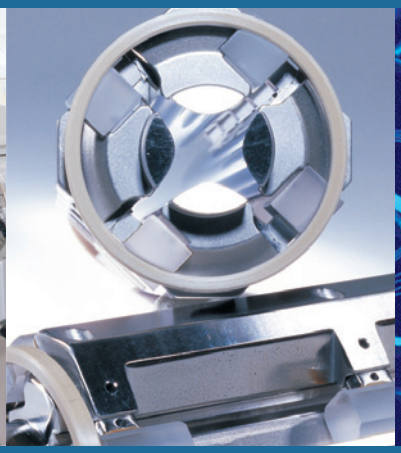
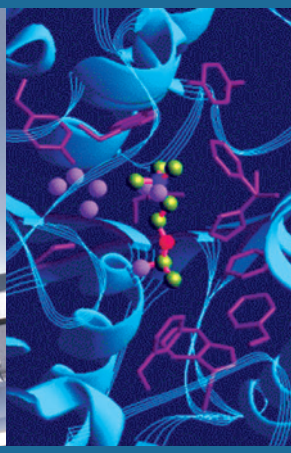
Thermo Fisher Scientific

GasBench II

Operating Manual

Revision A - 1118343

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Declaration of conformity according to ISO/IEC 17050-1:2004
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Name des Herstellers: manufacturers name nome produttore	Thermo Fisher Scientific
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GASBENCH

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rispetta le seguenti specifiche del prodotto

EMV (Störemissionen): EMC (emissions) EMC (emissioni)	EN 50081-1; EN 55022 class B
EMV (Störfestigkeit): EMC (immunity) EMC (immunità)	EN 61000-3-2, -3; EN 61000-4-2, -3, -4, -5, -6, -11; EN 61000-6-2; EN 50204
Elektrische Sicherheit: electrical safety sicurezza elettrica	EN 61010-1
Ergänzende Informationen: complementary information informazioni complementari	_____

Dieses Produkt erfüllt die EMV-Richtlinie 89/336/EWG und Niederspannungsrichtlinie 73/23/EWG.
This product complies with EMC directive 89/336/EEC and Low Voltage Directive 73/23/EEC.
Questo produtto rispetta la direttiva 89/336/EEC e la direttiva 73/23/EEC.

Bremen, Germany, 2. März 2007

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Read This First

Welcome to the Thermo Scientific, GasBench II system! The GasBench II is an interface for the Thermo Scientific family of advanced isotope ratio mass spectrometer (IRMS) detectors.

About This Guide

This *GasBench II Operating Manual* contains a description of the modes of operation and principle hardware components of your GasBench II. In addition, this manual provides step-by-step instructions for cleaning and maintaining your instrument.

Who Uses This Guide

This *GasBench II Operating Manual* is intended for all personnel that need a thorough understanding of the instrument (to perform maintenance or troubleshooting, for example). This manual should be kept near the instrument to be available for quick reference.

Scope of This Guide

This manual includes the following chapters:

- Chapter 1: "Preinstallation Requirements" outlines the site, power and gas requirements of the GasBench II.
- Chapter 2: "Hardware Components" outlines the layout of the GasBench II. It deals with autosamplers, sample trays and additional options as well as with the gas supply. The different needles are discussed. The chapter also describes online water removal, the Valco eight-port valve, the GC oven and the open splits.
- Chapter 3: "Isodat" outlines how to operate the GasBench II by the Isodat software. It deals with how to create a configuration, a method and a sequence. Different kinds of GasBench II methods are discussed. Another subject is carrying out Continuous Flow sample gas measurements using Dual Inlet for referencing. Results export to Excel® and autosampler programming are described as well.

- Chapter 4: "Basic Operations" explains basic tests as leak check, checking column flows, zero enrichment test (that is standard on/off test), linearity test and condition test. Other sections deal with starting an automated sequence, carrying out a performance test of the GasBench II, preparing phosphoric acid and handling sample vials.
- Chapter 5: "Measurement Procedures for Real Samples" outlines the measurement of the most common groups of samples as carbonates, DIC (that is dissolved inorganic carbon), breath gas, CO_2 in atmospheric concentrations, water equilibration (that is $^{18}O/^{16}O$ equilibration as well as $^{2}H/^{1}H$ equilibration). Another section explains how to operate the GasBench II in combination with the ConFlo IV.
- Chapter 6: "Options" outlines technical details about the standard options (carbonate option, cryo trap options, Denitrification Kit, PreCon) to be used together with the GasBench II. At the end of the chapter, information about the catalyst used in hydrogen equilibration is given.
- Chapter 7: "Technical Information" contains information about spare parts and consumables of the GasBench II. Sections about capillaries, water traps, reference open split, sample open split, GC oven and plug and measure adapters are presented as well.

Related Documentation

In addition to this guide, Thermo Fisher Scientific provides the following documents for the GasBench II:

- *ConFlo IV Operating Manual* (P/N 1224730)
- *Denitrification Kit for GasBench II - Installation Guide* (P/N 1214270).

Contacting Us

There are several ways to contact Thermo Fisher Scientific.

Assistance

For technical support and ordering information, **visit us on the Web**:

www.thermo.com/advancedms

Customer Information Service

cis.thermo-bremen.com is the Customer Information Service site aimed at providing instant access to

- latest software updates
- manuals, application reports, and brochures.

Note Thermo Fisher Scientific recommends that you register with the site as early as possible. ▲

To register, visit register.thermo-bremen.com/form/cis and fill in the registration form. Once your registration has been finalized, you will receive confirmation by e-mail.

Changes to the Manual

❖ **To suggest changes to this manual**

- Please send your comments (in German or English) to:

  Editors, Technical Documentation
  Thermo Fisher Scientific (Bremen) GmbH
  Hanna-Kunath-Str. 11

  28199 Bremen

  Germany

- Send an e-mail message to the Technical Editor at

  documentation.bremen@thermofisher.com

You are encouraged to report errors or omissions in the text or index. Thank you.

Typographical Conventions

This section describes typographical conventions that have been established for Thermo Fisher Scientific manuals.

Data Input

Throughout this manual, the following conventions indicate data input and output via the computer:

- Messages displayed on the screen are represented by capitalizing the initial letter of each word and by italicizing each word.
- Input that you enter by keyboard is identified by quotation marks: single quotes for single characters, double quotes for strings.
- For brevity, expressions such as "choose **File > Directories**" are used rather than "pull down the File menu and choose Directories."
- Any command enclosed in angle brackets < > represents a single keystroke. For example, "press **<F1>**" means press the key labeled F1.
- Any command that requires pressing two or more keys simultaneously is shown with a plus sign connecting the keys. For example, "press **<Shift>** + **<F1>**" means press and hold the <Shift> key and then press the <F1> key.
- Any button that you click on the screen is represented in bold face letters. For example, "click on **Close**".

Topic Headings

The following headings are used to show the organization of topics within a chapter:

Chapter 1 Chapter Name

Second Level Topics

Third Level Topics

Fourth Level Topics

Safety and EMC Information

In accordance with our commitment to customer service and safety, this instrument has satisfied the requirements for the European CE Mark including the Low Voltage Directive.

Designed, manufactured and tested in an ISO9001 registered facility, this instrument has been shipped to you from our manufacturing facility in a safe condition.

This instrument must be used as described in this manual. Any use of this instrument in a manner other than described here may result in instrument damage and/or operator injury.

Notice on Lifting and Handling of Thermo Scientific Instruments

For your safety, and in compliance with international regulations, the physical handling of this Thermo Scientific instrument *requires a team effort* for lifting and/or moving the instrument. This instrument is too heavy and/or bulky for one person alone to handle safely.

Notice on the Proper Use of Thermo Scientific Instruments

In compliance with international regulations: If this instrument is used in a manner not specified by Thermo Fisher Scientific, the protection provided by the instrument could be impaired.

Notice on the Susceptibility to Electromagnetic Transmissions

Your instrument is designed to work in a controlled electromagnetic environment. Do not use radio frequency transmitters, such as mobile phones, in close proximity to the instrument.

Safety and Special Notices

Make sure you follow the precautionary statements presented in this guide. The safety and other special notices appear different from the main flow of text. Safety and special notices include the following:

Warning Warnings highlight hazards to human beings. Each Warning is accompanied by a Warning symbol. ▲

Caution Cautions highlight information necessary to protect your instrument from damage. ▲

Note Notes highlight information that can affect the quality of your data. In addition, notes often contain information that you might need if you are having trouble. ▲

Identifying Safety Information

This guide contains precautionary statements that can prevent personal injury, instrument damage, and loss of data if properly followed. Warning symbols alert the user to check for hazardous conditions. These appear throughout the manual, where applicable. The most common warning symbols are:

Warning This general symbol indicates that a hazard is present that could result in injuries if it is not avoided.
The source of danger is described in the accompanying text. ▲

Warning High Voltages capable of causing personal injury are used in the instrument. The instrument must be shut down and disconnected from line power before service is performed. Do not operate the instrument with the top cover off. Do not remove protective covers from PCBs. ▲

Warning Strong magnetic fields are used in the instrument. Keep away from heart pacemakers, computers, credit cards, and any other magnetically sensitive device. Do not bring compressed gas cylinders within close proximity to the instrument. ▲

Warning Treat heated zones with respect. Parts of the instrument might be very hot and might cause severe burns if touched. Allow hot components to cool before servicing them. ▲

Warning Careless handling of cryogenic liquids might cause severe personal injury including frostbite. Wear protective clothing when operating this equipment including insulated gloves and face shield. ▲

Warning Wear gloves when handling toxic, carcinogenic, mutagenic, or corrosive/irritant chemicals. Use approved containers and procedures for disposal of waste solution. ▲

Warning **Laser Radiation** Avoid eye or skin exposure to direct or scattered radiation! ▲

In addition to the above described, every instrument has specific hazards. So, be sure to read and comply with the precautions described in the subsequent chapters of this guide. They will help ensure the safe, long-term use of your system.

General Safety Precautions

Observe the following safety precautions when you operate or perform service on your instrument:

- Before plugging in any of the instrument modules or turning on the power, always make sure that the voltage and fuses are set appropriately for your local line voltage.
- Only use fuses of the type and current rating specified. Do not use repaired fuses and do not short-circuit the fuse holder.
- The supplied power cord must be inserted into a power outlet with a protective earth contact (ground). When using an extension cord, make sure that the cord also has an earth contact.
- Do not change the external or internal grounding connections. Tampering with or disconnecting these connections could endanger you and/or damage the system.
- The instrument is properly grounded in accordance with regulations when shipped. You do not need to make any changes to the electrical connections or to the instrument's chassis to ensure safe operation.
- Never run the system without the housing on. Permanent damage can occur.
- Do not turn the instrument on if you suspect that it has incurred any kind of electrical damage. Instead, disconnect the power cord and contact a Service Representative for a product evaluation. Do not attempt to use the instrument until it has been evaluated. (Electrical damage may have occurred if the system shows visible signs of damage, or has been transported under severe stress.)
- Damage can also result if the instrument is stored for prolonged periods under unfavorable conditions (e.g., subjected to heat, water, etc.).
- Always disconnect the power cord before attempting any type of maintenance.
- Capacitors inside the instrument may still be charged even if the instrument is turned off.

- Never try to repair or replace any component of the system that is not described in this manual without the assistance of your service representative.
- Do not place any objects – especially not containers with liquids – upon the instrument. Leaking liquids might get into contact with electronic components and cause a short circuit.

Safety Advice for Possible Contamination

Hazardous Material Might Contaminate Certain Parts of Your System During Analysis.

In order to protect our employees, we ask you to adhere to special precautions when returning parts for exchange or repair.

If hazardous materials have contaminated mass spectrometer parts, Thermo Fisher Scientific can only accept these parts for repair if they have been properly decontaminated. Materials, which due to their structure and the applied concentration might be toxic or which in publications are reported to be toxic, are regarded as hazardous. Materials that will generate synergetic hazardous effects in combination with other present materials are also considered hazardous.

Your signature on the **Repair-Covering letter** confirms that the returned parts have been decontaminated and are free of hazardous materials.

The Repair-Covering letter can be ordered from your service engineer or downloaded from the **Customer Information Service** (**CIS**) site. Please register under http://register.thermo-bremen.com/form/cis.

Parts contaminated by radioisotopes are not subject to return to Thermo Fisher Scientific – either under warranty or the exchange part program. If parts of the system may be possibly contaminated by hazardous material, please make sure the Field engineer is informed before the engineer starts working on the system.

Contents

Figures

Tables

Chapter 1 Preinstallation Requirements

This chapter outlines the preinstallation requirements of GasBench II. It treats the following topics:

Site and Power Requirements

Note Check all items mentioned below by ☐ and confirm them by ☑. Then, send back this form to your Thermo Fisher Scientific Customer Support Organization. ▲

GasBench II is attached to Thermo Fisher Scientific isotope ratio mass spectrometers, for example DELTA V, and will be placed either on top of the IRMS or on a peripherals support table. The site requirements of the GasBench II are given in Figure 1-1.

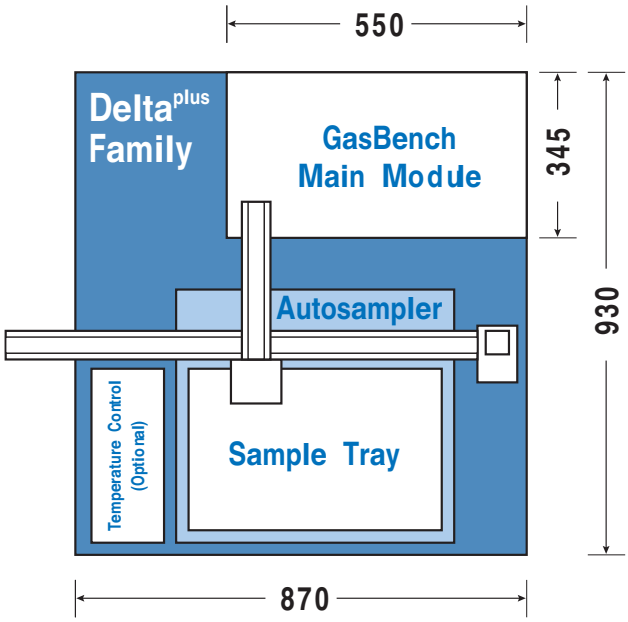


Figure 1-1. Site requirements of GasBench II*

*Dimensions given in mm

❑ **Note** The space required is 900 mm width×900 mm depth. ▲

❑ The GasBench II will be supplied by the IRMS line distributor. Therefore, the total IRMS power consumption will increase by 0.5 kW.

Gas Requirements

This section lists the required gases for installing the GasBench II and to subsequently perform different kinds of analyses.

Gas Requirements for Installation of GasBench II

These gases are required for installing the GasBench II by a Thermo Fisher Scientific service engineer.

Table 1-1. Gas requirements

	Purity	Pressure and usage
❑	He 5.0 (that is 99.999 %)	4 bar as carrier gas and to flush sample vials
❑	He 4.6 with 0.3 % CO_2 4.5 or alternatively He 4.6 with 0.5 % CO_2 4.5	4 bar for acceptance tests
❑	CO_2 (purity as mentioned in the Preinstallation Requirerments Guide of your IRMS)	as reference gas (pressure as mentioned in the Preinstallation Requirerments Guide of your IRMS)
❑	H_2 (purity as mentioned in the Preinstallation Requirerments Guide of your IRMS)	as reference gas (pressure as mentioned in the Preinstallation Requirerments Guide of your IRMS)

Gas Requirements for Water Equilibration

Table 1-2. Gas requirements for water equilibration

	Analysis and purity	Pressure and usage
❑	$^{18}O/^{16}O$ - He 4.6 with 0.3 % to 1 % CO_2 4.5	4 bar as auxiliary gas
❑	$^{18}O/^{16}O$ - CO_2 4.5 (that is 99.995 %)	4 bar as reference gas
❑	$^{2}H/^{1}H$ - He 4.6 with 2 % H_2 or alternatively $^{2}H/^{1}H$ - He 4.6 with 4 % H_2	4 bar as auxiliary gas
❑	$^{2}H/^{1}H$ - H_2 4.5 (that is 99.995 %)*	4 bar as reference gas

*Generated by electrolysis. Refer to topic "Water Equilibration ($^{2}H/^{1}H$ Equilibration)" on page 5-36.

Gas Requirements for Carbonates

Table 1-3. Gas requirements for carbonates

	Purity	Pressure and usage
❑	CO_2 4.5 (that is 99.995 %)	4 bar as reference gas

Gas Requirements for DIC (Dissolved Inorganic Carbon)

Table 1-4. Gas requirements for DIC (Dissolved Inorganic Carbon)

	Purity	Pressure and usage
❑	CO_2 4.5 (that is 99.995 %)	4 bar as reference gas

Note All stainless steel gas lines should be oil-free and preferably flame-dried. The connectors can be made either of stainless steel or brass. The gas lines, or gas tanks respectively, should be at a distance of 1-1.5 m to the instrument. ▲

Note All regulators should be oil- and fat-free and be specified for gases of high purity. The supply lines should terminate with 1/8“ male Swagelok®-type connectors. ▲

❑ Compressed air will be supplied by the compressed air distributor of the IRMS and should be between 2.8 bar and 4.8 bar (40 psi and 70 psi).

❑ **Note** Sometimes, it may be necessary to check the unit for leaks. Therefore, use an argon tank. ▲

❑ **Note** Thermo Fisher Scientific recommends installing a high capacity purifier (P/N 1140790) to ensure constant and affordable high quality of the helium carrier gas. ▲

Chapter 2 Hardware Components

This chapter outlines important hardware components of GasBench II. It treats the following topics:

Layout of GasBench II

This section outlines the layout of the GasBench II and important hardware components.

Figure 2-1. GasBench II next to CTC GC PAL autosampler

Figure 2-1 displays the GasBench II next to the CTC GC PAL autosampler. In Figure 2-2, the GasBench II has been arranged upon a DELTA V Plus.

Figure 2-2. GasBench II upon DELTA V Plus - front view

Figure 2-3 shows the front panel of the GasBench II with the pressure regulators and pressure gauges for the reference gases and helium, respectively.

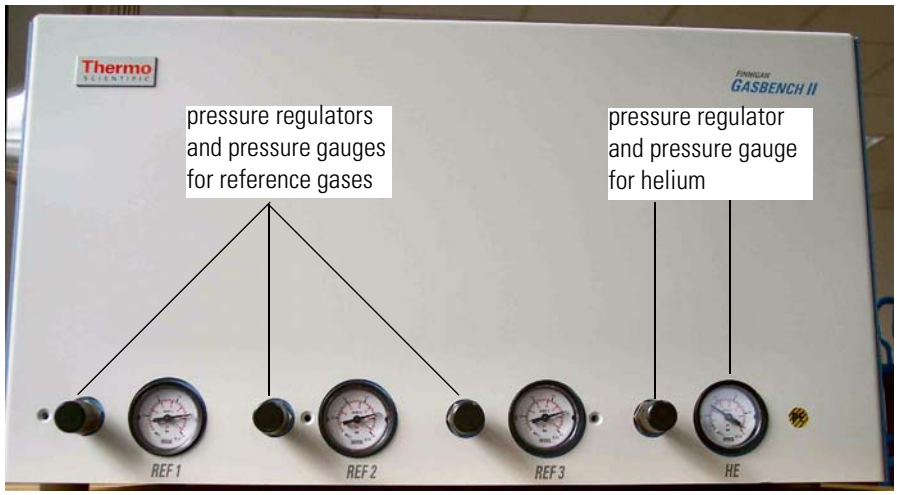
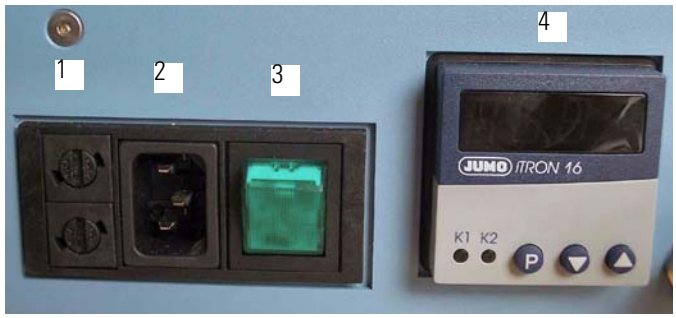


Figure 2-3. Pressure regulators and pressure gauges at front panel

Figure 2-4 displays the main fuses (T 3.15 A, L 250 V), the main power plug, the main power switch and the JUMO iTRON 16 temperature controller. They are all located at the lower left side panel.

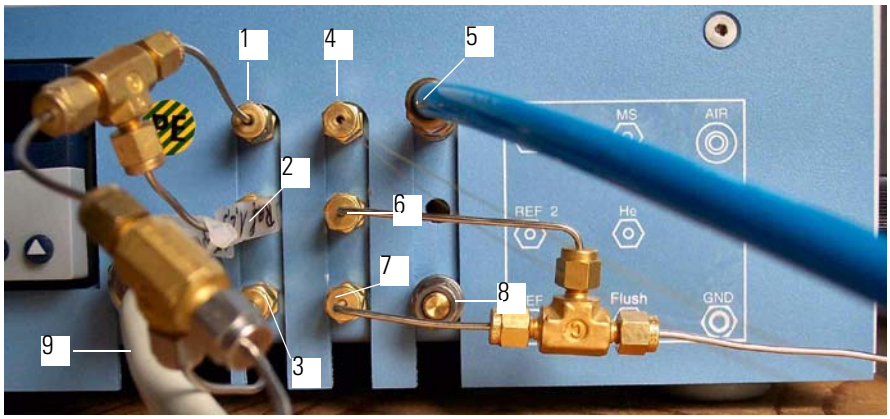


Labeled components: 1=main fuse, 2=main power plug, 3=main power switch (on/off), 4=JUMO iTRON 16 temperature controller

Figure 2-4. Power switch and JUMO iTRON 16 temperature controller

In Figure 2-5 the gas connections and the cable for connecting the GasBench II to the IRMS are shown. They are all located at the lower left side panel. See the connection scheme (Figure 2-27) as well.

Note For flush gases (CO_2 in He, H_2 in He, for example), a dedicated plug must be installed! ▲



Labeled components: 1–3=connections for reference gases, 4=capillary feedthrough to IRMS, 5=connection for compressed air, 6=helium carrier gas connection, 7=flush connection, 8=GND (ground), 9=cable for connection to IRMS

Figure 2-5. Gas connections at left side panel

Figure 2-6 shows the fan for H_2 exhaustion located at the upper left side panel.

Warning Explosion hazard. A leak in the hydrogen (H_2) supply may cause fire or an explosion! ▲

Figure 2-6. Fan at left side panel

Figure 2-7 shows the connections for optional cryo traps at the rear panel. Each of both optional cryo traps (trap 1, trap 2) has a control output (Control) and an output for compressed air supply (Supply).

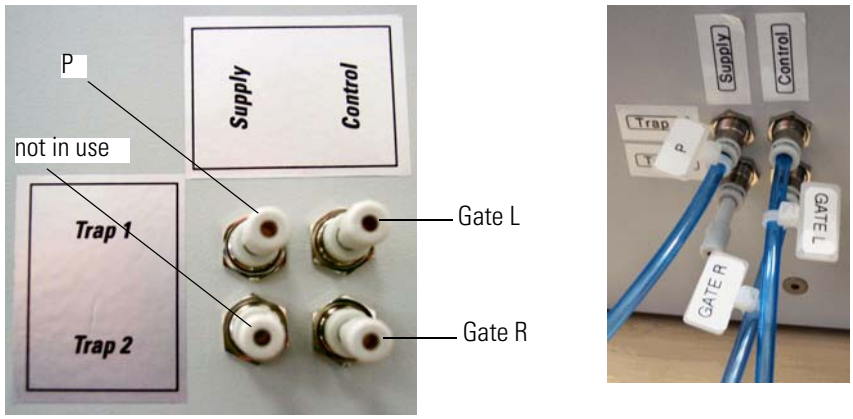
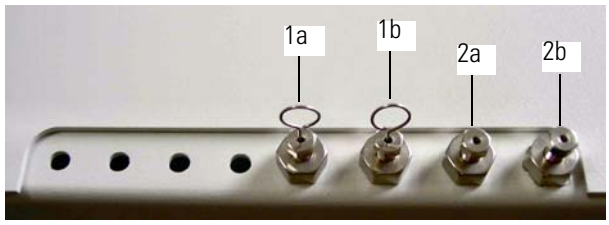


Figure 2-7. Ports for connecting optional cryo traps at rear panel

Figure 2-8 outlines the connections for the sample needles. They are located on top of the GasBench II. If you bought a second needle holder (complete), you can flush using a second needle. This will shorten the flushing time of a tray by 50 %.



Labeled components: 1a=flush connection for single needle flush, 1b=flush connection for dual needle flush, 2a=input of carrier gas into sample needle, 2b=output of carrier gas with sample gas to the first Nafion® water trap

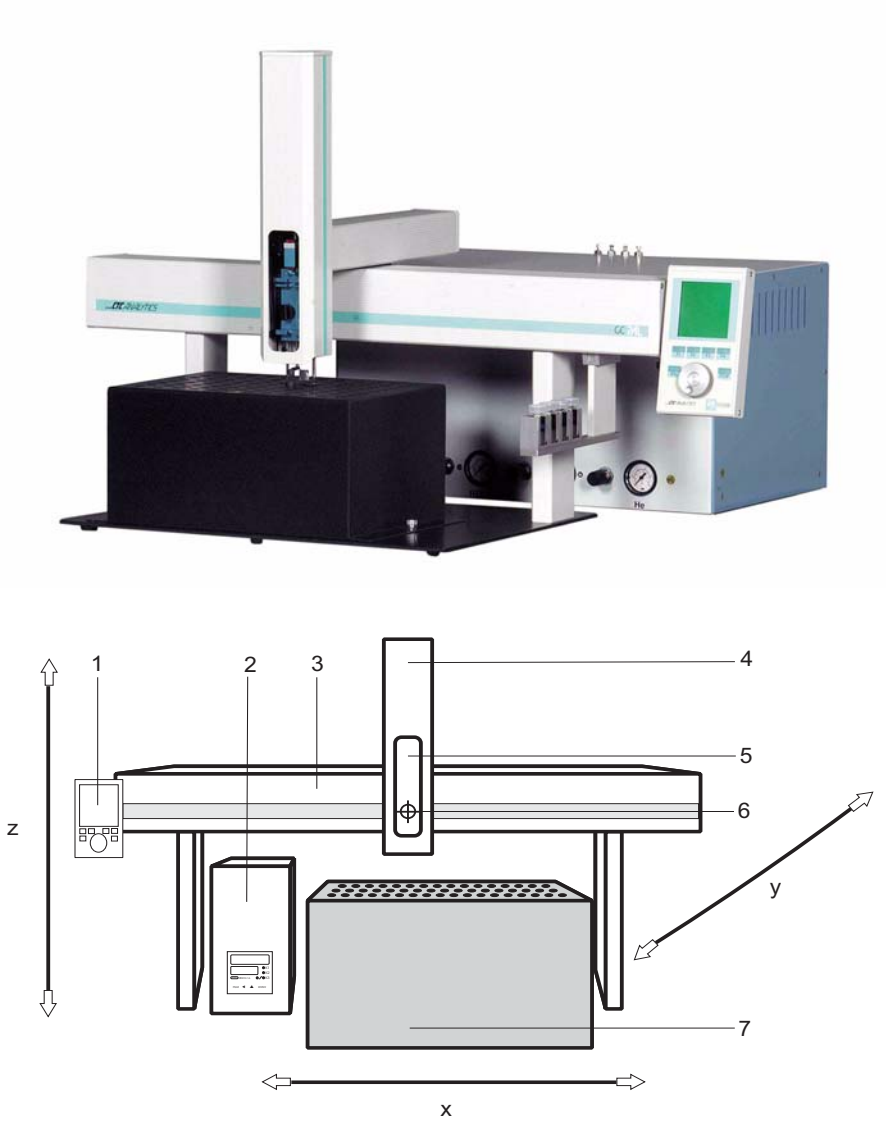
Figure 2-8. Connections for sample needles (view from rear panel)

In Figure 2-9 the GasBench II is shown after its cover has been removed.

Figure 2-9. GasBench II general survey - open

Autosampler

Figure 2-10 shows the GC PAL autosampler (P/N 1145540), the mounting parts (P/N 1125820) and the thermostated sample tray (P/N 1112800) or the sample tray for 96 sample vials of 10 mL size each, so-called exetainer®s (P/N 1112780).



Labeled components: 1=display and controls, 2=heating unit with JUMO iTRON 16 temperature controller, 3=syringe carrier, 4=injection head, 5=syringe, 6=position of sample needles, 7=sample tray

Figure 2-10. GC PAL autosampler and sample tray

Installing Autosampler

Note The x-axis is the long axis at the autosampler, whereas the y-axis is directed forward, and the z-axis downwards, respectively. ▲

❖ **To install the autosampler**

1. Unpack the box containing the components of the autosampler.
2. Screw the feet of the autosampler onto the base plate.

Note The base plate is not packed into the autosampler box, but into the box containing GasBench II. The feet, however, are packed into the autosampler box. ▲

3. Place the sample tray and the heating block onto the base plate. Therefore, the base plate has prefabricated cut-outs, where the heating block is simply inserted. Owing to its heaviness, the heating block must not be fixed by screws underside.
4. Unpack the temperature controller for the heating block. The lid of the heating block needs to be screwed sideways onto the heating block by two provided knurled head screws.

Note In case of the carbonate option, a cut-out must be rasped at the right rear edge of the lid. The cut-out will be used as feedthrough for the acid line of the acid reservoir. Usually, this is performed by a service engineer. ▲

5. Take out the z-arm.
6. Mount the x-axis guidance upon the feet and fasten it there using a Torx® screwdriver. Three Torx® screwdrivers are provided with the autosampler: 360/T10×80, 360/T20×100 and 360/T25×100.
7. Unscrew the retaining screws out of the y-arm.
8. Attach the z-arm at the y-arm. To fasten the z-arm, move the plunger entirely downward as this allows accessing the eyelets.
9. Remove the protective faceplate from the z-arm. This allows to plunge in the syringe from the front side later on.

Note When the autosampler is switched off (during installation, for example), in most cases the plunger falls completely down and can then be moved freely. However, the plunger cannot be moved when the autosampler is switched on. ▲

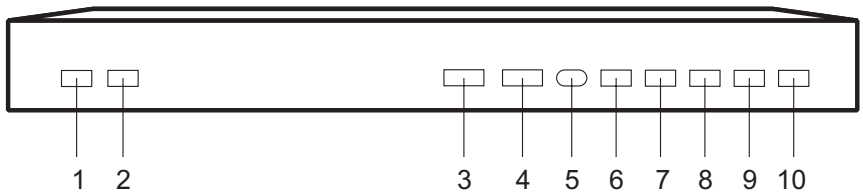
Connecting Autosampler

Caution Never unplug or connect any cables while the autosampler is switched on! This may lead to damage of the autosampler. ▲

Note for service engineers: The part number of the replacement fuse is P/N 1141420. ▲

❖ **To connect the autosampler**

1. Connect the serial cable of the autosampler to the serial port COM 1 of your computer.
2. Mount the autosampler display on the most convenient side of the autosampler. Connect the autosampler display to the rear panel of the autosampler by the serial cable. See pos. 8 (that is serial 3) in Figure 2-11.



Labeled components: 1=(Auxiliary 1) - Combi PAL only, 2=(Auxiliary 2) - Combi PAL only, 3=(Interface 1) - Combi PAL only, 4=(Interface 2) - Combi PAL only, 5=main power - connect to autosampler power supply, 6=LED, 7=speaker (buzzer), 8=Ser 3 - to autosampler display, 9=Ser 2, 10=Ser 1 - to host computer

Figure 2-11. X-arm rear panel (GC PAL or Combi PAL)

3. Connect the autosampler power supply to the mains supply and the autosampler.
4. Check the functioning of the autosampler and the COM port assignment by using the PAL loader software.
5. To start the autosampler press the **Start** button beneath **PAL Loader**.

Sample Trays Used with GasBench II

Depending on your particular application the following sample trays are to be used with the GasBench II:

- Non-thermostated sample tray (P/N 1112780)
- 6×9 sample tray (P/N 1212360)
- Thermostated sample tray (P/N 1112800)
- Cooled sample tray (P/N 1257090)

They will be discussed in detail below.

Non-Thermostated Sample Tray

Per default, the GasBench II is delivered without any sample tray. Therefore, a sample tray must additionally be ordered unless you have your own tray or you use the trays that are delivered together with the CTC autosampler.

For the GasBench II a standard CTC autosampler can be used (for DIC analysis, for example). Per default, the CTC autosampler is delivered with 76×1 mL or 98×2 mL trays containing described vial sizes. Those vials are not suitable for normal GasBench II analyses. The vials can be used for GasBench II and Flash HT or TC/EA coupling.

The non-thermostated sample tray, P/N 1112780, is suitable for equilibrium work or breath gas analysis. See Figure 2-12 and Figure 2-13.

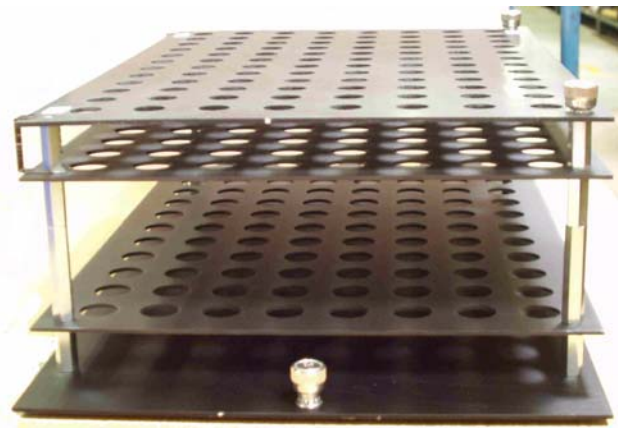


Figure 2-12. Non-thermostated sample tray - side view

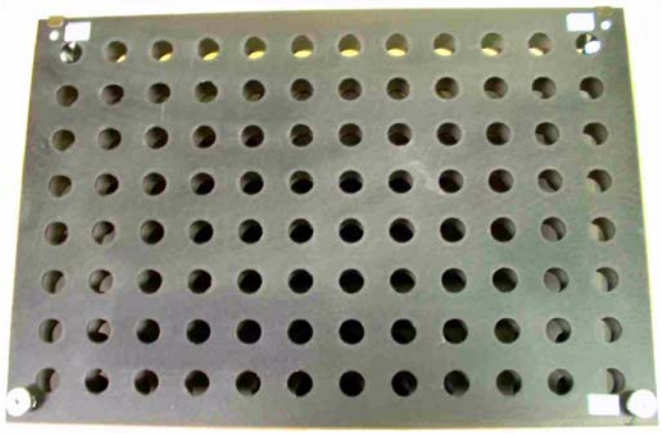


Figure 2-13. Non-thermostated sample tray - top view

6×9 Sample Tray

The 6×9 sample tray (P/N 1212360, Figure 2-14) is used for analysis of 20 mL special vials. It operates at ambient air temperature and is fixed to the mounting plate of the GasBench II. The fixing points are at the same positions as with the thermostated sample tray. The Denitrification Kit (P/N 1220010) uses this sample tray.

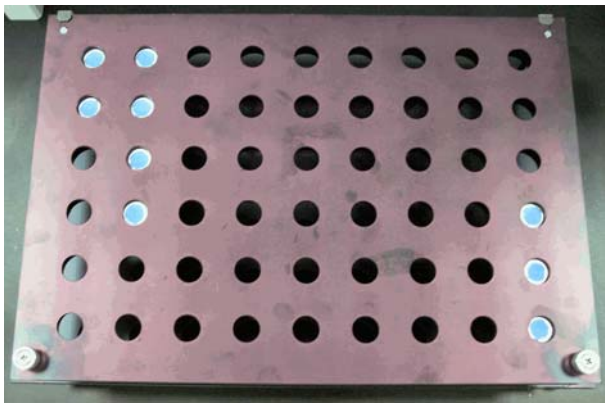


Figure 2-14. 6×9 sample tray - top view

The Kit for 6×9 Sample Tray & Vials (20 mL), P/N 1237520, contains

- headspace vial, type 4020 (P/N 1213410)
- tear-off seal, type 4020 (P/N 1213430)
- headspace septum, type 4020 (P/N 1213440)
- 20 mm E-Z crimper (P/N 1215100)

Programming CTC GC PAL Autosampler

Note This information must not be used for other purposes than reprogramming the autosampler for using the 6×9 sample tray. ▲

Caution Before changing the settings of the autosampler, read the autosampler manual. ▲

The following values are intended as reference values only. They come from a CTC GC PAL autosampler equipped with the Kit for 6×9 Sample Tray & Vials (20 mL) (P/N 1237520). Check the settings as described in the autosampler manual. If necessary, adjust them according to the application and the used vials or septa.

Note If you use another than the 6×9 tray, evaluate the needed parameters. Follow the instructions in the autosampler manual. ▲

1. Tray Types
   a. Insert new type (named GB 6×9)
   b. Insert values according to Table 2-1.

Table 2-1. Values to be inserted - tray types

Parameter	Value
Row Length Y	167.9 mm
Col Length X	267.6 mm
Spl Per Row	6
Spl Per Col	9
Tray Type Group	A
Vial height	75
Z Tolerance	5
Max Penetrat	20 mm
Min Penetrat	18 mm

2. Trays
   a. Insert the new tray
   b. Insert the values according to Table 2-2.

Table 2-2. Values to be inserted - trays

Parameter	Value
Tray holder	GB-Thldr
Tray Type Group	ABCD
Tray Type	GB 6x9
other values	evaluate by your system

Note These settings are also contained in the backup file GB 6×9 for Denitrification 2008-06-10.sss on your Isodat CD. You can transfer them to the CTC GC PAL autosampler by using the PAL Loader program. Refer to topic "GC PAL Loader Software" on page 3-65. Check the values as described in the autosampler manual. If necessary, adjust the settings. Be aware that the settings of the needles of the Denitrification Kit are saved with this .sss file as well. ▲

Thermostated Sample Tray

However, if temperature control is required for your application (carbonate analysis, equilibration measurements, high temperature stability measurements, for example) a thermostated sample tray, P/N 1112800, is in use. See Figure 2-15.

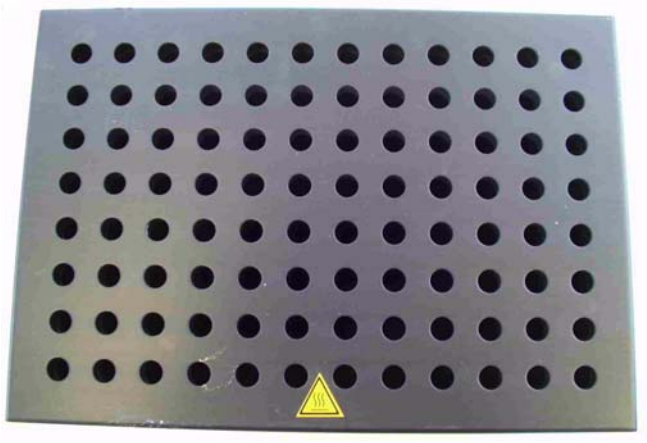


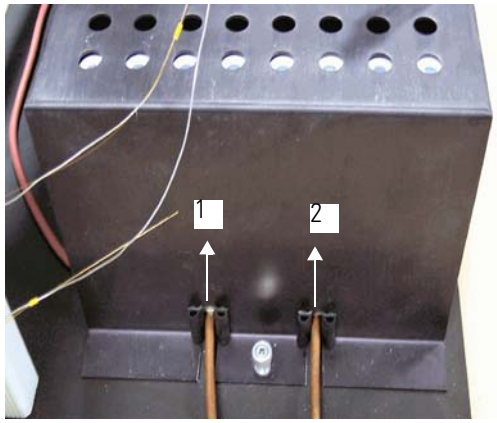
Figure 2-15. Thermostated sample tray - top view

When using the thermostated sample tray, take into account that:

- it is optimized for carbonate measurement. Refer to topic "Carbonates" on page 5-6.
- the delay between acid dosing and measurement is 1 h.
- the acid reservoir is thermostated.
- two columns cannot be used.

Cooled Sample Tray

The cooled sample tray, P/N 1257090, is a specially produced thermostated sample tray with liquid cooling option. It is used for cooled operation of samples. With water recirculators the ambient temperature of the samples can be cooled down by adding coolant additives (water/glycol mixtures, for example). The minimum temperatures of the cooling liquid can be reached as described in the specifications of the recirculator.



Labeled components: 1=cooling water in, 2= cooling water out

Figure 2-16. Screw connections for cooling lines

In Figure 2-16, the screw connections for the cooling lines (for entering and leaving water) are depicted. An outer diameter of 6 mm of the cooling lines is suitable.

Figure 2-17. Filter system (left) and filter cartridge (right)

Figure 2-17 (left) shows the filter system used to remove coarse particles, for example algae and fungi. An arrow on its lid indicates the flow direction of the water from the water recirculator to the sample tray.

Figure 2-17 (right) shows its filter cartridge. To exchange the filter cartridge, use the tool as shown in Figure 2-18 (right) and Figure 2-19.

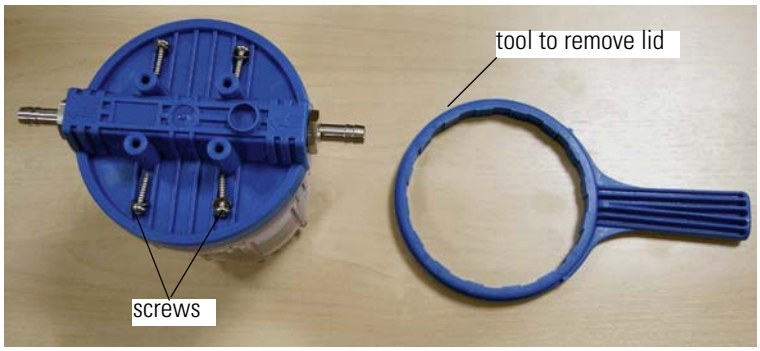


Figure 2-18. Filter system and tool to remove its lid

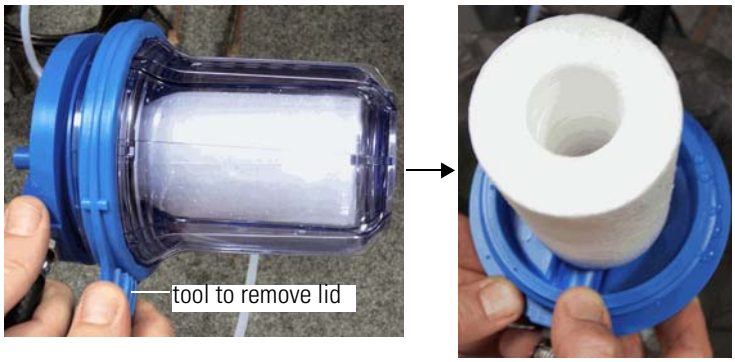


Figure 2-19. Exchanging filter cartridge

As an example for a water recirculator, Figure 2-20 shows the water in and water out connections of the DC10-K20 of Thermo Scientific. Table 2-3 summarizes its specifications.

Figure 2-20. Connections of water recirculator DC10-K20

Table 2-3. Specifications of water recirculator DC10-K20*

Parameter	Value
working temperature range [ºC]	-28 to 100
temperature accuracy [± K]	0.02
heater capacity 230 V [kW] heater capacity 115 V [kW]	2.0 1.2
cooling capacity [W] at 20 °C cooling capacity [W] at 0 °C cooling capacity [W] at -20 °C	320 205 75
maximum pressure of pump [mbar]	300
maximum flow rate of pump [L/min]	12.5
bath opening: w×l×d [cm]	13×10×15
maximum bath volume [L]	4.5
overall dimensions: w×l×h [cm]	23×46×58
net weight [kg]	29.8
voltage [V]	230 ± 10 % 115 ± 10 % 100 ± 10 %
frequency [Hz] for 230 V frequency [Hz] for 115 V frequency [Hz] for 100 V	50; 60 60 50-60
total wattage 230 V/115 V [VA]	2400/1600

*The water recirculator is delivered together with a bath cover and two olives for 8 mm ID tubing. Additionally, two Perbunan® tubings (8 mm ID and 2.5 m length each) suitable for the temperature range between -40 ºC and 100 ºC and four clamps for 8 mm ID tubings are included.

Additional Options for IRMS, Autosampler and Various Peripheral Couplings

When coupling the GasBench II with a TC/EA or a GC, special additional options for IRMS, autosampler and various peripherals have to be installed:

- Kit for simultaneous attachment of one GC PAL autosampler, PreCon interface and GasBench II
- Kit for simultaneous attachment of one GC PAL autosampler and sample trays of GasBench II to Flash EA, IRMS, Flash HT or TC/EA
- Kit for simultaneous attachment of one GC PAL autosampler to H-Device and GasBench II

Layout of 96 Sample Trays with 10 mL Vials

This section outlines the 96 sample trays (that is 8×12 and 12×8 trays) with 10 mL vials. The movement of the autosampler across the 8×12 tray is depicted in Figure 2-21 and Figure 2-22. It contains 96 holes with the properties summarized in Table 2-4. This CTC tray needs to be positioned below the CTC autosampler. Be aware to have sufficient free space below the x-arm of the CTC autosampler.

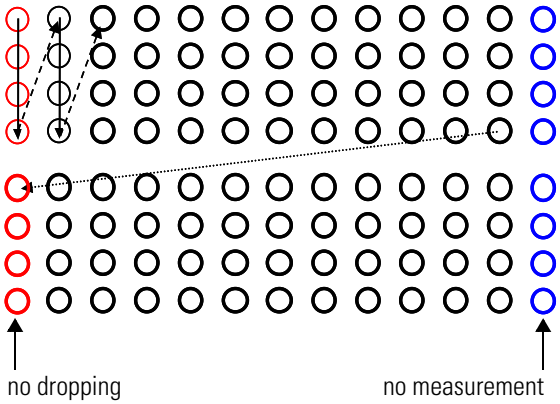


Figure 2-21. Autosampler movement across 8x12 tray (ex factory)

Table 2-4. Properties of tray holes

Parameter	Value
spacing of holes	26 mm×26 mm
diameter of holes	16 mm
depth of holes	85 mm

Alternatively, the 96 sample tray (12×8 tray, 8×12 tray), an 8×11 tray and an 11×8 tray can be programmed with the CTC software. To attach a CTC GC PAL tray, refer to the CTC Operating Manual.

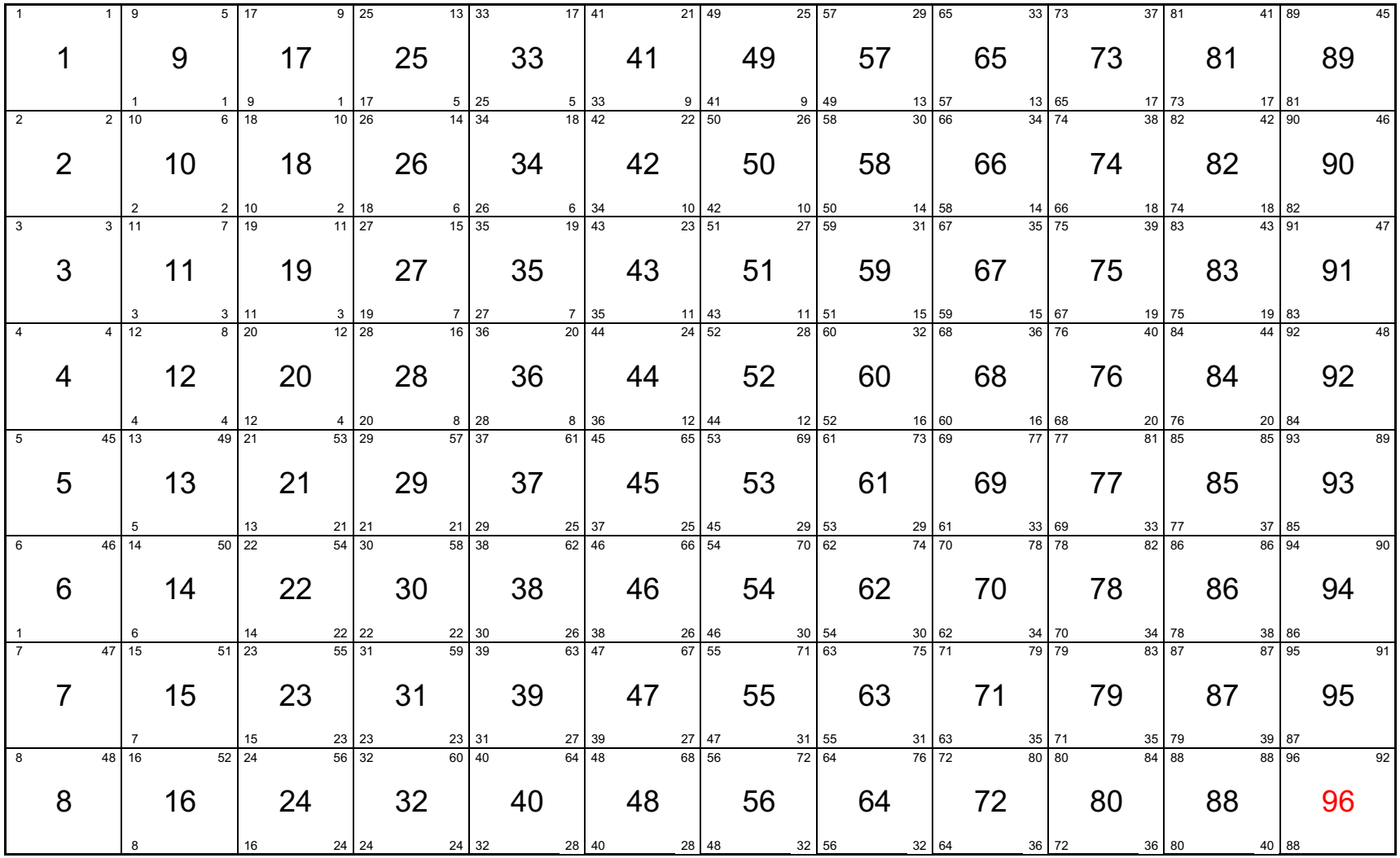
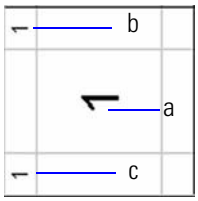
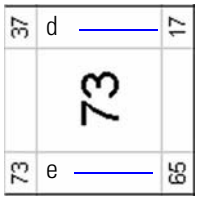


Figure 2-22. Sampling positions for 8×12 sample tray (non-thermostated and thermostated)



Labeled components: a=autosampler position in sequence, b=row number in sequence (carbonates), c=row number in sequence (equilibration)

Figure 2-23. Autosampler position and row number in sequence



Labeled components: d=dual needle flush, e flush fill

Figure 2-24. Dual needle flush and flush fill

Programming Temperature Controller for Thermostated Sample Tray and Cooled Tray

For programming the JUMO iTRON 16 temperature controller for GC oven, refer to topic "Programming Temperature Controller for GC Oven" on page 2-41. For details, refer to the manual of the JUMO iTRON 16 temperature controller.

Figure 2-25. JUMO iTRON 16 temperature controller

The temperature controller located externally allows controlling the sample tray temperature. Notice the three keys (see arrows in Figure 2-25):

P key	for programming; the values will be accepted automatically after 2 s.
Arrow Up key	to increase a particular value
Arrow Down key	to decrease a particular value

Manual Programming

❖ To perform Step 1 of programming

1. Press the **P** key and hold it for 2 s.
2. Pass through the menu until **Y.0** is displayed.
3. Again, press the **P** key and hold it for 2 s.
   a. Set **C111** to 003 (transducer type, Pt 100, 2-wire, for example).
   b. Set **C112** to 1 (number of decimal places and temperature unit, 1 and °C, for example).
   c. Set **C113** to 33 (controller type, for example double setpoint).
   d. Set **C115** to 1 (ramp function in °C/min).
   e. Set **C116** to 0 (outputs on fault, that is 0 %; minimum output limiting **Y.2** is effective).
   f. Set **SP.L** to 0 (lower setpoint limiting).
   g. Set **SP.H** to 80 (upper setpoint limiting).
   h. Set **OFFS** to 0 (process value correction).

❖ To perform Step 2 of programming

1. Again, press the **P** key and hold it for 2 s.
2. Press the **Arrow Up/Down** key to change values.
   a. Set **Pb.1** to 2.8 (proportional band 1).
   b. Set **Pb.2** to 2.8 (proportional band 2).
   c. Set **d.t.** to 35 (derivative time in s).
   d. Set **r.t.** to 135 (reset time in s).
   e. Set **CY.1** to 2 (cycle time 1 in s).
   f. Set **CY.2** to 2 (cycle time 2 in s).
   g. Set **db** to 0 (contact spacing).
   h. Set **HyS.1** to 0 (differential 1).
   i. Set **HyS.2** to 0 (differential 2).
   j. Set **Y.0** to 0 (working point in %).
   k. Set **Y.1** to 100 (maximum output in %).
   l. Set **Y.2** to 0 (minimum output in %).
   m. Set **d.F** to 5 (filter time constant in s).
   n. Set **rA.Sd.** to 9.99 (ramp slope in °C/h or °C/min).

Alternative: Automatic Programming

Let the temperature controller program itself automatically. Thereby, you do not need to specify all the parameters mentioned above on your own. For details, refer to the manual of the JUMO iTRON 16 temperature controller.

Gas Supply

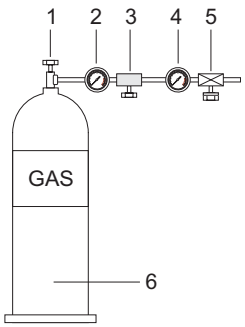
This section outlines first how to install gas tanks and to work with them. Then the gas connections for operating the GasBench II with the IRMS are described.

Gases in Use

For all applications, helium is needed as carrier gas. Its purity should be at least 99.999 % He. We recommend using a second cylinder switchover to prevent pressure loss during overnight operation and contamination by atmospheric gases during bottle change. A standard 50 L gas tank has a lifetime of half a year in continuous operation. For all applications with CO_2 as molecule of interest (that is water equilibration, DIC, or carbonates), CO_2 having a purity of 99.995 % CO_2 is recommended as reference gas. A 40 L tank will last longer than one year in continuous operation.

In case of CO_2 water equilibration, additionally a mixture of CO_2 in He is needed for headspace flushing. The purities are recommended to be as stated above for He and CO_2 respectively. A CO_2 content of 0.3% leads to an ideal signal height of 9 V. In case of H/D measurements, H_2 is needed as reference gas. Its purity should be 99.996 % H_2. In case of headspace flushing, a mixture of 4 % H_2 in He should result in a signal height of 9 V, which is optimal with regard to error margins.

Note The pressure of new gas tanks is up to 200 bar (helium tank). The pressure must be adjusted to approximately 4 bar using the pressure regulator mounted at the gas tank. ▲



Labeled components: 1=main valve, 2=manometer 200 bar (He), for pre-pressure, 3=line pressure regulator, 4=manometer 4 bar (He), 5=on/off valve, 6=high pressure gas tank

Figure 2-26. Gas tank

Installing Gas Tanks

❖ **To install the gas tanks**

1. Connect the reference gases.
2. Connect the measurement gases.
3. Connect the equilibration gases, that is the flush gases:
   Either [CO_2 + He] or [H_2 + He] are used as equilibration gases (0.5% CO_2 in He because of 50 V dynamic range).

Working with Gas Tanks

Before starting the system, a leak check must be performed outside the working area.

Warning It is strongly recommended to install the gas tanks firmly. Tumbling must definitely be prevented! ▲

Warning Explosion Hazard. A leak in the hydrogen (H_2) supply may cause fire or an explosion! ▲

❖ **To perform a leak check**

1. After mounting the reducing valve to the gas tank, both valves should be open (that is, the on/off valve and the reducing valve). See Figure 2-26.
2. Open the main valve for two or three seconds to let the gas purge the whole valve system. See Figure 2-26.
3. Close the on/off valve. Then close the main valve.
4. Mark the manometer positions of on/off valve and main valve and wait for 10–15 min.
5. If the manometer positions have changed, a leak may be present.
6. To detect the leak brush all valves and connections carefully with soap sud. A possible leak is indicated by gas bubbles.

Gas Connections

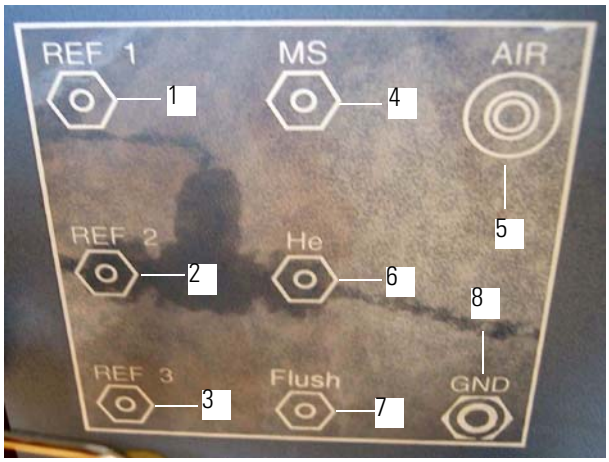
To operate GasBench II and the IRMS, several gases are needed either from gas tanks or from the main gas supply of the laboratory (compressed air, for example). See Figure 2-27 to locate the numbers. To operate the open split levers, the Valco valve and eventually the traps, compressed air of 4 bar is required (40-70 psi; see pos. 5 in Figure 2-27). It can be provided by the pressure regulator of the IRMS.

Use the quick release connection to connect the blue compressed air cable to the compressed air connectors of the IRMS. See Figure 7-2. As the IRMS has four connectors, four screws (wing unions for compressed air, quick release connections) are provided either with GasBench II or with the IRMS itself.

Two capillaries leading the gas flow to the mass spectrometer input valve must be installed. See pos. 4 in Figure 2-27. The connections 1 to 3 are used for the reference gases used in the various applications. Flush gases must be connected to the respective connector. For a detailed explanation, refer to topic "Measurement Procedures for Real Samples" on page 5-1.

Note When installing CO_2 reference gas tanks, keep in mind that standard high pressure tanks for CO_2 contain a liquid phase that is subject to fractionation when temperature changes. These tanks must be stored at constant temperature to obtain stable isotope values for your reference gas. ▲

Note When using hydrogen (H_2) as reference gas, it is necessary to shorten the internal flow restricting capillary (that is, the capillary leading from the reference pressure regulator to the open split, 3-fold) to approximately 50 % of its original length. This ensures that enough hydrogen enters the reference port of the mass spectrometer. See Figure 7-1, Figure 7-13, Table 7-1, and Table 7-2. ▲



Labeled components: 1–3=connections for reference gases, 4=capillary feedthrough to IRMS, 5=connection for compressed air, 6=helium carrier gas connection, 7=flush connection, 8=GND (ground)

Figure 2-27. Connection scheme at left side panel

Figure 2-27 shows the connection scheme at the left side panel.

It is intended to connect only one equilibration gas to the flush port. Ex factory, the helium inlet port is connected to a T-piece, which feeds the flush port with helium. The service engineer will connect helium at the upper inlet port and the required flush gas at the lower inlet port.

Needles for GasBench II

This section informs about the different needles that are in use with the GasBench II.

Sample Needle

The sample needle, P/N 1137020 (Figure 2-28), is located in the GC PAL autosampler. The correct connection is important to guarantee high GC performance. All sample needles pass a quality control ex-factory. Refer to topic "Connecting Sample Needle" on page 2-25.

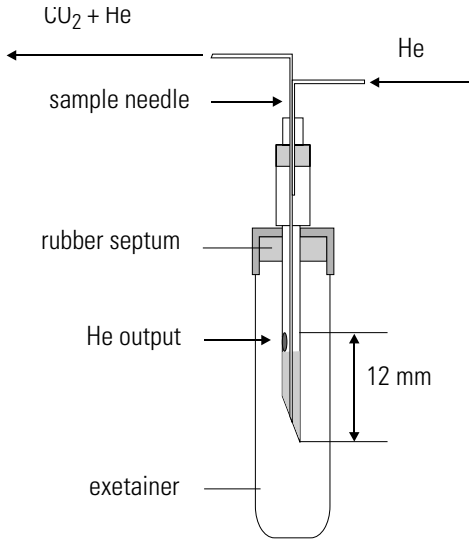


Figure 2-28. Sample needle

Note The sample needle is sometimes synonymously called transfer needle or measurement needle. ▲

Connecting Sample Needle

Connect the sample needle as outlined in Figure 2-29. The sample needle should direct the helium flow through the side hole and take up the sample through the needle tip. This ensures dead volume-free and therefore memory-free sampling. The CO_2 + He carrying capillary and the corresponding bulkhead connector should be marked by a flag. See Figure 2-29.

Now, helium gently moves CO_2 from the headspace of the Exetainer into the fused silica capillary within the needle tip. From here, the sample is transferred through the water removal (pos. 1, refer to topic "Principle of Online Water Removal" on page 2-30) and the Valco loop for GC injection. The helium flow should be at approximately 0.4-0.5 mL/min (measured at the vent of the Valco valve; see Figure 2-37).

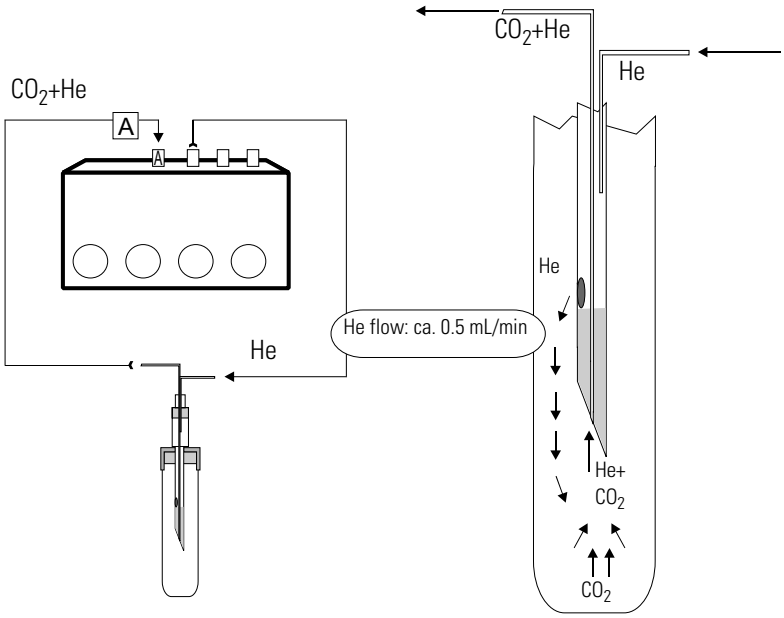


Figure 2-29. Connecting sample needle

Unclogging Sample Needle

The sample needle might be clogged by and by due to phosphoric acid crystallizing within the fused silica capillary.

