Finnigan™ GasBench II

Operating Manual

Revision A
111 8342

Thermo
ELECTRON CORPORATION

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Reparatur - Begleitkarte

Bitte vollständig ausfüllen

Repair-Covering Letter

Please fill in completely

Absender:
Dispatcher:

Geräte-Type:
Instrument Type:

Service-Nr.:
Service-No.:

Sie erhalten zur Reparatur unter unserer Bestell-Nr.:
You receive for repair under our Order No.: ----------

☐ **DOA**

☐ **Teil wurde nicht benutzt / part not used**

☐ **Teil wurde nur für Testzwecke verwendet / used for test purposes only**

☐ **Festgestellte Mängel oder deren Auswirkung:**
Established Defect or its Effect:

Bitte detaillierte Angaben machen / Please specify in Detail

Ein Austauschteil haben wir erhalten unter Kommissions-Nr.:
An Exchange Part already received with Commission No.:

Ja/Yes **Nein/No**

Die Anlage ist außer Funktion
The System is out of Function **Ja/Yes** **Nein/No**

Durch die nachfolgende Unterschrift bestätige(n) ich/wir, daß die o.g. Teile frei von gesundheits - schädlichen Stoffen sind, bzw. vor Ihrer Einsen - dung an Thermo Electron Bremen dekontami - niert wurden, falls die Teile mit giftigen Stoffen in Verbindung gekommen sind.

By signing this Document I am/we are certifying that the a.m. Parts are free from hazardous materials. In case the parts have been used for the analysis of hazardous substances I/we attest that the parts have been decontaminated before sending them to Thermo Electron Bremen.

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Name _____

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Tell us more... Let us know more about how you use this product:

My Organization Is: (Check one only)

- ❑ Commercial (for profit) lab
- ❑ Government lab
- ❑ Hospital / Clinic
- ❑ Research Institute
- ❑ University / College
- ❑ Veterinary
- ❑ Other _____

Job Function: (Check one only)

- ❑ Administration
- ❑ Lab Management
- ❑ Operator
- ❑ Other _____

My Primary Application Is: (Check one only)

- ❑ Analytical
- ❑ Biomedical
- ❑ Clinical / Toxicology
- ❑ Energy
- ❑ Food / Agriculture
- ❑ Forensic / Toxicology
- ❑ Pharmaceutical
- ❑ Research / Education
- ❑ Other _____

Reader Survey... Help us to improve the quality of our documentation by answering a few questions:

Finnigan GasBench II Operating Manual *Revision A 111 8342*

	Strongly Agree	Agree	Disagree	Strongly Disagree
The manual is well organized.	1	2	3	4
The manual is clearly written.	1	2	3	4
The manual contains all of the information I need.	1	2	3	4
The instructions are easy to follow.	1	2	3	4
The instructions are complete.	1	2	3	4
The technical information is easy to understand.	1	2	3	4
The figures are helpful.	1	2	3	4

Additional Comments: (Attach additional sheets if necessary.)

_____
_____
_____
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Tear this sheet from the manual, fold it closed, stamp it, and drop it in the mail.

fold

From _____

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Place Stamp Here

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Finnigan Advanced Mass Spectrometry
Product Marketing
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declaration of conformity according to EN 45014
Dichiarazione di conformità alla EN 45014

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manufacturers name:
nome produttore:

Finnigan MAT GmbH

Adresse des Herstellers:
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28197 Bremen
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erklärt, daß das Produkt
declares that the following product
dichiara che il seguente prodotto

GASBENCH

mit den folgenden Produktspezifikationen übereinstimmt:
complies with the following product specifications:
rispetta le seguenti specifiche del prodotto:

EMV (Störemissionen):
EMC (emissions):
EMC (emissioni):

EN 50081-1, EN 55011

EMV (Störfestigkeit):
EMC (immunity):
EMC (immunità):

EN 50082-2, EN 61000-4-2, -3, -4, -6, EN 50204

Elektrische Sicherheit:
electrical safety:
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EN 61010-1

Ergänzende Informationen:
complementary information:
informazioni complementari:

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This product complies with the EMC directive 89/336/EEC and the Low Voltage Directive 73/23/EEC.
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Bremen, Germany, 7. July 1998

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Head of Engineering:
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Finnigan MAT GmbH

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manufacturers address:
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complies with the following product specifications:
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EMV (Störemissionen):
EMC (emissions):
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EN 50081-1, EN 55011

EMV (Störfestigkeit):
EMC (immunity):
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Head of Engineering:
Responsabile construzione:

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Notice on the Proper Use of Thermo Electron Bremen Instruments

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

Safety and EMC Information

In accordance with our commitment to customer service and safety, these instruments have 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.

> **Caution.** 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.

Identifying Safety Information

This reference manual contains precautionary statements that can prevent personal injury, instrument damage, and loss of data if properly followed. All statements of this nature are called to your attention through the use of bold type and the following icons:

Warning! | Cold Surface! | Hot Surface | Strong Magnetic Field! | High Voltage!

Every instrument has specific hazards, so be sure to read and comply with the following precautions. They will help ensure the safe, long-term use of your system.

1. 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.
2. Only use fuses of the type and current rating specified. Do not use repaired fuses and do not short-circuit the fuse holder.
3. 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.

4. Do not change the external or internal grounding connections. Tampering with or disconnecting these connections could endanger you and/or damage the system.

> **Caution.** 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.

5. Never run the system without the housing on. Permanent damage can occur.
6. 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.)
7. Damage can also result if the instrument is stored for prolonged periods under unfavorable conditions (e.g., subjected to heat, water, etc.).
8. Always disconnect the power cord before attempting any type of maintenance.
9. 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.

> **Warning.** Avoid any contact of the system with liquids! Permanent damage can occur due to high voltage, e.g. leaking liquids might get into contact with electronic components and cause a short circuit.

Contents

Read This First

Welcome to the Thermo Electron, Finnigan GasBench II Operating Manual!

Finnigan GasBench II Operating Manual describes how to setup and use Finnigan GasBench II.

It includes the following chapters:

Chapter 1: Preinstallation Requirements summarizes requirements related to site, power and the various gases in use before operating Finnigan GasBench II.

Chapter 2: Hardware Components treats autosampler installation, sample tray and its temperature control, gas supply, measurement needle and flush needle, water removal, valco eight-port valve, GC oven and open splits.

Chapter 3: Isodat 2.0 Software describes how to start Isodat 2.0 and subsequently how to create a GasBench-related configuration.

Then, the chapter denotes how to create a new GasBench II method and a new GasBench II sequence in Isodat 2.0's Acquisition Mode. Various types of GasBench II methods are demonstrated as examples, including e.g. an autosampler, an acid pump or a PreCon. Finally, basics of autosampler programming are discussed.

Chapter 4: Basic Operations describes several test routines, e.g. leak check, checking column flows, zero enrichment test (that is, standard on/off test), linearity test and condition test.

The chapter ends pointing out how to start an automated sequence and summarizing Frequently Asked Questions (FAQ).

Chapter 5: Measurement Procedures for Real Samples deals with carbonates, Dissolved Inorganic Carbon (DIC), breath gas analysis, CO_2 in atmospheric concentrations and water equilibration (^{18}O and H/D, respectively).

Chapter 6: Options describes carbonate option and cryo traps option.

Chapter 7: Technical Information outlines test instructions, auxiliary parts and mechanical parts. It provides technical information about the capillaries in use and compressed air supply as well.

Changes to the Manual and Online Help

To suggest changes to this manual or the online Help, please send your comments to:

Thermo Electron (Bremen) GmbH
Finnigan Advanced Mass Spectrometry
Barkhausenstr. 2
D-28197 Bremen

Germany

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

Abbreviations

The following abbreviations are used in this and other manuals and in the online Help.

A	ampere
ac	alternating current
ADC	analog-to-digital converter
AP	acquisition processor
APCI	atmospheric pressure chemical ionization
API	atmospheric pressure ionization
ASCII	American Standard Code for Information Interchange
b	bit
B	byte (8 b)
baud rate	data transmission speed in events per second
°C	degrees Celsius
CD	compact disc
CD-ROM	compact disc read-only memory
cfm	cubic feet per minute
CI	chemical ionization
CIP	carriage and insurance paid to
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	depth
Da	dalton
DAC	digital-to-analog converter
dc	direct current
DDS	direct digital synthesizer
DEP™	direct exposure probe
DS	data system
DSP	digital signal processor

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	femto (10^{-15})
°F	degrees Fahrenheit
.fasta file	extension of a SEQUEST search database file
FOB	free on board
ft	foot
FTP	file transfer protocol
g	gram
G	giga (10^{9})
GC	gas chromatograph; gas chromatography
GC/MS	gas chromatograph/mass spectrometer
GND	electrical ground
GPIB	general-purpose interface bus
GUI	graphical user interface
h	hour
h	height
HPLC	high-performance liquid chromatograph
HV	high voltage
Hz	hertz (cycles per second)
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
k	kilo (10^{3}, 1000)
K	kilo (2^{10}, 1024)
KEGG	Kyoto Encyclopedia of Genes and Genomes
kg	kilogram

l	length
l	liter
LAN	local area network
lb	pound
LC	liquid chromatograph; liquid chromatography
LC IRMS	liquid chromatography isotope ratio mass spectrometer
LC/MS	liquid chromatograph/mass spectrometer
LED	light-emitting diode
µ	micro (10^{-6})
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
n	nano (10^{-9})
NCBI	National Center for Biotechnology Information (USA)
NIST	National Institute of Standards and Technology (USA)
OD	outside diameter
Ω	ohm
p	pico (10^{-12})
Pa	pascal
PCB	printed circuit board
PID	proportional / integral / differential
P/N	part number

P/P	peak-to-peak voltage
ppm	parts per million
psig	pounds per square inch, gauge
RAM	random access memory
RF	radio frequency
RMS	root mean square
ROM	read-only memory
RS-232	industry standard for serial communications
s	second
SIM	selected ion monitoring
solids probe	direct insertion probe
SRM	selected reaction monitoring
ss	stainless steel
SSQ®	single stage quadrupole
TCP/IP	transmission control protocol / Internet protocol
TIC	total ion current
Torr	torr
TSQ®	triple stage quadrupole
u	atomic mass unit
URL	uniform resource locator
V	volt
V ac	volts alternating current
V dc	volts direct current
vol	volume
w	width
W	watt
WWW	World Wide Web

Note. Exponents are written as superscripts. In the corresponding online Help, exponents are sometimes written with a caret (^) or with *e* notation because of design constraints in the online Help. For example:

MS^n (in this manual) Ms^n (in the online Help)

10^5 (in this manual) 10^5 (in the online Help)

Typographical Conventions

Typographical conventions have been established for Thermo Electron San Jose manuals for the following:

- Data input
- Boxed information
- Topic headings

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 represented in **bold face letters**. (Titles of topics, chapters, and manuals also appear in bold face letters.)
- 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 and a different font. For example, "click on **Close**".

Boxed Information

Information that is important, but not part of the main flow of text, is displayed in a box such as the one below.

> **Note**. Boxes such as this are used to display information.

