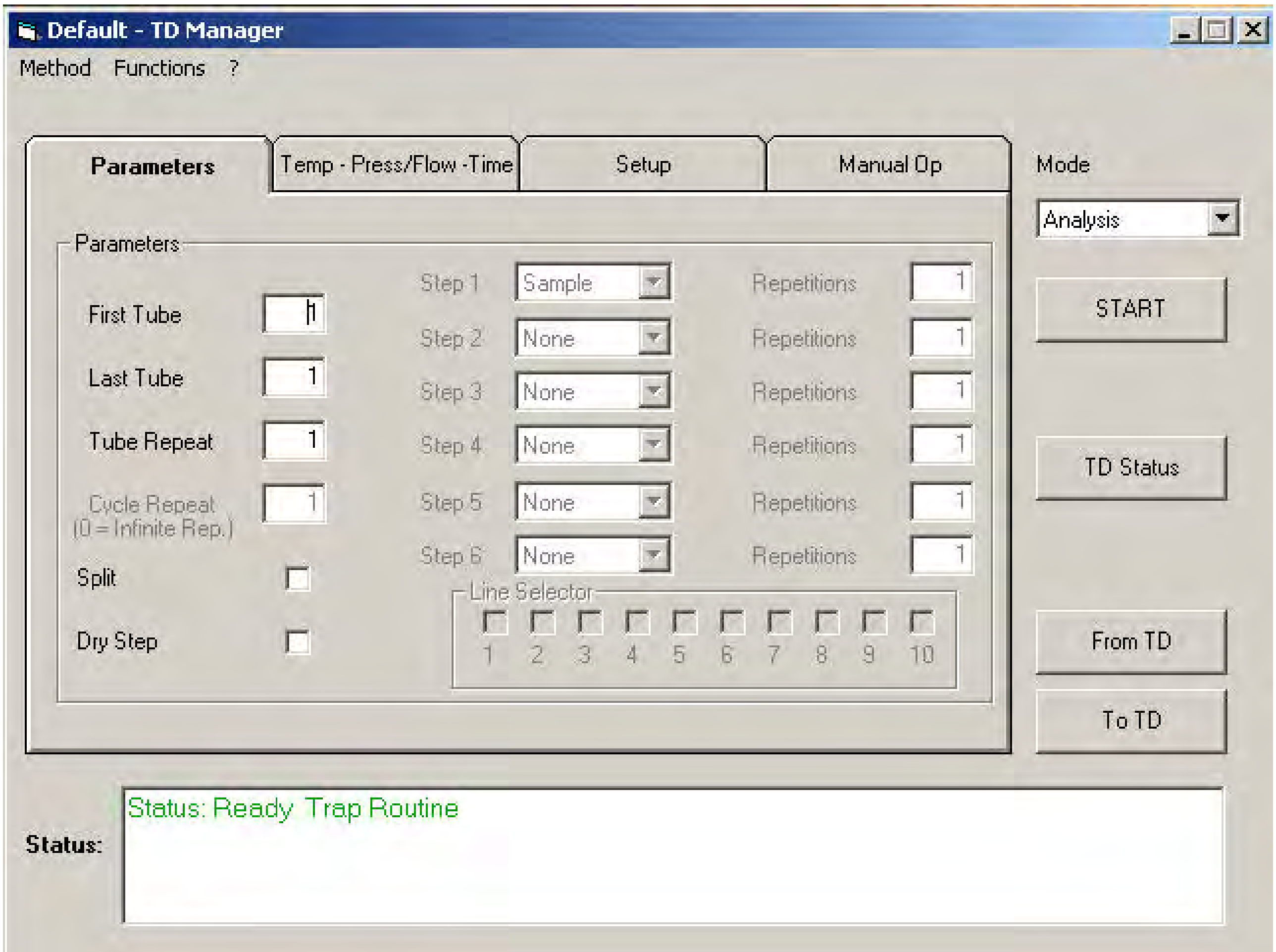
If the command is selected when the instrument is in Ready conditions, the sequence starts immediately. If the command is selected when the instrument is in Waiting condition, the Autostart function activates and the sequence will start automatically when the instrument is in Ready.

STOP

The *STOP* command will appear in the place of the *START* command when a sequence is running. It stops a sequence in progress at any time.
When a sequence is interrupted it is not possible to start again from the point where it was interrupted. At the next *START* it will start from the beginning.
To continue the sequence from the last sample analyzed, modify the method to start from the correct sample.

Parameters

Select the *Parameters* page (see Fig. 5-3) to set the sample parameters.



Mode: Analysis

Parameters

First Tube: 1
Last Tube: 1
Tube Repeat: 1
Cycle Repeat (0 = Infinite Rep.): 1
Split ☐
Dry Step ☐

Step 1	Sample	Repetitions	1
Step 2	None	Repetitions	1
Step 3	None	Repetitions	1
Step 4	None	Repetitions	1
Step 5	None	Repetitions	1
Step 6	None	Repetitions	1

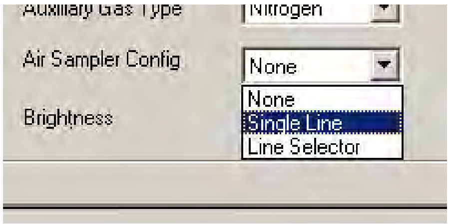
Line Selector: ☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ☐ 9 ☐ 10

Status: Status: Ready Trap Routine

Figure 5-3 - Parameters page

The active text boxes are written in black colour. They depend on the operative mode selected in the text box on the right upper corner.

At the same time, the available choice in the operative *Mode* text box depend on the *Air sampler config* selection in the *Setup* page (*None*, *Single Line* or *Line Selector*), as explained in the following table:



Air sampler config → *none*	Air sampler config → ***single line* or *line selector***
Analysis	Direct Sampling
Conditioning	Trap Routine
Multiple Desorption	
Trap Routine	

• Analysis	standard mode to perform complete analysis
• Conditioning	tube conditioning procedure
• Multiple Desorption	continuous extractions on the same sample
• Direct Sampling	to use for direct sampling when AIR Sampler device is installed
• Trap Routine	procedure for conditioning the trap

The table below shows the parameters available (written in black colour) for each operating mode in the standard configuration.

Warning

No selection is available in trap routine mode. Therefore it is important to place the followings according to the kind of selection in Air Sampler Config in Setup page:

\- *None* — *place a tube in position 1 of the carousel*
\- *Single Line or Line Selector* — *connect to the "BLANK" inlet a zero grade gas (i.e. Air or nitrogen) to perform the trap cleaning.*

Analysis	**Conditioning**	**Multiple Desorption**	**Direct Sampling***	**Trap Routine**
First Tube	First Tube	First Tube	-	-
Last Tube	Last Tube	Last Tube	-	-
Tube Repeat	-	Tube Repeat	-	-
-	-	-	Cycle Repeat	-
Split	-	Split	-	-
Dry Step	-	-	-	-
-	-	-	Step (1 to 6)	-
-	-	-	Repetitions	-
-	-	-	Line Selector**	-

* *Available only if the AIR Sampler (Single Line or Line Selector in Setup page) is configured*
** *Available only if Line Selector (in Setup page) is configured*

First Tube

Specifies the number of the first tube (1-50) analyzed with the active method.

Note: in the Trap Routine mode, this number specify the tube used for trap leak test and conditioning.

Last Tube

Specifies the number of the last tube (1-50) analyzed with the active method. The number of the last tube cannot be lower than the number of the first tube. In this case, the status window shows an error message and it is necessary to correct the setting.

Note: if one or more carousel positions between the first and last tube are empty, the instrument will diagnose a leak for that position and pass to the next.

Tube Repeat

Indicates the number of repetitions (1-100) for the same sample. The sequence of events is identical for all the repetitions.

Split

Selects the split option between the tube and the trap.
Select the split option (✓) if you want to eliminate part of the desorbed sample from the tube before it enters the trap, for example with highly concentrated samples.
Adjust the split flow rate by using the needle valve located on the backside of the instrument (see "*Gas Press Flow*" section in the *Manual Operation* paragraph of this chapter). To display the split flow rate select *TD Status* command and verify the *Split Flow* and the *Split Ratio*.

Dry Step

Select this option to eliminate water in the sample. Select the dry step option (✓) if you want to eliminate water from the sample before the primary desorption.
In this case you must set a time (*Dry Step* in the Temp-Press/Flow-Time page) and a temperature (*Dry Step* in the Temp-Press/Flow-Time page) for this phase.
The Dry Step time and temperature are available only if the Dry Step option in the "Command" page is enabled (✓).

Step 1 (up to Step 6)

In each step it is possible to choose among *None, Sample, Blank* and *Calibration*, depending on which order the operator wants the analysis to be performed.

Repetitions

In these text boxes it is possible to select the number of repetitions of each *Step* (1 - 100). The text box is active only if in the corresponding Step you have selected *Sample, Blank* or *Calibration*.

Cycle Repeat

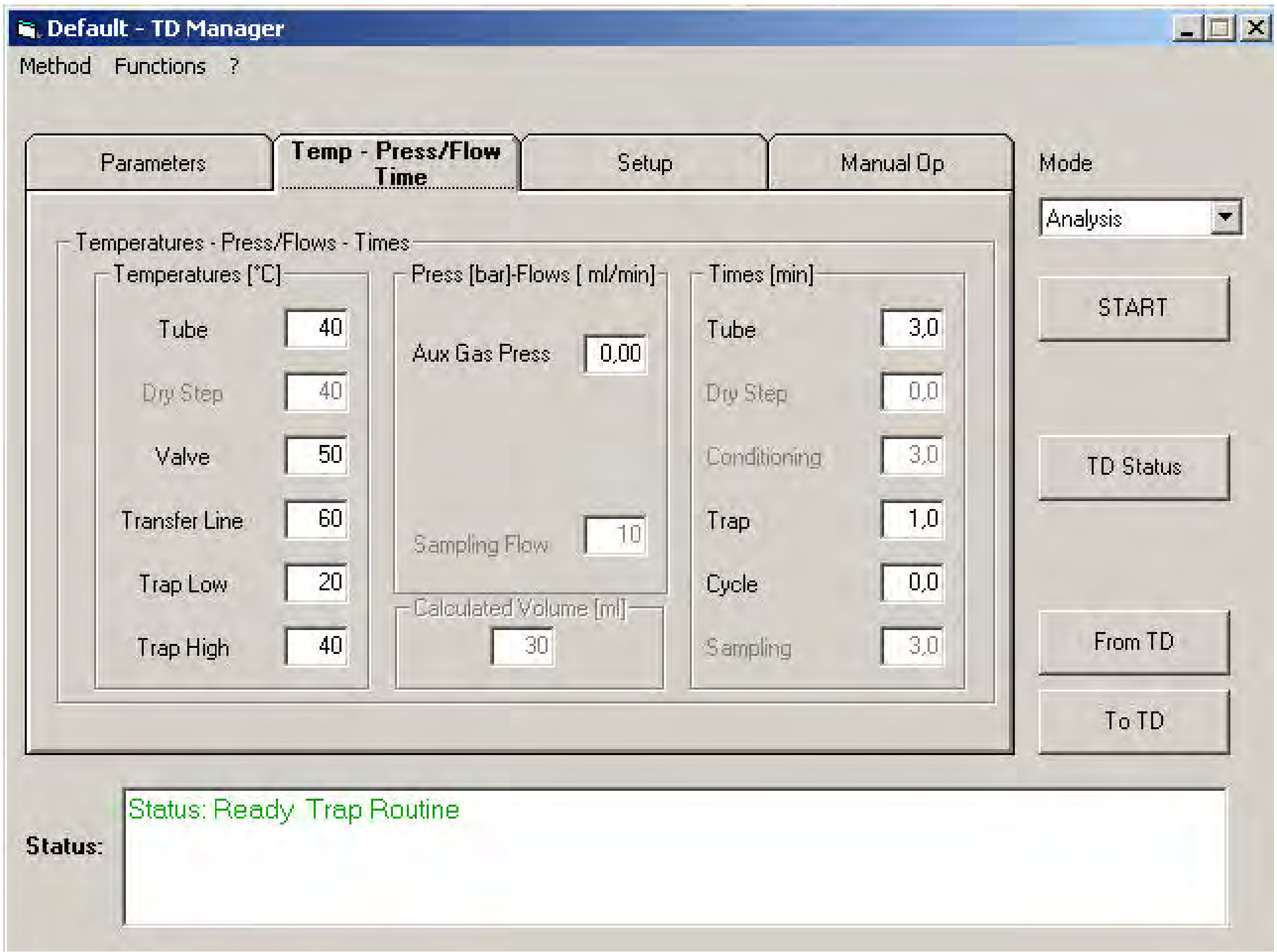
Indicates how many times the whole *step* cycle must be repeated (0 - 100).
0 refers to an infinite number of repetitions

Line Selector

This section is available only in the Line Selector configuration (*Setup* page). You have to select the number of the line (from 1 to 10) to be analyzed. The whole Step cycle will be performed one time for each sample line

Temp - Press/Flow - Time

Select the *Temp-Press/Flow-Time* page to set the operating parameters.



Mode: Analysis

Temperatures - Press/Flows - Times

Temperatures [°C]
Tube: 40
Dry Step: 40
Valve: 50
Transfer Line: 60
Trap Low: 20
Trap High: 40

Press [bar]-Flows [ml/min]
Aux Gas Press: 0,00
Sampling Flow: 10

Calculated Volume [ml]: 30

Times [min]
Tube: 3,0
Dry Step: 0,0
Conditioning: 3,0
Trap: 1,0
Cycle: 0,0
Sampling: 3,0

Status: Status: Ready Trap Routine

Figure 5-4 - Temp-Press/Flow-Time page

- Temperatures [°C] -

The *Temperatures* section on the left of the page contains the temperatures of all the heating and cooling devices.

The following table shows the parameters available (written in black colour) according to operating mode.

Analysis	**Conditioning**	**Multiple Desorption**	**Direct Sampling***	**Trap Routine**
Tube	Tube	Tube	-	-
Dry Step**	-	-	-	-
Valve	Valve	Valve	Valve	Valve
Transfer Line	Transfer Line	Transfer Line	Transfer Line	Transfer Line
Trap Low	-	Trap Low	Trap Low	-
Trap High	-	Trap High	Trap High	Trap High

* *Available only if the AIR Sampler (Single Line or Line Selector in Setup page) is configured*
** *Available only if the Dry Step in "Parameters" page is selected (✓)*

Tube

Indicates the temperature (40–400°C) used for heating the tube during the desorption phase. If a temperature set is higher than the maximum safety temperature, the software will display an error dialog box containing the correct parameter range. The operator must select OK and modify the value.
In the *Direct Sampling* and *Trap Routine* operating modes there is no tube treatment and this parameter is not available.

Dry Step

Indicates the temperature (30–100°C) of the tube during the *Dry Step* phase.
This parameter is available only if the *Dry Step* option (*Parameters* page) is active.

Valve

Indicates the heating temperature (50–300°C) of the switching valve.

Transfer Line

This is the transfer line temperature (50–290°C).

Trap Low

This is the lower trap temperature (-40–30°C). The trap is kept at this temperature during the tube desorption step.

Trap High

This is the upper trap temperature (30–450°C). The heating device heats up 3 minutes before start of the trap desorption phase. If a temperature set is higher than the maximum safety temperature the software will display an error dialog box containig the correct parameter range. The operator must select OK and modify the value.
The trap cooling and heating devices are not active in the Conditioning mode.

- Press [bar] - Flows [ml / min] -

The *Press-Flows* section in the middle of the page contains the text boxes to set the auxiliary gas pressure and the sampling flow rate values.

Aux Gas Press

Indicates the pressure (0.00–4.00 bar) of the gas used for desorbing the tube.

Sampling Flow

This text box is available only if the AIR Sampler is configured (see *Setup* paragraph in this chapter).
Represents the flow of the gaseous sample through the trap (10-100 Nml/min). All flows refer to Normal conditions (0°C and 1 atm). The flow measured by the instrument can differ from the flow measured with a bubble flowmeter because local and reference conditions are not the same

Calculated Volume

It shows the calculated sampling volume. It is the result of sampling flow multiplied by sampling time.