❖ **To unclog the sample needle**

1. Detach the fused silica capillary from the GasBench II in order not to destroy the Nafion® polymer of the water trap.
2. Fill an exetainer with methanol or acetone.
3. Heat it up to approximately 40 °C.
4. Use the pressure of the helium flow from the GasBench II through the steel capillary to pressurize the extainer.

If you have a setup of the GasBench II with a flush needle for flushing exetainers with gas (as used for water equilibration) you can connect the steel capillary even to this gas line and use a higher pressure. Be careful and put a beaker below the end of the fused silica capillary as methanol will run very fast as soon the line is unclogged.

5. A 0.1 mm i.d. capillary can be moved through the side hole or bottom end of the needle. Accidentally deposited septa butyl rubber from pinching might be removed that way.

Flush Needle

The flush needle is a modified sample needle (P/N 1137020). It operates for a normal 10 mL sample vial at enhanced flush flow to exchange the headspace of the sample from ambient air or to exchange with an equilibration gas (for example CO_2 in He, H_2 in He).

Connecting Flush Needle

The measurement needle will be changed. The fused silica capillary will be cut using a wafer or cutter approximately 10-20 cm from the top of the needle connection. This allows less restriction and a higher flow of flush gas through the sample vial and the needle.

Note If a sampling needle is defective, a measurement needle can be used as a sample needle. Connect the fused silica capillary of a flush needle with a 0.32-0.32 or fit-to-all press-fit connector. Refer to topic "GC Oven" on page 2-35. It is connected as a single version either to port 2a in Figure 2-8 or in dual needle version to ports 2a and 2b in Figure 2-8. For the dual needle version, one extra sample needle needs to be changed to a flush needle. ▲

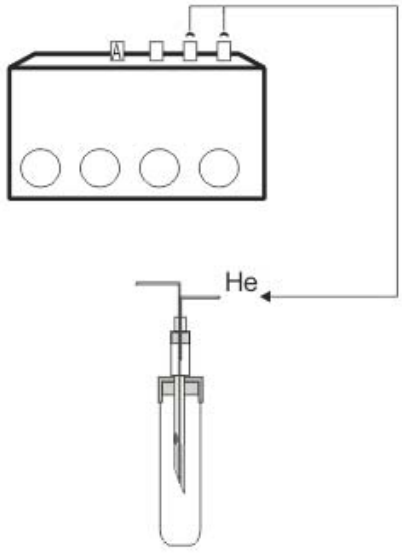


Figure 2-30. Connecting flush needle

With the flush needle, different flush flows and flush gases are in use:

- Flushing with helium (≈ 100 mL/min during 4-6 min) in case of carbonates and DIC.
- Filling with a gas mixture of 0.3-0.4 % CO_2 in helium and a flow of 50 mL/min makes the use of glove bags and glove boxes unnecessary.
- Filling of the sample vial headspace with CO_2 in He or H_2 in He.

Note It is possible to connect two flush needles and operate them simultaneously by using our dual needle holder (P/N 1137120). See pos. 2 and pos. 4 in Figure 2-31. The dual needle holder is part of the Installation Kit (P/N 1121060). See Table 7-2. For dual needle flush an extra sample needle can be cut at the 0.32 ID deactivated fused silica capillary. This enables dual needle flush using two flush needles. ▲

Mounting Syringe Needles into Autosampler

Figure 2-31 outlines the mounting of needles into the needle holder of the autosampler. The related parts are summarized in Table 2-5. The part number of the complete sample needle assembly is

- dual needle holder for CTC autosampler (P/N 1137120) and
- measurement needle (P/N 1137020)

Note The relative positions between two needles are fixed when inserted into the needle holder. See Table 6-1 and Table 7-1 for part numbers. ▲

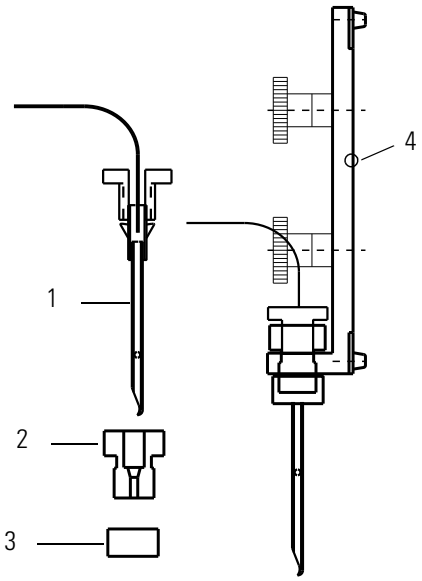


Figure 2-31. Mounting sampling or flush needles into needle holder

Table 2-5. Parts of Figure 2-31

No. in Figure 2-31	Designation	P/N
1	acid needle (any needle from flushing, measuring or acid)	1137030
2	acid needle holder	1175070
3	knurled nut, M8	1119170
4	dual needle holder for CTC autosampler	1137120

Figure 2-32. Dual needle holder for CTC autosampler - front view

Figure 2-32 shows the dismantled dual needle holder for CTC autosampler, P/N 1137120, in front view.

❖ **To insert the dual needle holder into the autosampler**

1. Mount the needles on the dual needle holder. See Figure 2-32.
2. Insert the dual needle holder into the autosampler. See Figure 2-33.

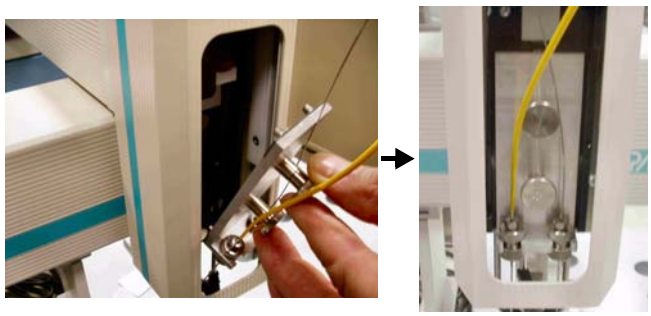


Figure 2-33. Inserting dual needle holder for CTC autosampler into AS

Note The dual needle setup exerts a strong force on the rubber straps. We recommend exchanging the rubber straps once a year. This is especially important, if you switch between Flash HT (fast injection) and GasBench II (slow injection). Contact your local CTC service for the Preventive Maintenance Kit (PAL PM, GC PAL). Refer to Kit for the simultaneous attachment of one GC PAL autosampler and sample tray of the GasBench II to FlashEA, IRMS, HT or TC/EA (P/N 1132201). ▲

Online Water Removal

The GasBench II is equipped with two on-line water removals. One of them is positioned in front of the Valco eight port valve, whereas the other one is used as a guard trap in front of the open split interface to the IRMS. The second water trap keeps the water background stable of helium coming from the GC column and the parts in front of it. See Figure 2-34.

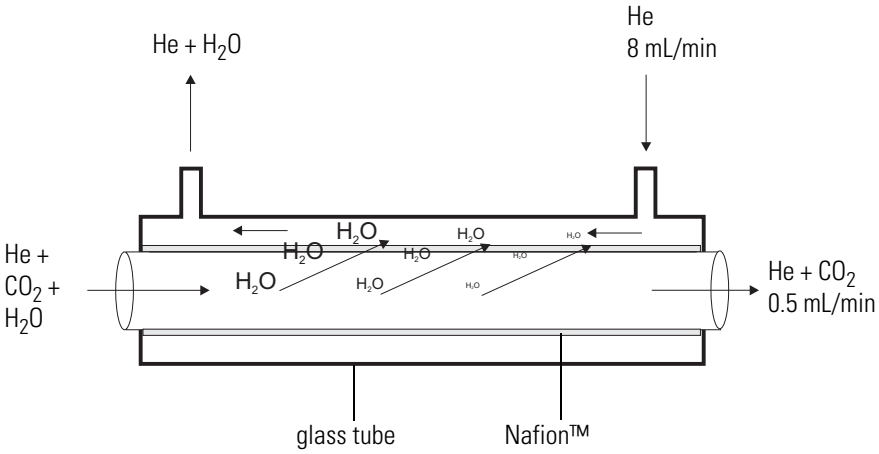


Figure 2-34. Schematic of online water removal

Principle of Online Water Removal

Water is removed from the transfer sample stream by a gastight but hygroscopic Nafion® tubing. The sample flow (He + CO_2 + H_2O, 0.5 mL/min) passes through the Nafion® tubing, which is mounted co-axially inside a glass tube. This glass tube, and therefore the outer surface of the Nafion® tube, is constantly kept dry by a He flow of approximately 8-20 mL/min.

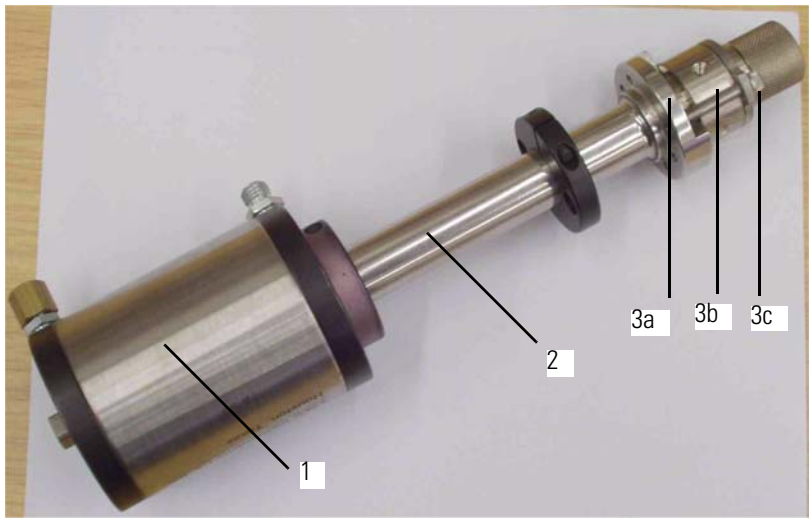
Owing to the water gradient through the Nafion® wall, any water in the sample flow will move through the Nafion®. A dry (He + CO_2) gas results, which flows towards the Valco loop. Alternatively, water-free nitrogen can be used for water removal.

Principle of Valco Eight Port Valve

The Valco eight port valve is an alternatively switching multiposition valve. It operates with dry, oil-free compressed air moving within an electropolished stainless steel body. It allows changing the gas flow by pneumatic port switch under vacuum conditions.

Parts of Valco Eight Port Valve

Figure 2-35 shows the Valco Eight Port Valve. The long shank allows to introduce the functional head into the oven as head and control are thermally separated by the distance. The chequered knob on top must be unscrewed, if you want to withdraw the rotor. After inserting the rotor, screw in the chequered knob again.



Labeled components: 1=compressed air control, 2=long shank, 3=functional head (3a=mounting plate, 3b=n-port, 3c=chequered knob)

Figure 2-35. Valco eight port valve - side view

Note Take the direction of the letter on top of the rotors into account. After exchange or cleaning, the positioning of the letter must exactly be the same as it was before! ▲

Note If the Valco valve leaks (argon background: switch to Instrument Control and measure Ar40 signal), as a first measure carefully clean the sensitive rotor. Therefore, refer to Technical Note 201: Operation Notes and Cleaning Instructions of Valco Instruments Co. Inc. (VICI) at www.vici.com. It is also part of your equipment.

Furthermore, refer to Technical Note 410: Multiposition Air Actuator O-Ring Replacement and to Technical Note 701: Operation Notes and Alignment Instructions, Air Actuated Multiposition Valves at www.vici.com. ▲

Load Mode vs. Inject Mode

The Valco eight port valve is used in a six port setup. Two ports are in "standby" for each injection mode. See Figure 2-36 and Table 2-6.

Table 2-6. Load mode vs. Injection mode of Valco eight port valve

Load mode	Inject mode
Ports 1 and 8 are in "standby".	The gas content of the sampling loop is directly transferred onto the GC column by the GC flow (2 mL/min, for example) via ports 5 ¦ 6 ¦ 3 ¦ 4.
The sample flow (He + CO_2) purges the sampling loop (100 mL, for example) via ports 2 ¦ 3 ¦ 6 ¦ 7.	The sample flow is directly connected to Vent via ports 2 ¦ 1.
The GC column is directly connected to the He pressure via ports 5 ¦ 4.	

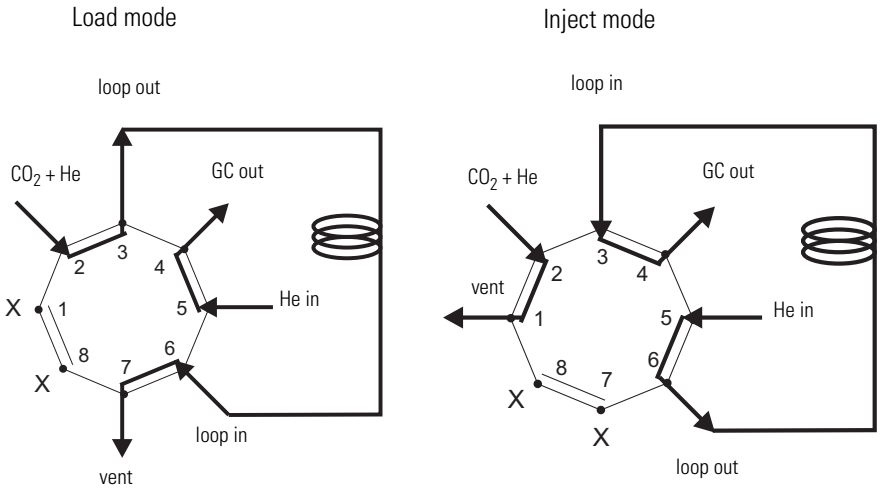


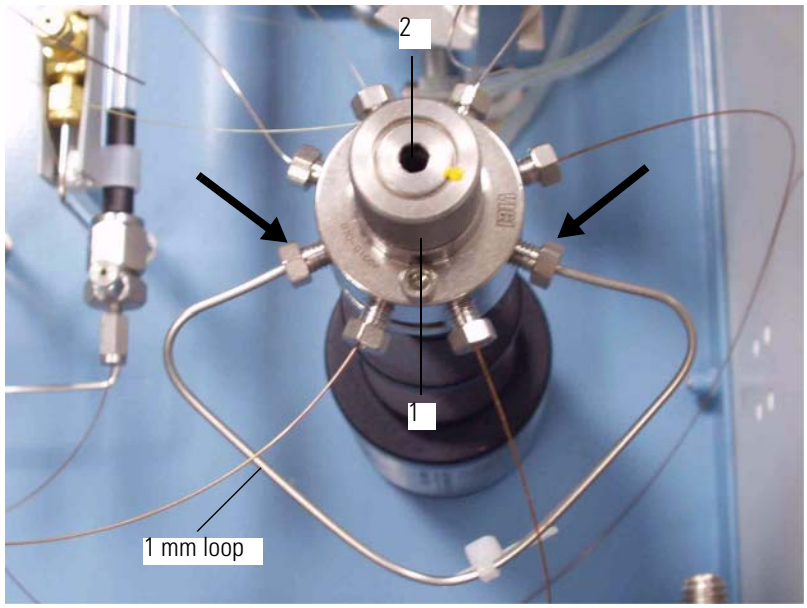
Figure 2-36. Valco eight port valve - Load mode vs. Inject mode

Changing Loop Size

Note Refer to Technical Note 201: Operation Notes and Cleaning Instructions of Valco Instruments Co. Inc. (VICI) at www.vici.com. It is also part of your equipment. Furthermore, for proper loop installation refer to Technical Note 105: Installing a Loop at www.vici.com. ▲

Caution Make sure the Valco valve is in Load Mode! Changing the loop in Inject Mode will interrupt the GC column flow. This will cause damage to the GC column. ▲

Caution Always use Valco stainless steel ferrules for mounting the loop! Refer to Technical Note 503: Fitting Instructions at www.vici.com. ▲



Labeled components: 1=chequered screw, 2=socket head screw

Figure 2-37. Valco valve with loop - top view

The arrows in Figure 2-37 show the two screws (1) and (2), which fasten the loop:

- The chequered screw (1) is used to fix the internal rotor, which is flexibly fitted within in the stator by a conical seal.
- The socket head screw (2) is used after fixing the internal rotor by the chequered screw. It allows adjusting the pressure acting from above upon the cone. By increasing this pressure, the internal rotor is tightened against the side walls.

❖ **To change the loop size**

1. Switch the Valco valve to Load Mode.
2. Open the nuts on Port 3 and Port 6. See Figure 2-37.
3. Replace the loop.Use loop sizes less than 250 mL for the two column types.
4. Tighten the nuts.
5. Inject the sample needle into a helium-filled vial and purge the loop before switching to Inject Mode.
6. At the Valco vent (port 7) check for a purge flow of 0.3-0.5 mL.

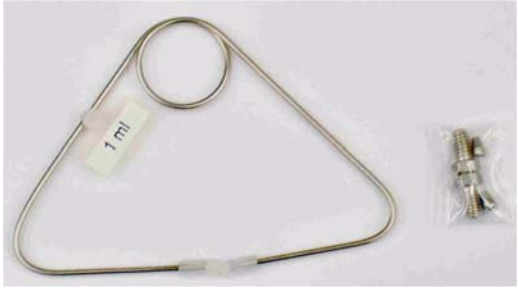


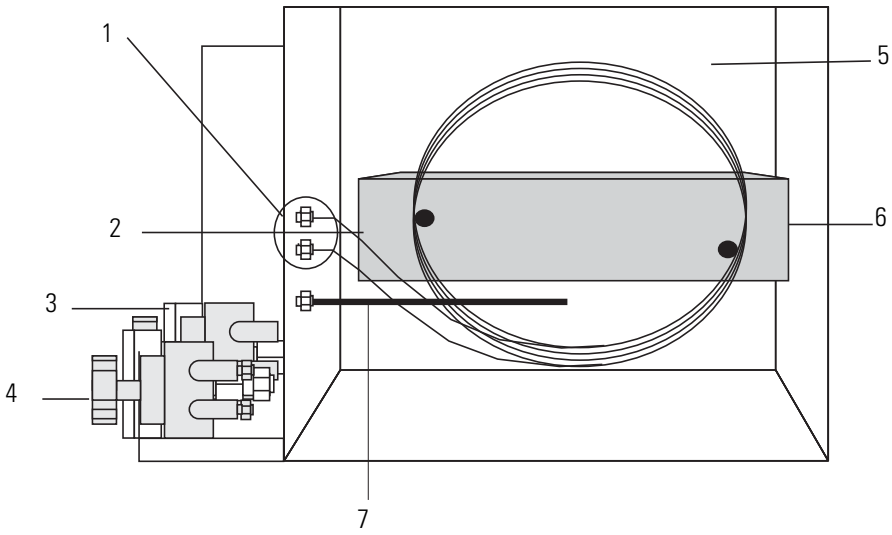
Figure 2-38. 1 mL loop

Figure 2-39. 2 mL loop

Figure 2-38 and Figure 2-39 are shown above as examples. Loops of 100 µL, 250 µL, and 1 mL are already part of your equipment provided by Thermo Fisher Scientific. If necessary, loops of even bigger volumes are available. The 1 mL loop and the 100 µL loop are very similar. For nitrogen analysis, also smaller loops (1 µL) are available.

GC Oven

The GC oven is either equipped with a “HayeSep D” micro-packed stainless steel column or a “PoraPlot Q” fused silica cap column (standard GC column). A JUMO iTRON 16 temperature controller and a type K thermocouple guarantee stable isothermal conditions. The opened right side panel of GasBench II shows the GC oven with the column. See Figure 2-40 and Figure 2-45 on page 2-39.



Labeled components: 1=in/out, 2=heater assembly, 3=manometer, 4=gauge, 5=GC box (inside view), 6=GC column (PoraPlot Q or HayeSep D), 7=thermocouple

Figure 2-40. GC oven - open

The GC column separates the different gas compounds released from the sample loop, N_2 and CO_2, for example. The compounds eluting from the GC column are transferred through the Nafion® trap and via open split into IRMS.

Caution Strictly avoid exceeding the maximum temperature of your column! ▲

Note The change of the setpoints must be validated with a temperature calibrated multimeter and a thermocouple attached to it. ▲

Type “PoraPlot Q” GC Column

This column type is used in the current versions of GasBench II and is part of your equipment. See Table 2-7.

Table 2-7. Properties of PoraPlot Q“ GC column

Parameter	Value
type	fused silica column
length	25 m
inner diameter	0.32 mm
helium pressure	10–12 psi (700–830 mbar)
helium flow	approximately 2-3 mL/min
GC column temperature	room temperature, that is 24 °C

Caution Strictly avoid exceeding the maximum temperature of the column! ▲

Caution Avoid fast pressure variations along the column (Δ p < 0.5 psi/s, that is Δ p < 34.5 mbar/s)! ▲

Type “HayeSep D” GC Column

This column type has been used in prior versions of GasBench. See Table 2-8.

Table 2-8. Properties of “HayeSep D“ GC Column

Parameter	Value
type	1/16” stainless steel micro-packed column
length	2 m
inner diameter	0.76 mm
packing material	polymer HayeSep D; 80/100 mesh
helium pressure	10–15 psi (700–1000 mbar)
helium flow	3–4 mL/min
GC column temperature	50–60 °C

Caution Strictly avoid exceeding the maximum temperature of the column! ▲

Step 1 - Accessing GC Column

Currently, the GC column is a static part of the GasBench II as it nearly never needs to be exchanged. Only maintenance is necessary from time to time. The GC oven is located at the right side of the GasBench II (front view).

❖ **To access the GC column**

1. When inserting the GC column for the first time or when exchanging it, first remove the cover of the GC oven (that is right side panel of the GasBench II). Therefore, unscrew all seven screws using an Allen wrench. See Figure 2-41.

Figure 2-41. GasBench II - right side panel being opened

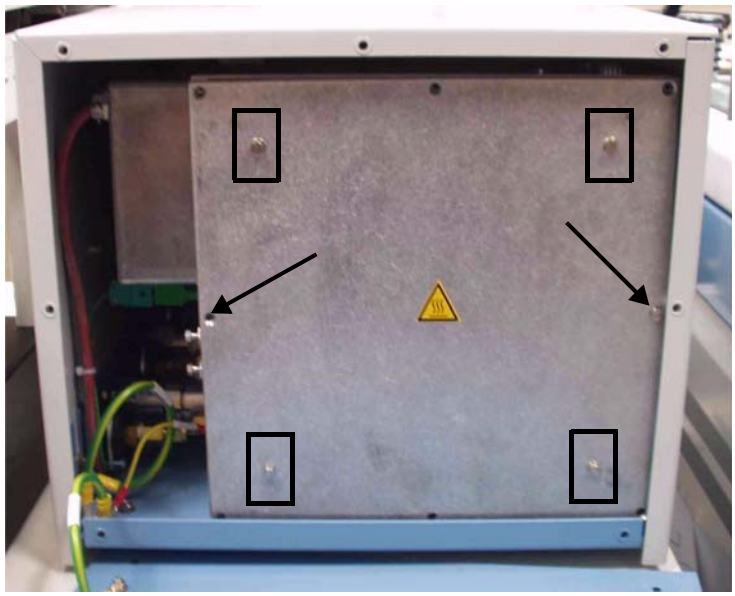


Figure 2-42. GasBench II - right side panel removed

2. Afterwards, remove the two screws marked by arrows in Figure 2-42.

Note Leave the remaining four screws untouched that are marked by rectangles in Figure 2-42, as they hold the insulation of the GC oven! ▲

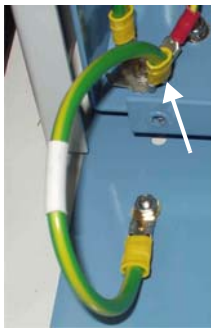


Figure 2-43. Grounding cable of right side panel

Each side panel has a grounding cable of its own to guarantee electrical security. Each grounding cable must be connected as shown in Figure 2-43 as an example for the right side panel. Furthermore, the top side and the oven housing are grounded as well.

Step 2 - Changing GC Column

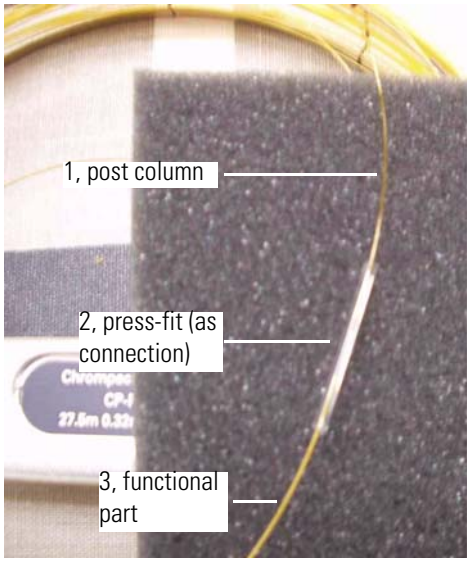
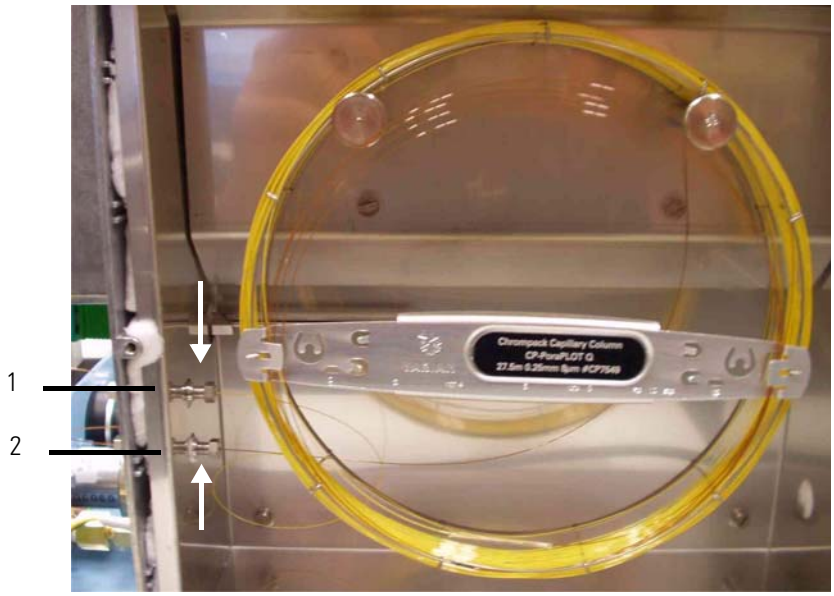


Figure 2-44. Junction between both parts of column

The GC column is now visible and consists of two parts:

- the functional part (light yellow; see pos. 3 in Figure 2-44). It is the packed part of the column, that is the plot part.
- the post-column (nearly transparent; see pos. 1 in Figure 2-44)

The connection between both parts is established by a press-fit (pos. 2 in Figure 2-44).



Labeled components: 1=GC in, 2=GC out

Figure 2-45. Column - installed*

*By default, the column is installed as 1=GC in and 2=GC out.

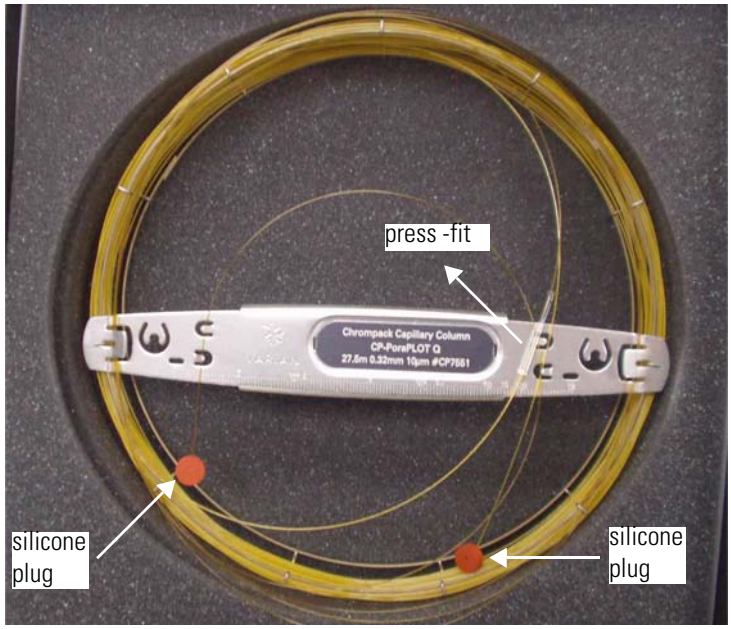


Figure 2-46. Column - with blocked ends

Figure 2-46 shows the ends of the column, which are blocked by silicon plugs.

❖ **To change the GC column**

1. Cut the silicon plugs off using a capillary cutter (wafer).
2. Insert each end into its bulkhead connection at the left side of the oven (see pos. 1 and pos. 2 in Figure 2-45) as follows:
   a. The bulkhead connection, which is connected to the Valco valve, is intended for the inlet of the column. It must be connected to the functional part of the column (light yellow).
   b. As the outlet, the post-column must be connected to the bulkhead connection that is directed towards the water trap 2. The water trap, in turn, leads to the diluter, that is to the open active split.

   The post-column (nearly transparent) acts as a particle trap, that is it prevents particles from reaching rear valves.
3. Screw the Swagelok® connection or Valco valve connection on as follows:
   a. Insert the respective ferrule.
   b. Newly cut the capillary off.
   c. Introduce the capillary.
   d. Carefully tighten the ferrule until the capillary can no longer be pulled back. Do not tighten the ferrules/connections too strong!

Caution If you want to tighten the ferrule further, it is absolutely necessary to perform a leak check first! Only tighten it further, if gas is still coming in after the leak test has been performed.
Act extremely carefully while opening and closing connections! Do not tighten any Swagelok® connection around the column too strong as this causes demolition!
Only connections made up by metal ferrules can be tightened strongly. Normally, the only connections to be touched by users are those of the column, the loop and for installing a flush needle or a sample needle, respectively. ▲

Note For detailed information about how to install the column in the GC, about conditioning, storage and description refer to the Capillary Column Test Report by Varian/Chrompack. It is part of your Varian/Chrompack capillary column. ▲

Programming Temperature Controller for GC Oven

The JUMO iTRON 16 temperature controller allows to control the temperature of the GC oven. It is located at the side panel of the GasBench II. See Figure 2-47.

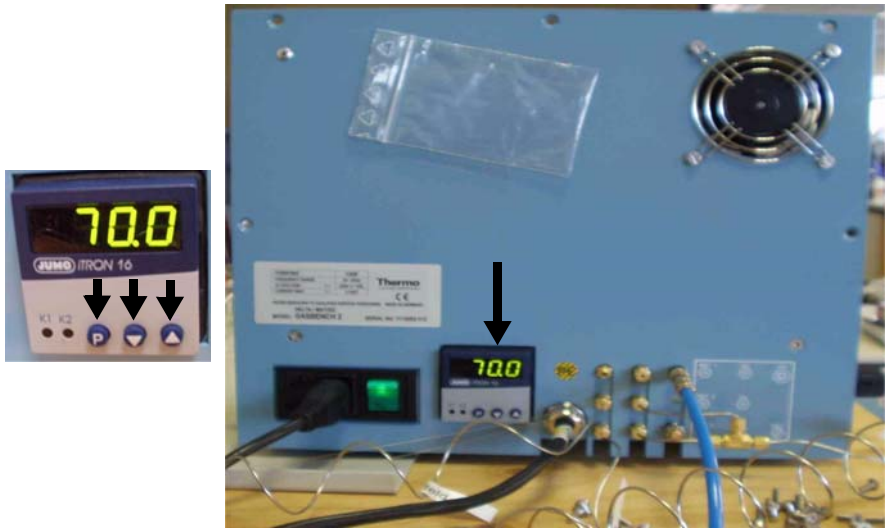


Figure 2-47. JUMO iTRON 16 temperature controller

Notice the three keys shown in Figure 2-47 (left):

P key	for programming; values will be accepted automatically after 2 s.
Arrow Up key	to increase a particular value
Arrow Down key	to decrease a particular value

Note The parameter values to be used for manual programming of the JUMO iTRON 16 temperature controller have been pre-set by the final test field of Thermo Fisher Scientific (Bremen). ▲

Note The change of the setpoints must be validated using a temperature-calibrated multimeter and a thermocouple attached to it. ▲

Caution Do not use Self Optimization of the JUMO iTRON 16 temperature controller. The GC column may be destroyed! The maximum temperature to be regulated by the JUMO iTRON 16 temperature controller may not exceed 150 °C! ▲

For details of manual programming, refer to the manual of the JUMO iTRON 16 temperature controller.

Open Splits

Within the GasBench II, two open splits are used to allow a continuous flow of the sample gas to the IRMS at atmospheric pressure:

- sample injection (active open split) and
- reference injection (reference open split)

Reference Injection

This section outlines the function of the reference section of the GasBench II. Three reference gases can be injected via a three-port open split interface. A He stream of 2 mL/min permanently flushes the interface tube (see Figure 2-48 and Figure 2-49). A permanent flow of 0.25 mL/min transports the content of the interface tube to the IRMS.

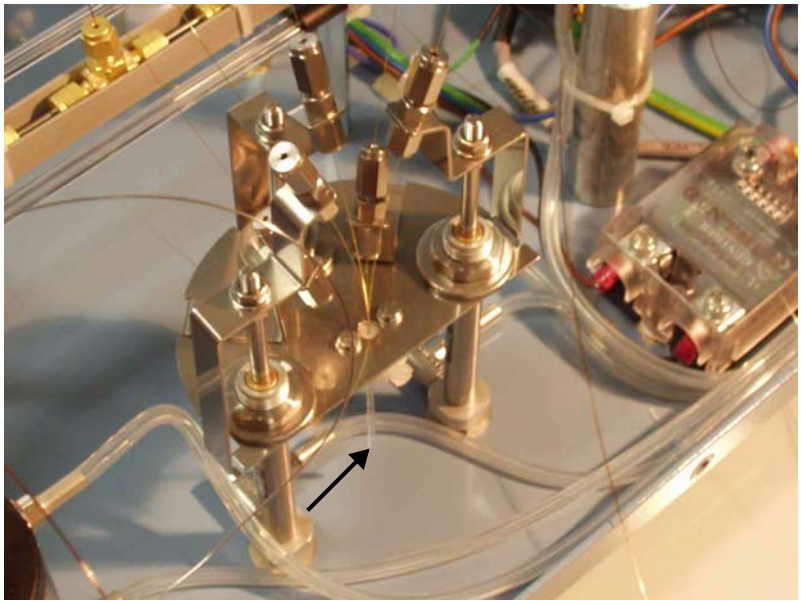


Figure 2-48. Reference inlet (open split)

Principle of Reference Gas Introduction

To inject a reference gas, the corresponding reference capillary moves to the bottom of the open split interface. See Figure 2-49. The reference gas, CO_2 for example, is then mixed with the 4 mL/min He flow. Now, 0.25 mL/min of this (He + CO_2) mixture is transferred to the IRMS resulting in a rectangular shaped reference gas pulse. The width of this pulse, 20 s for example, is defined by the time between injecting and removing the reference gas capillary.

Note No CO_2 or air must be visible in Instrument Control. Otherwise, the capillaries need to be redesigned. ▲

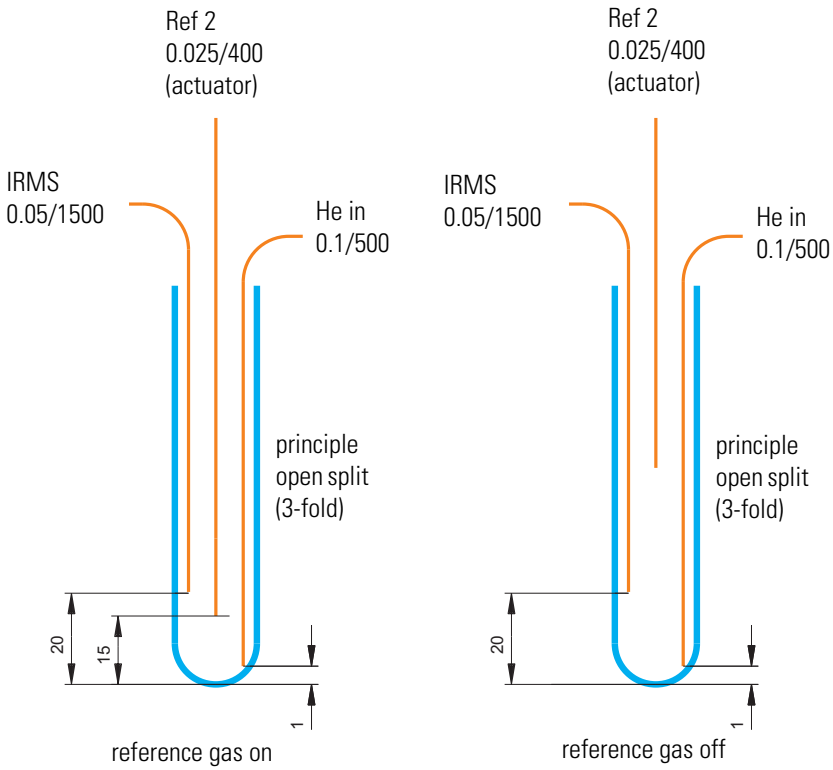


Figure 2-49. Principle of reference gas introduction

Sample Injection and Dilution

The sample injection (active open split) enables the injection of sample gas carried by helium flow into the IRMS. The sample gas is injected from below into a helium-purged mixing zone. Consequently, the gas pressure of the ion source is kept constant as defined by atmospheric pre-pressure, length and inner diameter of the capillary.

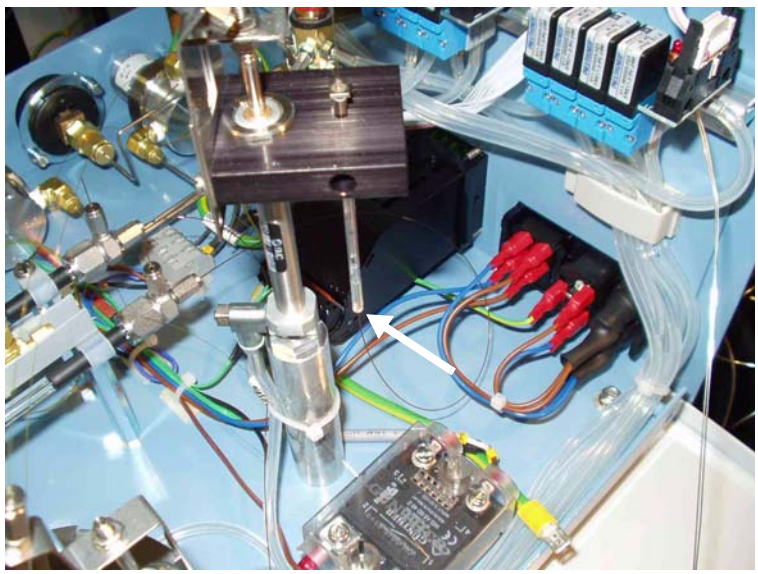


Figure 2-50. Sample inlet (open split)

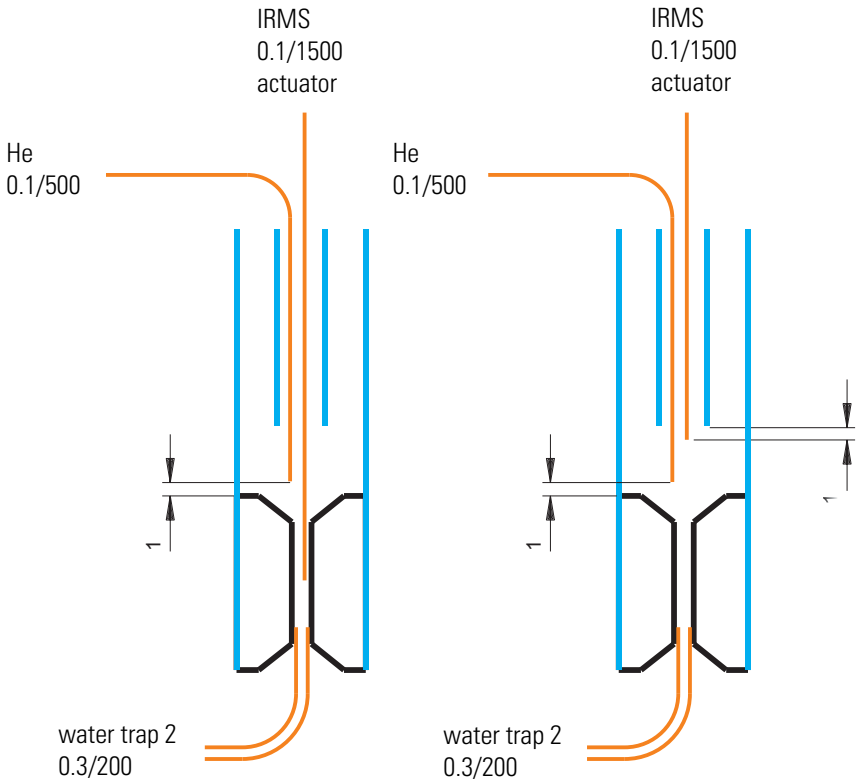


Figure 2-51. Sample injection and dilution

Principle of Active Open Split

The sample gas pressure is never ideally the same (for example, the amount of carbonates alternates). To be able to keep all CO_2 generated from different amounts of carbonates at a constant CO_2 pressure range, the active open split has been developed by Thermo Fisher Scientific.

Moving the IRMS capillary into the direct transfer connection (90-100 %) or mixing zone (1:4) enables to dilute the sample gas concentration within the helium flow.

- left side of Figure 2-51: no dilution
- right side of Figure 2-51: dilution active

The transfer of the sample stream into the IRMS is achieved via the open split. The capillary that leaves the second water trap enters the open split interface as well as the retractable sampling capillary of the IRMS. A third capillary (protection capillary) delivers a constant stream of dry helium, which purges the exit volume of the open split at any time.

"IN" position

- The IRMS capillary is moved to the bottom of the open split.
- The IRMS capillary "sniffs" the sample stream eluted by the capillary that comes from the second water trap.

"OUT" position

- The gas from the protection capillary mixes with the sample flow.
- The IRMS capillary "sniffs" the diluted sample stream.

Note Notice a difference between GC applications and GasBench applications: In case of GC applications, the mass spectrometer capillary is completely decoupled from GC. In case of GasBench applications however, only partial decoupling occurs. ▲

Chapter 3 Isodat

This chapter outlines how to operate the GasBench II by the Isodat software. It deals with the following topics:

Starting Isodat

❖ To start Isodat

1. Start Isodat by a double-click.

2. Start the Configurator.
   Choose **Edit > Reset Isotope MS**. See Figure 3-1.

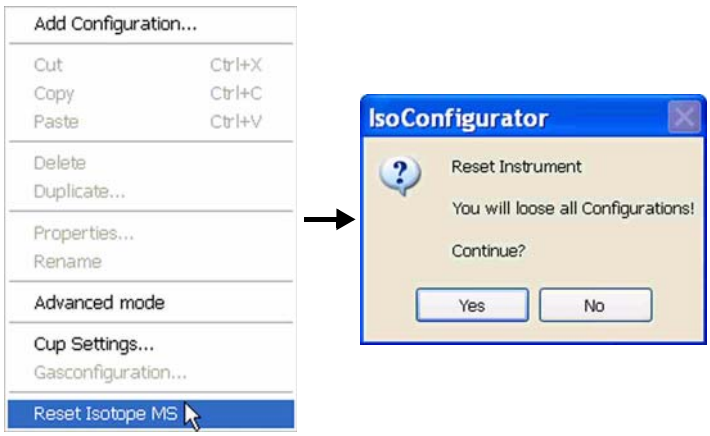


Figure 3-1. Reset mass spectrometer

3. Isodat is a software package that controls a family of mass spectrometers for isotope ratio measurements. As a first step, the user must select the mass spectrometer he wants to control by Isodat. Select your mass spectrometer, DELTA V, for example. See Figure 3-2.

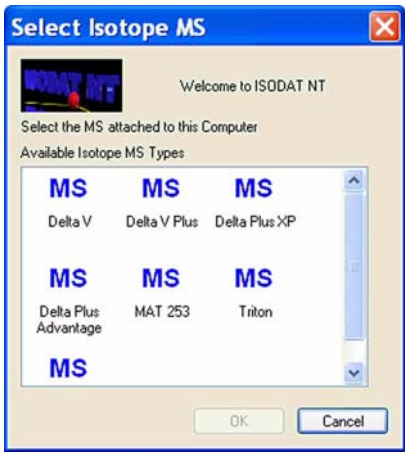
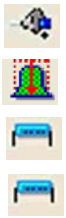


Figure 3-2. Selecting the mass spectrometer

4. In the Cup Settings window (See Figure 3-3.), do the following:



a. Look, whether the cups are installed or not installed.

b. Look at the Peak Center option of the cups.

c. Look at the Resistor values [Ω] of the cups.

d. Look at the Resistor 2 values [Ω] of the cups.

Refer to the delivered test protocol and compare it with your order.

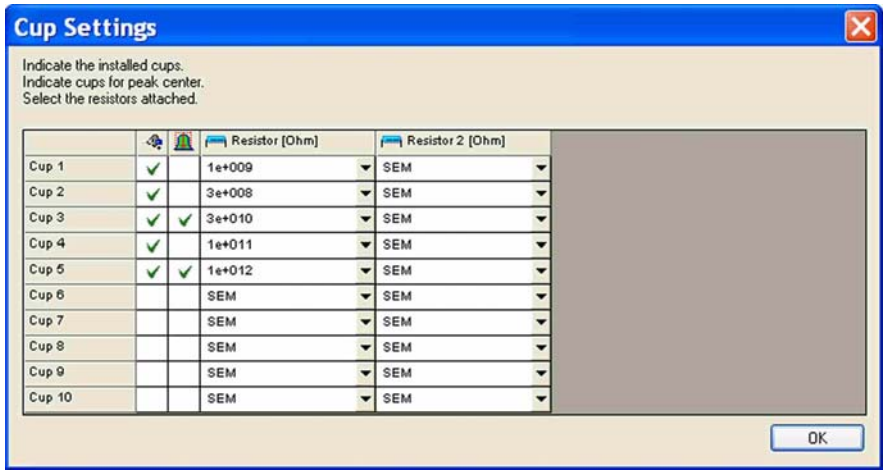


Figure 3-3. Cup Settings window

5. In the Gas Configuration Editor (Figure 3-4):

   Check for your particular configuration (CO2, for example) whether the masses are assigned correctly to the cups.

   Check calibration, Ratio Groups, magnet position and Peak Center Offset. The default values for magnet position are averaged experience values that cannot be checked and edited here, but later on during calibration procedure.

   The number of required cups (3, for example) is displayed together with the corresponding masses (m/z 44, m/z 45, m/z 46, for example) below the grid.

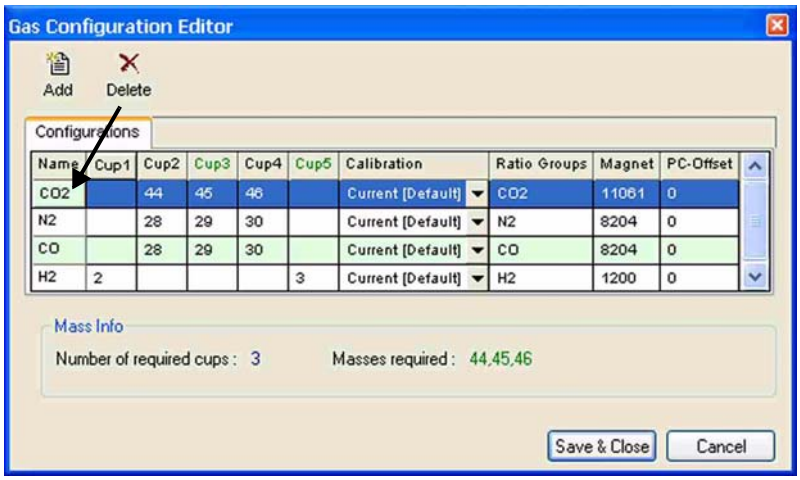


Figure 3-4. Gas Configuration Editor

6. Click on **Save & Close** to exit the Configurator.

7. Click **OK** to shut down and rest the instrument.

Figure 3-5. Resetting mass spectrometer

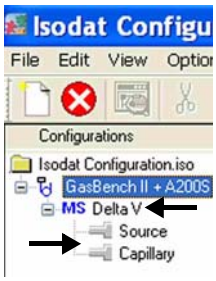
Creating a GasBench Configuration

❖ **To create a new GasBench II configuration**

1. Open the Configurator.

2. The appearing default configuration contains the mass spectrometer you previously specified, DELTA V, for example.

   Rename My Configuration by for example GasBench + A200S.



3. Click on both '+' signs to expand the mass spectrometer tree.

   The specified mass spectrometer becomes visible together with its Source port and Capillary port (see arrows).

4. Among the available GasBench II sets in the right pane, mark the one that matches your system, for example **GasBench + A200S Sampler**. Then, drag it to the Capillary port. See Figure 3-6.

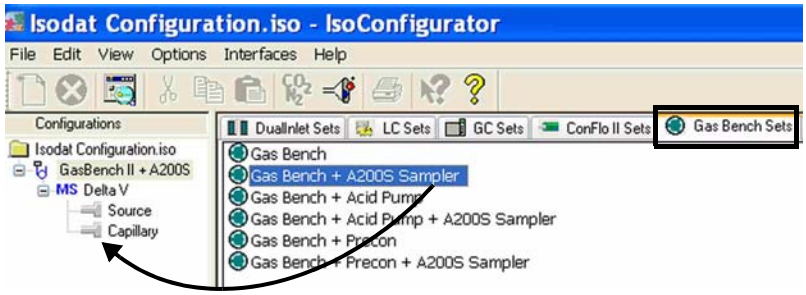


Figure 3-6. Appending GasBench II set to port

Figure 3-7. Optional hardware - Flush Fill, Trap and Trap 2

5. Select or deselect optional hardware, that is Flush Fill, Trap or Trap 2. See Figure 3-7.

   Confirm by **OK**.

Contrary to former times, GasBench II now always contains a Flush Fill. GasBench II can be used either without a trap or with one trap or with two traps. Traps are optional and provide additional opportunities.

Note In Isodat versions older than Isodat 2.0, occasionally software problems due to old scripts (that is .sct) occurred when no trap was installed. In Isodat 2.0 however, new scripts (that is .isl) are used eliminating this problem. ▲

6. The entire set has been appended to the Capillary port.
   Click on the various '+' signs to unfold the entire tree showing the individual components of the device. See Figure 3-8.

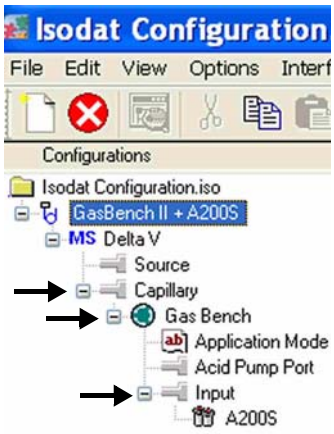


Figure 3-8. Complete set appended to Capillary port

7. Close the Configurator. All settings will be saved automatically.

Acquisition Mode

This section outlines Acquisition mode.

Starting Acquisition Mode and Activating Toolbars

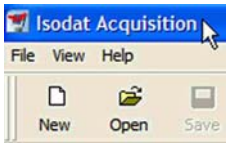
❖ **To start Acquisition mode**

1. Start Isodat by a double-click.

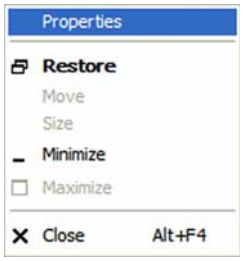
2. Start Acquisition.

   You are now able to run any application which gives you full control over the automated measurement.

❖ **To activate the toolbars**



1. Move your cursor to the title bar Isodat Acquisition. Right-click on it to display the shortcut menu.



2. Select **Properties**.

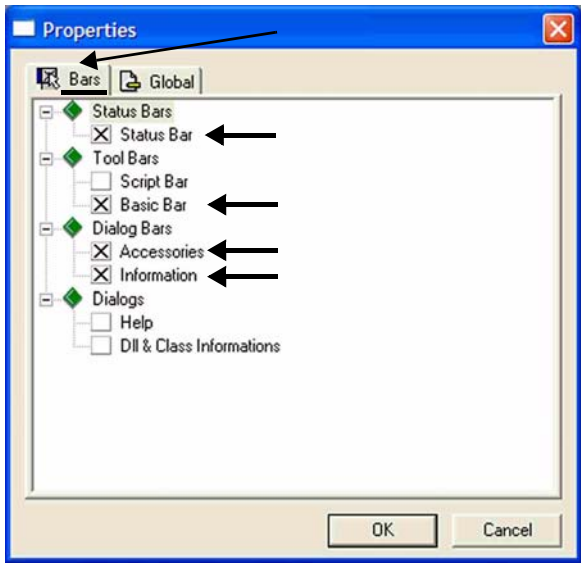


Figure 3-9. Visibility of individual toolbars

3. In the Properties dialog box, select the **Bars** tab. See Figure 3-9.
4. Select the toolbars to be displayed. We recommend to primarily select **Status bar**, **Basic bar**, **Accessories bar** and **Information bar**.
5. Confirm by **OK**. The bars will appear in the Acquisition window.

Components of Accessories Bar

Note It is important that you have already created a configuration that contains your IRMS, for example GasBench + A200S. Refer to topic "Creating a GasBench Configuration" on page 3-5. ▲

The Accessories bar contains important operating panels. If, in one instant, you do not see the Accessories bar, carry out the following steps.

❖ **To display the Accessories bar**

1. Mark the corresponding check box in the Bars tab. See Figure 3-10.

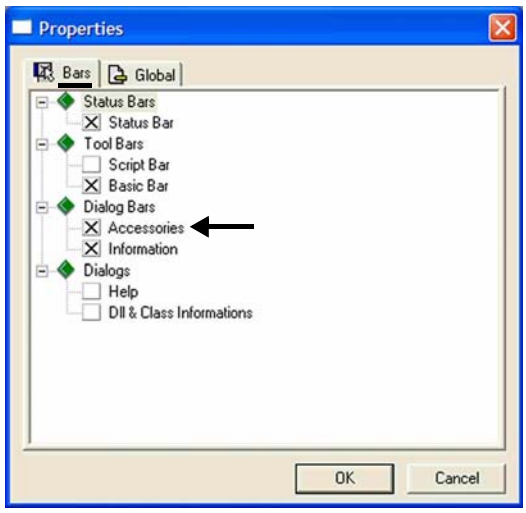


Figure 3-10. Displaying Accessories bar

As Figure 3-11 outlines, the Status bar displays

- the actual configuration (GasBench II + A200S, for example)
- the actual Gas Configuration (CO2, for example)

2. Click on the button of the active configuration tab to have the GasBench II + A200S configuration (Figure 3-12) available. Isodat will automatically refresh or switch to the GasBench II + A200S configuration.

3. Select just this configuration. See Figure 3-11.

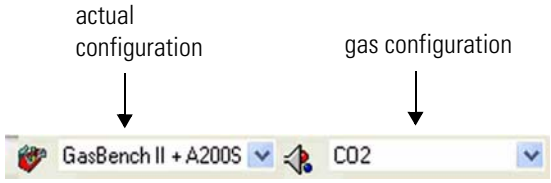


Figure 3-11. Status bar

The Accessories bar displays the selected configuration together with its configured features (as previously defined in the Configurator). See Figure 3-12.

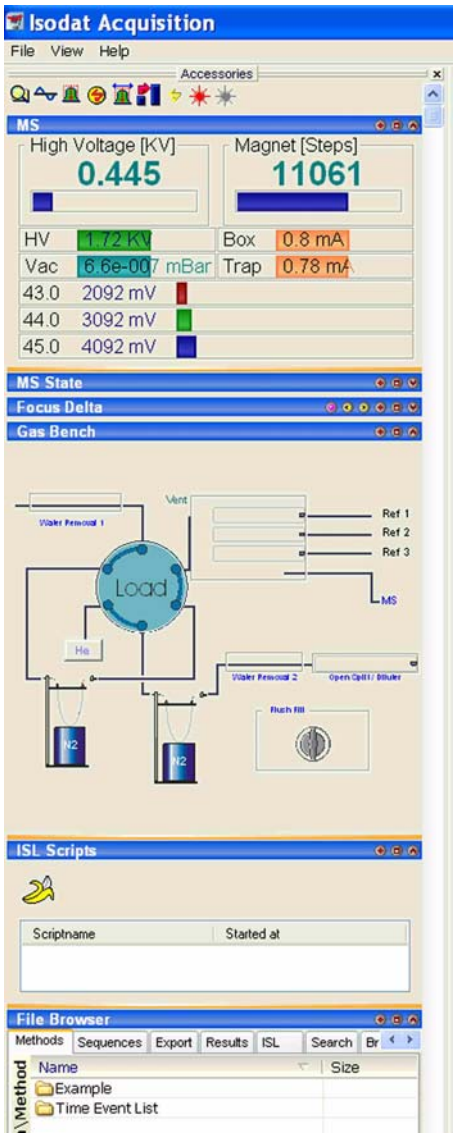


Figure 3-12. Components of Accessories bar

Troubleshooting - Error Messages

If an error message appears at the Status bar, check whether the configuration has been set up correctly. The most common error messages are:

- Plug&measure devices could not be found. See Figure 3-13.

Figure 3-13. Plug & Measure devices not found

It typically appears when the GasBench II plug&measure adapter has not or improperly been plugged into the IRMS. Refer to topic "Plug and Measure Adapters" on page 7-10.

- A configuration containing the acid pump has been selected although the acid pump is not in use.

  If you want to use this configuration anyhow, you must calibrate the acid pump. This is possible only in Fake Mode. After this calibration, a configuration containing the acid pump can even be used for equilibration measurements.

Changing Visibility of Components

❖ **To change visibility of components of Accessories bar**

1. Right-click on an arbitrary title bar (GasBench).

2. Click on the **Administrate Panels** button..

3. In the Accessories dialog box, mark the information to be displayed on the Accessories bar, for example MS State. See Figure 3-14.

4. Unmark the information not to be displayed on the Accessories bar, for example Object Properties. See Figure 3-14.

Figure 3-14. Marking or unmarking accessories

5. Confirm by **OK**. See Figure 3-14. The dialog closes, and enabled accessories will appear on the Accessories bar.

GasBench Window

The GasBench window, Figure 3-15, appears with any configuration containing a GasBench II, no matter whether an autosampler, an acid pump or a PreCon device additionally are attached to it.

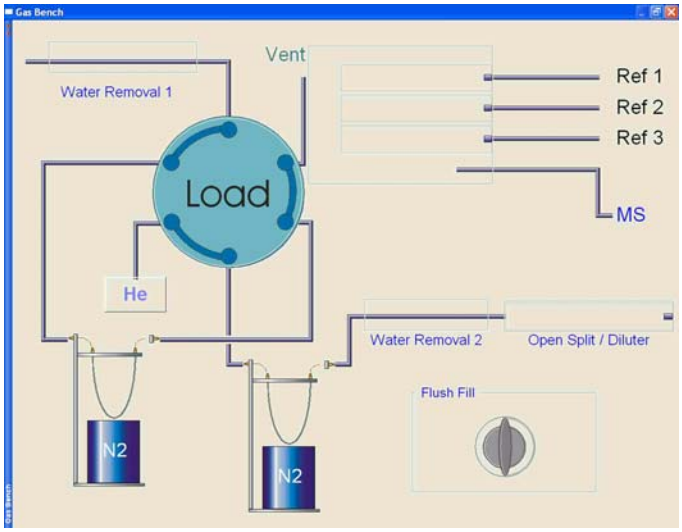


Figure 3-15. GasBench window

The GasBench window allows direct control of all GasBench II hardware components. Set or reset hardware components at any time, even during an acquisition.

Click on a graphical object to operate the specific devices, as there are flush fill valve, Valco valve, open split, reference ports and traps.

Acid Pump Window

If GasBench II is used with an acid pump, the corresponding configuration containing the acid pump must be selected in the Configurator first. Beneath the GasBench window, the Acid Pump window will appear (Figure 3-16).

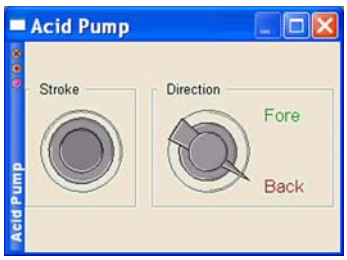


Figure 3-16. Acid Pump window

❖ **To configure the acid pump**

1. Adjust the number of acid drops per stroke at the acid pump. Refer to topic "Acid Pump Adjustment" on page 6-5.

2. This number must be communicated to Isodat. Therefore, right-click somewhere into the Acid Pump window.

3. Click on the **Calibrate...** button.

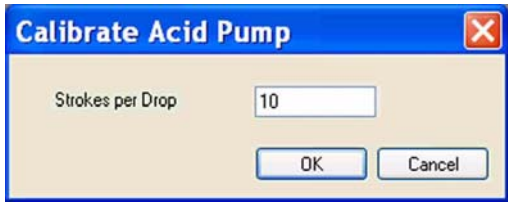


Figure 3-17. Number of acid drops per stroke

4. Type in the number of acid drops per stroke adjusted at the acid pump (default is 10) and confirm by **OK** (Figure 3-17).

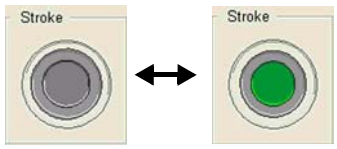


Figure 3-18. Stroke button

5. When you press the **Stroke** button, a single stroke of the acid pump will be carried out. The **Stroke** button, usually grey, changes its color to green for the duration of the stroke and returns to grey.

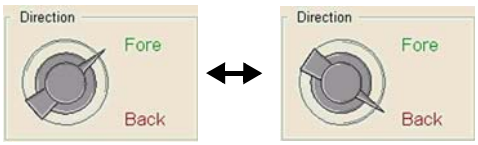


Figure 3-19. Positions of Direction button

You can switch between the positions Fore and Back by pressing the **Direction** button. Both buttons are used to directly control the acid pump. When you try them for the first time, check via the **Direction** button, whether the acid pump rotates forward by switching to **Fore**.

The **Stroke** button controls the rotation of the acid pump. A specific number of rotations is needed to produce one drop of acid. This number must be determined by the user and then be saved in the Isodat database using the **Calibrate** button. It appears after a right-click on the Acid pump window.

File Browser

The File Browser, also called File Browser bar, is accessible via the Accessories bar. It comprises various tabs, which are described in the following topics. See Figure 3-20.