Boxed information can be of the following types:

- **Note** – information that can affect the quality of your data. In addition, notes often contain information that you might need if you are having trouble.
- **Caution** – information necessary to protect your instrument from damage.
- **Warning** – hazards to human beings. Each Warning is accompanied by a Warning symbol.

Topic Headings

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

Chapter 1
Chapter Name

1.2 Second Level Topics

Third Level Topics

Fourth Level Topics

Fifth Level Topics

Reply Cards

Thermo Electron San Jose manuals contain one or two reply cards. All manuals contain a Customer Registration / Reader Survey card and some contain a Change of Location card. These cards are located at the front of each manual.

The Customer Registration / Reader Survey card has two functions. First, when you return the card, you are placed on the Thermo Electron San Jose mailing list. As a member of this list, you receive application reports and technical reports in your area of interest, and you are notified of events of interest, such as user meetings. Second, it allows you to tell us what you like and do not like about the manual.

The Change of Location card allows us to track the whereabouts of the instrument. Fill out and return the card if you move the instrument to another site within your company or if you sell the instrument. Occasionally, we need to notify owners of our products about safety or other issues.

Chapter 1
Preinstallation Requirements

1.1 Site and Power Requirements

> **Note.** Check all items mentioned below by ❑ and confirm them by ☑.
>
> Then, send back this form to your Thermo Electron Customer Support Organization.

Finnigan GasBench II is attached to Finnigan isotope ratio mass spectrometers, e.g. Finnigan Delta^{plus}XP, and will be placed either on top of the IRMS or on a peripherals support table.

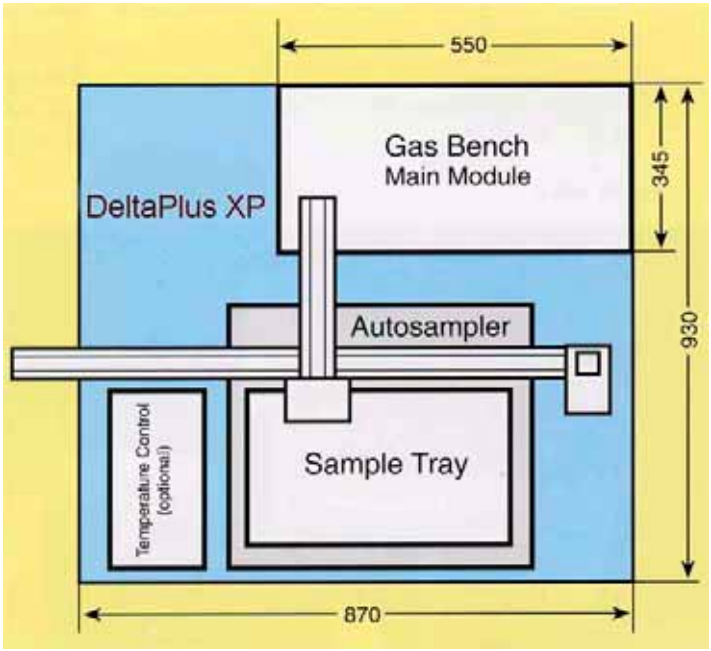


Figure 1-1. Site Requirements of GasBench II

> **Note.** The space required is 900 mm width * 900 mm depth.

❑

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

1.2 Gas Requirements

- He 5.0 (that is 99.999 %) 4 bar as carrier gas
- He 4.6 with 0.3 % CO_2 4.5 4 bar for acceptance tests

For Water Equilibration

- ^{18}O He 4.6 with 0.3 %-1 % CO_2 4.5 4 bar as auxiliary gas
  CO_2 4.5 (that is 99.995 %) 4 bar as reference gas
- HD He 4.6 with 2 % H_2 4 bar as auxiliary gas
  H_2 4.5 (that is 99.995 %) 4 bar as reference gas

For Carbonates

- CO_2 4.5 (that is 99.995 %) 4 bar as reference gas

For DIC (Dissolved Inorganic Carbon)

- CO_2 4.5 (that is 99.995 %) 4 bar as reference gas

Warning. All gas lines should be oil-free and preferably flame-dried. The gas lines, or gas tanks respectively, should be at a distance of 1 - 1.5 m to the instrument.

Warning. 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 40 psi and 70 psi.

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

Note. Thermo Electron (Bremen) recommends to install a high capacity purifier (Part No. 114 0790) to ensure constant and affordable high quality of the helium carrier gas.

Chapter 2
Hardware Components

2.1 GasBench II Layout

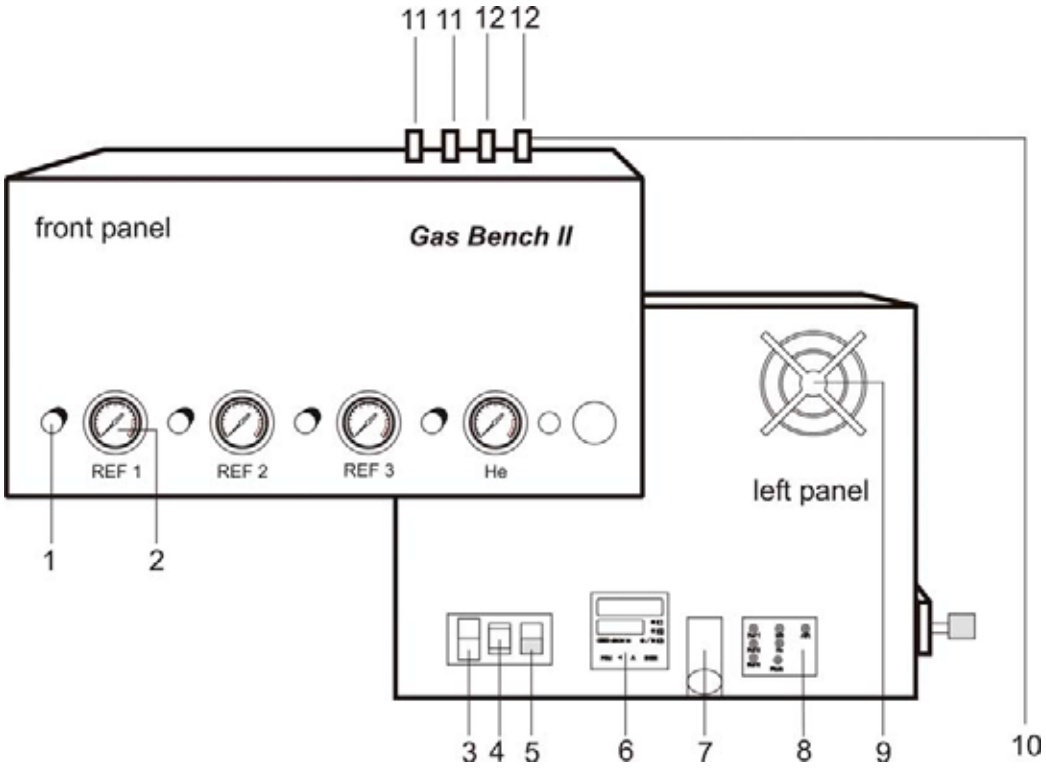


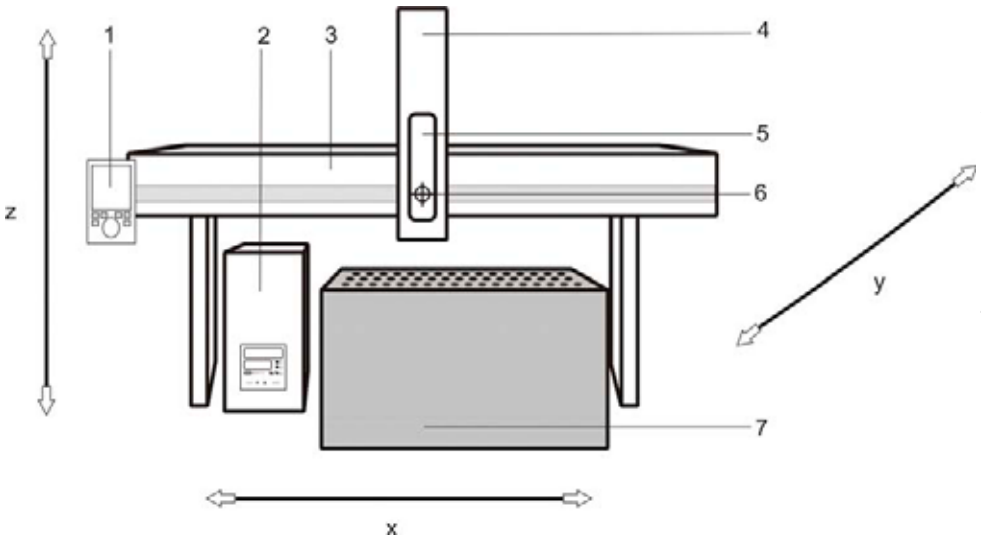
Figure 2-1. GasBench II Unit - Front and Left Side View

1. pressure regulator (e.g. reference gas 1)
2. pressure gauge (e.g. reference gas 1)
3. main fuse
4. main power plug
5. main power switch (on/off)
6. JUMO itron 16 temperature controller
7. cable for connection to IRMS
8. gas connection terminal (refer to Figure 2-14).
9. fan
10. connection terminals for sampling needles
11. sample/purge
12. purge

Figure 2-2. GasBench II with Kiel Carbonate Device and Delta^{Plus} Advantage - Front View

Figure 2-3. GasBench II General Survey - Open

2.2 Autosampler



1. display and controls
2. heating unit with JUMO itron 16 temperature controller
3. syringe carrier
4. injection head
5. syringe
6. position of measurement needles
7. sample tray

Figure 2-4. Schematic of Autosampler A200S and Sample Tray

Figure 2-5. Autosampler A200S and Sample Tray

Installing the 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.

1. Unpack the box containing the autosampler's components.
2. Screw the autosampler's feet 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 sample tray and heating block onto the base plate. Therefore, the base plate has prefabricated cut-outs, where the heating block is simply inserted. Due 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 kurled head screws.

> **Note.** In case of 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 together with the autosampler.
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 (e.g. during installation here), 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.

Torx Screwdrivers Provided with the Autosampler

- 360/T 10 * 80

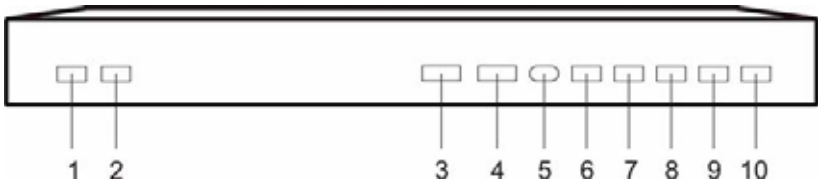
- 360/T 20 * 100
- 360/T 25 * 100

Connecting the Autosampler

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

Note for Service Engineer. Part No of replacement fuse is 114 1420.

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 **8**, that is serial 3, in Figure 2-6.
3. Connect the autosampler power supply to the mains supply and the autosampler.



