
PreCon

Operating Manual

PreCon - OPERATING MANUAL **Table of Contents**

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1. Introduction

The PreCon is an automated pre-GC concentration device. It has been developed for the high precision isotope analysis of atmospheric trace gases.

The interest in atmospheric trace gases such as N_2O and CH_4 has been increasing since global warming and the depletion of the ozone layer were found to be strongly connected to these gases.

The approximate concentrations of the trace gases N_2O and CH_4 in atmospheric air are:

0.3 ppm for N_2O
1.7 ppm for CH_4

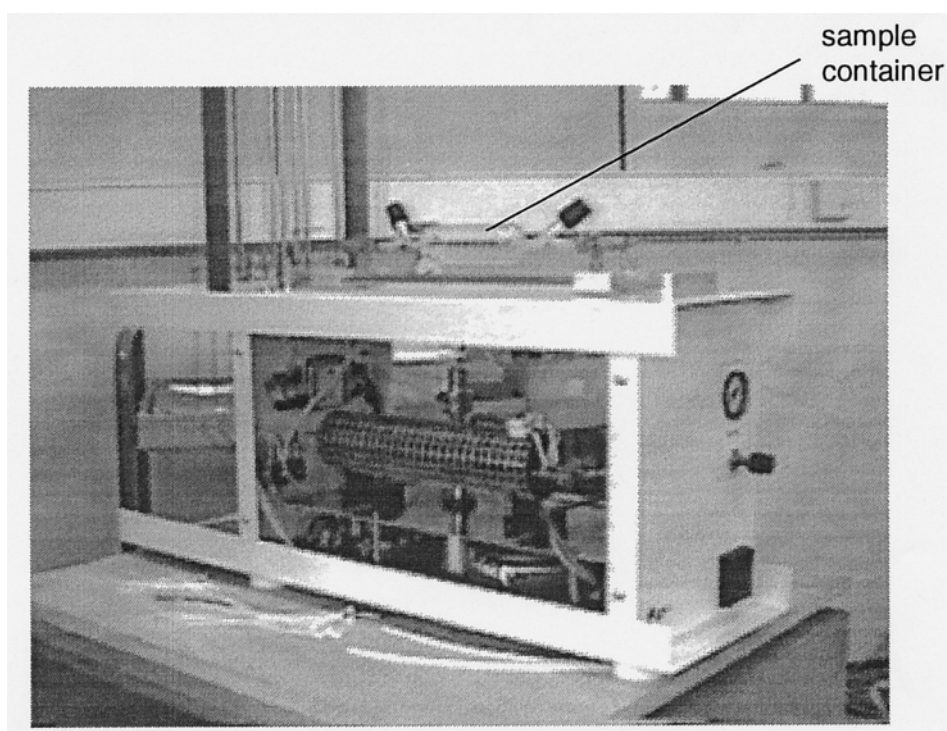
as compared to the concentrations of

Nitrogen	N_2	80%
Oxygen	O_2	17%
Argon	Ar	1%
Carbon dioxide	CO_2	0.036% or 360 ppm

In conventional (dual inlet) isotope analysis techniques, the required sample size for monitoring isotope ratios of atmospheric trace gases is high.

For CH_4 for instance, typically more than 50 liters of air per sample are necessary. Due to the use of Helium as a carrier gas for transporting, a large portion of the sample into the ion source of the mass spectrometer the PreCon method is able to provide isotopic information at the nanomole to picomole level.

Fig. 1 - 1

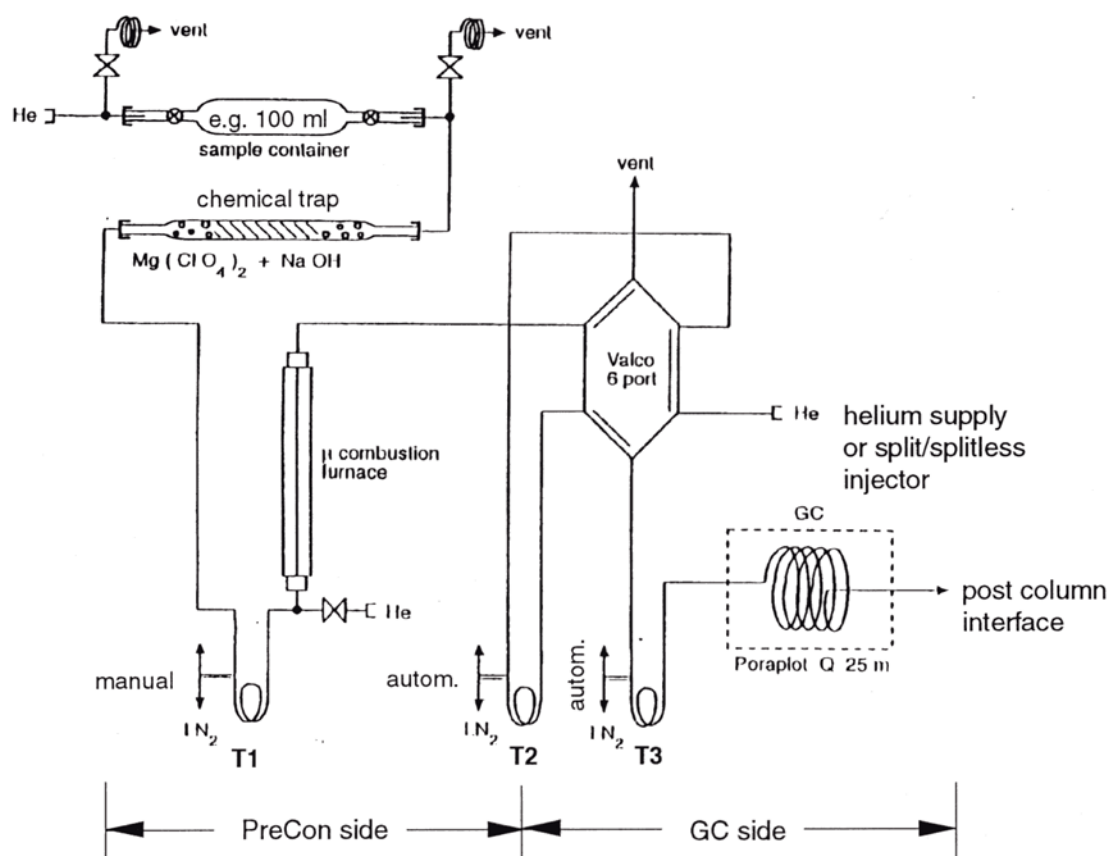


2. Principle of the PreCon

The PreCon collects N_2O or CO_2 (from combusted methane) derived from small air samples into a small diameter cold trap (-196°C) and interfaces it via a GC to an isotope ratio mass spectrometer for on-line isotope evaluation (see Fig. 2 - 1).

This irm-GCMS method is described in the following for the work with N_2O and CH_4 :

Fig. 2 - 1: Layout of the pre-GC concentration device (PreCon)



N_2O : Air samples of 100 ml size containing about 30 nanoliters of analyte gas are driven through a chemical trap (ascarite plus magnesium perchlorate) using a helium flow of 10-15 ml/min. Most of the CO_2 (efficiency > 99.99%) and H_2O is withheld in this trap. A small amount of the CO_2 all of the N_2O and most of the other air constituents escape this chemical trap.

For N_2O analysis, the manual cold trap T1 (see Fig. 2 - 1) downstream the ascarite trap is kept at room temperatures.

The combustion furnace is kept at $<200^{\circ}\text{C}$ (N_2O would be reduced to N_2 at higher temperatures).

Cold trap T2 samples the condensibles (N_2O and traces of CO_2) by removing them from the gas stream at -196°C .

T2 is an automated trap moving in and out of a liquid nitrogen filled Dewar. T2 forms the loop of a 6-port valve (VALCO) for sampling from the gas container and for the transfer from the concentration to the GC side. The GC side of the PreCon includes at the column head a cold trap T3 with an internal diameter of 0.5 mm. T3 acts as a cryofocus device for enhanced GC resolution. ²

The analyte components are transferred to cold trap 3 by removing trap T2 from the liquid nitrogen container.

GC analysis is started by removing T3 from the LN_2 reservoir.

CH₄: For the analysis of CH_4 the cold trap T1 is immersed into the liquid nitrogen Dewar manually. Here, all CO_2 that escaped the ascarite trap and all of the N_2O is removed from the helium stream.

Only components volatile at $\sim -196^{\circ}\text{C}$ pass the trap (N_2 , O_2 , Ar, CH_4 , CO) enter the μ -combustion reactor which is kept at about 1000°C . Oxidation takes place via contact with NiO, converting CH_4 to CO_2 and water. All oxidation products are frozen and transferred to the GC as described for N_2O .

Figures 2 - 2 and 2 - 3 show the peaks that elute from the GC-column.