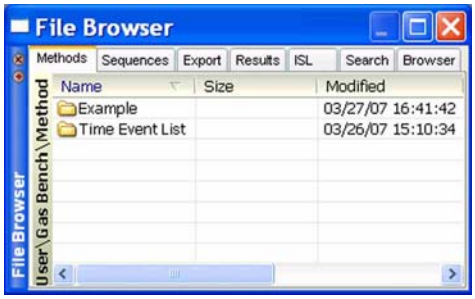


Figure 3-20. File Browser

Methods Tab

At Methods tab, Isodat methods can be saved. In the Example folder, predefined methods have been stored. Methods provide the complete description of a single measurement. They can be programmed or changed by the user. Refer to topic "Creating a New Method" on page 3-18.

Note You must create and save a new method on your own! The predefined methods delivered by Thermo Fisher Scientific in the Examples folders are only example files. They only show guidance through helpful default values, but must never be used for measurements!
Never overwrite an example file with a method created on your own! Depending on your software version, these examples may not work properly. ▲

Sequences Tab

At Sequences tab, Isodat sequences can be saved. In the Example folder, predefined sequences have been stored. Sequences contain the description of a sequence of single measurements (methods). They can be programmed or changed by the user. Different sequences have been predefined covering all basic measurements (in the Examples folder of the Sequences tab). Refer to topic "Creating a New Sequence" on page 3-50.

Note You must create and save a new sequence on your own! The predefined sequences delivered by Thermo Fisher Scientific in the Examples folders are only example files. They only show guidance through helpful default values, but must never be used for measurements!
Never overwrite an example file with a sequence created on your own! Depending on your software version, these examples may not work properly. ▲

Export Tab

At the Export tab, you can save your defined Isodat export templates. Edit voluminous amounts of acquisition data for your own data systems using export templates. Use the Result Workshop of Isodat to select and display particular aspects of your acquisition data.

Results Tab

The Results tab provides access to all previously acquired measurement results. It gives an overview of all results and is empty prior to the first measurement.

Note To easily transfer and store data at your place of choice (for example on a drive where data security is guaranteed), go to Results tab, perform a right-click there and then select **Set Path**. The basic path is automatically installed at C:\Thermo\Isodat NT\Global\User\Gas Bench\Results*.cf. For reasons of data security, we recommend using this feature frequently. ▲

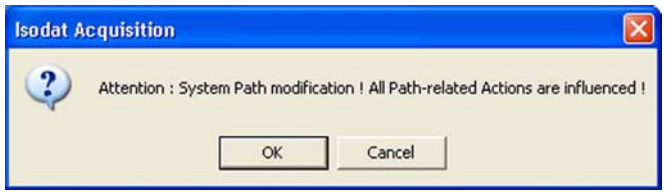


Figure 3-21. Modifying the result path

Modify the results path to a backup directory. From now on, all method, sequence and result files will be stored at a different location. See Figure 3-21.

ISL Tab

In the ISL folder, you will find only one single acquisition script for GasBench II (acquisition.isl). It is used for all possible configurations that can be selected in the Configurator. It is not necessary to change it. Refer to topic "Creating a GasBench Configuration" on page 3-5.

Note All acquisition scripts are usually named acquisition.isl, no matter to which application they belong. However, they are stored in separate application-related folders (for example in a particular GasBench II folder at C:\Thermo\Isodat NT\Global\ISL\GasBench). ▲

Calibrations Tab

The Calibrations tab shows the mass calibrations for the IRMS.

Scans Tab

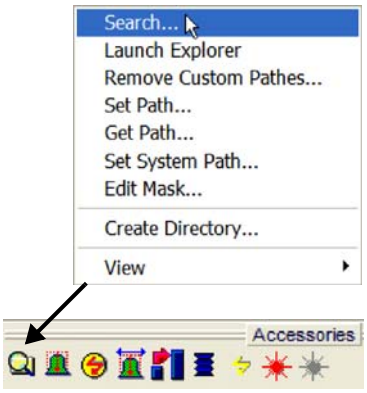
Any transient signal information (HV, ion current of a specific mass, time, electronic potential of an electrical lens, etc.) can be recorded in Instrument Control of Isodat. Recorded scans can be saved under the Scans tab.

Search Tab

The Search tab allows finding any result files of data acquisitions by pressing the **File Search** button . Like a file manager, it displays the results of a file search and allows moving files.

❖ **To perform a file search**

1. In the File Browser, click on the the **Results** tab.



2. Right-click somewhere onto the grid and select **Search**.

   Alternatively, click on the **File Search** button on top of the Accessories bar.

   The Isodat File Search window, Figure 3-22, will appear.

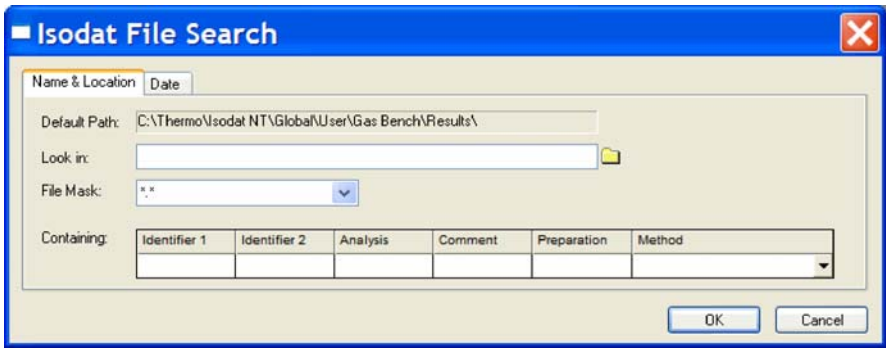


Figure 3-22. Isodat File Search window

3. At its **Name & Location** tab, numerical or alphabetical parameters can be entered for the search ('a' at Identifier 1, for example).

   At its **Date** tab, date-specific search criteria can be enabled. See Figure 3-23.

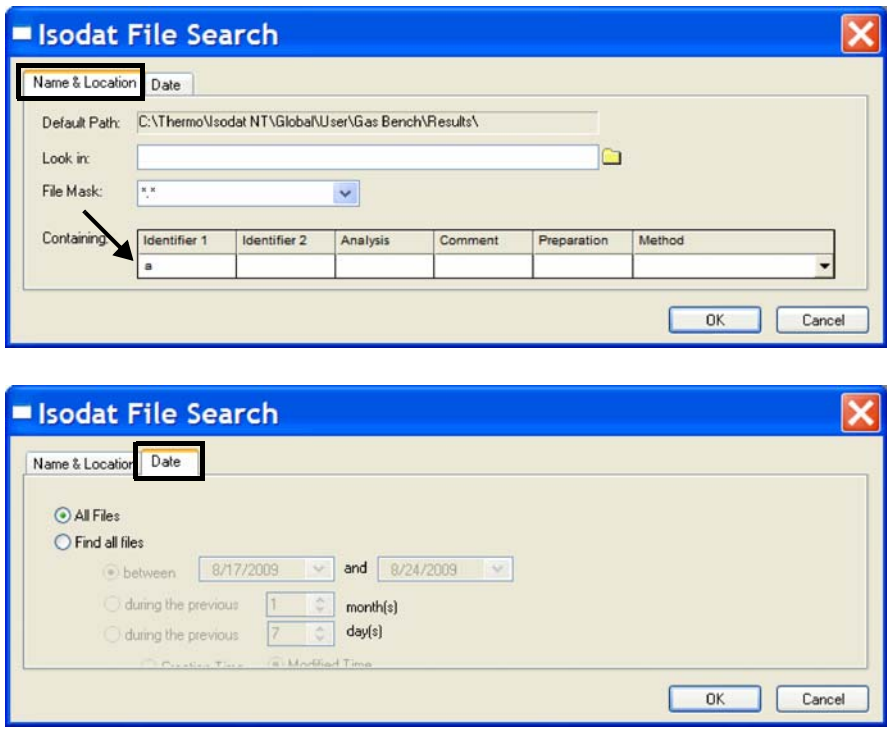


Figure 3-23. Entering parameters for file search

All files matching the search criteria will automatically be shown at the Search tab. See Figure 3-24.

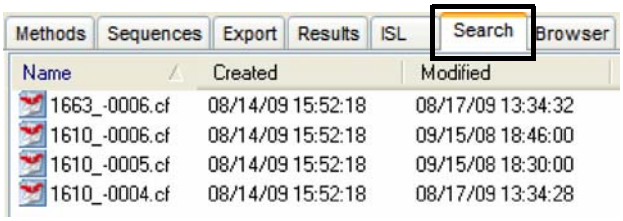


Figure 3-24. Files matching the search criteria

Browser Tab

If a Result Workshop document is open, this tab shows the objects that can be imported (methods, sequences, results, for example). A file manager that allows browsing to an arbitrary directory of your choice, even to a root of a harddisk drive. As with other file managers, files and folders can be created, moved or deleted.

Creating a New Method

The Acquisition mode of Isodat allows fully automated isotope ratio determination. All parameters relevant for data acquisition of a sample are stored in a method.

Note This section describes only the entries that are specific for operating the GasBench II. ▲

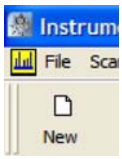
Note You must create and save a new method on your own!
The predefined methods delivered by Thermo Fisher Scientific in the Examples folder are only example files. They only show guidance through helpful default values, but must never be used for measurements!
Never overwrite an example file with a method created on your own!
Depending on your software version these examples may not work properly. ▲

❖ **To create a new method**

1. Open Acquisition mode.

2. Select a configuration suitable for your GasBench II application, for example GasBench + A200S.

3. Select the appropriate Gas Configuration for the intended measurement type, CO2, for example.



4. Press the **New** button to display the File New dialog box. See Figure 3-25.

5. Click on the **Method** icon.

6. Confirm by clicking on **OK**.

Proceed with topic "Structure of GasBench-Related Methods" on page 3-20.

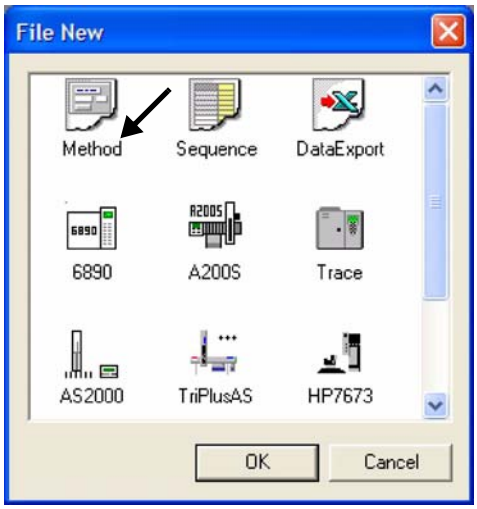


Figure 3-25. Creating a new method

Predefined Methods as Examples

For the sake of simplicity, predefined methods can be selected via the File Browser. See Figure 3-26. Use them only as examples! It would even be sufficient to deliver only one or at most two such predefined methods to cover all kinds of measurements.

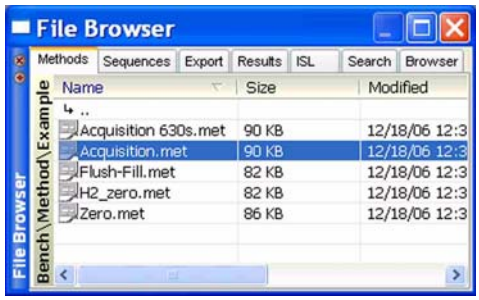


Figure 3-26. File Browser displaying predefined methods for GasBench II

❖ **To select an predefined method**

1. Click on File Browser's **Methods** tab.
2. Select the location where your own GasBench II methods are to be stored.

Note Do not mix them up with the predefined methods in the folder Examples! ▲

3. Double-click on your example method of choice, Acquisition.met, for example.

Instead of double-clicking on the example method of choice, drag and drop it to the Acquisition window right to the File Browser. The example method will be displayed. Proceed with topic "Structure of GasBench-Related Methods" on page 3-20.

Select between the example methods summarized in Table 3-1.

Table 3-1. Example methods for GasBench II

Method	Description
Acquisition 630s.met	considerably faster than Acquisition.met requires the column to be pre-heated to 70 °C
Acquisition.met	lasts longer than 1400 s used at ambient temperatures no longer recommended, as it is an older version (first basis method of GasBench)
Flush Fill.met	for flushing the samples prior to measuring them, that is during their preparation
H2_zero.met	for zero enrichment of hydrogen
Zero.met	to test the basic functions of the IRMS The reference gas is just switched on and off several times (10 or 100 pulses, for example) and one watches the obtained result. The more pulses you apply the more exact the result.

Structure of GasBench-Related Methods

The following method is a GasBench + Autosampler A200S method. It corresponds to the GasBench + Autosampler A200S configuration which results, if you have selected the GasBench + Autosampler A200S set in the Configurator before.

Other GasBench-related methods will be described in topic "Different GasBench II Methods" on page 3-40.

All GasBench methods are organized by the following pages: Instrument tab, Time Events tab, Evaluation tab, Peak Detection tab and Printout tab.

In Evaluation tab, Peak Detection tab, and Printout tab, the currently active gas configuration is indicated: for example Evaluation@CO2 alludes to CO2.

Instrument Tab

This section describes the parameters of the Instrument tab.

Experiment

In the Experiment section of the Instrument tab, the related configuration, gas configuration and acquisition script are displayed. A comment can be entered. See Figure 3-27 and Table 3-2.

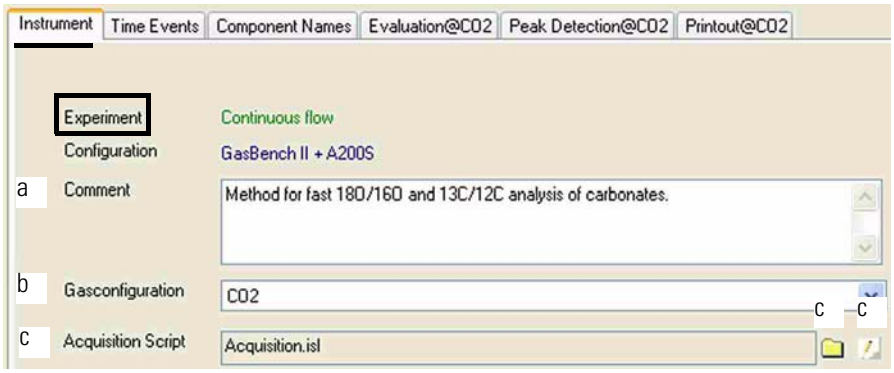


Figure 3-27. Instrument tab - Experiment

Table 3-2. Instrument tab - Experiment

No.	Parameter	Description
a	Comment	Per default, this field is empty. You can type in comments about method, acquisition script, time events, etc.
b	Gasconfiguration	Defines which Gas Configuration will be used for data acquisition, CO2, for example. Usually, the default entry can be accepted. Refer to the Status bar in topic "Components of Accessories Bar" on page 3-9.
c	Acquisition Script	Select an appropriate acquisition script by a click on the button. Acquisition.isl is the default entry and can usually be accepted. It controls the acquisition cycle. To edit the acquisition script, click on the button.

Note It should only be edited by users trained on script editing, debugging and error tracking. Otherwise, potential errors within scripts, which are due to editing, maybe difficult to be discovered afterwards. ▲

Isotope MS

In the Isotope MS section of the Instruments tab, the integration time of ion current data points is defined. See Figure 3-28 and Table 3-3. A peak center serves to focus all ion currents into the mass-specific Faraday cup center. Pre- and post-delays must be set to avoid failure of the peak center procedure (pre-delay) or unwanted peak center-related ion currents in the acquisition chromatogram (post-delay).

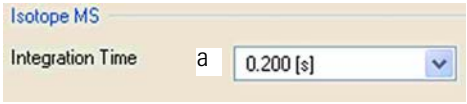


Figure 3-28. Instrument tab - Isotope MS

Table 3-3. Instrument tab - Isotope MS

No.	Parameter	Description
a	Integration Time [s]	time during which the current in the cups is integrated to form a data point triplet (0.2 s, for example).

Peak Center

In the Peak Center section of the Instrument tab, the parameters for the peak center are defined. See Figure 3-29 and Table 3-4.

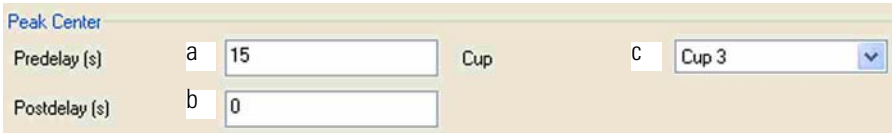


Figure 3-29. Instrument tab - Peak Center

Table 3-4. Instrument tab - Peak center

No.	Parameter	Description
a	Predelay [s]	After the valve is opened and the gas is let in (activation of reference gas), this waiting time elapses before the peak center procedure starts. Usually between 0 and 300 s
b	Postdelay [s]	waiting time after the end of the peak center until acquisition starts, 5 s, for example. Postdelay can thus be used to delay the measurement start, but is usually set to zero.
c	Cup	In the actual Gas Configuration, one cup must always be selected as the peak center cup. Normally, cup 3, the narrow center cup in a triple collector, is used. For all available cups and the peak center cup, see the Gas Configuration Editor (Figure 3-4).

Note The retention time should be set to the Reference Out value of the respective reference gas pulse in the time events list. This accommodates for the delay of 7-10 s associated with the gas passage through the capillary to the IRMS. ▲

Reference Device

Referencing with GasBench II can be performed with

- reference open split (reference ports 1 to 3) of the GasBench II
- ConFlo IV reference open split capability
- Dual Inlet bellow as reference injection (lecture bottles, bellow as reference storage). See Figure 3-30 and Table 3-5.

  At Dual Inlet peak center, the scripts for reference must be activated (automatic reference open split; reference gas automatic. Mark the Use Scripts checkbox in the lower part of Figure 3-30, with script for Reference On and script for Reference Off). For referencing, Switch On and Switch Off will appear in the time events list.

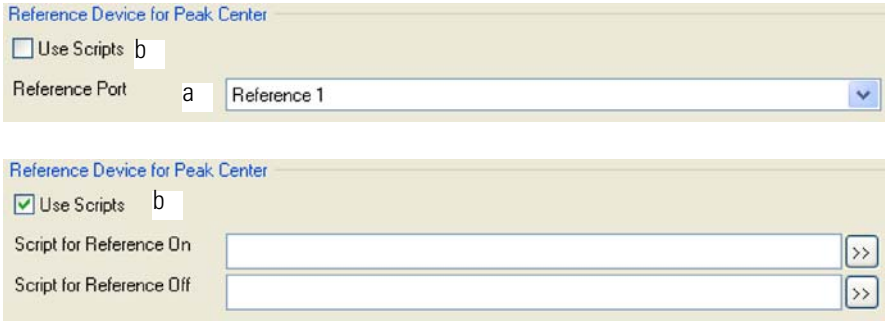


Figure 3-30. Instrument tab - Reference Device

Table 3-5. Instrument tab - Reference device

No.	Parameter	Description
a	Reference Port Reference 1 Reference 2 Reference 3	Select the Reference Port to connect the reference gas to, for example Reference 1. Choose between Reference 1, Reference 2 and Reference 3 as equivalent ports. See Figure 2-5 and Figure 2-27.
b	Use Scripts	Mark this checkbox to start an ISL script.

Always, only one reference gas is used, mostly CO_2. However, in case of hydrogen equilibration, H_2 is required as reference gas instead of CO_2. Some applications need N_2 as reference gas instead of CO_2.

Contrary to for example Elemental Analyzer applications, where two reference gases are necessary, no reference gas switches occur during GasBench II applications. Therefore, the Switch To column in the Time Events tab is empty.

GasBench

This section of the Instrument tab contains the GasBench II-related pre-settings of the Load mode (Transfer Time) and the Auto Dilution functionality. Advanced users can load extra scripts (for example to operate the GasBench II without time events). The extra scripts will be executed before data acquisition starts. See Figure 3-31 and Table 3-6.

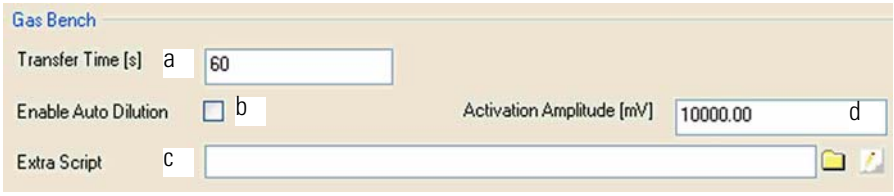


Figure 3-31. Instrument tab - GasBench

Table 3-6. Instrument tab - GasBench

No.	Parameter	Description
a	Transfer Time [s]	Time the autosampler needs to run from standby position to the vial and pierce (at least 15 s). GasBench II is in "Standby Mode" during this period.
b	Enable Auto Dilution	Enables the action of the open split
c	Extra Script	Refers to additional hardware of GasBench II, for example to traps which include the command scripts. Select an appropriate Extra Script by a click on the button. To edit the Extra Script, click on the button.
d	Activation Amplitude [mV]	Set the signal amplitude needed to activate auto dilution. Whenever a sample peak voltage exceeds this limit, the open split will be activated and dilution starts.

Note If additional time is needed between piercing the vial and starting the measurement, Transfer Time should be increased. ▲

Time Events Tab

After starting the chromatogram, the Time events list (Figure 3-32 and Figure 3-33) controls all operations during data acquisition. See Table 3-7 as well.

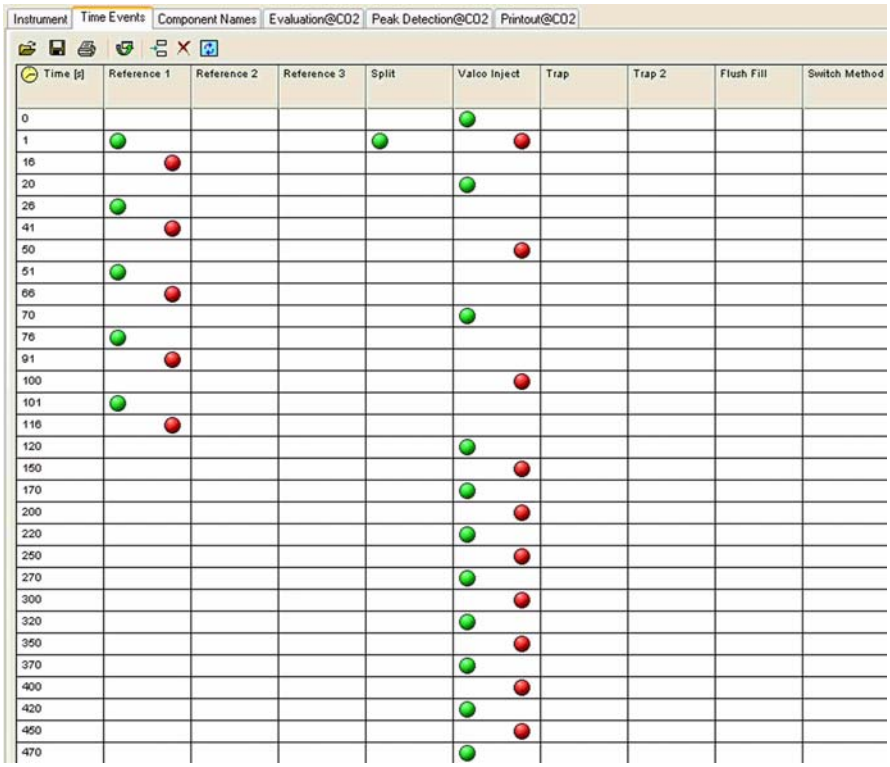
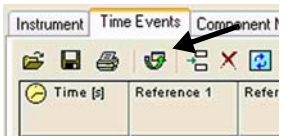


Figure 3-32. Time Events tab - Time events list

While editing the time events, keep in mind that it takes some time to flush the capillary from the sampling needle to the Valco valve (approximately 70 s). In the above sample, this time has elapsed during the subsequent acid dosing.

Under standard flow conditions, the time required to inject the whole gas sample into the GC should not be less than 15 s (loop: 100 µL; flow > 1 mL/min plus security). Allow at least 25 s for loading a 100 µL loop using a flow of 0.5 mL/min.

As no switch of gases occurs, the Switch Method column is currently not used in GasBench operation, that is it stays empty.



The display of the time events list can be enlarged pressing the **Big Edit View** button .

Lines can be inserted by using the right mouse button or by clicking on .

The time [s] at which a particular event will happen can be edited.

By a double-click on the field of a valve or by using the space bar you can set/toggle its status to active or inactive .

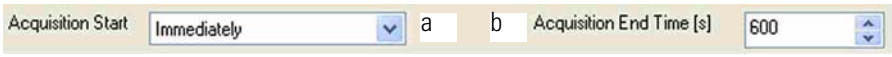


Figure 3-33. Time Events tab - Acquisition Start and Acquisition End Time

Table 3-7. Time Events tab - Acquisition Start and Acquisition End Time

No.	Parameter	Description
a	Acquisition Start 	defines the signal source to trigger the start of data acquisition. Choose between Immediately, by GC or by Enter Key. In the vast majority of cases, Immediately is used. By GC refers to a trigger signal from GC, whereas the user gives the trigger signal via keyboard at by Enter Key.
b	Acquisition End Time [s]	end time of data acquisition After Acquisition End Time, no further actions will be executed from the time events list. Allow some time to finish the last event before ending the acquisition.

Timing Considerations

When setting up the time events list keep in mind the different transition times through the various components of GasBench II.

When moving a reference capillary into the reference open split, the gas travelling towards the IRMS almost instantaneously changes its composition. However, it takes about 5 s for the mixture to arrive in the ion source. This is the time the gas needs to travel the capillary length.

When injecting a sample to the GC via the Valco valve, several factors influence the travel time of the gas to the IRMS:

- First of all, the flow velocity of the gas through the length of the GC capillary determines the required time. The flow velocity in turn is determined by the helium pressure at the central helium control of GasBench II.

- Additionally, the material of the actively separating part of the GC column causes different gases to travel at different velocities (retention).
- Finally, column oven temperature biases this time difference.

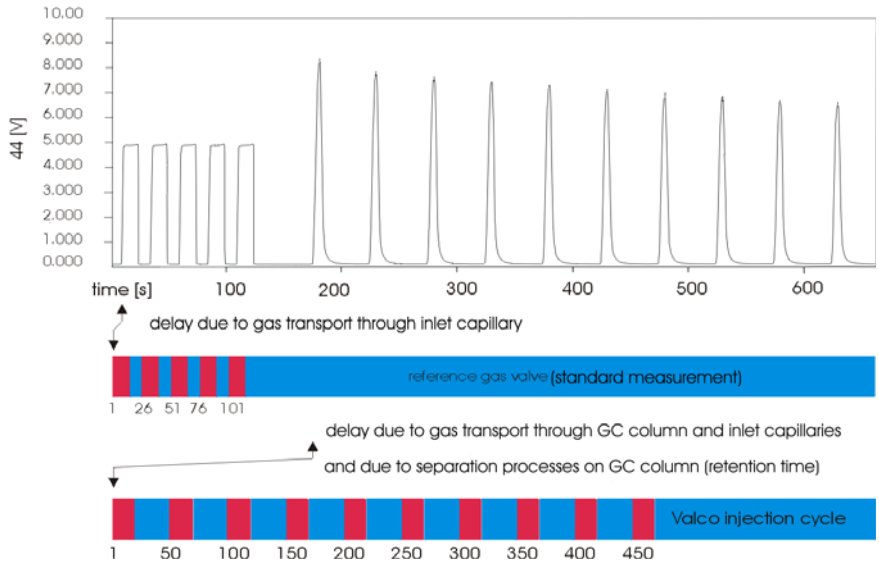


Figure 3-34. Timing considerations

Component Names tab

Hitherto, Component Names tab, Figure 3-35, is of no importance for GasBench applications, because only one sample gas is investigated.

Component Names tab is mostly important for GC measurements as many different substances having retention times of their own can be eluted from the GC column. If the system is sufficiently stable, each retention time can be assigned to its corresponding component, that is substance. Isodat is supposed to find and designate each substance in the chromatogram.

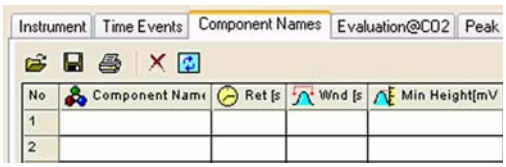


Figure 3-35. Component Names tab

Evaluation Tab

In Evaluation tab, parameters used after acquisition for data evaluation purposes are specified. Particularly, all or some of the isotope ratios defined in the Ratio Editor of Isodat can be calculated.

Evaluation Type

Here, the references and their true values are subsumed. Refer to the Standard Editor of Isodat. See Figure 3-36, Figure 3-37 and Table 3-8.

Note Never mix up the values of various references! ▲

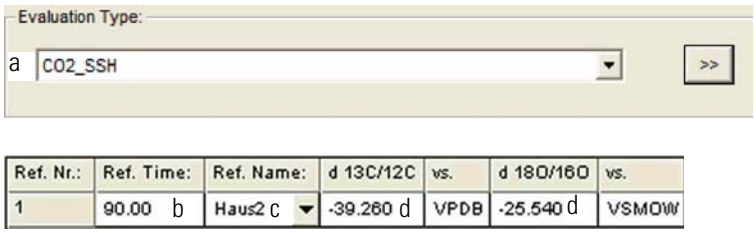


Figure 3-36. Evaluation tab - Evaluation type

Table 3-8. Evaluation Tab - Evaluation type

No.	Parameter	Description
a	Evaluation Type None CO2_SSH CO2_CRAIG	Select an appropriate ion correction for CO_2 data evaluation from the list: "None", "CO2_SSH" (default) or "CO2_Craig". Press the >> button to add own scripts for ion corrections.
b	Ref. Time [s]	Enter the retention time, 90.00 for example, of the standard peak(s) defined in the time events list, which are used for calculating the corresponding δ value(s). See Figure 3-32. If the assigned time for standard peak detection falls in between the Peak Start and Peak Stop marks of a peak, this peak will be used for δ value calculation.
c	Ref. Name Haus2 IAEA CO2 CO2 Lab.Tank CO2_zero Air	1. Select a Ref. Name from your standard database set in the Standard Editor, "Haus2", for example (Figure 3-37) or 2. Edit the related δ values (Figure 3-37). In this case, "User Defined" will be shown at Ref. Name. 3. New standards can be created in the Standard Editor.
d	$\delta^{13}C/^{12}C$ $\delta^{18}O/^{16}O$	Manually add δ values for the reference peak.

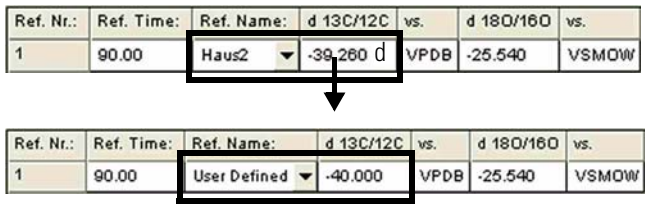


Figure 3-37. Evaluation Tab - Editing δ values

Note The retention time should be based on the Reference Out time of the respective reference gas pulse (in the time events list). This accommodates for the delay of 7-10 s associated with the gas passage through the capillary to the IRMS. ▲

Note For correct reporting of sample δ values, the data entered in the $\delta^{13}C/^{12}C$ field or in the $\delta^{18}O/^{16}O$ field must resemble the true isotopic values of your reference gas. ▲

Peak Detection Tab

The Peak Detection tab allows configuration and parameter settings for numerical evaluation of the sample and reference peak ion currents and calculation of areas to obtain isotope ratios.

Detection Types

The Detection Types checkboxes define the use of peak detection, background detection and major mass ion current for isotope ratio determination. See Figure 3-38 and Table 3-9.

Note We recommend keeping the default values! ▲

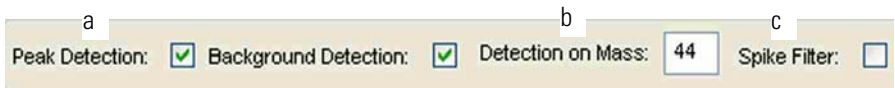


Figure 3-38. Peak Detection Tab - Peak detection and Background detection

Table 3-9. Peak Detection tab - Detection types

No.	Parameter	Description
a	Peak Detection vs Background Detection	Mark the respective checkboxes, if you want to perform a peak detection or background detection, respectively.
b	Detection on Mass	Type in the corresponding detection mass, for example m/z 44 in case of CO_2.
c	Spike Filter	Mark this checkbox to apply a moving average filter to the collected data in order to exclude electrical noise present in your environment.

Detection Parameters

Based on the mass trace derived from the ion beam which was chosen as the detection trace, the peak detection is performed. Ideally, the major ion beam is chosen as the detection trace due to its best signal-to-noise ratio.

The recognition of the beginning and ending times of peaks is the first step in data processing. The instantaneous rate of change of the signal is determined using a five point smoothing for each data point. Beginning and end of each peak are then determined based on user-selected slope thresholds. The peak top is characterized by the slope changing sign. All peak detection criteria of the method must be fulfilled to validate a peak.

Peak detection parameters are virtual parameters used in peak detection. Default values for Start Slope, End Slope, Peak Min Height and Background Type are shown in Figure 3-39 and Table 3-10 can usually be accepted.

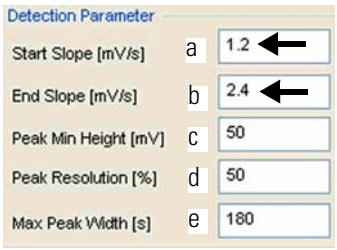


Figure 3-39. Peak Detection tab - Detection parameters

Table 3-10. Peak Detection tab - Detection parameters

No.	Parameter	Description
a	Start Slope [mV/s]	Controls the portion of the peak that is included in the integration. Lower values will result in capturing more of the peak slopes.
b	End Slope [mV/s]	Controls the portion of the peak that is included in the integration. Lower values will result in capturing more of the peak slopes.
c	Peak Min Height [mV]	Limits the number of reported peaks as it allows to exclude small ones from evaluation.
d	Peak Resolution [%]*	Overlapping peaks may not occur in GasBench II applications as they would indicate a gross error leading to worthless measurements: The signal of residual air together with CO_2 acts as an interference. The column has to separate these two components, because residual air produces NO_2 and N_2O in the ion source, which can hardly be pumped off. Additionally, a peak on m/z 46 occurs, which could coincide with a CO_2 peak and thus would lead to considerable shifts of the δ value. Furthermore, during the ten repetitions one runs the risk of coincidence with the CO_2 peak, if the timing is wrong. This results in a massive shift of the δ value as well. Therefore, clearly separated peaks are a crucial measure of precaution to be taken!
e	Max Peak Width [s]	Broader signals will not be recognized as peaks.

*After start and top of a peak have been found, its end must be looked for. The peak end will be determined from peak slope. As soon as the slope of the flattening peak falls below the value defined for the peak end, the peak end is found. Peak resolution is the percentage value to which the signal must decrease (in relation to the peak maximum) before the search of the peak end begins. x % peak resolution correspond to (100-x) % of the peak maximum.

Note Higher start slopes (that is 1.2 mV/s instead of 0.2 mV/s for other applications) and end slopes (that is 2.4 mV/s instead of 0.4 mV/s for other applications) have experimentally proven to yield a slightly smaller standard deviation in the final result over the ten repetitions performed in every chromatogram. This is valid for systems running stable for a longer time. See arrows in Figure 3-39. ▲

Background Parameters

For the determination of backgrounds for transient ion current signals, different background detection algorithms and detection procedures can be applied. See Figure 3-40 and Table 3-11.

Sample-related ion currents - integrated in order to determine isotope ratios - are determined by subtracting the background from the gross signal at each point. The automatic procedures assume that background levels are constant across the width of each peak.

Note Background correction within continuous flow isotope ratio determinations may strongly influence the final isotope ratios. The background algorithms described in this section should be used carefully. In difficult background situations, other than the individual background can be useful, but need to be cross-checked on their effects. ▲

Note The smaller sample peaks are in relation to the background, the higher the influence of background determination and correction upon the result. ▲

Note In case of hydrogen isotope ratio determination, the same background algorithm as for H_3^+ determination should be used in order to reduce possible errors. ▲

Note All isotope ratios of results (including H_3 factor determination) must use the same background detection type and parameterization. ▲

Note Some of the background algorithms (as dynamic background, base fit background, time-based background) cannot be run during a measurement. Instead, these will be calculated by a re-evaluation after the measurement is finished. ▲

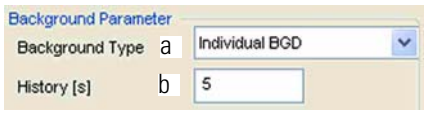


Figure 3-40. Peak Detection tab - Background parameters

Table 3-11. Peak Detection tab - Background parameters

No.	Parameter	Description
a	Background Type Individual BGD Single BGD Calc Mean BGD Median Mean BGD Low Pass Filtered BGD Dynamic BGD BaseFit BGD Skimmed BGD TimeBased BGD	It has been proven experimentally that the background type is important for GasBench II measurements. HD equilibration and CO_2 equilibration require different background types: Mostly, especially for all CO_2 applications, "Individual Background" yields the best results, whereas H_2 evaluates best with "Low Pass Filtered Background".
b	History [s]	defines a window prior to the peak start point where the algorithm searches for the minimum amplitude

Individual Background

The individual background is defined as the lowest running five point average among the data points preceding a peak start. The history size of the data buffer for the individual background determination is based on seconds and can be edited in the method. For each individual peak the background values are determined, and δ values are calculated using the individual background values.

Single Background

The single background is a special version of the individual background. The individual background value for the first peak during data acquisition is determined and applied to all subsequent peaks.

Time-Based Background

The time-based background is the same as single background except for the time interval where the background is measured. Instead of using the individual background of the first peak, the time interval for background definition can be freely selected.

Dynamic Background (for GC applications)

The dynamic background algorithm adapts a background function over the entire GC run. The user-defined step width allows background data points to be taken. Outliers are determined, and a smoothened background curve with point-to-point slopes is applied to the detected GC peaks.

Base Fit Background

The base fit background is an algorithm version of the dynamic background.

Low Pass Filtered Background

In this background algorithm, each background point is smoothened by its preceding point. The strength of influence is user-definable by the τ-factor. This background has advantages for small peaks on a noisy background (for GC applications or special GasBench II applications as O_2, Ar, etc.).

Mean Background

This background algorithm uses the same strategy as the individual background. By contrast however, it defines the mean of data points for smoothening. It is useful in case of very smooth backgrounds.

Median Mean Background

This background algorithm uses the same strategy as the individual background. The smoothening however, is quite different and is based on mean and median of the data points. An algorithm using comparisons of means and medians is applied in order to find the optimal background.

Timeshift

For each peak, the ion current traces are integrated separately from start to stop before an isotope ratio is formed.

Since isotopically substituted species in general are separated chromatographically, for example different isotopic species of CO_2 derived from the effluent peak have different times of appearance. These shifts in chromatographic retention times ("time shifts") are detected and taken into account by fitting a parabolic function to each of the detected peaks and shifting the integration intervals to align with each other.

Example: the m/z 45 and m/z 46 peaks are shifted accordingly to align with the m/z 44 peak.

Note Reference gas pulses are not subject to time shift correction. ▲

As chromatographic peaks emanate from a GC column, an isotope effect is noticed during their detection: a slight delay of heavy isotopes' signal positions occurs compared to those of lighter ones. When integrating chromatographic peaks, this needs to be compensated by a timeshift (detection trace is fixed; the other traces are time-adjusted to the detection trace).

Reference pulses however, lead to square peaks. Here, no timeshift is necessary, because they simply are fed into the open split and do not emanate from a GC column. On square peaks, one does not want to perform a timeshift, whereas on chromatographic peaks, one wants to do.

The shape of a chromatographic peak or a square peak can be characterized by its height/width ratio. The factor f is dimensionless and defined as:

$$f = \frac{A_{raw}}{h \times w}$$

with:

A_{raw} raw area of the chromatographic or square peak (in Vs)

h peak height (in V)

w peak width (in s)

As square peaks and (gaussian) chromatographic peaks are considerably different with respect to f, this factor can be used for peak discrimination. It ranges between 0 and 1. A high f value alludes to square peaks, a low one to chromatographic peaks. Its default value 0.55 should be satisfactory for most chromatogram types.

In any chromatographic system however, chromatographic peaks may sometimes occur that are of quite similar shape as are square peaks. Thus, although a peak is no square peak, it might wrongly be identified as such. In this case, it is recommended to change the default value of f.

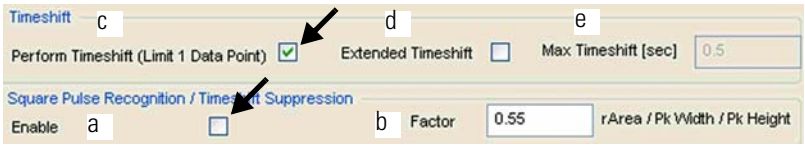


Figure 3-41. Peak Detection Tab - Auto square pulse recognition / timeshift suppression

Table 3-12. Peak Detection tab - Time shift

No.	Parameter	Description
a	Enable	Mark the Enable checkbox to automatically detect square peaks and suppress the timeshift correction of square peaks. If you unmark Enable and simultaneously mark Perform Timeshift, timeshift correction will be enabled for all peaks. See arrows in Figure 3-41. As default, Enable is unmarked, because old chromatograms might have been calculated without automatic square peak detection. In case of recalculating them, Enable can be marked to include now automatic detection.
b	Factor f	Its default value 0.55 should be satisfactory for most chromatogram types. In any chromatographic system however, chromatographic peaks may sometimes occur that are of quite similar shape as are square peaks. Thus, although a peak is no square peak, it might wrongly be identified as such. In this case, it is recommended to change the default value.

Table 3-12. Peak Detection tab - Time shift, continued

No.	Parameter	Description
c	Perform Timeshift	If Perform Timeshift is unmarked, no timeshift correction will be performed on any peak. Decide, whether you additionally want automatic square peak detection/suppression of timeshift correction to be performed or not. As an example, you can perform a timeshift and additionally let the square peaks be automatically detected. If you do not want to detect them automatically, you can define ranges instead where a timeshift will be performed or not (for example in case of many different peak shapes, one single factor f might not be sufficient). Marking Enable is only useful, if you simultaneously also mark Perform Timeshift.
d	Extended Timeshift	The normal timeshift corrects the different peak top positions on the individual traces to maximally one data point. Extended Timeshift removes this restriction.
e	Max. Timeshift [s]	If Max. Timeshift > 0, it limits the correction to a maximum time interval t_1-t_2.

Note In no case apply the timeshift correction on a reference pulse (square peak)! ▲

Post Evaluation Filter Parameters

The post evaluation filter paramter serves to remove small peaks from the background detection of subsequent big peaks. Formerly, smaller peaks were detected via detection parameter settings (Peak Min Height and Peak Width, for example).

Post evaluation filter parameters take into account those smaller peaks for background detection of subsequent bigger peaks. See Figure 3-42 and Table 3-13.

Figure 3-42. Post evaluation filter parameters

Table 3-13. Peak Detection tab - Post evaluation filter parameters

No.	Parameter	Description
a	Peak Min Height Filter [mV]	The normal peak height criterion (detection parameter) allows excluding small peaks. Sometimes however, these small peaks are immediately followed by a big peak. If you discard such a small peak, the following big peak may place its background over the small peak. In case the small and the big peak pass into each other, the second peak (that is, the big one) gets the background value of the small peak. In case the small peak is missing, the area before the big peak is taken as the background. Therefore, a small value for the minimum peak height is usually chosen. After data evaluation, one then discards the small peaks.
b	Max Peak Width Filter [s]	For the peak width, the same principle as outlined for the peak height in a is valid.

Printout tab

In Printout tab, the use of printout templates is controlled. See Figure 3-43 and Table 3-14.

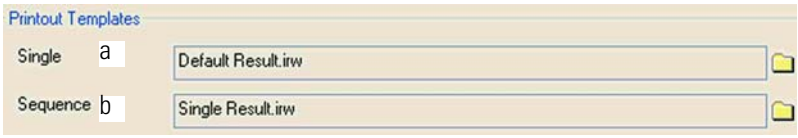


Figure 3-43. Printout Tab

Table 3-14. Printout Tab

No.	Parameter	Description
a	Single	Selects a print template from the Result Workshop for an individual printout per sample.
b	Sequence	Selects a print template from the Result Workshop for a reduced printout per sample within a sequence summary.

Saving a Method

After you met all your decisions throughout the tabs of the method, you must save it.

Note You must create and save a new method and a new sequence on your own! The predefined methods and sequences delivered by Thermo Fisher Scientific in the Examples folders are only example files. They only show guidance through helpful default values, but must never be used for measurements! ▲

Note Never overwrite an example file with a method or sequence created on your own! Depending on your software version these examples may not work properly. ▲

❖ To save a method

Do one of the following:

Click on the **Save** button to save a method previously created on your own.

Click on the arrow and choose **Save as...** to optionally choose a new name and folder for the currently active method (single document). See Figure 3-44.

Give the method a significant name, for example similar to the sequence it corresponds to. Keep the extension .met.

Confirm by **Save**.

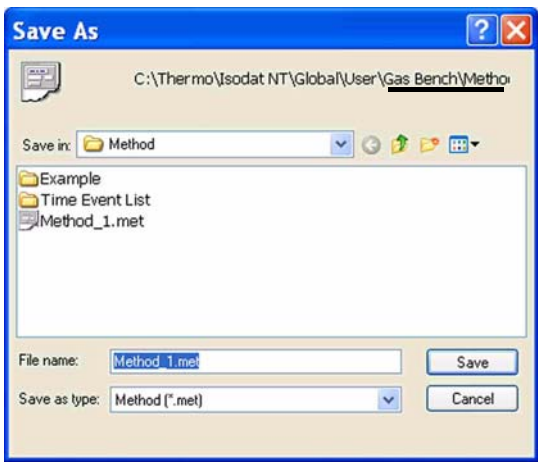


Figure 3-44. Saving a method

Note The particular folder containing the currently active method is shown. See Figure 3-44.
Choose the folder above the Example folder, not the Example folder itself! This ensures not to mix or even overwrite the predefined example method with your own method. ▲

Click on the ▾ arrow and choose **Save All** to save all currently active Isodat documents (methods, sequences, result files, Result Workshop files, for example). They will be stored without changing names and folders.

Different GasBench II Methods

Depending on the particular GasBench set chosen in the Configurator, different configurations will result as depicted in topic "Creating a GasBench Configuration" on page 3-5.

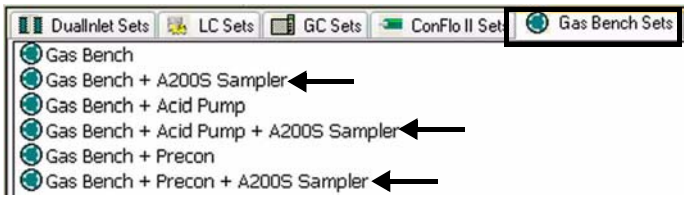


Figure 3-45. GasBench sets chosen in Configurator

- GasBench II can be used alone. In this case, choose GasBench.
- In most cases however, GasBench II is used together with an autosampler, for example the A200S.

Note GC PAL and Combi PAL must be treated as A200S. ▲

Therefore, mostly choose between the following GasBench sets shown by the arrows in Figure 3-45:

- GasBench + A200S Sampler
- GasBench + Acid Pump + A200S Sampler
- GasBench + Precon + A200S Sampler

Different configurations will in turn lead to different corresponding methods. The particularities in the tabs of the various possible methods will be described one by one now. For general information about the structure of GasBench methods, refer to topic "Creating a New Method" on page 3-18.

GasBench Method

If you use GasBench II alone and therefore choose GasBench as set in Figure 3-45, the corresponding method GasBench will result. It shows no particularity. Refer to topic "Creating a New Method" on page 3-18.

GasBench + A200S Sampler Method

If you use GasBench II together with an A200S autosampler and therefore choose GasBench + A200S Sampler as set in Figure 3-45, the corresponding method GasBench + A200S will result. Refer to topic "Creating a New Method" on page 3-18.

GasBench + Acid Pump + A200S Sampler Method

If you use GasBench II in combination with an acid pump and an A200S autosampler and therefore choose GasBench + Acid Pump + A200S Sampler as set in Figure 3-45, the corresponding method GasBench + Acid Pump + A200S will result.

Acid Pump

As a particularity on the Instrument tab, the following parameters for acid pump control can be adjusted. See Figure 3-46 and Table 3-15.

Figure 3-46. Instrument tab - Acid pump

Table 3-15. Instrument tab - Acid pump

No.	Parameter	Description
a	Drop Count Forward	number of drops pumped while the pump is in forward position (that is, releasing acid from the acid needle)
b	Drop Count Backwards	number of drops pumped while the pump is in backwards position (that is, retracting acid)
c	Delay [s]	waiting time between two strokes

To ensure that no drop remains sticking, acid is first pumped in, before the acid pump is switched over in order to draw it back again. Owing to the negative pressure, a drop sticking at the tip should thus be drawn backwards into the bulk volume.

Note A standard GasBench II can be used with acid pump even though an acid pump is not installed! To do so, set Drop Count Forward and Drop Count Backwards both to zero. ▲

GasBench + PreCon + A200S Sampler Method

If you use GasBench II in combination with a PreCon plus an A200S autosampler and therefore choose GasBench + Precon + A200S Sampler as set in Figure 3-45, the corresponding method GasBench + Precon + A200S autosampler will result.

Experiment

At Experiment, the parameters Configuration, Comment, Gas Configuration and Acquisition Script are summarized. At Configuration, the configuration selected previously appears (GasBench II+PreCon+A200S, for example).

Figure 3-47. Experiment part of Instrument tab

Note The acquisition script acquisition.isl is stored in a particular folder PreCon. See arrow in Figure 3-47. ▲

PreCon

PreCon is a medium flow (20 mL/min) preconcentration device for small concentrations of N_2O, CH_4, N_2 and CO_2. It can be operated together with GasBench II or Trace GC IRMS.

The script that controls PreCon is integrated here. Specify its name and location. See Figure 3-48.

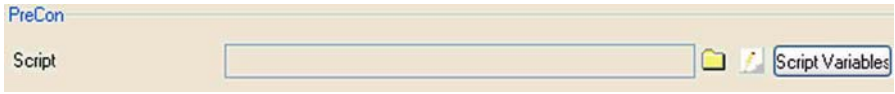


Figure 3-48. Instrument tab - PreCon

As Figure 3-49 shows, the folder \Thermo \Isodat NT\ Global\ ISL\PreCon contains the following selection:

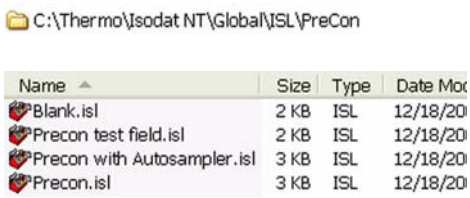


Figure 3-49. Files in folder PreCon

Table 3-16. ISL scripts in folder PreCon

ISL script	Function
Blank.isl	to perform blank measurements
Precon test field.isl	used in our test field
Precon with Autosampler.isl	to run PreCon in combination with the GC PAL belonging to GasBench II
Precon.isl	to run PreCon in combination with GasBench II

Time Events Tab

Additionally, the Time events tab contains entries for all the components in PreCon, for example Valco valve and additional traps.

Continuous Flow Sample Gas Measurements Using Dual Inlet for Referencing

For any continuous flow measurement, reference injection can be applied with a Dual Inlet. A Dual Inlet, P/N 1082862, must be installed with the Delta series or the MAT 253 isotope ratio mass spectrometer. Any Isodat version greater than Isodat 2.0 can be used to reference the isotope ratios of a sample with a Dual Inlet referene gas injection.

The reference gas flask ("lecture bottle") is attached to the reference gas bellow of the Dual Inlet. Reference gas bottles (usually 1 L at 10 bar pressure of CO_2) can be ordered at gas suppliers. The quality of the reference gas must be as required in the Preinstallation Requirements Guide of your IRMS.

Gas suppliers even guarantee a predefined isotope ratio of the purchased gas. In any case, we recommend referencing the samples against the internationally accepted scale of international standards reported by the IAEA. Refer to topic "Carbonates" on page 5-6.

Configuring an IRMS Peripheral (for Example GasBench II) in Isodat

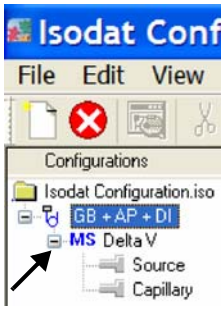
The Dual Inlet and the IRMS peripheral need to be configured in the Configurator of Isodat. The IRMS method must be set up to be able to use a Dual Inlet for peak centering and as a reference gas injector for online measurements (reference gas peaks in a sample gas run).

Connecting a Dual Inlet as Reference Device to a GasBench II

❖ **To connect a Dual Inlet to a GasBench II using the Configurator**

1. Open the Configurator.

2. Click on the **New** button to create a new configuration.



3. Give it a significant name, GB+AP+DI, for example.

   Click on the + sign of your IRMS to open the complete tree structure (see arrow).

4. Click on the GasBench Sets tab. Among the GasBench sets, choose for example GasBench + Acid Pump + A200S Sampler as the hardware set. Drag and drop it to the Capillary connection port of the IRMS. See Figure 3-50.

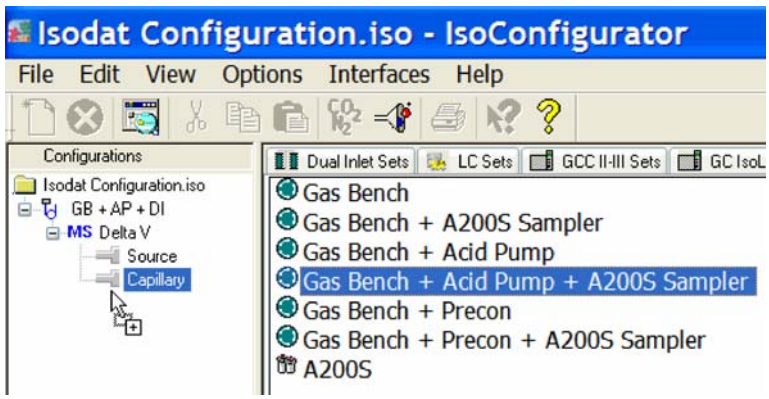


Figure 3-50. Dragging GasBench set to capillary port

5. Add the Dual Inlet by clicking on the Dual Inlet Sets tab and dragging and dropping the simple Dual Inlet hardware set to the Source connection port of the IRMS. See Figure 3-51.

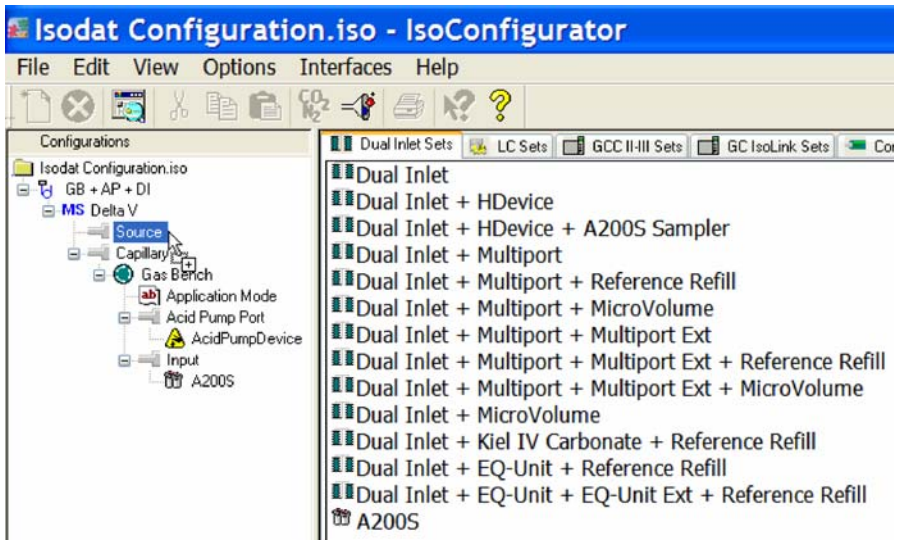


Figure 3-51. Dragging Dual Inlet set to source port

GasBench and Dual Inlet will appear at the Capillary and Source connection port, respectively. See Figure 3-52.

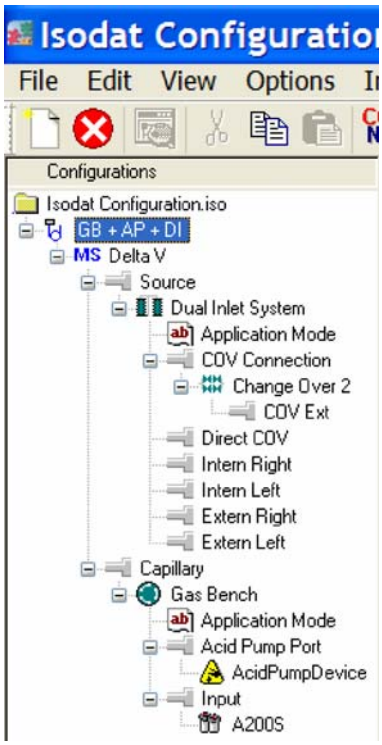


Figure 3-52. Configuration containing GasBench and Dual Inlet

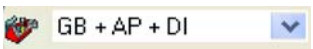
Note To add the Dual Inlet to this Continuous flow configuration ( ), switch to Advanced Mode. The Dual Inlet system will not work in Dual Inlet mode ( ). As soon as a continuous flow configuration is added however, the configuration will automatically switch to a Continuous Flow configuration ( ). ▲

Using Dual Inlet for Peak Centering in a GasBench II IRMS Method

Analysis with IRMS requires peak centering of the ion currents used for isotope ratio determination of sample and reference gas.

❖ **To incorporate Dual Inlet scripts into the IRMS method to be able to carry out a peak center**

1. Open the Acquisition.



2. Select the configuration which uses GasBench II and Dual Inlet for referencing.

At the Accessories bar, GasBench II, acid pump and Dual Inlet will be symbolized by individual panels. See Figure 3-53.

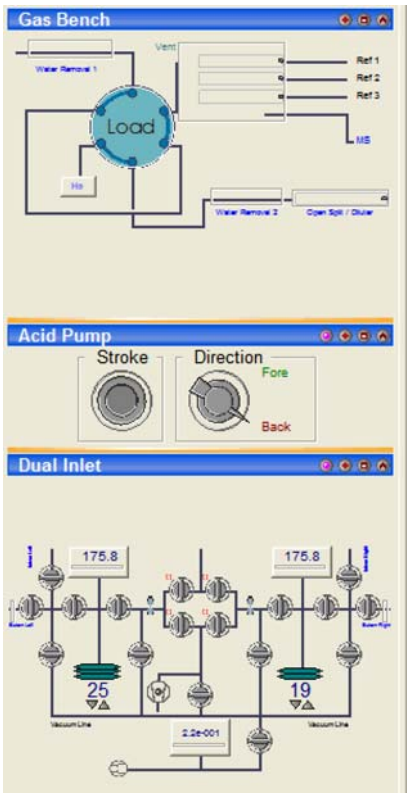
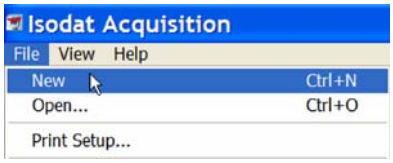


Figure 3-53. Hardware components as separate panels

3. Create a new IRMS method by clicking either on the **New** icon or by choosing File > **New**.



4. Double-click on the **Method** icon. See Figure 3-54.

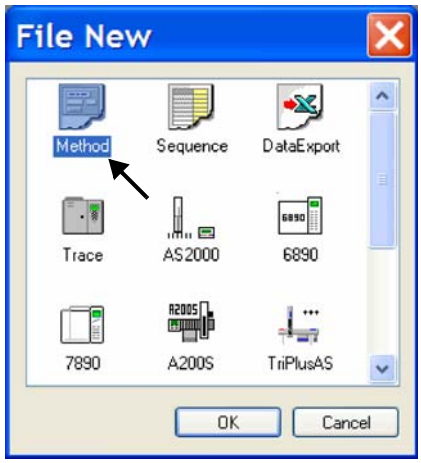


Figure 3-54. Creating a new method

The new method will show up with its Instrument tab.

The reference device controls the device configuration used for a peak center with Dual Inlet. Figure 3-55 shows the Reference Device section of the Instrument tab.

Figure 3-55. Reference Device section of Instrument tab

5. Mark the Use Scripts checkbox to automatically show the script for Reference On and Reference off. See Figure 3-56.

Figure 3-56. Script for Reference On and Reference off

6. At Script for Reference On, click on the >> button. Browse to the folder C:\Thermo\Isodat NT\Global\ISL\ChangeOver and choose the script file CovRt.isl to open the right reference gas bellow for introducing reference gas from the right bellow into the IRMS ion source.

7. At Script for Reference Off, click on the >> button. Browse to the folder C:\Thermo\Isodat NT\Global\ISL\ChangeOver and choose the script file Covcl.isl to close the changeover valve (COV). See Figure 3-57.

Figure 3-57. Choosing the script files

Note Before using the Dual Inlet as automated reference gas inlet system, the reference gas must be introduced manually into the reference gas bellow. The reference gas pressure of the bellow needs to be adjusted to the amplification mode of the Faraday cup collector. Consequently, the reference gas pressure is adjusted at maximum to the maximum signal read-out of the mass spectrometer (50 V). For the example of CO_2 reference gas, we recommend a signal read-out of 1 V to 5 V. Usually, this signal will be in the range of transient signals in Continuous Flow applications. For operation of the Dual Inlet refer to the Operating Manual of the IRMS (either MAT 253 or Delta series instrument). If the right bellow is used for referencing, the left-side Dual Inlet bellow shall be evacuated during sample measurement. ▲

Using Dual Inlet for Reference Gas Injection in the GasBench II Online Chromatogram

The injection of reference gas (reference gas pulses) into the IRMS ion source is controlled at the Time Events tab of the IRMS method. To see the COV Close, COV Left (for left referencing), Cov Right, scroll down at the right scroll bar and at the lower scroll bar to the right.

In Figure 3-58, an example is shown about how the reference gas pulses are positioned in the time events list, if sample measurements with ten sample peaks and three reference gas peaks shall appear.