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 2-6. Syringe Carrier Rear Panel (GC PAL or Combi PAL)

2.3 Sample Trays

Layout

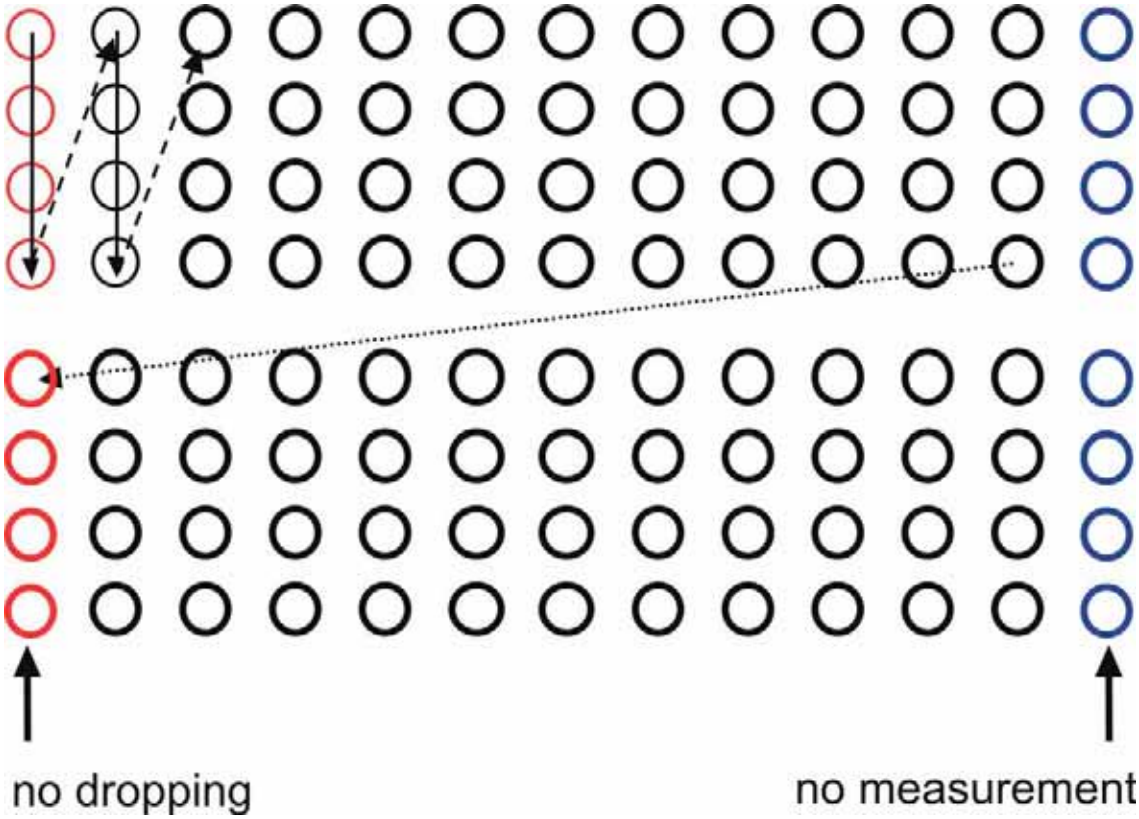


Figure 2-7. Schematic of Autosampler Movement across the Trays (Ex Factory)

The trays contain 96 holes:

- spacing of the holes is 26 mm * 26 mm
- diameter of the holes is 16 mm
- depth of the holes is 85 mm

Per default, Finnigan GasBench II is delivered with a ***non-thermostated*** sample tray, Part No. 111 2780, suitable for equilibrium work or breath gas analysis. See Figure 2-8 and Figure 2-9.

Figure 2-8. Non-Thermostated Sample Tray - Side View (Part No. 111 2780)

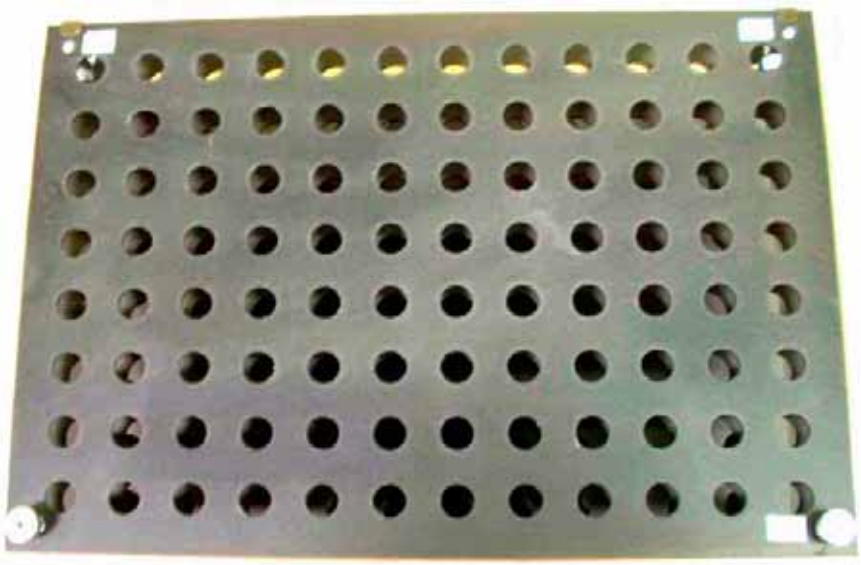


Figure 2-9. Non-Thermostated Sample Tray - Top View (Part No. 111 2780)

However, if temperature control is required for your application, the ***thermostated*** sample tray, Part No. 111 2800, is used. See Figure 2-10.

When using this sample tray, take into account that:

- it is optimized for carbonate measurement (refer to **Carbonates** on page 5-6).
- the delay between acid dosing and measurement is 1 hour.

- the acid reservoir is thermostated.
- two columns can not be used.

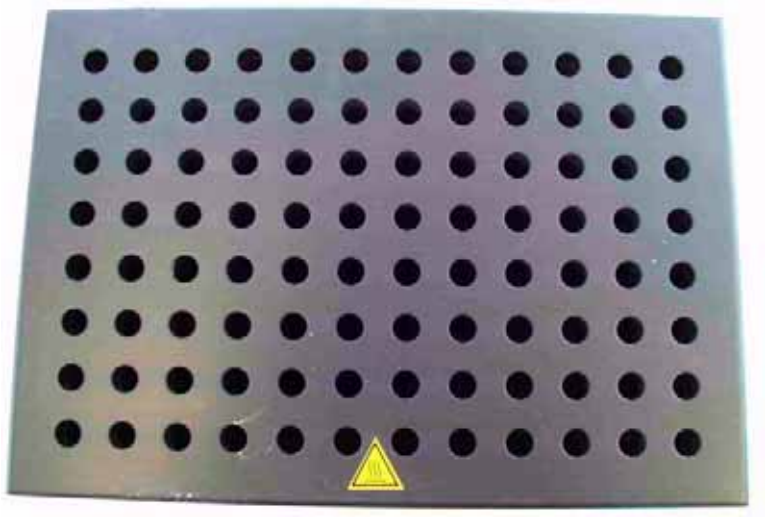


Figure 2-10. Thermostated Sample Tray - Top View (Part No. 111 2800)

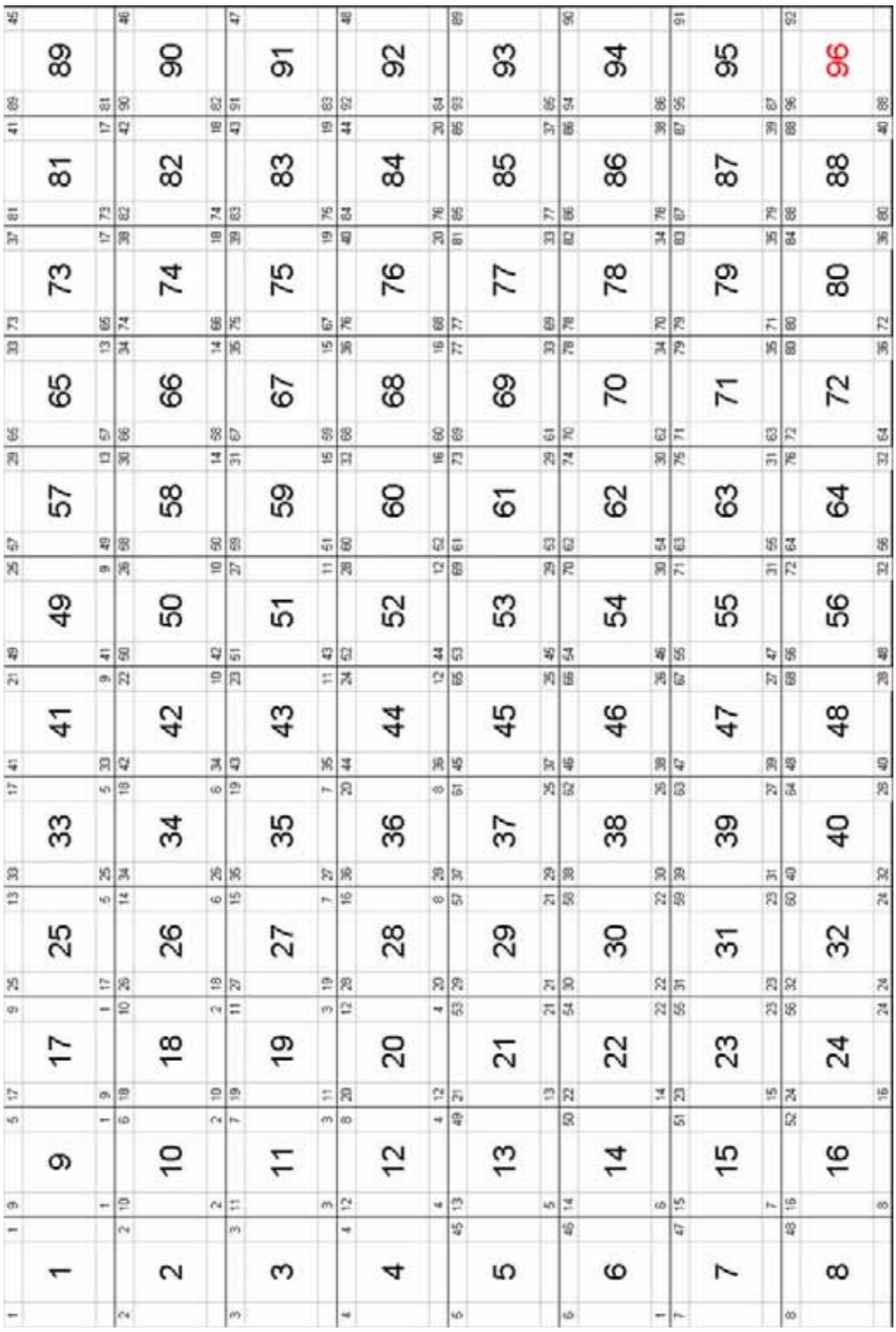
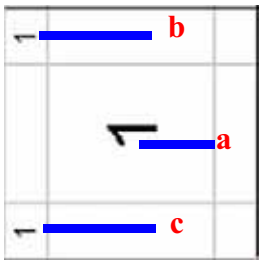


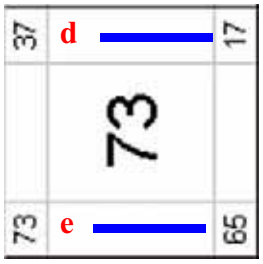
Figure 2-11. Sampling Positions as Defined in the "Tray 01" Object in the Autosampler Memory and Crosslink to Sequence Lines within Sequence Examples



a autosampler position in sequence

b row number in sequence (carbonates)

c row number in sequence (equilibration)



d double needle flush

e flush fill

Programming JUMO itron 16 Temperature Controller for Sample Tray

For programming JUMO itron 16 temperature controller for ***GC oven***, see **Programming JUMO itron 16 Temperature Controller for GC Oven** on page 2-32. For details refer to Jumo itron 16 temperature controller manual.