Fig. 2 - 2

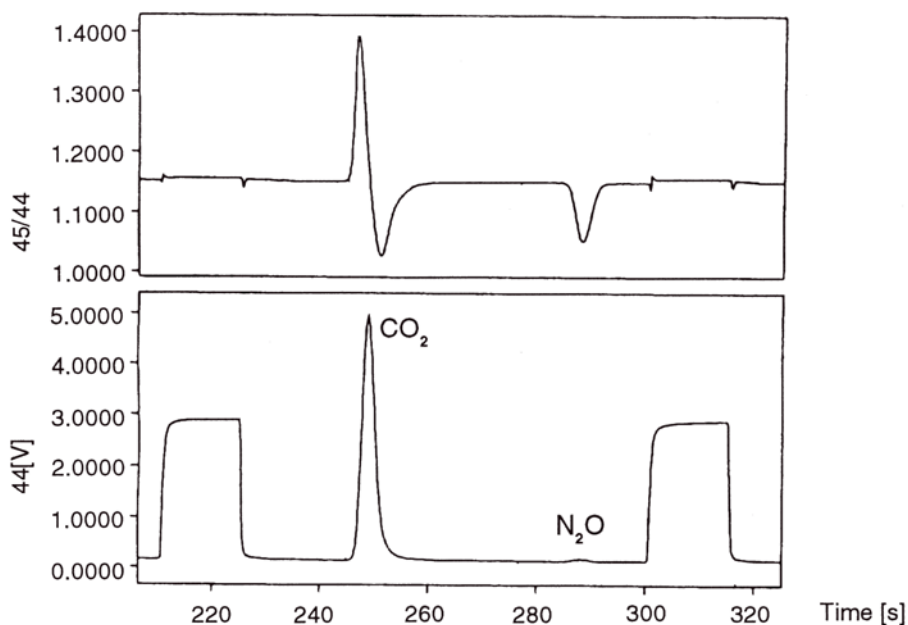
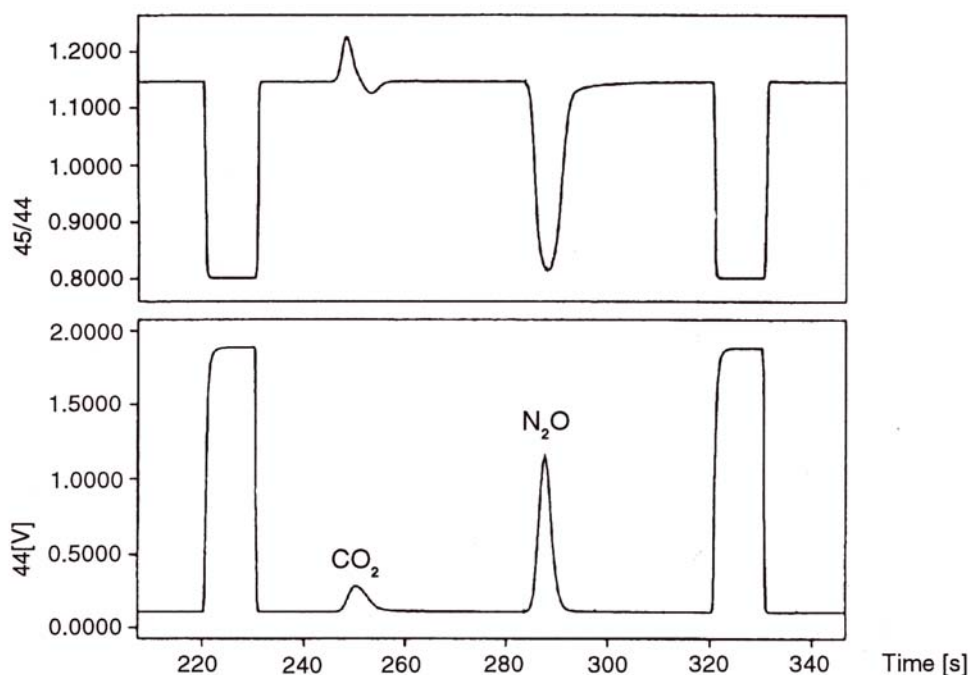


Fig. 2 - 3

In both cases, CO₂ elutes first, N₂O second. The time difference between the two peaks is ~40 seconds.

Due to the chromatographic separation of the isotopomers with the heavier component eluting first, the trace for the ratio 45/44 of CO₂ exhibits a typical S-shape. The square peaks are reference gas injections.

Due to the presence of Ni in the hot furnace, very small amounts of N₂O may be produced during oxidation, which leave a faint response on the irm/GCMS intensity trace.

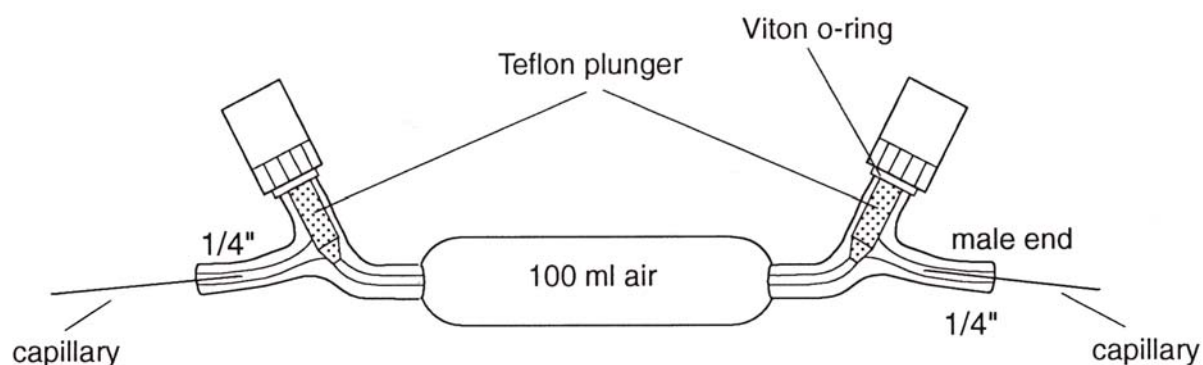
3. The PreCon Hardware:

The PreCon unit usually is positioned at the left hand side of the GC-Box or the GC/C interface. It consists of two parts: a high flow part (20-25 ml helium flow) on the PreCon side and a low flow part (1- 2 ml helium flow) on the GC side (see Fig. 2 - 1, general schematic). The 6-port valve (VALCO) together with the cold trap T2 links the preconcentration part to the GC column. The individual parts of the PreCon are described in the following:

3.1 Sample Container:

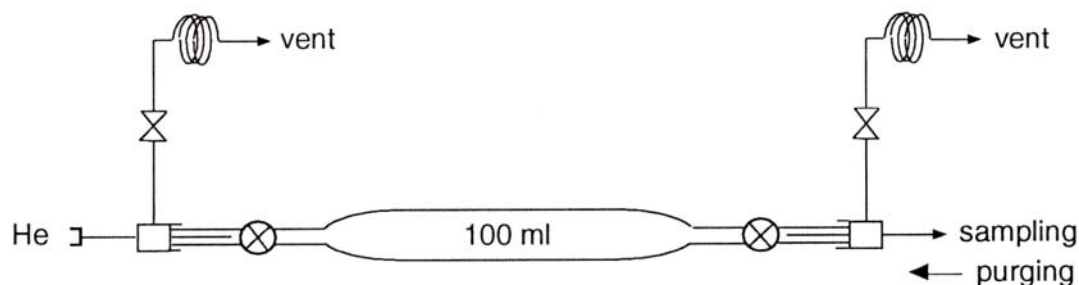
The glass sample container is located on top of the PreCon (see photo, Fig. 1 - 1). Each air sample has to be loaded manually by mounting the glass tube into the corresponding carriage.

Fig. 3 - 1: Sample container



Loading of the sample requires working in a clean environment to avoid contamination. The sample container has two entries (see Fig. 3 -1) sealed with Teflon plungers and (1/4") male ends. The connecting capillaries must be inserted into the 1/4" ends of the sample container. To avoid blanks from ambient air both ends of the container are flushed with helium gas (see Fig. 3 - 2).

Fig. 3 - 2: Helium supply of sample container



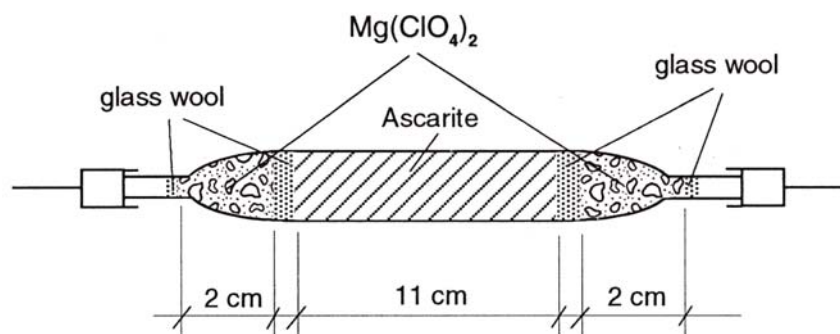
A continuous flow of helium purges all connecting capillaries via two different pathways to provide a very clean working environment.

Hint: To avoid air blanks from sample loading ensure that both capillaries are mounted as deep as possible into the male ends and purge both sides with helium for at least 2 minutes.

To start sampling the sample container valves must be opened and closed manually. All following procedures are software controlled (e.g. valves, traps etc.).

3.2 Chemical Trap:

Fig. 3 - 3: Chemical trap



The chemical trap is filled with $\text{Mg}(\text{ClO}_4)_2$ and NaOH on support (= 'ascarite'). This trap captures close to 99.99 % of the CO_2 from the air sample. H_2O is also withheld in the trap and removed from the helium gas stream, whereas N_2O and Methane CH_4 escape the ascarite trap quantitatively. For removal of CO from the air sample, some Schuetze reagent (I_2O_5) may be included in the filling.

3.3 Cold traps:

There are two fully automated traps (T2,T3) and a manually operated cold trap (T1) in the PreCon. All traps consist of stainless steel capillaries of different internal diameters diving into a liquid nitrogen (LN_2) bath.

Trap T1: This manually operated cold trap is filled with Ni wires.

It captures all CO_2 that escaped the ascarite trap and all other condensables by freezing it from the analyte stream.

The Ni wires prevent the frozen CO_2 ice particles to be blown away by the fast helium stream. The helium flow must not exceed 15 ml/min.

Trap T2: The trap T2 is a stainless steel tube (1 mm i.d.) filled with Ni wires for quantitative trapping. This automated trap may be moved in and out of the Dewar by means of an air actuated piston. This trap freezes all N_2O from the air sample or the combusted CO_2 derived from CH_4 oxidation. It forms the sampling loop of the 6-port valve (VALCO). Depending on the valve position, trap T2

belongs to both sides of the PreCon device: To the preconcentration side with the Valco valve switched to the loop position (loading) and to the GC side with the Valco valve switched to the vent position (injecting). Please refer to the chapter 3.5: 6-port valve.

Trap T3: This small diameter trap (0.5 mm i.d.) is also made of stainless steel. The analyte components are transferred from the larger trap T2 into this smaller trap and frozen again.

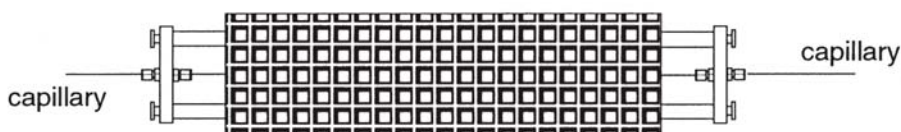
From trap T3, GC analysis is started by removing the trap from the liquid nitrogen container. T3 is also called the column head trap.

Hint: For further improving the GC performance the stainless steel capillary of T3 (0.5 mm i.d., length about 4m) may be replaced with a deactivated fused silica capillary (0.3 mm i.d.).

3.4 Combustion reactor:

The combustion reactor is an alumina tube of 0.8 mm i.d. filled with 3 Ni wires (0.13 mm). It oxidizes methane to carbon dioxide and water at temperatures of about 1000°C.