- Times [min] -

The *Times* section on the right of the page contains the text boxes to set the duration of operating steps.
The table below shows the displayed parameters according to operating mode

Analysis	**Conditioning**	**Multiple Desorption**	**Direct Sampling***	**Trap Routine**
Tube	-	-	-	-
Dry Step	-	-	-	-
-	Conditioning	-	-	-
Trap	-	Trap	-	Trap
Cycle	-	Cycle time	-	Cycle
-	-	-	Sampling	Sampling

***** *Available only if the AIR Sampler (Single Line or Line Selector in Setup page) is configured*

Tube

Sets the duration of the primary tube desorption phase (3.0–999.9 min). A minimum time of 3 minutes is necessary for heating the trap.

Dry Step

Sets the duration of the Dry Step phase (0.0-999.9 min).
This parameter is available only if the Dry Step option (*Parameters* page) is active.

Conditioning

Indicates the duration of conditioning for each tube (3.0-999.9 min).

Trap

Indicates the time of the trap heating phase (0.0-999.9 min).

Cycle

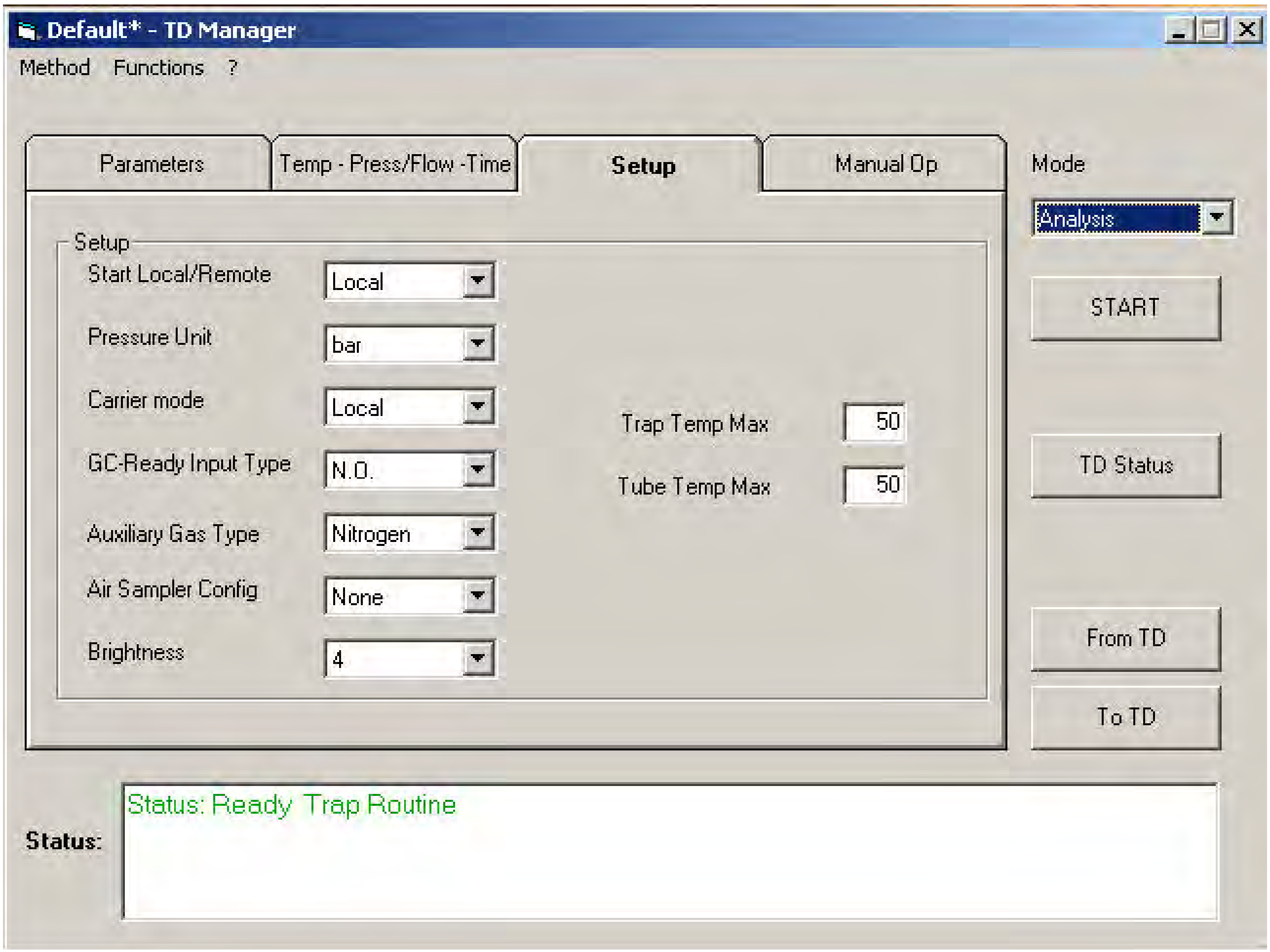
Indicates the time interval (0.0– 999.9 min) between one desorption and the next. This time must at least coincide with the time the gas chromatograph requires for effecting the analysis and returning to Ready conditions. In this way, the second tube and the following ones can undergo desorption before the previous analysis has been completed and the GC is in Ready conditions.
This parameter is only active if the instrument start has been configured for local control. The parameter is not considered if the instrument start is in remote control mode (see *Setup* paragraph in this chapter).
In the *Multiple Desorption* mode this phase has a minimum setting of eight minutes longer than trap time, so that all the events can be carried out. If you set a cycle time shorter than trap time added by eight minutes, when you send the method to TD, an error dialogue window ("Cycle Time is too low. Can't proceed") will be displayed. You must select OK and modify the value.

Sampling

Represents the duration of the sampling through the trap (3.0 - 999.9 min).

Setup

Select the *Setup* page to configure the Master TD.



Mode: Analysis

Setup

Start Local/Remote: Local

Pressure Unit: bar

Carrier mode: Local

GC-Ready Input Type: N.O.

Auxiliary Gas Type: Nitrogen

Air Sampler Config: None

Brightness: 4

Trap Temp Max: 50

Tube Temp Max: 50

Status: Status: Ready Trap Routine

Figure 5-5 - Setup page

Start Local / Remote

This function establishes the control method between the Master TD and the gas chromatograph. By selecting *Local*, the sampling sequence starts without verifying the condition of the gas chromatograph. The second tube and the following ones will be sampled at regular time intervals defined by the *CycleTime* parameter.
By selecting *Remote* the sequence can only be started if the gas chromatograph is in the Ready condition. Each subsequent tube will be sampled when the gas chromatograph registers a Ready condition. The *CycleTime* parameter no longer has any effect.

Pressure Unit

In this text box you can select the pressure measurement unit choosing among bar, psi and kPa. The default unit is bar.

Carrier Mode

This text box is used to select whether the instrument must indicate only the presence or absence of carrier gas or display the carrier gas pressure value.
The default value provides the reading of the pressure value because the carrier gas is usually supplied and controlled by the gas chromatograph.

GC-Ready Input Type

With this function it is possible to configure the type of contact from the gas chromatograph as a *ready* signal. Master TD is configured to be connected to a gas chromatograph with a relay which is Normally Open (N.O.) and the *Ready* signal is produced by closing a contact, which is how DANI gas chromatographs operate.
Select the N.C. option if the gas chromatograph connected to the Master TD has a Normally Closed relay and produces a *Ready* signal by opening a contact.

Auxiliary Gas Type

The flow rates displayed for Split and Vent flows depend on the type of gas used for primary desorption.
Select the auxiliary gas type choosing among Hydrogen, Nitrogen and Helium.

Air Sampler Config

With this function it is possible to configure the AIR Sampler device.
The default selection is None, which means that Master TD isn’t configured to work with AIR Sampler.
Master TD can control the AIR Sampler when you select Single Line or Line Selector.
Choose *Single Line* when the AIR Sampler has the standard configuration and *Line Selector* when the AIR Sampler is equipped with the line selector option (check the ten inlets on the back side of the AIR Sampler)

Trap Temp Max

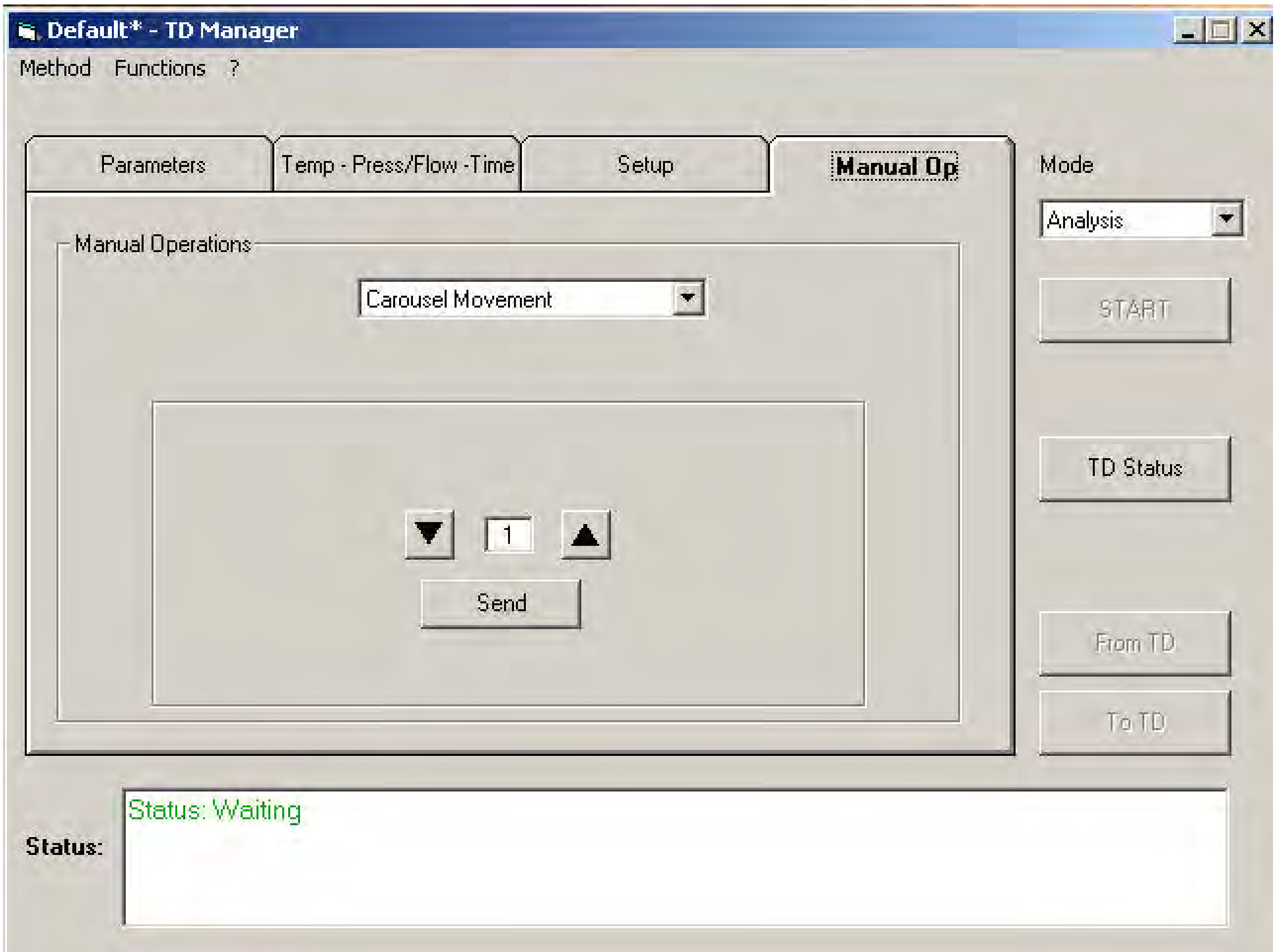
Sets the maximum trap safety temperature (50 - 450°C) based on the maximum temperature to use for the trap sorbent material.
If a trap temperature above the maximum is set in the method, an error dialogue window ("Trap Temp Max < Trap High Temp. Can't proceed") will be displayed when you send the method to TD. You must select OK and modify one of the two values.

Tube Temp Max

Sets the maximum tube safety temperature (40 - 400°C) which depends on the maximum temperature to use for the tube sorbent material.
If a tube temperature above the maximum is set in the method, an error dialogue window ("Tube Temp Max < Tube Temp. Can't proceed") will be displayed when you send the method to TD. You must select OK and modify one of the two values.

Manual Op

In this page it is possible to enable or disable some electrical and pneumatic devices in manual mode separately from each other.
The options selectable in this page are particularly useful for diagnostic operations or for setting up analysis.
Select the *Manual Operation* page



Status: Waiting

Figure 5-6 - Manual Op page

The visualization in the combo box depends on the manual operation selected in the text box menu in the middle of the page.

Carousel Movement

Use this function to load or remove tubes from the carousel. You can rotate the carousel in one direction or the other clicking ▲ , ▼ or inserting directly the number of the position desired (e.g. insert 24 if you want the tube 24 to be under the heater). When you change page, the carousel will automatically return to the standby position which is number 1 under the heater.

Tube Movement

Click ▲ to lift up the tube under the heater, or ▼ to let it down.

Sampling Valve

There are two keys: ON and OFF. When the sampling valve is ON, the ON key is green and only the OFF key is available and viceversa. Click the available key to change the sampling valve status.

Trap Shifting

There are two keys: PELTIER and HEATER. Click PELTIER when you want to shift the trap in the cooling zone and click HEATER if you want to shift the trap in the heating zone. The green colour of the key indicates the actual trap position. The two keys become both yellow during the trap movement.

Split Valve

There are two keys: OPEN and CLOSE. When the split valve is OPEN, the OPEN key is green and only the CLOSE key is available and viceversa. Click the available key to change the split valve status.

Vent Valve

There are two keys: OPEN and CLOSE. When the vent valve is OPEN, the OPEN key is green and only the CLOSE key is available and viceversa. Click the available key to change the vent valve status.

Injection Valve

There are two keys: TRAP and BY-PASS. When the option TRAP is selected (the relative key is green) the gas carrier flows through the trap to the GC. When you click BY-PASS the gas carrier flows directly to the GC by-passing the trap.

Gas Press/Flow

The *Gas Press/Flow* option allows you to control the pneumatic circuit. It contains a submenu with three groups (see the table below). Whenever you select one group, the options in the combo box change as follows:

Desorption Gas	Tube Split	Carrier Gas
Aux Gas Flow (ml/min)	Split Flow (ml/min)	Carrier Gas (bar)
Aux Gas Press (bar)	Split Ratio (1:--)	

The numbers displayed are all actual values that means they can't be modified, with the exception of AUX GAS PRESS parameter which has a set and an actual value. Click SEND when you want to send the new set value to the Master TD.

To setup the analysis flow rates, insert a tube and lift it with the *Tube Movement* function; enter an AUX GAS PRESS value and read the desorption flow rate (AUX GAS FLOW); if necessary open the split solenoid valve with the *Split Valve* function and adjust the flow rate using the needle valve on the backside of the instrument: display both the SPLIT FLOW and the SPLIT RATIO (see *Setting and Starting Up a method* chapter).
The CARRIER GAS function indicates the presence or the lack of pressure on the carrier gas line (numeric value when the carrier gas control is local, and ON/OFF when the carrier gas control is remote).

All flows refer to Normal conditions (0°C and 1 atm). The flow rate measured by the instrument can differ from the flow rate measured with a bubble flowmeter because local and reference conditions are not the same.

Counters

This function visualizes the *Valve Counter* and the *Trap Heaters Counter*. These are both actual values and can't be modified.

The *Valve Counter* function indicates how many times the valve has been activated. This information is used by technical assistance personnel to evaluate the use of the instrument.

The *Trap Heaters Counter* indicates how many times the trap has been heated. This information makes it possible to evaluate when is the best time to replace the trap sorbent. However, the duration depends on the type of material and the temperature that is used.

Heaters - Mechanical Test

These two functions require a password and must be used only by DANI authorized technical personnel.

When DANI Air Sampler is configured, there are some more device options that can be manually enabled. You can find the following additional options in the scroll bar in the middle of the page:

Air Sampler Pump

There are two keys: ON and OFF. When the Air Sampler pump is switched ON, the ON key is green and only the OFF key is available and viceversa. Click the available key to change the Air Sampler pump status.

Inlet Line

There are two keys: ▲ and ▼. Click them to select SAMPLE, BLANK or CALIBRATION to activate the corresponding solenoid valve.

Line Selector

There are two keys: ▲ and ▼. Click them to select the number (from 1 to 10) of the solenoid valve you want to activate

Method menu

New

Creates a new method. When invoked a new file *"Default"* is created. Temperature, pressures, times and the other parameters in the pages are set to the minimum value.
No file may be saved under the name Default.