The temperature controller, located externally, allows controlling sample tray temperature. Notice the three keys (see arrows in Figure 2-12):

- ***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)

Figure 2-12. JUMO itron 16 Temperature Controller for Sample Tray

Step 1 of Programming

- Press the ***P*** key and hold it for 2 s.

- Pass through the menu until ***Y.0*** is displayed.
- Again, press the ***P*** key and hold it for 2 s.

Set ***C111*** to 003 (transducer type, e.g. Pt 100, 2-wire).

Set ***C112*** to 1 (number of decimal places and temperature unit, e.g. 1 and ºC).

Set ***C113*** to 33 (controller type, e.g. double setpoint).

Set ***C115*** to 1 (ramp function, that is, ramp function in ºC/min).

Set ***C116*** to 0 (outputs on fault, that is 0 %; minimum output limiting ***Y.2*** is effective).

Set ***SP.L*** to 0 (lower setpoint limiting).

Set ***SP.H*** to 80 (upper setpoint limiting).

Set ***OFFS*** to 0 (process value correction).

Step 2 of Programming

- Again, press the ***P*** key and hold it for 2 s.
- Press the ***Arrow Up/Down*** key to change values.

Set ***Pb.1*** to 2.8 (proportional band 1).

Set ***Pb.2*** to 2.8 (proportional band 2).

Set ***d.t.*** to 35 (derivative time in s).

Set ***r.t.*** to 135 (reset time in s).

Set ***CY.1*** to 2 (cycle time 1 in s).

Set ***CY.2*** to 2 (cycle time 2 in s).

Set ***db*** to 0 (contact spacing).

Set ***HyS.1*** to 0 (differential 1).

Set ***HyS.2*** to 0 (differential 2).

Set ***Y.0*** to 0 (working point in %).

Set ***Y.1*** to 100 (maximum output in %).

Set ***Y.2*** to 0 (minimum output in %).

Set ***d.F*** to 5 (filter time constant in s).

Set ***rA.Sd.*** to 9.99 (ramp slope in ºC/h or ºC/min).

Alternative: Automatic Programming

Let the temperature controller program itself automatically. Thereby, you don’t need to specify all the parameters mentioned above on your own.

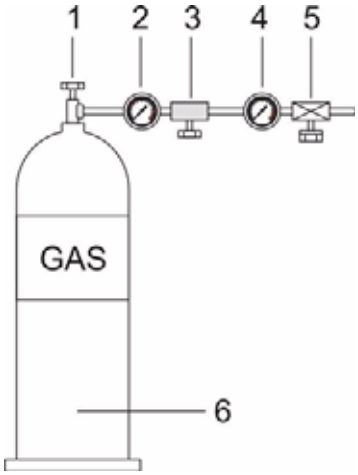
2.4 Gas Supply

Gases in Use

For all applications helium is needed as carrier gas. Its purity should be at least 99.999 % He. We recommend to use a second cylinder switchover to prevent pressure loss during overnight operation. 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 2 % H_2 in He should result in a signal height of 9 V, which is optimal with regard to error margins.

Warning. 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.



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 2-13. Gas Tank

Installing the Gas Tanks

1. Connect the ***reference*** gases:
2. Connect the ***measurement*** gases.

3. Connect the ***equilibration*** gases, that is ***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 the Gas Tanks

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

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

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

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 2-13).
2. Open the main valve for two or three seconds to let the gas purge the whole valve system (see Figure 2-13).
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.

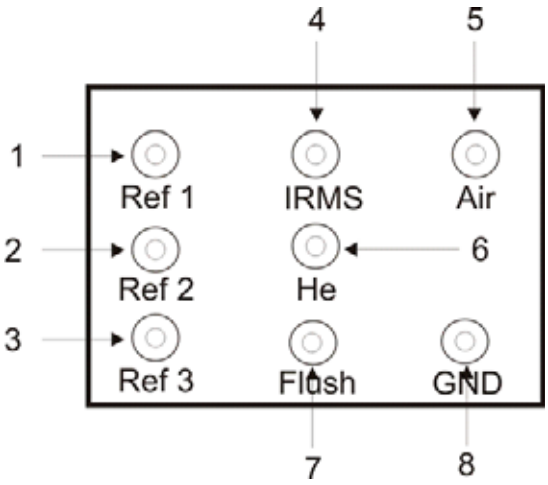
Gas Connections

To operate GasBench II and the IRMS, several gases are needed either from gas tanks or from the laboratory's main gas supply (e.g. compressed air). Refer to Figure 2-14 to locate the following 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 also Pos. 5 in Figure 2-14). It can be provided by the pressure regulator of the IRMS. Two capillaries leading the gas flow to the mass spectrometer input valve must be installed (see Pos. 4 in Figure 2-14). 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 detailed explanation, refer to **Measurement Procedures for Real Samples** on page 5-1.

Warning. 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.

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 mass spectrometer's reference port. Refer to Figure 7-8, Figure 7-9 and Table 7-8.

Use the quick release connection to connect the blue compressed air cable to the compressed air connectors of the IRMS. See Figure 7-10. 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.



1 - 3 connections for reference gases
4 capillary feedthrough to IRMS
5 connection for compressed air
6 He carrier gas connection
7 flush connection
8 GND (ground)

Figure 2-14. Connection Panel of Gas Bench II

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 reqired flush gas at the lower inlet port.

2.5 Measurement Needle

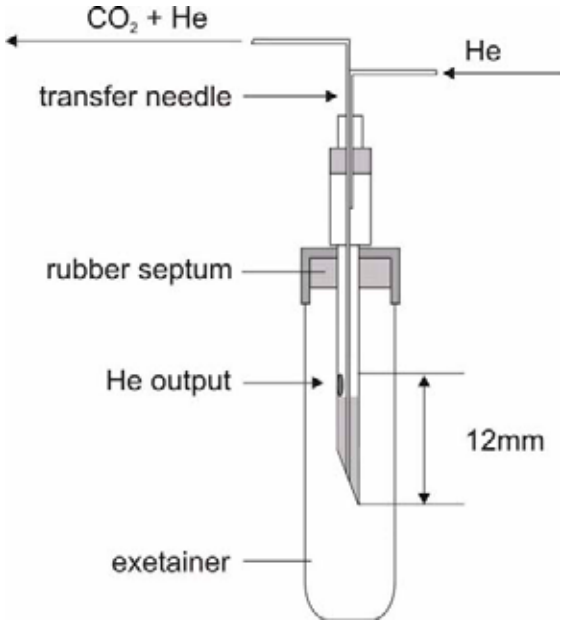


Figure 2-15. Measurement Needle

> **Note.** The measurement needle is sometimes synonymously called transfer needle.

The measurement needle is located in the Combi Pal autosampler. The correct connection is important to guarantee high GC performance. Refer to **How to Connect the Measurement Needle** on page 2-16.

How to Connect the Measurement Needle

Connect the measurement needle as outlined in Figure 2-16. The measurement needle should direct the He 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 2-16. Now, helium gently moves CO_2 from the exetainer's headspace into the fused silica capillary within the needle tip. From here, the sample is transferred through the water removal (**1**, see **Principle of On-Line Water Removal** on page 2-21) and the valco loop for GC injection. The He flow should be at approximately 0.4 - 0.5 ml/min (measured at the vent of the valco valve; see Figure 2-25).

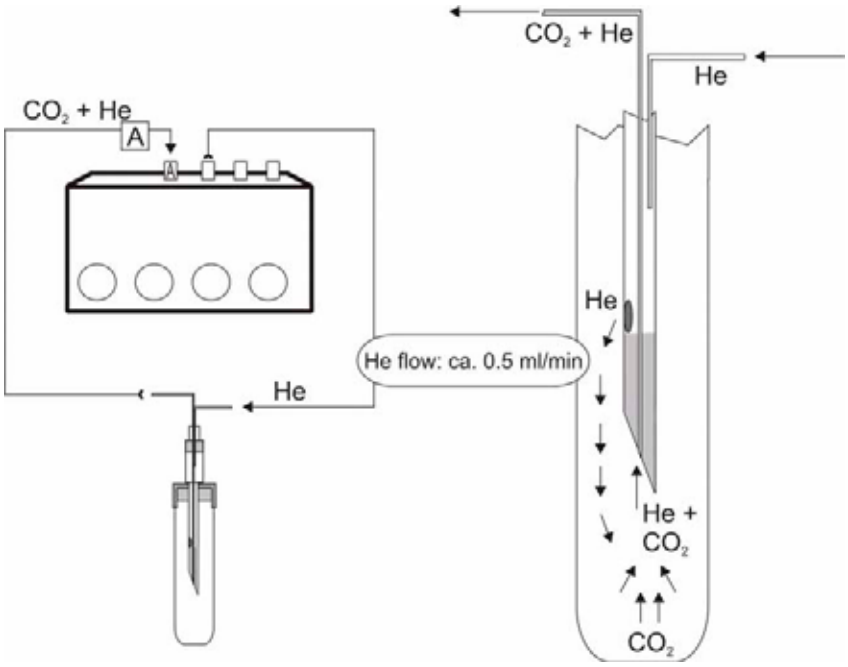
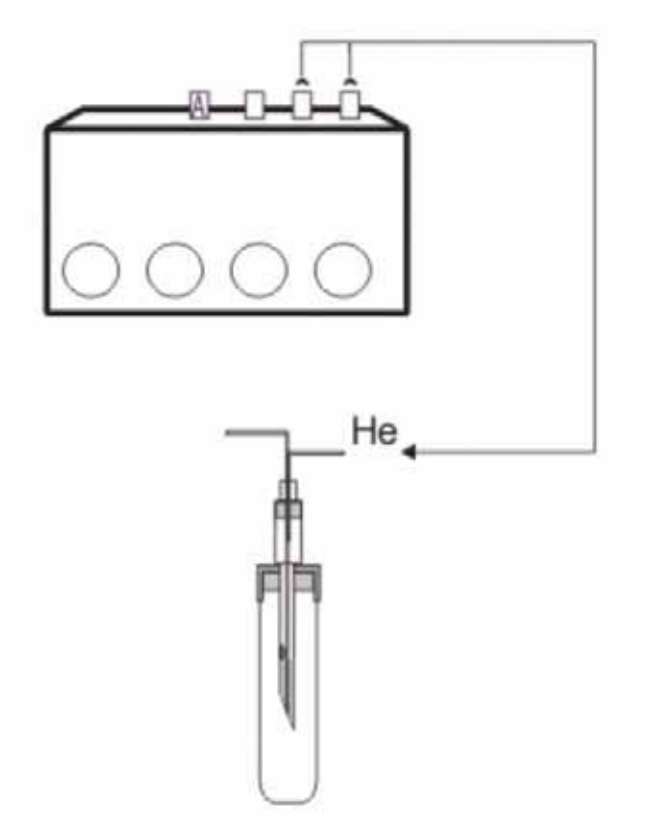