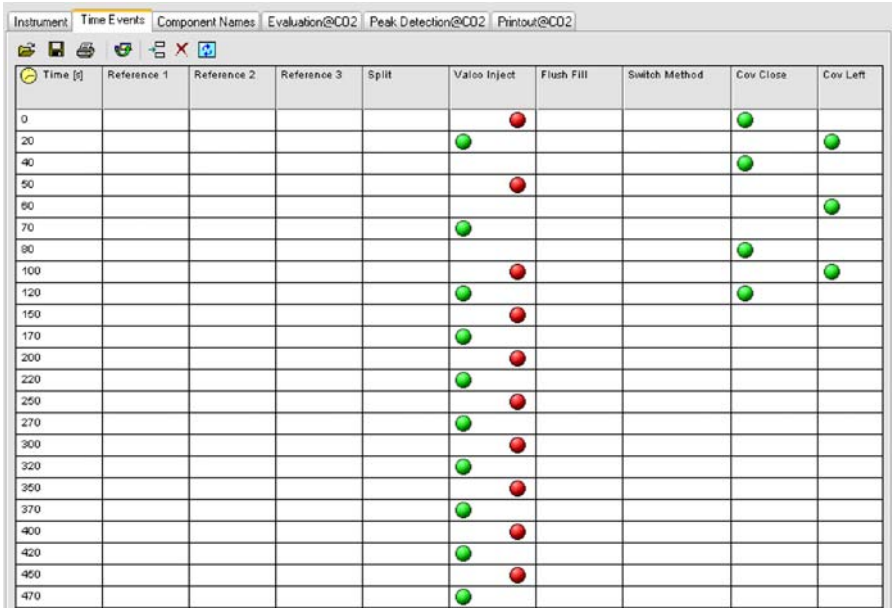


Figure 3-58. Example for reference gas pulses in time events list

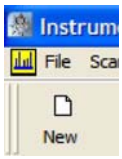
Creating a New Sequence

After creating and saving a method (refer to topic "Creating a New Method" on page 3-18), a sequence must now be created as follows.

Note As with methods, you must create and save a new sequence on your own! The predefined sequences delivered by Thermo Fisher Scientific in the Examples folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! ▲

Note Never overwrite an example file with a sequence created on your own! Depending on your software version these examples may not work properly. ▲

❖ **To create a new sequence**



1. Click on the **New** button to display the File New dialog box. See Figure 3-59.

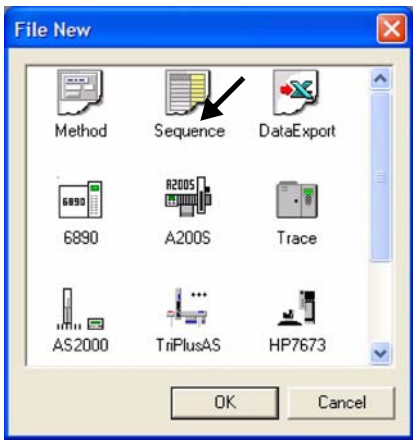


Figure 3-59. Creating a new sequence

2. Click on the **Sequence** icon to display the Sequence properties dialog box. See Figure 3-60.

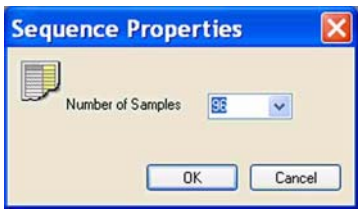


Figure 3-60. Specifying number of samples

3. Specify the number of samples, 96, for example and confirm by **OK**.

Note In case of carbonates, 80 samples can be measured, leading to 88 lines. The first row cannot be measured as it is not accessible by the acid needle without destroying the sample needle.
The last row cannot be measured as it is not accessible by the sample needle without destroying the acid needle. In case of equilibrations, all 96 lines can be filled. Refer to topic "Sample Trays Used with GasBench II" on page 2-9. ▲

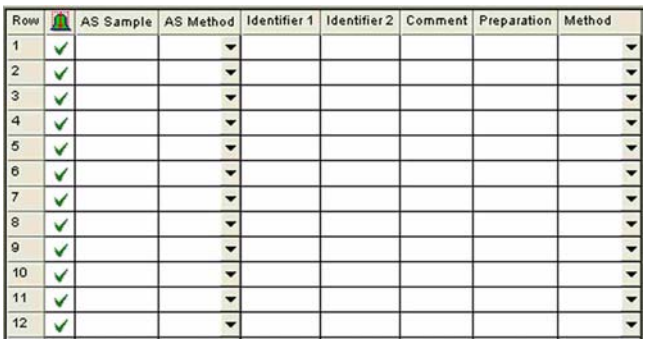


Figure 3-61. Sequence grid - first 12 lines

The appearing sequence grid, Figure 3-61, contains information about the individual samples bundled together in the sequence. See Table 3-17.

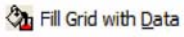
Note Individual columns (Row or AS Sample, for example) can be copied from example sequences. ▲

Table 3-17. Sequence grid

Parameter	Description
Row	Each row refers to an individual sample.
Peak Center 	Marking it ✓ allows performing a peak center procedure prior to measuring the particular sample. This ensures the peak to be in the middle of the cup. As this standard procedure is time-consuming, save a lot of time by omitting some peak centers. The device is sufficiently stable to operate during a certain time period without a peak center.
AS Sample	The number between 1 and 96 indicates the position of the sample to be measured in the tray. Refer to topic "Sample Trays Used with GasBench II" on page 2-9, Figure 2-21 and Figure 2-22.

Table 3-17. Sequence grid, continued

Parameter	Description
AS Method	Autosampler method, can be selected from the pulldown list. In most cases, only the internal methods (that is Internal No 1 to Internal No 9) are in use. Usually, even only two or three of them are applied. After setting up the autosampler with the corresponding backup file: Autosampler method Internal No 7 corresponds to Flush Fill.met. Autosampler method Internal No 9 corresponds to Acquisition 630s.met. Autosampler method Internal No 8 corresponds to Acquisition.met (old method, no longer recommended). Thus, in a sequence used for flushing, always select method Internal No 7 in each line. In a sequence used for all kinds of measurements, always select method Internal No 9 in each line (or method Internal No 8 in each line, but no longer recommended).
Identifier 1 Identifier 2	optional; mostly used to identify the particular sample.
Comment	optional; add an arbitrary comment concerning the particular sample.
Preparation	optional; add an arbitrary comment concerning sample preparation.
Method	important; the IRMS method edited in topic "Creating a New Method" on page 3-18 can be selected here from the pulldown list. By selecting it here, you determine the particular IRMS method to be used indeed during measurement. Without a selection from the pulldown list, no measurement will take place. Instead, the error message "No valid method found in sequence grid" will occur.



Note After you typed data in only one cell of the sequence grid, easily fill each of its columns: right-click the column and choose the **Fill Grid with Data** command. ▲

Saving a Sequence

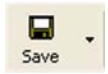
Note The predefined sequences in the Examples folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! ▲

Note Never overwrite a sequence example file with a sequence you created! Depending on your software version, these examples may not work properly. ▲

As done with a method (refer to topic "Saving a Method" on page 3-38), after defining the new sequence you must save it before it will start.

❖ **To save a sequence**

Do one of the following:



Click on the **Save** button to save a sequence previously created on your own.

Click on the arrow and choose **Save as...** to optionally choose a new name and folder for the currently active sequence (single document).

Give the sequence a significant name, for example similar to the method it corresponds to. Keep the extension .met. See Figure 3-62. Confirm by **Save**.

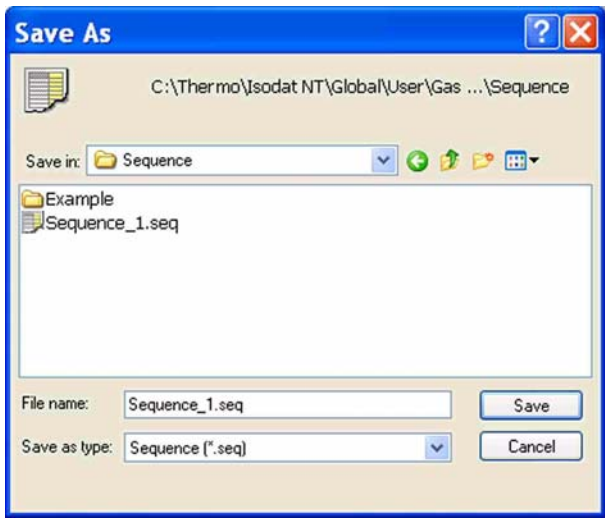


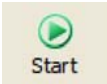
Figure 3-62. Selecting folder for sequence

Note Notice that the particular folder is shown that contains the currently active sequence. See Figure 3-62. Choose the folder above the Example folder, not the Example folder itself! This ensures not to mix or even overwrite the predefined example sequence with your own sequence. ▲

Click on the arrow and choose **Save All** to save all currently active Isodat documents (methods, sequences, result files, Result Workshop files, for example). They will be stored without changing names and folders.

Starting a Sequence

❖ To start a sequence



1. Press the **Start** button.
2. Define parameters for Results Export, Printout and Sequence Scripts as follows. See Figure 3-63.

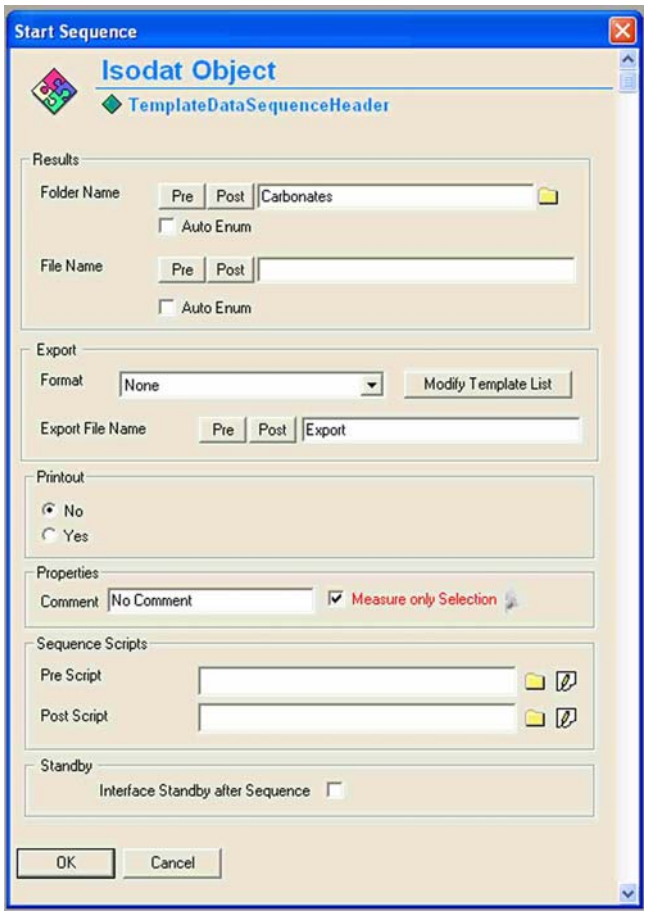


Figure 3-63. Defining parameters for handling results

Results

At Results, the storage path of result files and its naming conventions are defined. See Figure 3-64 and Table 3-18.

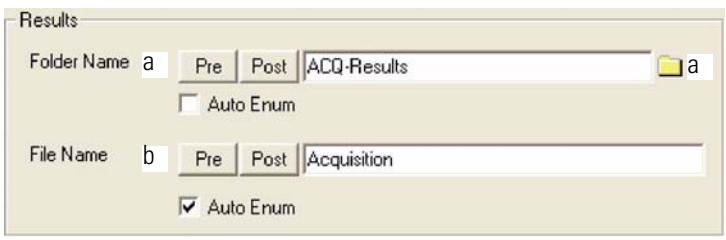


Figure 3-64. Defining path for results storage

Table 3-18. Defining path for results storage

No.	Parameter	Description
a	Folder Name	Define a folder for results storage. To choose another folder than the proposed one, browse via .
b	File Name	Within the defined folder, define a file for results storage.

Use the **Pre** and **Post** buttons to automatically create meaningful folder names and file names (for example ACQ-Results as file folder and Date as a postfix will result in a folder ACQ-Results_080725, if the acquisition was started the 25th of july 2008).

Folder and path for storage of single result data will be set at the Results tab of the File Browser. If no entry is made at Folder Name (pos. a in Figure 3-64), the result data will be stored directly at the Results tab without creating a particular folder.

Note For Pre file names, we recommend choosing analysis number. This allows ordering the files in the results folder according to its once defined acquisition. ▲

Export

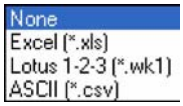
At Export, an Excel export file can be created according to the user-defined Excel export templates. It is saved under the name before (Pre) and after (Post). The name is typed into the blank line (here as Export). See Figure 3-65 and Table 3-19.

Starting the sequence acquisition will immediately create an Excel export file and save it into the cache memory.

Figure 3-65. Defining parameters for results export

Note The data is exported into an Excel file into the cache memory, if an online-evaluation was enabled in the sequence grid. Before this Excel file is saved into the cache memory, it is evaluated by Isodat. Do not open this file with a file browser or with the File Browser of Isodat without saving it under a different file name. Re-open this cache memory file, when you are sure that the result file will not be saved into the cache memory right after you opened it! If done so, subsequent data is not lost, but the acquisition chromatogram will not be visible. ▲

Table 3-19. Defining parameters for results export

No.	Parameter	Description
a	Format	Define the format of result data to be exported via the .wke template. Choose between “None”, “Excel”, “Lotus” and “ASCII”. 
b	Export File Name	Name the export file.

Note Text strings exceeding 256 characters in one row will be truncated when exporting result data in Excel® format (.xls). However, in case of export in Lotus format (.wk1) or ASCII format (.csv), no truncation of information will happen. ▲

Printout

Printouts can be created right after a single data acquisition (c in Figure 3-66) or after finishing the entire sequence(b in Figure 3-66). See Table 3-20as well.

Figure 3-66. Defining parameters for results printout

Table 3-20. Defining parameters for results printout

No.	Parameter	Description
a	Yes/No	Decide, whether you want a printout (Yes) or not (No).
b, c		If you want a printout, choose between: one printout per sequence (b) or one printout per sample (c)

Properties

Comments concerning all result files of a sequence can be entered here. They will be saved together with the sequence and are available after loading it later on. Only special vials can be measured as a selection in the sequence list. See Figure 3-67 and Table 3-21.

Figure 3-67. Properties box - comment

Table 3-21. Properties box - comment

No.	Parameter	Description
a	Comment	Type an arbitrary comment applied to all result files in this sequence.
b	Measure only Selection	Mark, if only specific vials are to be measured (1-7, for example). The checkbox is active, if a selection in the sequence list has been made. Only samples in connected lines (that is without an interception between them) can be measured by "Measure only Selection". Scattered runs however, are not possible.

Sequence Scripts

Advanced users can program predefined or postdefined sequences before an individual sequence is started. For example, valve operation could be started before a sample measurement sequence would start. See Figure 3-68 and Table 3-22.

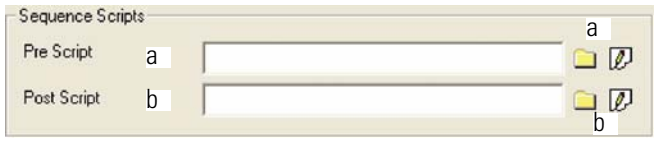


Figure 3-68. Selecting ISL scripts to be executed

Table 3-22. Selecting ISL scripts to be executed

No.	Parameter	Description
a	Pre Script	Select an ISL script (*.isl) to be executed before the sequence.
b	Post Script	Select an ISL script (*.isl) to be executed after the sequence.

Standby

Standby of the device after the sequence has been executed can be chosen here. See Figure 3-69 and Table 3-23.

Figure 3-69. Standby

Table 3-23. Standby

No.	Parameter	Description
a	Interface Standby after Sequence	Advanced users may add additional interfaces which can be put on idle by ISL script language.

Finally, confirm by **OK**. The measurement will be started. If an error message indicates low memory, close other applications. Refer to Chapter 5: "Measurement Procedures for Real Samples".

Note In GasBench II Standard mode, neither standby nor pre- or postscript sequence scripts exist. Only advanced users should use this tool and in this case should perform an Isodat backup prior to any changes! ▲

Predefined Sequences as Examples

For the sake of simplicity, predefined sequences can be selected via the File Browser. Use them only as examples! It would even be sufficient to deliver only one or at most two such predefined sequences to cover all kinds of measurements.

❖ **To display a predefined sequence**

1. Click on the **Sequences** tab of the File Browser. See Figure 3-70.

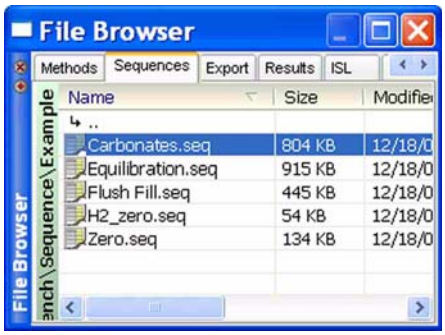


Figure 3-70. Predefined sequences as examples

2. Double-click on your example sequence of choice, Carbonates.seq, for example.

Note Do not mix up your own sequences with the predefined sequences in the folder Examples! Therefore, choose a separate folder for your own GasBench II sequences. ▲

Instead of double-clicking on the example sequence of choice, drag and drop it to the Isodat Acquisition window right to the File Browser. The sequence grid will be displayed. Select between the example sequences shown in Table 3-24.

Table 3-24. Example sequences

Sequence	Usage
Carbonates.seq	for all carbonate measurements
Equilibration.seq	for all equilibration measurements
Flush Fill.seq	for flushing the samples prior to measuring them, that is during their preparation
H2_zero.seq	as Zero.seq, but uses H2 as gas configuration.
Zero.seq	to test the basic functions of the IRMS. The reference gas is just switched on and off several times (10 or 100 pulses, for example), and one watches the obtained result. The more pulses you apply the more exact is the result.

The sequence for carbonate measurements (Carbonates.seq) differs just slightly from the one for equilibration measurements (Equilibration.seq): in the latter, only the number of acid drops has been reset to zero.

The sequence for HD equilibration, Equilibration.seq, is also used for CO_2 equilibration: only the reference gas inlet must be changed and the reference gas be switched in the time events list.

Method-Sequence Correspondence

Each predefined method corresponds to a predefined sequence and vice versa. See Table 3-25.

Table 3-25. Method-sequence correspondence

Method	Corresponding sequence
Zero.met	Zero.seq
Flush Fill.met	Flush Fill.seq
Acquisition 630s.met	Carbonates.seq and Equilibration.seq
Acquisition.met As an older method, Acquisition.met is no longer recommended.	Carbonates.seq and Equilibration.seq
H2_zero.met	H2_zero.seq

Excel Export

Figure 3-71 shows a simple Excel Export template created for GasBench II using the Excel Export Editor. It can be used as an example for creating a customized export template. In all cases, the columns listed in the right pane of Figure 3-71 should be exported:

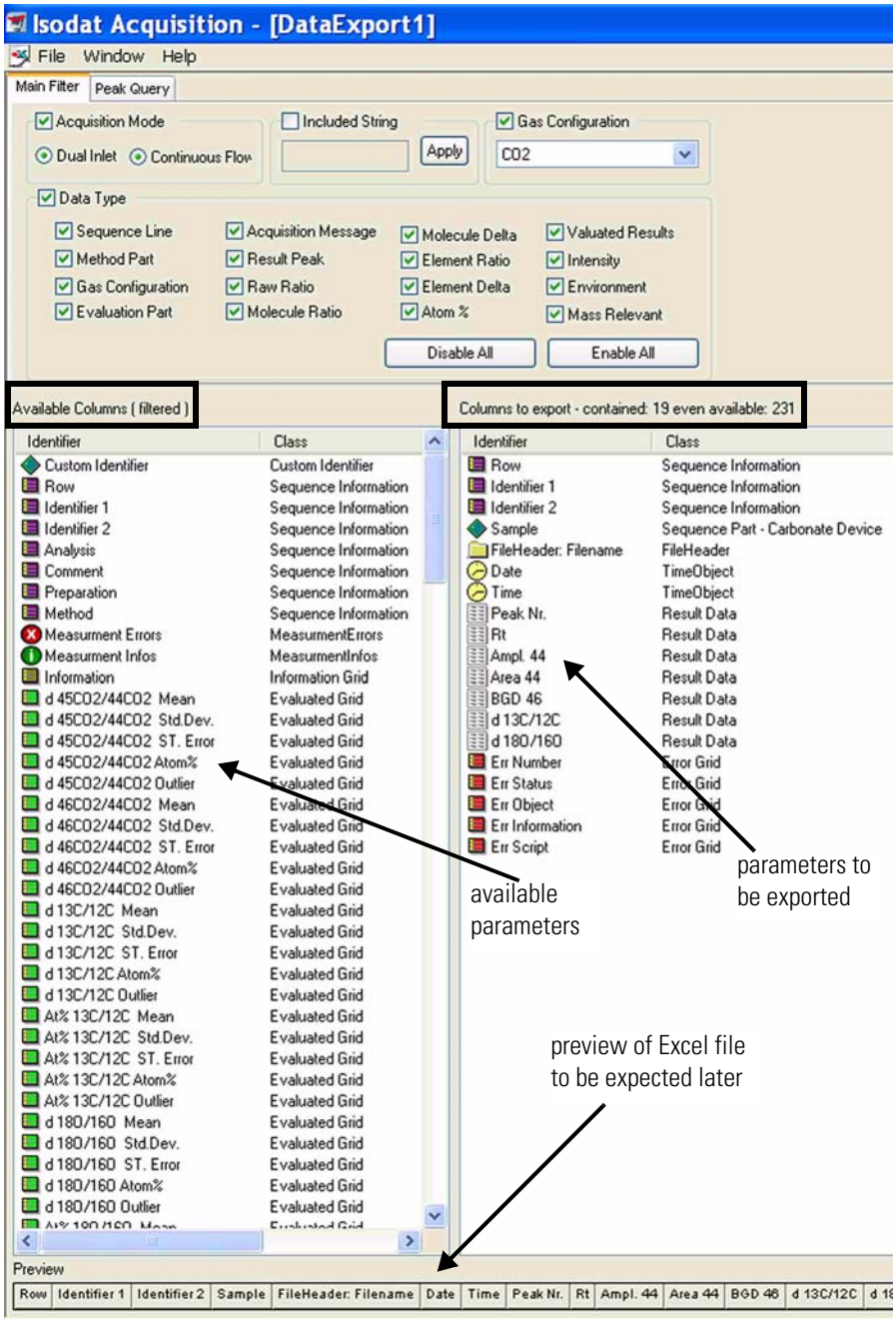


Figure 3-71. Excel Export module with basic output parameters

An Excel export template is valid for the export of one sheet within an Excel file (.xls). Several Excel export templates yield several sheets.

Performing Excel Export

This section outlines how an Excel Export is performed.

❖ **To perform an Excel Export**

1. Click on the Results tab of the File Browser. Results are listed there as cf-files. Mark the cf-files of your choice. See Figure 3-72.

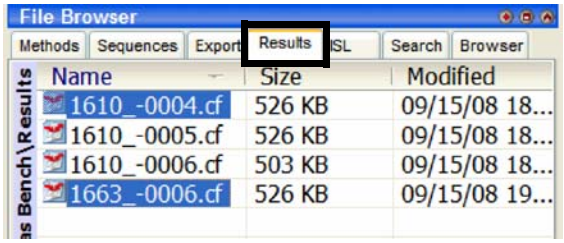


Figure 3-72. Selecting cf-file(s) at Results tab of File Browser

2. With the cf-files of choice marked, perform a right-click and select **Re-Process**. See Figure 3-73.

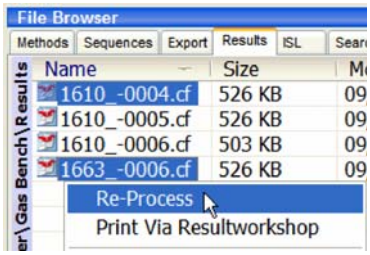


Figure 3-73. Reprocessing selected cf-files

3. In the appearing Re-proccess window, the name of the Excel file to be exported is shown at File Name. Click on the **Add** button. See Figure 3-74.

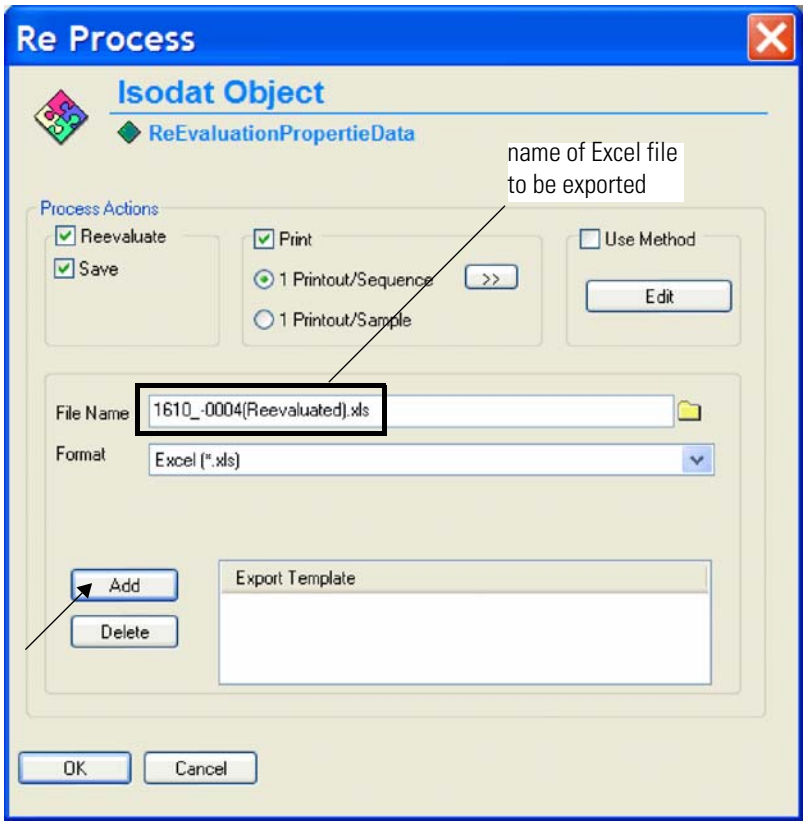


Figure 3-74. Add button in Reevaluation window

4. Browse to the WK 1 Export Templates folder. The user-defined export templates are listed as wke-files. Select all of them and click on the **Open** button. See Figure 3-75.

Note The number of wke-files you select will determine the structure of the Excel file to be exported. ▲

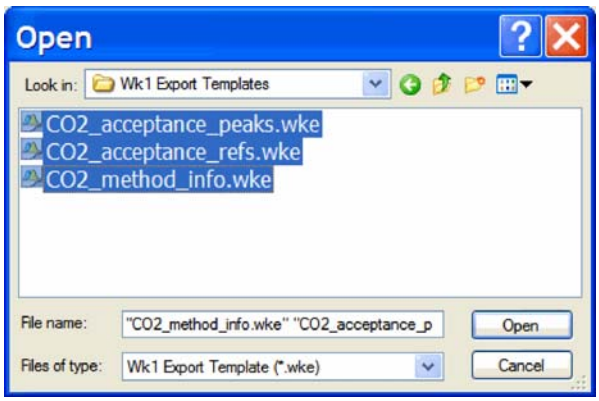


Figure 3-75. Selecting user-defined export templates

5. The selected user-defined export templates will appear in the Re-Process window. See Figure 3-76.

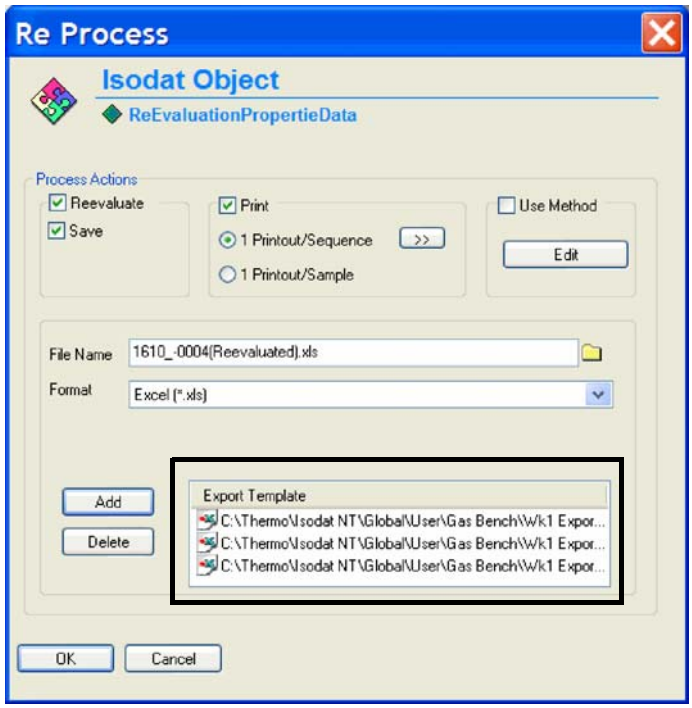


Figure 3-76. Selected export templates

6. Confirm by **OK**. The export will be carried out. See Figure 3-77.

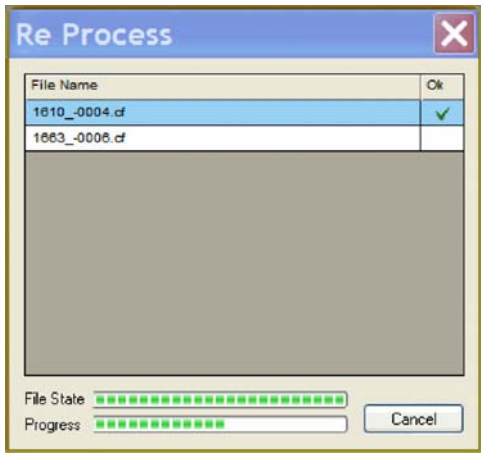
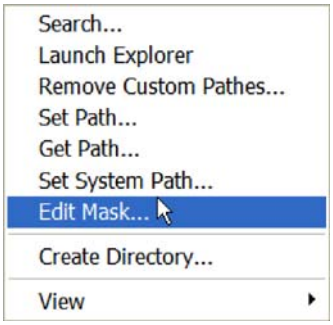


Figure 3-77. Export being carried out

The generated Excel export file ...(Reevaluated).xls has been saved.



7. To let the generated Excel export file appear at the Results tab, modify the file mask by right-clicking somewhere on the File Browser and then selecting **Edit Mask...**.

8. In the Modify Mask window (Figure 3-78), enter "*.xls;*.*" as new file types to be additionally displayed in the File Browser. Separate the file types by semicolons from the file formats already listed.

Figure 3-78. Editing mask by new file formats to be displayed

The Excel export file appears now at the Results tab. See lower part of Figure 3-79.

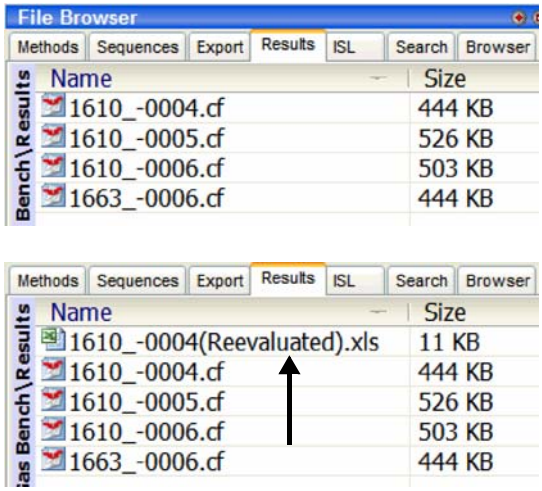


Figure 3-79. Excel export file visible at Results tab after editing mask

9. Open the Excel export file by dragging and dropping it from the Results tab into your open Excel application.

Note The Excel sheet comprises three tabs. This corresponds to the number of wke-templates you selected in Figure 3-75 (three, for example). See arrows in Figure 3-80. ▲

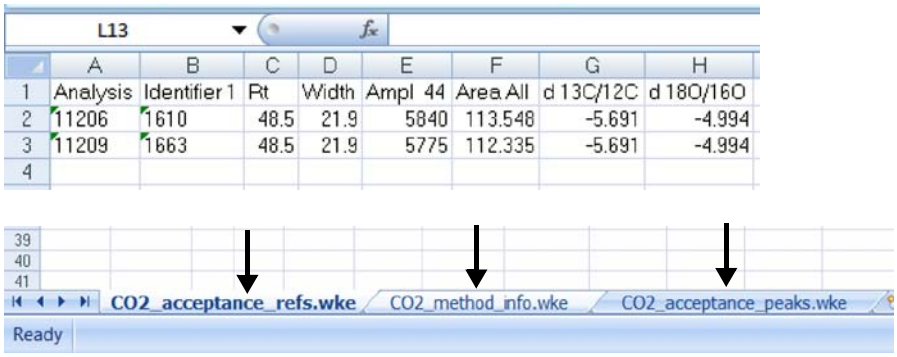


Figure 3-80. Exported Excel sheet with three tabs

Autosampler Programming

The CTC PAL parameter settings are changed via the control panel. The complete parameter setting is saved on an electronically programmable read-only memory (EPROM) on the electronic board of the CTC autosampler. To backup the complete parameter setting, the CTC PAL loader software is used.

GC PAL Loader Software

All autosampler settings, positions and methods that include timing are entered directly into the memory of the autosampler via the panel of the autosampler. All changes of autosampler programming are effective immediately. To save a copy of the memory contents of the autosampler, use the PAL loader software provided with your Combi PAL or GC PAL. This software package allows to read the memory of the autosampler and to save its contents to a backup file on your hard disk. Using the same program, the memory contents of the autosampler can be restored via a backup file. Thus, these backup files contain the autosampler settings needed for the different applications. Some exemplary backup files are provided by Thermo Fisher Scientific as PAL-GASBENCH V2.33 021031.sss.

Using GC PAL Loader Software

For any GC PAL, a loader software is provided, which needs to be installed on your computer. It is necessary for adjusting the autosampler settings. As a stand-alone software, it can be installed independently of Isodat.

❖ **To install the GC PAL loader software**

1. Start the loader software. Communication between computer and autosampler is now possible via the COM Port.
2. Default installation location is: Program Files > PAL > Loader. Note the two subfolders Backup and Update. Save the file PAL-GASBENCH V2.33 021031.sss in the subfolder Update.
3. Open the GC PAL loader software via Start > Programs > PAL System **> PALLoader**.
4. Perform a backup of the default autosampler configuration.
5. Wait until backup is complete.
6. On your Isodat CD, look for the GC PAL folder. It contains two files with autosampler settings adjusted ex factory, PAL-GASBENCH V2.33 021031.sss (one for Combi PAL and one

for GC PAL). The latest version is available also on CIS, that is on our Customer Information System.

7. Copy these two files to the GC loader's update folder.

8. Press **Update** and select the PAL-GASBENCH V2.33 021031.sss file. Perform the update.
   The autosampler-related file PAL-GASBENCH V2.33 021031.sss will be installed automatically. This may last some minutes.

First Touch

In this section, the usage of the autosampler display and its key functions are described.

The display of the autosampler shows four function keys, F1, F2, F3 and F4. See Figure 3-81. Pressing a function key leads to a specific submenu, where F1, F2, F3 and F4 may have completely different meanings. Thereby, a wide-branched system of commands will be accessible.

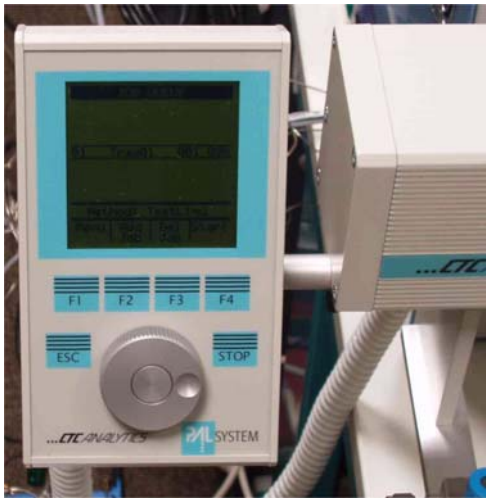


Figure 3-81. Autosampler display - general

Table 3-26 and Figure 3-82 show the meaning of the four function keys in the Start menu.

Table 3-26. Function keys in Start menu

Function key	Meaning
F1	Menu
F2	Add Job
F3	Delete Job
F4	Start

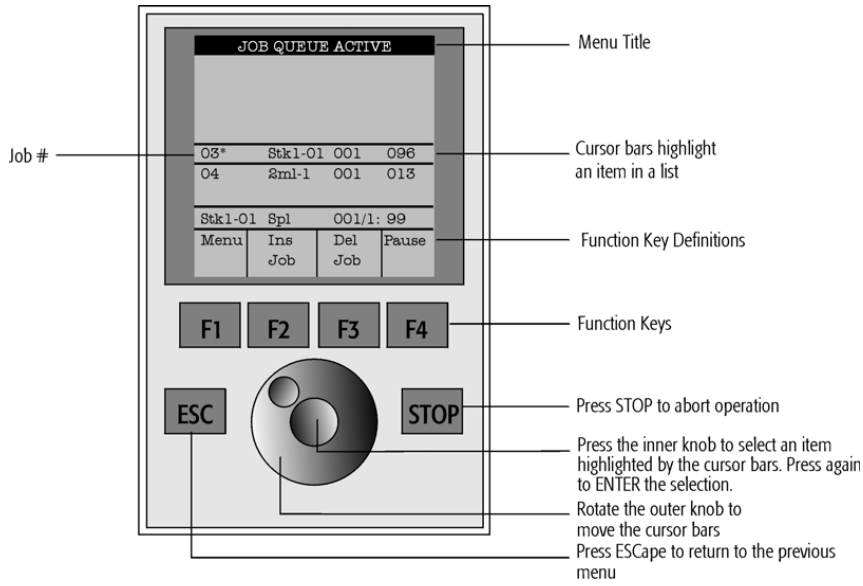


Figure 3-82. Autosampler display - Start menu

For the hierarchically structured menu a navigation sheet delivered by CTC is used. See Figure 3-83 and Figure 3-84. All programmable parameters and in which structure they are programmed are described within this navigation sheet.

To find an individual parameter within the memory of the autosampler, press the **Menu** button (**F1**) on the panel of the autosampler. You will see a menu on the panel that allows to step down further into the parameter tree.

To inspect the subtrees, locate the highlighted bar above the menu entry using the dial and press the center knob on the dial.

To access some more critical parameters press **F3** and the center knob simultaneously.

To locate all parameters of the object “tray holders”, follow the path given in Table 3-27.

Table 3-27. Path to locate parameters of object “tray holders“

Menu **F1**

→ Methods

Utilities

Logfile

Info

Setup **F3**

→ Ident

Access

Sounds

Time

SYSTEM

SERVICE

Objects → Vials

SYRINGES

TRAY TYPES

Tray Holders

Trays

Wash Stations

Injectors

VALVES

AGITATORS

POSITIONS

PATHS

Sync Signals

Out Signals

Events

Table 3-28. Commands for menu navigation

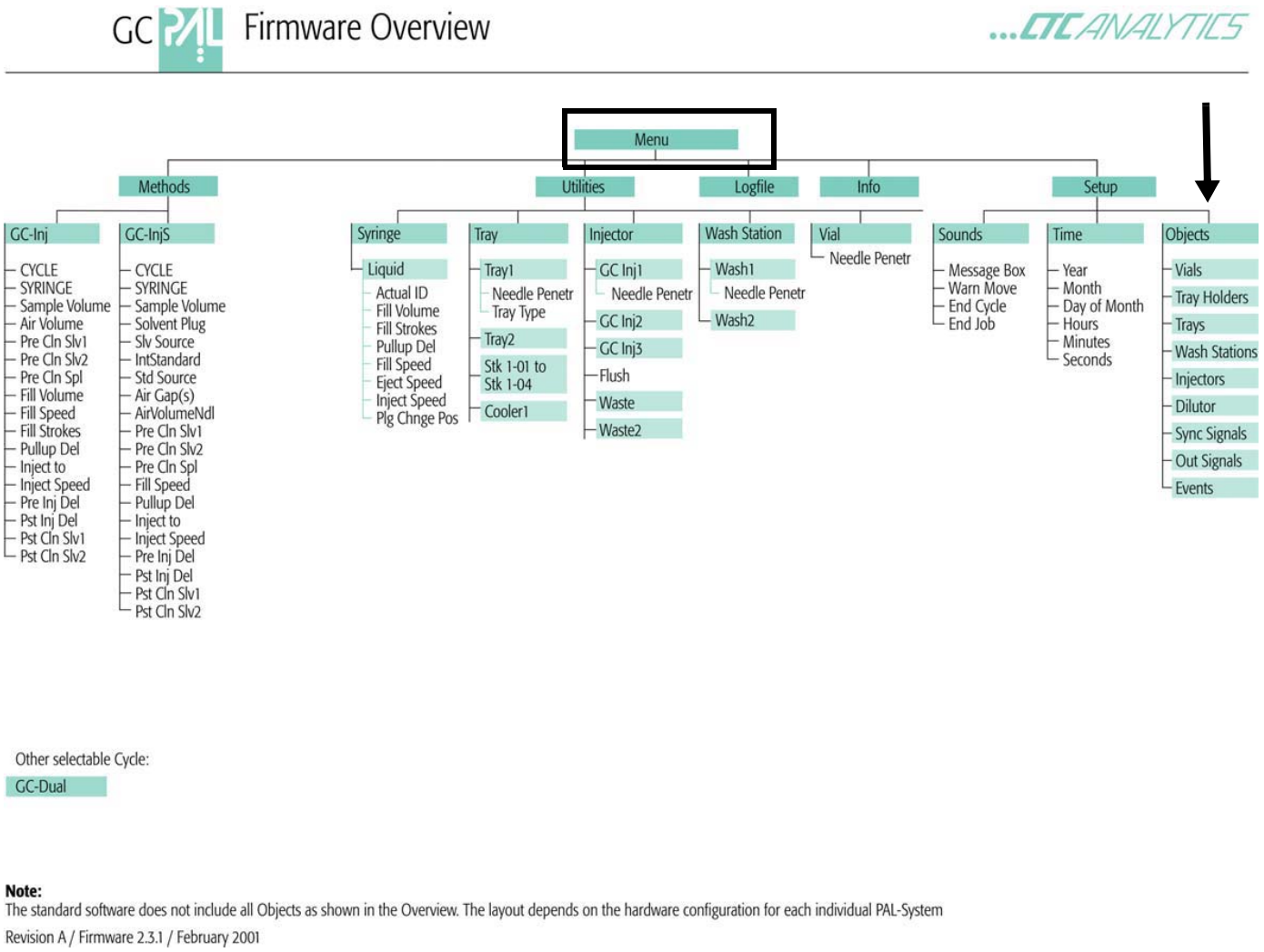
Command	Function
ESC	leads you back to the previous menu Press it repeatedly to go back to the main menu.
Home	directly leads you back to the main menu (mostly F4)
Stop	stops the autosampler during operation For example, when a sequence is being performed in Isodat, the autosampler is running and can only be stopped by the Stop command.

Note Enter is the center knob on the autosampler's dial. If you press Enter alone, that is without F3, you only get access to the entries that are not uppercase.
The additional entries, which are UPPERCASE, cannot be accessed directly when passing through the autosampler's menus. Press the **F3** key once (at the position of the arrow shown above) followed by **Return** at the autosampler to access them.Thereby, sensitive entries that lead to large-scale changes, are protected against clumsy access.
This principle is valid for the entire tree of commands shown above: at any position within the tree, F3 leads to additional commands. ▲

The autosampler commands can be classified into several groups:

- tray-related commands
- tray holder-related commands (for example the tray holders which are used; dimensions, that is the number of rows and columns)
- positioning of the autosampler in order to adjust sample positions
- adjustment of the needle holder

Figure 3-83 and Figure 3-84 have been taken from *CTC Analytics PAL SYSTEM User Manual*.



Note:
The standard software does not include all Objects as shown in the Overview. The layout depends on the hardware configuration for each individual PAL-System

Revision A / Firmware 2.3.1 / February 2001

Figure 3-83. Autosampler adjustment - tree of hardware commands (Main menu)

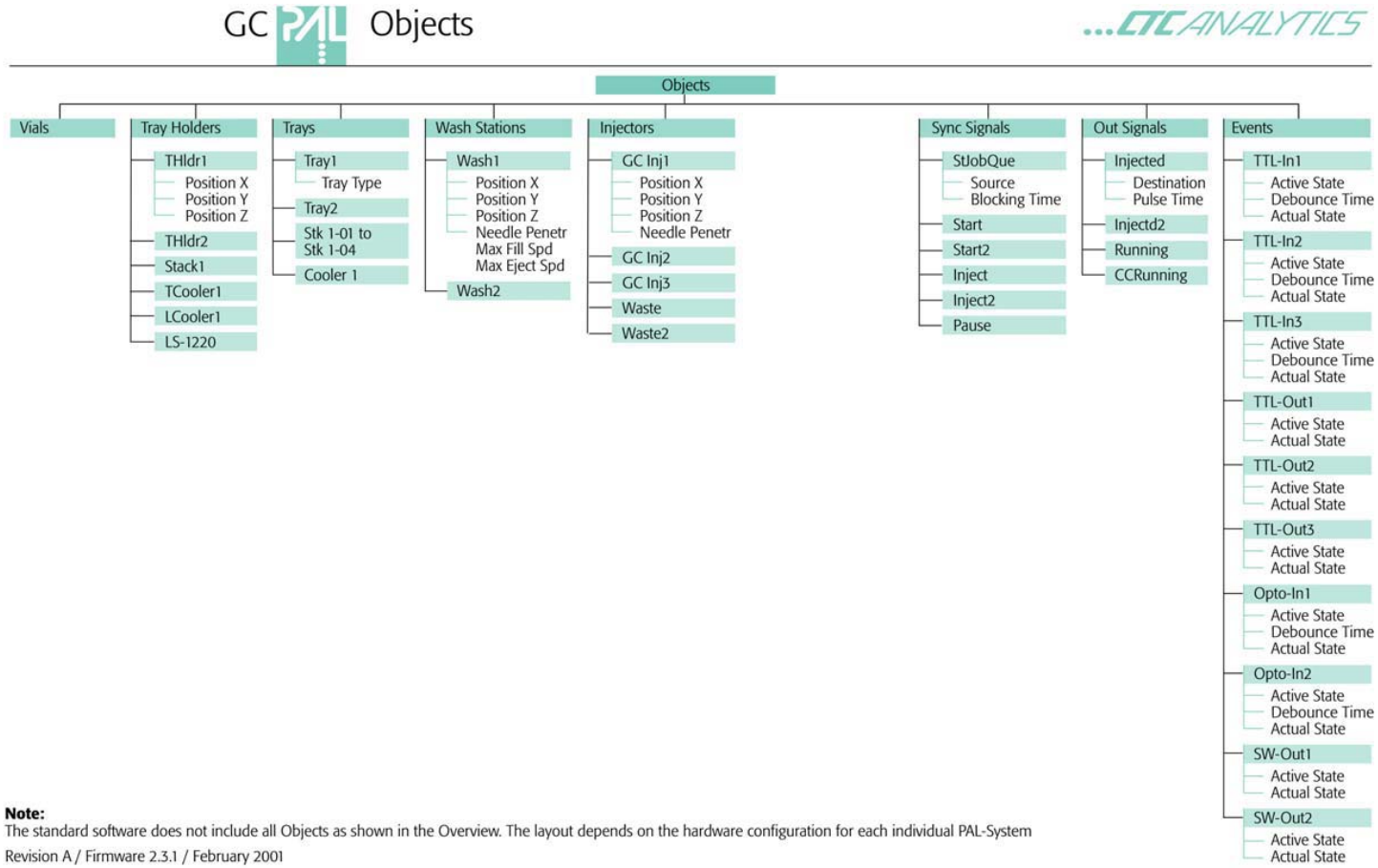


Figure 3-84. Autosampler adjustment - tree of hardware commands (Objects submenu)

Adjusting Autosampler Tray Position

Note This is to readjust the GasBench tray. In general, the trays are predefined and preinstalled using the file PAL-GASBENCH V2.33 021031.sss on your Isodat CD. Refer to topic "GC PAL Loader Software" on page 3-65. If preinstallation and configuration have already been performed, redirect into the menu of the autosampler by **ESC**. Refer to topic "First Touch" on page 3-66. ▲

❖ **To adjust the autosampler tray position**

1. Remove the needles to avoid damaging them.
2. Click Home > Manual Setup > F3 > Object Trays > **Tray 01**
3. Click Home > Manual Setup > F3 > Object Trays > **Holder**.

   Two tray holders will appear:

   GasBench tray holder (without numerical designation) and

   GasBench tray holder #2.

   GasBench tray holder #2 refers to a 96 sample tray setup with a specific sample positioning, for example. This positioning is not discussed here, but it can be performed in the same way as GasBench tray holder.
4. Go to Gas Bench tray holder.

Example for Adjusting: GasBench Tray Holder

❖ **To adjust the GasBench tray holder**

1. Go to the positioning variables x, y, z.
2. To prevent the sample tower from crushing into the tray, set the positioning variables x, y, z to zero.
3. Determine the dimensions of the tray relative to the zero position of the autosampler. Again, readjust only, if the dimensions are false or if a different tray is in use.
4. Each position, that is x, y or z, can be configured by turning the wheel to the correct dimensions.

Using Autosampler Method

We use the compatibility mode of the autosampler, where the autosampler emulates the behavior of an AS200 autosampler. Therefore, only ten different methods can be used, and they must be named A200S-0 to A200S-9. Initially, the autosampler uses three methods for GasBench II, which are shown in Table 3-29.

Table 3-29. Autosampler methods for GasBench II

Autosampler method	Used for
A200S-7	flushing
A200S-8	carbonates
A200S-9	equilibration

Their main difference is the duration during which the sample needle will stay injected in the headspace of the vial. This time is given by the method parameters Fill strokes and Pullup delay according to the equation:

$$\text{time for one sample} = (\text{fill strokes} + 1) \times \text{pullup delay}$$

The settings in the following example, which is taken from the A200S-8 method, result in a sampling time of 682 s.

Table 3-30. Example for CTC autosampler method

Parameter	Value
Cycle	LC-Inj
Syringe	10 µL
Sample Volume	1.0 µL
Air Volume	0 nL
Pre Cln Slv 1	0
Pre Cln Slv 2	0
Pre Cln Spl	0
Fill Speed	5.0 µL/s
Fill Strokes	10
Pullup Del	62 s
Inject to	NONE
Inject Speed	50 µL/s
Pre Inj Del	0 ms
Pst Inj Del	0 ms
Pst Cln Slv 1	0
Pst Cln Slv 2	0

Table 3-30. Example for CTC autosampler method, continued

Parameter	Value
Vlv Cln Slv 1	0
Vlv Cln Slv 2	0

Testing Autosampler

You can test the communication of the autosampler independently of Isodat.

❖ **To test the autosampler**

1. Open a “hyperterminal” to be found in the Start menu under: Start > Programs > Accessories > Communications > **Hyperterminal**.

2. Use the settings summarized in Table 3-31.

Table 3-31. Settings for testing austosampler

Item	Value
serial port	COM 1
baud rate	9600 baud
number of stop bits	1
parity	no parity
flow control	NONE

3. Type in the following command:

   #010000 (request status)

   The autosampler should respond with:

   #010001 (STANDBY) or
   #01w002 (READY), (BUSY, if w > 0)

4. Finally, order the sampler to execute method M on sample NNN in

   TRAY01: #99MNNN

Chapter 4 Basic Operations

This chapter explains basic operations to be performed with GasBench II. It treats the following topics:

Leak Check

To check whether the IRMS is ready to operate, close the inlet valve and run a mass scan from 3000 magnet steps to 12000 magnet steps. Use the cup with the largest amplification factor (cup 3 with 3×10^{10} Ω). It should look more or less like Figure 4-1 or Figure 4-2, respectively.

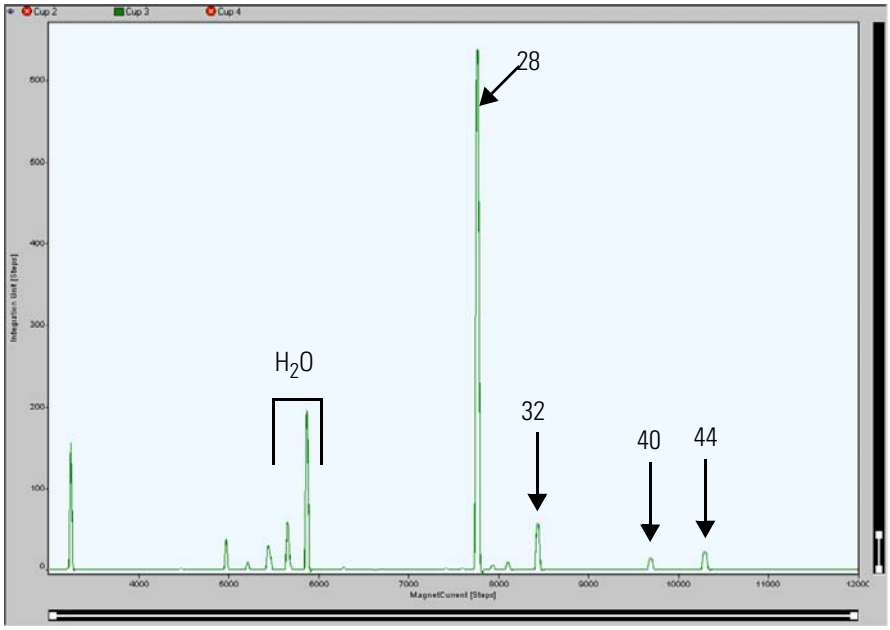


Figure 4-1. Mass spectrum of background gas composition (for Delta^{Plus} XP)

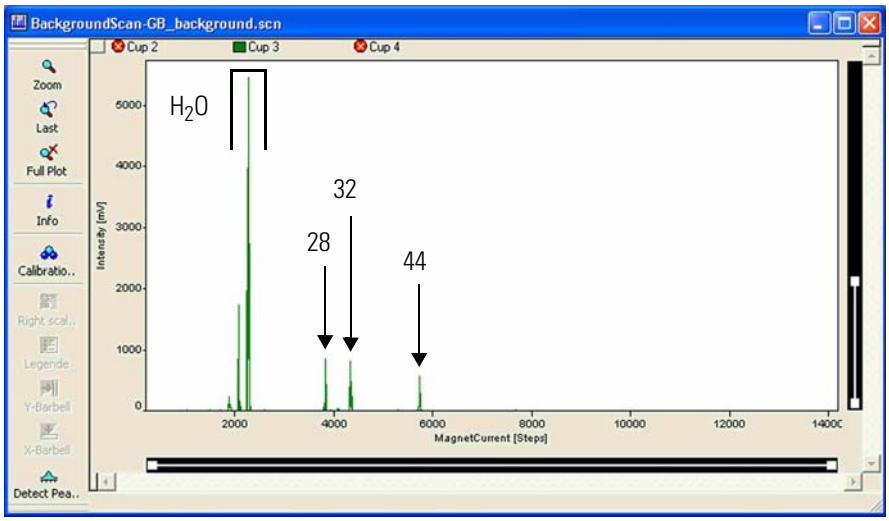


Figure 4-2. Mass spectrum of background gas composition (for MAT 253)

The mass scan shows the composition of the background gas in the source region and informs about the amount of gases present. Try to identify the following patterns and compare them with the maximum values below.

Water

For the isotope ratio measurement, the water background must be stable to ensure the principle of identical treatment of all samples and standard samples.

Water contains ions of m/z 16, m/z 17 and m/z 18. It appears at magnet current values approximately between 5300 steps and 6000 steps. The peak intensity should be at most 1 V. The peak shape of m/z 16 and m/z 18 should look as in Figure 4-2. The intensity ratio of the three peaks is 1:2:4.

Air

In principle, air response changes the stability of ion source ionization. Therefore, it is important to avoid any leakage of air into the ion source and the GasBench II system.

Air contains ions of m/z 28, m/z 32, and m/z 40. It appears around magnet current values of approximately 7800 steps, 8500 steps, and 9700 steps, respectively. The maximum intensity for m/z 40 is 30 mV. The intensity ratio of the three peaks is 4:1:0.7.

Carbon Dioxide

Any CO_2 interference from a source other than the sample CO_2 changes the accuracy of the isotope ratio of samples. Therefore, a constant CO_2 response or better no CO_2 response shall be visible during measurement.

CO_2 contains ions of m/z 28 (CO) and m/z 44 (CO_2). It appears around magnet current values of approximately 7800 steps and 10300 steps, respectively. The intensity of m/z 44 must be less than 50 mV. The CO portion can easily be confused with nitrogen from air.

If air appears in the spectrum, check the IRMS for leaks, for example by using argon from a tank. In case of a too high water level, heat out the IRMS using the source heaters for at least 12 h. When a high water level is present in the source, usually some air is leaking into the mass spectrometer as well.

Once this check has been performed within the given limits, open the inlet valve and repeat the mass scan. If air appears in the spectrum again, check all gas connections at GasBench II for air leaks. Do not forget to check all connections under excess pressure as they may leak, too. The best way to find leaks in the excess pressure section is to use a standard soap solution (SNOOP®, for example), which is applied to the connectors. Small bubbles appear when gas is leaking.

Caution The connection between plot column and safety column located in the GasBench II oven is critical. ▲

Caution Be careful when tightening the connectors. Do not use excessive force. Tighten only, if you are absolutely sure that the connection is leaking. ▲

If the water level is too high after the leak check, heat out the GC column at 140 °C overnight. The GC column accumulates water by and by and releases it when heated. The water level only decreases after prolonged heating and continues to fall for some time even after heating is switched off (provided that there are no leaks).

Leak testing is especially laborious in the gas sampling section. A leak in this section has no continuous connection to the mass spectrometer. Instead, the Valco eight port valve needs to be switched to introduce a portion of the gas stream into the IRMS.

Caution When checking this section comprising sample bottle, sampling needle connectors, water trap and the appropriate connectors at the Valco valve, be extremely careful not to overtighten the connections.

When replacing ferrules in this section, be sure to use only the listed Valco ferrules. Refer to Technical Note 503: Fitting Instructions at www.vici.com. ▲

Checking Column Flows

For optimal operation, certain flows in GasBench II must be within a specific range. The bubble flow meter supplied with GasBench II can be used to check various flows throughout the system. Fill the small rubber ball with some soap solution and press it until bubbles appear in the inlet region. Connect the inlet tube to the capillary under test. The bubbles should then be transported along the tube by the gas flow under inspection. By measuring the time needed to fill a certain volume, the flow at the inlet tube can be calculated.

The flow through the sample needle should be checked regularly before each run using a flow meter. Measure at the exhaust capillary at the Valco valve, which is connected to port 7. Measure, while a closed bottle is attached to the sample needle and while the Valco valve is in Load mode. For normal operation, the flow should be in the range between 0.5 and 0.8 mL/min. Measuring at the exhaust of the loop allows checking the complete sample transfer path.

To check the flow through the flushing needle, a bottle must be connected and the flush valve be open. This flow is measured at the open exhaust capillary at the bottle connection of the flushing needle and should be in the range between 100 and 150 mL/min for normal operation.

Checking the flow in the GC column is more difficult. Because the GC column itself is the restriction for the gas flow, the flow can only be measured behind the column. The best point is the exit of the GC column. Carefully remove the capillary that leads to the second water trap and measure the flow, which should be between 1 and 1.5 mL/min for normal operation.

Caution During removal of the capillary be careful when you tighten the ferrule. Excessive force may lead to destruction of the ferrule or even the bulkhead connector at the GC housing. ▲

Zero Enrichment Test (Standard On/Off Test)

Provided that GasBench II has no leak (refer to topic "Leak Check" on page 4-2), the Zero Enrichment test and Linearity test (refer to topic "Linearity Test" on page 4-10) can be performed using the standard acquisition scripts.

The final test for the overall performance of GasBench II and IRMS is the Zero Enrichment test (also called Standard On/Off test). To perform it, fill an arbitrary number of sample bottles with a test mixture of 0.3‰ CO_2 in He and start an acquisition. Use the acquisition method and printout templates supplied during installation of Isodat. A single result printout should look as shown below.

Check for each chromatogram, whether the ratio baseline is flat. Large peaks in the baseline of 44/46 just in front of each sample CO_2 peak point towards air contaminating the sample. Check whether the sample bottle was properly closed. If, in the intensity plot, a peak larger than 100 mV appears just in front of the CO_2 peak, the result must be discarded.

In all other cases, calculate the standard deviation $\sigma(O_2)$ of the ten sample peaks of one sample. It should be less than 0.05‰ for all measurements. This result is called "internal error".

The "external error" is the standard deviation of the mean values of all measurements. It should be less than 0.08 ‰ for $\delta^{18}O/^{16}O$ and less than 0.06 ‰ for $\delta^{13}C/^{12}C$.

If this is obtained, you are ready to measure carbonates (refer to topic "Carbonates" on page 5-6), DIC (refer to topic "Dissolved Inorganic Carbon (DIC)" on page 5-22), or water equilibration. Refer to topic "Water Equilibration ($^{18}O/^{16}O$ Equilibration)" on page 5-33 and to topic "Water Equilibration ($^{2}H/^{1}H$ Equilibration)" on page 5-36.

Run a sequence using the standard on/off method, that is zero.met.