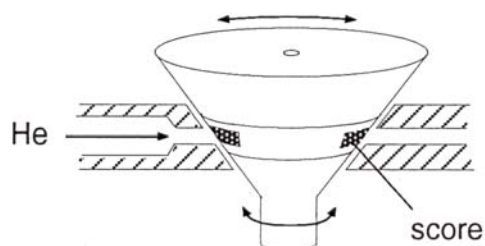
Fig. 3 - 4: Combustion furnace



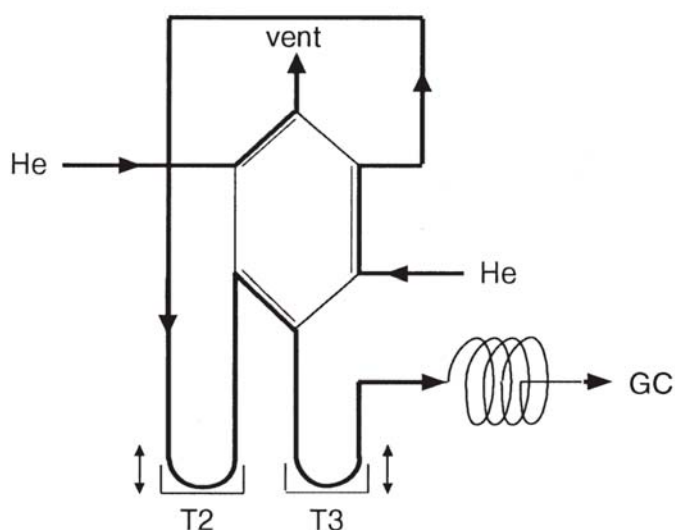
No additional carbon containing substances are allowed to be present at this point.

3.5 The 6-port valve (Valco):

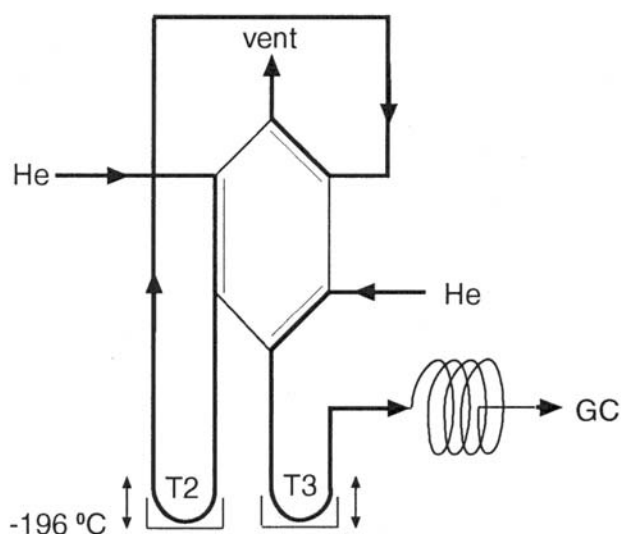
The 6-port valve represents the switch between the PreCon side and the GC side of the PreCon. It is a rotating valve, rotating between two fixed positions. The rotorhead (see Fig. 3 - 5) contains three grooves, which form different pathways for the helium gasflow, depending on the positions of the grooves and the capillaries.

Fig. 3 - 5: Valco valve rotorhead

A clockwise rotation leads to the vent mode.

Fig. 3 - 6: Vent mode

The helium stream on the PreCon side is vented without passing through the sampling loop. On the GC side the helium flow passes the sampling trap T2 and the column head trap T3 to inject the sampled components into the GC column. A counter clockwise rotation of the Valco Valve leads to the load mode.

Fig. 3 - 7: Load mode

This mode is the sampling mode. During sampling, the sampling trap T2 is cooled with liquid nitrogen until most of the sample has passed the PreCon side of the system.

There should be a short delay before lowering the sampling trap in order to flush the system from any accumulated carbon. The sampling time is about 15 minutes. During this time all CO₂ derived from CH₄ by oxidation is frozen out into trap T2. At the same time, only helium passes through trap T3 and supplies the GC column.

To transfer the sample to the GC side, the Valco valve must be rotated to the vent position (T3 is at -196°C). The sampling trap T2 is removed from liquid nitrogen and the analyte components are transferred to trap T3. Here they are frozen again. GC analysis is started by removing the T3 from the liquid nitrogen container.

4. PreCon Software:

4.1 PreCon Software Installation:

The ISODAT PRECON software is shipped on a diskette labeled 'PRECON.WRK' with the delivery of each PreCon unit. The diskette includes a number of executable files and corresponding resource files in addition to those used by the standard ISODAT software. Software requirements: Successfully installed ISODAT and GCC software.

NOTE: The PreCon software has to be installed under the same configuration as the GCC is installed. It may be installed after the standard ISODAT software installation.

Proceed as follows:

Exit the ISODAT program: Press the key <ALT> and simultaneously on the keyboard
type: quit

You are returned to the root directory: C:\(root)
Now switch to the subdirectory ISOTST: Type: cd\isotst
and activate the installation program: Type: install

The ISODAT Installation Menu is displayed.

Activate the related submenus:
Type: 6 for GC/ConFlo Installation Menu
Type: 4 for PreCon Installation

The program will ask:
Please enter the configuration to be installed (A/B/C/D): B

NOTE: Be sure to copy the PreCon files to the GCC configuration already installed.

Configuration is already installed. Continue ? Yes
The program will now copy all PreCon files to the configuration desired and create backup files.
After copying files the program will ask:

Please select the correct hardware address: 36 or 52
The default address is 36
Answer with Yes for address 36. Address 52 is used normally for the internal Multiport!
Please answer exactly and pay attention to the type of parameters to be entered:
numeric i.e. 0,1 ...
or alpha-numeric i.e. Y,N

CAUTION: There is no check of parameters entered and wrong input may cause a faulty system installation.

After the installation is completed, return to the main menu and exit the installation program. Start the ISODAT system software again by re-booting.

4.2 The PreCon Screen:

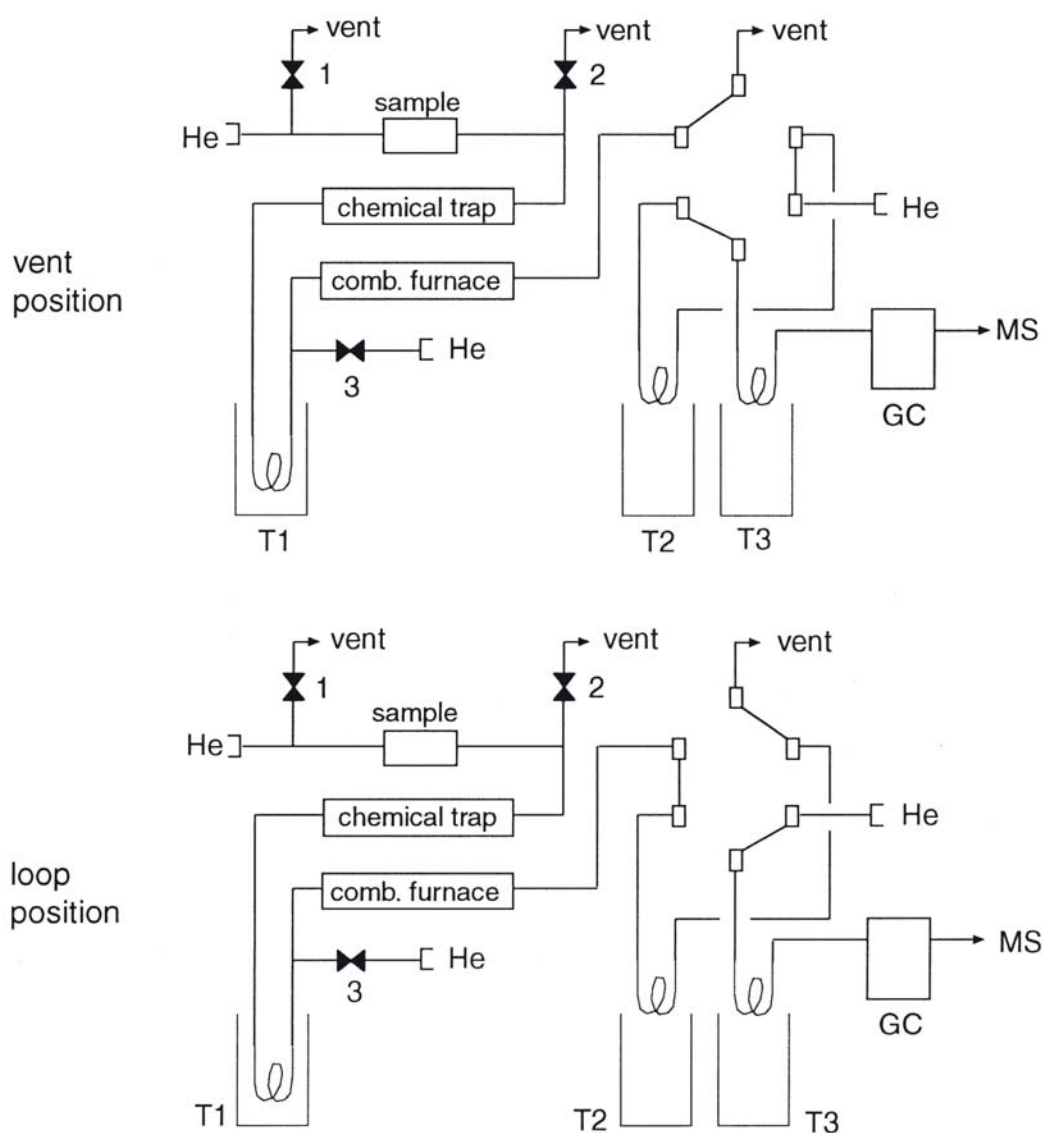
Check if the installation was successful.

Move to the configuration of the respective PreCon, installation/support environment and activate the <GC/Interface> program. A new screen output 'PRECON' is now added to the system.

Click on the 'PreCon' screen with a left mouse click.

A PreCon schematics is displayed on the screen:

Fig. 4 -1: Preparation/concentration interface screen



Function keys:

<HARDCOPY>: Send current screen output to the printer

<KBD INPUTx> Keyboard input. Enter the following parameters for a PreCon action:

vent: the 6 - port valve is switched into vent
or inject position, indicated by the red lines

loop: Valco valve is switched to the load or loop
position for the sampling procedure

Vxop: V = valve, x = number of valve, op = open

Vxcl: Valve number X closed

Txon: Trap number X is on, means the cooling is on

Txoff: Trap number X is off (cooling off)

NOTE: All valves, traps and the vent or loop position of the 6-port valve may also be switched manually via mouse click

<CHECK PROC>: Activation of the check procedure. The program starts checking all process parameters of the PreCon process file step by step. The PreCon process or 'prc' file is described below:

Click <SKIP-> or <SKIP+> function keys with a left mouse click or use the keyboard function keys F7 to move to the previous and shift F7 to move to the next process parameter.