Figure 2-16. Connection of Measurement Needle

2.6 Flush Needle

How to Connect the Flush Needle



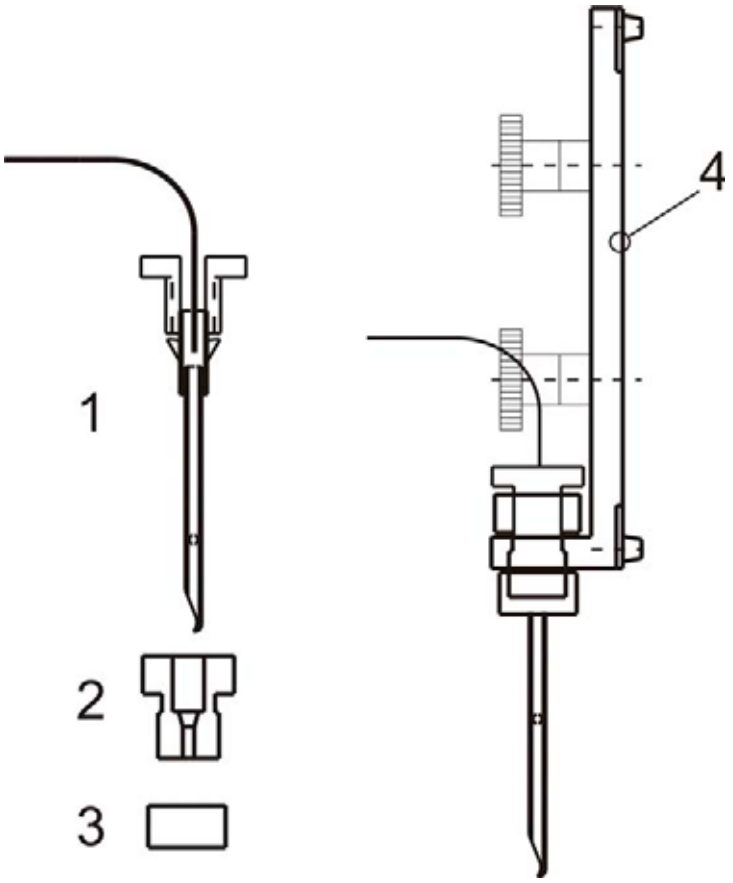
- Flushing with He (~ 100 ml/min during 4 - 6 min) in case of carbonates and DIC
- Filling with a gas mixture of 0.3 - 0.4 % CO_2 in He and a flow of of 50 ml/min makes the use of glove bags and glove boxes unnecessary.

Figure 2-17. Connection of Flush Needle

> **Note.** It is possible to connect two flush needles and operate them simultaneously by using our double needle holder (Part No. 113 7120). Refer to Pos. 2 and Pos. 4 in Figure 2-18.
> The double needle holder is part of the Carbonate Kit (Part No. 064 4520). Refer to Table 6-1.

2.7 Mounting Syringe Needles into Autosampler

Figure 2-18 outlines the mounting of needles into the autosampler's needle holder. Notice that the relative positions between two needles are fixed when inserted into the holder. See **Carbonate Option (Part No. 113 2471) - Components** on page 6-2 for the part numbers.



1 any needle from flushing, measuring or acid

2 supporting screw
Refer to needle holder, Part No. 113 7080.

3 nut

4 single needle holder or double needle holder (complete, Part No. 113 7120)

Figure 2-18. Mounting Sampling or Flush Needles into Needle Holder

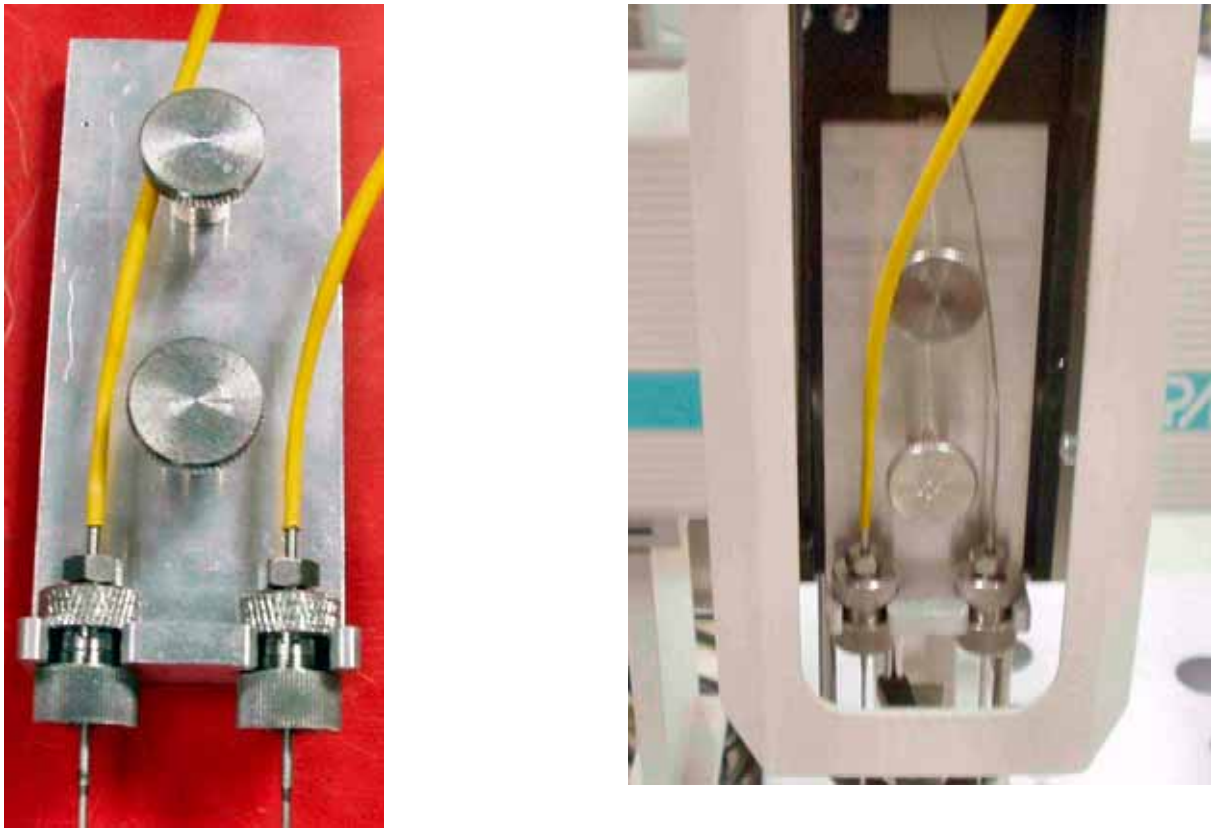


Figure 2-19. Double Needle Holder (Dismantled, left and within the Autosampler, right)

Figure 2-20. Inserting Double Needle Holder into Autosampler

2.8 On-Line Water Removal

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.
See Figure 2-21.

Principle of On-Line 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 ml/min. Due 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.

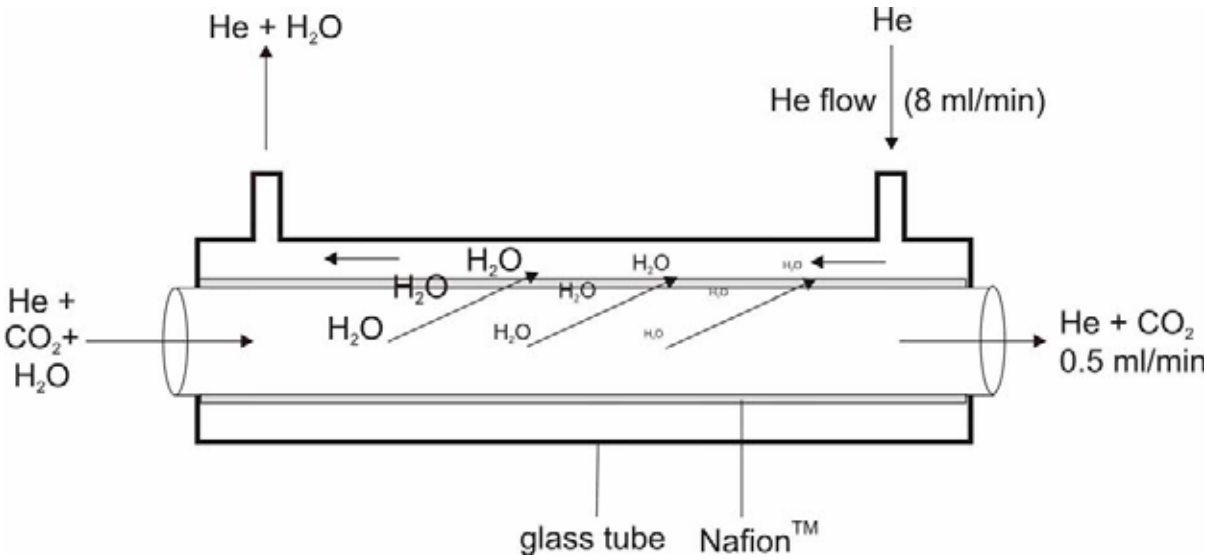
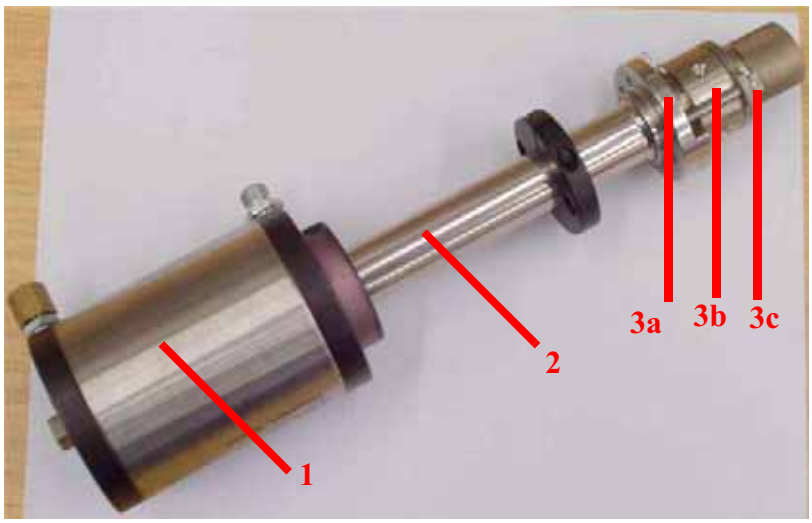


Figure 2-21. Schematic Online Water Removal

2.9 Principle of Valco Eight Port Valve



1 compressed air control

2 long shank; allows to introduce the functional head into the oven as head and control are thermally separated by the distance.

3 functional head; consists of a mounting plate **3a**, a n-port **3b** and a chequered knob on top **3c**.