Note The amplitude of m/z 44 must be between 4 V and 5 V. This refers to the cup having a resistor of 3×10^9 Ω, that is usually Cup 2, where m/z 44 is measured under standard conditions. All necessary information is given in the Gas Configuration Editor. Refer to topic "Creating a GasBench Configuration" on page 3-5. ▲

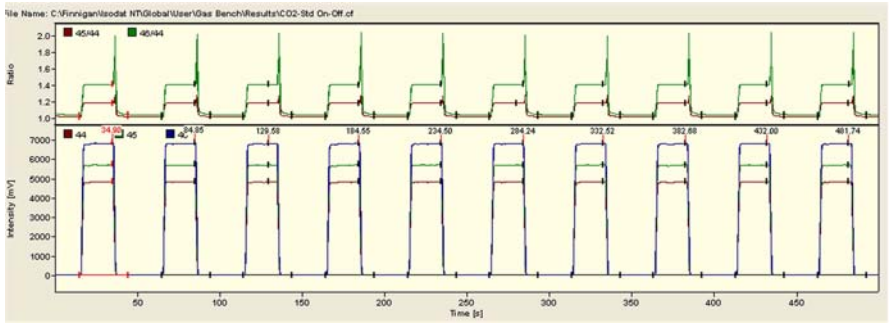


Figure 4-3. Zero enrichment - chromatogram

Note If the capillaries got entangled, the reference gas peaks shown in Figure 4-3 begin to differ in peak height. ▲

CO2 | Error | Extended | Sequence Line

Peak Nr.	Rt [s]	Width [s]	Ampl. 44 [mV]	BGD 44 [mV]	BGD 45 [mV]	BGD 46 [mV]	Area All [Vs]	R 45CO2/44CO2	d 13C/12C [per mil] vs. VPDB	d 18O/16O [per mil] vs. VSMOW
1	34.9	29.5	4843.635	7.401	8.867	10.957	95.113	0.0119844	-0.0403999953	0.0083090491
2	84.9	29.5	4850.178	6.750	8.075	10.051	95.178	0.0119849	0.0000171315	0.0172742706
3*	129.6	29.5	4822.312	6.768	8.051	10.050	95.067	0.0119849	0.0000000000	0.0000000000
4	184.5	29.5	4843.289	6.793	8.104	10.121	94.991	0.0119846	-0.0235142430	-0.0338557016
5	234.5	29.5	4835.014	6.819	8.137	10.119	95.164	0.0119848	-0.0046782666	-0.0189323045
6	284.2	29.3	4822.259	6.842	8.204	10.234	95.066	0.0119845	-0.0291343755	-0.0357779845
7	332.5	29.5	4834.253	6.859	8.217	10.231	95.128	0.0119848	-0.0003728474	-0.0411926241
8	382.7	29.5	4829.114	6.875	8.207	10.234	95.041	0.0119850	0.0109096230	-0.0420390676
9	432.0	29.5	4825.737	6.894	8.228	10.245	95.170	0.0119848	0.0005798929	-0.0429669210
10	481.7	29.3	4821.359	6.899	8.245	10.256	95.132	0.0119848	0.0002116145	-0.0524993646

Figure 4-4. Zero enrichment - result grid

❖ **To obtain the standard deviation of all ten peaks**

d 13C/12C [per mil] vs. VPDB
-0.0403999953
0.0000171315
0.0000000000
-0.0235142430
-0.0046782666
-0.0291343755
-0.0003728474
0.0109096230
0.0005798929
0.0002116145

1. Click on the column header, for example of the d 13C/12C [per mil] vs. VPDB column. It will be highlighted completely. The same principle is valid for the d 18O/16O [per mil] vs. VSMOW column.
2. Right-click on the column header to display the shortcut menu.

3. Choose **Calculate** to show online calculations of the single result (Figure 4-5). With this tool, advanced users can already approximate results and stablility of measurements during online data acquisition (standard deviation and linearity, for example).

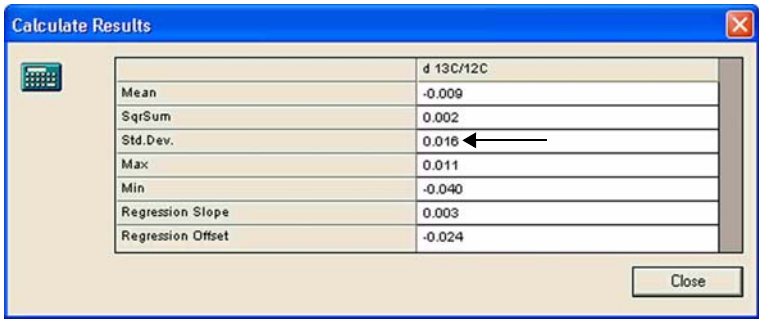


Figure 4-5. Calculate results

Note The standard deviation (for example of the ten sample peaks; internal error) must be less than 0.1 ‰ for $\delta\ ^{18}O$ and $\delta\ ^{13}C$. ▲

Testing Reference Gas Inlet Ports

If the Zero Enrichment test was unsuccessful, check the reference gas inlet ports.

❖ **To check reference gas inlet ports**

1. Check the dimensions of your fused silica reference gas capillary as shown in topic "Open Splits" on page 2-42.
2. Check the distances of your reference gas capillaries as they should be set up in topic "Open Splits" on page 2-42. Use the GasBench window as a part of the Accessories window.
3. The functionality of all three fused silica reference gas capillaries can be tested:
   a. No bending shall occur.
   b. Transfer of reference gas (if installed) must be possible.
   c. Mechanical and air pressure movements must be possible.

Caution Do not cut any of the capillaries inside GasBench II! ▲

4. If 3a.) or 3b.) is out of order, the following checks can be performed:
   a. Loosen the upper straight connector screw of the reference gas capillary so that the capillary can be moved with ease.
   b. Take out the capillary.
   c. Cut off approximately 1 cm from the capillary.
   d. Readjust the capillary in the straight connector.

Caution Avoid any blockage of the capillary! ▲

   e. Check for the correct distances of the capillaries inside the reference open split.
   f. Tighten the capillary carefully until no movement is possible by hand anymore.

Caution Do not overtighten the capillary! ▲

Check 3a.) and 3b.). If either of them is out of order, pass again through all steps 4a.) to 4f.).

Linearity Test

The mass spectrometers normally used together with GasBench II (that is Delta series and MAT 253) are not ideally linear. This means that the measured δ value depends on the actual amplitude (peak height). With each IRMS, a certain slope is guaranteed, for example 0.05 ‰/V for the Delta series. To check for this effect and to ensure proper operation, the following linearity test should be performed from time to time.

Run a sequence using the method zero.met. While the method is running, vary the reference gas pressure to obtain different peak heights for the various pulses. Plot peak height versus δ value for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ respectively. Determine the slope.

Note If the GasBench II is coupled to a ConFlo IV, the linearity test will be performed automatically. Refer to the *ConFlo IV Operating Manual*, P/N 1224730. ▲

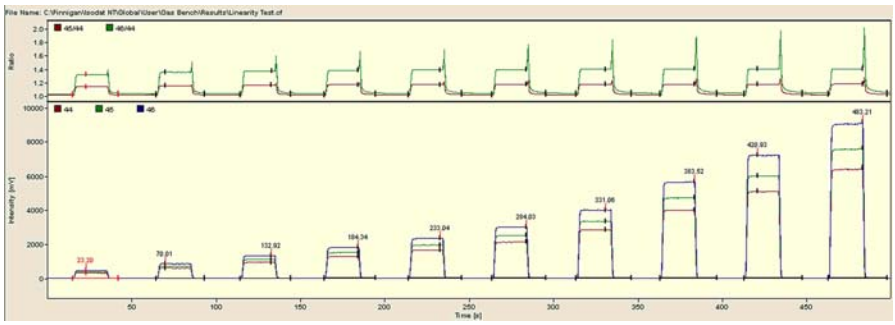


Figure 4-6. Linearity test - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Rt [s]	Width [s]	Ampl. 44 [mV] a	BGD 44 [mV]	BGD 45 [mV]	BGD 46 [mV]	Area All [Vs]	R 45CO2/44CO2	d 13C/12C [per mil] vs. VPDB b	d 18O/16O [per mil] vs. VSMOW c
1	23.2	27.2	330.475	6.385	7.589	9.229	6.333	0.0119856	0.0525950567	0.4434196816
2	70.0	28.6	608.808	7.052	8.369	10.237	11.905	0.0119855	0.0538517979	-0.0002045676
3*	132.9	29.7	941.904	7.464	8.862	10.813	18.481	0.0119849	0.0000000000	0.0000000000
4	184.3	30.3	1291.421	7.829	9.281	11.319	25.267	0.0119852	0.0363528147	-0.1012398761
5	233.0	31.6	1663.908	8.157	9.708	11.884	32.720	0.0119845	-0.0219037244	-0.2031053355
6	284.0	32.0	2140.433	8.449	10.059	12.220	42.047	0.0119845	-0.0265884027	-0.2091772941
7	331.1	32.8	2852.487	8.735	10.410	12.708	56.137	0.0119846	-0.0088587106	-0.2968846352
8	383.5	33.6	4021.943	9.157	10.886	13.246	79.185	0.0119847	-0.0050016053	-0.3096256787
9	420.9	34.3	5114.933	9.633	11.442	14.048	100.828	0.0119846	-0.0065581097	-0.3708753995
10	483.2	35.1	6470.237	10.059	11.936	14.732	126.650	0.0119847	0.0053447480	-0.4068704781

Figure 4-7. Linearity test - result grid

❖ **To obtain the linearity of all ten peaks**

1. Click on the column header of the Ampl. 44 column (a in Figure 4-7). It will be highlighted.
2. Select all amplitude values of this column and transfer them to a spreadsheet file as x-values.
3. Click on the column header of the d 13C/12C column (b in Figure 4-7). It will be highlighted.
4. Select all δ values values of this column and transfer them to a spreadsheet file as y-values.
5. In the spreadsheet file, plot the δ values vs. the amplitude values. The slope of the δ(A) diagram is the linearity.

Instead of the δ values of the d 13C/12C column (b in Figure 4-7), you can alternatively plot the δ values of the d 18O/16O column (c in Figure 4-7) against the amplitude values of the Ampl. 44 column (a in Figure 4-7).

Note Linearity should be less than 0.05 ‰/V. ▲

Condition Test

A simple way to check the condition of GasBench II alone, that is without a set of individual sample vials, is to gently flush the sample line with a 0.3–0.5 % (CO_2 in He) mixture. The check should be performed using a filled container of a larger volume, 500 mL, for example. The following parameters can be optimized by this check:

- temperature and flow of GC column (PoraPlot Q)

  GC temperature changes the separation between peaks belonging to the same sample injection (aliquot). GC column flow shifts all GC peaks in time: higher flows mean shorter retention times and vice versa.

- retention time and GC peak shapes (DtR N2/CO2)

  Retention time depends on column type. Peak shapes tend to be tailed, if the column is heavily used and needs recovering. Refer to topic "GC Oven" on page 2-35.

- time delay between METHOD/PROCESS (Dt loop injections)

  Use this type of condition test when changing the timing in order to control the results of manipulations to the time events list.

- loop size (10-250 mL; sensitivity vs. peak shape)

  Different loop sizes require different times for loading and injecting the loop. Calculate load times from loop volume and sample needle flow. Calculate inject times from loop volume and GC column flow. Allow extra times for safety.

- IRMS sensitivity (length of transfer line)

  Frequently check the sensitivity of the whole apparatus by this test.

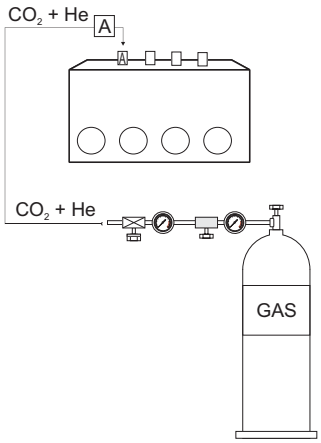


Figure 4-8. Basic test for sample section (autosampler and bottles excluded)

Starting an Automated Sequence

Prior to starting an automated sequence of valuable samples, the GasBench II shall be checked for certain items:

- Frequently check the sample needle, flush needle and acid needle for remainders of the vial septa. Small parts can be removed using a syringe tip. Check the flow through the sample needle (0.5-0.8 mL/min) at the exhaust (vent) connection of the Valco eight port while a sample is connected.
- From time to time, at least once a month, heat out the GC column. Set the temperature regulator to 140 °C and keep this temperature constant for 12 h.
- From time to time, check whether the water background of the IRMS is within acceptable limits, that is less than 3 V.
  Refer to topic "Water" on page 4-3.
- Check the sample needle fused silica capillary for remnants of phosphoric acid or water. Remove droplets before starting the analysis.

To start an automated sequence click on the **Start** button in Isodat Acquisition.

Preparing a Test Sample

The basic principle of the GasBench II technique is the measurement of any gas (CO_2, for example) from the headspace in a vial. Therefore, it is unimportant for the GasBench II measurement how the gas was produced and released into the headspace. For a basic system check (that is, with no sample involved), a gas mixture is ideal.

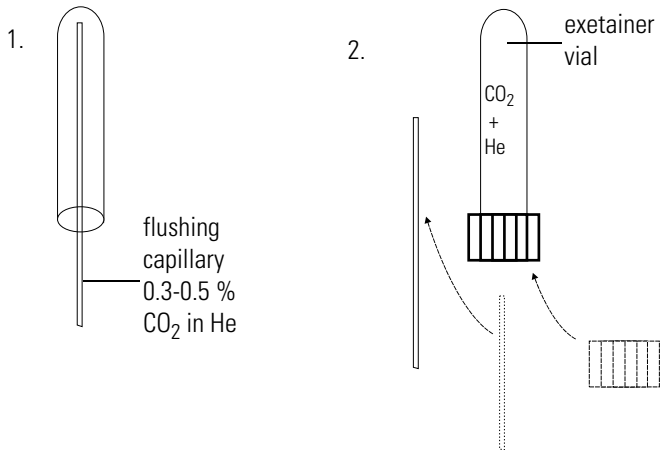


Figure 4-9. Flushing an empty exetainer for preparation of a test sample

Prepare this gas into an exetainer by flushing the vials with a mixture of 0.3-0.5 % CO_2 in He. The flow should be about 100 mL/min. Hold the tube upside down onto the flushing capillary for approximately 20 s and close the tube immediately after flushing. See Figure 4-9.

A more convenient way to fill the (He + CO_2) mixture into an exetainer vial is to use the flushing needle (refer to topic "Flush Needle" on page 2-27) together with the Combi PAL autosampler. To fill the exetainer properly, each tube is rinsed for approximately 5 min with (He + CO_2) at a flow rate of 100 mL/min.

Note To guarantee high performance, the exetainer should be washed prior to using it. Refer to topic "Manual Cleaning of Sample Vials" on page 4-20 and to topic "Machine Cleaning of Sample Vials" on page 4-21. ▲

After Preparing a Test Sample

After preparation of the test sample there are two possibilities to proceed:

- The user can take a predefined sequence as a guideline for a measurement.
- The user must define a method for a measurement.

Using a Predefined Sequence

At Sequence tab, predefined sequences may be chosen. The predefined parameters in the sequence can be copied and pasted into a new sequence file and be saved under a different name.

❖ **To use a predefined sequence**

1. Make sure that the IRMS is calibrated.
2. Make sure that the vials are prepared and placed in the tray.
3. Select an appropriate line in the sequence.
4. Press the **Start** button.

Defining a Method

The topic "File Browser" on page 3-14 gives an overview about what can be defined and seen by using the Method tab within the File Browser.

Note In this section, only the method entries that are specific for operating the GasBench II will be described. ▲

It is recommended to perform a peak center prior to the acquisition. Define CO_2 as a reference three times (duration: 20 s) and take the middle one as standard.

Table 4-1 lists ten loop switches for ten sample peaks on the GC column. It explains time event settings (reference gas injection, load and inject timing) of the GasBench II.

Table 4-1. Ten loop switches for ten sample peaks on GC column

Time	Action
1-100 s	sampling line and Valco valve are rinsed with (sample + He).
200 s	first injection of the loop onto the GC column (Inject mode)
230 s	loop is in Load Mode again.
230-270 s	Valco loop is filled with (sample + He).
270 s	second injection of the loop onto the GC column (Inject mode)…

Each line of the sequence list refers to a specific analysis. It combines the position of the specific sample (1) with the Combi PAL method (9), a preprocess file or any valve actions before data acquisition and the respective acquisition method.

Note When the sequence is finished, calculate all the averaged results for all vials. The standard deviation of these newly obtained results must be less than 0.1 ‰ for both $\delta\ ^{13}C$ and $\delta\ ^{18}O$. ▲

A measurement can be significantly shortened by analysis of only four to five sample peaks.

Performance Test of GasBench II

From time to time, take a look at the checklist shown below. It outlines the performance achievable by the system GasBench II plus IRMS. Check all mentioned items.

❖ **To test the performance of the GasBench II**

1. A basic test must be performed, that is testing the IRMS alone.
2. Perform a Zero Enrichment test outlined in topic "Zero Enrichment Test (Standard On/Off Test)" on page 4-6.
3. Carry out a Linearity test as described in topic "Linearity Test" on page 4-10.
4. Ensure that also the sample side (that is Valco valve, GC column) operates properly by performing the Condition test as described in topic "Condition Test" on page 4-12.
5. Carry out a Zero Enrichment test with vial. The filling can be performed manually or automatically.
6. Only if all the previous items are performed to specifications, carry out the measurement.

Preparing Phosphoric Acid

Warning While preparing and handling phosphoric acid, strictly adhere to the safety measures! Wear protective clothing, protective gloves, and a face mask. Goggles are not sufficient! Operate under a fume hood. Operate according to the material safety data sheet (MSDS). ▲

Caution For use with GasBench II, never use phosphoric acid with densities above 1.92 g/cm^3! This will inevitably cause the acid pump to get clogged. ▲

Phosphoric acid with densities between 1.90 g/cm^3 and 1.92 g/cm^3 is prepared on the basis of 99 % phosphoric acid. No phosphorous pentoxide needs to be added at all.[1]

H_3PO_4 is available in brown glass containers that contain 500 mL of 99 % phosphoric acid (P/N 1112640). Because the phosphoric acid is crystallized at 25 °C, carefully heat it in its brown glass container until it becomes liquid.

Note Do not heat the phosphoric acid in a non-glass container! ▲

Caution Check the fused silica capillary of the measurement needle for droplets of remnant phosphoric acid every day and for droplets of water (DIC) which may contain phosphoric acid. Phosphoric acid will destroy the Nafion water trap, the Valco valve rotor and the PoraPlot GC column! ▲

[1]For a discussion of preparation methods, refer to the following publications:

J. Burman, O. Gustafsson, M. Segl and B. Schmitz: A simplified method of preparing phosphoric acid for stable isotope analyses of carbonates. *Rapid Commun. Mass Spectrom.* 2005, **19**, 3086–3088

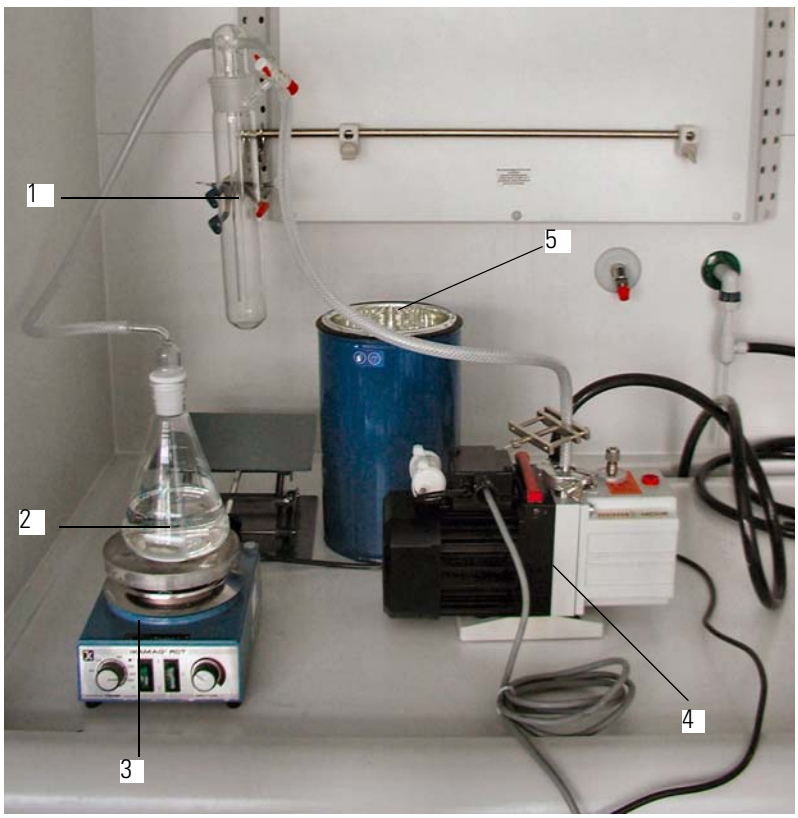
E.A. Wachter and J.M. Hayes: Exchange of oxygen isotopes in carbon dioxide–phosphoric acid systems. *Chem. Geol. (Isotope Geoscience Section)* 1985, **52,** 365–374

Checking Density of Phosphoric Acid

If necessary, allow the acid to cool down to room temperature and check its specific density as shown in Figure 4-10. If it is less than 1.92 g/cm^3, remove the water. Refer to topic "Removing Water from Phosphoric Acid" on page 4-18.

Figure 4-10. Checking density of phosphoric acid

Removing Water from Phosphoric Acid



Labeled components: 1=500 mL water trap, 2=phosphoric acid, 3=hot plate and magnetic stirrer, 4=vacuum pump, 5=dewar vessel for liquid nitrogen

Figure 4-11. Removing water from phosphoric acid

Figure 4-11 shows the apparatus that can be used to remove water (and absorbed gases) from phosphoric acid. Excess water is removed by freezing it in a liquid nitrogen trap under low vapor pressure. This apparatus can be used to regularly dewater prepared 95 % H_3PO_4.

Handling 99 % Phosphoric Acid

Handling during a measurement:

- Keep the phosphoric acid in a closed container within a heating cabinet at 70 °C.

Handling when no measurement is performed:

- Keep the phosphoric acid in a closed container in a heating cabinet at above 50 °C.
- Keep the phosphoric acid in a tightly closed container at 25 °C. Use Parafilm® to seal the screw cap. In case of recrystallization, carefully heat it anew and check its density.

Handling Sample Vials

The sample vials used for carbonate measurements should be free of organic and inorganic contaminations before they are loaded with carbonate. You can clean the sample vials either manually or automatically in a dishwasher.

To ensure the complete removal of all residues, consider the following recommendations for cleaning the vials:

- Never use plastic containers, only use glassware! Especially, do not use acetone in plastic bottles!
- Only use liquid detergents and no detergent in powder form.
- Use only deionized water for cleaning. Last rinsed water must be at least reversed phase water.

Manual Cleaning of Sample Vials

❖ **To clean the sample vials manually**

1. Fill up the vials with warm diluted phosphoric acid (that is phosphoric acid plus warm distilled water) and leave them for eight hours. Alternatively, put the vials into distilled water immediately after analysis.
2. Repeatedly rinse the vials with distilled water using a washing bottle. Best rinse it twice in deionized water of 70 °C.

Note You may rinse it a third time in millipore water or reversed phase deionized water (resistance ≤ 2 MΩ). ▲

3. Rinse the vials with acetone using a washing bottle, too. This helps to dry the vials faster. Acetone does not impact isotope results. This ensures removal of residual water that may contain acid-soluble minerals as well.

Note As a disadvantage, acetone always contains residues. Therefore, the vials should be dried upside down. ▲

4. Dry the vials in a drying chamber at 72 °C for one hour, if acetone was used or up to 2.5 hours, if no organic solvent was used to dry the vials. Cover them with aluminum foil to protect them against contamination.

Machine Cleaning of Sample Vials

Used sample vials can be cleaned automatically in a laboratory dishwasher made of stainless steel. The dishwasher must be connected to deionized water of high quality.

❖ **To clean the sample vials automatically**

1. Immediately after analysis, put the vials into distilled water.
2. Use automated liquid detergent dosing containing 0.5–1% of KOH or NaOH (suggested dergent: neodisher® LM3, manufacturer: Dr. Weigert; see www.drweigert.de).
3. Use automated liquid neutralization dosing containing 0.1% of acetic acid or citric acid (suggested dergent: neodisher® Z, manufacturer: Dr. Weigert; see www.drweigert.de).
4. Rinse twice. If only deionized water is available, a third manual cleaning step with at least reversed phase deionized water is mandatory.
5. Dewater the vials with acetone (acetone does not impact isotope results). However, this step is not mandatory.
6. If possible, dry the vials turned upside down.

Chapter 5 Measurement Procedures for Real Samples

This chapter outlines the measurement procedures for various common sample types. It treats the following topics:

Introduction

The scope of this section is to generally explain main applications, schematic gas flow and the headspace gas sampling procedure with GasBench II.

The GasBench II is an universal on-line interface, which allows automated isotope ratio determination of small gas samples (isotopic characterizations of CO_2 or N_2 between 200 nmol and 20 mmol of total sample size). The gas, that is CO_2, can either

- be part of the original gas sample (breathed air, for example) or
- be released from liquid or solid phase into the headspace of the sample vial by different sample preparation methods (for DIC, carbonates) or
- be added to the original water sample (equilibration).

Using a gentle stream of helium, the CO_2 in the headspace of a sample container continuously passes through a Valco sampling port. Multiple analysis is achieved by switching the contents of the sample loop into a GC column every 90 s. Each switch corresponds to starting GC separation of the sample coming from the loop.

GasBench II is supported by a Combi PAL autosampler for fully automated transfer of the gas samples which are contained in a sample tube with a septum top. GasBench II covers a large variety of application areas. The same device can be used in:

- Hydrology (determination of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ from water samples),
- Global Change Research ($^{13}C/^{12}C$ determination of dissolved inorganic carbon, DIC, from ocean water or fresh water) or
- Paleoclimatology (simultaneous $^{18}O/^{16}O$ and $^{13}C/^{12}C$ determination from carbonates of various sources).

Furthermore, it is possible to introduce traps for cryofocusing methane and other trace gases in air mixtures or to determine $^{13}C/^{12}C$ concentrations in breath gas. The abilities in equilibration of oxygen and hydrogen isotopes can widely be used in food authentification.

The GasBench II system consists of the following components:

- a user programmable autosampler
- a gas sampling system
- a maintenance-free water removal system
- a loop injection system

- an isothermal gas chromatograph (GC)
- an active open split interface
- a reference gas injection system with three reference ports
- an optional LN2 trap for cryofocusing
- an optional acid dosing system

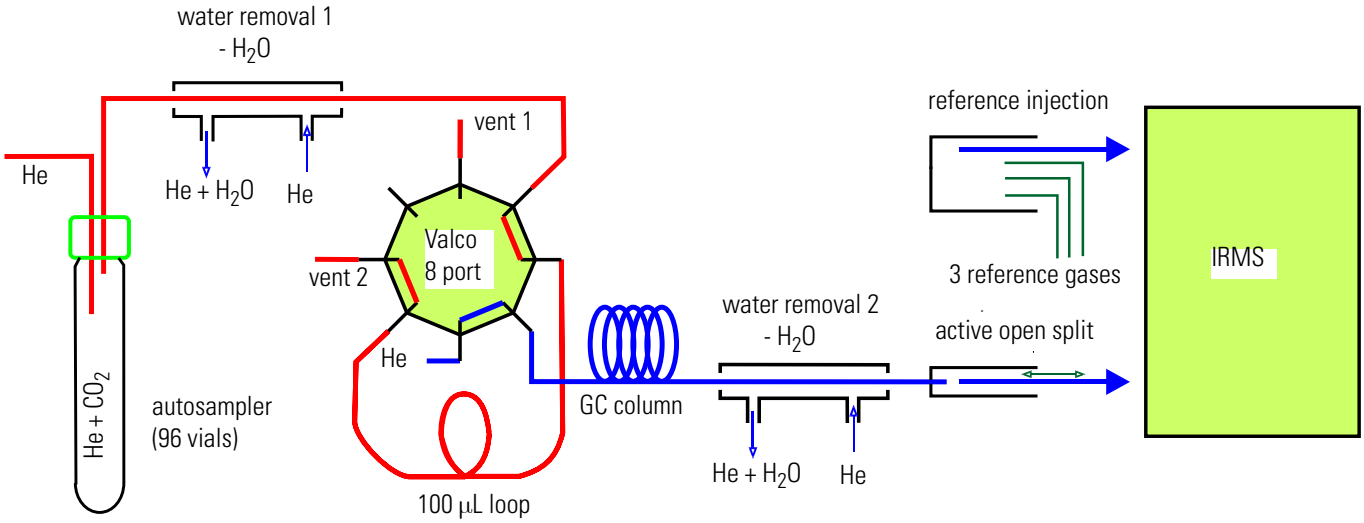


Figure 5-1. Schematic of GasBench II components

Note For a description of the basic principles of Continuous Flow, see Habfast, K.: Advanced Isotope Ratio Mass Spectrometry I: Magnetic Isotope Ratio Mass Spectrometers. Chapter 3 in: Platzner, I.T., ed., *Modern Isotope Ratio Mass Spectrometry*, 1997, p. 11-82, John Wiley & Sons Ltd. ▲

In all types of measurements the isotopic composition of a sample gas is compared to the isotopic composition of a reference gas. GasBench II consists of a reference inlet system that allows to use three different reference gases (Reference 1 or Reference 2 or Reference 3; only one of them per measurement. See Figure 3-30).

Usually, CO_2 and H_2 are choosen to cover all applications mentioned above. Reference gases are expected to be clean and stable with respect to their isotopic compositions. For a gas tank that contains a liquid phase like CO_2 this means absolute temperature stability.

The sample gas is fed into GasBench II by a specially designed headspace sampling needle. By a helium overpressure, the gas will be transported through the capillaries into GasBench II where a drying stage removes water from the sample gas mixture. Otherwise, it tends to clog the Valco valve or the mass spectrometer inlet valve.

The sample loop is filled with the analytic mixture. Refer to topic "Principle of Valco Eight Port Valve" on page 2-31. A portion of the sample gas mixture is cut from the continuous stream by switching the Valco valve to the inject position. The portion is injected into the GC column, where a separation in time between CO_2 and other gas components takes place.

To decouple the overpressure section of GasBench II from the mass spectrometer's vacuum chamber, the gas mixture passes a second water trap and enters the open split arrangement. While a fixed amount of the gas mixture travels to the mass spectrometer, the excess gas leaves the split to the surrounding atmosphere.

The different gases contained in the original mixture arrive at the mass spectrometer source separated by polarity. Using a Poraplot Q, no time difference can be detected for O_2, N_2, H_2, and He. Their travel time along the column is approximately 120 s depending on column pressure and temperature. CO_2 needs about 20 s longer, while more polar compounds like water or ethanol may travel 300 to 500 s or get stuck on the column and "bleed off" only when the column is heated.

Headspace Sampling

In standard setup that is used for equilibration, DIC, and carbonate analysis, the sample gas is taken from the headspace of a sample bottle. In all of these cases, the gas to be measured is not identical to the substance whose isotopic value should be determined. This leads to numerous complications in sample preparation, sampling technique, and results interpretation.

First of all, the isotopic abundances in the liquid phases are different from those in the gas phase. This effect is most striking when measuring hydrogen isotopic ratios: here, the abundance of the heavier isotope in the gas phase is approximately four times lower than in the liquid phase due to thermodynamic mechanisms. The abundance of this isotopic dilution effect is described by a number usually denoted as α factor.

Note The α factor for HD is 4.00 and about 1.04 for CO_2 from dissolved CO_2. Refer to Friedman, I. and O'Neill, J.R.: *Compilation of stable isotope fractionation factors of geochemical interest*. Chapter KK in: Fleischer, M., ed., Data of geochemistry, 6th ed., 1977, U.S. Geological Survey Professional Paper 440. ▲

In equilibration techniques, the gas to be measured is added to the headspace. This requires the air in the headspace to be exchanged with helium or a mixture of helium and the gas to be analyzed. It is assumed that, after some time, an isotopic equilibrium is reached between the gas

in the headspace and the molecules in the liquid. Only then, the gas mixture can be analyzed. In carbonate analysis, the gas to be measured is released from the carbonate material by adding phosphoric acid.

A similiar idea leads to DIC measurements. In both cases, the air in the headspace must be replaced prior to the reaction by helium which is inert and thus will not influence GC analysis. Measurement timing must take into consideration the times reqired for the reactions mentioned above as well as the times the autosampler needs to perform its injections. Nevertheless, one can use a single acquisition script for all analysis types.

If you take care of the reference gas settings in the method (that is the reference port setting in the Instrument tab and the reference port switching in the time events list), you can use the same method and sequence for all GasBench II standard work. It is comprehensible that acqisition script, method and sequence must satisfy the most complicated of all measurements, that is carbonate analysis.

Note Isotope ratio measurements with the GasBench II can be performed especially quickly by using short methods. Recording only a few sample peaks considerably increases the number of samples measurable per day. ▲

Carbonates

In order to measure carbonates, you need the carbonate option. Refer to topic "Carbonate Option" on page 6-2. This option contains special borosilicate vials suitable for carbonate analysis. The soda glass vials delivered with the basic GasBench II package are not suitable for carbonate analysis. Furthermore, the option contains blue exetainer caps to be used with a heated tray.

In this section, simultaneous measurement of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios in calcite, aragonite (that is, mainly $CaCO_3$) or dolomite (that is $MgCO_3$) will be covered. The latter is subject to a lot of discussion, and results should be discussed carefully. The idea is to react the carbonate species with phosphoric acid to yield CO_2 that carries an image of the isotopic value of the carbonate ion CO_3^{2-}.

Dual Needle Setup

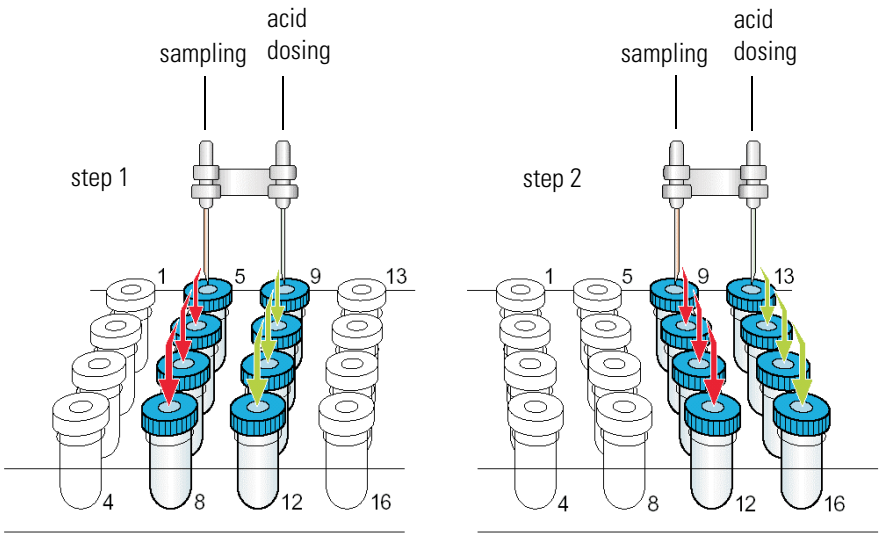


Figure 5-2. Defining the sequence - dual needle setup

The dual needle setup allows acid dosing to a sample while measuring another one. Refer to Figure 5-2, Table 5-1 and to topic "Flush Needle" on page 2-27. While the right needle transports acid to a bottle filled with helium, the left needle takes sample gas from the headspace.

Carbonates in Brief

For optimized carbonate reaction and best performance results, carbonate sampling, the measurement procedure and contaminant-free, best performed chromatograms are explained in this section.

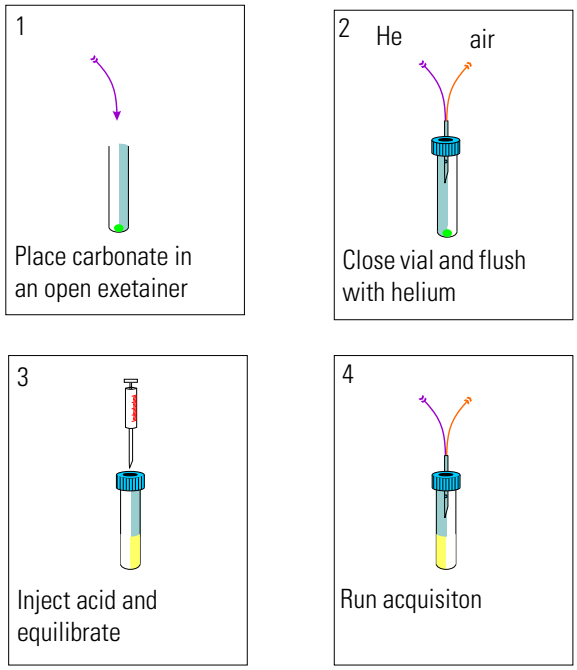


Figure 5-3. Sample preparation for carbonate measurement

❖ **To perform a carbonate measurement**

1. Heat the tray to 72 °C. This will speed up the reaction between the carbonates (that is mainly $CaCO_3$) and phosphoric acid (that is H_3PO_4) and shortens the time required to reach isotopic equlibrium.
2. Place 50-600 µg of solid, carbonate-containing sample (dolomite, calcite, foraminifera, for example) into a clean sample vial.
3. Close the vial with a new cap and a new septum.
4. Place the vials within the tray.
5. Ensure that the rinsing/filling needle is properly mounted in the autosampler.
6. Depending on your flushing needle setup, either choose the flush or dual needle flush sequence. Select the appropriate line numbers and start the sequence. By default, the sequence is set up to flush each vial with a helium stream of 100 mL for 5 min.
7. Ensure that the sampling needle is properly mounted in the autosampler.

8. Ensure that the GasBench II is absolutely free of contaminants (phosphoric acid and water in the fused silica capillaries).

Note It is strongly recommended to choose a dual needle setup (that is sample needle plus acid needle) for fully automated measurement of carbonates. This ensures proper timing of the measurement. Mount the sampling needle on the left side of the dual needle holder of the autosampler. ▲

9. Start the analysis sequence with a dual needle setup. Refer to topic "Dual Needle Setup" on page 5-6. Use the Carbonates sequence. Select the appropriate lines.

   The method used in connection with this sequence ensures that the following steps will take place:

   a. Dosage of H_3PO_4 using our automatic device. Reaction between the carbonate-containing sample and H_3PO_4 begins.[1] CO_2 will be released into the headspace.

   b. Waiting for about 1 h for equilibration of the CO_2.

   c. During measurement, helium enters the system, and a mixture of helium and CO_2 (as the sample gas) passes to the GasBench II.

Note The vials on the positions 1–9 are neither filled with carbonates nor with acid, but they will be flushed with helium. These vials are used as dummies for the sampling needle while the acid needle is dosing the phosphoric acid in vials 9 to 16.
The analysis pathway follows the positions 1–4, 9–12, 17–20 and so on. This defines a reaction time four times as large as the acquisition time for a single sample. Refer to Figure 5-2, Table 5-1, Figure 2-28 and to topic "Creating a New Sequence" on page 3-50. ▲

If everything operates properly, you should receive a result chromatogram for each sample that looks like the one shown in Figure 5-4.

---

[1] Formation of carbon dioxide from limestone

When dropping water-free phosphoric acid upon limestone (that is calcite or aragonite), phosphates of calcium, carbon dioxide and water will be formed. Possible reactions are:

$$3\ CaCO_3 + 2\ H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3\ H_2O + 3\ CO_2$$

$$CaCO_3 + 2\ H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + CO_2$$

$$CaCO_3 + H_3PO_4 + H_2O \rightarrow CaHPO_4 \cdot 2\ H_2O + CO_2$$

Notice that water is formed in each step.

Results of a Carbonate Measurement

Figure 5-4 shows the chromatogram of a typical carbonate measurement and Figure 5-5 the corresponding result grid.

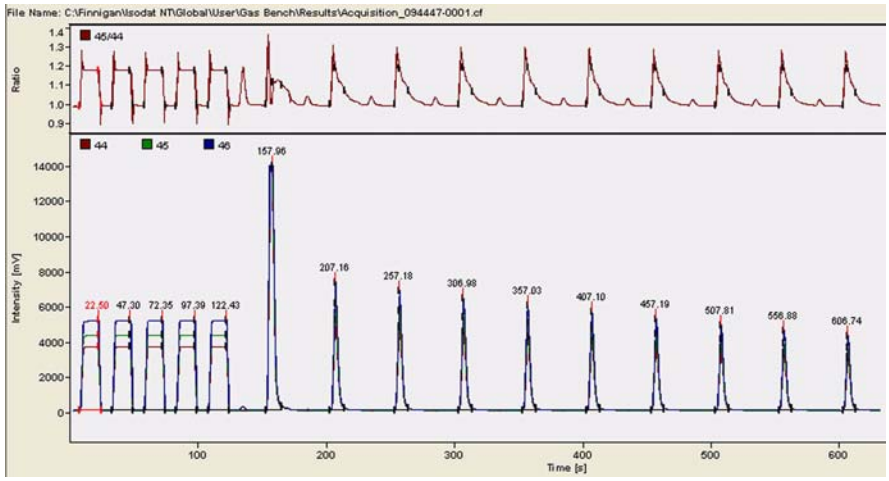


Figure 5-4. Carbonate measurement - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	End [s]	Width [s]	Ampl. 44 [mV]	BGD 46 [mV]	Area All [Vs]	d 13C/12C [per mil] vs. VPDB	d 18O/16O [per mil] vs. VSMOW
1	8.0	22.5	24.8	16.8	3635	123.1	50.505	0.204	0.331
2	33.0	47.3	49.6	16.6	3635	125.6	50.602	0.065	0.022
3	58.1	72.3	74.6	16.6	3638	126.3	50.671	-0.056	-0.122
4*	82.8	97.4	99.7	16.8	3646	126.0	50.669	0.000	0.000
5	107.9	122.4	124.7	16.8	3649	126.5	50.728	-0.063	-0.182
6	152.9	158.0	165.8	12.8	13883	127.6	58.622	-84.115	-180.865
7	203.4	207.2	214.2	10.8	5122	126.1	18.582	9.287	13.157
8	253.4	257.2	264.0	10.6	4774	125.7	17.295	9.309	13.344
9	303.2	307.0	313.8	10.6	4461	125.5	16.110	9.372	13.413
10	353.3	357.0	363.6	10.3	4187	125.0	15.011	9.561	13.610
11	403.3	407.1	413.6	10.3	3917	124.6	14.051	9.585	13.529
12	453.4	457.2	463.7	10.3	3646	124.2	13.083	9.585	13.579
13	504.0	507.8	514.1	10.1	3405	123.8	12.139	9.615	13.604
14	553.1	556.9	562.9	9.8	3184	123.4	11.288	9.705	13.643
15	603.0	606.7	612.8	9.8	2986	123.1	10.599	9.657	13.496

Figure 5-5. Carbonate measurement - result grid*

*The arrow shows the overranged peak no. 6.

- The first peak may be overranged. Due to the open split action the subsequent peaks are in range.
- Almost no signal occurs on m/z 46 between the CO_2 peaks.
- Decreasing peak height indicates proper transport of the sample/helium mixture.

Note We use the term “chromatogram“ even though it may not be a chromatogram in a narrower sense. However, one obtains ten or less repetitions of the same sample, that is of the same small chromatogram. ▲

Linearity Correction

The system GasBench II-IRMS with its different gas flows and slightly varying temperatures is never perfectly linear. To achieve the best possible result with respect to both accuracy and stability, either tune your instrument to optimal conditions in every run or apply a mathematical correction for the effects.

The effects that influence fractionation of masses by the system include temperature first of all. Temperature variations change the viscosity of helium and thereby affect flow speeds. They also change the δ value of your reference gas, if you use a pressurized CO_2 tank with a liquid phase inside.

Note Refer to Grootes, P.M., Mook, W.G. and Vogel, J.C.: Isotopic fractionation between gaseous and condensed carbon dioxide. Zeitschrift für Physik **221**:257-273 (1969). ▲

Experiment-to-experiment variations of fractionation occur, if you tune the source or change the timing of the acquisition. More reasons for applying corrections to the signal-to-δ value-scale and to the measured-to-real δ value-scale can easily be found. This topic, “Linearity Correction“, covers the relationship between measured δ value and signal height. The relationship between measured δ value and real δ value will be covered at topic “Referencing vs. VPDB” on page 5-13.

Table 5-1 shows an uncorrected result, that is raw data from a series of measurements of the same sample.

Table 5-1. Raw data example to illustrate linearity correction

Position	Bottle number	Weight	Average area	$\delta^{13}C$	$\delta^{18}O$
1	dummy sample	0	11.40	-39.332	-5.838
2	dummy sample	0	16.46	-39.662	-0.380
3	dummy sample	0	11.58	-39.401	-1.342
4	dummy sample	0	17.38	-39.532	-2.523
9	CaCO3 Merck	100	12.53	-30.292	-12.049
10	CaCO3 Merck	41	3.63	-29.885	-12.154
11	CaCO3 Merck	39	3.57	-30.083	-12.219
12	CaCO3 Merck	112	9.96	-30.333	-12.171
17	CaCO3 Merck	77	7.18	-30.198	-12.070

Table 5-1. Raw data example to illustrate linearity correction, continued

Position	Bottle number	Weight	Average area	$\delta^{13}C$	$\delta^{18}O$
18	CaCO3 Merck	188	19.02	-30.350	-12.054
19	CaCO3 Merck	80	6.29	-30.193	-12.192
20	CaCO3 Merck	34	3.42	-30.196	-12.277
25	CaCO3 Merck	72	6.82	-30.199	-12.296
26	CaCO3 Merck	139	13.63	-30.340	-12.230
27	CaCO3 Merck	176	15.19	-30.381	-12.170
28	CaCO3 Merck	147	15.11	-30.390	-12.107
33	CaCO3 Merck	38	3.16	-30.155	-12.250
34	CaCO3 Merck	78	6.52	-30.316	-12.386
35	CaCO3 Merck	142	12.93	-30.374	-12.208
36	CaCO3 Merck	67	5.78	-30.330	-12.373
41	CaCO3 Merck	36	3.69	-30.356	-12.370
42	CaCO3 Merck	48	5.14	-30.130	-12.157
43	CaCO3 Merck	12	0.51	-29.484	-12.100
44	CaCO3 Merck	311	32.57	-30.449	-11.849
49	CaCO3 Merck	52	5.29	-30.501	-12.250
50	CaCO3 Merck	303	32.99	-30.394	-11.827
51	CaCO3 Merck	48	4.06	-30.289	-12.235
52	CaCO3 Merck	26	2.14	-30.309	-12.211
57	CaCO3 Merck	143	13.47	-30.474	-12.196
58	CaCO3 Merck	108	10.79	-30.437	-12.205
59	CaCO3 Merck	48	2.55	-30.292	-12.346
60	CaCO3 Merck	201	9.84	-30.445	-12.097
65	CaCO3 Merck	21	1.58	-30.411	-12.387
66	CaCO3 Merck	57	5.64	-30.323	-12.340
67	CaCO3 Merck	250	25.03	-30.474	-12.035
68	CaCO3 Merck	235	24.41	-30.511	-12.031
73	CaCO3 Merck	86	9.23	-30.441	-12.149

If you plot the δ value versus the peak area or the peak amplitude, which is strictly proportional to it, a graph like the one shown in Figure 5-6 will be obtained.

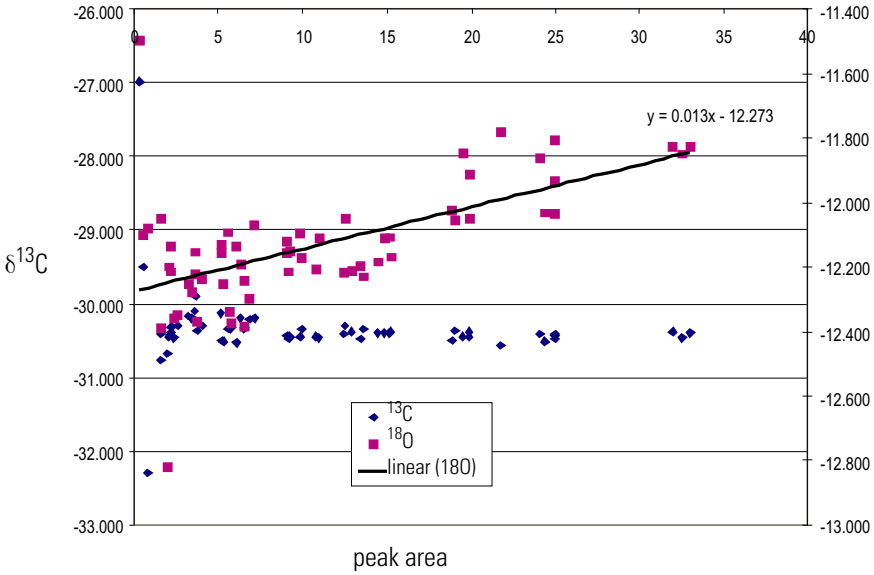


Figure 5-6. Measured δ value versus peak area for a set of measurements*

*same sample but different sample amounts

Experience teaches that the functional dependence between δ value and peak area (or peak amplitude) always is a linear one. Thus, within the statistical error limits all results are distributed along a line with a small slope. The slope is small (0.013 ‰/Vs for $^{18}O/^{16}O$ and 0 ‰/Vs for $^{13}C/^{12}C$ in the example above), but depends on all of the the factors mentioned above. The following correction procedure is recommended:

The correction can be approximated by a linear function δ_{meas} (A):

$$\delta_{meas} = m \times A + \delta_{real}$$

δ_{meas} denotes the measured δ value, δ_{real} the real one. *A* describes the peak area.

Determine the correction factor *m*, that is the slope, from reference samples (that is working standards) by plotting the measured δ value for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ δ_{meas} versus peak area or peak amplitude.

The correction factor δ_{real} must be evaluated from absolute standards (IAEA). For an explanation in detail refer to topic "Referencing vs. VPDB" on page 5-13.

To achieve proper results you need to include working standards in your sequence of measurements. It is absolutely necessary to keep all possible sources of fractionation constant during the sequence. The reference samples (that is working standards) should be well distributed in the sample tray. To obtain a proper estimate for the slope, sample amount should vary. Furthermore, this procedure allows quality control during the entire data acquisition.

Referencing vs. VPDB

All carbonate δ values must be referenced to the international standard VPDB (Vienna Pee Dee Belemnite), the successor of PDB as PDB is exhausted. However, VPDB with $\delta^{13}C = 0$ and $\delta^{18}O = 0$ as one would expect, does not exist. Instead, standards exist which are related to this virtual, that is unreal definition. See Table 7-7.

Note Refer to "Reference and intercomparison materials for stable isotopes of light elements". In: IAEA-TECDOC-825, IAEA, ed., Vienna, 1995. ▲

At present, there are a couple of primary standards available from IAEA and NIST, respectively, with given δ values for $^{18}O/^{16}O$ and $^{13}C/^{12}C$. To determine the actual δ value of a sample relative to VPDB, measure standard and sample under the same conditions and perform the following procedure:

1. Determine the δ value of your working standard.
2. Calibrate versus known standards supplied by IAEA or NBS.
3. Use a primary standard to determine the δ value of the reference gas.
4. With *x* meaning working standard and *z* denoting VPDB, the following equation is valid. Refer to topic "Remark on the Strange Mathematics of δ Values" on page 5-15:

$$\delta_z^x = \frac{\delta_y^x \cdot \delta_z^y}{1000} + \delta_y^x + \delta_z^y$$

and

$$\delta_z^y \neq \delta_y^z$$

with:

x working standard
y gas
z absolute standard, that is VPDB

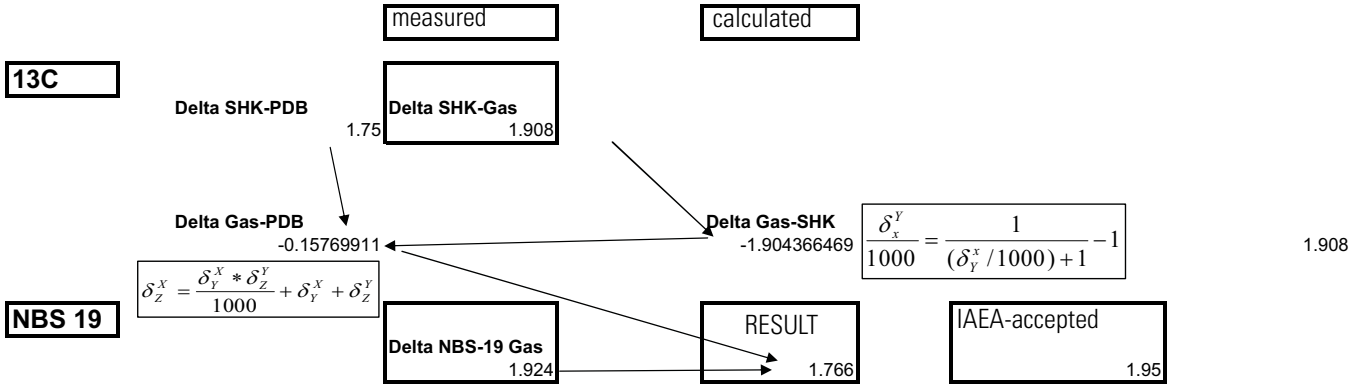


Figure 5-7. Calculation example*

*SHK designates Solnhofen limestone.

Figure 5-7 depicts an example for obtaining δ values specified against VPDB starting from measured and corrected δ values.

The examples comprises the following steps:

1. Determine absolute δ value of the primary standard.
   In this example:

$$\delta_{PDB}^{SHK} = 1.750$$

2. Invert the measured value for primary standard versus gas used:

$$\delta_{Gas}^{SHK} = 1.908$$

Thus:

$$\delta_{SHK}^{Gas} = -1.903$$

3. Determine the absolute δ value of the gas used today with the aid of the equation:

$$\delta_z^x = \frac{\delta_y^x \cdot \delta_z^y}{1000} + \delta_y^x + \delta_z^y$$

Thus:

$$\delta_{PDB}^{Gas} = -0.157$$

4. Use this value and any measured sample δ vs. reference gas to calculate the δ value of sample vs. PDB with the aid of:

$$\delta_z^x = \frac{\delta_y^x \cdot \delta_z^y}{1000} + \delta_y^x + \delta_z^y$$

Thus:

$$\delta_{\text{PDB}}^{\text{NBS 19}} = 1.767$$

In this case, the result is incorrect.

Remark on the Strange Mathematics of δ Values

The δ definition:

$$\delta_y^x = \left(\frac{R_x}{R_y} - 1\right) \cdot 1000$$

with:

$\delta^x{}_y$ **δ** value of x against y
R_x raw ratio of x (that is A_{13}/A_{12})

can be rearranged:

$$\frac{R_x}{R_y} = \frac{\delta_y^x}{1000} + 1$$

As x and y are only arbitrary notations and thus can be interchanged, an analogous equation for $\delta^y{}_x$ can be written:

$$\frac{R_y}{R_x} = \frac{\delta_x^y}{1000} + 1$$

Considering reciprocity:

$$\frac{R_y}{R_x} = \frac{1}{(R_x / R_y)}$$

Combination of both equations yields the relationship between $\delta^x{}_y$ and $\delta^y{}_x$ we were aiming at:

$$\frac{\delta_x^y}{1000} = \frac{1}{\frac{\delta_y^x}{1000} + 1} - 1$$

This shows indeed:

$$\delta_x^y \neq \delta_y^x$$

The δ definition results in the following rule when calculating a δ value with an intermediate result, which is always the case when referencing to a gas or a working standard:

$$\delta_z^x = \left(\frac{R_x}{R_z} - 1\right) \cdot 1000 = \left(\frac{R_y \cdot R_x}{R_y \cdot R_z} - 1 - \frac{R_y}{R_z} + \frac{R_y}{R_z} - \frac{R_x}{R_y} + \frac{R_x}{R_y} - 1 + 1\right) \cdot 1000$$

$$\delta_z^x = \left(\frac{R_y \cdot R_x}{R_y \cdot R_z} - \frac{R_y}{R_z} - \frac{R_x}{R_y} + 1 + \frac{R_y}{R_z} + \frac{R_x}{R_y} - 1 - 1\right) \cdot 1000$$

$$\delta_z^x = \left(\left(\frac{R_x}{R_y} - 1\right) \cdot \left(\frac{R_y}{R_z} - 1\right) + \left(\frac{R_x}{R_y} - 1\right) + \left(\frac{R_y}{R_z} - 1\right)\right) \cdot 1000$$

$$\delta_z^x = \frac{\delta_y^x \cdot \delta_z^y}{1000} + \delta_y^x + \delta_z^y$$

This equation has been used above (special case: working standard x, absolute standard z, that is VPDB). Refer to topic "Referencing vs. VPDB" on page 5-13.

Ion Correction

The isotopic composition of a compound A is expressed by its δ value, δ_A,

$$\delta_A = 10^3 \cdot \left(\frac{R_A}{R_{ST}} - 1\right)$$

Here, δ_A is given in ‰. R_A denotes the isotope ratio of compond A and R_{ST} the defined isotope ratio of a standard sample.

Examples

Here, the ion correction for carbon is given for the masses m/z 44, m/z 45 and m/z 46.

1. Carbon[2]

$$\delta^{13}C = 10^3 \cdot \frac{(^{13}C/^{12}C)_{SA} - (^{13}C/^{12}C)_{ST}}{(^{13}C/^{12}C)_{ST}}$$

[2]As usual, the index SA refers to sample and the index ST to standard.

2. Oxygen (measured as CO_2)[2]

$$\delta^{18}O = 10^3 \cdot \frac{(^{18}O/^{16}O)_{SA} - (^{18}O/^{16}O)_{ST}}{(^{18}O/^{16}O)_{ST}}$$

For CO_2, the IRMS measures the 45/44 and 46/44 ratios. M/z 45 comprises $^{13}C^{16}O_2$ as well as $^{12}C^{17}O^{16}O$, so that the 45/44 ratio is different from the ratio $^{13}C/^{12}C$ by a correction regarding the ratio $^{17}O/^{16}O$ in the sample or standard. Therefore,

$$R_{45} = \frac{^{13}C^{16}O_2 + ^{12}C^{17}O^{16}O}{^{12}C^{16}O_2} = \frac{^{13}C}{^{12}C} + 2 \cdot \frac{^{17}O}{^{16}O} = R_{13} + 2 \cdot R_{17}$$

In this equation, the definitions

$$R_{45} = \frac{\text{signal (m/z 45)}}{\text{signal (m/z 44)}}$$

and

$$R_{13} = \frac{\text{isotopic abundance (m/z 13)}}{\text{isotopic abundance (m/z 12)}}$$

(similarly for R_{17} etc.) are used.

Ion correction routines must be applied to the measured ratios in order to account for the additional ion species contributing to the measured ratios. Likewise, other ion species must be subtracted from the 46/44 ratio for oxygen in CO_2, the 65/64 and 66/64 ratios for sulfur, and the 34/32 ratio for elemental oxygen[3].

The ^{17}O correction applied in Isodat follows the suggestions given by Santrock and coworkers[4] with:

$$R_{17} = K \times R^a_{18}$$

using a = 0.516 and K = 0.0099235.

The δ values of the working standard against an international standard must be known.

[3]H. Craig: Isotopic standards for mass spectrometric analysis of carbon dioxide. Geochimica Cosmochimica Acta, **12** (1957) 113-140.

[4]J. Santrock, S.A. Studley and J.M. Hayes: Isotopic analyses based on the mass spectrum of carbon dioxide. Analytical Chemistry, **57** (1985) 1444-1448.

Common Pitfalls

In this section, some failures possible with GasBench II are described. You are responsible for cleanliness of all lines and leak-tightness. The GasBench II allows long time highest performance. It is explained how a chromatogram of GC Poraplot gas separation looks like using the GasBench II. The addition of a chromatogram - visual as one - allowing peaks from the first injection to appear under the injection chromatogram of the third one, is outlined.

Retention Times

Whenever the user needs to create or modify the methods used for any of the possible applications, the timing of the injection events becomes important. In order to understand the required timing, you need to understand how the substances injected to the chromatographic column (a Poraplot Q is used as default) behave. As a general statement substances are delayed relative to the carrier gas (usually helium) while travelling along the column. This delay is called retention time, and on a Poraplot Q column the retention is higher, if the substance is more polar.

In Figure 5-8 you see a sample chromatogram for a Poraplot Q chromatographic column. Retention times are given for several substances, for example ethanol has a retention time of 3.73 min, equal to 224 s. It is important to keep in mind that retention times are strictly temperature and flow dependent. The retention time for ethanol in the example below is given at a column temperature of 150 °C. Other column temperatures cause other retention times.

In general, lower temperatures yield higher retention times. As an extreme, if the temperature is below a certain limit, the substance may not leave the column. This is the case for instance for water, if the column temperature is 21 °C.

composition of test mixture:
1.0 % of each component in methanol

Peak No.	Ret. time [min]	Component
1	3.73	ethanol
2	5.28	acetone
3	6.77	diethylether
4	7.18	n-pentane
5	12.24	ethylacetate
6	15.70	n-hexane

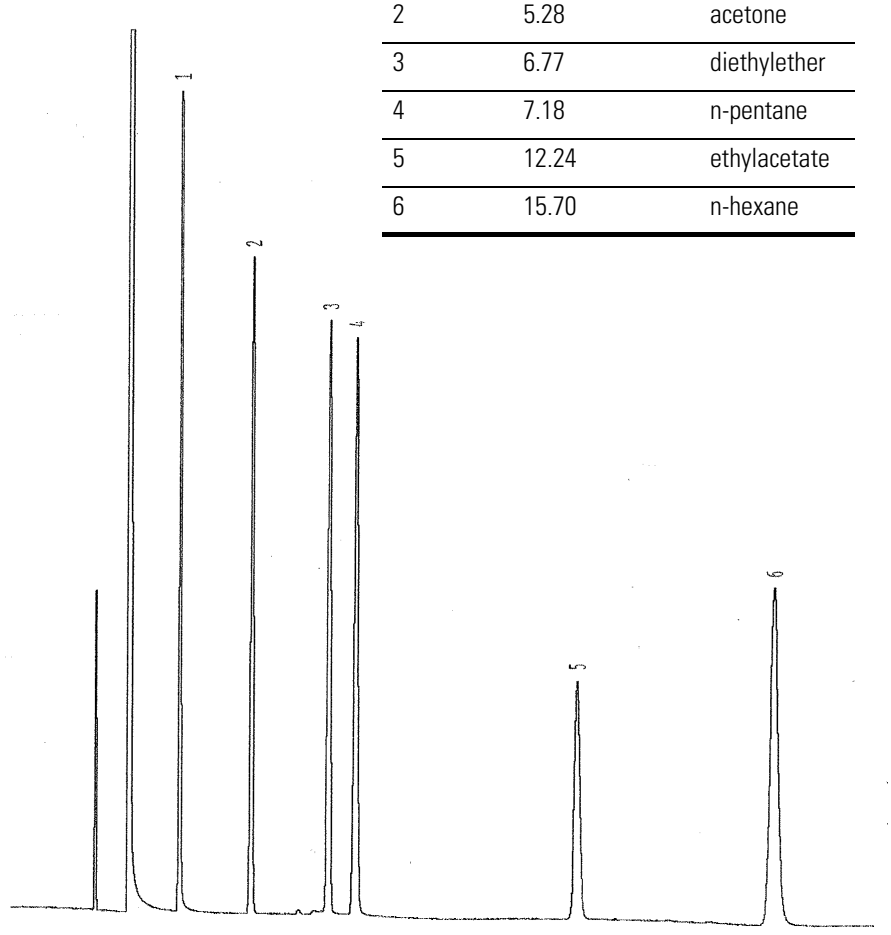


Figure 5-8. Sample chromatogram for Poraplot Q column

The substances that are of interest in GasBench II applications, namely CO_2, H_2O, Ar, O_2 and N_2, have much shorter retention times than the methanol given above. Under the normal conditions that we set in the GasBench II - that is flow 1.5 mL/min and temperature 70 °C - O_2 and N_2 arrive in the mass spectrometer about 120 s after the injection. CO_2 arrives after 150 s.