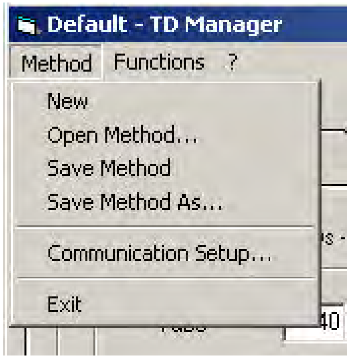


Figure 5-7 - Method menu

Open Method

Selects and opens a method. When invoked, the opened *Open* dialog box enables the user to select the method. The method will be then loaded and its name displayed in the TD Manager window title bar.

Save Method

Saves the method. If a new file has to be saved, this command has no effect. In this case use *Save Method As* instead. The *"Default"* name is reserved for new, as yet not saved files.

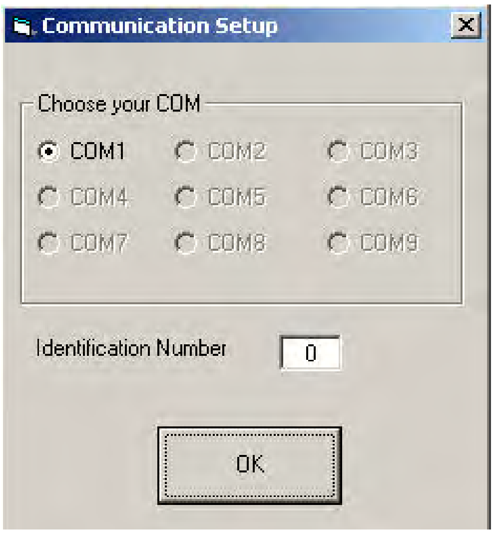
Save Method As

Saves a method under a selected name and/or to another directory. The command opens the *Save As* dialog box. Here a new name can be entered or a new directory selected.

Communication Setup

The command opens a configuration window. It appears the first time the user click on the TD Manager icon or selecting *Communication Setup* from the *Method* menu.

The number of the *COM* port must correspond to the number of the PC's serial port where Master TD is connected.
Selecting the wrong *COM* number will not allow the communication between TD Manager and Master TD.



Choose your COM
● COM1 ○ COM2 ○ COM3
○ COM4 ○ COM5 ○ COM6
○ COM7 ○ COM8 ○ COM9

Identification Number: 0

Functions menu

Method Sequence

The command opens the window below.
The option must be enabled checking the Method Sequence text box on the left.
The user can select up to four saved methods to be managed in sequence by Master TD. When complete, the sequence can be sent to Master TD using the command *To STD* on the right.

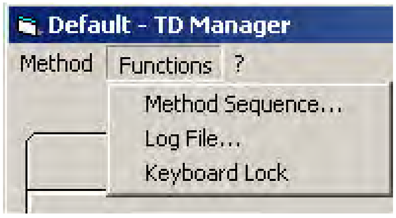
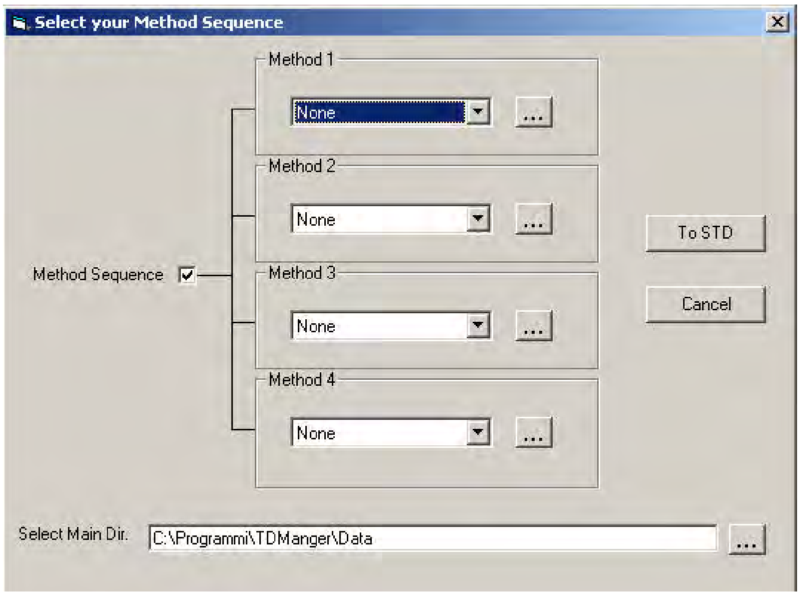


Figure 5-8 - Functions menu

Log File

Contains information regarding the last 100 sampling sequences. The last sequence carried out in chronological order is memorized as RUN 1, the previous as RUN 2 and so on.
For each new sequence the LOG FILE updates the information recorded in RUN 1 with those of



Method Sequence ☑

Method 1: None
Method 2: None
Method 3: None
Method 4: None

Select Main Dir.: C:\Programmi\TDManger\Data

the last sequence and moves all the others by one position.
The information on the hundredth previous sequence is lost.
For each sequence the method used to perform the sequence and operating mode are shown.

Keyboard Lock

Disables the TO TD key to avoid, for example, accidental modification of a method. When selected a check sign appears on the left and a red note is written in the status window.

Note: the keyboard is automatically locked while a method is being carried out and it is impossible to unlock it.

"?" menu

About

Contains information about the TD Manager version.

Developing a method

Principle of thermal desorption

Thermal desorption consists in extracting volatile compounds from a matrix using heat and a flow of inert gas and transferring them directly to an analytic system, normally a gas chromatograph.

Sampling

The samples can be gathered by trapping volatile compounds present in a gaseous matrix in a tube containing an opportune sorbent (figure 6-1) or by inserting a solid sample directly into a tube (Figure 6-2).

Two-stage desorption

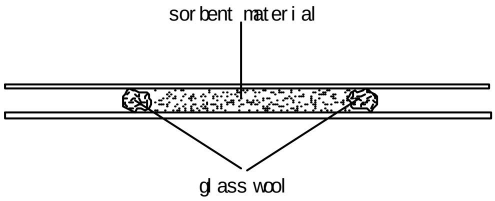


Figure 6-1- Tube filled with sorbent material

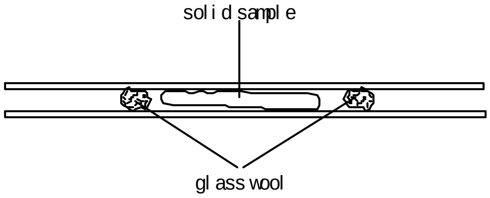


Figure 6-2 - Tube with solid sample

Compounds which are thermally extracted from a tube can be directly transferred to a chromatograph column, according to techniques called “single stage” (Figure 6-3). However, this procedure, although simple, transfers compounds in such a wide band that it impairs chromatographic separation.

This problem is resolved by concentrating the compounds desorbed from the tube on a focalization device to transfer them to the analytic column and with a further heating in a volume of gas reduced as much as possible. This technique, called “double step desorption” can be performed in two ways with:

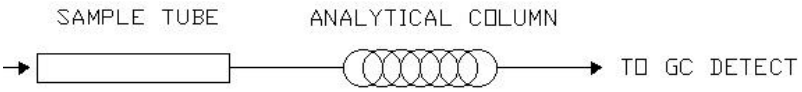


Figure 6-3 - Single stage desorption

- cryfocalization on capillary column
- focalization on a packed trap

In the first instance the volatile compounds are focalized in a section of capillary column kept at a very low temperature (Figure 6-4). This system requires the use of cryogenic fluids and is easily subject to the formation of ice with subsequent block of the transfer fluid.

In the other case, the use of a trap filled with sorbent and electrically cooled has the advantage of retaining the quantity of even very volatile compounds without requiring the use of cryogenic fluids and notably limiting the risk of ice formation, but guaranteeing a sufficiently quick desorption to produce peaks compatible with capillary columns (Figure 6-5).

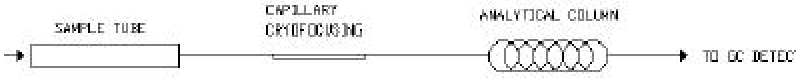


Figure 6-4 - Cryofocusing

The later is the solution adopted by the Master TD thermal desorber.

Fields of application

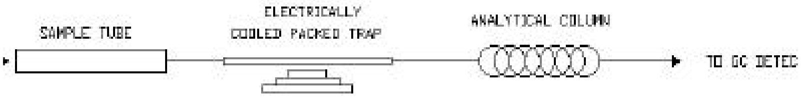


Figure 7-5 - Focusing on cold packed trap

Thermal desorption can be applied to almost any compound normally analyzed by gas chromatography in an interval of truly broad concentrations (from ppt to percentages).
The main field of application is for environmental analysis to identify the volatile and semi-volatile organic contaminants in the atmosphere and in work environments and emissions from building materials and products for domestic use.
Thermal desorption is also widely used to extract volatile organic substances present in matrices which cannot be directly injected into a gas chromatograph such as solid samples, emulsions, saline solutions etc. The principal applications regard identifying the residual solvents in pharmaceutical products, in wrapping and packing, monomers in polymers, analysis of flavor and fragrances, foods and beverages, exhaust etc.

The application limits of thermal desorption obviously involve compounds which cannot be analyzed by gas chromatography, compounds which deteriorate at temperatures lower than those required for their desorption.

Method Objectives

Setting an analytical method must have the following objectives:

- Completely (or almost totally) desorb the compounds in question from the tube
- Completely trap the desorbed compounds in the trap
- Quantitatively elute the compounds from the trap and transfer them in the narrowest band possible to the analytical column.

The parameters used to reach these analytical objectives are:

- tube desorption, high and low temperature
- time of tube desorption and trap desorption
- flow of tube desorption, carrier gas and split
- type and quantity of sorbent.

Temperatures

Tube desorption temperature

Select the tube heating temperature so that the desired compounds are completely desorbed from the tube. The temperature must be as high as possible taking into consideration the maximum temperature limit of the sorbent and the thermal stability of the compounds. However, it is unadvisable to desorb at a temperature near the temperature limit: the higher the temperature the greater the deterioration of the sorbent material and the consequent release of contaminating substances.
In tubes filled with different sorbents the temperature limit of the most heat sensitive sorbent needs to be considered.

The list below shows the temperature limits for some sorbents and the use temperature normally adopted for desorption.

Material	Max.temperature (°C)	Desorption temperature (°C)
Tenax TA	350	300
Tenax GR	350	300
Porapak Q	250	225
Porapak N	180	180
Carbotrap Carbopack Anasorb GCB1	>400	325
Chromosorb102	>250	225
Carbosieve S-III Carboxen 1000 Anasorb CMS	400	325
Molecular Sieves 13X	350	300

Lower trap temperature (adsorption)

Select the lower trap temperature so that the amount of substance desired is recovered. The minimum selectable temperature is - 40°C but -5°C is usually sufficient for trapping most compounds, as long as an appropriate sorbent is used.

Higher trap temperature (desorption)

The higher trap temperature must guarantee total desorption of the focalized compounds in a time short enough to concentrate the compounds in a reduced volume of gas.
Again in this case the temperature is limited by the maximum use temperature of the sorbent and the thermal stability of the compounds, as well as for the tube desorption temperature.

Note: in some cases the trap sorbent may be different from the tube sorbent and thus have a different thermal stability.

Times

Primary desorption time

The tube desorption time must be such as to guarantee, along with the flow rate and desorption temperature, total extraction of the compound in the shortest amount of time possible, this is to increase productivity over time. Desorption time normally varies between 15 and 30 minutes, based on the flow rate and desorption temperature.

Trap desorption time

The trap desorption time must be such as to guarantee total transfer of the compounds to the gas chromatograph column. A slightly longer time ensures that the trap is clean and free from any interference which could appear in subsequent analyses.

Flow rates

Auxiliary gas flow rate

The tube desorption flow rate must be optimized so that total extraction of the compounds is achieved in a relatively short time at the same time facilitating focalization in the trap.

Flow rates which are too low can limit extraction and increase the desorption time. Flow rates which are too high can make it difficult to retain the compounds in the trap. Normally 30-50 mL/min is used. The use of higher flow rates is advisable for desorbing heat sensitive compounds, when the temperature is limited.

When the split option is used, the total effective desorption flow rate is given by the split rate and the gas rate at the vent outlet. By using the split it is possible to desorb with a higher flow rate keeping a limited adsorption rate in the trap. Because the split reduces the absolute quantity of sample transferred to the trap it can only be applied to sufficiently concentrated compounds.

Trap desorption flow rate

The trap desorption rate must guarantee, along with the temperature, a total transfer of the substances and as quickly as possible to the gas chromatograph column.

The minimum flow rate for transfer compatible with capillary columns is around 7-8 mL/min. The flow of carrier gas in the trap is given by the sum of the column flow rate and the split flow rate at the injector. Thus, when using high resolution capillary columns (0.25-0.32 mm inner diameter) with column flow rates around 0.5-2.0 mL/min, it is necessary to regulate the split to a minimum flow rate of 5-10 mL/min to ensure a sufficiently fast transfer. Since using the split reduces the absolute quantity of sample entering the column, the sensitivity limit is reduced.

Actually, the absolute quantity of sampled and pre-concentrated substances in the tube is practically always high enough to ensure a sufficient sensitivity even in split conditions and with a non-specific detector such as a flame ionization detector.

High split flow rates can be used when treating highly concentrated samples to prevent saturating the analytical column.

It is possible to work without the split and to introduce 100% of the desorbed sample into the analytical column if using semi-capillary type (0.53 mm or greater inner diameter) or packed columns which normally work with carrier gas flow rates above 8 -10 mL/min.

Type and quantity of sorbent

Tube sorbent

Select a sorbent which has a sufficient capacity for trapping the desired compounds.

The table below provides some guidelines for selecting a sorbent. For more information refer to the numerous methods published on active or diffusive sampling and the subsequent thermal desorption of volatile and semi-volatile compounds or the indications suggested by sorbent or pre-filled tube manufacturers.

Sorbent	Volatility interval (approx.)	Examples
Carbotrap C Carbopack C Anasorb GCB2	from n-C8 to n-C20	Alkylbenzenes and aliphatics with volatility between n-C8 and n-C16
Tenax TA	b.p. from 100°C to 450°C from n-C7 to n-C26	Aromatics. Apolar compounds (b.p.>100 °C) and less volatile polar compounds (b.p.>150°C)
Tenax GR	b.p. from 100°C to 450°C from n-C7 to n-C30	Alkybenzenes, PAH and PCB in vapor phase and like Tenax TA
Carbotrap Carbopack B Anasorb GCB1	from (n-C4) n-C5 to n-C14	Wide range of VOC including ketones, alcohols, aldehydes (b.p.>75°C) and all apolar compounds in the specified volatility range
Chromosorb 102	b.p. from 50°C to 200°C	Wide range of VOC including less volatile compounds of oxygenated and halogenated CH2Cl2
Chromosorb 106	b.p. from 50°C to 200°C	Wide range of VOC including hydrocarbons from n-C5 to n-C12. Also suitable for oxygenated volatile compounds.
Porapak Q	b.p. from 50°C to 200°C	Wide range of VOC including oxygenated compounds
Porapak N	b.p. from 50°C to 200°C	Specific for volatile nitriles; acrylonitrile and propionitrile. Also suitable for pyridine, volatile alcohols from EtOH, MEK, etc.
*Spherocarb	b.p. from -30°C to 150°C from C3 to n-C8	Suitable for highly volatile compounds like VCM, ethylene oxide, CS2 and CH2Cl2. Also suitable for polar volatiles e.g. MeOH, EtOH and acetone.
*Carbosieve S-III *Carboxen 1000 *Anasorb CMS	b.p. from -60°C to 80°C	Suitable for extremely volatile compounds such as hydrocarbons C3 and C4, volatile halogenated substances and Freon.
**Molecular Sieves	b.p. from -60°C to 80°C	Specific for 1,3-Butadiene and N2O.

** These sorbents are slightly hydrophilic. If the sampling is done in a very humid atmosphere (RH>90%), the trapping capacity of these sorbents decreases approximately 10 times.*

*** This sorbent is highly hydrophilic. It is unadvisable to use it in particularly humid atmosphere.*

If more than one sorbent is suitable for the specific application, select the most hydrophobic to limit water being trapped and the one with the least production of adulteration.

If the sample is composed of a mixture of compounds with a wide range of boiling points, it is useful to use tubes with more than one sorbent (multi-layer). Multi-layer tubes are also advisable when the sample composition is unknown because the combination of sorbents makes it possible to trap almost all the compounds.