The chequered knob must be unscrewed, if you want to withdraw the rotor. After inserting the rotor, screw in the chequered knob again.

Figure 2-22. Valco Eight Port Valve - Side View

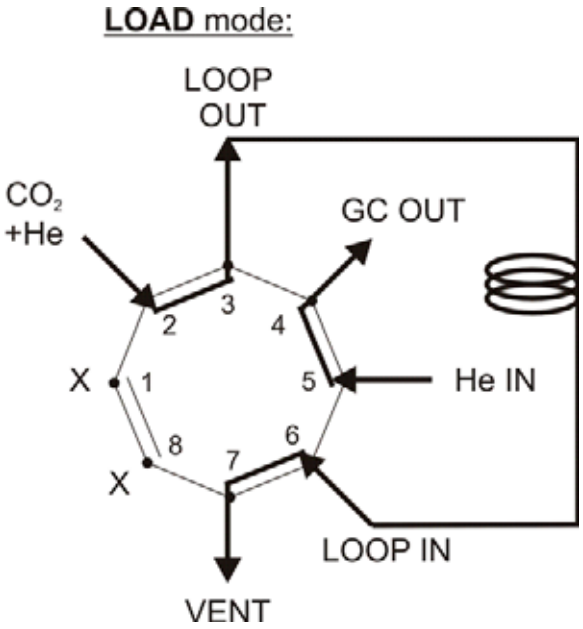
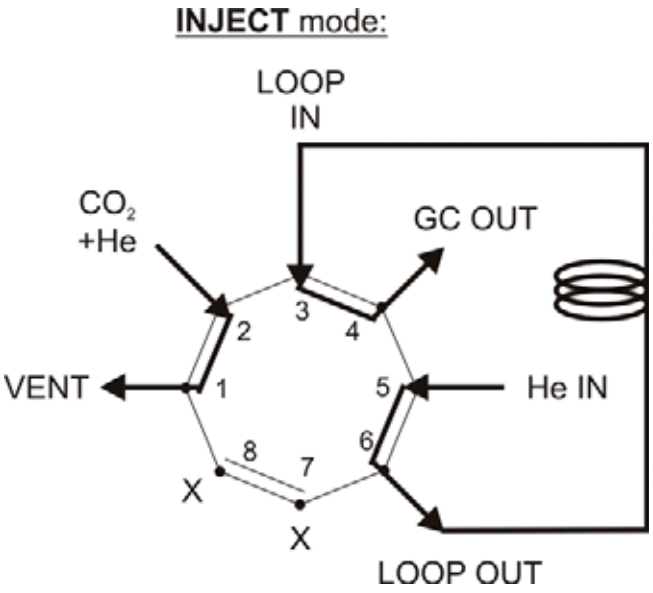


Figure 2-23. Valco Eight Port Valve - Load Mode

The Valco eight port valve is used in a six port setup. Two ports are in "standby" for each injection mode.

1. ***Load*** Mode

   - Ports 1 and 8 are in "standby".
   - The sample flow (He + CO_2) purges the sampling loop (e.g. 100 µl) via ports 2 ¦ 3 ¦ 6 ¦ 7.
   - The GC column is directly connected to the He pressure via ports 5 ¦ 4.



2. ***Inject*** Mode

- The gas content of the sampling loop is directly transferred onto the GC column by the GC flow (e.g. 2 ml/min) via ports 5 ¦ 6 ¦ 3 ¦ 4.
- The sample flow is directly connected to Vent via ports 2 ¦ 1.

Figure 2-24. Valco Eight Port Valve - Injection Mode

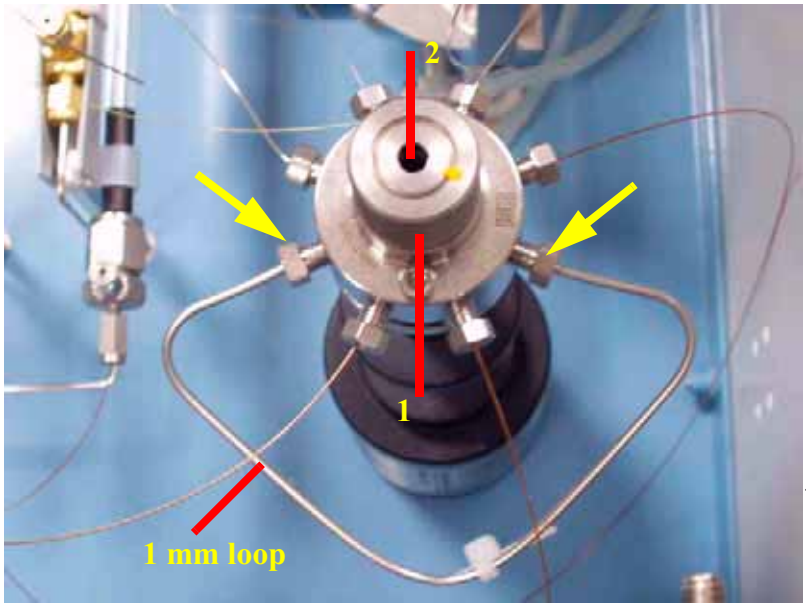
How to Change the Loop Size

Note. Refer to the valco documentation, that is Valco Instruments Co. Inc. (VICI): Technical Note 201: **Operation Notes and Cleaning Instructions**. It is part of your equipment.

Warning. Make sure the Valco is in Load Mode!

Changing the loop in Inject Mode will interrupt the GC column flow. This will cause damage to the GC column.

Warning. Always use Valco stainless steel ferrules for mounting the loop.



The arrows in Figure 2-25 show the two screws, which fasten the loop.

1 chequered screw; is used to fix the internal rotor, which is flexibly fitted within in the stator by a conical seal.

2 socket head screw; is used after fixing the internal rotor by the chequered screw.

The socket head screw allows to adjust the pressure acting from above upon the cone.

By increasing this pressure the internal rotor is tighted against the side walls.

Figure 2-25. Valco Valve with Loop - Top View

1. Switch the Valco to Load Mode.
2. Open the nuts on Port 3 and Port 6. Refer to Figure 2-25.
3. Replace the loop.Use loop sizes less than 250 ml for the two column types.
4. Tighten the nuts.
5. Inject the measurement 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.

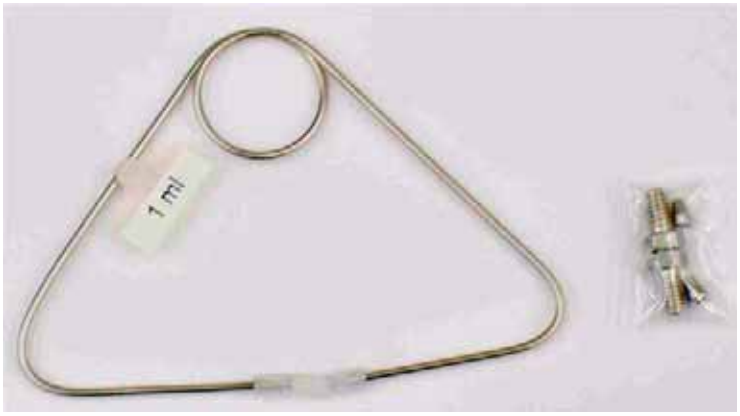


Figure 2-26. 1 ml Loop

Figure 2-27. 2 ml Loop

Figure 2-26 and Figure 2-27 are shown above as examples. Loops of 100 µl, 250 µl and 1 ml are already part of your equipment provided by Thermo Electron (Bremen). If necessary, loops of even bigger volumes are available. The 1 ml loop and the 100 µl loop are very similar.

2.10 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. 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 2-28 and Figure 2-32.

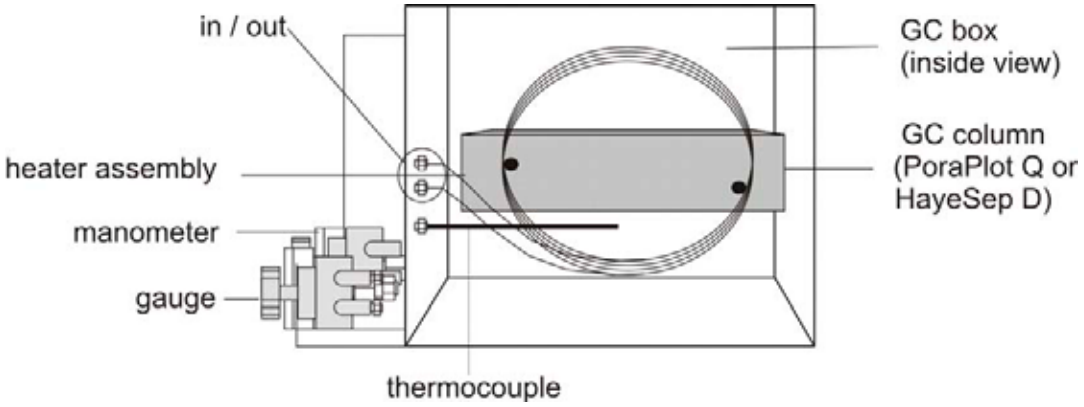


Figure 2-28. GC Oven - Open

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

Type "PoraPlot Q" GC Column

This column type is used in the current versions of GasBench II and part of your equipment.

Warning. Avoid fast pressure variations along the column ($\Delta p < 0.5$ psi/s)!

Table 2-1. Properties of "PoraPlot Q" GC Column

type	fused silica column
length	25 m
inner diameter	0.32 mm
helium pressure	10 - 12 psi
helium flow	approximately 2 ml/min
GC column temperature	room temperature (that is, 24 °C)

Type "HayeSep D" GC Column

This column type has been used in prior versions of GasBench.

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

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
helium flow	3 - 4 ml/min
GC column temperature	50 - 60 °C

Step 1 - Accessing the GC Column

Currently, the GC column is a static part of 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 GasBench II (front view). 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 GasBench II). Therefore, unscrew all seven screws using an allen wrench. See Figure 2-29.

Figure 2-29. GasBench II - Right Side Panel Being Opened

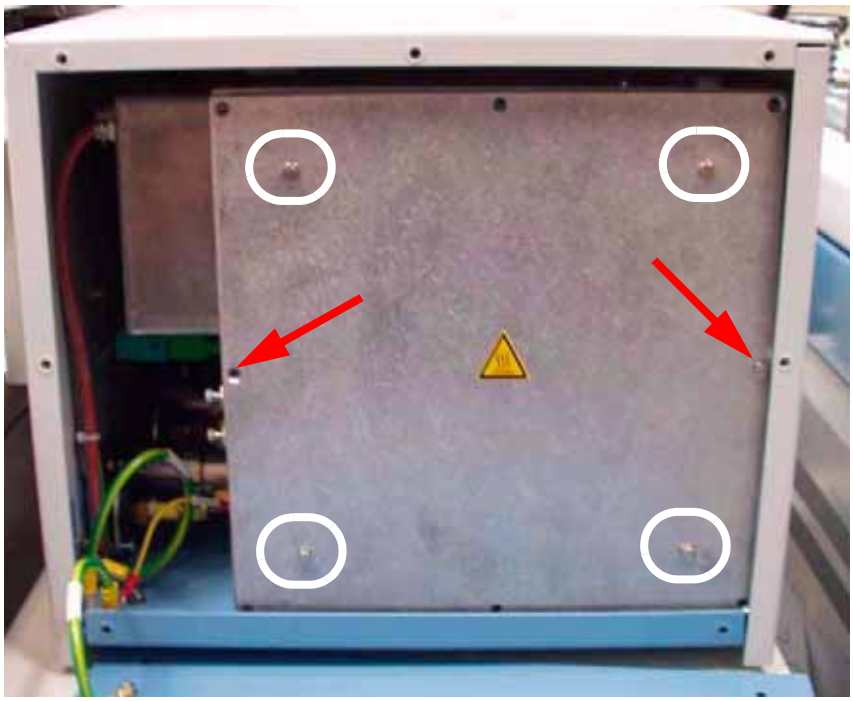


Figure 2-30. GasBench II - Right Side Panel Removed

Afterwards, only remove the two screws marked by arrows in Figure 2-30.