If water is present in the substance mix in the loop, it will arrive after about 300 s. The situation is complicated furthermore by the repeated loop injection that is normally performed to enhance the accuracy of the measurement. This repeated loop injection causes the peaks to “stack” in the chromatogram thus sometimes hiding important impurities. This is outlined in Figure 5-9 which shows combined chromatograms.

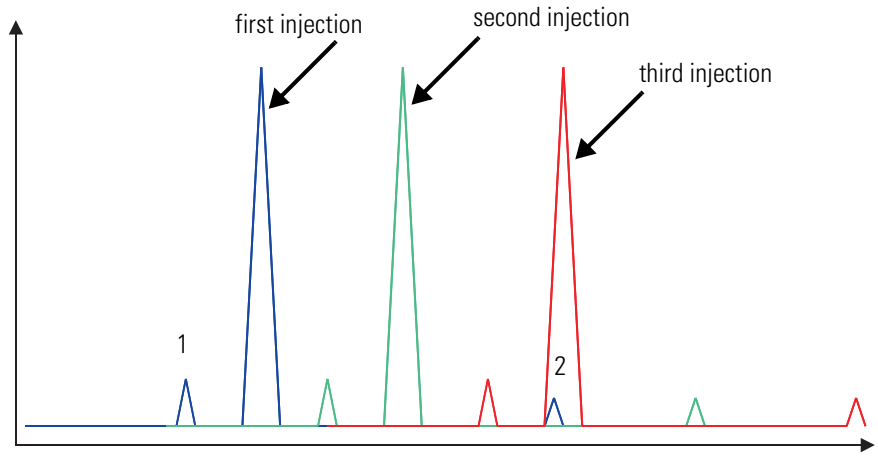


Figure 5-9. Upon retention times - combining chromatograms

The following features are then typical for the chromatogram:

1. Air peak precedes CO_2. See pos. 1 in Figure 5-9.
2. Water peak may follow CO_2 but must not interfere with CO_2. See pos. 2 in Figure 5-9.
3. Additional peaks, for example due to solvents, must not interfere with CO_2.

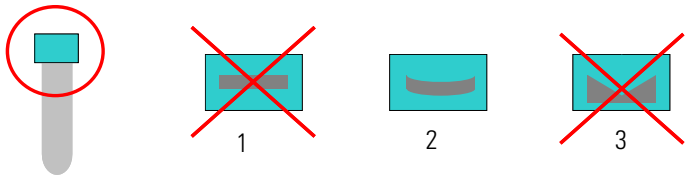
Wasting Acid

Due to improper adjustment of the acid pump, acid drops may be deposited on the septa. If so, acid can enter the sample needle and travel towards the Valco valve.

Caution Acid entering the sample needle must be avoided under all circumstances! Severe damage to water trap and Valvo valve will result! Refer to topic “Acid Pump Adjustment” on page 6-5. ▲

Handling Septa

Ensure that the sample vials are screwed down correctly in order to be really closed. See Figure 5-10.



Labeled components: 1: will not be leaktight, 2: fits correctly, 3: will develop fissures and tends to be cut by the needle

Figure 5-10. Correct handling of septa

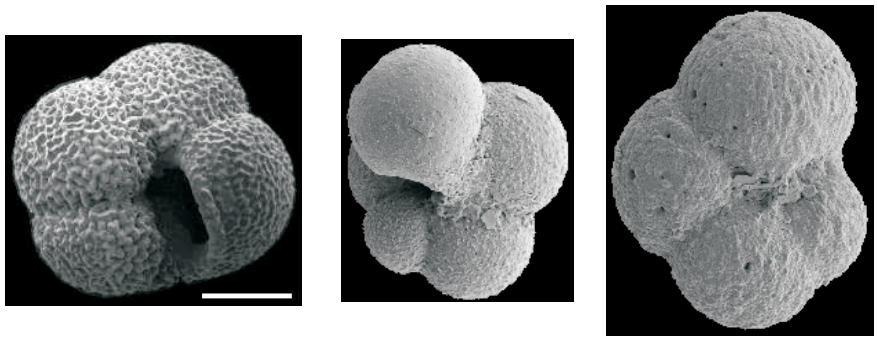
Water Condensation beneath Septa

During equilibration, when tray temperature is only slightly above room temperature, water vapor condenses benath the septa. This effect is unavoidable and usually poses no problem. Once the septa have been punctured by the needle, these water droplets accumulate to one large drop. If now this particular vial will be measured again, there is a significant chance to pick up this drop. This results in water travelling towards water trap and Valco valve, possibly clogging the system.

Note Therefore, never measure equilibrated samples twice! ▲

Neogloboquadrina Pachyderma (Ehrenberg, 1894)

Neogloboquadrina pachyderma is the most abundant planktonic foraminifer of high latitudes. See Figure 5-11. As any planktonic foraminifer, it avoids low-salinity and shallow waters. The left-coiled morphotype prevails at lowest temperatures and occurs throughout the Arctic Ocean.



Left-coiled specimen, umbilical view, scale bar 0.1 mm

Right-coiled (dextral) specimen, umbilical view

Left-coiled (sinistral) specimen, umbilical view

Figure 5-11. Neogloboquadrina pachyderma

Dissolved Inorganic Carbon (DIC)

Dissolved Inorganic Carbon (DIC) is of large interest for global carbon cycle research, metabolic research and carbon flux studies of different water sources. The isotope ratio determination of DIC helps to identify and quantify processes within those different scientific areas.

Dissolved Inorganic Carbon (DIC) in Brief

The preparation of DIC samples for $^{13}C/^{12}C$ isotope ratios with GasBench II is explained briefly in this section. The preparation prior to phosphoric acid reaction is performed in different ways. Each of these ways have different advantages and disadvantages:

1. Field collection of DIC samples and poisoning in the field.

   Store the samples in destinated sample vials. Add a sample to a preflushed sample vial containing phosphoric acid in the laboratory. See Figure 5-12.

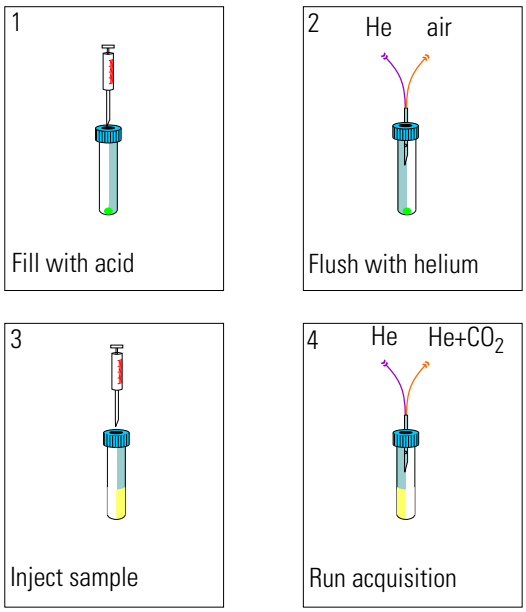


Figure 5-12. Sample preparation for Dissolved Inorganic Carbon (DIC) measurement

2. Field collection of DIC samples in helium-preflushed sample vials adding phosphoric acid to the samples in the field

The disadvantage of the first method is the poisoning with $HgCl_2$. An advantage is the stopping of any bacterial degradation changing the original isotopic $^{13}C/^{12}C$ ratio of DIC.

The second approach has the advantage of clean analysis, but implies the possibility of biological degradation, if the analysis in the laboratory is not performed fast enough.

When real samples are collected, they must be poisoned using a saturated $HgCl_2$ solution to stop all biological activity.

Warning Danger of Poisoning! Strictly avoid any exposure to the severely toxic $HgCl_2$! Always wear protective gloves. Refer to your supplier's Material Safety Data Sheet (MSDS) for proper handling. ▲

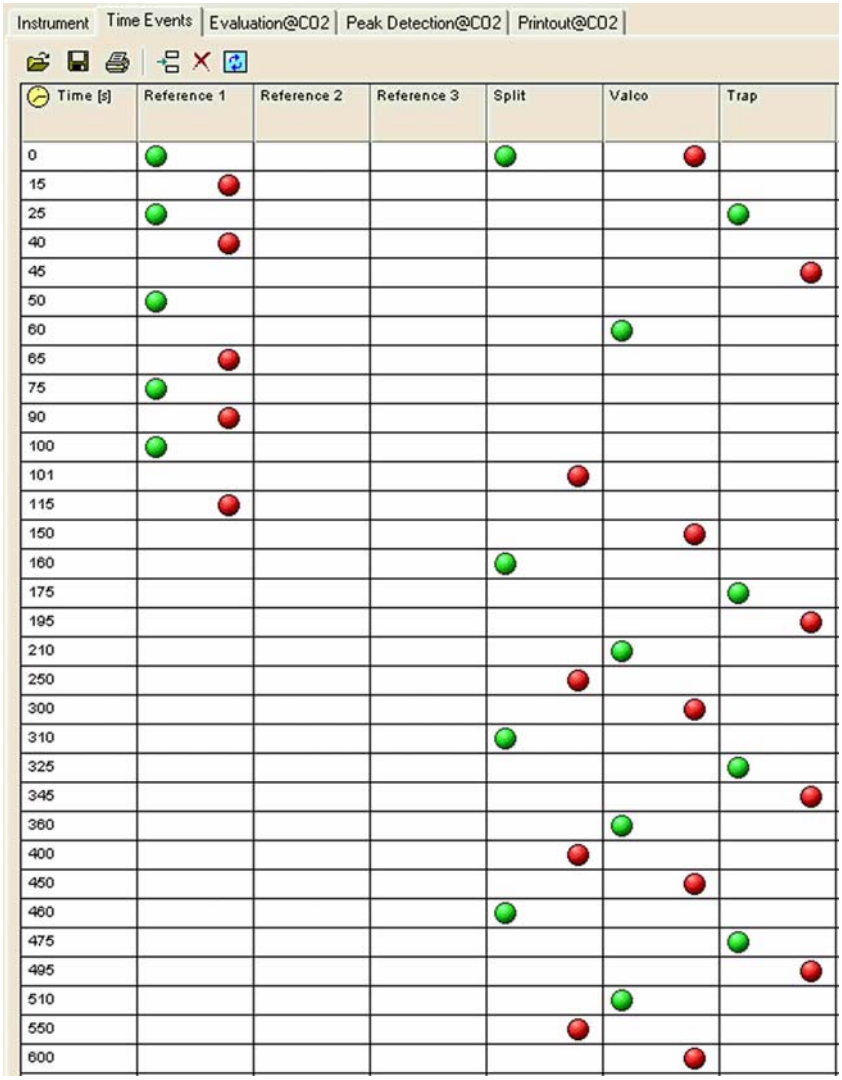


Figure 5-13. Dissolved Inorganic Carbon (DIC) measurement - time events list (partly)

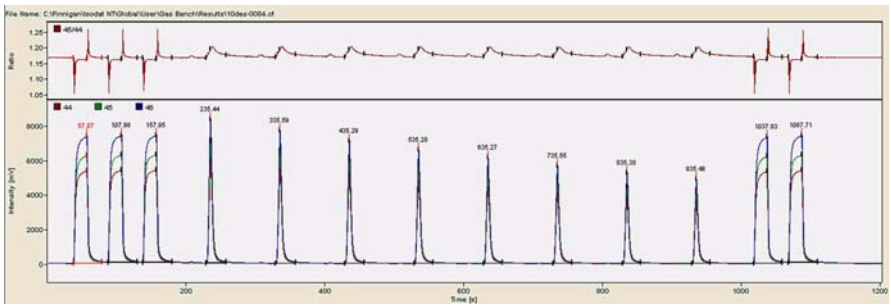


Figure 5-14. Dissolved Inorganic Carbon (DIC) measurement - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 46 [mV]	BGD 44 [mV]	Area All [Vs]	δ 13C [‰] vs. VPDB	δ 18O [‰] vs. VSMOW
1	38.1	57.9	41.8	5383	7357	43.1	100.161	-28.539	0.083
2	88.2	108.0	42.3	5370	7340	89.7	101.763	-28.626	-0.047
3*	138.1	157.9	42.5	5370	7340	96.4	100.966	-28.620	0.000
4	229.7	235.4	29.0	5925	8323	55.7	33.485	1.036	27.156
5	329.5	335.6	28.5	5464	7668	41.9	31.039	1.127	27.216
6	429.3	435.3	28.0	5064	7102	38.4	28.932	1.155	27.113
7	529.2	535.3	27.7	4684	6577	36.4	26.994	1.118	27.151
8	629.2	635.3	27.2	4357	6115	35.0	25.197	1.044	27.074
9	729.3	735.5	27.0	4038	5671	33.8	23.410	1.025	26.957
10	829.3	835.4	26.5	3745	5256	32.8	21.745	1.027	26.790
11	929.4	935.5	26.0	3478	4883	31.9	20.256	0.966	26.710
12*	1018.3	1037.8	41.3	5367	7337	32.1	98.588	-28.620	0.000
13	1068.2	1087.7	42.0	5367	7342	82.2	100.776	-28.763	-0.192

Figure 5-15. Dissolved Inorganic Carbon (DIC) measurement - result grid

In the following section, common pitfalls with the preparation of DIC samples prior to analysis with the GasBench II are discussed.

- Almost no signal occurs on m/z 46 between the CO_2 peaks.
- Decreasing peak height indicates proper transport of sample/helium mixture.

Caution When filling a number of tubes from the same water standard, do not fill them from a sealed vessel with septum. A negative pressure will be created that could cause fractionation. ▲

Caution When filling real samples, use a new syringe for each sample. When running standards for acceptance tests, a single syringe is sufficient. Care must be taken to allow any ocean water to remain on the inside of the septum! ▲

Note Wipe the outside of the needle prior to puncturing the septum. When filling the flushed vial with ocean water, do not puncture the septum in the center, but close to the edge. ▲

If samples are stored for a longer period (that is for several months), only use large sample amounts (above 100 mL). This avoids isotopic fractionation due to evaporation. Carefully close the bottles using parafilm. Avoid headspaces filled with air and store them in a cooler at 4 °C.

To maintain water as a working standard stable in isotopic composition over a longer time, it has been proven useful to store them in large canisters. Use at least a 50 L stainless steel barrel and vent it using only dry inert gas, N_2, for example. It is not dissolved in the water and thus the CO_2 content will not change.

❖ **To perform a DIC measurement (see** Figure 5-12**)**

1. Fill some drops (about 30 µL) of 45 % to 98 % H_3PO_4 into an empty vial. Refer to topic "Preparing Phosphoric Acid" on page 4-17 for instructions on how to prepare phosphoric acid as well.

   For DIC measurements, smaller concentrations of H_3PO_4 can be used, simplyfying the addition of H_3PO_4 into the vials.

2. Close the vial and place it in the tray.

3. Exchange the headspace (that is via the needle, helium streams in and replaces the gas in the vial, which in turn streams out of it).

4. Inject the sample (about 700 µL) through the septum into the closed vial using a syringe. CO_2 will be released from these different origins and will then be mixed with the helium in the headspace.

Note A syringe must be used to prevent the sample from contacting and exchanging with ambient air. ▲

5. Allow 18 h to equilibrate.

6. Finally, the sample will be measured.

Referencing Strategies for DIC

For referencing the $^{13}C/^{12}C$ isotope ratios of working standards and samples to the international VPDB scale, different analytical procedures exist.

a. Analysis of a solid carbonate standard (NBS 19 or working standard carbonate material) prior to analysis of DIC samples. For the working standard, baking powder ($NaHCO_3$, pro analysis) can be used.

b. Running a working standard as a DIC standard (dissolved in deionized water; remove CO_2 via ultrasonification). The working standard will be prepared in different concentrations to make an area correction of the $^{13}C/^{12}C$ ratios of samples possible. Refer to topic "Carbonates" on page 5-6. The concentration must reflect the DIC concentration range of the samples.

Note The liquid $NaHCO_3$ will be prepared before each analysis to avoid contamination of the standard $NaHCO_3$ with CO_2 coming from atmospheric air. ▲

Note For different bicarbonates, different $^{13}C/^{12}C$ acid fractionation factors exist. ▲

Breath Gas Analysis

Isotopic analysis of breath CO_2 has important applications in physiology, ecology and medicine. $^{13}C/^{12}C$ of CO_2 in breath (breath gas analysis) helps identifying *Helicobacter pylori* and is used in metabolic research. *Helicobacter pylori* is one of the major elicitors to cause stomach ulcer and stomach cancer.

To detect the occurrence of *Helicobacter pylori*, ^{13}C-labelled urea is given to the patient. Demethylization of the bacteria is detected in the ^{13}C-enriched CO_2 of breath. The $\delta^{18}O$ of CO_2 reflects $\delta^{18}O$ values of body water. It matches the $\delta^{18}O$ of drinking water or from food sources (fruits with high water content).

Using Autodiluter for Blanking

The atmospheric mixture used here contains lots of nitrogen and oxygen that severely distort operation of the source when reaching the inlet. To avoid this, the autodiluter arrangement has been modified to guarantee extreme dilution.

❖ **To obtain the modification**

1. Loosen the two screws
2. Move the small metal plate that limits the movement of the autodiluter's pneumatic lever fully upwards. See arrows in Figure 5-16.

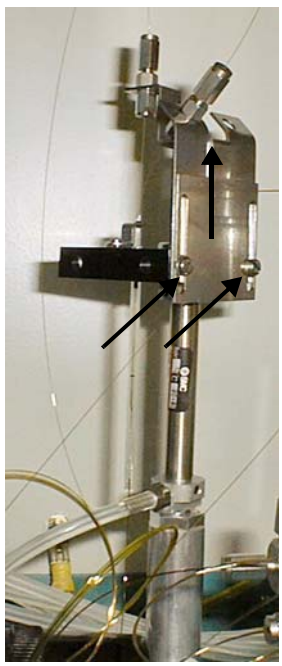


Figure 5-16. Adjusting open split for blanking

Additionally, the capillary feeding the split with helium needs to be retracted into the inner glass tube. See Figure 5-16 and Figure 5-17.

When unlimited in movement, the lever moves the capillary leading from the autodiluter to the IRMS into the inner tube of the autodiluter. In this position, the capillary samples almost entirely helium, and the dilution factor is larger than 100.

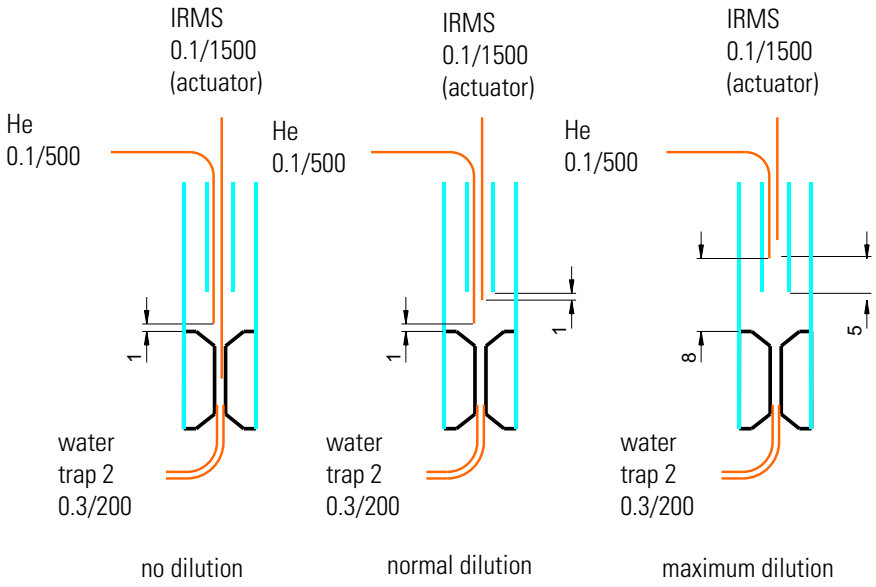


Figure 5-17. Principle of blanking

Results of Blanking

The retraction of the IRMS capillary into the inner glass tube results in an almost 100 % dilution of the sample gas signal with helium. In Figure 5-18 and Figure 5-19, the chromatogram and the respective result grid are shown, if a 100 % dilution is applied.

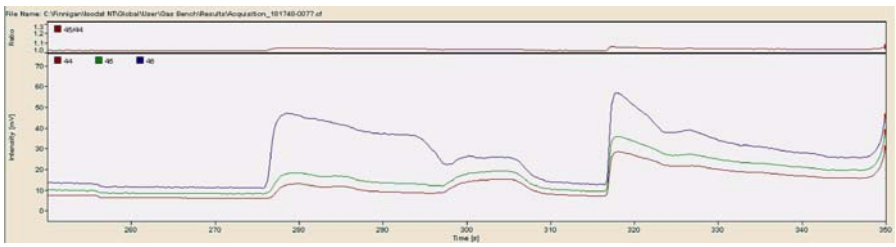


Figure 5-18. Blanking - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 46 [mV]	BGD 46 [mV]	Area All [Vs]	δ 13C [‰] vs. VPDB	δ 18O [‰] vs. VSMOW
1	6.8	21.1	18.6	6597	9.1	66.551	0.322	0.188
2	31.6	46.1	18.9	6605	13.6	67.624	0.189	0.074
3	56.6	71.2	18.9	6601	14.9	67.769	0.026	0.053
4*	81.7	96.2	18.6	6610	15.3	67.713	0.000	0.000
5	106.7	121.3	18.6	6619	15.6	67.673	-0.042	-0.034
6	199.7	203.8	10.6	12952	21.4	19.841	16.942	33.333
7	350.0	355.0	10.1	10263	25.6	17.249	17.131	33.472
8	499.9	504.2	9.6	9202	24.8	15.067	17.109	33.565
9	650.0	654.0	9.4	8699	22.8	13.425	17.255	33.646
10	799.8	803.5	9.3	8502	20.8	12.137	17.210	33.574
11	950.1	954.7	9.6	6300	19.1	10.877	17.375	33.612
12	1100.3	1104.5	9.1	6070	19.3	9.859	17.384	33.503
13	1247.8	1251.6	8.6	5622	18.3	8.494	17.308	33.666

Figure 5-19. Blanking - result grid

Blanking with Sample Open Split of New Design

Another possibility to perform blanking is the use of one of the Flush ports. Refer to topic "Connecting Flush Needle" on page 2-27.

Connect a capillary (ID = 0.3 mm) to the Flush port and feed it into the sample open split instead of the original capillary (0.1/500; see Figure 7-5). Set the appropriate time events Flush Fill on and off instead of moving the split in and out as given in Figure 5-23.

Breath Gas Analysis in Brief

To perform breath gas analysis, the sample loop of the Valco valve must be replaced by a 10 µL volume. Refer to topic "Changing Loop Size" on page 2-32.

❖ **To perform a breath gas analysis**

1. Fill empty sample vials with breath using a straw.
2. Close them with a fresh cap and septum. Place them in the sample tray.
3. Perhaps, you should modify the method as descibed in topic "CO_2 in Atmospheric Concentrations" on page 5-31.
4. A sequence of its own is not necessary. Instead, use the equilibration sequence Equilibration.seq to perform a measurement.

Results of Breath Gas Analysis

For breath gas analysis, the GasBench II chromatogram looks different from a normal chromatogram for equilibration or carbonate measurements. Blanking is used, and therefore N_2O gas (production in the ion source coming from N_2 in air) or breath is removed.

High water contents in breath may result in less precision of $\delta^{18}O$ in CO_2 results, if water is not quantitatively removed. Adding a magnesium perchlorate tube helps to quantitatively remove breath water.

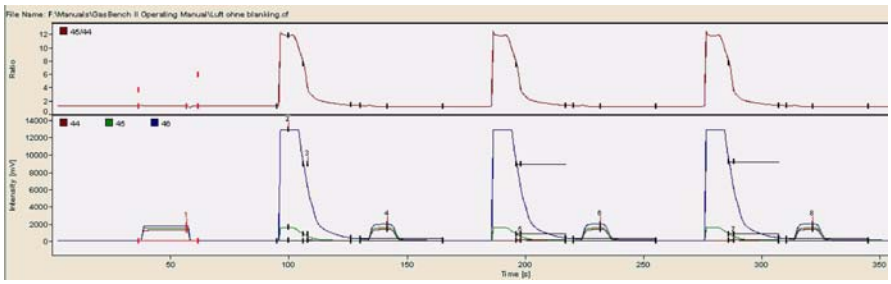


Figure 5-20. Chromatogram of plain analysis (without blanking)

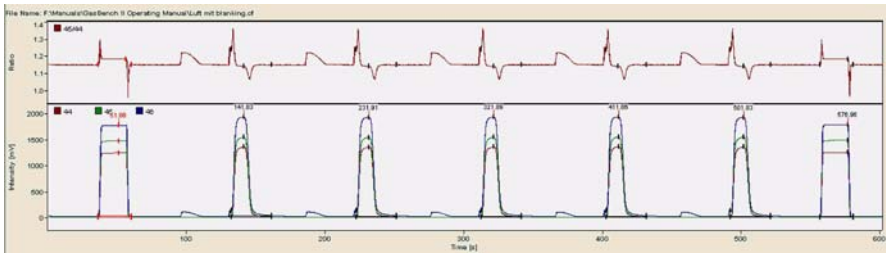


Figure 5-21. Chromatogram of analysis (with blanking activated)

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	BGD 44 [mV]	BGD 45 [mV]	BGD 46 [mV]	Area All [Vs]	δ 13C [‰] vs. VPDB	δ 18O [‰] vs. VSMOW	AT% 13C [%]
1*	37.0	51.9	23.9	1245	3.6	4.1	21.8	25.085	-3.489	-18.360	1.101843
2	132.8	141.8	29.1	1357	3.4	3.8	21.0	14.849	-43.652	4.258	1.057905
3	222.8	231.9	29.2	1355	3.3	3.7	20.2	14.812	-43.777	3.993	1.057768
4	312.8	321.9	29.2	1357	3.2	3.7	19.7	14.823	-43.692	3.526	1.057861
5	402.9	411.9	29.0	1362	3.2	3.6	19.0	14.908	-43.651	2.817	1.057906
6	492.7	501.8	28.9	1356	3.2	3.6	18.6	14.842	-43.626	3.213	1.057933
7*	557.1	577.0	23.9	1256	3.9	4.4	18.6	25.243	-3.489	-18.360	1.101843

Figure 5-22. Result grid of analysis (with blanking activated)

Note Take into account the different ordinate scales when comparing Figure 5-20 and Figure 5-21. ▲

CO_2 in Atmospheric Concentrations

The analysis of $\delta^{13}C$ of CO_2 in air is to measure different flux rates of CO_2 coming from different carbon sources in the environment. It is largely used for keeling plots and for example for eddy correlation studies.

Editing a Method

To measure CO_2 in atmospheric concentrations, create a method and save it under a reasonable name, for example Acquisition 630s mod for air.met.

Note The method differs only with respect to the Time Events list from Acquisition 630s.met used for carbonate measurements. ▲

Select it from the Methods tab of the File Browser. Then, double-click or drag and drop it into the Acquisition window of Isodat. Refer to topic "Predefined Methods as Examples" on page 3-19 and to topic "Creating a New Method" on page 3-18.

Time Events Tab

Similar to breath gas analysis, blanking is used to avoid production of N_2O. Refer to topic "Breath Gas Analysis" on page 5-27.

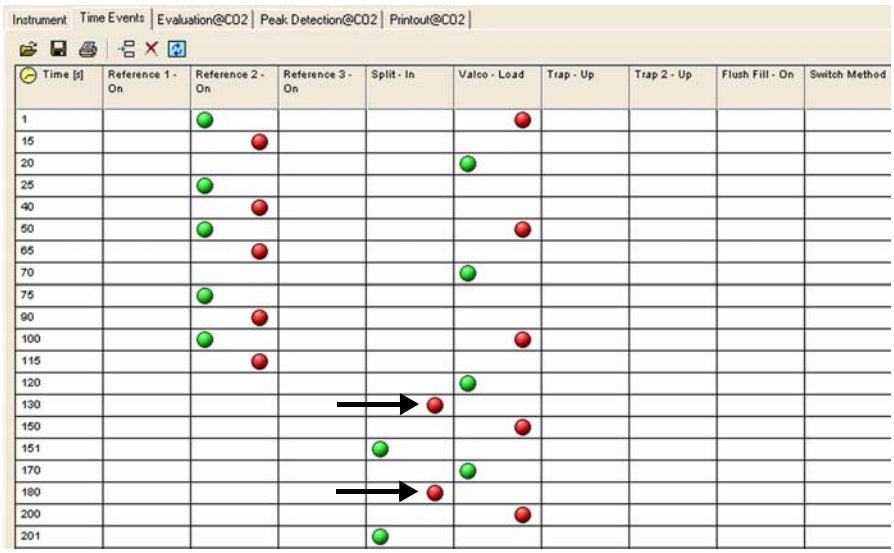


Figure 5-23. CO_2 in atmospheric concentrations - time events list using blanking

Note Note the differences compared with the Time Events list of Acquisition 630s.met used for carbonate measurements:

Whenever you expect an air peak in the chromatogram, it must be masked out. This is achieved by setting the split to dilution position, that is off in the Split-In column during these time intervals. The split will thus move upwards, that is it is pulled out causing dilution.

Setting the split on, in the Split-In column will stop dilution. The split will be pushed in again. This ensures that most of the sample can be measured. Overall, this change between on and off positions takes place ten times. ▲

Figure 5-24. CO_2 in atmospheric concentrations - time events list - Acquisition

Results

Using the Time Events list will result in a chromatogram without air response (N_2O, for example). See Figure 5-25 and Figure 5-26.

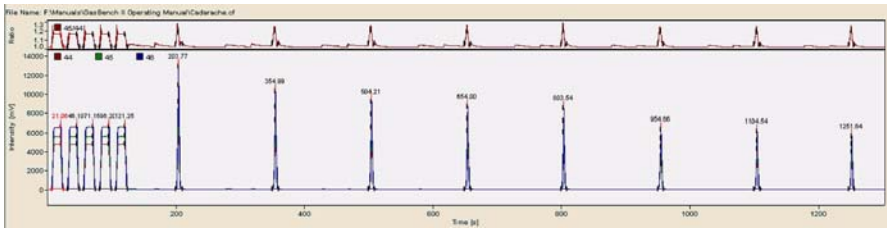


Figure 5-25. CO_2 in atmospheric concentrations - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 46 [mV]	BGD 46 [mV]	Area All [Vs]	δ 13C [‰] vs. VPDB	δ 18O [‰] vs. VSMOW
1	6.8	21.1	18.6	6597	9.1	66.551	0.322	0.188
2	31.6	46.1	18.9	6605	13.6	67.624	0.189	0.074
3	56.6	71.2	18.9	6601	14.9	67.769	0.026	0.053
4*	81.7	96.2	18.6	6610	15.3	67.713	0.000	0.000
5	106.7	121.3	18.6	6619	15.6	67.673	-0.042	-0.034
6	199.7	203.8	10.6	12952	21.4	19.841	16.942	33.333
7	350.0	355.0	10.1	10263	25.6	17.249	17.131	33.472
8	499.9	504.2	9.6	9202	24.8	15.067	17.109	33.565
9	650.0	654.0	9.4	8699	22.8	13.425	17.255	33.646
10	799.8	803.5	9.3	8502	20.8	12.137	17.210	33.574
11	950.1	954.7	9.6	6300	19.1	10.877	17.375	33.612
12	1100.3	1104.5	9.1	6070	19.3	9.859	17.384	33.503
13	1247.8	1251.6	8.6	5622	18.3	8.494	17.308	33.666

Figure 5-26. CO_2 in atmospheric concentrations - result grid

Water Equilibration ($^{18}O/^{16}O$ Equilibration)

This section outlines water equilibration ($^{18}O/^{16}O$ equilibration).

$^{18}O/^{16}O$ Equilibration in Brief

❖ **To perform an $^{18}O/^{16}O$ equilibration**

1. Fill the sample into the clean open exetainer vial (10 mL) by using an adjustable pipette with disposable pipette tips. It is not necessary to pierce the septum using the needle. The filling volume should be 0.5 mL.
2. Close the vial and place it into the autosampler tray.
3. The flushing gas is a mixture of He and CO_2, that usually has already been properly mixed and filled into a He/CO_2 tank. Open the He/CO_2 tank connected to the flush gas input.
4. Increase the pressure to result in a flow of the He/CO_2 mixture of approximately 100–150 mL/min at the vent of the flush needle. When using a new gas mixture, wait for 10–15 min until all the lines are completely filled with this new mixture, that is until it is ensured that the former gas mixture has been completely exchanged with the new one.

Note The flush needle is sometimes synonymously called flushing needle, rinsing needle, or filling needle. Accordingly, one speaks of flush valve and flush connection. ▲

5. Ensure that the flush needle is properly mounted in the autosampler.
6. Depending on your hardware, use the flush sequence or the dual needle flush sequence to fill the vials automatically. By default, the sequence is set up to flush each vial with a helium stream of 100 mL for 5 min. Refer to topic "Creating a New Sequence" on page 3-50.
7. Close the He/CO_2 mixture tank when the flush sequence is finished.
8. Wait for approximately 18 h for proper equilibration.
9. Start the measurement sequence. Refer to topic "Creating a New Sequence" on page 3-50.

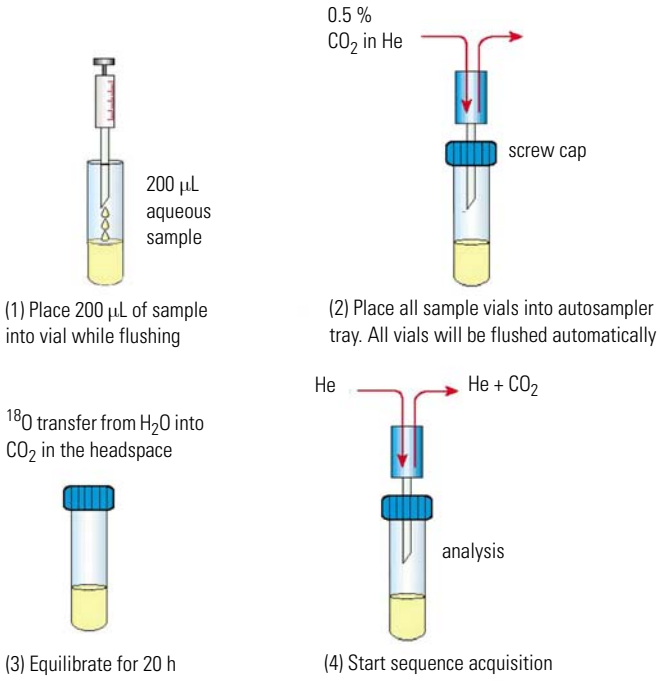


Figure 5-27. Sample preparation for $^{18}O/^{16}O$ equilibration

Note Salt water needs to be equilibrated for a maximum of 2-5 days to improve accuracy of sample results. ▲

Temperature Control of Sample Tray

For high precision $^{18}O/^{16}O$ equilibration, the temperature of the sample tray needs to be stabilized. Two operation modes are available:

- Passive tray at room temperature, that is 21 °C

  The thermal mass of the cast aluminum tray and its isolation allow keeping the temperature control of the tray deactivated. Only long-term drifts in tray temperature will occur within a certain time interval. Placing reference samples allows correcting for possible temperature drifts (one reference sample for six unknown samples, for example).

- Active temperature control at 24 °C

  Ensure that room temperature is approximately 5 °C below the set tray temperature. Check the temperature stability over several hours. The controller readout may not alter by more than 0.1 °C.

Referencing versus VSMOW

Referencing can be performed either using the complete and precise mathematical pathway outlined in topic "Carbonates" on page 5-6 or using the simplified scheme given in topic "Water Equilibration ($^{2}H/^{1}H$ Equilibration)" on page 5-36.

Note Refer to Reference and intercomparison materials for stable isotopes of light elements. In: IAEA-TECDOC-825, IAEA, ed., Vienna, 1995. See also Table 7-7. Also refer to Nelson, S.T.: A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. Rapid Communications in Mass Spectrometry **14**:1044-1046 (2000). John Wiley & Sons Ltd.. ▲

Results

This section shows a typical chromatogram and result grid of a water equilibration ($^{18}O/^{16}O$).

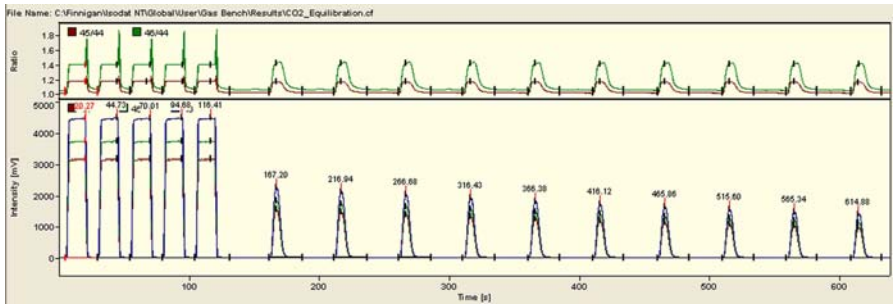


Figure 5-28. Water equilibration ($^{18}O/^{16}O$) - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Rt [s]	Width [s]	Ampl. 44 [mV]	BGD 44 [mV]	BGD 45 [mV]	BGD 46 [mV]	Area All [Vs]	R 45CO2/44CO2	d 13C/12C [per mil] vs. VPDB	d 18O/16O [per mil] vs. VSMOW
1	20.3	24.7	3168.949	8.261	9.853	13.342	45.741	0.0119844	-0.0404715422	-0.0247573364
2	44.7	25.1	3172.385	8.261	9.853	13.342	46.454	0.0119848	-0.0049358485	-0.0271250732
3	70.0	24.7	3162.652	8.261	9.853	13.342	46.106	0.0119846	-0.0193904556	-0.0185544341
4*	94.7	25.1	3175.371	8.261	9.853	13.342	46.452	0.0119849	0.0000000000	0.0000000000
5	116.4	27.0	3174.137	8.261	9.853	13.342	46.171	0.0119847	-0.0148408892	0.0355349526
6	167.2	25.5	1558.924	10.026	11.930	16.165	9.362	0.0120095	1.2898437380	24.8855176293
7	216.9	25.7	1474.518	9.898	11.790	15.890	8.873	0.0120101	1.3322078285	25.0623807066
8	266.7	25.1	1402.154	9.747	11.593	15.696	8.406	0.0120106	1.3767898590	25.1197961709
9	316.4	24.9	1328.000	9.621	11.475	15.481	7.964	0.0120098	1.3009168171	25.1052293560
10	366.4	24.2	1260.666	9.556	11.396	15.345	7.555	0.0120093	1.2616982998	25.0541138496
11	416.1	23.8	1194.149	9.483	11.269	15.184	7.162	0.0120103	1.3478018448	25.0422751081
12	465.9	24.2	1135.574	9.385	11.185	15.013	6.809	0.0120081	1.1514021328	25.0579538020
13	515.6	24.2	1075.597	9.304	11.069	14.915	6.456	0.0120102	1.3427602406	24.9632988890
14	565.3	23.2	1019.809	9.254	10.998	14.690	6.118	0.0120095	1.2709751780	25.3041357725
15	614.9	23.4	965.837	9.152	10.891	14.630	5.801	0.0120090	1.2395511347	24.9201001991

Figure 5-29. Water equilibration ($^{18}O/^{16}O$) - result grid

Water Equilibration ($^2H/^1H$ Equilibration)

This section outlines water equilibration ($^2H/^1H$ equilibration).

$^2H/^1H$ Equilibration in Brief

In case of any hydrogen equilibration, perform the following steps keeping the tray at room temperature. Refer to topic "Temperature Control of Sample Tray" on page 5-34.

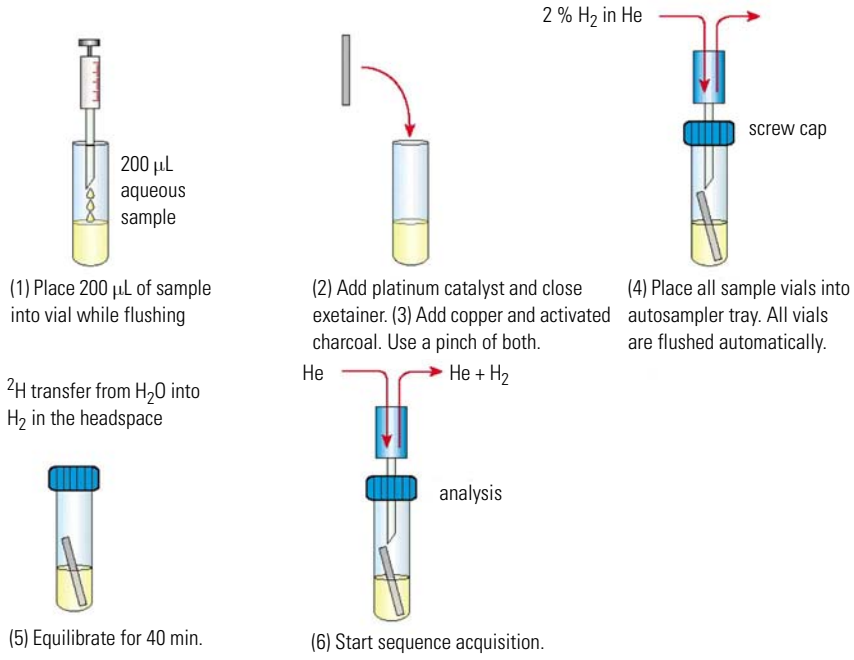


Figure 5-30. Sample preparation for $^2H/^1H$ equilibration

❖ **To perform a hydrogen equilibration**

1. Insert the sample into vials and insert the catalytic platinum sticks. Refer to topic "Catalyst for Hydrogen Equilibration" on page 6-26 for a description of the catalyst.

   This is done to avoid formation of H_2S and to remove adsorbed water molecules on dissolved organic carbon (DOC). Activated charcoal adsorbs dissolved organic carbon (DOC).

2. Flush all samples with 2 % H_2 in helium. Run a flushing sequence. Refer to topic "Creating a New Sequence" on page 3-50. The equilibration is finished within 40 min. It is not necessary to wait additional time.

3. Exchange the rinsing needle with the sampling needle. There are various needle sets using the same needle type: one set of needles exists for flushing (that is rinsing needle) and another one for measuring (that is sampling needle). The rinsing needle is used to rinse the vials: the recurrent capillary must be broken off at 20 cm to let the rinsing agent pass into ambient air. In case of the sampling needle, the recurrent capillary leads into the GasBench II.

4. Run a mesurement sequence. Refer to topic "Creating a New Sequence" on page 3-50.

Note The addition of activated charcoal and copper pieces increases the accuracy of results. ▲

Note Salt water needs an increased equilibration time. ▲

Preparing an $^2H/^1H$ Measurement

This section outlines how to prepare a $^2H/^1H$ measurement.

Preparing an $^2H/^1H$ Method

When preparing a method for $^2H/^1H$ equilibration, choose **Low pass filtered** background. In case of $^2H/^1H$ equilibration, this background algorithm yields better results than the **Individual** background algorithm recommended for CO_2 measurements.

H_3 Factor

Due to timing considerations, the H_3 factor needs to be corrected. Experience shows that correcting the H_3 factor by 0.5 units is sufficient in most cases. Determine the exact value by reevaluating whole sequences with the goal to minimize internal errors.

Adjust Hydrogen Calibration

We provide no special procedure to adjust the mass scale for $^2H/^1H$ measurements. Instead, you must set the calibration manually.

❖ **To adjust the hydrogen calibration**

1. Switch the reference H_2 on.
2. Set the mass spectrometer to approximately 1000 magnet steps.
3. Press the right mouse button on the magnet steps value.
4. Select **Pass to Gas Configuration**.

5. Force the IRMS to jump to m/z 2 for instance by changing the Gas Configuration to **CO2** and back to **H2**.
6. Carefully adjust the magnet steps value to hit the peak center and repeat the last two steps.
7. The setting is precise enough, if the jump finds 50% of peak intensity.

From now on, the IRMS will always correctly jump to m/z 2 and m/z 3.

Adjust Reference Signal Height

To achieve optimal performance it must be possible to set the reference signal height to 8 V. Therefore, it is necessary to cut the flow restricting capillary by 30% from its original length.

Note Ask your service engineer upon installation of GasBench II to do this. ▲

Referencing versus VSMOW

When performing water equilibration with its larger error bars and accuracy requirements compared to carbonate measurements, it is possible to use a simplified calculation scheme.

Note Refer to Nelson, S.T.: A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. Rapid Communications in Mass Spectrometry 14:1044-1046 (2000). John Wiley & Sons Ltd.. ▲

This eliminates the need to worry about the water-to-gas fractionation factor α as well as using the complicated δ value equations explained in topic "Remark on the Strange Mathematics of δ Values" on page 5-15.

❖ **To reference versus VSMOW**

1. Assume you measured the following values for the two primary standards VSMOW and SLAP and one sample GISP. See Table 5-2.

Table 5-2. Values of VSMOW, SLAP and GISP

Standard	Measured value	Accepted value (IAEA)
VSMOW	- 650	0
SLAP	- 757	- 428
GISP	- 697	- 189.73

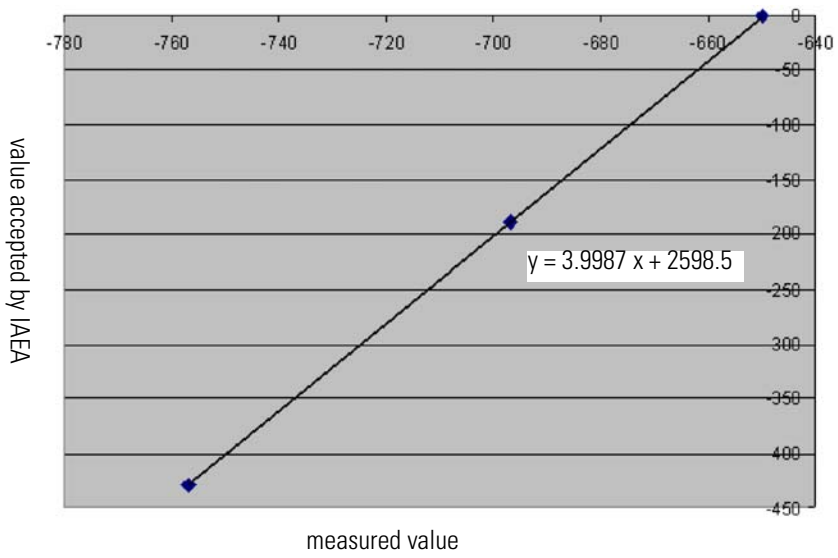


Figure 5-31. Measured δ values vs. accepted values

2. Plot the measured δ values versus the accepted values (IAEA) as given in the example above (Figure 5-31).

3. Determine a trend line that fits the two primary standards, in this case:

$$\text{accepted value (IAEA)} = 3.99 \times \text{measured value} + 2598.5$$

4. From this equation deduce the accepted values of the samples. In this case, GISP would yield a value of 188.59 which is fairly good compared to the accepted value given above.

Adjusting Electron Energy

If the ionization energy (electron energy) is set to above 100 eV, doubly charged He ions (that is He^{2+}) are formed in the ion source. Because they have a significant mass difference to H_2^+ (Δ_m = 0.5%), their presence leads to peak shape distortion. See Figure 5-32. Setting the electron energy below 100 eV considerably prevents He^{2+} formation.

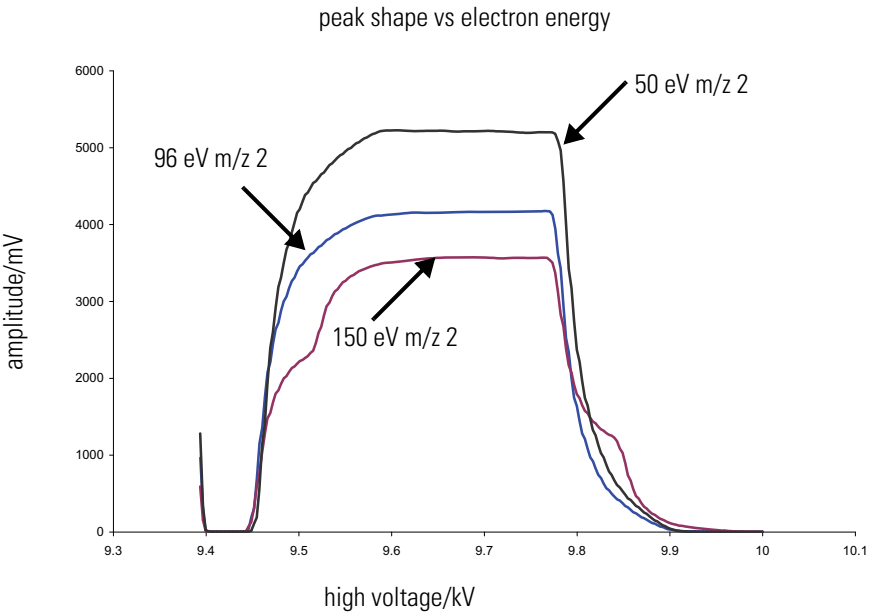


Figure 5-32. Peak shape scan for m/z 2 under different electron energy conditions

Determining Optimal Setting of Electron Energy

❖ **To achieve the optimal setting of the electron energy**

1. Perform a peak center with reference on.
2. Switch the reference off.
3. Record the signal intensity on m/z 2 versus the electron energy. See Figure 5-33.

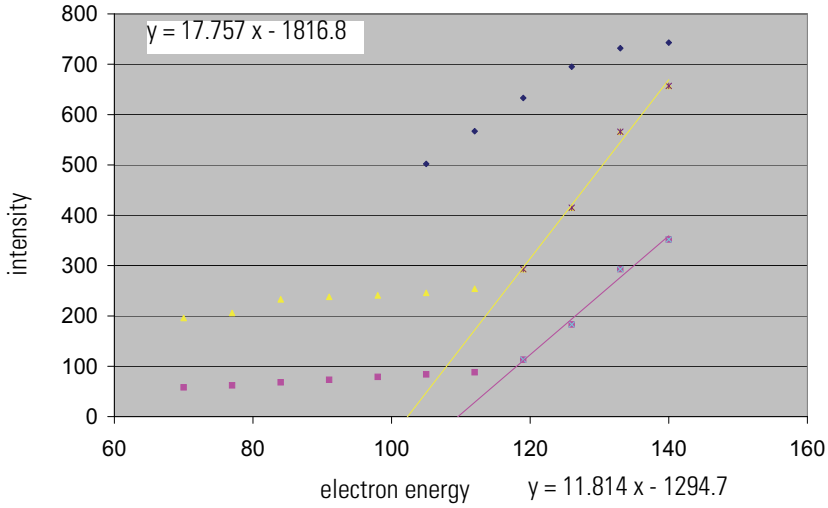


Figure 5-33. Signal intensity on m/z 2 vs. electron energy

The optimal setting is just below the appearance of the He^{2+} signal, where the sensitivity for H_2 is optimal.

Note For further information, refer to Field, F.H. and Franklin, J.L.: Electron Impact Phenomena, pp. 244, 1957, Academic Press. ▲

Results

Figure 5-34 shows a sequence line for water equilibration (H/D). In Figure 5-35 and Figure 5-36, the corresponding chromatogram and the result grid are depicted, respectively.

H2 | Error | Extended | Sequence Line

Line		AS Sample	AS Method	Identifier 1	Identifier 2	Comment	Method
13	✓	25	>Internal No 9	H2_Equilibration-empty-vial	HDBroenst	200ul	GB_H2\H2_sample-zero-on-off.met

Figure 5-34. Water equilibration (H/D) - sequence line

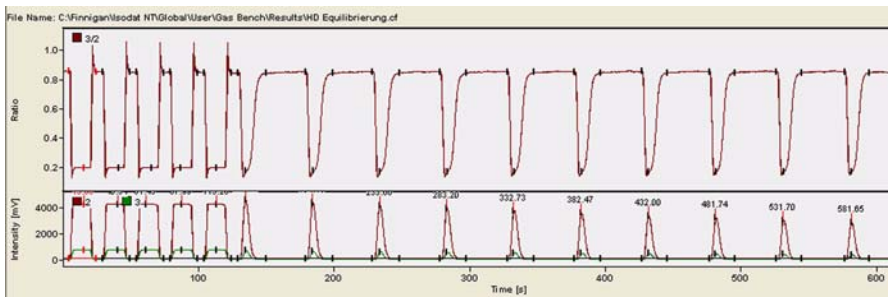


Figure 5-35. Water equilibration (H/D) - chromatogram

H2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 2 [mV]	Ampl. 3 [mV]	BGD 2 [mV]	BGD 3 [mV]	Area All [Vs]	d 2H/1H [per mil] vs. VSMOW
1	4.6	15.9	20.1	4163.104	678.629	94.704	66.291	59.664	-704.6292876581
2	29.5	40.3	20.1	4159.171	676.948	96.253	66.865	60.420	-705.1174246827
3	54.3	61.4	20.1	4154.121	675.990	96.758	66.943	60.376	-705.0888370417
4*	79.2	88.0	20.1	4158.018	676.808	97.134	67.019	60.434	-705.0000000000
5	104.3	113.3	19.9	4165.310	678.561	97.471	66.941	60.066	-705.0231499927
6	129.6	134.6	20.3	4507.296	628.112	97.663	66.742	22.137	-771.3099704087
7	179.1	184.1	20.3	4302.290	589.089	96.221	66.853	20.998	-772.1366049160
8	228.6	233.7	19.6	4087.487	549.124	95.936	66.796	19.852	-771.9840873102
9	278.2	283.2	19.9	3871.657	510.392	95.763	66.633	18.744	-771.9223315247
10	327.9	332.7	19.9	3667.605	475.314	95.618	66.431	17.696	-771.3439768402
11	377.7	382.5	19.0	3470.959	442.071	95.509	66.329	16.672	-771.0606303511
12	427.2	432.0	19.0	3287.745	411.110	95.425	66.363	15.753	-771.7245158400
13	476.9	481.7	18.8	3111.868	382.983	95.330	66.395	14.914	-771.6717305681
14	526.7	531.7	18.8	2949.896	357.793	95.322	66.503	14.139	-772.4198754619
15	576.8	581.6	18.4	2790.626	333.125	95.202	66.484	13.461	-772.0906609478

Figure 5-36. Water equilibration (H/D) - result grid

Sample Amount Considerations for Both Water Equilibration Types

In this section, the sample amount needed for both types of water equilibration is estimated via an approximate calculation. It helps to decide whether a mass balance calculation needs to be performed for a particular sample or not.

Depending on how much gas of a particular δ value has been filled into the headspace and how much water has been added to the sample (δ value unknown), a final δ value between these two original δ values will result.

Remember that 1 mol of water equals 18 mL and 1 mol of an ideal gas commensurates to 22.4 L.

One sample vial contains 12 mL, that is 12/22400 mol $\approx 5.357 \times 10^{-4}$ mol of an ideal gas. We do not use pure CO_2, but 0.5 % CO_2 in He and consider this mixture to be an ideal gas. Therefore, one sample vial contains (12/22400) × 0.005 mol $CO_2 \approx 2.679 \times 10^{-6}$ mol CO_2.

Let us return to the water: 1 mL of water equals 1/18 mol of water. Using 1 mL of sample in the sample vial yields 10000 times more oxygen atoms in the water phase compared to the gas phase.

As a good estimation, we can therefore assume the isotope value of the gas to be equal to the initial isotope value of the sample. This means, the isotope value will not shift, but the gas will indeed take the original value of the sample. Thus, using 1 mL (or 500 µL or 200 µL) of sample, no mass balance calculation is required.

Operating GasBench II with ConFlo IV

This topic outlines how to connect and operate the GasBench II with the ConFlo IV.

The ConFlo IV is a universal continuous flow interface to a DELTA series or MAT 253 IRMS. It has two high-flow sample gas connection ports (for EA) and one low-flow sample gas connection port (for a GasBench II or a GC).

It is equipped with three sample gas dilution systems in order to adjust the sample gas signal. Five reference gas ports are permanently connected for referencing. This allows automated H_3 factor determination and linearity tests of different gases. Refer to the *ConFlo IV Operating Manual*, P/N 1224730, for further details.

Note Until now, the GasBench II in combination with the ConFlo IV is not a launched product. Only advanced users shall connect the GasBench II to the ConFlo IV. The GasBench II in combination with the ConFlo IV is not supported by Thermo Fisher Scientific. Thermo Fisher Scientific assumes no responsibility and will not be liable for any failure that might result from any improper GasBench II to ConFlo IV installation, even if the information in this Operating Manual is followed properly. ▲

Connecting GasBench II to ConFlo IV

To install the ConFlo IV itself and for its preinstallation requirements, refer to the *ConFlo IV Operating Manual*, P/N 1224730.

When assembling the hardware, establish the sample gas connection to the ConFlo IV. The ConFlo IVmust already be in operation.

The GasBench II must be connected to the low-flow port of the ConFlo IV. The “sample dilution 1” step of the automated sample gas dilution procedure replaces the formerly known autodilution of the GasBench II.

❖ **To connect the GasBench II to the ConFlo IV**

1. Close the needle valve of the GasBench II sample and reference capillaries.
2. Cut the sample capillary that connects the water trap 2 to the sample open split (see Figure 5-3). Use a press-fit to connect the 0.32 mm ID fused silica capillary to the water trap 2. See Figure 5-37.

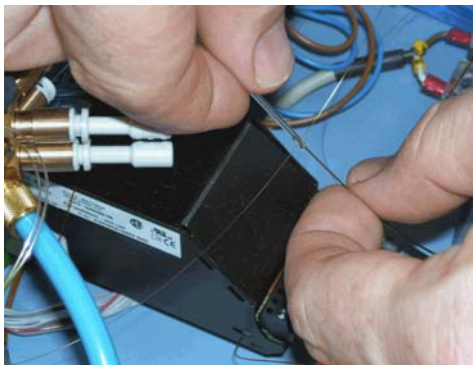


Figure 5-37. Cutting sample transfer capillary to IRMS

3. Connect one end of a 0.32 mm ID fused silica capillary (P/N 1004640) to a 0.32 mm ID-0.32 mm ID press-fit (BgB-Analytik™, P/N 1137430, for example). See Figure 5-3.

4. Connect the 0.32 mm ID fused silica capillary to the LF port of the ConFlo IV. See Figure 5-38 which shows the low flow connector for the sample gas capillary of the GasBench II at the rear panel of the ConFlo IV.

Figure 5-38. Low flow connector for GasBench II sample gas capillary

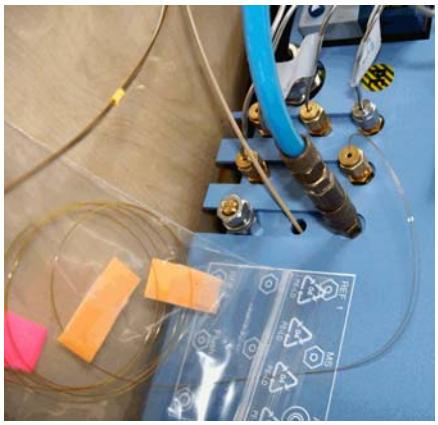


Figure 5-39. Feedthrough of sample gas capillary to LF port of ConFlo IV

Note We recommend leading the 0.32 mm ID fused silica capillary through the hole beneath the compressed air connection of the GasBench II. See Figure 5-39 (feedthrough of the new sample gas capillary to low flow port of the ConFlo IV). ▲

Note To connect the ConFlo IV to the reference gas capillary of the IRMS, refer to the *ConFlo IV Operating Manual*, P/N 1224730. ▲

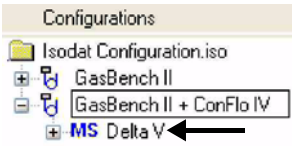
Creating a Configuration for GasBench II and ConFlo IV

The GasBench II in combination with a ConFlo IV must be operated by Isodat 3.0 or higher.

❖ **To create a configuration for the GasBench II together with a ConFlo IV**

1. Open the Configurator.

2. Click on the **New** button in the upper left corner.



3. Give the new configuration a significant name, for example GasBench II + ConFlo IV.

   Then click on the + sign at MS to open the tree structure (see arrow).

4. Pass to Advanced mode by selecting Edit > **Advanced Mode** and confirming by **OK**.

5. In the right pane, click on the **GasBench II Sets - ConFlo IV** tab. See Figure 5-40.

Figure 5-40. Selecting correct tab

6. From the appearing sets select **ConFlo IV + GasBench**. See Figure 5-41.

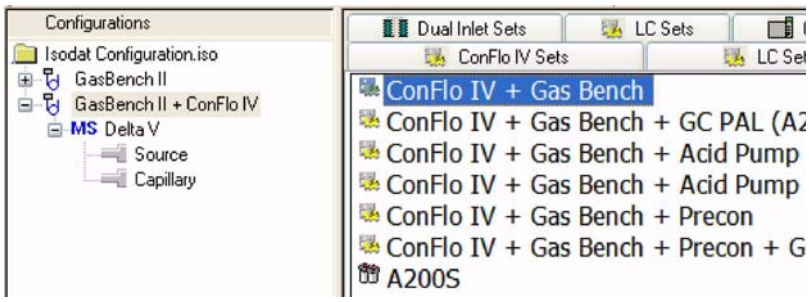


Figure 5-41. Selecting correct set from tab

7. Drag and drop the **ConFlo IV + GasBench** set to the Capillary symbol in the left pane. See Figure 5-42.

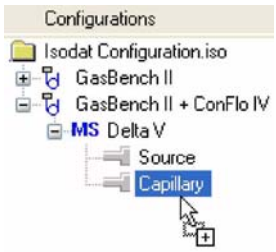


Figure 5-42. Drag and drop of set to capillary symbol

8. Select Flush Fill, one trap or two traps as optional hardware components. See Figure 5-43.

Figure 5-43. Selecting optional hardware components

9. The ConFlo IV + GasBench set will then be appended to the capillary port. See Figure 5-44.

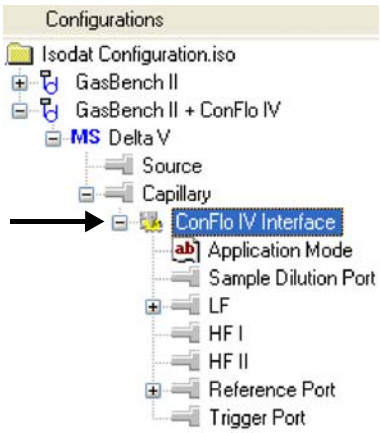


Figure 5-44. Set appended to capillary port

Clicking on the + signs will unfold the tree structure and reveal the individual hardware components. See Figure 5-45.