Note: multi-layer tubes can only be used for active sampling.

In multi-layer tubes the sorbents are placed in order of increasing adsorption capacity (from the weakest to the strongest). The sample must enter from the end with the weakest sorbent and flow towards the strongest sorbent.

Desorption must occur in the opposite direction, from the strongest to the weakest. In this way, the compounds with higher boiling points are trapped first and desorbed first and do not come into contact with the sorbent with a greater adsorption capacity.

Figure 6-6 shows an example of a multi-layer tube.

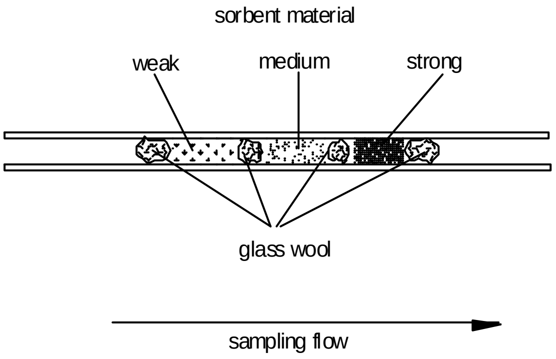


Figure 6-6 - Example of a multilayer tube

Note: it is unadvisable to fill a tube with two sorbents with very different maximum desorption temperatures because it is difficult to perfectly condition the most resistant one without causing deterioration to the less stable one.

The quantity of material inside the tube is normally given in terms of length of the filled section, referred to a standard inner diameter of 5 mm, or in weight.

The tubes contain from 200 to 1000 mg of sorbent depending on the density, for example approximately 250 mg of porous polymers (Tenax, Chromosorb, Porapak) and 500 mg of graphitized carbon or carbon molecular sieves. The recommended mesh size, even if not exclusive, is 60-80 mesh.

The length of the filled section must not exceed the heating area and thus approximately the center 6 cm. The sorbent is held at the two ends by glass wool plugs or special stainless steel retention springs and gauzes.

Note: glass tubes have an inner diameter of 4 mm. Thus with the same length the amount of sorbent is less.

Trap sorbent

Since the trap can operate at temperatures below room temperature and because it must maintain the compounds for a relatively short time, a few minutes, normally it can be filled with a sorbentwith a lower retention capacity than that used in the tube.

The table below gives some guidelines on trap sorbent based on the sorbent used in the tube.

Tube sorbent	Trap sorbent
Carbotrap C Carbopack C Anasorb GCB2	Tenax or Carbopack C
Tenax TA	Tenax
Tenax GR	Tenax
Carbotrap Carbopack B Anasorb GCB1	Tenax or Carbopack B
Chromosorb 102	Double layer CB+CMS or Chrom102
Chromosorb 106	Double layer CB+CMS or Chrom106
Porapak Q	Double layer CB+CMS or Porapak Q
*Spherocarb	Double layer CB+CMS or Spherocarb
*Carbosieve S-III *Carboxen1000 *Anasorb CMS	Double layer CB+CMS or only CMS
**Molecular sieves	Double layer CB+CMS or only CMS
Double layer Tenax + CB	Tenax
Double layer Carb B + CMS	Double layer CB+CMS
Triple layer Carb B+Carb C + CMS	Double layer CB+CMS

** These sorbents are slightly hydrophilic. If the sampling is done in a very humid atmosphere (RH>90%), the trapping capacity of these sorbents decreases approximately 10 times.*
*** This sorbent is highly hydrophilic. It is unadvisable to use it in particularly humid atmosphere.*

Master TD desorbs the trap in counter-current so it is possible to use multi-layer traps for sampling in a wide range of boiling points.
Instructions for filling and replacing the trap are in the *Maintenance* chapter.

Using the split

Split between tube and trap

The desorber is fitted with a split outlet between the tube and trap. When the SPLIT option is selected in the method, the outlet remains open during the tube desorption phase. The split outlet gas rate is regulated by a needle valve on the backside of the instrument (See "*Settings and operation*" paragraph in *Operation* chapter to learn how to set the split flowrate).
By activating the SPLIT function, part of the desorbed sample is eliminated and part is refocalized in the trap.
The split ratio expresses the ratio between vent outlet gas rate and split outlet gas rate.
For example, if the vent flow rate is 30 mL/min and the split flow rate is 120 ml/ min, the display will show split ratio 1 : 4.

The fraction of sample transferred to the trap is calculated with the following formula:

$$\%\,\textit{sample to the trap} = \frac{\textit{vent flow rate}}{(\textit{split flow rate} + \textit{vent flow rate})} \times 100$$

In the case above, 20% of the sample desorbed by the tube is transferred to the trap and the remaining 80% is eliminated at the split.
Since the gas flow rate which actually passes through the tube is given by the sum of the two flow rates, the use of the split, applied to highly concentrated samples, makes it possible to increase the desorption gas flow, facilitating the extraction of compounds from the tube and maintaining a relatively low flow in the trap which improves trapping.

Split between trap and analytical column

The split between the trap and analytical column is used when working with capillary columns to increase the desorption flow in the trap and transfer the compounds to the analytical column in a narrow band.
The desorber, connected to the column by the gas chromatograph injector, uses the split function of the gas chromatograph.
The sample fraction which passes from the trap to the column is determined by the ratio between the split outlet gas rate and the column flow rate.

$$\%\,\textit{sample to the column} = \frac{\textit{column flow rate}}{(\textit{column flow rate} + \textit{GC split flow rate})} \times 100$$

If the split between the tube and trap is going to be used at the same time as the one between the split and injector, the percentage of sample which is introduced into the column is calculated with the following formula:

$$\%\,\textit{sample to the column} = \frac{\textit{vent flow rate}}{(\textit{split flow rate} + \textit{vent flow rate})} \times \frac{\textit{column flow rate}}{(\textit{column flow rate} + \textit{GC split flow rate})} \times 100$$

For example, by considering the following flow rates:

vent flow rate	30 ml/min
split flow rate	120 ml/min
column flow rate	2 ml/min
injector split flow rate	8 ml/min

the percentage of sample transferred to the column is 4% of the quantity desorbed by the tube.

Using the “Dry Step”

The *Dry Step* function involves passing a flow of inert gas in the tube at a relatively low temperature for a set amount of time to eliminate any water present in the sample before desorption, to prevent transferring a large quantity of water to the trap and then to the analytical column.

Even though the *Dry Step* function is available, it is important that the first precautionary measure taken with very humid samples be to use highly hydrophobic sorbents and thus limit as much as possible the amount of water trapped at the source.

In selecting operating conditions, evaluate the possible leakage of more volatile substances together with the water by comparing recovery with and without *Dry Step*.

Calibration

Calibration of the STD-GC system requires the use of a procedure which is as close as possible to actual sampling conditions.

Calibration with gaseous mixtures

In the event of gaseous samples (atmosphere, air in work environments etc.), the best procedure consists in loading a tube with the required quantity of compounds through a gaseous calibration standard. This can be done in two ways:

- *Using standard atmospheres*
  Prepare a standard atmosphere with a concentration of substances and humidity level as similar as possible to the sample atmosphere. The standard atmosphere must be loaded in the active sampling tube at the same flow rate conditions used for the sample.
- *Using concentrated pressurized standard calibration mixtures*
  If a gas cylinder with a concentrated standard mixture is available, sample a known volume (between 0.5 and 5.0 ml) using a sampling valve with a metering loop so as to introduce the same absolute quantity of substance collected for a normal sample.
  Introduce the standard from the sampling end of a conditioned tube and flow with at least 10 times the volume of the capillary with a pure inert gas to completely transfer the contents from the valve to the tube.

Calibration with liquid mixtures

When it is not practical to use gaseous standards, it is possible to calibrate with liquid standards in two ways:

- *Vaporizing a liquid standard through an injector.*
  Connect the sampling end of a pre-conditioned tube to an injector for packed columns. Keep the injector at room temperature and adjust the flow rate to approximately 100 mL/min of pure inert gas. With a normal syringe for liquids introduce a volume of liquid through the injector.
  The solvent and the substances will enter the tube in a vapor phase. For standards containing less volatile compounds than C12 it is opportune to slightly heat the injector (approximately 50 °C).
  Wait until all the substances and solvent have passed from the injector to the tube. Use a very pure solvent and, if possible, more volatile than the substances to be analyzed. In addition, it is preferable to choose a solvent which is not retained by the sorbent (for example Methanol on Tenax or CarbopackB): in this case leave the tube connected until all the solvent has been eliminated (approximately 5 minutes in the specified conditions).
  If the mixture contains highly volatile compounds select a solvent which separates easily from the compounds to be analyzed (for example Ethyl Acetate) or use a gaseous standard.
  The concentration of the standard must be calculated so as to introduce an absolute quantity of substances that is the same size as that expected from the sample collection in a volume of liquid between 0.5 and 10.0 µL.
  If using an untreated solvent, it is possible to introduce higher volumes (5-10 µl) improving the accuracy of the introduction. If using a treated solvent it is advisable to introduce reduced volumes (0.5-1.0 µL) of more concentrated solutions to minimize interference caused by the solvent peak.
  At the end disconnect the tube and hermetically seal it.
- *Direct introduction of a liquid standard.*
  Introduce a volume of liquid directly from the tube outlet end. The sample must be deposited “behind” the sorbent bed so that during desorption the compounds pass the sorbent simulating actual adsorption conditions as much as possible.

Standard certified tubes are available on the market which can be used to check the accuracy of the analytical system.

Calculating the concentration of the liquid standard

The concentration of the standard must be calculated so as to introduce an absolute quantity of substances of the same size as that expected from sample collecting.
The mass of a substance present in a volume of air is calculated using the Boyle’s law according to which a mole of pure gas occupies approximately 22.4 liters at 25 °C and atmospheric pressure.

Considering, for example, Benzene (mol. wt. 78) calculate:

- 1 mole of benzene gaseous weighs 78 g and occupies 22.4 l
- 1l of pure Benzene gaseous weighs 3.19 g
- 1l of an atmosphere containing 100 ppm of Benzene contains 319 ug of Benzene
- 1l of an atmosphere containing 1ppm of Benzene contains 3.19 ug of Benzene
- 1l of an atmosphere containing 1 ppb of Benzene contains 3.19 ng of Benzene

Considering a Benzene concentration in the atmosphere between 0.5 and 25 ppb, if a 5 l volume of air is sampled, the mass of Benzene introduced with a liquid standard must be between 8 and 400 ng.

In the event of diffusive sampling (see *Sampling techniques* chapter), knowing the U diffusive uptake rate of the tube and the sampling time it is possible to calculate the absolute quantity of substance according to the formula:

$$U\,(ng\,ppm^{-1}\,\mathrm{min}^{-1}) = \frac{adsorbed\,mass\;(ng)}{atm.conc.\,(ppm)\times \mathrm{exp.}time(\mathrm{min})}$$

In the case of Benzene, the diffusive uptake rate (U) of a standard dimension tube, filled with Tenax GR, at 25°C and atmospheric pressure is 1.81 ng ppm^{-1} min^{-1}, where ppm is the atmospheric concentration and min the exposure time.
If an atmospheric concentration of 1 ppm is expected and an exposure time of 8 hours (480 min) it is possible to calculate that the benzene mass calculated will be approximately 850 ng.
A solution at 0.1% can be prepared and 1 ul injected in the tube to introduce approximately 1 ug.

Sampling techniques

Tubes for thermal desorption are used with gas and solid samples by applying different sampling techniques.

For gas samples the following techniques are used:

- diffusive sampling
- active sampling

Diffusive sampling

Diffusive sampling (also called passive sampling) is a simple, low-cost air sampling procedure. It does not involve initial costs for purchasing sampling pumps and the consequent maintenance expenses; it is also the method preferred by workers involved in monitoring campaigns as it the small, light-weight simple sampler does not affect their normal working habits.

Principle of diffusive sampling

Diffusive samplers are exposed to the air for a certain period of time. The organic vapors migrate inside the tube by diffusion and are trapped by the sorbent.

The mass of a substance which spreads from the environment in a certain sorbent is determined by an equation derived from the first of Fick’s law:

$$m_s = \frac{A \cdot D \cdot (\rho_1 - \rho_2) \cdot t}{l} \qquad (1)$$

where:

m_s = mass equals the substance adsorbed by diffusion (µg)
A = surface of the sampling tube section (cm^2)
D = diffusion coefficient in the compound air (cm^2/min)
ρ_1 = concentration of the substance in the air outside the tube (µg/cm^3)
ρ_2 = concentration of the substance near the sorbent (µg/cm^3)
l = distance between the end of the tube and the sorbent (cm)
t = sampler exposure time (min)

In ideal conditions, ρ_2 is equal to 0 because the sorbent, due to effect of the adsorption mechanism, reduces the concentration of the substance and acts as a force for the diffusion along distance *l*.

In these conditions, from the equation (1), for $\rho_2 = 0$, **the diffusive uptake rate *U*** is defined as:

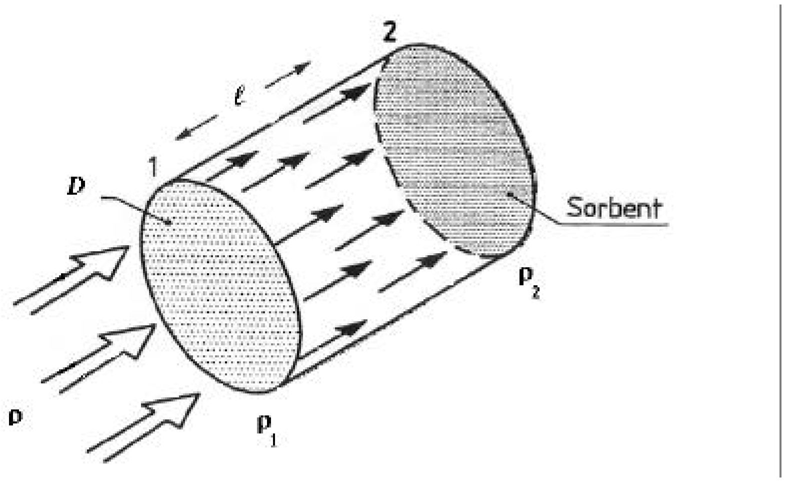


Figure 7-1 - Operating principle of diffusive sampling

$$U = \frac{A \cdot D}{l} = \frac{m_s}{\rho \cdot t} \qquad (2)$$

The diffusive uptake rate U expresses the speed at which a diffusive sampler is able to collect the substance from the atmosphere .
If the diffusion coefficient D of a substance in a certain sorbent and the dimensions of the sampling tube (A and l) are known it is possible to calculate the diffusive uptake rate U for that substance and that sorbent. U dimensions are in cm^3/min.

Once the U value is known, the concentration C of a substance in the sampled atmosphere, in µg/m^3, can be calculated with the following formula:

$$C = \frac{m_s}{U \cdot t} \cdot 10^6 \qquad (3)$$

where:

C = substance concentration in µg/m^3
m_s = mass of the substance present in the tube, in µg
U = diffusive uptake rate, in cm^3/min
t = sampling time, in minutes

Note: to bring a value calculated in the above manner to reference pressure and temperature conditions, for example 25 °C and 101 Kpa, calculate:

$$C_{corr} = C \cdot \frac{101}{P} \cdot \frac{T + 273}{298} \qquad (4)$$

where:

C_{corr} = concentration of substance corrected to reference conditions, in µg/m^3
P = sampled air pressure, in Kpa
T = sampled air temperature, in °C.

Much more often the diffusive uptake rate is expressed in ng.ppm^{-1}.min^{-1}. These dimensions are more practical to use as they can be directly correlated with the concentration of the substance in the gas expressed in ppb.