> **Note.** Leave the remaining four screws that are marked by white circles untouched, as they hold the isolation of the GC oven!

Figure 2-31. 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 2-31 as an example for the right side panel. Furthermore, the top side and the oven housing are grounded as well.

Step 2 - Changing the GC Column

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

- the functional part (light yellow, see **3** in Figure 2-34). It is the packed part of the column, that is the plot part.
- the post-column or pre-column (nearly transparent; see **1** in Figure 2-34)

The junction between both parts is established by a press-fit and shown as **2** in Figure 2-34.

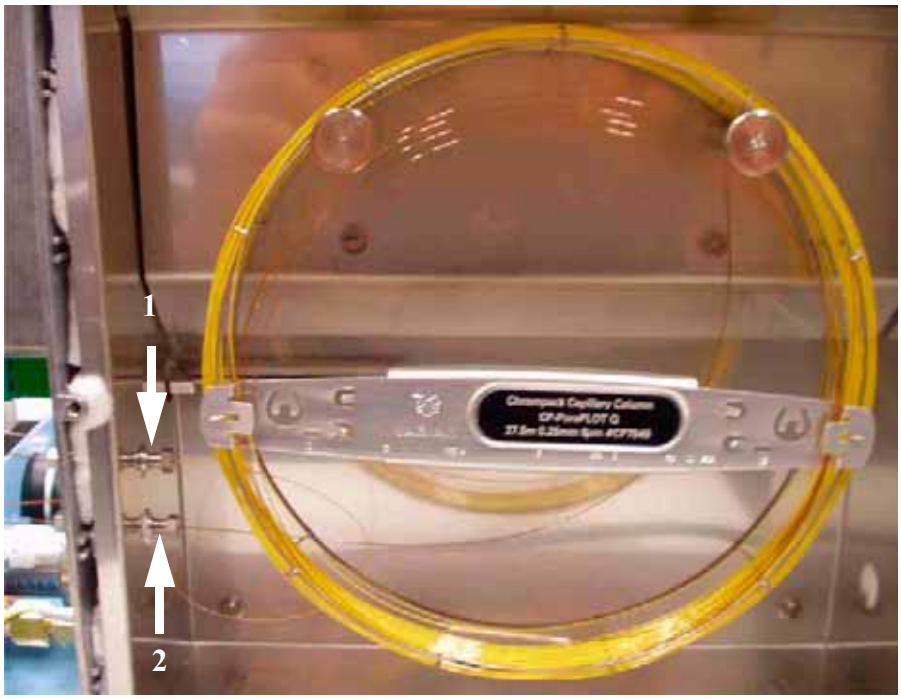


Figure 2-32. Column (Installed)

Figure 2-33. Column (with Blocked Ends)

Figure 2-33 shows the ends of the column, which are blocked by silicon plugs.

- Cut the silicon plugs off using a capillary cutter.
- Thereafter, insert each end into its bulkhead connection at the left side of the oven (see **1** and **2** in Figure 2-32) as follows:
  - The bulkhead connection, which is connected to the valco, is intended for the inlet of the column. It must be connected to the functional part of the column (light yellow).
  - As the outlet, the post-column must be connected to the bulkhead connection that is directed towards the water trap. 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.
- Screw the Swagelok® connection or valco connection on as follows:
  - Insert the respective ferrule.
  - Newly cut the capillary off.
  - Introduce the capillary.
  - Carefully tighten the ferrule until the capillary can no longer be pulled back. Do not tighten the ferrules/connections too strong!

Warning. 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 **Installation of the column in the GC**, **Conditioning**, **Storage** and **Description** refer to **Capillary Column Test Report** by Chrompack®. It is part of your Chrompack® capillary column.

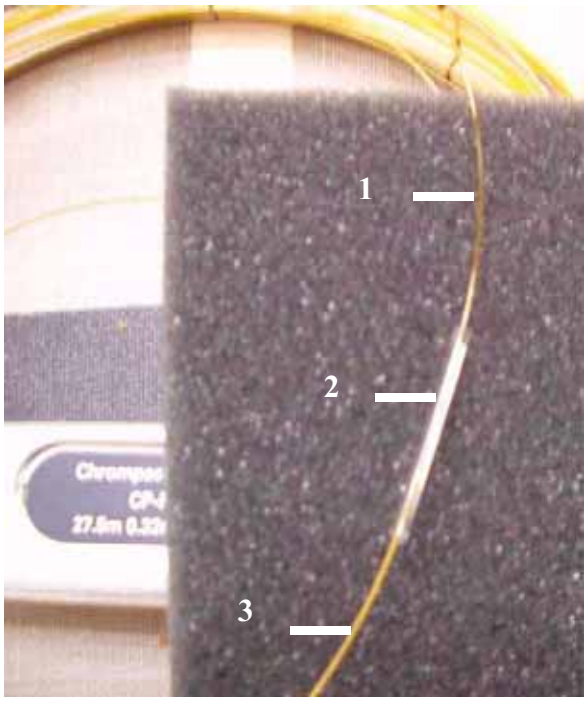


Figure 2-34. Junction between Both Parts of the Column

Programming JUMO itron 16 Temperature Controller for GC Oven

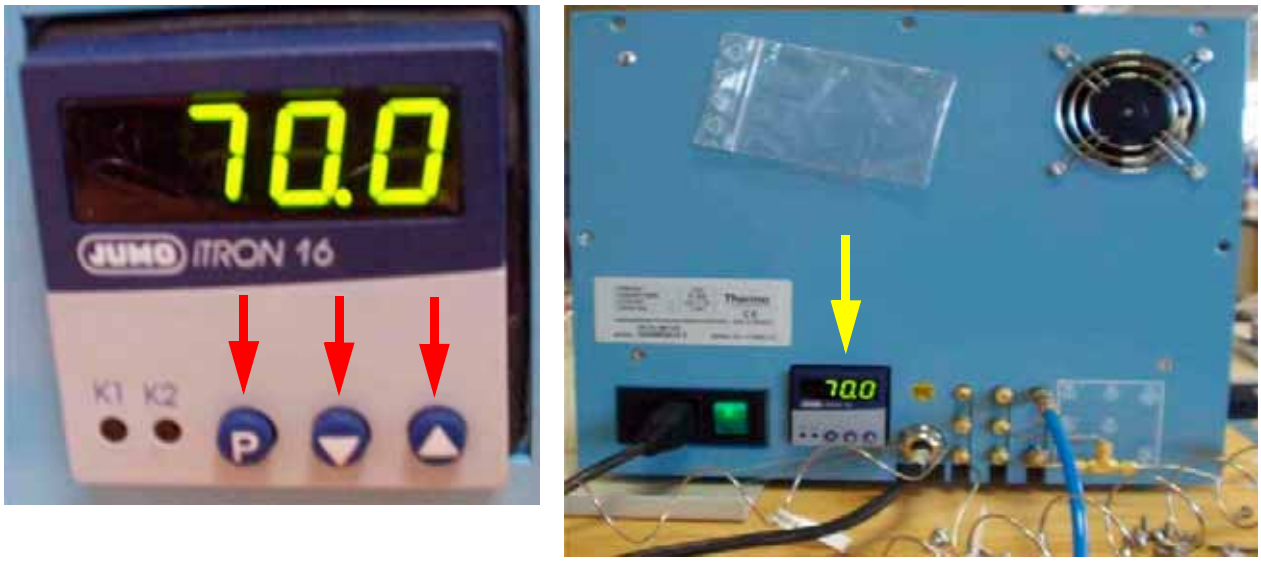


Figure 2-35. Jumo itron 16 Temperature Controller

The temperature controller, located at the side panel of GasBench II, allows to control the temperature of the GC oven. Notice the three keys:

- ***P*** key
  (for programming; values will be accepted automatically after 2 s).
- ***Arrow Up*** key
  (for increasing a particular value)
- ***Arrow Down*** key
  (for decreasing a particular value)

Programming - Step 1

- Press the ***P*** key and hold it for 2 s.
- Pass through the menu until ***Y.0*** is displayed.
- Again, press the ***P*** key and hold it for 2 s.

  Set ***C111*** to 043 (transducer type, e.g. NiCr-Ni, K).

  Set ***C112*** to 1 (number of decimal places and temperature unit, e.g. 1 and ºC).

  Set ***C113*** to 33 (controller type, e.g. double setpoint).

  Set ***C115*** to 0 (ramp function, that is ramp function off).

Set ***C116*** to 0 (outputs on fault, that is 0 %; minimum output limiting ***Y.2*** is effective).

Set ***SP.L*** to 0 (lower setpoint limiting).

Set ***SP.H*** to 200 (upper setpoint limiting).

Set ***OFFS*** to 0 (process value correction).

For details refer to Jumo itron 16 temperature controller manual.

Programming - Step 2

- Again, press the ***P*** key and hold it for 2 s.
- Press the ***Arrow Up/Down*** key to change values.

Set ***Pb.1*** to 9.1 (proportional band 1).

Set ***Pb.2*** to 0.9 (proportional band 2).

Set ***d.t.*** to 61 (derivative time in s).

Set ***r.t.*** to 243 (reset time in s).

Set ***CY.1*** to 50.4 (cycle time 1 in s).

Set ***CY.2*** to 50.4 (cycle time 2 in s).

Set ***db*** to 0 (contact spacing).

Set ***HyS.1*** to 0 (differential 1).

Set ***HyS.2*** to 0 (differential 2).

Set ***Y.0*** to 0 (working point in %).

Set ***Y.1*** to 100 (maximum output in %).

Set ***Y.2*** to 0 (minimum output in %).

Set ***d.F*** to 6.5 (filter time constant in s).

Set ***rA.Sd.*** to 0 (ramp slope in ºC/h or ºC/min).

For details refer to Jumo itron 16 temperature controller manual.

Alternative - Automatic Programming

Let the temperature controller program itself automatically. Thereby, you don’t need to specify all the parameters mentioned above on your own. For details refer to Jumo itron 16 temperature controller manual.

2.11 Open Splits

Reference Injection

This chapter outlines the functioning of the reference section of 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 also Figure 2-36 and Figure 2-37). A permanent flow of 0.25 ml/min transports the content of the interface tube to the IRMS.