Example of a PreCon process file:

V1op,V2op,V3op

t2off,t3off

enter ('mount sample.press <ENTER>'):screen output

loop

delay (3) 3 seconds

vent

delay (3)

loop

delay (60)

enter 'open sample valves, press <ENTER>'

V1cl (see above)

V2cl

delay(20)

V3cl

delay (40)

t2on

delay (700) 'Freeze sample in T2'

vent

delay (20)

t3on

delay (60)'Freeze T3¹

```
t2off
delay (340) 'Freeze sample T2 -> T3'
t3off
start GC (GC starting command)
```

<RUN PROC>: The PreCon procedure is carried out one time

<HELP>: Gives an overview of the process commands

4.3 Programming the PreCon Unit:

To operate the PreCon a special PreCon process or 'prc' file must be created after the PreCon Installation is finished. All actions to be carried out by the PreCon are written into the PRECON.PRC file (PRC = process) located in the ISOTST subdirectory. Edit the PRECON.PRC using any standard text editor by switching to another console ('<ALT> S' and '<CTRL> 4'). An example is given above.

Note: Please save the PreCon.prc as e.g. Precon.bak before implementing changes.

4.4 PreCon Application Software:

a. <SINGLE ACQ(uisition)>:

For concentrating the trace gases from air, each sample must be mounted manually into the sample carriage. A multiple sample acquisition - <SEQUENCE ACQ> uisition - therefore is not available with the PreCon device. The Single Acquisition program is located in the ACON environment of the respective GCC configuration. The program initiates isotopic analysis of a single sample preconcentrated by the PreCon device and transferred to the Mass Spectrometer via the GCC or GC/GP interface.

Activation of the program displays the editorial page. All required inputs may be edited here, see table:

Table 4-1: Acon start single sample

```
>>> ANALYSIS <<<
      SAMPLE IDENT      : test      /      /
      COMMENT
      METHOD
      NAME              : PRECON
      FILE OUTPUT
      FILENAME          :
      LIST TYPE         :
      FILE TYPE         :
      SAVE DATA TO DATABASE : COL
```


F5 < Measure>
 < Print >
 < STD DIR >
 < SAVE >
 < METH DIR >

Explanation of the possible entries:

SAMPLE IDENT: Sample identifiers
COMMENT: User defined
METHOD NAME: PreCon

Sample identifiers and the method name are entries that will be used as keywords for retrieving acquired data from the database

FILE OUTPUT:

FILENAME: Drive/path/file name
LIST TYPE: Format1...6
FILE TYP: ASCII, DIF or LOT

These entries can be used to automatically generate a data file that can be retrieved with a spreadsheet program.

SAVE DATA TO THE DATABASE:

If data shall be saved to the database, enter COL. Else, data will not be stored

Functions and procedures:

<METHOD DIR>: This function allows to select a method for the analysis to from the method directory. Activation of this function key displays the available methods in a pop up list. To select a method: point the name with the mouse cursor and click the left mouse button. To transfer the selected method to the editorial input line: click the right mouse button.

NOTE: To start an acquisition at least one method must be defined.

<STD.DIR>: Displays all available standards.
<PRINT >: Sends the editorial page to the printer for printout.
<SAVE>: Saves the editorial page input.

<MEASURE>: This function starts the acquisition. The information 'WAITING FOR PEAK JUMPING AND PEAK CENTER READY' will be displayed on the screen.

After the system is ready, up to four different screens are available:

GC-ACQ-1

PRECON

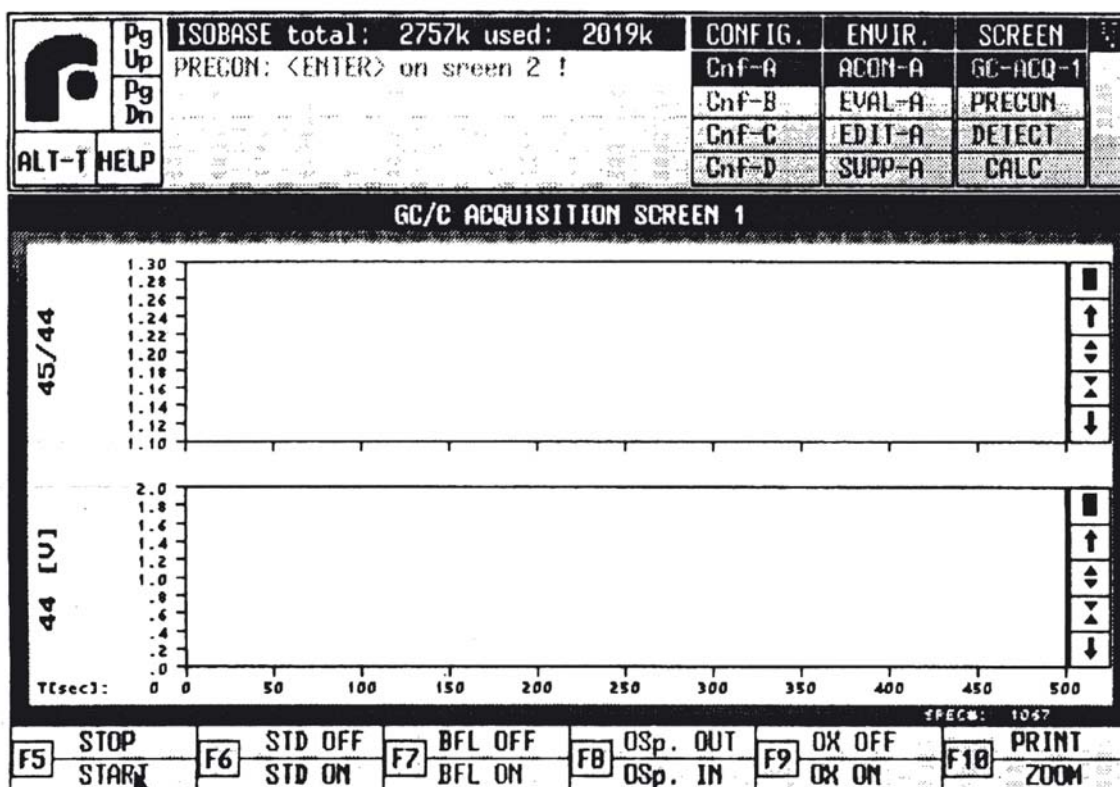
DETECT

CALC

GC-ACQ-1 screen:

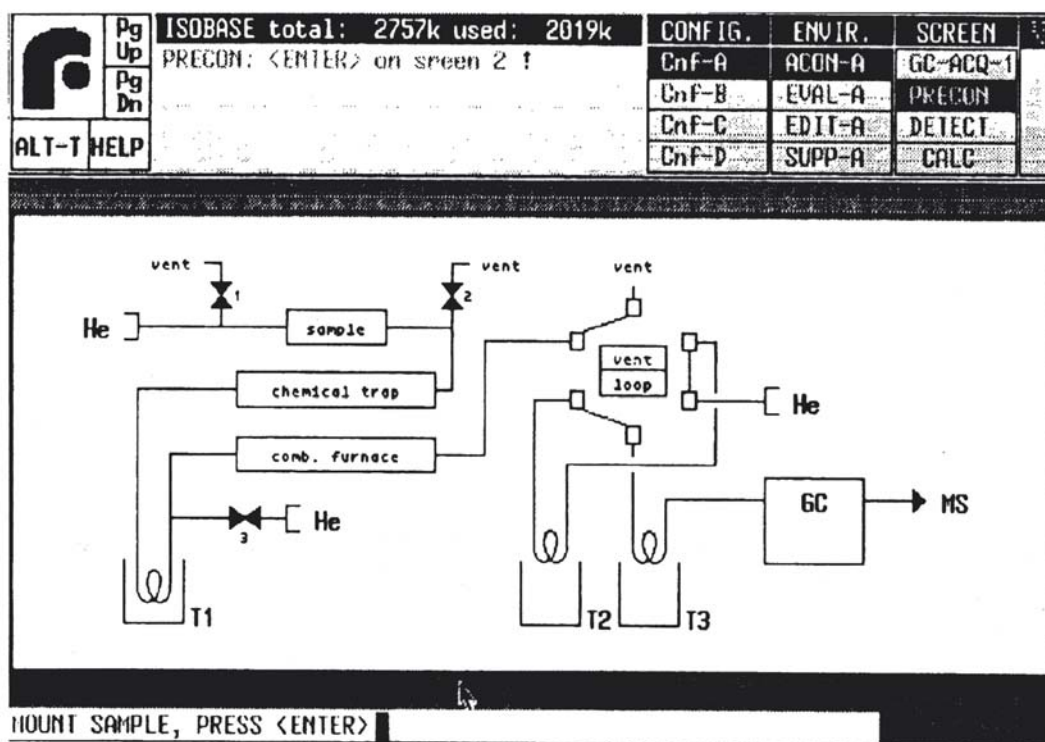
The GC-ACQ-1 screen displays the intensity of the 44 ion current and the 45/44 ratio trace [V] versus time for CO₂ or N₂O (see figure 4 - 2).

Fig. 4 - 2



PRECON screen: The PRECON screen displays the general schematics of the PreCon (see figure 4 - 3).

Fig. 4 - 3



DETECT screen: All peaks detected are listed. Only one function key is available: <HARDCOPY> sends the total list of peaks to the printer.

CALC screen: All detected peaks are calculated after the run is completed and listed here.
(For more information on the peak calculation, please refer to the GCC Manual, chapter: 3.1 GENERAL).

<START>: The <START> function key is present only when the GC-ACQ-1 screen is activated. A single acquisition may be started only by this function key.
After the system has been started a message: PRECON: <ENTER> on screen 2 ! will be displayed in the upper information box.
Switch to the PRECON screen for further information about the action in the PreCon.
The message: MOUNT SAMPLE, PRESS <ENTER> tells you to mount the PreCon sample manually into the respective Pre-Con carriage.
Press <ENTER> when ready.
Now the acquisition is actually started.
A message: PRECON: process running...

indicates the process. All process parameters and delay times will be displayed on the screen stepwise, until:

PROCESS: Start GC is displayed.

To follow the GC-Acquisition switch to the GC-ACQ-1 screen. The Acquisition ends with a printout of the acquired data according to the selected printout format in the method.

<STOP>: Use the <STOP> function key to manually stop and save the acquisition.