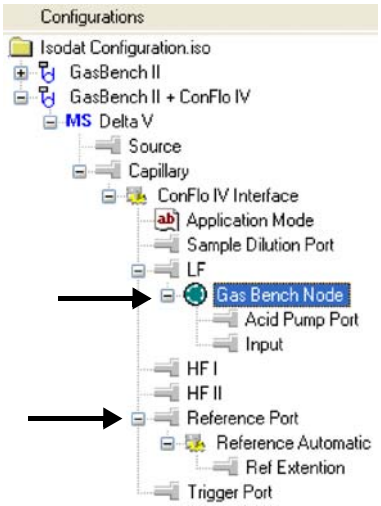


Figure 5-45. Complete tree structure of appended set

Further Steps for Preparing a Measurement

After a configuration has been created, perform the following steps to prepare a measurement.

1. Create methods with and without autodilution.
2. Create sequences.
3. Use the Sequence Scheduler, for example to perform an automated H_2 stability test, a H_3 factor determination, an immediate sample measurement or to set up a sequence for Elemental Analyzer plus GasBench II. Refer to the *ConFlo IV Operating Manual*, P/N 1224730.

Note Using the Sequence Scheduler of the GasBench II together with a high flow peripheral (as is for example Flash EA, Flash HT, TC/EA) is not in the responsibility of Thermo Fisher Scientific! Offline experiments prove however that a switch from GasBench II to HF or vice versa can be performed within 1-3 h, for example for equilibration applications. ▲

An examplary schedule is given to show how effective GasBench II measurements can be performed in combination with a ConFlo IV.

1. Automated $^{18}O/^{16}O$ and $^{2}H/^{1}H$ analysis of water, for example:
   a. Sequence Scheduler with HT-EA on $^{2}H/^{1}H$
   b. Sequence Scheduler method with idle or stability tests at the same time
   c. Stand-alone GasBench II equilibration
   d. Sequence Scheduler for $^{18}O/^{16}O$ analysis with a GasBench II short method (that is, four sample peaks)

Panels in Isodat Acquisition for Operating GasBench II with ConFlo IV

Isodat uses a simple flow scheme for the GasBench II, if connected to a ConFlo IV. See Figure 5-46.

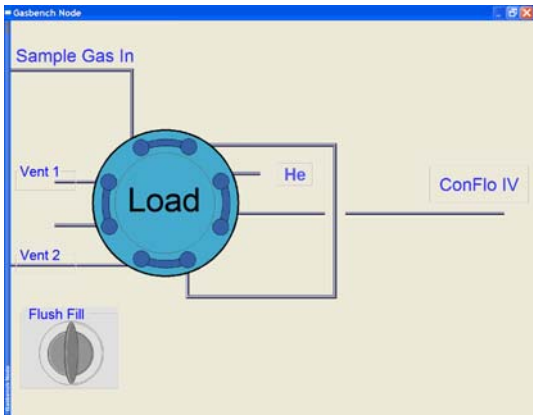


Figure 5-46. Flow scheme for GasBench II with ConFlo IV in Isodat

The ConFlo IV has two panels on the Accessories toolbar - either ConFlo IV Diagnosis or ConFlo IV Interface. The ConFlo IV is directly connected to the second water trap and therefore to the GC out fused silica connection.

Peak Center and Reference Gas Injection Using ConFlo IV

The reference port in Reference Device can be configured in the Isodat Configurator (via Edit > **Advance Mode** in the Configurator) either as Reference Automatic or Reference Manual.

The Instrument tab of the Isodat method shows the integration of the ConFlo IV as reference device with Reference Automatic. See Figure 5-47.

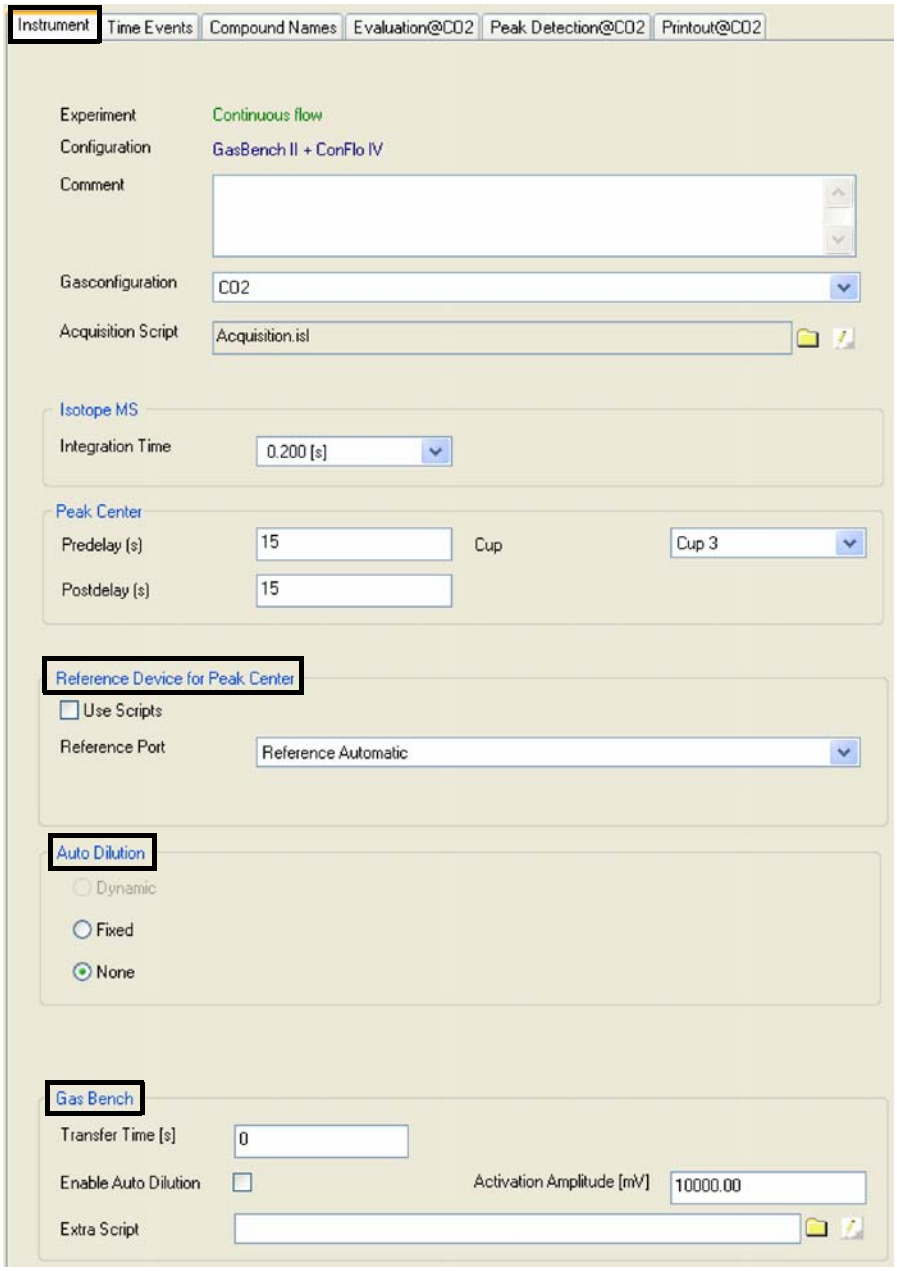


Figure 5-47. Instrument tab for GasBench II with ConFlo IV

Reference Device passes information to Isodat which gas shall be used to perform the peak center. As manual reference device, Ref I Capillary or Ref II Capillary can be chosen for the first peak center. See Figure 5-48.

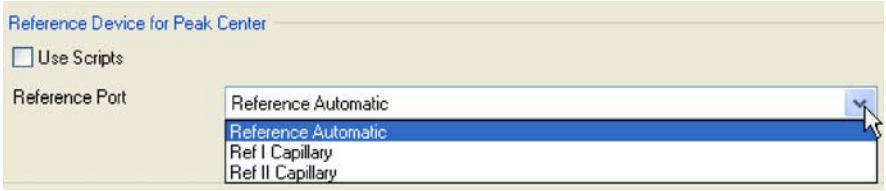


Figure 5-48. Reference Device: Ref I Capillary or Ref II Capillary

The different dilution capabilities of the reference gas can be switched at Autodilution. Refer to the *ConFlo IV Operating Manual*, P/N 1224730.

The GasBench II is integrated as GasBench. The autodilution of the GasBench II sample gas flow is switched or enabled in GasBench. In other words, the first low flow sample gas dilution step (Valves 1 & 2 in) enables the dilution of the sample gas flow by a quarter of the total flow transfer (none diluted mode).

Isodat scripting automatically enables this functionality of the former Autodiluter of the GasBench sample gas open split. No incorporation of other extra scripts is required. Activation of the sample gas flow auto dilution is enabled by changing the activation amplitude threshold.

CO_2 Zero Method for GasBench II with ConFlo IV

The CO_2 enrichment test using GasBench II together with ConFlo IV is described in this section. The time events list using CO_2 enrichment test in Reference Automatic mode is depicted in Figure 5-49.

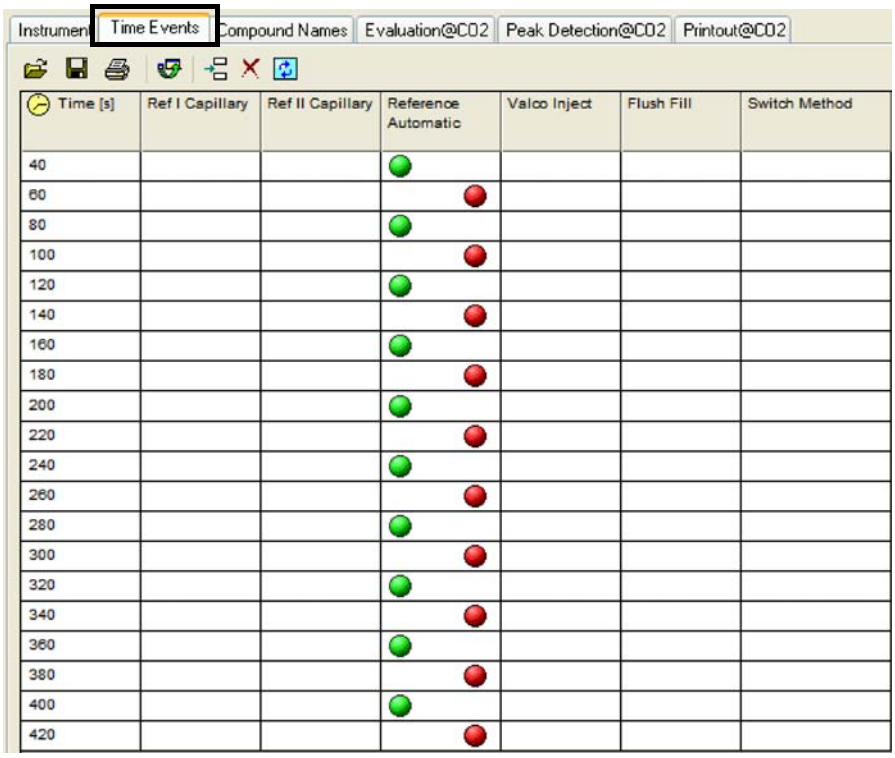


Figure 5-49. Time events list for CO_2 enrichment test

If Reference Automatic has been chosen, Isodat automatically switches the reference gas capillary in for the configured gas to be measured. If a peak jump is performed (switch method), Isodat automatically switches to the next gas required.

For manual reference gas switch, you must predefine the gas in the ConFlo IV Interface panel. This means, at a peak jump the software only moves the reference gas capillary in or out.

For manual activation of the reference gas peaks in the GasBench II chromatogram, either Ref I capillary or Ref II capillary are switched as the gas is set in the active gas configuration.

For a single CO_2 zero enrichment run, the time events list (Figure 5-49) is used. Isodat automatically switches the valves and the capillary according to the definition of the CO_2 reference gas switch in the ConFlo IV Interface panel.

CO_2 Linearity of GasBench II with ConFlo IV

The ConFlo IV automatically increases the gas pressure of the reference gas to the ion source by reducing the dilution of reference gas by dilution capillaries. Before performing an automated linearity sequence, you have to perform an automatic reference gas dilution calibration. Refer to the *ConFlo IV Operating Manual*, P/N 1224730.

For the GasBench II, the automatic linearity script being used for the CO_2 linearity test has not been installed with Isodat.

1. Therefore, identify the script Linearity determination acq.isl in the folder C:\Thermo\Isodat NT\Global\User\Conflo IV Interface**GC Device\ISL**. See arrow in Figure 5-50.

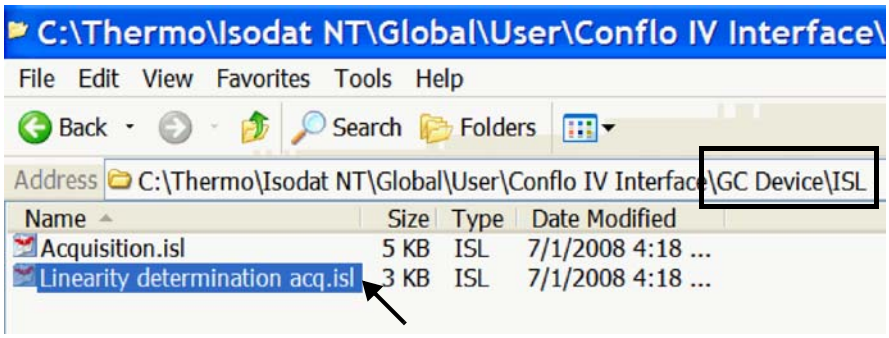


Figure 5-50. Identifying linearity script for the CO_2 linearity test

2. Copy it to the folder C:\Thermo\Isodat NT\Global\User\Conflo IV Interface**Gasbench Device\ISL**. See arrow in Figure 5-51.

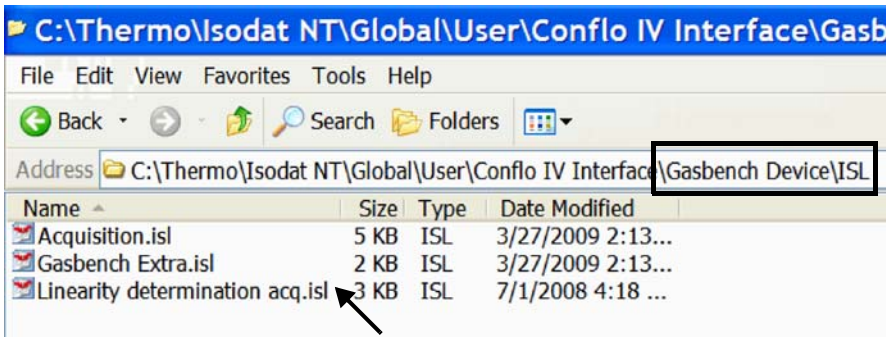


Figure 5-51. Linearity script for the CO_2 linearity test in new folder

3. Open the ConFlo IV zero method described at "CO_2 Zero Method for GasBench II with ConFlo IV" on page 5-51 and save it with a different name, for example CF IV Automated CO2 linearity.met.

4. In the Instrument tab of the method, change the acquisition script to Linearity determination acq.isl by using the button. See Figure 5-52.

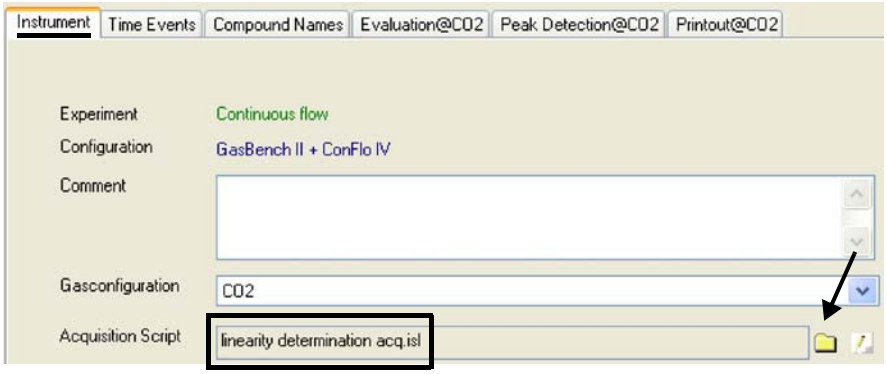


Figure 5-52. Changing acquisition script to Linearity determination acq.isl

5. Save the new method.

6. Open a sequence and open the method CF IV Automated CO2 linearity.met. Start the sequence with the linearity run. See Figure 5-53.

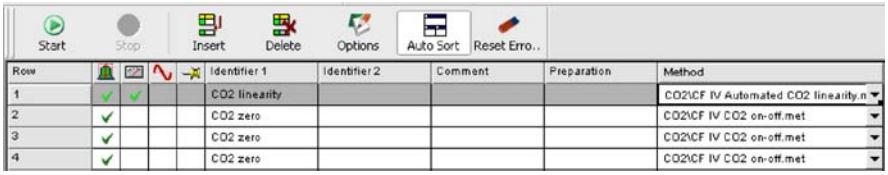


Figure 5-53. Starting sequence with linearity run

7. During normal measurements, a linearity run can be performed.

CO_2 Determination Using GasBench II with ConFlo IV

This section gives an example of an automated CO_2 determination using GasBench II with ConFlo IV. Figure 5-54 shows a chromatogram and the appropriate result grid.

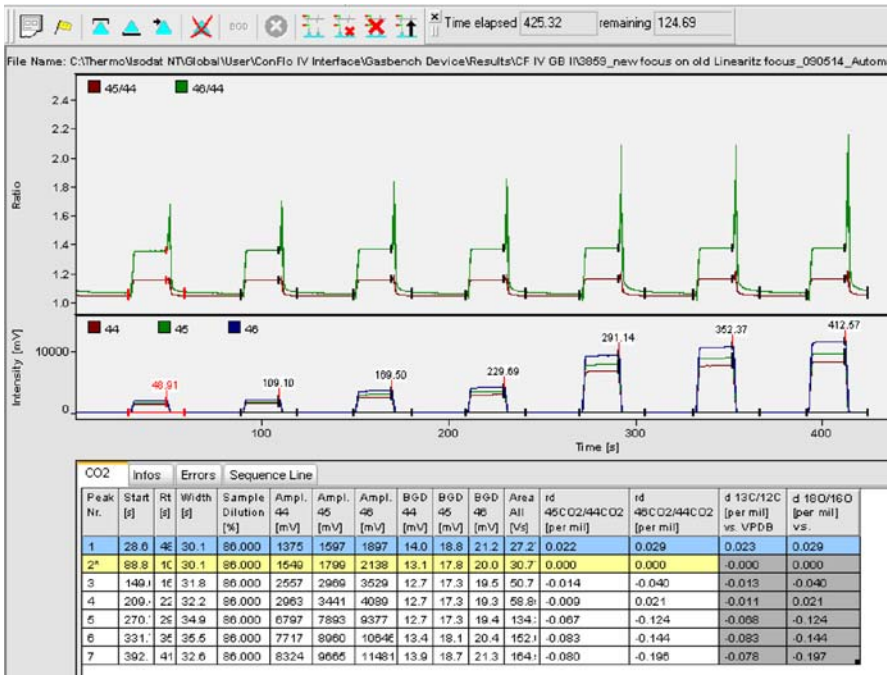


Figure 5-54. CO_2 determination using GasBench II and ConFlo IV

CO_2 Equilibration Using GasBench II with ConFlo IV

In this section, CO_2 equilibration using GasBench II with ConFlo IV is discussed briefly. In the Instrument tab of the method, mark the **Fixed** radio button and set Reference Intensity to 8000 mV (that is, use a fixed reference dilution of 8 V to meet the sample area). See Figure 5-55.

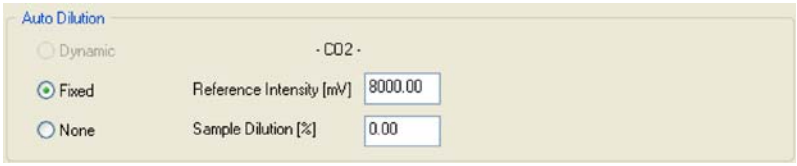


Figure 5-55. Setting Reference Intensity in Instrument tab

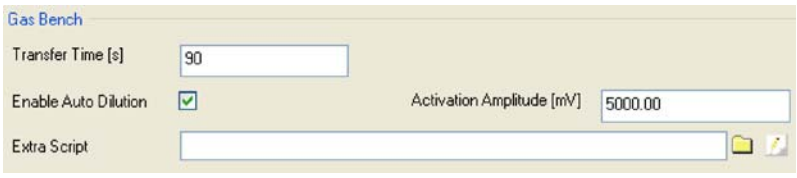


Figure 5-56. GasBench II parameters in Instrument tab

Chapter 6 Options

This chapter outlines technical details about the standard options to be used together with GasBench II. It treats the following topics:

Carbonate Option

The carbonate option (P/N 1132471) is used to measure $\delta\ ^{13}C/^{12}C$ and $\delta\ ^{18}O/^{16}O$ values simultaneously from carbonates. It allows for fully automated measurements of calcite, dolomite, foraminifera, or bulk sediments.

Components of Carbonate Option

Important parts of the carbonate option are summarized in Table 6-1.

Table 6-1. Components of carbonate option

Pos.	Qty.	Designation	P/N
1	1	acid pump with connector	1137301
2	1	acid needle	1137030
3	1 (500 g)	phosphoric acid	1112640
4	1	acid tube	1137070
5	1	clamp 1×4 DIN 72571	0370010
7	1	warning label for corrosive substances	1121230
8	2	warning label to wear protective goggles	1137310
9	1	O-ring, 47,22×3,53, Viton®	1061810
10	1	acid needle holder	1175070
11	1	knurled nut, M8	1119170
12	1	front ferrule, 1/16", stainless steel, silver-plated	0520910
13	1	rear ferrule, 1/16", stainless steel	0520940
14	1	O-ring, 14×10, Viton®	0553520
15	1	hollow nut with 1/16" boring	1137390
16	1 package*	sample vials (borosilicate glass, 12 mL), caps and septa (all washed)	1168790
17	1 sample	$CaCO_3$, as working standard	1147090

*P/N 1168790: a package consists of 100 sample vials made of borosilicate glass, 300 caps and 300 septa to hermetically close the vials. Sample vials, caps and septa are all washed. Alternatively, unwashed sample vials are available (P/N 1168770).

Caution Ensure that only blue caps are used when using the carbonate option! See pos. 16 in Table 6-1. Other caps are not dimensionally stable at the elevated temperatures. ▲

Placement of Components

❖ **To place the components of the carbonate option**

1. Place the acid reservoir in the rightmost row of the sample tray and the acid pump behind the tray. Connect them using the tubing supplied with the reservoir. See Figure 6-5.
2. Do not cut the tubing length. The small diameter tubing is for venting the reservoir. Place it beneath the cover of the tray.
3. To ensure proper closing of the tray cover, a small cut must be made at the edge of the cover using a file.
4. Connect the acid needle tubing to the acid pump (see Figure 6-4) and place the needle in the dual needle holder on the right side. See Figure 2-31.
5. Place the sampling needle in the left slot of the dual needle holder.

Acid Pump

Note For calibrating the acid dropping velocity of the acid pump and for a description of its parts, refer to the *FMI Instructions Manuals* at www.fmipump.com, for example to the *Quick Start Instructions* and to the *Parts Identification Sheet H431-02* (model RHOCKCLF). ▲

Figure 6-1 shows the switches that have been deactivated by Thermo Fisher Scientific in the modified version. Direction and volume pumped per stroke are accessed externally via an additional device.

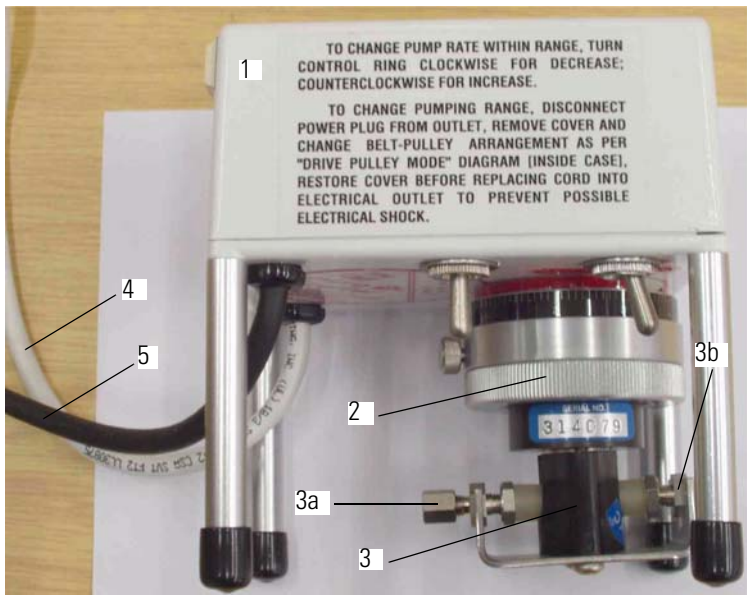


Figure 6-1. Acid pump - side view

Table 6-2 summarizes important parts of the acid pump.

Table 6-2. Parts of acid pump

No. in Figure 6-1	Designation
1	control housing
2	important adjusting screw, used to adjust the volume pumped per stroke (via its mark). Refer to the calibrating instructions on top of the acid pump. This volume pumped per stroke is then reported to Isodat. Refer to topic "Instrument Tab" on page 3-21 as well.
3	head of pump (within a polypropylene housing); shows 3a and 3b
3a and 3b	metric screw connections for the stainless steel pipes Usually, the inlet 3a is on the left and the outlet 3b on the right. For the layout of these metric screw connections, see Figure 6-4.
4	power cable
5	cable with a push button at its end Pushing the button triggers a single stroke at the pump manually.

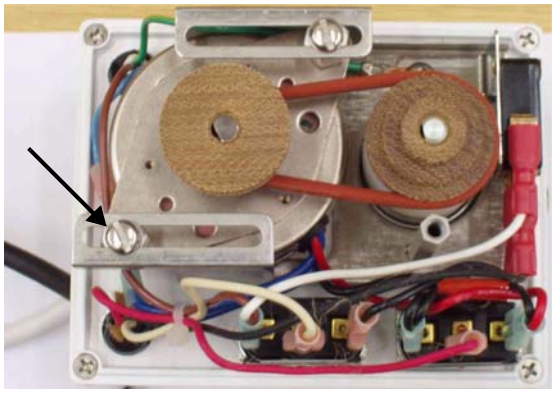


Figure 6-2. Acid pump - top view (open)

The acid pump can be operated at three drive levels, that is at different rotational speeds, which are described inside the control housing. See pos. 1 in Figure 6-1.

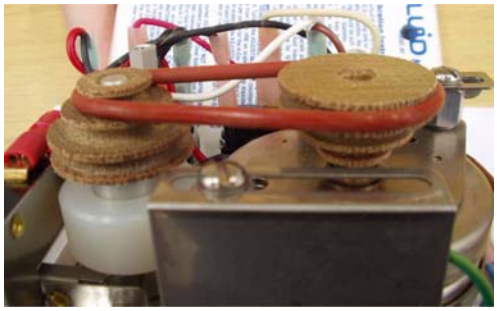


Figure 6-3. Acid pump - side view (open)

Operate the acid pump at slow rotational speed. This means, the rubber ring should be mounted on top, as shown in Figure 6-3 (usual adjustment; sometimes ex factory also in the middle).

Warning Always pull the plug out of the socket before opening the control housing! ▲

Note If the tension of the rubber ring is not sufficient, open the two screws shown in Figure 6-2. Then pull the motor in one direction so that the tension of the rubber ring increases. ▲

Acid Pump Adjustment

For proper function, the acid pump needs to be adjusted prior to operation.

❖ **To adjust the acid pump**

1. Set the pump to minimal pumping volume. This allows exact dosing of the acid and pumping the viscous concentrated phosphoric acid. Follow the instructions on the acid pump housing.
2. Adjust the pumping volume until you obtain one drop of acid by every 10 pump strokes. Use the manual switch at the pump to force a single stroke. Wait between single strokes for at least 30 s.

These settings are a precondition for retracting the acid from the needle tip. This also avoids spoiling the acid to the septum.

Note It may be useful to set a larger pumping volume during the initial filling of pump and tubing. ▲

Caution Never use solvents to test the pump, as the rubber-made O-rings might be destroyed! ▲

For details about how to communicate this acid pump adjustment to Isodat, see Figure 3-16.

Electrical Connection of Acid Pump

In order to connect the acid pump, a plug and measure adapter (pnm adapter for acid pump, P/N 2052660) is needed. Refer to topic "Plug and Measure Adapters" on page 7-10 for details.

Avoiding Clogging of Acid Pump

Acid clogging may occur after improper handling of the acid pump, phosphoric acid preparation and using phosphoric acid thereafter. We recommend using only pure phosphoric acid as prepared according to topic "Preparing Phosphoric Acid" on page 4-17.

Clogging of phosphoric acid in the acid delivery capillaries of the acid pump, the phosphoric acid capillaries of the GasBench II and acid needle can be avoided, if one takes care:

- to use only pure phosphoric acid (99 %, that is of 1.92 g/cm^3 density).
- not to use phosphoric acid of higher density as it would crystallize inside the acid pump head and the capillaries. A crystal core may be formed. After cleaning, even a small crystal may lead to crystallization again due to its reduced lattice energy, and therefore to repeated clogging.
- to avoid any leakage between the acid container and the tip of the acid needle. A leakage may lead to clogging of acid inside the acid pump head.

Caution For use with the GasBench II, never use phosphoric acid with densities above 1.92 g/cm^3! This will inevitably cause the acid pump to be clogged. If chromium oxide or hydrogen peroxide are added, this may lead to clogging of the acid capillaries and unwanted supply of ions from the stainless steel capillaries. ▲

Treatment of Acid Pump, if Clogged

If acid clogging has occurred, clean all capillaries and the acid pump head with hot water for a long time. Remove all remnants of water using methanol.

Warning Methanol is toxic by ingestion! Carefully read and strictly behave according to the safety regulations and the material safety data sheet (MSDS). ▲

If crystallization cannot be avoided, exchange the pump head (P/N 1157620) by a new one.

Note If a leak occurs, air bubbles come out of the acid needle while pumping. Check daily prior to analysis! Usually, a leak may have occurred at the straight connectors of the acid pump head. If necessary, exchange the bulk head connectors and O-rings. See Table 6-3. Avoid too tight connections of the bulk head connectors. The thread into the polymer of the acid pump head may wear out. Too strong connections may lead to damage of the acid pump head thread and therefore to leakage. In this case, you need to exchange the acid pump head (P/N 1157620) by a new one. ▲

Connecting Acid Needle

❖ **To connect the acid needle**

1. Connect the acid needle to the bulk head connector.
2. Tighten the thread of the bulkhead connector with an intermediate suitable O-ring and a correctly directed metal seal.
3. Check for air bubbles at the tip of the acid needle. Leak tightness is indicated by absence of air bubbles.

Note If no drops appear, check whether the flow direction has been correctly set in the software. See Figure 6-5. ▲

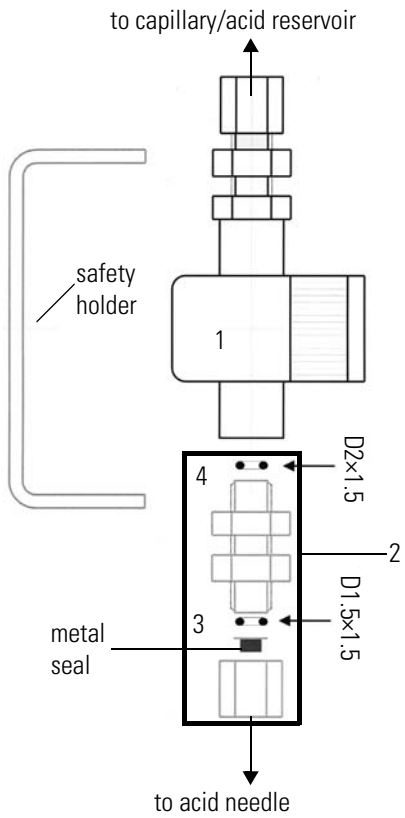


Figure 6-4. Details of pump head arrangement of seals

Table 6-3. Parts in Figure 6-4

Pos. in Figure 6-4	Qty.	Designation	P/N
1	1	pump head for acid pump	1157620
2	1	bulkhead connection (SERTO, 2 mm)	1141450
3	2	O-ring (1.5x1.5)	1141460
4	2	O-ring (2x1.5)	1147070

Note In Figure 6-4 and Table 6-3, the O-rings (3) and (4) are not part of the bulkhead connection (2), however the metal seal is! ▲

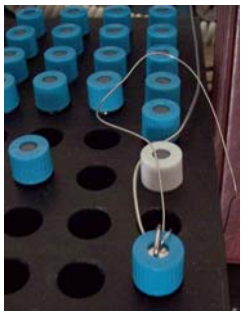


Figure 6-5. Placement of acid reservoir bottle in tray

Connect the acid reservoir (P/N 1137070) to the acid pump using the appropriate O rings and connectors as given in Figure 6-4.

Figure 6-5 shows the standard placement of the reservoir bottle in the heated tray. Place the acid pump beside the tray and feed the 1/16" stainless steel capillary underneath the tray cover to the acid pump.

Note Strictly observe the sequence of O-rings and metal seal parts given in Figure 6-4. Otherwise, the assembly might not seal to air, and then the pump will not deliver acid. ▲

Note When mounting the acid needle in the dual needle holder setup, only use the adapter (P/N 1175070, Figure 6-6)! This adapter has a slightly bigger bore diameter than the original adapter and can be recognized by a groove around the knurl. ▲

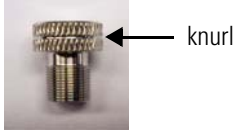


Figure 6-6. Acid needle holder

Cryo Trap Options

The basic problem to deal with is that a very small sample has to be analyzed from a relatively big gas volume. The Thermo Fisher Scientific cryo-option now renders this possible using the so-called GasBench II cryo-option. Two different types of the cryo-option can be delivered:

- Cold trap, P/N 1121300 (that is single trap version), comprising only one trap
- Dual cold trap, P/N 1141000 (that is comprising two traps)

In the Cold trap (that is single trap version), either a stainless steel capillary or a fused silica capillary is used depending on gas flow and sample amount. Both types of capillaries are used within the Dual cold trap, namely the fused silica capillary follows the stainless steel capillary. The general idea of the cryo-option is to obtain higher peak shapes by analyzing small samples in bigger gas volumes.

The cryo traps option contains an automated lever used to move a sample loop in and out of a Dewar filled with a cooling agent (to be supplied by the customer). By filling the Dewar with liquid nitrogen, substances like carbon dioxide, water, methane, or nitrous oxides can be frozen out (trapped). Via proper timing, it is possible to collect these substances in the trap and yield high amplitudes from low concentrations.

Operation Principle

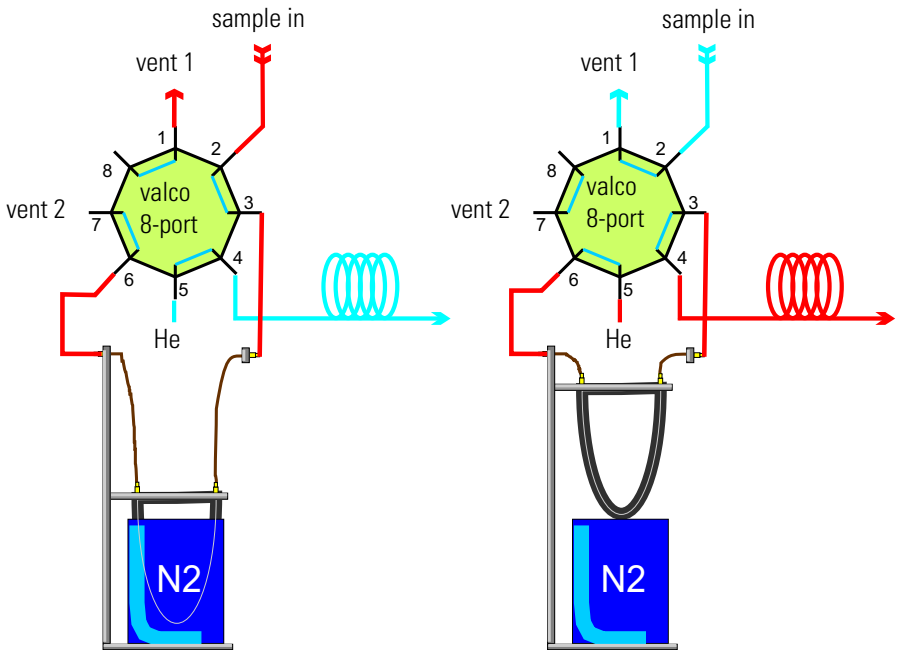


Figure 6-7. Fused silica trap connection for Cold trap

A sample loop is formed from a portion of a 3 m long piece of fused silica tubing. The rest of the full length is used to connect the trap setup to the Valco valve. The complete scheme replaces the standard sample loop that comes with GasBench II. See Figure 6-7.

According to the time event list of the method, the trap is moved into liquid nitrogen (LN2) at regular intervals to achieve accumulation of CO_2 in the cold spot of the sample loop. When released from the Dewar, the trap heats up without significant time delay, and the CO_2 starts to travel towards the GC of GasBench II. Due to cryo focusing (Dual cold trap, see Figure 6-15) the peak shape is extraordinary sharp. The grade of CO_2 enrichment can be determined by varying the time during that the loop stays in liquid nitrogen (accumulation time).

Procedure

This topic outlines the function of the Dual cold trap.

1. In a first step, the sample gas is carried through the sample needle into the nickel-filled stainless steel capillary by a gas flow of approximately 5–15 mL/min. There, the sample is frozen (Load Mode). In this case, the big surface of the stainless steel capillary plays an essential role as the entire sample can be frozen along a short distance. The stainless steel capillary is introduced into the sample gas flow instead of the loop of the Valco port that has been within the sample gas flow so far. For exchanging the loop, refer to topic “Changing Loop Size” on page 2-32.

2. After switching the Valco valve from Load Mode to Inject Mode, the entire sample is carried over into the fused silica capillary and frozen a second time.

3. Inject the sample gas into the IRMS by a continuous flow of less than 3 mL/min. Due to the lower diffusion in the fused silica capillary compared to the stainless steel capillary, a better peak shape will be achieved.

Cryo Trap Option with Cold Trap (Single Trap)

Figure 6-8 shows a schematic of the Cold trap (that is single trap version).

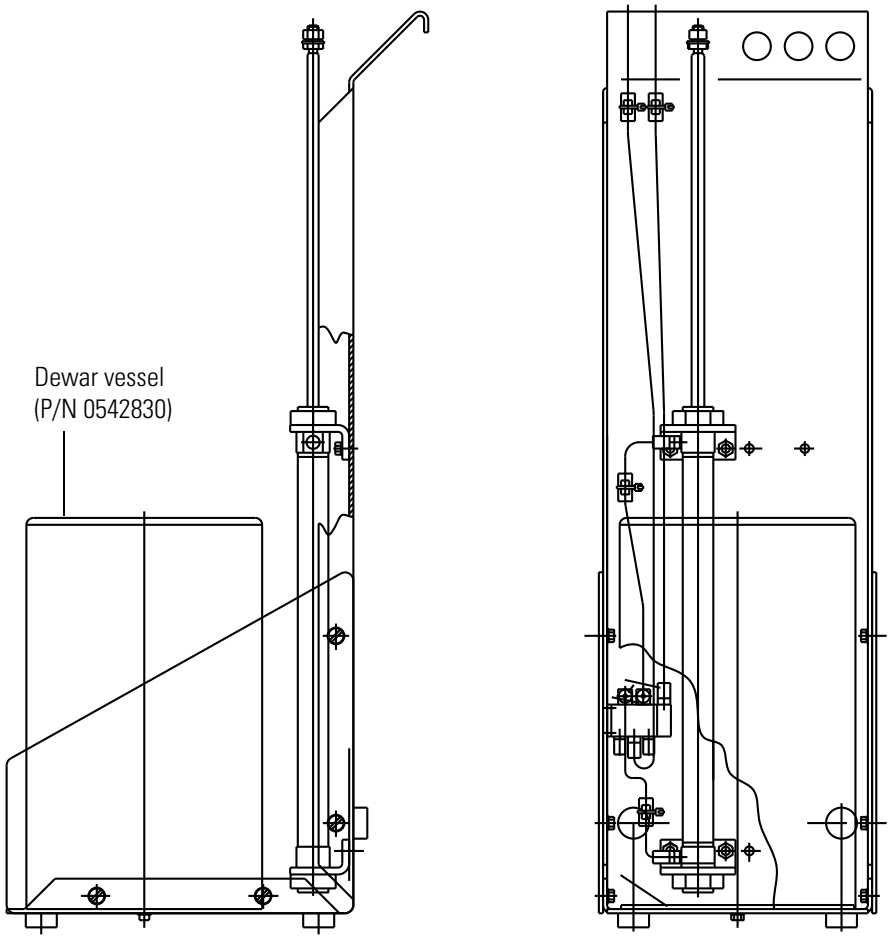


Figure 6-8. Cold trap (that is single trap version)

Cryo Trap Option with Dual Cold Trap

Figure 6-9 shows a schematic of the Dual cold trap, P/N 1141000.

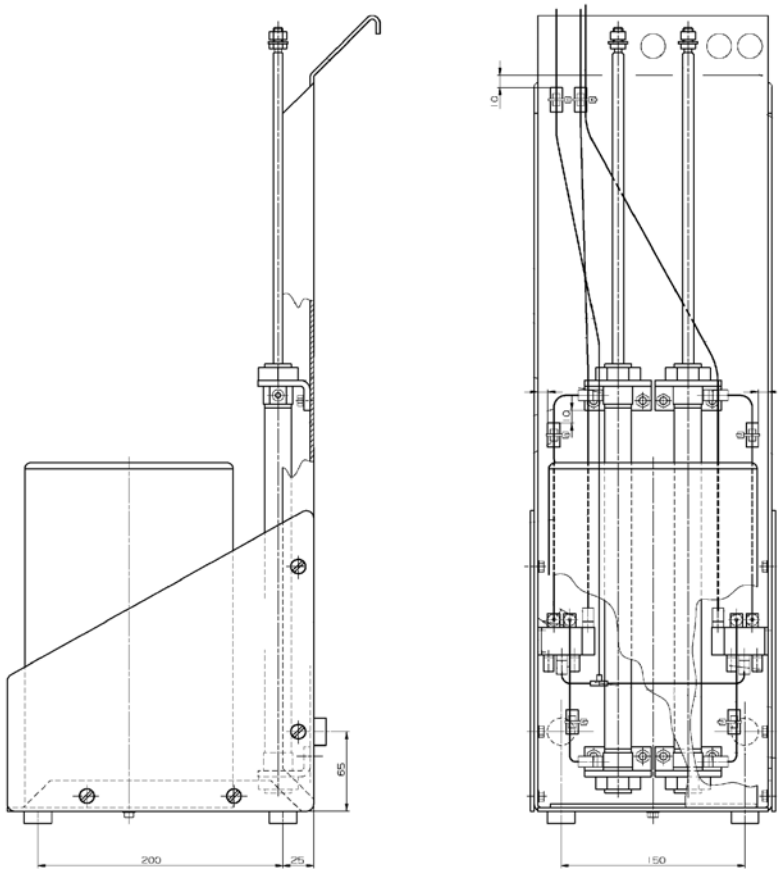


Figure 6-9. Dual cold trap

Important Parts of Both Cold Trap and Dual Cold Trap

Table 6-4 summarizes some important parts of both Cold trap (P/N 1121300) and Dual cold trap (P/N 1141000).

Table 6-4. Important parts of Cold trap and Dual Cold Trap

Designation	P/N	Qty.
cryo trap for GasBench II (mounted)	P1141250	1
nickel trap for GasBench II (mounted)	P1141260	1
capillary, 1/16"×0.8 mm	0605470	0.6 m

The cryo trap (P/N 1141250, Figure 6-10 left) can be used to trap water, carbon dioxide, and nitrous oxide but is not suitable for trapping nitrogen. The nickel trap (P/N 1141260, Figure 6-10 right) is equipped with a nickel wire that can be used to adsorb/trap nitrogen in this trap when submerged in liquid nitrogen.

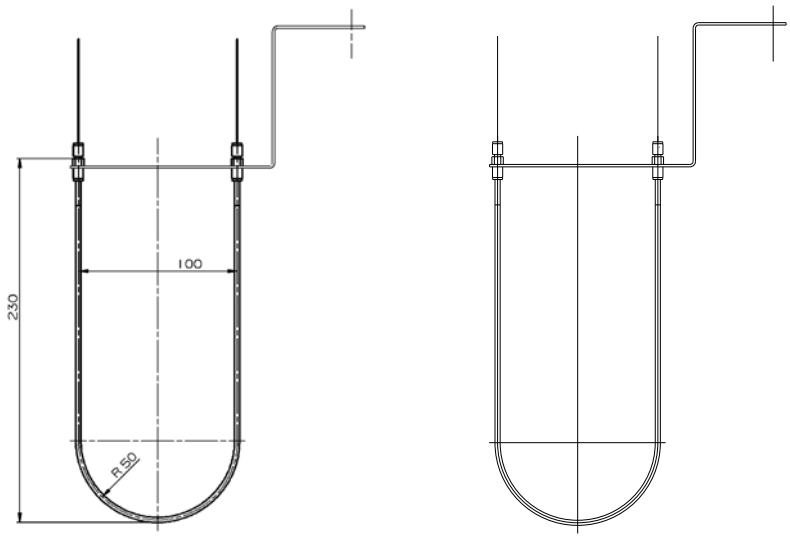


Figure 6-10. Cryo trap (left) and nickel trap (right)

Compressed Air Supply

Figure 6-11 shows the compressed air schematic of the Cold trap and the Dual cold trap. For a dual trap arrangement, trap 2 is added to the rack.

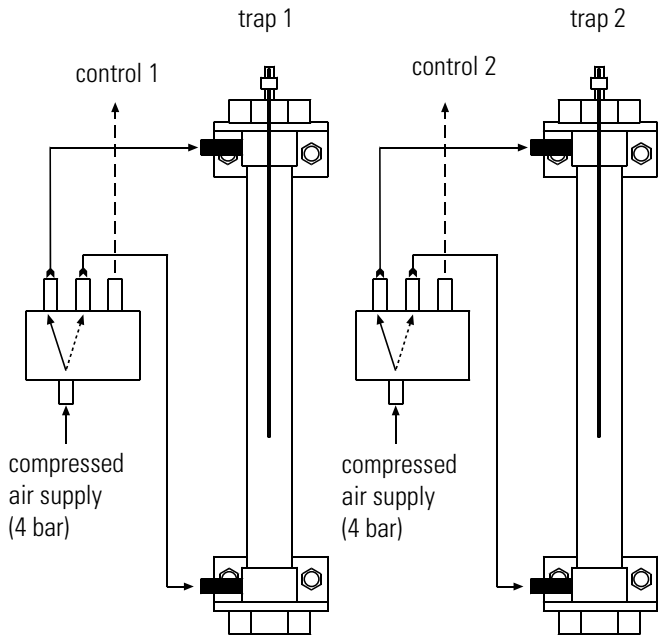


Figure 6-11. Compressed air schematic of Cold trap (trap 1) and Dual cold trap (trap 1 and trap 2)

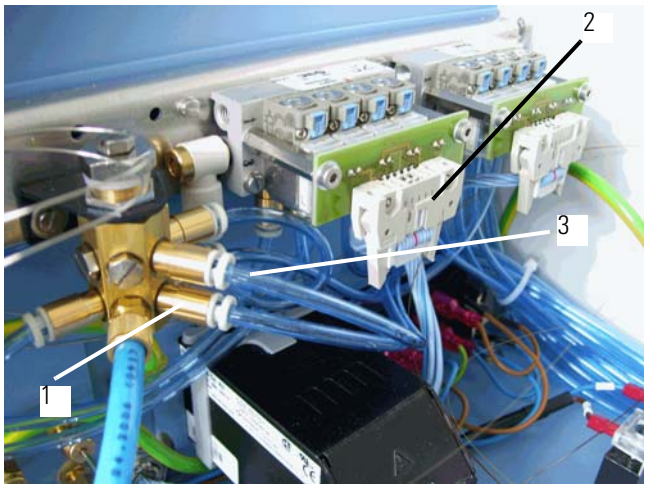
For connecting compressed air supply and control lines, see Figure 7-12 and Figure 7-13. The compressed air supply should always be set to approximately 4 bar.

Connecting Cold Trap and Dual Cold Trap

This topic informs about how to connect the Cold trap and the Dual cold trap.

Figure 6-12. Compressed air connections for Cold trap and Dual cold trap

In Figure 6-12 and Figure 6-13, the compressed air connections for the Cold trap and the Dual cold trap are shown (interior view).



Labeled components: 1=P for Cold trap and Dual cold trap, 2=Gate Right to Dual cold trap (trap 2), 3=Gate Left to feedthrough for cold trap (trap 1)

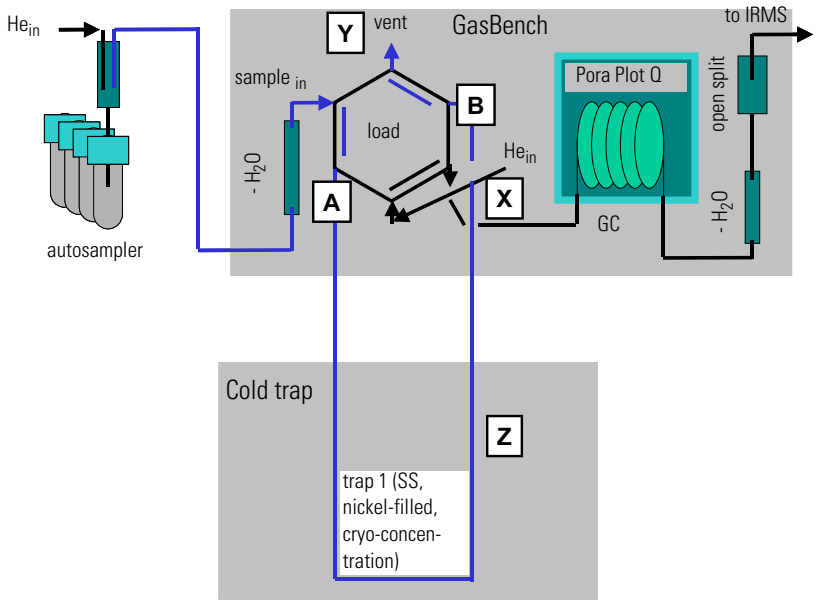
Figure 6-13. Compressed air connections for Cold trap and Dual cold trap

Notes for GasBench II Trapping System

The trapping system of the GasBench II is used to pre-concentrate or for peak sharpening. Additionally, it is used to trap and clean sample gas (N_2O from CO_2, for example) and to use it as an injection concentration to be able to switch from a medium flow to a normal gaschromatographic flow (that is, 2-3 mL/min).

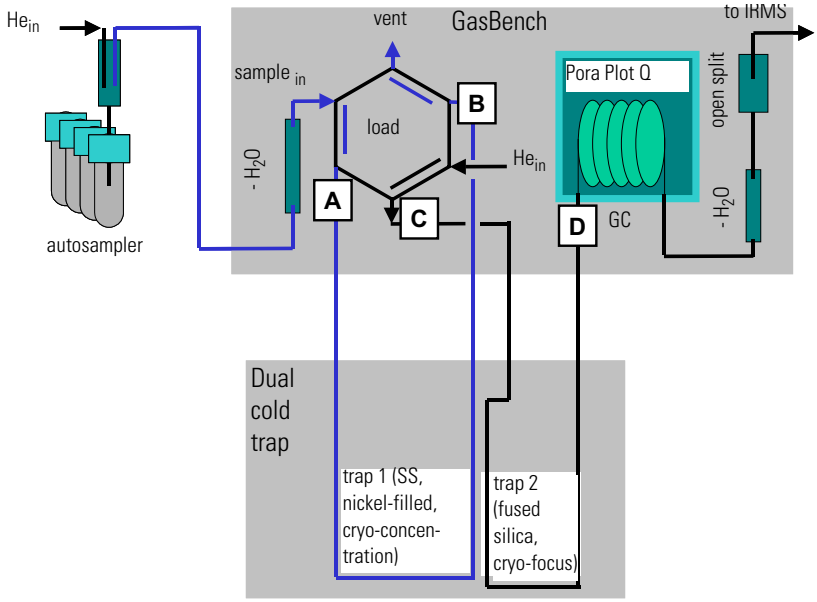
The Cold trap serves as a cryogenic pre-concentration unit for flows in the range of the GC column flow, that is 0.5-5 mL/min. Depending on the GC performance needed, a fused silica trap (0.32 mm fused silica tubing from Valco port A to port B) for very sharp GC peaks or a nickel-filled stainless steel trap (ID 1 mm) resulting in broad GC peaks can be used. In case of the stainless steel trap, the sample flow can also be increased up to 15 mL/min.

Note A longer fused silica capillary needs to be installed in the vent exit (Y) of the Valco valve to avoid freezing of ambient air into the trap. See Figure 6-14 (Cold trap) and Figure 6-15 (Dual cold trap). ▲



Labeled components: A=injector loop in, B=injector loop out, X=change He in and sample out at Valco, Y=vent capillary needs to be prolonged, Z=depending on the sample flow, the capillary of trap 1 may be made of SS, fused silica or be nickel-filled.

Figure 6-14. Cold trap



Labeled components: A=injector loop in, B=injector loop out, C=injector to trap 2, D=trap 2 to GC column

Figure 6-15. Dual cold trap

Table 6-5. Volumes of traps

No.	inner diameter ID (mm)	volume V (µl/m)
1	0.32	80
2	1.0	780

Now, general remarks are added to be taken care of during installation of Cold trap and Dual cold trap.

- Before releasing ferrules in the Valco valve, slowly reduce the He pressure in GasBench II to zero.

Note Close the needle valve leading into the ion source before reducing the He pressure. ▲

- The Dual Trap system serves as a cryogenic pre-concentration unit for flows in the range of the GC column flow (0.5-15 mL/min) including a cryogenic focusing trap in front of the GC column.
- The cryofocusing trap is a fused silica trap (0.32 mm fused silica tubing from Valco port C to port D) for very sharp GC peaks. It also serves as a mediator between high sampling flows and low GC flows (the sample is dissolved in other gases. Here, the fraction that can be frozen out is collected from a bigger gas amount. To collect this fraction completely, high throughputs through the trap are used during a long period of time).

- The cryogenic pre-concentration trap is a nickel-filled stainless steel trap (ID 1 mm) connected from Valco port C to port D.
- An application for one trap is given in topic "CO_2 in Atmospheric Concentrations" on page 5-31.
- Before releasing the ferrule in the bulkhead union in front of the GC column, slowly reduce the He pressure in GasBench II to zero.

Trapping of N_2 at -196 °C

Liquid nitrogen can be adsorbed on silica gel or nickel surfaces at about -196 °C. Thus, it is possible to collect and cryofocus nitrogen for analysis by using a trap operating with liquid nitrogen. The trap used with GasBench II is equipped with a nickel wire to perform N_2 trapping.

Note When applying this kind of trap, keep in mind that other air compounds like CO_2 or water will also be collected therein. ▲

Denitrification Kit

This section provides information about the working principle of the Denitrification Kit (P/N 1220010) and the Denitrification Kit for GasBench II including AS Kit (P/N 1249300).

The following parts are not provided with the Denitrification Kit and must be purchased additionally:

- GasBench II (P/N 1114262)
- Dual cold trap (P/N 1141000)
- CTC PAL GC autosampler (part of GasBench II)

Figure 6-16 shows the autosampler with the Denitrification Kit and the Autosampler Parts for Denitrification Kit installed.

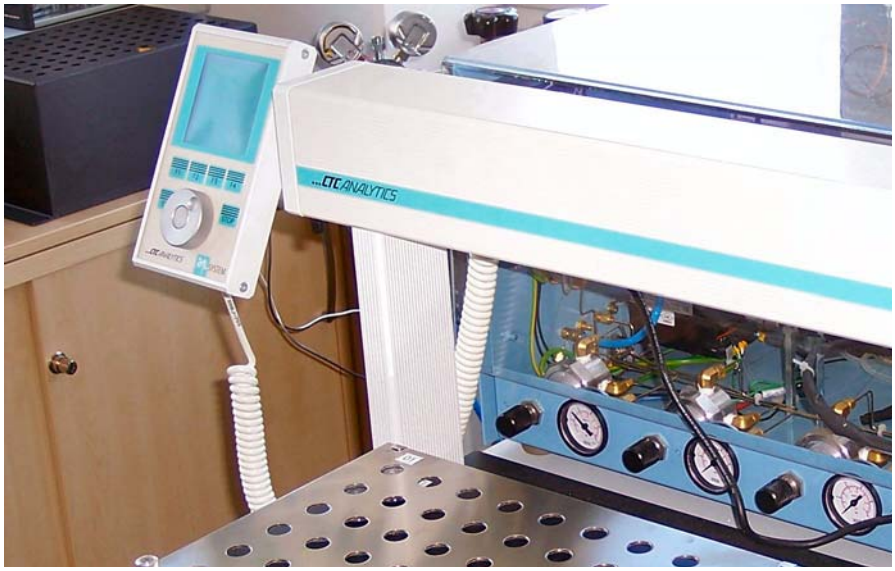


Figure 6-16. Autosampler with Autosampler Parts for Denitrification Kit

For instructions about how to assemble its parts, refer to *Denitrification Kit for GasBench II - Installation Guide* (P/N 1214270).

The Denitrification Kit is an option for the Thermo Scientific GasBench II. It allows, for example, measuring gaseous nitrogen or nitrogen oxides created by biological decomposition of nitrate samples or by chemical reduction using cadmium. Additionally, N_2O > 1 ppm can be analyzed. Refer to the following literature:

McIlvin M.R., Altabet M.A. Chemical conversion of nitrate and nitrite to nitrous oxide for nitrogen and oxygen isotopic analysis in freshwater and seawater. Anal. Chem. 2005, **77**, 5589-5595.

Sigman, D.M., Casciotti, K.L., Andreani, M., Barford,C., Galanter, M., Böhlke, J.K. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Anal. Chem. 2001, **73**, 4145-4153.

Working Principle

Figure 6-17 shows the working principle of nitrogen analysis with the GasBench II. The red frame indicates the parts of the Denitrification Kit.

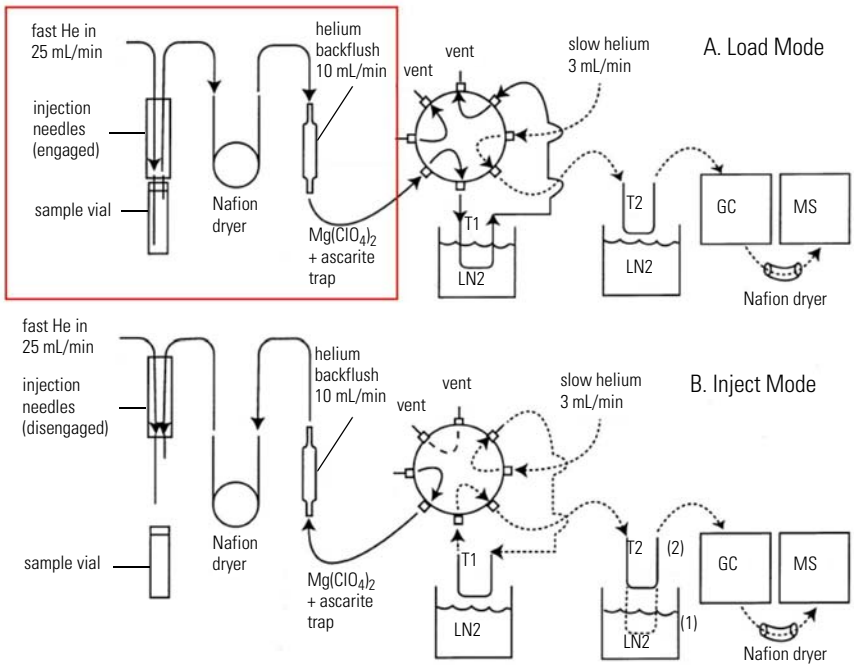


Figure 6-17. Working principle of Denitrification Kit

The description of the measurement method itself is beyond the scope of this section. For detailed information, refer to the following scientific paper and the papers cited therein:

Casciotti, K. L., Sigman, D. M., Galanter Hastings, M., Böhlke, J. K., Hilkert, A. Anal. Chem. 2002, **74**, 4905-4912.

Cold Trap and Dual Cold Trap

The two cold traps shown in Figure 6-17 are not part of the Denitrification Kit. They are part of the Dual cold trap (P/N 1141000), which must be purchased separately. Refer to topic "Cryo Trap Options" on page 6-9. If a Cold trap (P/N 1121300) was purchased earlier, a second Cold trap is required.

T1 (Trap 1) is connected with a stainless steel capillary (length of 950 mm, 1/16" OD, 0.8 mm ID) whereas T2 (Trap 2) is connected with a fused silica capillary (length of 560 mm, ID 0.32 mm).

Assembling Parts of Denitrification Kit

In this section, a general description about how the Denitrification Kits (either P/N 1220010 or P/N 1249300) operate is given. As a guideline for assembling the parts of the Denitrification Kit, use the schematic shown in Figure 6-18.

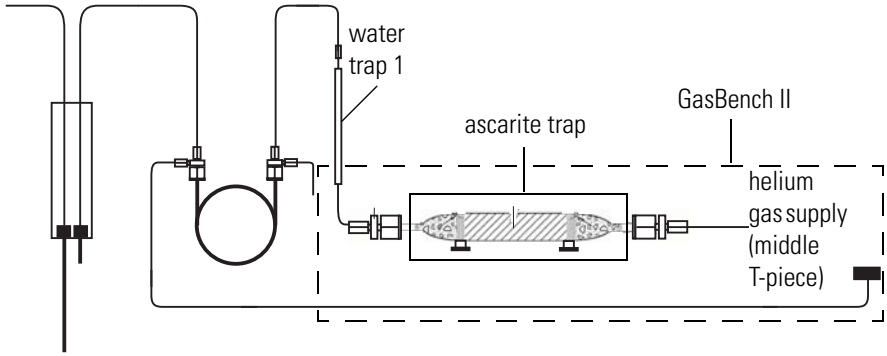


Figure 6-18. Assembling parts of Denitrification Kit

After assembling the Denitrification Kit, check whether the assembly is gas-tight. Flush the assembly with nitrogen or argon and monitor the signal in the mass spectrometer. Use the following parameters:

- cup for m/z 28 (N_2) or m/z 40 (argon)
- amplification factor 3×10^{10}

Parts Lists

This section contains the list of the kits included in the Denitrification Kit for GasBench II (P/N 1220010) and of the kits included in the Denitrification Kit for GasBench II including AS Kit (P/N 1249300).