Diffusive uptake rates in µg/m^3 and ng.ppm^{-1}.min^{-1} can be correlated to each other with the following expression:

$$U' = U \cdot \frac{M}{24{,}5} \cdot \frac{P}{101} \cdot \frac{298}{T + 273} \qquad (5)$$

where:

U' = diffusive uptake rate in ng.ppm^{-1}.min^{-1}
M = substance molecular weight
24.5 = molar weight of a gas at 25 °C and 101 KPa
P = sampled air pressure, in KPa
T = sampled air temperature, in °C

Once the value *U'* is known, the concentration *C'* of a substance in the sampled air, expressed in ppb, can be calculated with the following formula:

$$C' = \frac{m_s}{U' \cdot t} \cdot 10^6 \qquad (6)$$

where:

C' = substance concentration in ppb
m_s = mass of the substance present in the sampling tube, in µg
U' = diffusive uptake rate, in ng.ppm^{-1}.min^{-1}
t = sampling time, in minutes

Sampling tube requirements

The application of the Fick’s law expressed by equation (1) requires that the sampler be exposed to an atmosphere in stable conditions.
Some environmental conditions can cause a deviation of conditions from ideal to non-ideal and thus determine a variation in sampler performance compared to those foreseen. Environment air speed is one of these factors.
Various studies have evaluated the affect of air speed in relation to the dimensions of the sampler tube and have concluded that tubes with a relatively small exposure surface *A* and a relatively long section *l* between the end of the tube and the sorbent are practically not affected by the air speed.
Tubes with A= 0.2 cm^2 and *l* = 1.5 cm comply with these specifications and are considered reference standards to the point that all diffusive sampling methods written by the main official international agencies, such as HSE (UK Health and Safety Executive) ISO (International Organization for Standardization) and NIOSH (US National Occupational Safety and Health) refer to uptake diffusive rates *U* and *U'* experimentally defined for many solvents and the main sorbents, for tubes with the above dimensions.

These types of tubes, suitable for the Master TD sampler and other automatic samplers, are available on the market with various sorbents.
The dimensions are normally given in inches and refer to the inner diameter and length (1/4" x 3.5" respectively).
Normally, the end of a tube is marked with an outer groove and represents the sampling end. The sorbent, located 15 mm from the outer edge is kept in place by a stainless steel gauze. On the other end, a stainless steel spring, or a glass wool plug holds the sorbent (Figure 7-2).

During sampling, the sampling end must be sealed with a diffusive cap, that is equipped with a metal membrane with a surface corresponding to the tube diameter, which allows the air to diffuse. The other end must be sealed with an airtight cap.

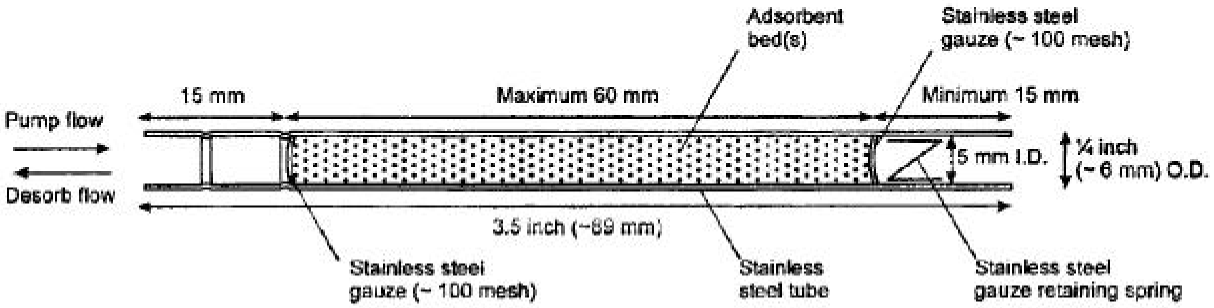


Figure 7-2 - Diffusive sampling tube

Using the diffusive uptake rate

The diffusive uptake rates given in the literature can be used to calculate the substance in sampled air by directly applying the formulas (3) or (6) depending on the measurement unit chosen, as long as the tubes used are of the above dimension specifications.
The table below gives examples of the diffusive uptake rates *U* and *U'* for some solvents and sorbents(*).

Compound	**Sorbent**	**Diffusive uptake rate**	
		$cm^3\ min^{-1}$	**$ng\ ppm^{-1}\ min^{-1}$**
1.3 Butadiene	Molecular sieves 13X	0.59	1.3
Benzene	Porapak Q Tenax GR	0.42 0.57	1.37 1.81
Styrene	Tenax TA	0.47	2.0
1,1,1 Trichloroethane	Chromosorb 106 Tenax GR	0.42 0.54	2.3 2.92
Ethyl Acetate	Chromosorb 106 Tenax TA	0.49 0.4	2.0 1.6
Ethylene Oxide	Spherocarb	0.88	1.6

(*) from Health and Safety Executive (1995) *Methods for the Determination of Hazardous Substances* - Volatile organic compounds in air - Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography. MDHS 80. HSE London

However, the user must consult the original data source to verify the applicability with the pertinent sampling conditions. Significant differences in diffusive uptake rates can be detected for example based on tube exposure time and atmospheric concentration (for example work environment or urban atmosphere).

If the diffusive uptake rate is not available for a specific compound, a “theoretical” value can be calculated with formula (2) by using the diffusion coefficient *D* provided in the literature or it can be determined experimentally by sampling a series of tubes in parallel and determining the absolute quantity compared to an independent method, for example by analyzing a known volume in a standard mixture.

Application of diffusive sampling

Diffusive sampling can only be applied to tubes filled with a single sorbent because with a second sorbent it would be impossible to comply with the 1.5 cm distance from the tube end.
Consequently, the application of each individual sampling is restricted to compounds trapped by the same sorbent.
To broaden the application to different compounds, it is necessary to expose various tubes at the same time filled with sorbents with different specifications.

Radial symmetry diffusive sampling

Brief mention needs to be given to the sampling device called *TD Radiello®* (*), available on the market and compatible with the Master TD desorber.

This device is a cylindrical passive sampler. Its diffusive surface is composed of the cylinder, the sorbent is contained in a smaller coaxial cylinder. The diffusive surface is comprised of a microporous high density polyethylene (HDPE) structure while the sorbent cartridge is comprised of a stainless steel mesh, sealed at the end and filled with an opportune sorbent.

After sampling, the sorbent cartridge, removed from the porous container and inserted in an empty steel tube, can be subjected to thermal desorption like a traditional sampling tube. The dimensions are such that it adapts perfectly to a standard 1/4 x 3.5 inch tube.

Radial symmetry sampling offers a greater diffusive uptake rate compared to axial sampling for the same substance and sorbent, because the diffusive surface is much higher.

This makes it possible to sample, in relatively short exposure times (8-24 hours) much higher absolute quantities of substance, comparable with those of an active sampling

** Fondazione Salvatore Maugeri registered trademark - IRCS, Padua - Italy*

Active Sampling

In active sampling, the air sample is suctioned through the sampling tube by a pump with a constant flow and for a determined amount of time. The concentration of substances in the air is calculated by comparing the absolute quantity of compounds trapped by the sorbent to the volume of sampled air.

The main advantage of active sampling is the possibility of using more than one sorbent in the same tube, and thus to trap compounds in a wide boiling range with a single sampling. The various sorbents can be placed in the same tube, separated from each other by glass wool (multilayer tube) or in different tubes connected in series. In both cases, during sampling the sorbents need to be placed in an order of increasing adsorbent capacity.

During sampling the caps need to be removed from both ends.

The sampling flow direction must be indicated because desorption must occur in the opposite direction.

Flow rates to apply vary normally between 10 and 200 mL/min; for standard tubes with 1/4 inch diameter, the optimum flow rate is 50 mL/min; greater flow rates can be used for relatively short times (10 min.).

Flow rates which are too low (< 10mL/min) can be affected by a diffusion effect, while excessive flow rates can cause a “breakthrough” effect, that is leaking of the sample from the flow outlet end.

Active sampling is a valid alternative to diffusive sampling particularly when diffusive uptake rate data not available or reliable or when the predicted substance concentration is very low.

While the lower sensitivity limit, in active sampling, is basically established by the sensitivity if the detector and the quality of the blank, the upper limit is determined by the adsorbent capacity, as well as the linear dynamics of the entire gas chromatograph system and the possibility of splitting the sample.

Breakthrough volume

Sampling efficiency is quantitative (100%) only if the sampling capacity of the sorbent is not surpassed. In this case, sample would leak from the sampling tube.
The sorbent capacity is defined as the maximum air volume that can be sampled before a significant quantity of substance elutes from the tube and is measured as the *breakthrough volume*.

Breakthrough volume defines the affinity a sorbent has for a certain substance and is thus specific for each sorbent/substance association.
A sorbent with a higher breakthrough volume has a greater adsorbent capacity compared to a sorbent with a lower breakthrough volume for the same substance.
Normally, the breakthrough volume is defined as the volume of air contained in an gaseous organic compound with a known concentration which can pass through a tube before the concentration of the compound in the gas leaking out reaches 5% of the inlet gas concentration (Figure 7-3).

The *breakthrough volume* is directly established by passing a standard atmosphere at a constant flow through a sampling tube, connecting the outlet gas directly to a detector and continuously measuring the detector response. The detector response will be zero as long as the sorbent in the tube is able to trap the compound. When the gas compound starts the leak the response to the detector will increase up to a maximum point and remain constant.

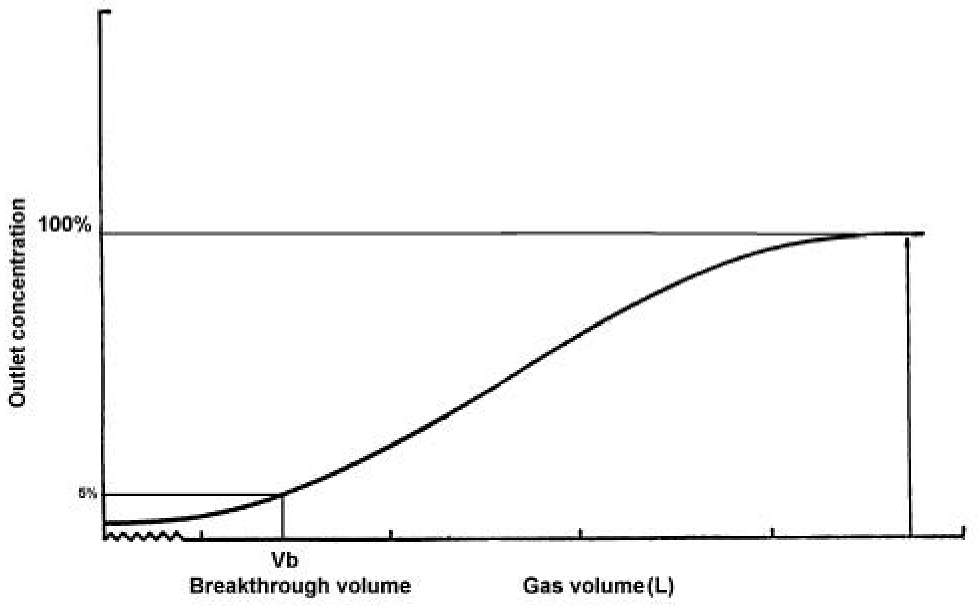


Figure 7-3 - Breakthrough volume

The breakthrough volume, expressed in liters, is calculated by measuring the time, expressed in minutes, which has passed from the beginning of elution up to when the response corresponds to 5% of the maximum value and multiplying it by the value of the gas flow, expressed in L/min.
The adsorbent capacity of some sorbents is greatly affected by humidity. If sampling is going to be done in air with a high level of humidity, the breakthrough volume must be calculated using a standard humidified atmosphere.

Retention volume

Since a standard atmosphere at a constant flow is not always readily available, there is an indirect method for evaluating the adsorbent capacity of a sorbent: this method establishes the *retention volume*, that is the volume of carrier gas needed to elute a small amount of organic vapor from a tube, measured at the highest peak (Figure 7-4).

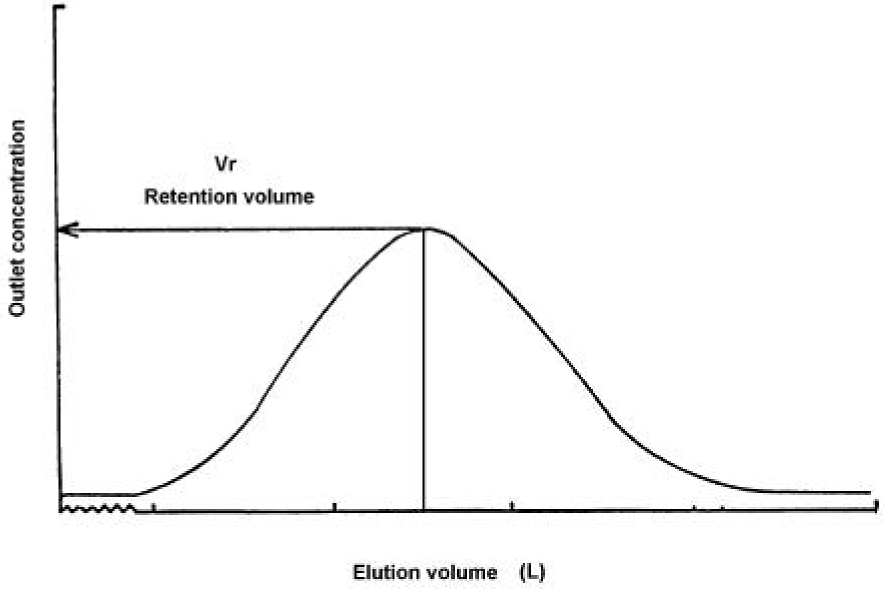


Figure 7-4 - Retention volume

The tube containing the sorbent is connected directly between the injector and gas chromatograph detector using inert connections. A reduced volume of a gaseous mixture of the substance is introduced into the tube and eluted with air or carrier gas. The retention volume, expressed in liters is obtained by multiplying the peak retention time, in minutes, by the carrier gas flow, in L/min. Since elution at room temperature would lead to unreasonable retention times, it is necessary to effect various repetitions at higher temperatures, selected so that the peak has a convenient retention time (between 2 and 20 minutes) and extrapolate the retention time to a temperature of 20 °C.

“Safe sampling volume”

Since different factors, such as sampling temperature, flow rate, presence of humidity and the concentration of the sample, can reduce the adsorption capacity of a sorbent, it is never advisable to work at the limit of a breakthrough volume.

To guarantee a certain safety margin in sampling operations, a *Safe Sampling Volume* has been established, that is the maximum volume which can actually be sampled. The Safe Sampling Volume (SSV) corresponds to 70% of the breakthrough volume or 50% of the retention volume. The SSV values calculated in the two different ways do not always match. The most reliable value is the one calculated directly, that is by breakthrough volume, even if the chromatograph method is a sufficiently reliable indication of the adsorbent capacity of a sorbent, except for samples with a high level of humidity or at a high concentration.

SSV values are available in the literature for various sorbents and the most common volatile organic solvents, most of which are established with the chromatograph method.
The SSV value is expressed in liters or liters/g of sorbent.

The table below gives examples of retention volume and SSV values for some compounds and sorbents (*).

Compound	**Sorbent**	**Desorption temp. (°C)**	**Retention Vol.(L)**	**Safe Sampling Vol. (L)**
Benzene	Chromosorb 106 (300mg)	160	53	26
	Tenax TA (200 mg)	120	12.5	6.2
1,1,1 Trichloroethane	Chromosorb 106 (300mg)	140	54	27
	Spherocarb (300mg)	290	$1.8x10^4$	$8.0x10^3$
Ethyl Acetate	Chromosorb 106 (300mg)	150	39	20
	Tenax TA (200mg)	120	7.2	3.6

(*) from Health and Safety Executive (1993) Methods for the Determination of Hazardous Substances - Volatile organic compounds in air - Laboratory method using pumped solid sorbent tubes, thermal desorption and gas chromatography. MDHS 72. HSE London

Preparing the sample

The following series of operations is required for preparing and analyzing the sample:

- filling the sampling tube
- conditioning the sampling tube
- conditioning the septa
- storing the sampling tubes
- sampling
- analysis

Filling the sampling tube

Filling with sorbent

There are tubes on the market, both in stainless steel and glass, already filled with sorbent and of suitable dimensions for STD 1000 sampler. The outer dimensions are 1/4 x 3.5 inches, the inner diameter is 5 mm for stainless steel tubes and 4 mm for glass tubes. Pre-filled tubes are available both unconditioned and pre-conditioned.

The preparation of these tubes is in compliance with principle international methods and thus their use is highly recommended.
However, if the tubes are going to be personally prepared, it is first necessary to set-up empty tubes in stainless steel or glass. Use stainless steel tubes for most cases and save the glass tubes for sampling labile compounds (e.g. sulfur compounds).
The tubes can be filled with one or more sorbents which have been pre-conditioned (see the following paragraph). The material must be placed in the central part of the tube, so that it corresponds with the area heated by the instrument, in addition, a distance of at least 15 mm must be left at each end, to prevent diffusion during active sampling.