NOTE: If <ALT><T> is used to instantaneously terminate the acquisition, data will not be saved nor printed.

All active function keys are indicated in red.

Use

<STD OFF>	to switch the standard off
<STD ON>	or on
<BFL OFF>	to switch the backflush off
<BFLON>	or on
<OSP OUT>	to move the open split out
<OSP IN>	or in
<OX OFF>	to stop the oxidation process
<OX ON>	or start
<PRINT>	Sends the graphical output to the printer
<ZOOM>	This function key allows to zoom graphs displayed with the function keys without using the mouse.

PreCon Method parameters:

To start an acquisition at least one PreCon method has to be defined, as mentioned above.

NOTE: If there is no method available yet, create a method first by using the <METHOD EDITOR> located in the respective Edit environment of your GCC configuration.

The PreCon acquisition method has the following descriptors:

PROMODE	for the process mode
PROCESS	for the sample handling (prior to data acquisition)
EXPERIMENT	for measurement (during data acquisition)
FORMAT	for data output

Change the parameters of an already defined method with the functions:

<PROMODE>: Select mode: PreCon

<PROCESS>: Define the process parameters
STD.MEAS. [SEC]
ON OFF Retention time of standard peaks
e.g. 10 30
BACKFLUSH [SEC]
ON OFF
e.g. 0 1
OPEN SPLIT [SEC]
IN OUT
e.g. 1 0
REOXIDIZE [SEC]
ON OFF
e.g. 0 1

<EXPERIMENT>: Define STANDARD PORT
and SAMPLE PORT to 5 (external inlet)

<FORMAT>: Define the data output parameters

Table 4 - 2

METHOD METHANE 1 PPM

>>> EXPERIMENT <<<

COMMENT

COMMENT :PreCon

GAS

GASNAME :CO₂
CUP # 1 :44.0
CUP # 2 :45.0
CUP # 3 :46.0
RATIO 1 X/Y :45.0 / 44.0
RATIO 2 X/Y :46.0 / 44.0

CHANGEOVER

COV PORT #1 :VAR. VOLUME 1
COV PORT #2 :VAR. VOLUME 2
COV PORT #3 :
COV PORT #4 :
STANDARD PORT # :5
SAMPLE POER # :5

MEASURE

PEAKCENTER :YES
MASS :45.0
STORAGE OFFSET TIME [SEC] :5
ACQ. END TIME [SEC] :498

PEAK DETECT

STARTING SLOPE [mV/ SEC] : **0.200**
 ENDING SLOPE [mV/ SEC] : **0.400**
 MIN. AMPLITUDE [V] : **0.050**

PEAK CALCULATION

BACKGROUND TYPE : **I**
 TYPE T STARTTIME : **20**
 TYPE T ENDTIME : **30**
 SOURCE CALIBRATION : **NO**

STANDARD PEAKS

1	:	125	DELTA	:	-42.000
2	:	0	DELTA	:	0.000
3	:	0	DELTA	:	0.000
4	:	0	DELTA	:	0.000
5	:	0	DELTA	:	0.000
6	:	0	DELTA	:	0.000
7	:	0	DELTA	:	0.000
8	:	0	DELTA	:	0.000

>>>PROCESS

<<< **MODE : PRECON**

	STD MEAS. [SEC]		BACKFLUSH [SEC]		OPEN SPLIT [SEC]		REOXIDIZE [SEC]	
	ON	OFF	ON	OFF	IN	OUT	ON	OFF
1:	10	30	0	1	1	0	0	1
2:	60	80	0	0	0	0	0	0
3:	110	130	0	0	0	0	0	0
4:	0	0	0	0	0	0	0	0
5:	0	0	0	0	0	0	0	0
6:	0	0	0	0	0	0	0	0
7:	0	0	0	0	0	0	0	0
8:	0	0	0	0	0	0	0	0
9:	0	0	0	0	0	0	0	0

	STD MEAS. [SEC]		BACKFLUSH [SEC]		OPEN SPLIT [SEC]		REOXIDIZE [SEC]	
	ON	OFF	ON	OFF	IN	OUT	ON	OFF
10:	0	0	0	0	0	0	0	0
11:	0	0	0	0	0	0	0	0
12:	0	0	0	0	0	0	0	0
13:	0	0	0	0	0	0	0	0
14:	0	0	0	0	0	0	0	0
15:	0	0	0	0	0	0	0	0
16:	0	0	0	0	0	0	0	0
17:	0	0	0	0	0	0	0	0
18:	0	0	0	0	0	0	0	0

>>> FORMAT

<<< **MODE : FORMAT**

PRINTER

LIST TYPE : LONG
 GRAPHICS : NO

5. How to start a PreCon Analysis:

5.1 Hardware Requirements:

To start the PreCon Analysis several hardware requirements have to be checked:

- PreCon:
 - The liquid nitrogen Dewar should be filled
 - The helium purity should be 99.999% or better.
The helium pressure in the PreCon for standby and reoxidation should be about 5 psi. Start an analysis with helium pressures of about 20 psi.
 - In case of methane (CH_4) determination, make sure that trap T1 is immersed into the liquid nitrogen Dewar and the oxidation reactor is at temperatures of 1000 °C. Before starting the μ combustion reactor for the first time, make sure the reactor is properly oxidized by oxidizing it at least once overnight with a pure oxygen sample (pressure 5 psi, low flow).
 - For N_2O determinations trap T1 has to be inactive and the oxidation reactor should be set to room temperatures.
- GC Interface:
 - Column: Use a Pora PLOT Q column, length 25 m, 0.32 mm i.d.
 - GC Injector: Set split mode to 1:20 or higher for helium supply of the trap T3 and the GC column.
 - GC Parameters: 25 °C isothermal, 10 psi He headpressure
 - In case a GCC interface is connected to the system be sure to deactivate both the oxidation and the reduction reactors.
(Set to RT) RT= room temperature
 - Valves: Backflush off, Open Split in, Reoxidize off

5.2 Software Requirements:

- PreCon.PRC: Ensure sufficient preconcentration and transfer times relating to the sample volume (20 ml/100 ml/500 ml).
- Method: Define a method for both applications CH_4 or N_2O . The only difference is the delta value of the reference peak.
- Reference gas: For CH_4 the reference gas is CO_2
For N_2O the reference gas is N_2O .

5.3 Start single Sample Acquisition:

- Activate editorial page (ACON environment, Single Sample)
- Edit identifiers and select method
- Prepare acquisition (Press <F5>)
- Switch to screen 2 ('PreCon')
- Follow the commands prompted in the command line

of the 'PreCon' page:

'Mount sample, press ENTER'

'Open sample valves, press ENTER'.

5.4 GC performance Requirements:

- Minor traces of CO₂ collected from the carrier gas need to be separated from the N₂O peak by at least 30 sec (40 sec is better).
- The background detected for the N₂O peak should not exceed the background of the CO₂ peak by more than 1 mV (= 2 counts on the 44 trace).
- The isotope ratio 45/44 of CO₂ exceeds that of N₂O by about 350‰ (!). Thus, any CO₂ left as a background under the N₂O peak will interfere considerably and reduce the accuracy of the background determination and correction.

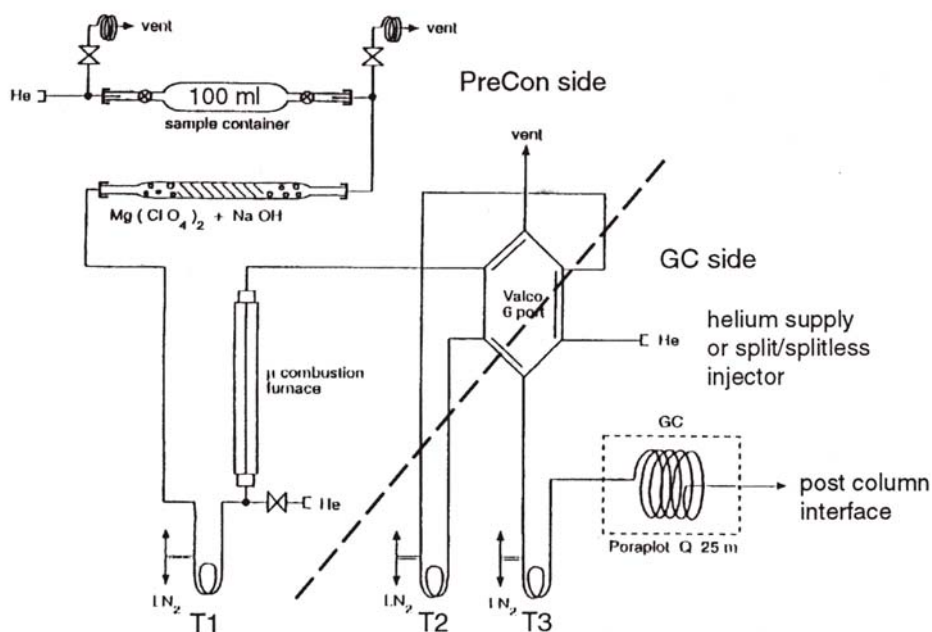
6. PreCon Assembly and Basic Tests

6.1 Introduction

The PreCon is designed for the preconcentration of trace gases in air or other samples and their high precision isotope analysis. Using the PreCon gives the advantage to analyze trace gases with concentrations in the low ppm to ppb range (e.g. Methane 1.7 ppm, N₂O 300 ppb) using air sample sizes of 100 ml and less.

The PreCon consists of two parts: a high flow part of 20 - 25 ml/min (PreCon side) and a low flow part of 1- 2 ml/min helium flow (GC side). Trap T2 belongs to both sides depending on the Valco valve being switched to vent or load mode. The PreCon is linked between the GC injector and the GC capillary column in the GC/C interface or the GC/GP interface.

Fig. 6 - 1: General Schematic of the PreCon



6.1.1 Assembly

The position of the PreCon usually is on the left hand side of the GC-Box or the GC/C interface.

- Connect all peripherals to compressed air, driver boards, helium and power supplies (see Figure 6 - 2a+b). The quality of the helium should be at least 99.996%.
- Connect all transfer capillaries between PreCon, GC-Box and GP-Interface or GC/C. Connect the transfer capillaries to the IRMS (see Figure 6 - 3a+b), keep the ion source still closed.