Denitrification Kit of GasBench II

Table 6-6 summarizes the kits included in the Denitrification Kit for GasBench II (P/N 1220010).

Table 6-6. Kits included in Denitrification Kit for GasBench II

Designation	P/N	Qty.
Ascarite Trap Kit for Denitrification Kit	1245230	1
Water Trap Kit for Denitrification Kit	1245240	1
Injection Kit for Denitrification Kit	1245250	1
Installation Kit for Denitrification Kit	1245260	1
Denitrification Kit for GasBench II - Installation Guide	1244270	1

Denitrification Kit of GasBench II Including AS Kit

Table 6-7 summarizes the kits included in the Denitrification Kit for GasBench II including AS Kit (P/N 1249300).

Table 6-7. Kits included in Denitrification Kit for GasBench II including AS Kit

Designation	P/N	Qty.
Denitrification Kit for GasBench II	1220010	1
Ascarite Trap Kit for Denitrification Kit	1245230	1
Water Trap Kit for Denitrification Kit	1245240	1
Injection Kit for Denitrification Kit	1245250	1
Installation Kit for Denitrification Kit	1245260	1
Denitrification Kit for GasBench II - Installation Guide	1244270	1
Kit for 6×9 Sample Tray & Vials	1237520	1

PreCon

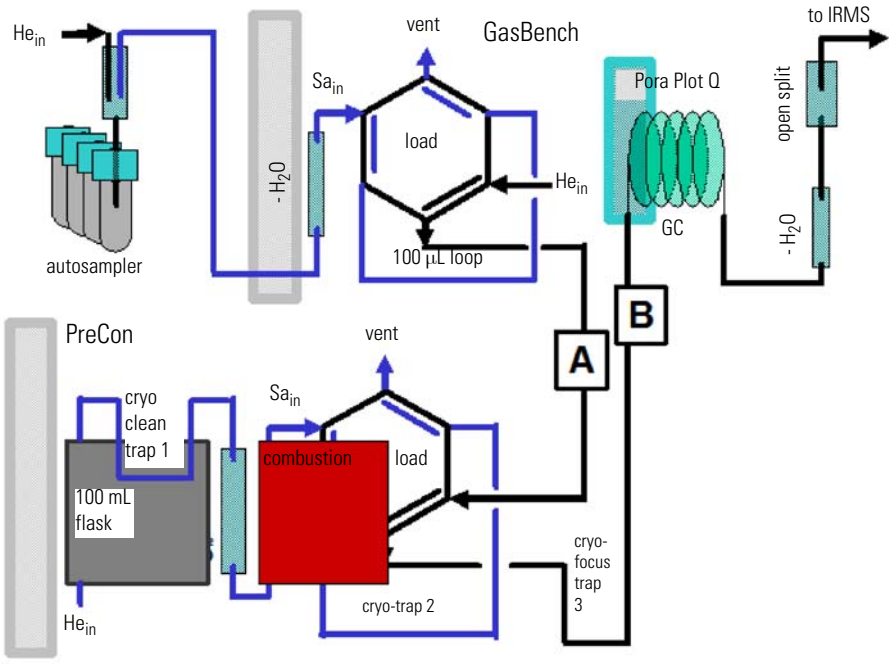
The PreCon is an additional peripheral to either GasBench II or Trace GC IRMS. It is used to concentrate subambient gas concentrations (CO_2 in soils, N_2 in water, noble gases), to clean noble gases from air etc., to concentrate ambient N_2O, CO_2 and CH_4 and to combust CH_4 to CO_2 for $^{13}C/^{12}C$ ratio determination of CH_4.

Introduction

The PreCon is designed for the preconcentration of trace gases in air or other samples in order to perform high precision isotope analysis. It allows to analyze trace gases with concentrations in the low ppm to ppb range (methane 1.7 ppm, N_2O 300 ppb, for example) using air sample sizes of 100 mL or less.

The PreCon consists of two parts: a high flow part with helium flows of 20–25 mL/min (PreCon side) and a low flow part of 1–2 mL/min helium flow (GC side).

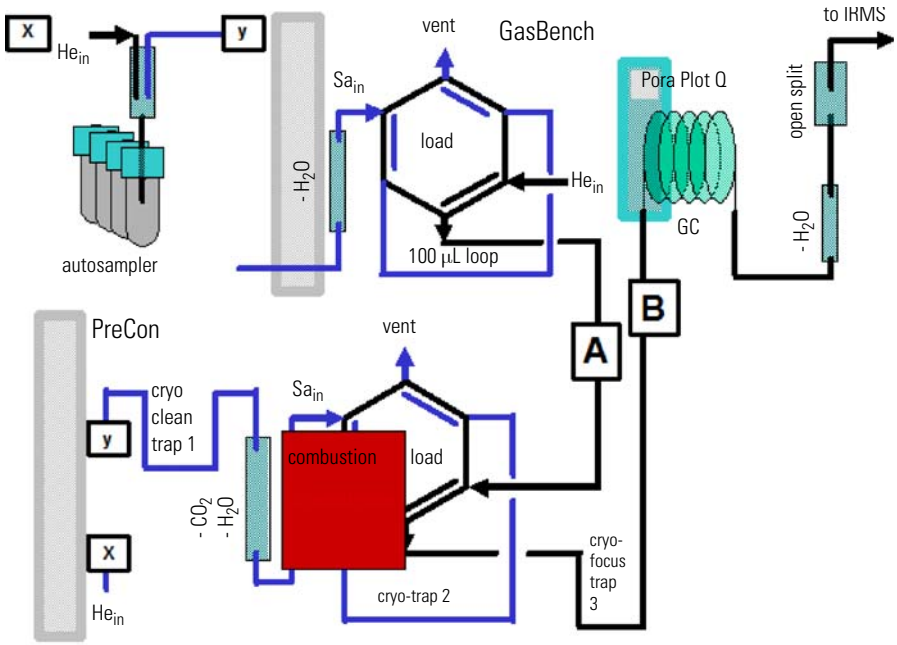
Trap T2 belongs to both sides depending on the Valco valve being switched to Vent or Load mode. The PreCon is linked into the GasBench II after the sample loop, but in front of the GC capillary column. See Figure 6-19. If the PreCon Valco valve is in Load mode, the GasBench II can be used normally.



Labeled components: A=injector to PreCon, B=trap 3 to GC column

Figure 6-19. Connection of PreCon to GasBench II for parallel operation

Alternatively, the autosampler of the GasBench II can be used with the PreCon, if the sample bottle is removed and the sampling needle is connected to the sample bottle ports. In this setup, it is not possible to use the GasBench II normally.



Labeled components: A=injector to PreCon, B=trap 3 to GC column

Figure 6-20. Alternative setup where PreCon uses autosampler of GasBench II*

*x must be connected to x, and y to y.

Connecting PreCon to GasBench II

Note Before attaching the PreCon to the GasBench II ensure that the inlet valve of the mass spectrometer is closed and the helium supply at the GasBench II and the PreCon is shut off. ▲

The mechanical position of the PreCon is usually on the left hand side of the GasBench II interface. Connect all peripherals to compressed air, electronics, helium and power supplies. The helium quality should be according to the pre-installation requirements.

❖ **To connect the PreCon to the GasBench II**

1. Connect the capillary designated as “Injection” (see Figure 6-21) to the vent port of the Valco valve of the GasBench II (see Figure 6-22).
2. Connect the capillary designated as “Column” to the Column inlet of the GasBench II. See Figure 6-23.

Figure 6-21. PreCon inlet and outlet connections

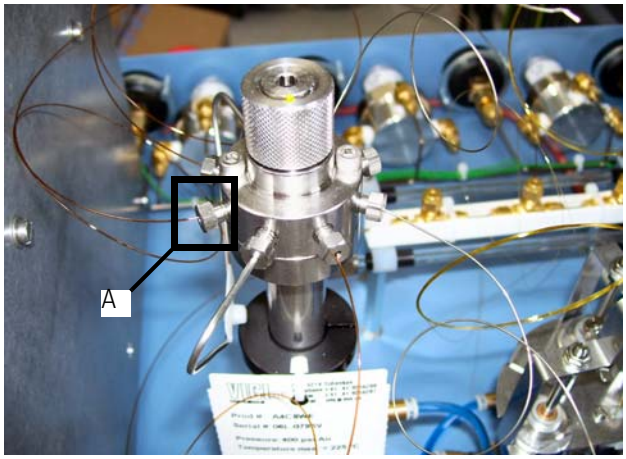


Figure 6-22. PreCon connection (A) at Valco valve of GasBench II

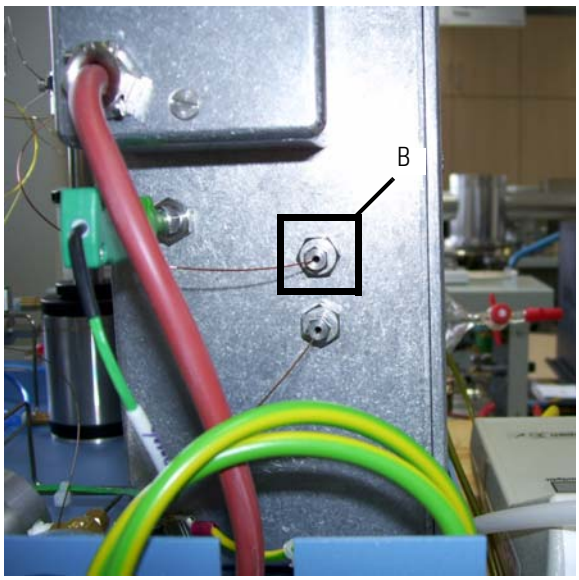


Figure 6-23. GasBench II-GC input connection (B)

Leak Check of 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 PreCon/GC/GP.

❖ **To check the helium supply lines for leaks**

1. Adjust the main supply to 5 bar.
2. Close all helium pressure reduction units at the front panels of the PreCon and the GasBench II.
3. Close the main supply. The pressure may not drop within 30 min or longer.

Setting up an Isodat Method

❖ **To set up an Isodat method for PreCon**

A suitable configuration must have been already created.

1. When setting up a new method, in its Instrument tab select the acquisition script found in the folder C:\Thermo\Isodat NT\Global\User\Gas Bench\ISL\PreCon. See Figure 6-24.

Figure 6-24. Selecting acquisition script for PreCon method

2. Depending on your hardware setup, in the Instrument tab select an appropriate PreCon script from the folder C:\Thermo\Isodat NT\Global\ISL\PreCon. See Figure 6-25.

Figure 6-25. Selecting PreCon script for PreCon method

Additional scripts exist, if the time events list of the IRMS method is not used. The events will be switched for the PreCon preparation steps by the script. Reference peaks will be switched in the time events list!

Catalyst for Hydrogen Equilibration

The catalyst required for hydrogen equilibration (P/N 1091831) is a platinum stick that is partly covered with platinum powder. See Figure 6-26. It is delivered in a box containing 50 pieces.

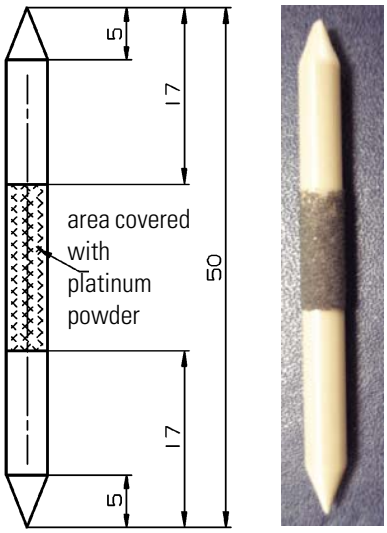


Figure 6-26. Catalyst for hydrogen equilibration*

*The distances are given in mm.

Refer to topic "Water Equilibration ($^2H/^1H$ Equilibration)" on page 5-36 for a description of its usage.

Chapter 7 Technical Information

Note This chapter is intended for use by trained Thermo Fisher Scientific personnel only. Thermo Fisher Scientific discourages use by and denies liability for the consequences of use by other than Thermo Fisher Scientific personnel. ▲

This chapter contains technical information about different fundamental parts of GasBench II. It treats the following topics:

Note The individual parts to be found in the spare parts lists mostly refer to adjacent figures. However, not all off them are intended to be bought separately. Instead, it may be more reasonable to buy an entire superordinate unit that contains the individual part of interest. ▲

Spare Parts and Consumables of GasBench II

The GasBench II consists of the

- GasBench II basic module, P/N 1187500, and the
- GasBench II installation kit, P/N 1121060.

Table 7-1 summarizes selected spare parts and consumables taken from the GasBench II basic module (P/N 1187500).

Table 7-1. Parts taken from GasBench II basic module

Pos. in Figure 7-1	P/N	Designation	Qty
13	P1002605	water trap GC-C III	2
20	0674552	JUMO iTRON 16 temperature controller	1
21	0281310	solid state relais, 10 A	1
84	9000342	seal ferrule, Valco, FS1.5 (pack with 5 pieces)	2
86	1004640	capillary, fused silica, ID 0.3 mm	2 m
88	1060170	ferrule, 1/16", GVF2/003	7
89	0674910	capillary, fused silica, not deactivated	4.4 m
91	1004850	ferrule, 1/16", GVF/003	2
94	0543380	capillary tubing, fused silica, 0.05	7.5 m
95	1045480	capillary, fused silica, 0.075, 2 m	1
126	1121170	bulkhead union (valco)	6

Table 7-2 summarizes selected spare parts and consumables taken from the GasBench II installation kit (P/N 1121060).

Table 7-2. Parts taken from GasBench II installation kit

Pos. in Figure 7-1	P/N	Designation	Qty
1	1168770	borosilicate vial, 12 mL, unwashed	100
8	1121070	disposable syringe, 1 mL (pack with 100 pieces)	1
9	1121080	disposable needle (pack with 100 pieces)	1
23	1137080	adapter GasBench needle to needle holder	2
24	1119170	knurled nut M8	2
32	P1114290	gas supply line	4
33	1137020	measurement needle	2
34	0171911	PoraPlot Q capillary column, 25 m × 0.32 mm	1
-	0674790	ferrule, 1/8"-1/16", Teflon	4
-	1004640	capillary, fused silica, ID = 0.3 mm	4 m
-	1137390	hollow nut with 1/16" boring	2

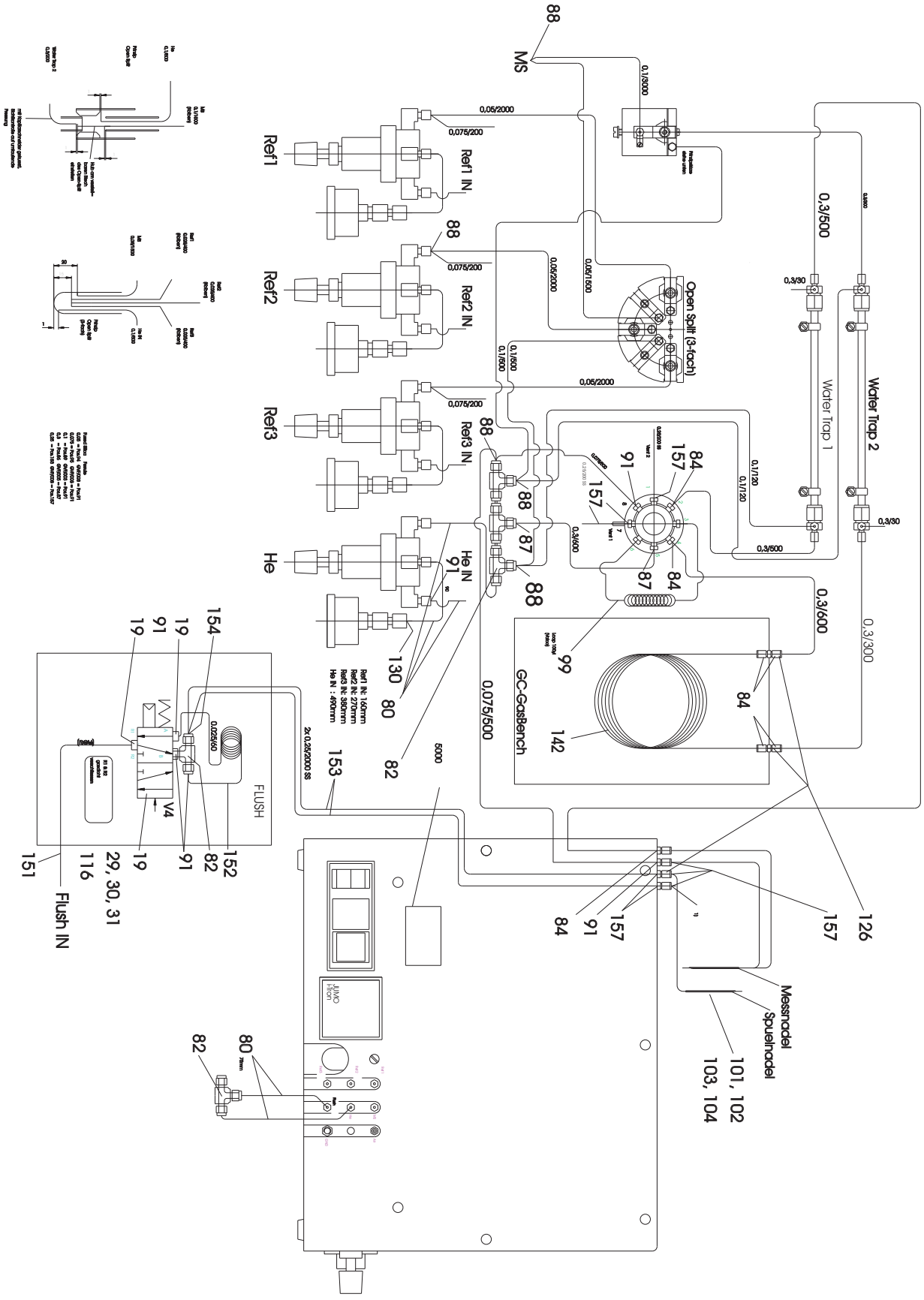


Figure 7-1. Tubing scheme of GasBench II (P/N 1114262)

Figure 7-1 shows the tubing scheme of the GasBench II.

Note For better visualization, the scheme can be downloaded at the CIS of Thermo Fisher Scientific (Bremen) as a pdf file. It can then be printed on larger paper size, for example DIN A3. ▲

In Figure 7-2 the compressed air scheme of the GasBench II (P/N 1114262) is displayed.

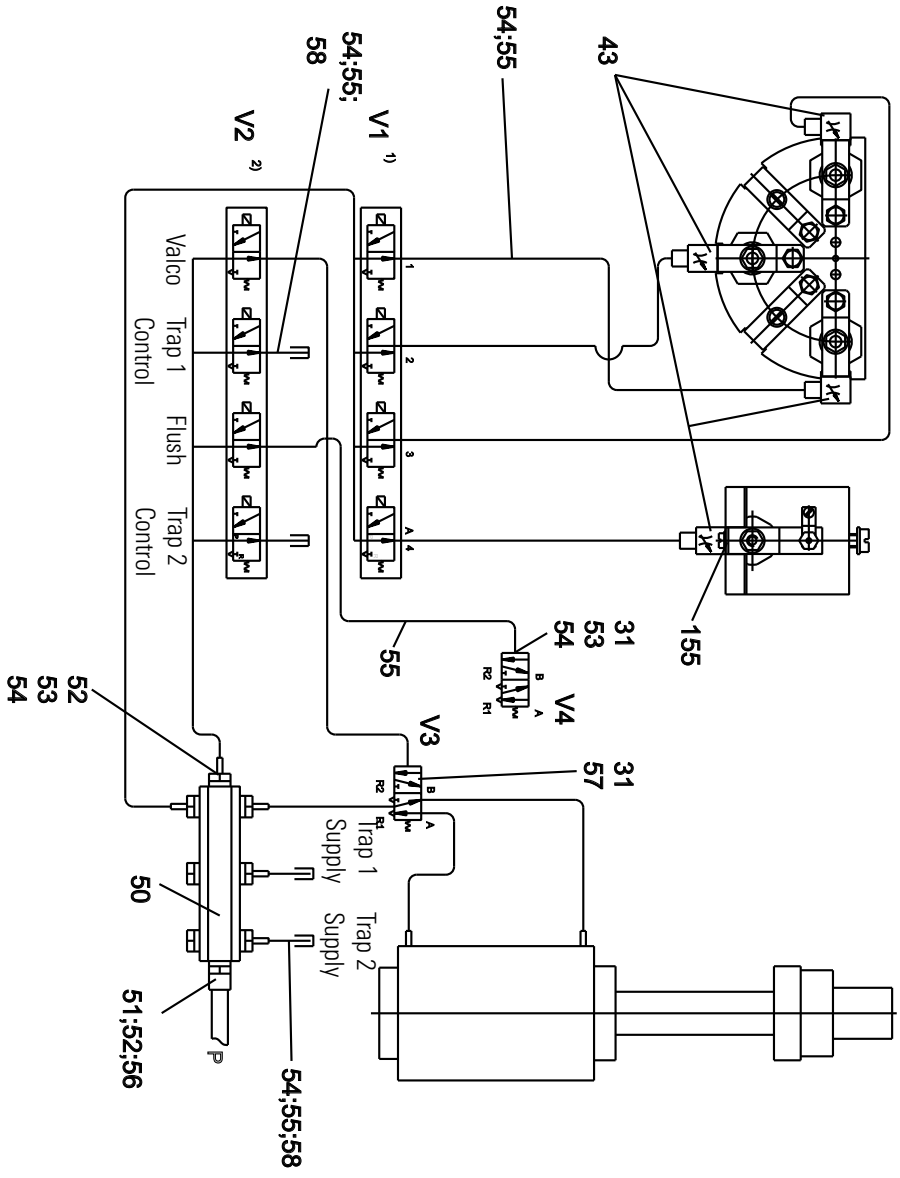


Figure 7-2. Compressed air scheme of GasBench II (P/N 1114262)

Capillaries

The GasBench II contains two groups of capillaries:

- capillaries that connect two points in the gas flow scheme

  usually of size ID = 0.32 mm

  length not important.

- capillaries that control flows

  All the capillaries that start from the central gas distribution T-piece belong to this group. There are:

  Two capillaries (0.1/500) that support the open splits with 2 mL/min of helium each.

  Two capillaries (0.1/250) for 4 mL/min of helium to water trap

  One capillary (0.075/1000) for 0.5 mL/min to sample needle

An exception is the column itself. It acts as its own flow restriction (1.5 mL/min).

Water Trap

This section schematically outlines the water trap (P/N 1002605) together with selected spare parts and consumables.

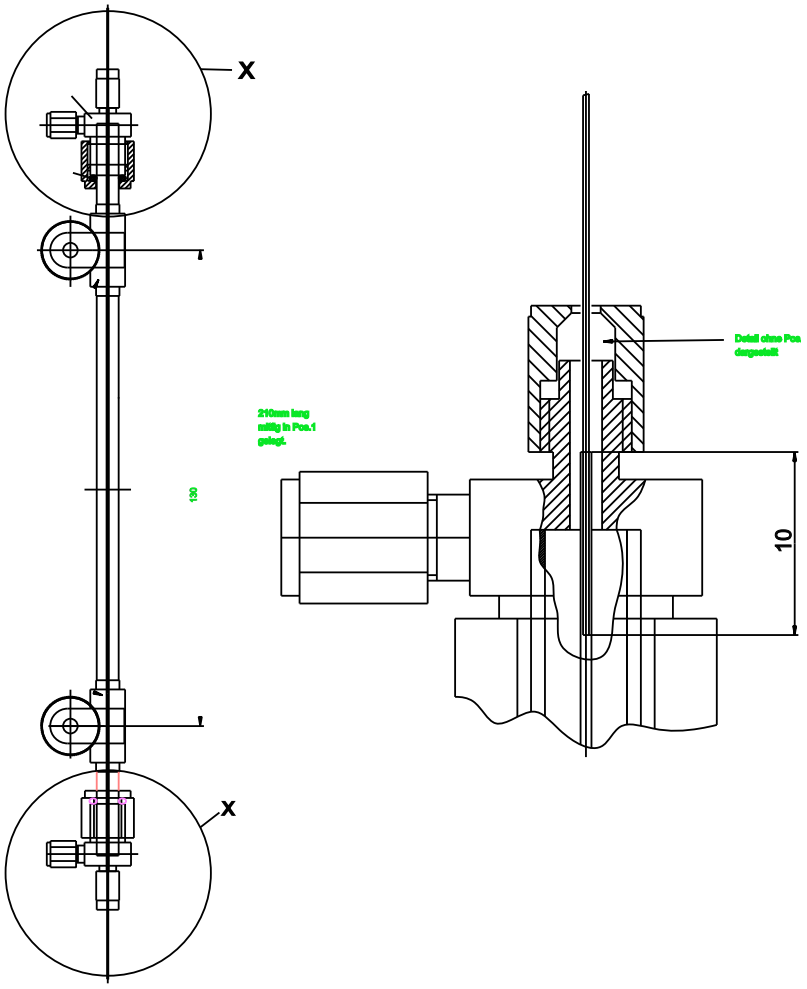


Figure 7-3. Water trap

Table 7-3. Selected spare parts and consumables of water trap

Designation	P/N	Qty.
Nafion tubing for gas dryer, ID = 0.3 mm	0743390	0.25 m
ferrule, 1/16”, GVF/005	0566390	3
ferrule, 1/16”, GVF/003	1004850	1

Reference Open Split

Figure 7-4 shows the reference open split (P/N 1096570). Table 7-4 summarizes important parts.

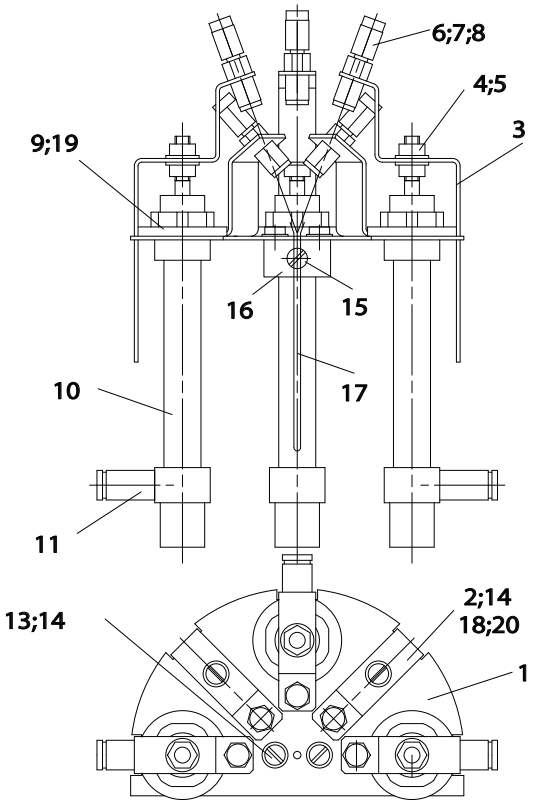


Figure 7-4. Reference open split

Table 7-4. Selected spare parts and consumables of reference open split

Pos. in Figure 7-4	P/N	Designation	Qty.
8	1004850	ferrule, 1/16", GVF/003	5
17	1041800	glass tube for reference open split	1

Sample Open Split

Figure 7-5 shows the sample open split, P/N 1041761. The glass tube of the sample open split (pos. 5 in Figure 7-5) has an ID of 0.8 mm and the P/N 1183040.

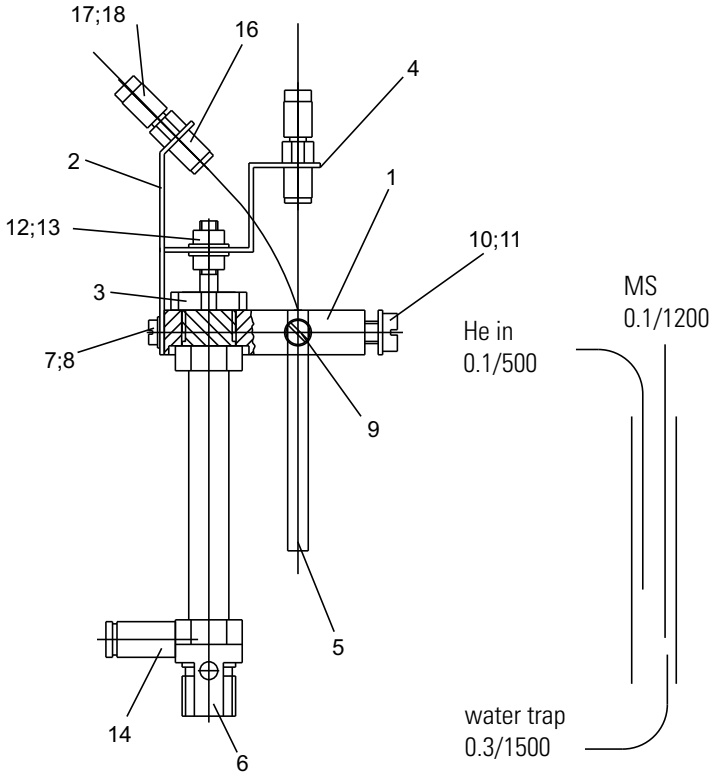


Figure 7-5. Sample open split

GC Oven

Figure 7-6 shows the GC oven (P/N 1121100).

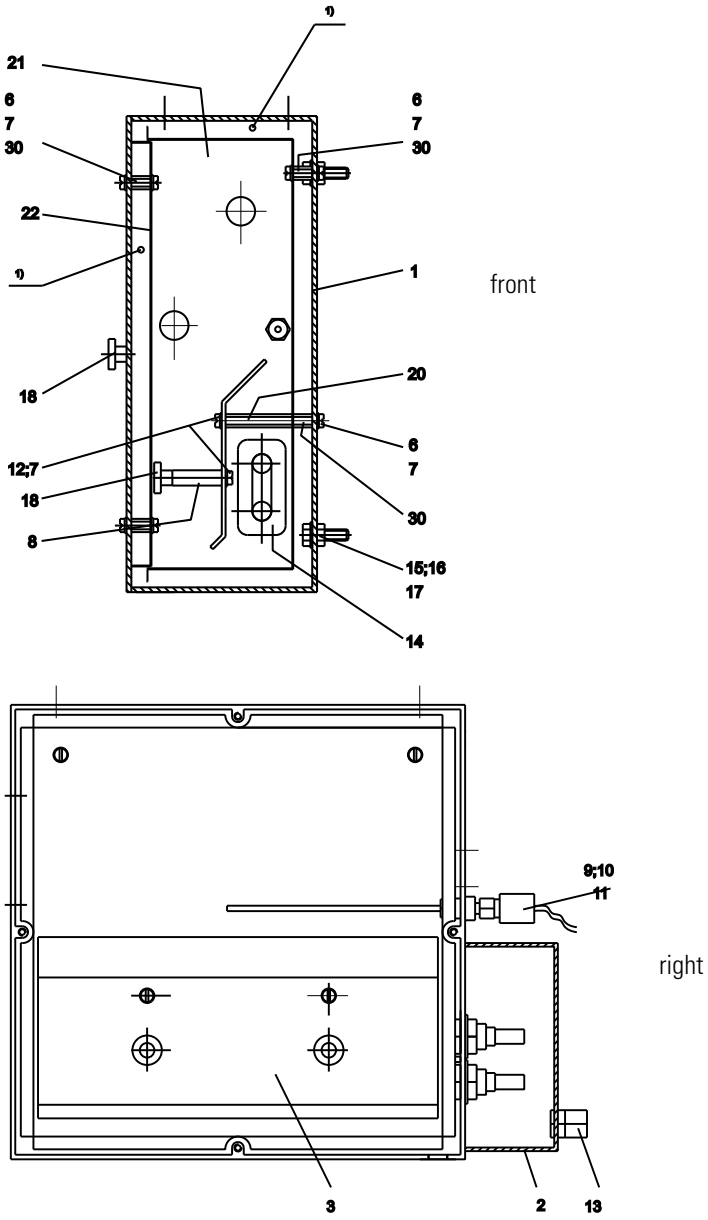


Figure 7-6. GC oven - front and right

The thermocouple (type K) and the ribbed radiator given in Table 7-5 are two especially important parts of the GC oven.

Table 7-5. Selected spare parts and consumables of GC oven

Pos. in Figure 7-6	P/N	Designation	Qty.
10	1061390	thermocouple (type K)	1
14	1123061	ribbed radiator, 240 W	1

Plug and Measure Adapters

An arbitrary peripheral can be connected to any of the five SUB D connectors of the IRMS. Refer to the Operating Manual of the IRMS.

Each peripheral has its own plug and measure code. This code is encoded either in the cable to the device or in a plug and measure adapter. This is also used for downward compatibility using an old peripheral. The instrument recognizes the kind of peripheral and the SUB D connector used for it automatically, when a configuration requires this device. Otherwise, for example when the device cable is unplugged accidentally, an error message will be displayed.

Plug and Measure Adapter for GasBench II

On the plug and measure adapter (pnm adapter, P/N 2052660) for GasBench II, two addresses have already been adjusted by Thermo Fisher Scientific via the two coding switches:

pnm-ID first device
S1 = 8
S2 = 0

Plug and Measure Adapter for Acid Pump

A plug and measure adapter (pnm adapter, P/N 2052660) is also needed to connect the acid pump. On this plug and measure adapter for the acid pump, two addresses have already been adjusted by Thermo Fisher Scientific via the two coding switches. See arrows in Figure 7-7.

pnm-ID
S1 = 8
S2 = 1

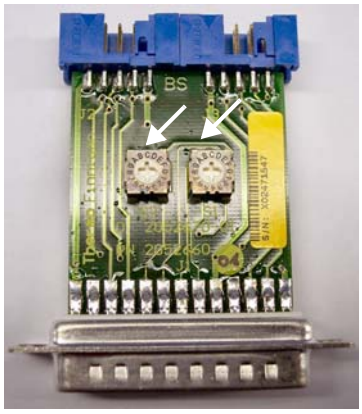


Figure 7-7. Plug and measure adapter for acid pump

Adjusting Plug and Measure Adapters

The plug and measure adapter (pnm adapter, Figure 7-8) is pre-configured at the factory for a defined option, GasBench II, for example). A supplementary reconfiguration by the user is not recommended. The plug and measure adapter is connected to one of the five identical SUB D ports of the IRMS. The peripheral is then connected to the IRMS via the bottom port of the pnm-adapter.

Peripherals are identified by the settings of the turn switches and the jumpers. The turn switches are used to specify the pnm-ID for the peripheral (for example, for the acid pump, set S1 to 8 and S2 to 1). The jumpers are also used to identify the kind of peripheral that is connected to the IRMS. If indicated, the lowest two contacts of the plug socket at the pnm-adapter (either socket J3 or J2) are cut short from outside of the pnm-adapter.

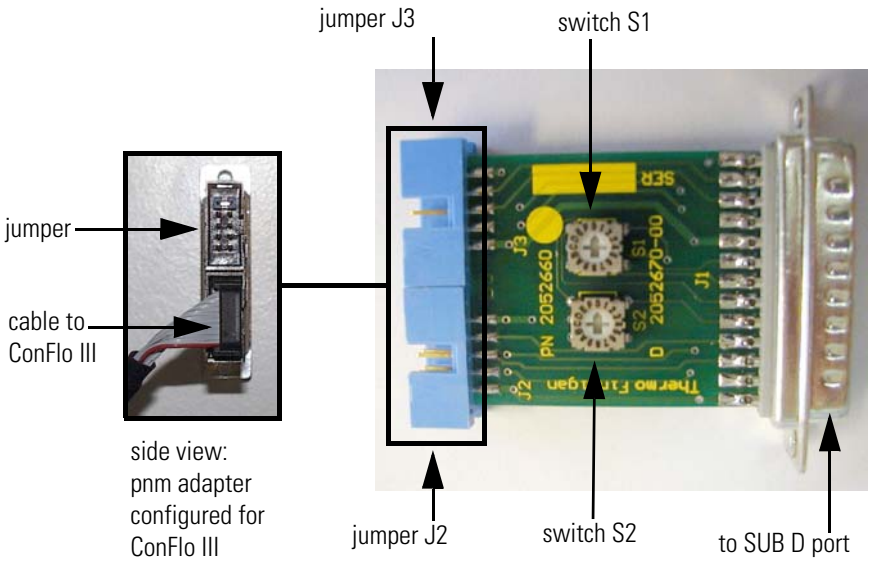


Figure 7-8. Plug and measure adapter

Note Some external options are connected to the SUB D ports without using the plug and measure adapter. ▲

Grounding Cable for Peripherals

Peripherals which are operated by a plug and measure adapter, must be connected to the IRMS by a grounding cable. It is not necessary for peripheral devices, which already run using a new cable (PreCon, GP Interface).

The peripheral is connected to the IRMS by a PE cable (bolt as grounding contact). See Figure 7-9 for the bolt and the grounding cable at the MAT 253 (left) and at the DELTA series (right).

Figure 7-9. Grounding cable at MAT 253 (left) and DELTA series (right)

Configuration of Plug and Measure Devices

Five SUB D ports are located at the rear side of the mass spectrometer. The external option is recognized, because it is encoded with a pnm ID. The electronics recognizes that an option is connected to a certain port, and which kind of option it is.

Table 7-6. Settings for plug and measure devices

Peripheral	pnm-ID* 1st Device		pnm-ID† 2nd Device		Jumper pin 9/10‡	New cable**	Cable P/N	
	S2	S1	S2	S1			1st Device	2nd Device
ConFlo II/III	0	2	0	3	J3			
GCC II/III	0	4	0	5	J3			
GasBench II	0	8	0	9				
PreCon	0	A	0	B		Yes	2054620	2054630
ProRef	0	C	0	D	J3			
MultiInlet	0	E	0	F				
acid pump	1	8	1	9	J2			
GC/GP	1	0	1	1		Yes	2054640	2054650
Dual Inlet			0					
MP1			0					
MP2			0					
TC1			0					
TC2	1	2	1	3				

*by switches inside the pnm-adapter or by shortcuts inside the cable.

†if two instruments of the same type are installed.

‡if indicated, the lowest two contacts of the plug socket at the pnm-adapter, that is either socket J3 or J2, are cut short (from the outside of the pnm-adapter).

**No pnm-adapter. Instead, it is necessary to exchange the cable.

Note The TubeCracker second bank is applied to two ports of the inlet board for external options. Therefore, it has a pnm-number. ▲

Using Peripherals with another IRMS

The options GasBench, PreCon or TubeCracker are available in two versions:

- one for Delta^{plus}XP, Delta^{plus}Advantage, or MAT 253
- one for Delta^{plus}, Delta^{plus}XL, or MAT 252.

Practice has shown that in some laboratories, options are not always connected to the same mass spectrometer, especially the Continuous Flow options like GasBench and PreCon. Depending on the analytical problem, they are sometimes transferred from one mass spectrometer to another. It is possible to switch between the newer generation mass spectrometers (Delta^{plus}XP, Delta^{plus}Advantage or MAT 253) and the older generation, when the subsequent important guidelines are followed.

- Applying an older peripheral device to a newer generation IRMS

  Use a plug and measure device. In case of PreCon and GP-Interface use a new connection cable. Each option delivered after June 2002 is delivered with the necessary hardware. For older devices, order a plug and measure device or a connection cable.

- Applying a peripheral device ordered with or for a newer generation mass spectrometer to an older generation IRMS.
  Connect the connection cable to the driver board.

  For most peripherals the driver board supplied with the older generation IRMS can be used directly.

  For peripherals like GasBench, PreCon or TubeCracker it is recommended to order a dedicated driver board.

Alternatively, a new address can be assigned to the driver board delivered with the older generation IRMS.

Caution Never put the plugs of the peripheral connection cable into the wrong socket on the driver board! Serious damage of the driver board may occur, which is not covered by any warranty.
On the other hand, if the jumpers are set to a wrong address, the device cannot be addressed, but nothing will be damaged. ▲

- Applying an option using an IEEE interface (HDO device, for example) delivered with an older generation IRMS to a newer generation IRMS. Install an additional IEEE interface.

IAEA Primary Standards

Calibrating versus international standards requires users to have their own specimens of Primary Standards. Primary Standards are exclusively distributed by the IAEA via agencies in Europe and the US. The reference list shown in Table 7-7 is taken from *IAEA TECDOC 825* and the *IAEA Analytical Quality Control Services Reference Materials Catalogue 2002-2003*.

Table 7-7. IAEA Primary Standards

Name	Nature		Isotopic ratio	δ [‰]	Reference standard
V-SMOW	water	$^{2}H/^{1}H$	(155.761 ± 0.05) x10e-6 (1) (155.751 ± 0.08) x10e-6 (2) (155.601 ± 0.12) x10e-6 (3)	0	VSMOW
		$^{18}O/^{16}O$	(2005.20 ± 0.45) x10e-6 (4)	0	VSMOW
		$^{17}O/^{16}O$	(379.91 ± 0.8) x10e-6 (5)	0	VSMOW
SLAP	water	$^{2}H/^{1}H$	(89.021 ± 0.05) x10e-6 (1) (89.12 ± 0,07) x10e-6 (2) (88.88 ± 0.18) x10e-6 (3)	-428.0 (6)	VSMOW
		$^{18}O/^{16}O$	(1893.91 ± 0.45) x10e-6 (7)	-55.50 (6)	VSMOW
NBS-19	calcite	$^{13}C/^{12}C$		1.95 (8)	VPDB
		$^{18}O/^{16}O$		-2.20 (8)	VPDB
				28.6 (9)	VSMOW
			Intercomparison materials		
GISP	water	^{2}H		-189.73 ± 0.87	VSMOW
		^{18}O		-24.784 ± 0.075	VSMOW
NBS-18	calcite	^{13}C		-5.029 ± 0.049	VPDB
		^{18}O		-23.035 ± 0.172	VPDB
IAEA-CO-1	calcite	^{13}C		2.48 ± 0.025	VPDB
		^{18}O		-2.437 ± 0.073	VPDB
IAEA-CO-8	calcite	^{13}C		-5.749 ± 0.063	VPDB
		^{18}O		-22.667 ± 0.187	VPDB
IAEA-CO-9	$BaCO_3$	^{13}C		-47.119 ± 0.149	VPDB
		^{18}O		-15.282 ± 0.093	VPDB

Refer to: *IAEA-TECDOC-825*: Reference and intercomparison materials for stable isotopes of light elements. Proceedings of a consultants meeting held in Vienna, 1-3 December 1993. International Atomic Energy Agency (IAEA).

Refer to Chapter 5.2 Environmental Level, pp. 55 in: IAEA Analytical Quality Control Services Reference Materials Catalogue 2002-2003. First edition, January 2002. Edited by Analytical Quality Control Services, International Atomic Energy Agency, P.O. Box 100, A-1400 Vienna.

Outdated Version

The GasBench II now allows using the third reference inlet for reference gases. Refer to topic "Reference Device" on page 3-23. No more pressure regulator is required to adjust Flush Fill. Instead, use the pressure reducer of the reference gas tank. Refer to topic "Optional hardware - Flush Fill, Trap and Trap 2" on page 3-5.

As no additional pressure regulator is available when flushing with helium (when preparing carbonates, for example), control the flush gas amount by timing. Therefore, in the time events list of the method, use the Flush Fill - On column to switch helium flow on and off. Refer to topic "Time Events tab - Time events list" on page 3-25.

The flush gas amount recommended is 500 mL. This means to switch on Flush Fill for 300 s, if the flow is 100 mL/min. Adjust the time to smaller values, if the flow is higher or to higher values, if the flow is lower. For details, see Figure 7-4 and Figure 7-5.

Figure 7-10 shows the outdated version of GasBench II (P/N 1114260) in top view. Figure 7-11 depicts it in side view. In Figure 7-12, its compressed air schematic is given. Figure 7-13 shows its tubing scheme.

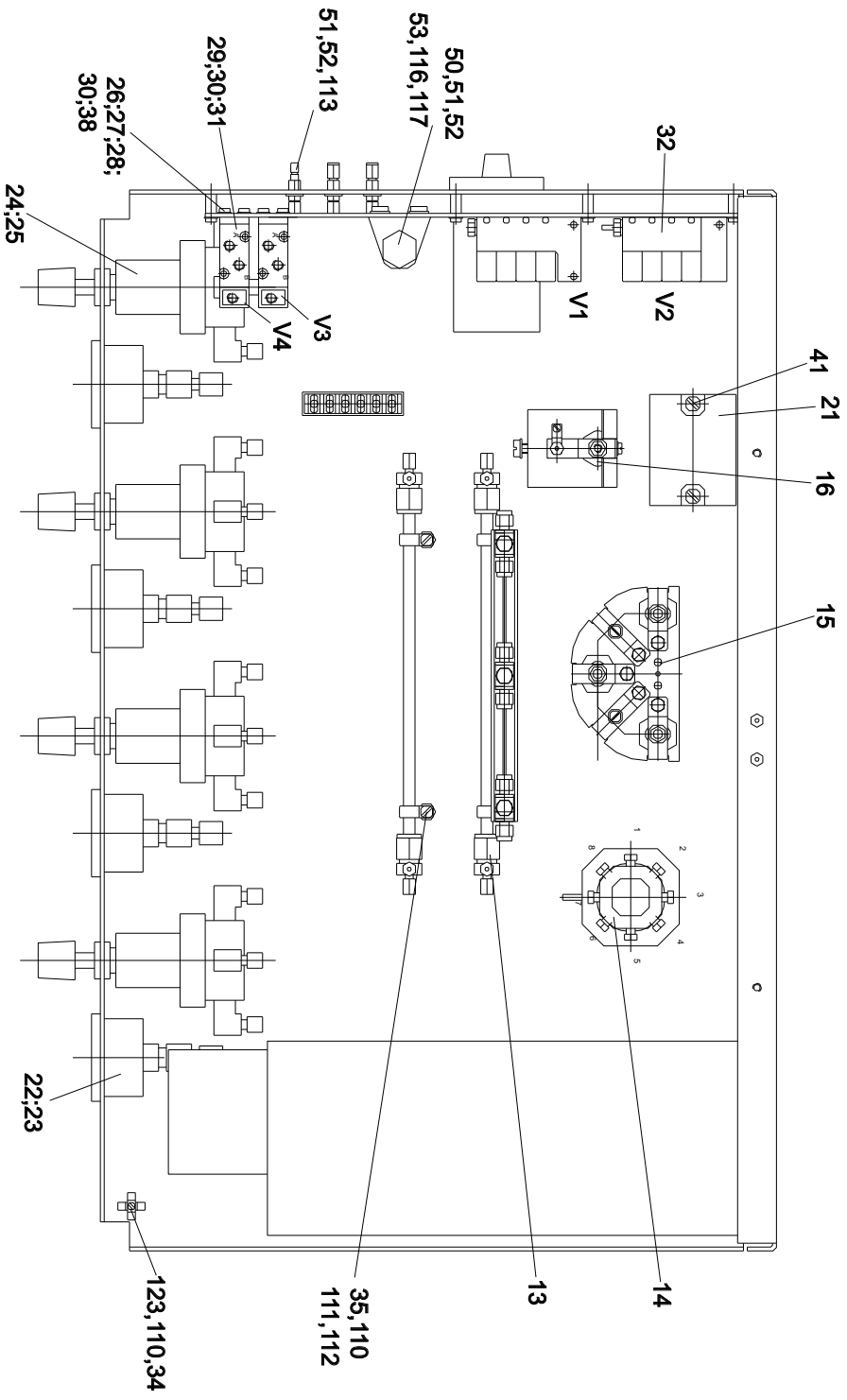


Figure 7-10. GasBench II - top view (outdated, P/N 1114260)

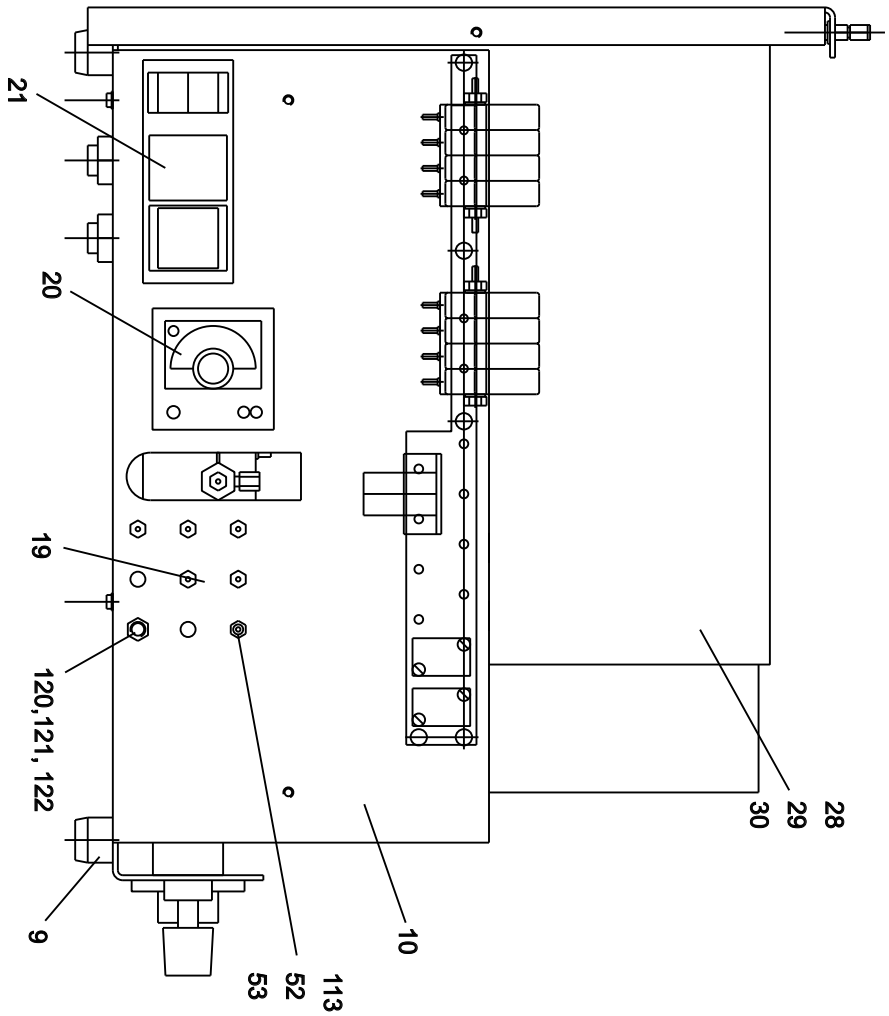


Figure 7-11. GasBench II - side view (outdated, P/N 1114260)

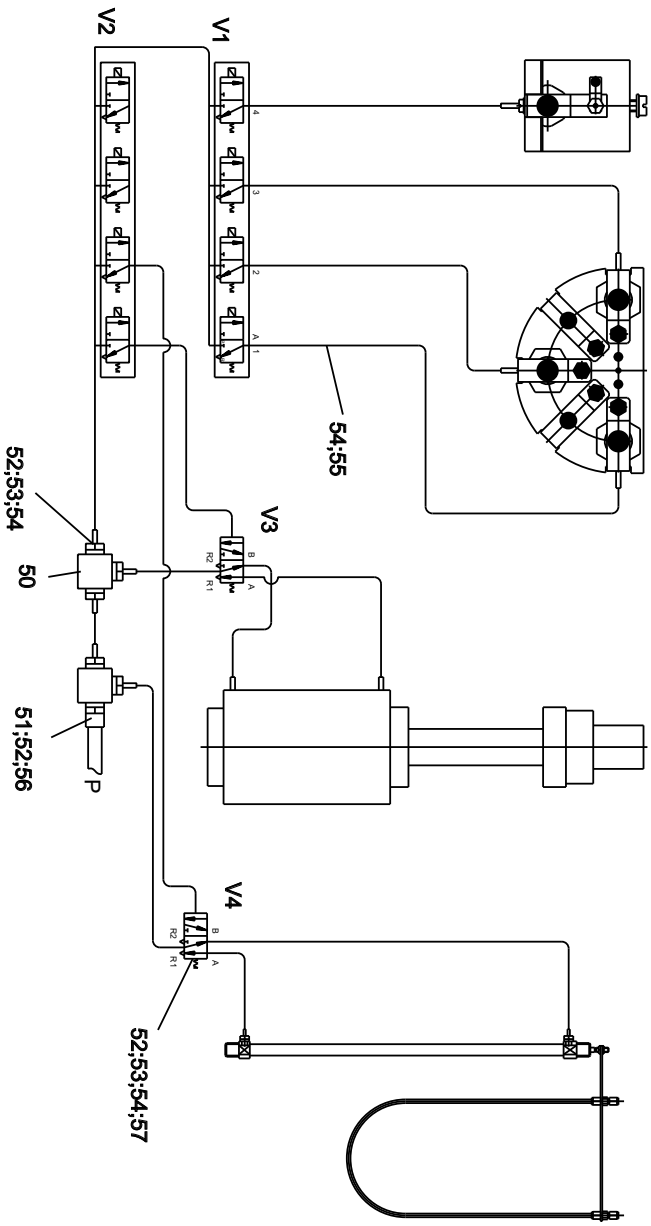


Figure 7-12. Compressed air schematic of GasBench II (outdated, until 2002, P/N 1114260)

Figure 7-13 shows the tubing scheme of the outdated version of GasBench II (P/N 1114260).

Note For better visualization, the scheme can be downloaded at the CIS of Thermo Fisher Scientific (Bremen) as a pdf file. It can then be printed on larger paper size, for example DIN A3. ▲

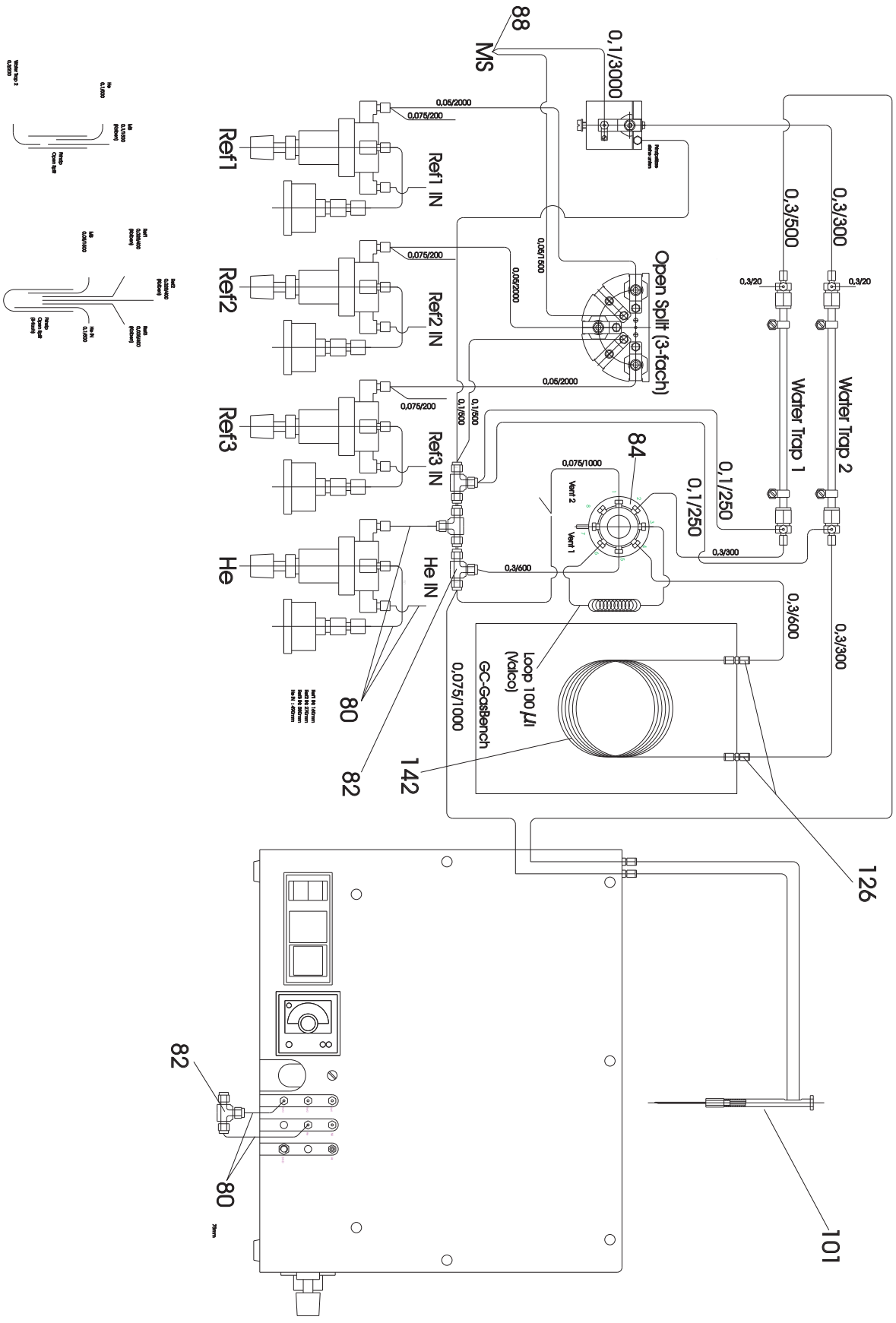


Figure 7-13. Tubing scheme of GasBench II (outdated, until 2002, P/N 1114260)

Glossary

This section lists and defines terms used in this manual. It also includes acronyms, metric prefixes, symbols, and abbreviations.

A

A ampere

ac alternating current

ADC analog-to-digital converter

AP acquisition processor

API atmospheric pressure ionization

ASCII American Standard Code for Information Interchange

B

b bit

B byte (8 b)

baud rate data transmission speed in events per second

C

°C degrees Celsius

cfm cubic feet per minute

CI chemical ionization

CID collision-induced dissociation

cm centimeter

cm^3 cubic centimeter

CPU central processing unit (of a computer)

CRC cyclic redundancy check

CRM consecutive reaction monitoring

<Ctrl> control key on the terminal keyboard

D

d depth

Da dalton

DAC digital-to-analog converter

dc direct current

driver A device-specific control program that enables a computer to work with a particular device.

DS data system

DSP digital signal processor

E

EI electron ionization

EMBL European Molecular Biology Laboratory

<Enter> Enter key on the terminal keyboard

ESD electrostatic discharge

ESI electrospray ionization

eV electron volt

F

f femto (10^{-15})

°F degrees Fahrenheit

forepump The pump that evacuates the foreline. A rotary-vane pump is a type of forepump.

ft foot

FTP file transfer protocol

FWHM Full Width at Half Maximum

G

g gram

G Gauss; giga (10^9)

GC gas chromatograph; gas chromatography

GC/MS gas chromatograph / mass spectrometer

GUI graphical user interface

H

h hour

h height

HPLC high-performance liquid chromatograph

HV high voltage

Hz hertz (cycles per second)

I

ICIS™ Interactive Chemical Information System

ICL™ Instrument Control Language™

ID inside diameter

IEC International Electrotechnical Commission

IEEE Institute of Electrical and Electronics Engineers

in inch

I/O input/output

ion optics Focuses and transmits ions from the ion source to the mass analyzer.

ion source A device that converts samples to gas-phase ions.

K

k kilo (10^3, 1000)

K kilo (2^{10}, 1024)

KEGG Kyoto Encyclopedia of Genes and Genomes

kg kilogram

L

l length

L liter

LAN local area network

lb pound

LC liquid chromatograph; liquid chromatography

LC/MS liquid chromatograph / mass spectrometer

LED light-emitting diode

log file A text file, with a .log file extension, that is used to store lists of information.

µ micro (10^{-6})

M

m meter

m milli (10^{-3})

M mega (10^6)

M^+ molecular ion

MB Megabyte (1 048 576 bytes)

MH^+ protonated molecular ion

min minute

mL milliliter

mm millimeter

MS mass spectrometer; mass spectrometry

MS MS^n power: where n = 1

MS/MS MS^n power: where n = 2

MS^n MS^n power: where n = 1 through 10

m/z Mass-to-charge ratio. An abbreviation used to denote the quantity formed by dividing the mass of an ion (in u) by the number of charges carried by the ion. For example, for the ion $C_7H_7^{2+}$, *m/z*=45.5.

N

n nano (10^{-9})

NCBI National Center for Biotechnology Information (USA)

NIST National Institute of Standards and Technology (USA)

noise Any random disturbance that obscures the clarity of a signal.

O

OD outside diameter

Ω ohm

outlier A calibration data point that does not appear to correlate to other calibration data points within experimental error.

P

p pico (10^{-12})

Pa pascal

PCB printed circuit board

PE protective earth

PID proportional / integral / differential

P/N part number

P/P peak-to-peak voltage

ppm parts per million

psi pounds per square incH

R

RAM random access memory

relative standard deviation A measure of the dispersion of a group of measurements relative to the mean of the group. Relative standard deviation is expressed as a percentage of the average value. The percent relative standard deviation is calculated as:

$$\%RSD = 100\ (S / \bar{X})$$

where S is the standard deviation and $\bar{X}$ is the sample mean.

RF radio frequency

RMS root mean square

ROM read-only memory

rotary-vane pump A mechanical vacuum pump that establishes the vacuum necessary for the proper operation of the turbomolecular pump. (Also called a roughing pump or forepump.)

RS-232 An accepted industry standard for serial communication connections. This Recommended Standard (RS) defines the specific lines and signal characteristics used by serial communications controllers to standardize the transmission of serial data between devices.

S

s second

serial port An input/output location (channel) for serial data transmission.

SIM selected ion monitoring

SRM selected reaction monitoring

standard deviation In statistics, the standard deviation is a measure of the dispersion of a group of measurements. For example, masses, times, or intensities. Standard deviation is calculated as follows:

$$s = \sqrt{Var(x_i...x_N)}$$

where Var (Xi...XN) is the variance.

See also relative standard deviation.

T

TCP/IP transmission control protocol / Internet protocol

TIC total ion current

Torr A unit of pressure, equal to 1 mm of mercury and 133.32 Pa.

turbomolecular pump A vacuum pump that provides a high vacuum for the mass spectrometer and detector system.

U

u atomic mass unit

UHV ultra high vacuum

V

V volt

V ac volts alternating current

V dc volts direct current

vol volume

W

w width

W watt

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Numerics

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Thermo Fisher Scientific Inc.
81 Wyman Street
P.O. Box 9046
Waltham, Massachussetts 02454-9046
United States

www.thermo.com

Thermo SCIENTIFIC