> *Note: if preparing tubes for diffusive sampling, in order to be able to refer to diffusive uptake rate data provided in the literature, steel tubes must be used (5 mm inner diameter) and the distance between the end of the sampling tube and the sorbent bed must be exactly 15 mm (see “Sampling techniques” chapter).*

The tubes can contain from 200 to 1000 mg of sorbent depending on its density - for example, 250 mg of Tenax TA, 300 mg of Chromosorb 106 or 500 mg of Carboxen 569.

The material is treated inside the tube by placing a plug of approximately 1 cm of preconditioned glass or quartz wool at each end.
The sorbent must not be compressed inside the tube to prevent excessive pressure drop.

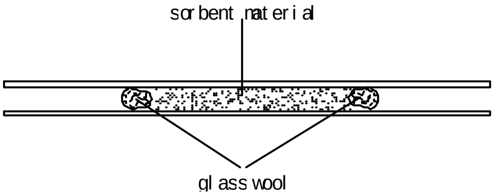


Figure 8-1- Tube filled with sorbent material

For the same reason it is advisable to use sorbent material with a mesh size which is not too fine (normally between 60 and 80 mesh) to prevent the particles from passing from the sampling tube into the instrument. It is advisable to sieve the sorbent to eliminate the finer particles.

Note: use silanized glass wool only for sampling labile compounds (sulfur or nitrogen compounds) and in this case do not use a desorbing temperature above 250°C.

If using more than one sorbent, these need to be added in increasing order of adsorbent capacity, the weakest sorbent closer to the sampling end, separating them with approximately 3 mm of pre-conditioned glass or quartz wool.

Note: it is not advisable to fill the same tube with sorbents that have maximum desorbing temperatures which differ by more than 50 °C as it would be impossible to completely condition or desorb the most stable without damaging the one most susceptible to heat.

Preconditioning the sorbent

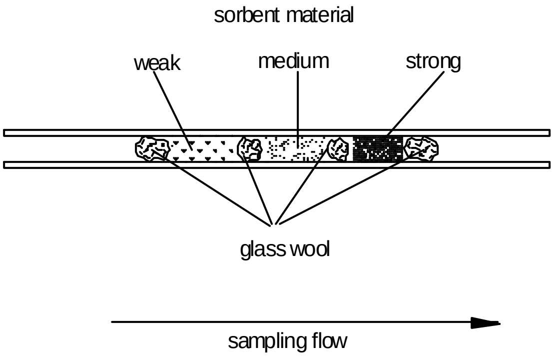


Figure 8-2 - Example of a multilayer tube

It is advisable to heat condition the sorbent before using it to fill tubes.
Condition each sorbent by leaving it for at least one night (> 16 hours) under a flow of inert gas at a temperature which is 25 °C less than the maximum temperature given for that sorbent (see table 1). Keep it in a clean and inert atmosphere during cooling, storage and tube filling.

Filling with solid samples

If the tube is going to be filled with a solid sample, place it in the central part and secure it with two plugs of glass wool.
The most suitable solids usually have a high surface/mass ratio and total extraction is almost always guaranteed: these are, for example powders, films, fibrous or granular materials.

Conditioning the tube

Before using, the tubes need to be conditioned at a temperature which is slightly higher than the temperature used for desorption.

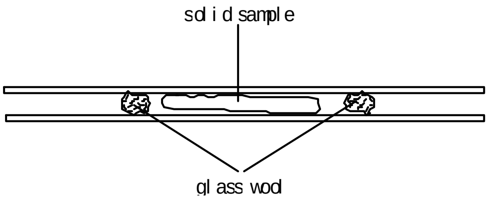


Figure 8-3 - Tube with solid sample

Conditioning can be done directly on the instrument, using the *Conditioning* operating mode (see *Operation* chapter), in this way, the impurities desorbed from the material are eliminated to the outside without passing through the trap.
Normally, a conditioning time of 10 minutes is sufficient with a diffuse uptake rate of 100 mL/min. Conditioning temperatures for the various sorbents are provided in the table below.

Note: if more than one sorbent is put in the tube, do not exceed the conditioning temperature for the most heat sensitive sorbent.

Conditioning must be done in counter-current which means that the gas flow in the tube must be in the opposite direction of the sampling flow

Sorbent	Maximum Temp. (°C)	Conditioning Temp. (°C)
Tenax TA	350	330
Tenax GR	350	330
Carbotrap Carbotrap C Carbopack B, C Carbograph TD-1	>400	350
Chromosorb 102 Chromosorb 106	250	250
Porapak Q	250	225
Porapak N	180	180
Spherocarb	>400	400
Carbosieve S-III Carboxen 1000	400	350
Molecular Sieves	350	330
Tenax/Carbopack B	350	330
Carbopack B/Carbosieve S-III	400	350

After conditioning check the cleanliness of the tube by carrying out a desorption in the conditions used for analysis. If the cleanliness is not acceptable, repeat the conditioning procedure.
If the tube is re-used right after an analysis, it is not necessary to repeat conditioning. Instead, it is a good idea to re-condition it if it is re-used after a long time or if its origin is uncertain.
If opportune precautionary measures are adopted, the tubes can be subjected to up to 100 sampling and desorption cycles before the sorbent needs to be replaced.

Deterioration is normally indicated by a reduced retention capacity of one or more analytes. For this, it is advisable to check the tube retention volume (see *Sampling techniques* chapter) after a certain period of use.

Conditioning the septa

In order to undergo analysis, the tubes must be equipped with a specific closing system for Master TD sampler, the same for each end, consisting of a silicone rubber septum and perforated aluminum cap.

The surface of the septum which faces the interior of the tube is coated with Teflon. Septa are available in 5 mm and 4 mm diameters for steel and glass tubes, respectively.
Before using them, it is advisable that the septa undergo a conditioning procedure to prevent any volatile substances adsorbed from the atmosphere from being released during desorption and thus interfering with analysis results.
To do this, it is advisable to submit the septa to a flow of inert gas for at least one night (16 hours) at

a temperature of 200 °C and to cool them in a clean atmosphere.
Then store them in a closed, sealed container in an inert atmosphere to prevent subsequent contamination.

Storing the tubes

The tubes must always be kept closed in a clean atmosphere.
If they have not been used recently, they must be re-conditioned before use.
After sampling, it is advisable to analyze the sample as soon as possible.
In this case, close the tube by inserting a rubber septum and cap in each end. Position the tube in the instrument carousel with the sampling end facing up for counter-current desorption.

> *Note: the septa for stainless steel tubes and glass tubes are different and can be easily distinguished by their color: blue for stainless steel and red for glass.*

If the tube cannot be analyzed immediately, it is advisable to use storage caps composed of a brass cap and PTFE seal.
It has been demonstrated that this type of closing keeps the sample undamaged for a long time, even up to a year.
Replace the storage caps with the septa and perforated caps only at the time of analysis.

Sampling

It is important to always identify the sampling inlet end. Some tubes have an arrow which indicates the sampling direction.

For diffusive sampling it is important that at the sampling end a distance of 15 mm between the edge of the tube and sorbent bed be left if reference is going to be made to the diffusive uptake rate data provided in the literature (see *Sampling techniques* chapter).
Before sampling remove the cap at this end and replace it with a diffusion cap. The other end must remain closed.
During air exposure, the tube must be protected from extreme atmospheric agents (for example: rain, strong wind) and must not come into contact with aerosol or particulate matter.
The exposition time normally varies from 8 hours, for monitoring work sites, up to 4 weeks for monitoring outdoor or indoor environments. Shorter periods can be used, but naturally they cause a reduction in the sampled mass and the overall sensitivity of the method.

As a guideline, below are the collected mass values based on atmospheric concentration and sampling diffusive uptake rate* for an 8 hour exposure time.

Sampling diffusive uptake rate ng/(ppm* min)	**Up = 1.3**	**Up = 1.5**	**Up = 1.7**	**Up = 2.0**	**Up = 2.5**
Concentration					

1000 ppm	0.624 mg	0.72 mg	0.816 mg	0.96 mg	1.2 mg
10 ppm	6.24 µg	7.2 µg	8.16 µg	9.6 µg	12.0 µg
1 ppm	0.624 µg	0.72 µg	0.816 µg	0.96 µg	1.2 µg
100 ppb	62.4 ng	72 ng	81.6 ng	96.0 ng	120.0 ng
10 ppb	6.24 ng	7.2 ng	8.16 ng	9.6 ng	12.0 ng
1 ppb	0.624 ng	0.72 ng	0.816 ng	0.96 ng	1.2 ng

* *The sampling diffusive rate refers to standard dimension tubes (5 mm inner diameter)*

For active sampling it is also important to identify the flow direction during sampling to be able effect desorption in counter-current.
In particular, when the tube contains more than one sorbent, sampling must be done with increasing adsorbent capacity, from the weakest to the strongest.
Connect the pump to the end nearest the strongest sorbent with a rubber tube. Adjust the flow rate to sample the required volume (see "*Sampling techniques*" chapter) in the time available.
The pump flow rate must be selected so that it does not exceed, in the established sampling time, the SSV of any of the required analyzing compounds.

If a long sampling time is required, to achieve a certain concentration averaged out over time, the pump flow rate must consequently be reduced. Obviously, bearing in mind these limits, the greater the sampled volume the lower the minimum quantity detected.
Typical examples of sampling conditions are:

- 16 mL/min for sampling 1 L of air in 1 hour
- 67 mL/min for sampling 4 L of air in 1 hour
- 10 mL/min for sampling 1800 mL of air in 3 hours
- 40 mL/min for sampling 2700 mL of air in 3 hours

The best flow rate for 1/4 inch tubes is 50 mL/min, even if it is possible to use flow rates between 5 and 200 mL/min without changing the retention volume.
However, avoid using flow rates under 10 mL/min because they could cause errors due to diffusion effects.
It is advisable not to sample a volume less than 300 mL for any reason.

The table below provides a guideline for collected mass values based on volume of air sampled and concentration of sample "X" with molecular weight =100.

Sample type	**Concentration**	**Mass sampled in 1 L**	**Mass sampled in 2 L**	**Mass sampled in 10 L**
Polluted urban area	10 - 250 ppb	40 -1000 ng	80 ng - 2 µg	0.4 - 10 µg
Indoor environment	1-100 ppb	4 - 400 ng	8 - 800 ng	40 - 4 µg

Av. benzene exp.	~ 3 ppb	11 ng	22 ng	110 ng
Normal urban area	1 -10 ppb	4 - 40 ng	8 - 80 ng	40 - 400 ng
Normal rural area	0.1 - 1 ppb	0.4 - 4 ng	0.8 - 8 ng	4 - 40 ng
Forest	0.25 - 2.5 ppb	1 - 10 ng	2 - 20 ng	10 100 ng
Very pure air	0.025 - 7.5 ppb	0.1 - 30 ng	0.2 - 60 ng	1 - 300 ng
Antarctic air	15 - 50 ppt	60 -200 pg	0.12 - 0.4 ng	0.6 2 ng

At the end of sampling, in both cases, immediately close the tube with caps for analysis, if this is going to be done immediately, or with storage caps.

Note: never use adhesive labels, markers or other material containing solvents for identifying the tubes.

Always write down the sampling conditions (exposure time, diffusive uptake rate, temperature and atmospheric pressure) measured at the beginning and end of sampling.
If the sample is important, and above all if there is some uncertainty as to whether the sampling or analysis will be successful, it is advisable to sample another tube at the same time, for example using a lower flow rate with active sampling.

Analysis

When the analysis is done, the tube must be closed with a septum and a perforated cap at both ends.
If it is closed with storage caps, remove them and replace with appropriate ones.
Insert the tube in the carousel so that the sampling end is facing up so that desorption is done counter-current.
Always analyze also a "blank" tube, that is a tube prepared, conditioned and stored in the same conditions as the sample but not submitted to the sampling procedure.

Use the "*Analysis*" operating mode and set the opportune operating parameters (see "*Developing a method*" and "*Setting and starting up a method*" chapters).

Air Sampler

Description

DANI Air Sampler is an automatic sampler to be joined with Master TD to analyze volatile compounds in gaseous samples.
Volatile compounds can be sucked into the Master TD focusing trap from canisters, sampling bags, or gas streams.
DANI Air Sampler was designed to automate and enhance the mesurement of trace level in air. It's ideal for unattended field or on-plant operation.

Sampling valve

The sampling system is composed of three solenoid valves

External connections

DANI Air Sampler has the following external connections:

- power supply
- RS232 serial output
- Connection to Master TD

The connections are located on the back of the instrument (see *Installation* section).

Pneumatic

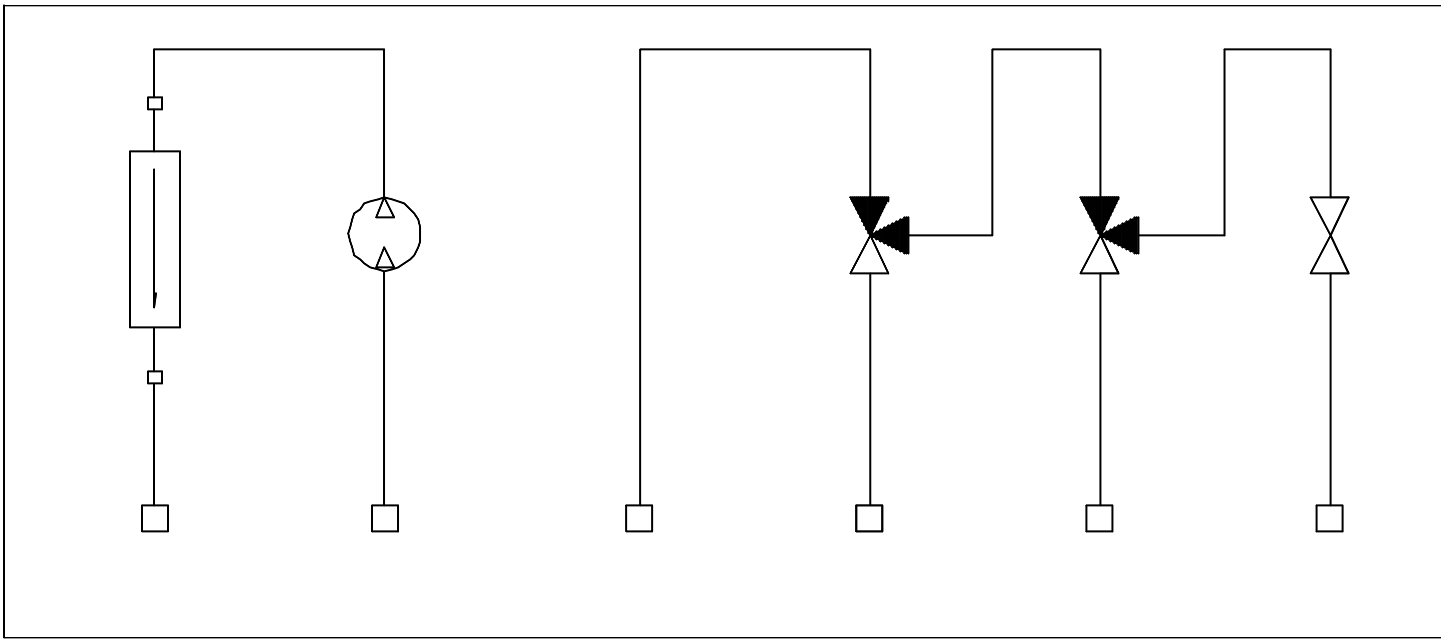
The instrument is equipped with four separeted inlets on the back:

- BLANK for the blank gas
- CAL GAS for the calibration gas
- SAMPLE for the sample gas
- FROM SAMPLER for the stream coming from Master TD (pneumatic line connected to Master TD *"VENT"* outlet)

and two outlets:

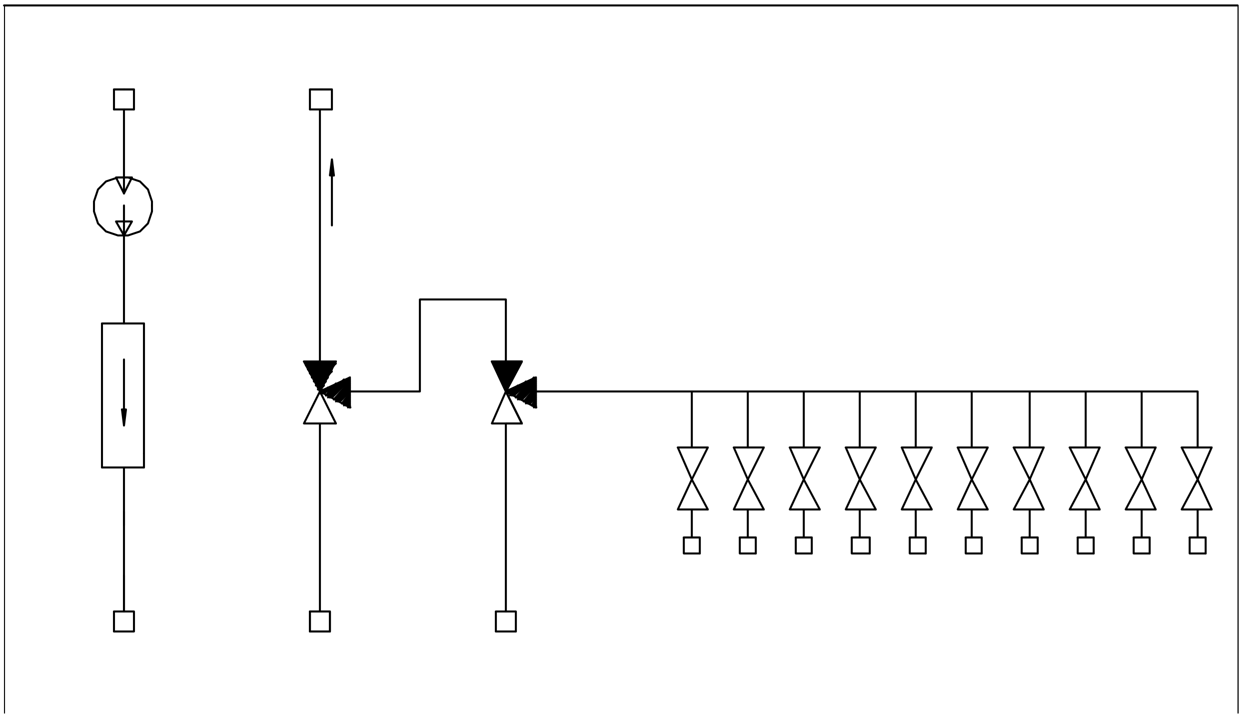
- VENT
- TO SAMPLER for the stream going to Master TD (pneumatic line connected to Master TD "*SAMPLE IN"* inlet)

The gas to be analysed is sucked by the pump through the Master TD trap. The flow rate is electronically regulated by the mass flow controller (MFC). Three solenoid valves (BK, CAL and SAM) provide the gas line selection.