- Leak Check on helium supply lines: This check can only be performed, if a pressure meter is available in the main helium supply line to the PreCon/GC/C or Pre-Con/GC/GP interface.
Set the main supply to 5 bar. Close all three helium pressure reduction units at the front panels of the PreCon, GC/GP or GC/C (counter clockwise). Close the main supply. The pressure may not drop within 30 min or longer.
- Check Clipboard Cards and Valves: Switch on and off all valves using the Interface Control in ISODAT. Watch the LED lights on the pneutronics or clipboard cards. Watch all pneumatic valves and pistons moving.

Fig. 6 - 2a: PreCon-GC/GP driver card lines, helium and compressed air supply lines

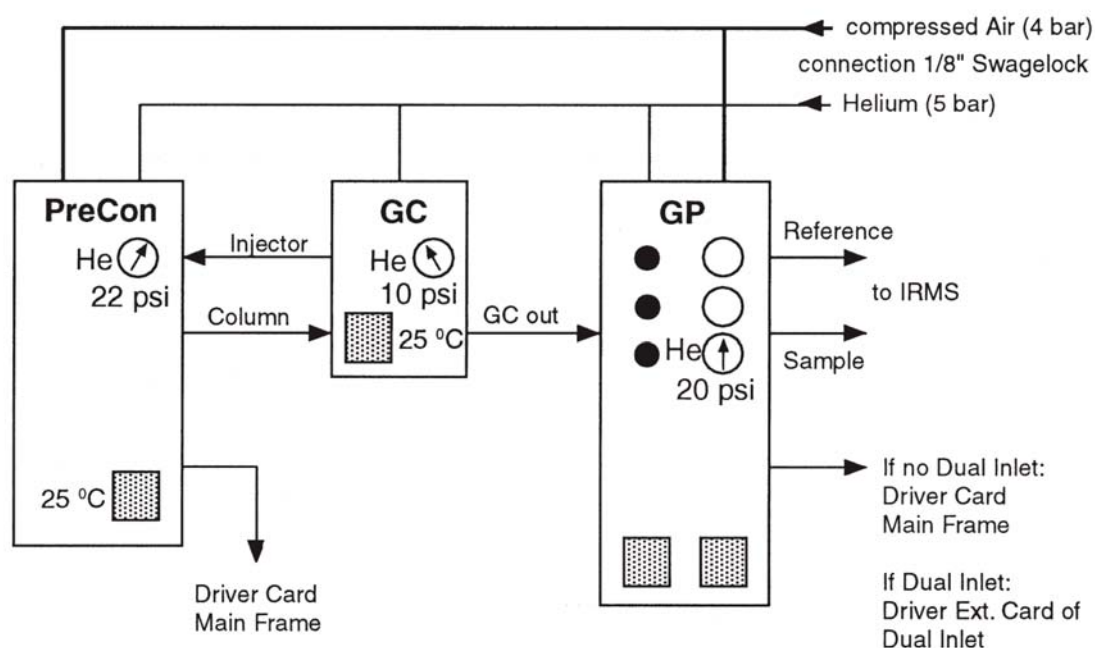


Fig. 6 - 2b: PreCon-GC/C driver card lines, helium and compressed air supply lines

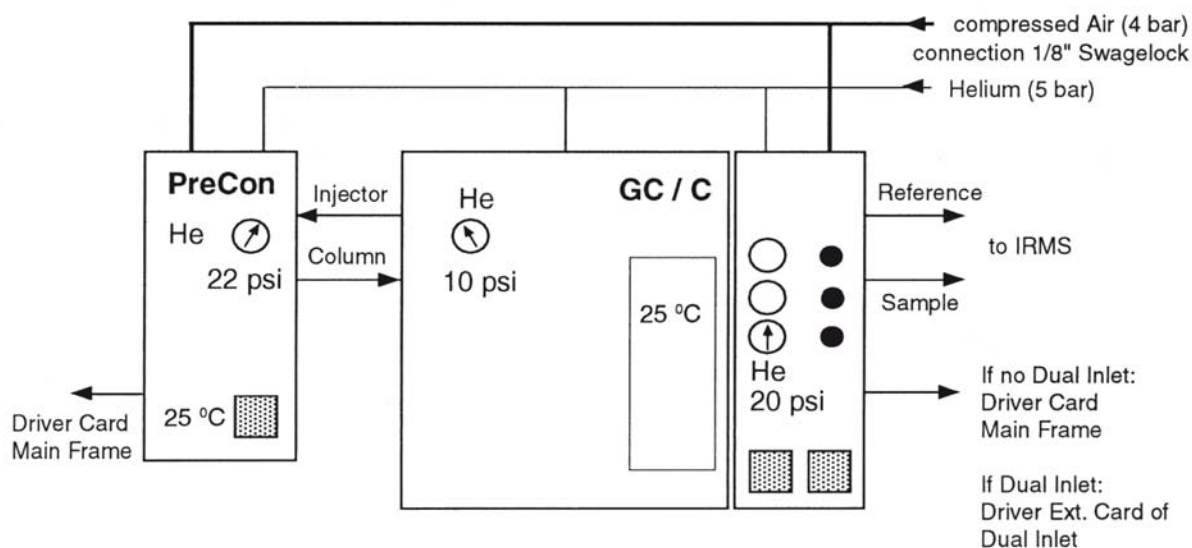


Fig. 6 - 3a: PreCon-GC/GP transfer lines

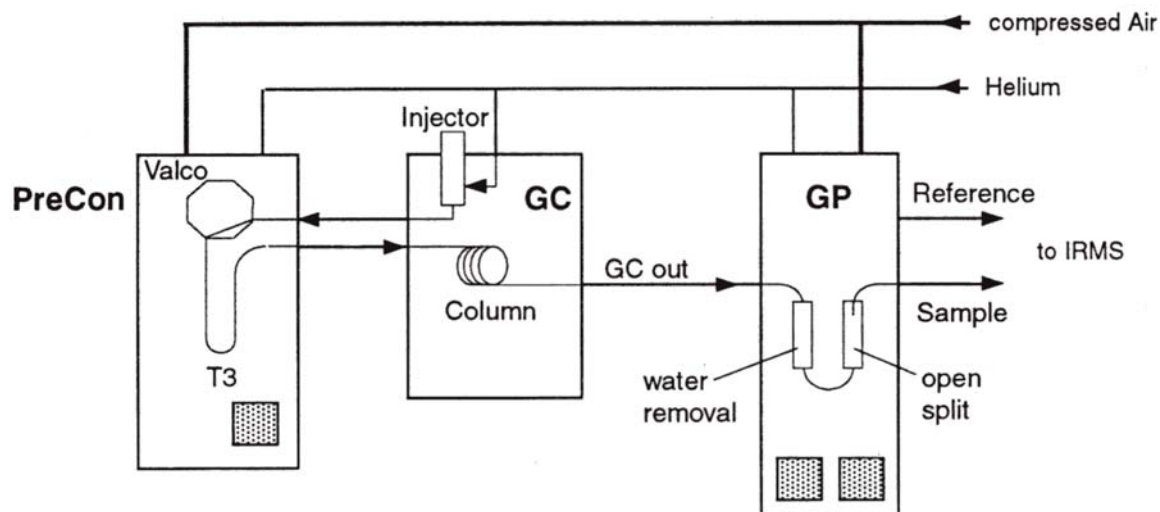


Fig. 6 - 3b: PreCon-GC/C transfer lines

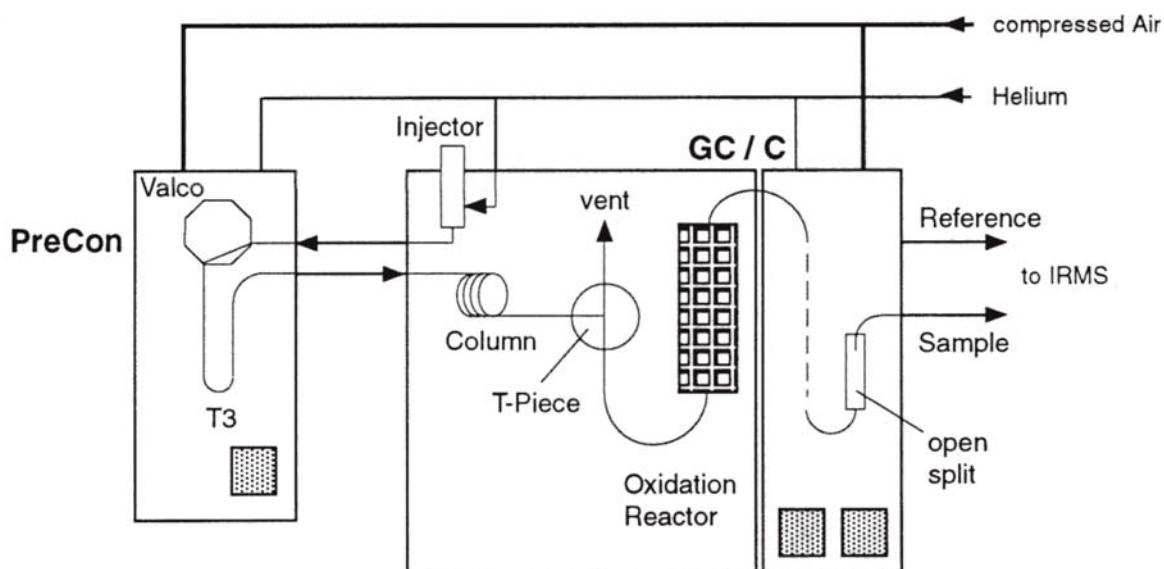
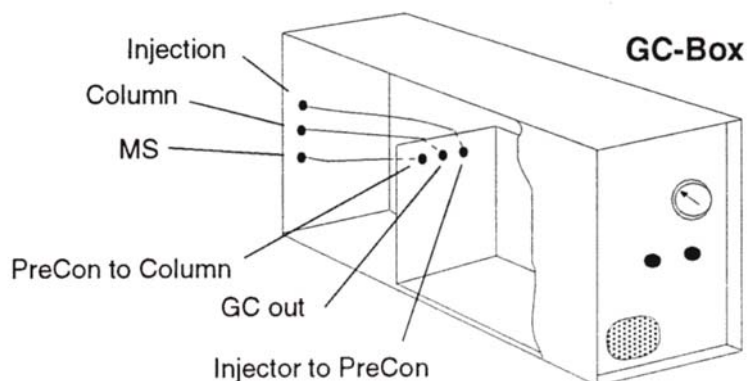