Air Sampler - pneumatic scheme

In case the LINE SELECTOR option is installed, ten inlets are available on the back of the instrument to select different sample lines. Each inlet is connected to a solenoid valve. One sample line is always opened at a time, according to a user defined sequence.



Air Sampler - line selector **option**

Technical specifications

Hardware	option to Master TD (Sequential Thermal Desorber)
Control	fully controlled by Master TD operating in *direct sampling* mode
Sampling rate	10 - 100 Nml/min (reference conditions 0°C, 1 atm)
Sampling time	3 - 120 min
Sample repetitions	up to 100
Cycle repetition	up to 100 or infinite
Total sampled volume	on display
Inlets	sample - calibration - blank
Inlet fittings	6MB, 1/8” SW with adapter
Line selector (optional)	10 sampling lines with plug-in connectors for 4x2 mm PTFE tubing
Inlet P max	1 bar
Inlet P min	0.3 bar vacuum
Flow control	mass flow electronic control
Outputs	RS232 serial output for software control
Power supply	120/240 V with selector, 50 - 60 Hz, 150 VA
Sample path	deactivated stainless steel
Sampling cycle	user defined between *sample*, *calibration* and *blank*
Sample frequency	user defined
Repeatability (RSD%)	better than 3%
Compliant with EPA TO14-TO15	canister sampling methods
Dimensions	width 200 mm, depth 450 mm, height 220 mm
Weight	16 kg

Installation

Enviromental conditions

DANI Air Sampler must be installed in an environment with suitable temperature and humidity conditions for best operation and long life.
The DANI Air Sampler can operate in a temperature range from 0 to 40°C and in a relative humidity range from 5 to 95%. Maximum altitude is 2000 meters.
However, the instrument performs best at 20-25°C room temperature and relative humidity of 40-50 %.
Exposure to corrosive, gaseous, liquid or solid substances can damage the material used in DANI Air Sampler and therefore must be avoided.

Positioning

DANI Air Sampler must be joined with DANI Master TD. It's necessary a free surface space approximately 25cm wide and 75cm deep suitable to support 16kg close to the left side of the thermal desorber.
It's necessary to free the backside of the Air Sampler (at least 20cm) from any kind of obstacles to make the assembling operations easier (connection of canisters, sampling bags or on-line sampling tubing).

Electrical power supply

Power voltage

DANI Air Sampler is equipped with a power supply with manual voltage level selection. It can operate at 240 or 120 VAC and a frequency range between 50 and 60 Hz.
Mains supply voltage fluctuations have not to exceed +/-10% of the nominal supply voltage

Power supply cable

For the safety of the operator the instrument is grounded through the three-conductor power line cord, according to International Electrotechnical Commission (IEC) regulations. Therefore, the cord must be inserted in a socket equipped with a correctly connected earth ground contact. Make sure the socket is grounded.
Before connecting the instrument to the power supply, make sure that the switch on the back of the instrument is in the "OFF" position. Insert the cable into the socket and then flip the switch to "ON".

Pneumatic supply

DANI Air Sampler is connected to DANI Master TD with two pneumatic lines: one from Master TD *"VENT"* outlet , to AIR SAMPLER *"FROM SAMPLER"* inlet; and the other from AIR SAMPLER *"TO SAMPLER"* outlet, to Master TD *"SAMPLE IN"* inlet.
Use deactivated stainless steel tubes in the circuits in contact with the sample, and stainless steel tubes for the other connections. To make long distance connections or to have high flows, use tubes with larger internal diametres. DANI gives a tubing standard equipment suitable in most cases.
The gas inlets are on the back of the instrument. Each inlet consists of a bulkhead union for 6MB fittings. Connect the tubing as described in the *"installation"* chapter of the manual.

Pneumatic connection to Master TD

Modify the pneumatic circuit inside the DANI Master TD as follows:

- Remove the pneumatic section cover and the sampling valve insulation
- Unscrew the fitting from the port no. 6 of the sampling valve using a 7mm wrench as shown in the picture 9-1
- Connect the deactivated stainless steel shaped tubing (cod. 1300 540 010) between port no.6 of the sampling valve and the bulkhead *"SAMPLE IN"* inlet, inside the Master TD (Figure 9-2)

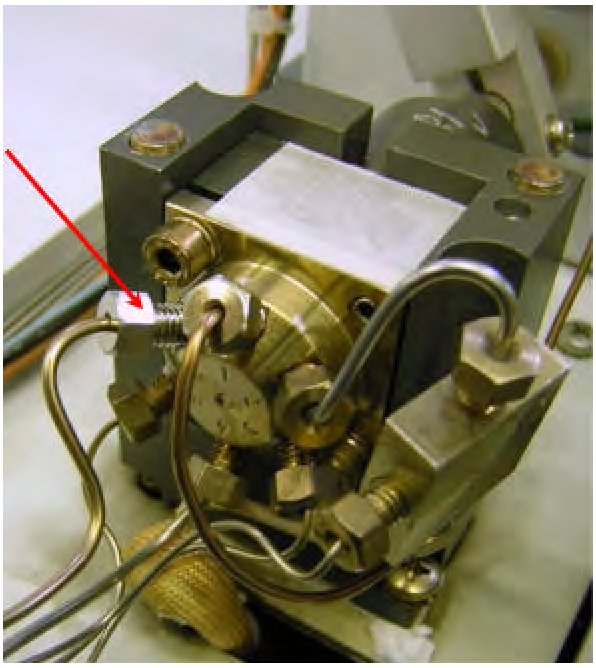


Figure 9-1 - Sampling valve

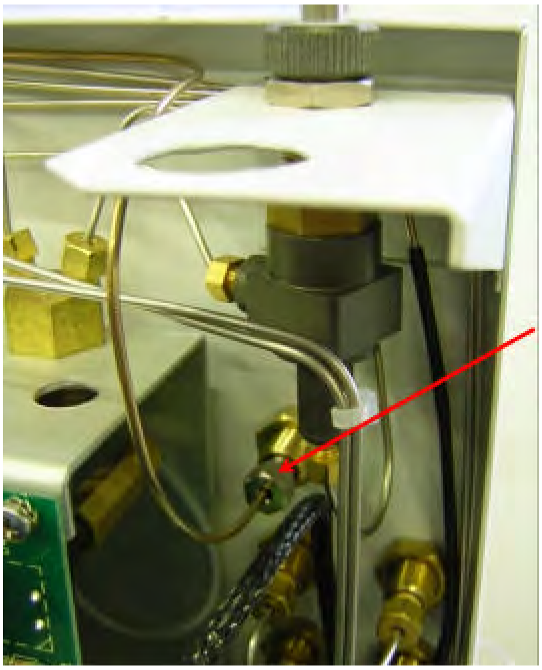


Figure 9-2 - SAMPLE-IN bulkhead

- Remove the green restriction (Figure 9-3) and connect the tubing directly to the flowmeter (Figure 9-4)
- Replace the sampling valve insulation and the pneumatic section cover

Figure 9-3 - Master TD original version

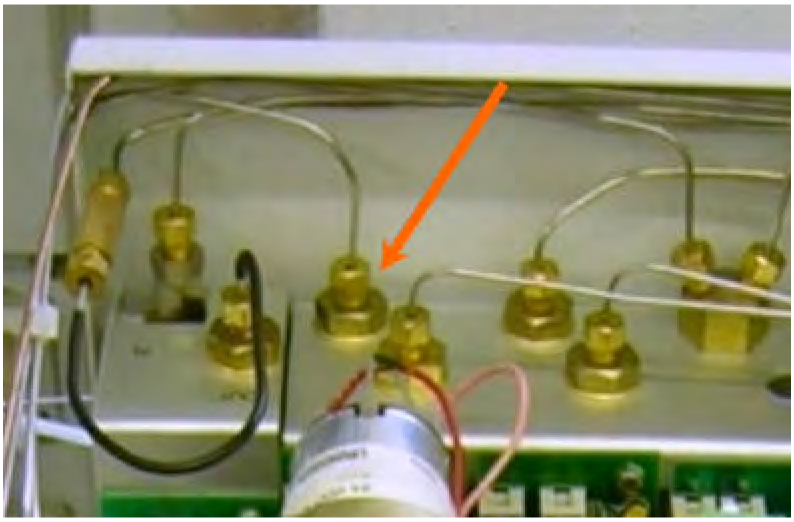


Figure 9-4 - Flowmeter

- Cut the deactivated tubing (cod. 130 050 2508) at the proper length and fit it with a 6MB brass fitting (cod. 230 000 3140) and an aluminium seal (cod. 230 603 3281) at both ends
- Install this tubing between the Master TD *"SAMPLE IN"* inlet with the Air Sampler *"TO SAMPLER"* outlet
- Connect the Master TD *"VENT"* outlet with the Air Sampler *"FROM SAMPLER"* inlet, using a stainless steel tube

Electrical connection to Master TD

- Connect the Master TD *"I.D."* outlet with Air Sampler *"SAMPLER"* inlet using the cable cod. 5103 509 009
- Verify the line voltage selected in the little window on the right side of the on/off line switch of the Air Sampler (115 or 230 Vac). If the value is not correct, remove the fuseholder and the voltage selector insert. Replace the insert in the right position and the fuseholder.

Attention!!!

Switch off the instrument and remove the power cord before the voltage selection changing or the fusedrawer removing.

AIR SAMPLER single line

AIR SAMPLER line selector

- Connect the power cord and switch on the Air Sampler
- Be sure that the Air Sampler is already ON when you switch ON the Master TD.

Configuration

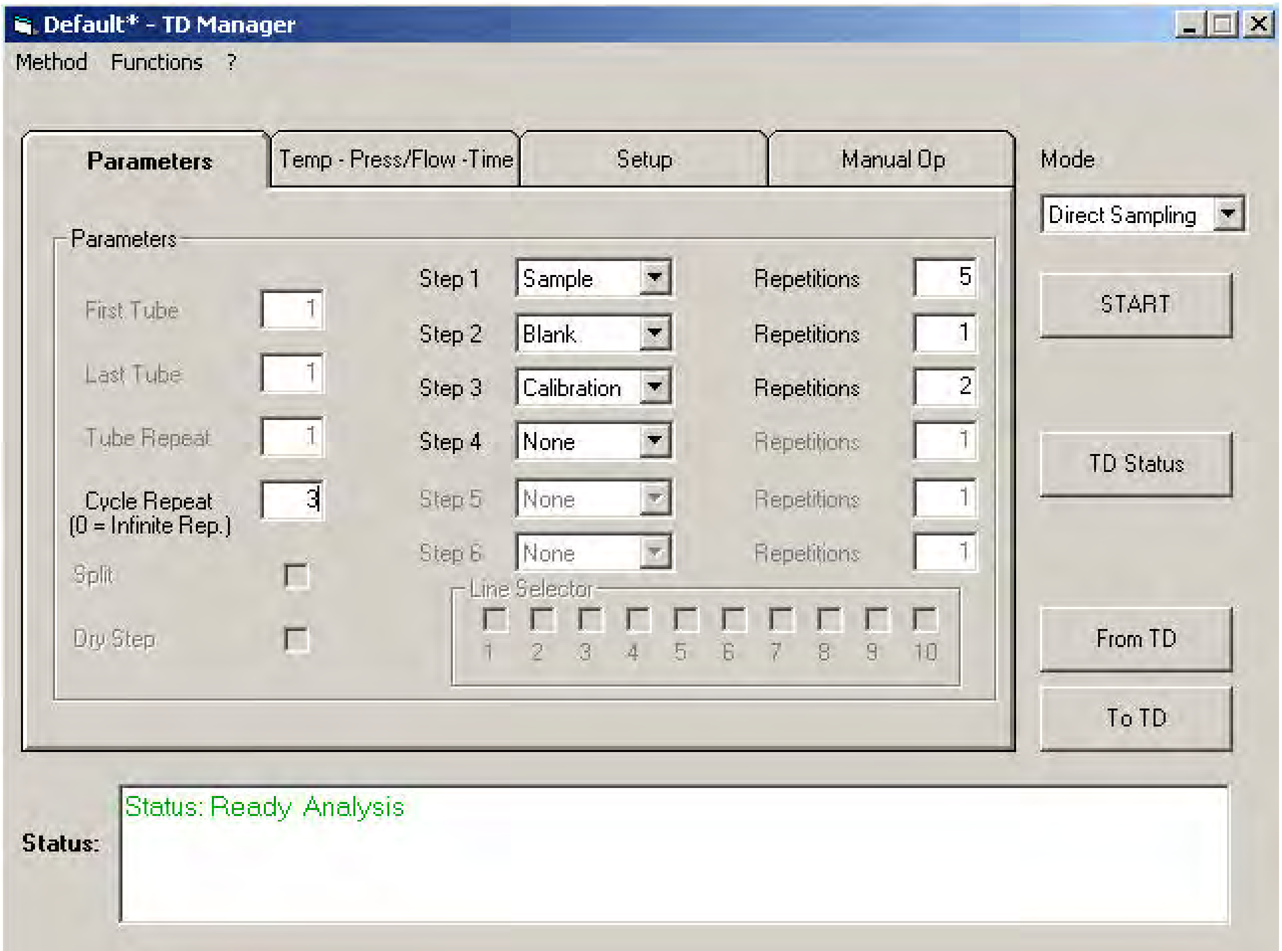
DANI Air Sampler is entirely controlled by Master TD. To control the Air Sampler, Master TD must be configured (see *Air Sampler Config* in *Setup* paragraph of *"Operation-TD Manager"* chapter).

Choose *Single Line* when the AIR Sampler has the standard configuration and *Line Selector* when the AIR Sampler is equipped with the line selector option (check the ten inlets on the back side of the AIR Sampler)

Programming examples

Setting of a sequence in “SINGLE LINE” configuration

You want to process a sample 5 times, then you want to perform 1 blank and 2 calibrations, repeating the whole cycle 3 times.
Fill in the *Parameters* page of the TD Manager as follows:



Parameters

First Tube 1
Last Tube 1
Tube Repeat 1
Cycle Repeat (0 = Infinite Rep.) 3
Split ☐
Dry Step ☐

Step 1	Sample	Repetitions	5
Step 2	Blank	Repetitions	1
Step 3	Calibration	Repetitions	2
Step 4	None	Repetitions	1
Step 5	None	Repetitions	1
Step 6	None	Repetitions	1

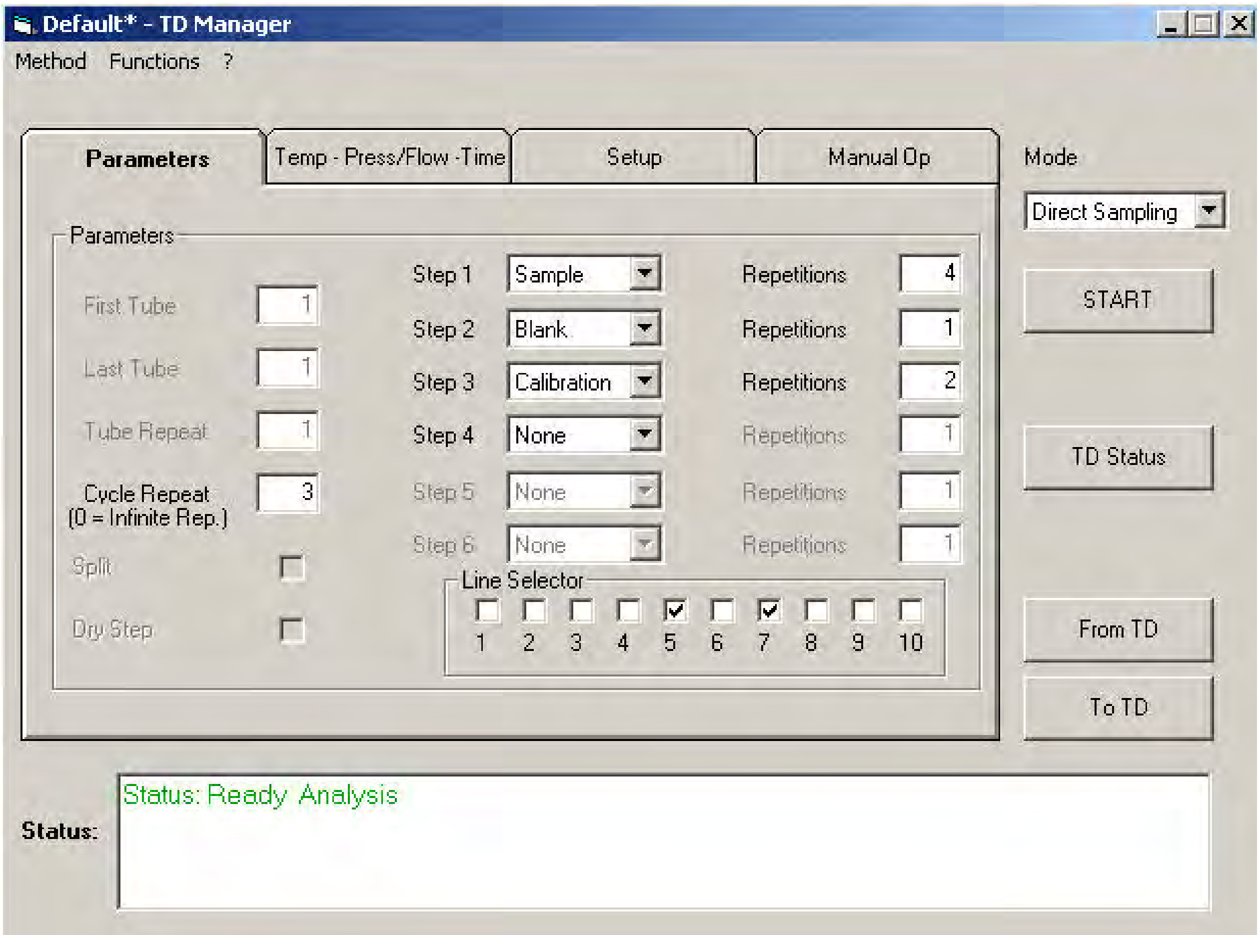
Line Selector
☐ 1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ☐ 9 ☐ 10

Mode: Direct Sampling

Status: Status: Ready Analysis

Setting of a sequence in “LINE SELECTOR” mode

You want to process the samples from inlets no. 5 and 7 of the line selector.
For each line you want to perform 4 analysis of the sample, 1 blank and 2 calibrations. You want to repeat the whole cycle 3 times.
Fill in the *Parameters* page of the TD Manager as follows:



Parameters

First Tube 1
Last Tube 1
Tube Repeat 1
Cycle Repeat (0 = Infinite Rep.) 3
Split ☐
Dry Step ☐

Step 1	Sample	Repetitions	4
Step 2	Blank	Repetitions	1
Step 3	Calibration	Repetitions	2
Step 4	None	Repetitions	1
Step 5	None	Repetitions	1
Step 6	None	Repetitions	1

Line Selector

☐	☐	☐	☐	☑	☐	☑	☐	☐	☐
1	2	3	4	5	6	7	8	9	10

Mode: Direct Sampling

Status: Status: Ready Analysis

Error messages

This chapter describes the error and alarm messages that come out when an instrument fault occurs, and how to correct them.
The error and alarm messages are displayed in the lower part of the status box of the TD Manager window.

Alarm: Temp Probe Shorted

The message ALARM: TEMP PROBE SHORTED appears if a temperature probe shorts when the instrument is already on. This is a general message. To identify the shorted probe turn the instrument off then on.
During the autotest the specific alarm message will appear, for example: ALARM: TRAP HIGH TEMP PROBE SHORTED
Contact the Technical Service Department to have the probe replaced.

Warning: Temp Probe Open

The message WARNING: TEMP PROBE OPEN appears if a temperature probe is open when the instrument is already on. This is a general message. To identify the open probe turn the instrument off then on.
During the autotest the specific alarm message will appear, for example: WARNING: TUBE TEMP PROBE OPEN
Contact the Technical Service Department to have the probe replaced.

Alarm: Motor Error

If a fault with one of the instrument motors occurs, a specific error message will appear in the status box of the TD Manager window:

- ALARM: TRAY MOTOR ERROR
- ALARM: TUBE MOTOR ERROR
- ALARM: SAMPLE VALVE ERROR
- ALARM: TRAP SHIFT ERROR

for the carousel rotation, tube lifting, valve rotation and trap shift motors, respectively.
Turn off the instrument and, if it is possible, remove the cause of the fault. If the fault continues contact the Technical Service Department.

Alarm: Trap Set Over Max Temp

The message ALARM: TRAP SET OVER MAX TEMP appears when the upper trap temperature (TRAP HIGH TEMP) entered is higher than the maximum safety temperature set in the Setup page of the TD Manager.
The alarm is removed by modifying one of the two parameters.

Alarm: Tube Set Over Max Temp

The message ALARM: TUBE SET OVER MAX TEMP appears when the tube desorption temperature (TUBE TEMP) entered is higher than the maximum safety temperature set in the Setup page of the TD Manager.
The alarm is removed by modifying one of the two parameters.

Alarm: Trap Actual Over Max Temp

The alarm ALARM: TRAP ACTUAL OVER MAX TEMP appears when, due to a fault with the temperature control, the actual temperature of the trap exceeds the maximum value set. If the cause is an incorrect setting, modify it. If not, contact the Technical Service Department.

Alarm: Tube Actual Over Max Temp

The alarm ALARM: TUBE ACTUAL OVER MAX TEMP appears when, due to a fault with the temperature control, the actual temperature of the tube exceeds the maximum value set. If the cause is an incorrect setting, modify it. If not, contact the Technical Service Department.

Alarm: Leak Test Failed

The message ALARM: LEAK TEST FAILED is displayed when the system does not pass the leak test. A bad seal can be caused by a leak in a tube, if diagnosed during the *Analysis* mode, or also in the trap if diagnosed during the *Trap Routine* mode. This warning is accompanied by the message CHECK LOG FILE which suggests to read the information contained in the *Log File* function (open the *Functions* menu of the TD Manager).
Both messages disappear by opening the Log File function.

Alarm: Run Aborted - Check Log File

The message ALARM: RUN ABORTED CHECK LOG FILE is displayed when a sequence of analyses is not completed because the gas chromatograph has not reached a Ready condition, not even after the 10 minute wait provided for introduction.

Read the information contained in the *Log File* function (open the *Functions* menu of the TD Manager) to check at which sampling or repetition the sequence was interrupted.
This message is displayed also when there is a problem in the Air Sampler during the *Trap Routine* mode. Open the *Log File* function to check what it is.

Warning: Tube Pressurized

This message is displayed during the Manual Operation if the operator wants to move the tube down when it is still pressurized. In fact, if the auxiliary gas pressure is over 0.05 bar, the movement is stopped and the following message is displayed: WARNING TUBE PRESSURIZED

Set an auxiliary gas pressure value = 0 before moving the tube down.

Error: Aux Gas Press

The message ERROR: AUX GAS PRESS is displayed when the instrument is not supplied by the correct auxiliary gas pressure. Check if the auxiliary cylinder is empty or not connected or if the manometer pressure isn't high enough for the pressure requested.
If the fault continues contact the Technical Service Department.

Maintenance

ATTENTION!!

ALWAYS DISCONNECT THE POWER SUPPLY CORD BEFORE OPENING THE INSTRUMENT

Removing the trap

To disassemble the trap proceed as follows:

- Switch off the instrument
- Withdraw the power cord
- Turn off all the gases
- Uncover the right upper part of the instrument by unscrewing the 2 front screws located on the two sides and gently moving the lid backward.

Attention

To prevent accidentally breaking the trap, absolutely avoid touching it when it is under tension. The slightest pressure or twisting can cause it to break.

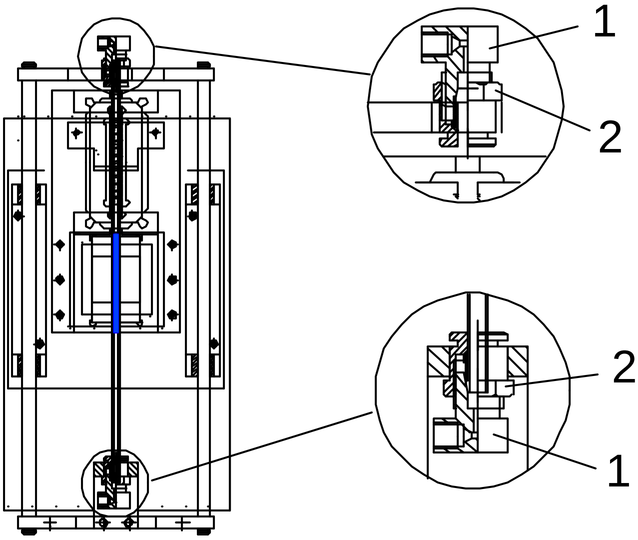


Figure 11-1 - Focusing trap fittings

Immobilize the fitting connected to the gas line (1- Figure 1) and use a 12 mm wrench to loosen the hex head screw (2 - Figure 1) at each end.

- First completely unscrew the front hex head screw and remove the fitting from its position by slightly shifting it to the side and being careful to retrieve the seal.

- Remove the fitting from the opposite end without taking out the trap.
- Slightly push the trap towards the bottom to retrieve the seal at the other end.
- Retrieve the trap by completely removing it from the front part

Filling the trap

DANI has three types of pre-filled traps

- full trap in Tenax GR (60-80 mesh)
- dual layer trap - Carbosieve S-III + Carbotrap
- full trap in Tenax TA (60-80 mesh)

It is highly recommended to use these traps.

To fill a trap proceed as follows:

- Get a new empty trap or empty the one being used, after disassembling it from the instrument, gently pushing the filling with a rigid tube approximately 1 mm in diameter (for example a glass rod or stainless steel tube)
- Insert a glass wool plug approximately 10 mm in length and push it until it is 63 mm from the end of the trap (see Figure 12-2).
- Place the trap vertically on a work surface with the open end facing up.
- Insert a small funnel in the open end.
- Add enough sorbent so that a length of approximately 40 mm is filled, settle the sorbent by gently and frequently hitting the trap.
- Do not compress the filling.
- Insert another glass wool plug 10 mm in length and push it until it touches the filling.
- If the trap needs to be filled with more than one sorbent, first put in the strongest material and then the weakest, separating the sorbents with a minimum quantity of glass wool (approximately 1 mm). Add the amounts of the various materials in the desired proportions so that the total length is equal to 40 mm.

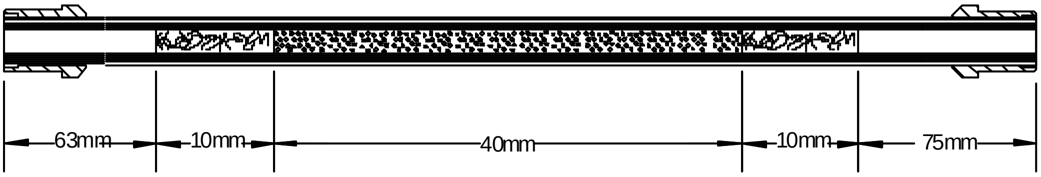


Figure 11-2 - Trap filling drawing

Assembling and conditioning the trap

To assemble a new trap proceed as follows:

- Gently insert the trap from the front part of the instrument following the alignment of the holes and paying attention to the direction. The end with the greater empty volume (75 mm) must face the back of the instrument.

Attention

Trap filling is not symmetric so it is essential to insert the trap in the right direction.

- Gently push it towards the bottom so that it slightly comes out from the hex head screw.
- Put on the Teflon seal with the cone part facing the end of the trap.
- Secure the back fitting by screwing the hex head screw with a 12 mm wrench. Before finishing the seal, gently press the trap to the bottom and then tighten until the hex head screw offers a slight resistance.
- Insert the Teflon seal with the cone part facing the end of the trap at the front end and secure the fitting by gently screwing the hex head screw until it offers a slight resistance.

Attention

To obtain a pneumatic seal for the trap just tighten until there is a slight resistance. Too much tightening can easily break the trap.

- Reinsert the power supply cable and turn on the instrument.
- Supply the carrier gas.
- Select a method and set:

MODE	Trap Routine
TUBE	1
TRAP HIGH TEMP	based on material
TRAP TIME	30
AUX GAS PRESS	1 bar

- Set the conditioning temperature based on the type of sorbent (see the table on page 8-4).
- Insert an empty tube with its septa and caps in position 1 on the carousel.
- Click START to begin the conditioning procedure with a leak test of the pneumatic system including the tube and trap. If the system is not sealed this message appears: LEAK TEST FAILED - CHECK LOG FILE
- Gently tighten the fitting ¼ of a turn and repeat the procedure. If necessary, check the tube.
- If the system is sealed, the instrument continues conditioning the trap with the set temperature conditions and for the set time.
- Put the cover back on the front part and secure it with the two screws located on both sides.

Replacing the needle

The transfer line needle is connected to the line by a fitting and a stainless steel ferrule. To replace the needle:

- Use a 7 mm wrench to support the fitting and with another 7 mm wrench unscrew the needle.
- Replace the needle and tighten the fitting until sealed. It is not necessary to replace the stainless steel ferrule on the tube.

Check the seal by closing the tube outlet, for example with a septum, and pressurizing the carrier gas line.

Cleaning the instrument

Only the smooth external surfaces of the instrument should be cleaned.
Turn off the instrument, remove the power supply cable from the outlet and let any hot parts cool down.

Only use a slightly damp cloth. Do not use alcohol or other solvents.

Handling precautions

If it is necessary to move the instrument, the following precautionary measures should be taken:

- Remove the tubes from the carousel
- Remove the quartz trap following the instructions in the *Removing the trap* paragraph in this chapter .
- Remove the needle from the transfer line.
- Use the original packing to transport the instrument. Do not turn the instrument upside down.

Consumables

Part.no	Description
1260 905 002	Septa D5 for stainless steel tube, set of 100
1260 904 002	Septa D4 for glass tube, set of 100
6310 220 050	Cap for tube Master TD
6310 220 051	Diffusive cap for tube Master TD
6310 220 041	Stainless steel tube Master TD, empty, set of 10
1270 510 002	Focusing trap, empty
9291 409 006	Focusing trap filled withTenax GR
9291 409 007	Focusing trap, double layer
9291 409 008	Focusing trap filled withTenax TA
2306 095016	Ferrule 10M D4 PTFE for focusing trap, set of 10
2322 590 003	Transfer line needle