Fig. 6 - 4: GC-Box internal back plate, capillary connectors and passing through



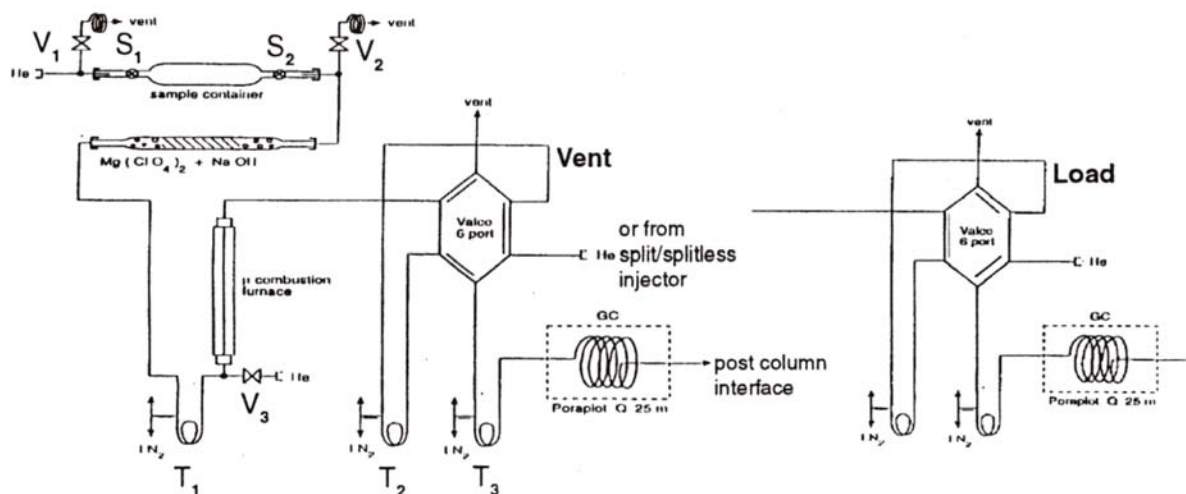
6.1.2 Setup for Basic Checks

- Connect a 3 - 5 m deactivated fused silica capillary instead of the PPQ column to the transfer capillary from the PreCon (see Fig. 6 - 4). Increase the injector pressure to ca. 3 psi. The measured flow at the column end should be 2 - 3 ml/min. Set the split flow of the split/splitless injector to 20 ml/min and the septum purge to 2 - 5 ml/min.
- Connect the end of the fused silica capillary to the GC-out of the GC-Box. In case of the GC/C-Interface, connect the fused silica capillary to the Valco T- or X-piece in the GC oven.
- Set the helium pressure of the GP or the Combustion Interface to 20 psi.
- Place the empty spare glass chemical trap to the Cajon supports inside of the PreCon instead of the filled chemical trap.

Do not mount the filled chemical trap at this state to prevent damage

- Place a sample container to the Cajon supports on top of the PreCon; open both sample valves (S1, S2).
- Open valves V1, V2, V3 in the Interface Control window.
- Set the PreCon helium pressure to 22 psi.

Fig. 6 - 5



6.1.3 Flow Checks

If there are active Backflush valves in the GC/GP like in the GC/C interface, the sum of the column flow and the backflush flow (ca. 2 ml/min) can be measured at the backflush vent (see Fig. 6 - 3b) on top of the GC. For further GC/C flow checks, please refer to the GC/C Setup and Performance Tests (in preparation).

Check for	Valve settings ¹⁾	Flow Rates	Remarks
He Supply at V1	□V1, ■V2, V3, no Container (S1, S2)	20—25 ml/min at the Cajon connector at V1	Make sure there is no leak at the vent of V1
Backflush flow at Valco vent	■V1, V2, V3; □S1, S2 ↑Vent	20 - 25 ml/min at the Valco vent	↑vent or ⇒Load may not alter the flow rate
Backflush flow at V1 vent	■V1, V2, V3; □S1, S2 ↑Vent	20 - 25 ml/min at the V1 vent	Checking leaktightness of the V1 vespel valve seat ²⁾
Backflush flow at V2 vent	□V1, V2, V3; □S1, S2 ↑Vent	15 - 20 ml/min at the V2 vent	Checking leaktightness of the V2 vespel valve seat ²⁾
Sampling flow at Valco vent without T2	□V1, V2, V3; ■S1, S2 ↑Vent	18 - 22 ml/min at the Valco vent	Checking the whole line: from V1 to Valco vent
Sampling flow at Valco vent with T2	□V1, V2, V3; ■S1, S2 ⇒Load	18 - 22 ml/min at the Valco vent	Checking the whole line: incl. Ferrules of T2.

- ¹⁾ □Vx, □Sx: valves closed; ■Vx, ■Sx: valves open;
V1 - 3: pneumatic valves 1 -3; S1 - 2: manual sample valves 1 - 2;
⇒Load: Valco 6-port in LOAD mode; ↑Vent: Valco 6-port in VENT mode;
T1 -3: Cryo traps 1 - 3 (T1: manual; T2 - 3: pneumatic)

- ²⁾ For pneumatic valves, please refer to the SGE maintenance information (startup kit)

6.1.4 Leak Checks

Only start with Leak Checks when all flow checks are within the given ranges
Before starting any leak checks by monitoring the background Argon levels or using an Argon jet, first, **a baseline level of the Argon from the Helium supply** has to be measured.

- Switch on the Backflush (F7), Open Split out (^F8) in the Interface Control window
- Activate m/z 40 on the middle cup ($R = 3 \times 10^{10}$ W) (F5) in the Instrument Control window
- Carefully open the needle valve to the ion source (turn off the filament temporary)
- The source pressure should read $1 - 2 \times 10^{-6}$ mbar (*DELTA^{plus}*, penning gauge) or $4 - 6 \times 10^{-6}$ mbar (MAT 252, ion gauge)

The Argon baseline level usually should be < 20 mV. Ensure that there is no leak in the supply line or the pressure-controlling unit in the GP or Combustion interface. For a more detailed leak detection use a low Argon flow from a jet (Ar gas tank). Also, refer to the Precon Performance Tests. If you are sure that all plumbings in the Helium supply line are leak tight, the Argon background level relates to Argon contaminations in the Helium gas tank. All further tests relate to this baseline value, and should be as close as possible to it.

GC side

For a more detailed leak test of the GP or GC/C interface, please refer to "GC Tests" of the "Precon Performance Tests" or the GC/C Setup and Performance Tests (in preparation).

Try to get as close as possible to the baseline Argon level

Checked Parts	Valve settings ¹⁾	Ar signal - baseline ²⁾	Remarks
Injector ³⁾ , ferrules of T3 at Valco 6-port capillary connector, GP or GC/C	⇒Load	< 20 mV	GP or GC/C back flush off, open split in!
Injector, ferrules of T3+T2 at Valco 6-port (2,3,4,5), capillary connector, GP or GC/C	↑Vent	< 20 mV	↑Vent or ⇒Load may not alter the argon signal

- 1) ☐Vx, ☐Sx: valves closed; ☒Vx, ☒Sx: valves open;
V1 - 3: pneumatic valves 1 - 3; S1 - 2: manual sample valves 1 - 2;
⇒Load: Valco 6-port in LOAD mode; ↑Vent: Valco 6-port in VENT mode;
T1 - 3: Cryo traps 1 - 3 (T1: manual; T2 - 3: pneumatic)

- 2) Instr. Control readout - Baseline = Leaks from checked parts

- 3) For a better detection of leaks in the injector, decrease the split flow rate

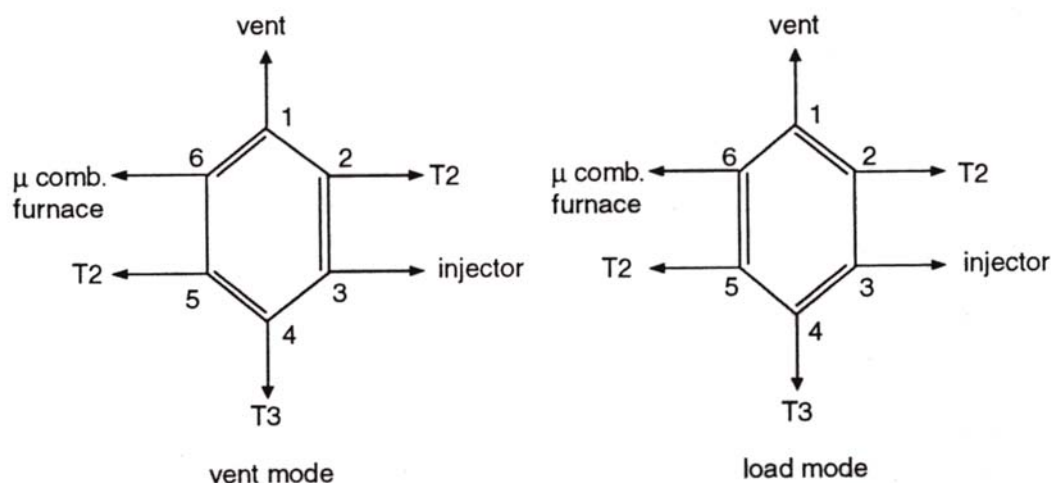
6.1.5 PreCon side

Only start with Leak Checks when all flow checks are within the given ranges

The PreCon side has no direct link to the GC flow path and the IRMS. Therefore, a direct leak check monitoring Argon is not possible. To perform a direct leak check, the transfer capillary from the open split to the ion source will be used as a probe in the Valco vent on top of the PreCon.

- Close the needle valve to the ion source
- Remove the 100 μm i.d. fused silica transfer line from the open split
- Carefully place it in the vent exit of the Valco 6-port valve (easy open split) Fix it with some tape to prevent disconnection and venting the IRMS
- Activate m/z 40 on the middle cup ($R = 3 \times 10^{10}$ W) (F5) in the Instrument Control window. For a better monitoring of also fast changes press F7 (screen update speed)
- Carefully open the needle valve to the ion source (turn off the filament temporary)
- The source pressure should read $1 - 2 \times 10^{-6}$ mbar (*DELTA^{plus}*, penning gauge) or $4 - 6 \times 10^{-6}$ mbar (MAT 252, ion gauge)
- Switch on the filament

Fig. 6 - 6: Valco 6-port valve; port numbers and flow directions



Try to get as close as possible to the baseline Argon level

Checked ferrules at	Valve settings ¹⁾	Ar signal - baseline ²⁾	Remarks ³⁾
V3, μ comb. furnace, Valco ports: 1, 6	■V1, V2, V3; □S1, S2 ↑Vent	< 10 mV	
V3, μ comb. furnace, Valco ports: 1, 2, 5, 6	■V1, V2, V3; □S1, S2 ⇒Load	< 10 mV	↑Vent or ⇒Load may not alter the argon signal
For the next test, first open the sample valves (■S1, S2); close valve 1 (□V1); wait for rinsing the sample container 4); close valve 2 (□V2) wait for pressure build up in the sample container (1 - 2 min); close valve 3 (□V3)			
V1, V2, chem. trap, V3, μ comb. furnace, Valco ports:	□V1, V2, V3; ■S1, S2 ↑Vent	< 10 mV	
V1, V2, chem. trap, V3, μ comb. furnace, Valco ports: 1, 2, 5, 6	□V1, V2, V3; ■S1, S2 ⇒Load	< 10 mV	↑Vent or ⇒Load may not alter the argon signal

- 1) □Vx, □Sx: valves closed; ■Vx, ■Sx: valves open;
 V1 - 3: pneumatic valves 1 -3; S1 - 2: manual sample valves 1 - 2;
 ⇒Load: Valco 6-port in LOAD mode; ↑Vent: Valco 6-port in VENT mode;
 T1 -3: Cryo traps 1 - 3 (T1: manual; T2 - 3: pneumatic)
- 2) Instr. Control readout - Baseline = Leaks from checked parts
- 3) For a better detection of leaks in the injector, you can reduce the flow rate in the PreCon (ca. 10 psi headpressure)
- 4) To rinse the sample container completely, increase the helium pressure to 22 psi and wait for ca. 30 min.

For a more detailed detection of leaks using a jet with Argon from a gas tank and further tests, please refer to the "PreCon Performance Tests".

Before continuing testing,

- close the ion source
- place the transfer line into the open split
- open valves 1 - 3
- mount the chemical trap to the Cajon supports inside of the PreCon

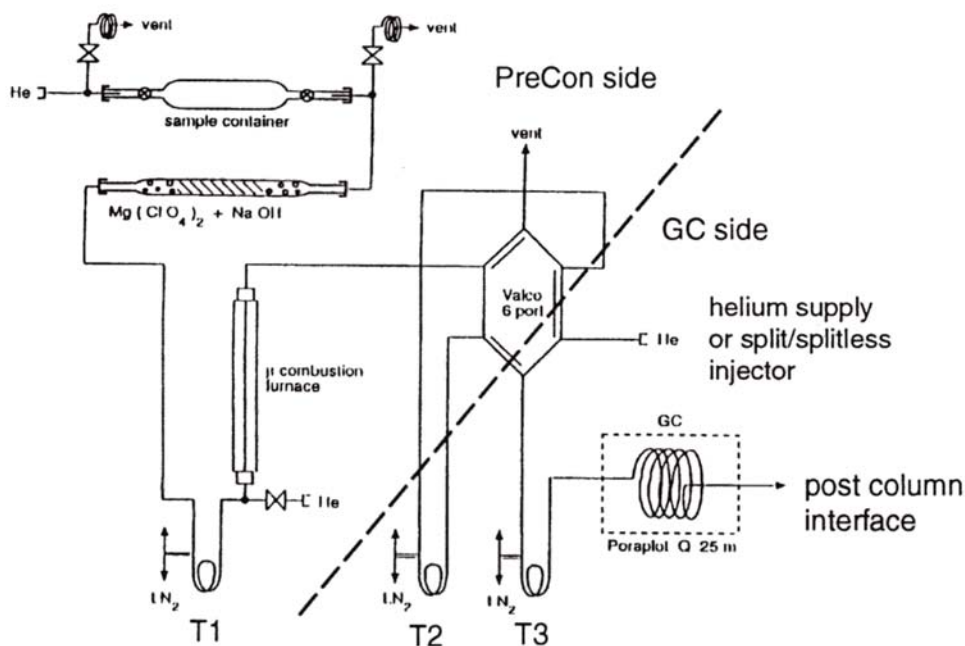
6.2 PreCon Performance Tests

6.2.1 Introduction

The PreCon is designed for the preconcentration of trace gases in air or other samples and their high precision isotope analysis. Using the PreCon gives the advantage to analyze trace gases with concentrations in the low ppm to ppb range (e.g. Methane 1.7 ppm, N₂O 300 ppb) with air sample sizes of 100 ml and less.

The PreCon consists of two parts: a high flow part of 20 - 25 ml/min (PreCon side) and a low flow part of 1 - 2 ml/min helium flow (GC side). Trap T2 belongs to both sides depending on the Valco valve being switched to vent or load mode. The PreCon is linked between the GC injector and the GC capillary column in the GC/C interface or the GC/GP interface.

Fig. 6 - 7



6.2.2 GC Tests

The GC Tests are checking the GC/GP or the GC/Combustion Interface together with the GC part of the PreCon for leaks, optimal transfer and GC performance. The GC part of the PreCon consists of trap T3 ('column head') and part of the Valco valve connected to the Split/Splitless injector and trap T3. Ensure that the Valco valve is in 'LOAD' position.

1. GC column

Mount the PoraPLOT Q column carefully into the GC oven. This column is sensitive to fast pressure changes (pressure changes should be less than 1 psi per second).

Please follow the PPQ set-up instructions

GC parameters: 10 psi, 25°C (room temperature), Split 10 - 20 ml/min, Backflush off (GCC II), open split in

2. Transfer Test

Inject 3 to 4 μ J of air. Detect the m/z 40 peak (Argon) on the cup with 3×10^{10} W. Note the transfer time. The peak should be sharp and intensive.

Inject 3 to 4 μ J of breath. Time and shape of the m/z 44 (on 3×10^{10} W) peak should be as similar to the argon peak as possible.

3. Leak Test

Use some Argon gas flowing gently through a jet (very low flow). Monitor m/z 40 (3×10^{10} W). Check all connectors in the tested gas line.

Always check from the IRMS to the GC injector and if needed to the Helium supply.

4. Blank Test

Freeze trap T3 for 5 to 6 min in liquid nitrogen. Release trap T3 to room temperature. Monitor m/z 44, 45, 46 on the CO₂ cup configuration in Instrument Control or run an acquisition in GC Combustion mode (CO₂). If all other tests show good results, this test should give you information on the CO₂ contamination in the Helium supply.

5. GC Performance Test

Prepare a mixture of CO₂ and N₂O. E.g. 10 ml vial (exetainer) + 100 μ l N₂O + 100 μ l CO₂. Inject 10 μ l of this mixture freezing it in T3. Release trap T3 to room temperature (GC start). Both peaks should show a good peak shape of similar height. CO₂ elutes before N₂O; the difference in retention time between both peaks should be 25 to 30 seconds or more. The background in front of the N₂O peak should be less than 1 mV higher than background in front of the CO₂ peak. As an alternative more close to reality, a mixture of 10 ml of ambient air and 100 μ l of N₂O can be used. The chromatogram then should look similar to Fig. 6 - 8.

6.2.3 PreCon Tests

The tests on the preconcentration side of the PreCon (20 to 25 ml/min) are special tests to check for leaks and 100% transfer from the sample flask to trap T2 at the Valco valve.

Take care that the chemical trap is properly filled, the Combustion Reactor is at ambient temperature, a sample container or, instead, the empty spare chemical trap is mounted in the sample support, the PreCon headpressure is 20 - 22 psi.

1. Basic Tests

Check flows at the vent of the Valco valve in Straight (valves 1, 2, 3 closed; valves of sample flask open!) and Backflush (valves v1, v2, v3 open) mode of the PreCon. Flows should be in the range of 20 to 25 ml/min. For more tests, you can check in load and in vent mode. If more detailed tests at the valves v1, v2, v3 seem to be necessary, please refer to the capillary schematics.

2. Leak Test

The best and most convenient way to check for leaks is to use Argon flushing on the fittings and to monitor the response at the vent of the Valco valve. Close the needle valve to the IRMS ion source. Remove the 100 μ m i.d. fused silica transfer line from the open split and insert it carefully into the vent exit of the Valco valve on top of the PreCon. Reduce the flow in the PreCon (headpressure ca. 10 psi). Test each fitting starting from the Valco valve backwards to the sample support and to the helium supply. Monitor m/z 40 (3×10^{10} W) on the potentiometric recorder or in Instrument Control.

You can increase the screen update speed in Instrument Control pressing F7.

In the same mode, you can also perform a very basic blank test. Freeze T1 for some minutes (vent mode) and release to room temperature. Freeze T2 for some minutes (load mode) and release to room temperature. Freeze T2 for some minutes and release to room temperature while T1 is active. Record with the potentiometric recorder or use the GCC acquisition mode.

6.2.4 Combined PreCon / GC/GP Tests

Take care that all modifications from the other tests are changed back to standard mode.

1. Blank Test

You can perform the blank test still using the empty spare chemical trap tube instead of a sample mounted in the sample support. Keep the oxidation reactor still cold.

Test for a CO₂/N₂O blank using the default PreCon procedure.

The response of the N₂O should be less than 1 mV. The response of the CO₂ should be similar to the T3 blank test. The retention time should be the same as in the GC test when freezing the sample in T3.

Ensure that the sample container or tube is well rinsed with helium.

2. N₂O Reproducibility Test

Use all sample containers delivered and evacuate or rinse them with helium to give all containers a similar history. Fill the containers all within a short time range (for ambient air) by evacuating them and opening outside of the laboratory; or flush them using a roughing pump or using a sample from a commercial gas cylinder.

The best sample to check the reproducibility on the PreCon is a mixture of 0.3 ppm N₂O and 1.7 ppm CH₄ in Synthetic Air in a commercial 10 l gas cylinder. This gas can also be used to state the long-term performance of the overall system.

Use the default PreCon procedure. The GC performance should be comparable to Fig. 6 - 8.

The reproducibility should meet both specifications for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

3. CH₄ Reproducibility Test

In advance to the CH₄ test heat the combustion reactor to 1000 - 1100 °C. Condition the reactor overnight with a sample container of 100 % O₂ at reduced flow (ca. 5 - 10 psi).

Use all sample containers delivered and evacuate or rinse them with helium to give all containers a similar history. Fill the containers all within a short time range (for ambient air) by evacuating them and opening outside of the laboratory; or flush them using a roughing pump or using a sample from a commercial gas cylinder.

The best sample to check the reproducibility on the PreCon is a mixture of 0.3 ppm N₂O and 1.7 ppm CH₄ in Synthetic Air in a commercial 10 l gas cylinder.

This gas can also be used to state the long-term performance of the overall system.

Use the default PreCon procedure. Ensure that trap T1 is active. The reproducibility should meet specifications for $\delta^{13}\text{C}$.

Fig. 6 - 8 Mass 44 and Isotope Ratio Trace of a N₂O Measurement