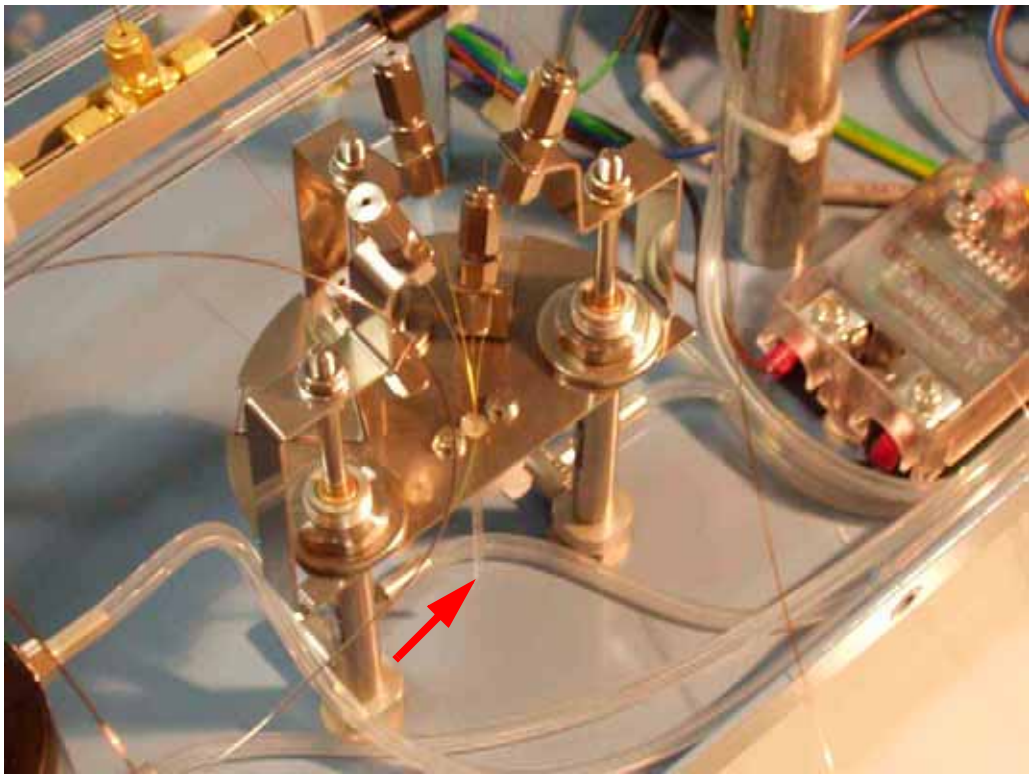


Figure 2-36. Reference Inlet (Open Split)

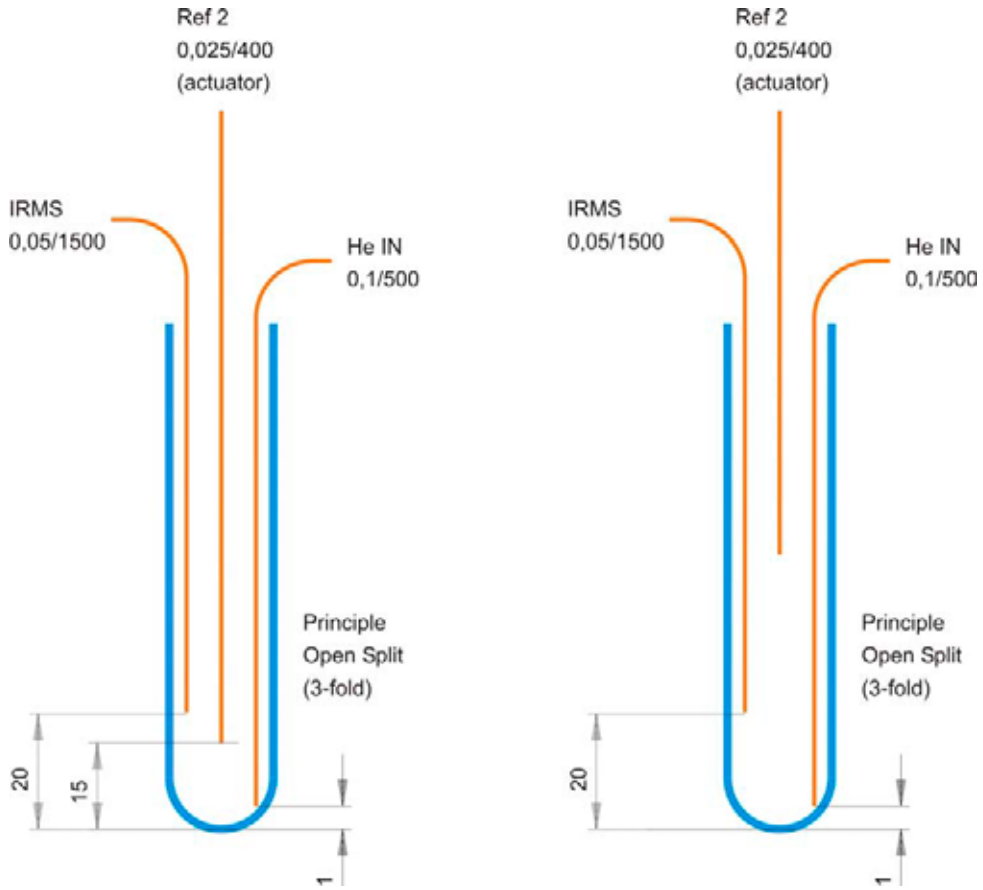


Figure 2-37. Principle of Reference Gas Introduction

Principle of Reference Gas introduction

- left side: reference gas ***on***
- right side: reference gas ***off***

To inject a reference gas, the corresponding reference capillary moves to the bottom of the open split interface (see Figure 2-37). The reference gas, e.g. CO_2, 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, e.g. 20 s, is defined by the time between injecting and removing the reference gas capillary.

Sample Injection and Dilution

Figure 2-38. Sample Inlet (Open Split)

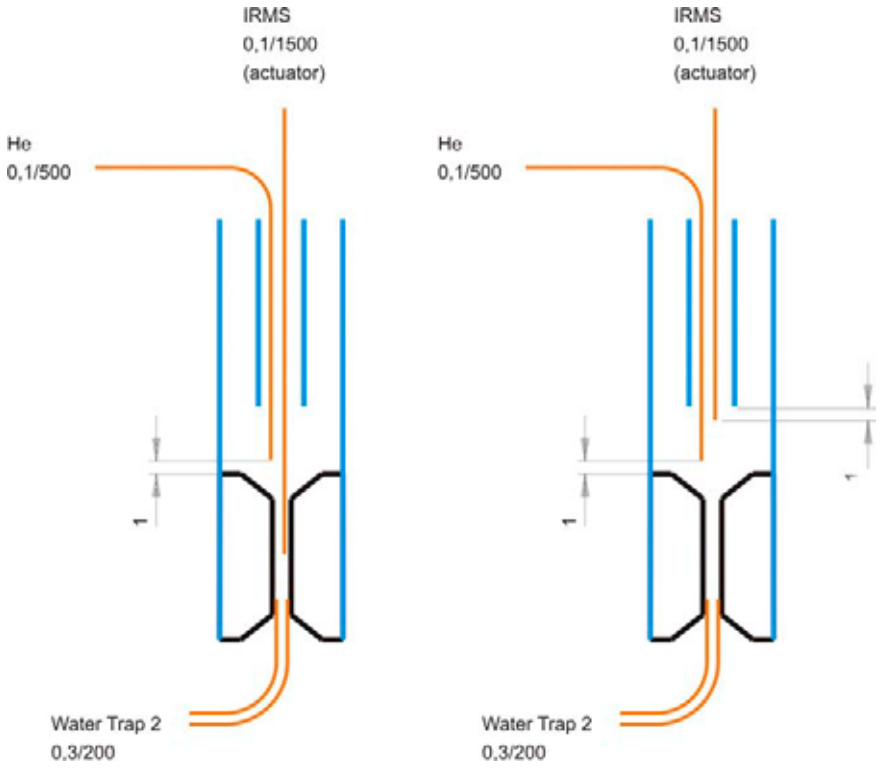


Figure 2-39. Sample Injection and Dilution

Principle of Active Open Split

- left side: no dilution
- right side: 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.

"OUT" position

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

"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.

Note. Notice a difference between GC applications and GasBench applications:

In case of GC applications, the mass spectrometer capillary is completely decoupled from GC.

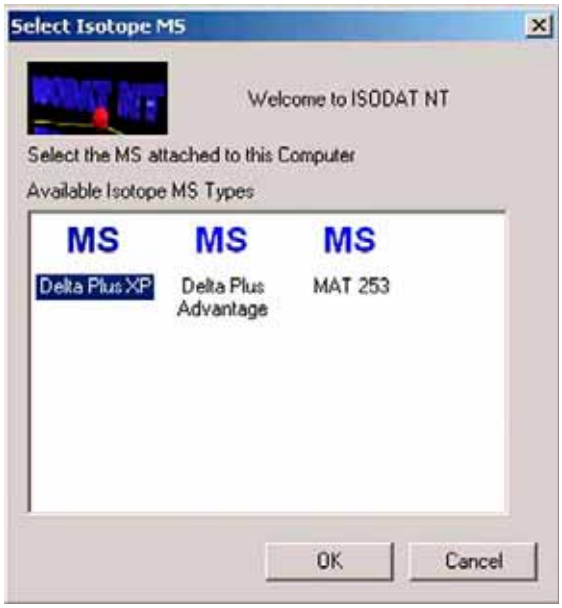
In case of GasBench applications however, only partial decoupling occurs.

Chapter 3
Isodat 2.0 Software

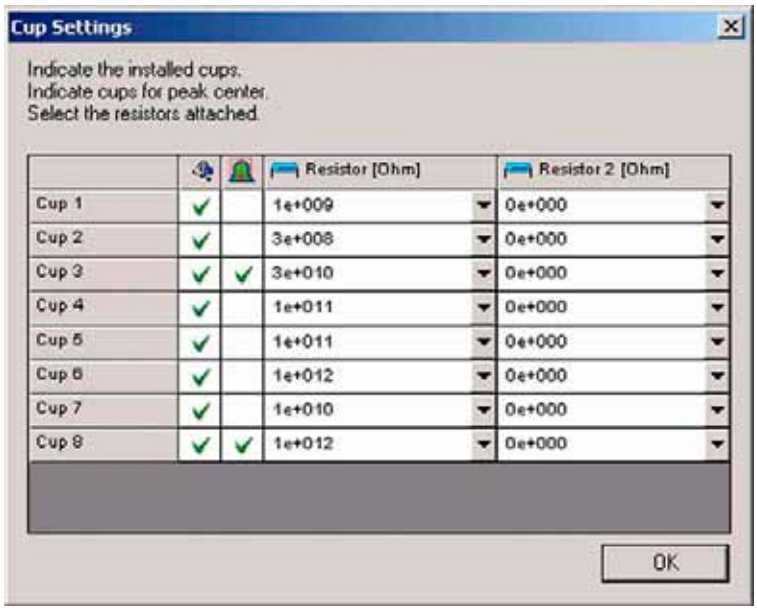
3.1 Starting Isodat 2.0

- After installing Isodat 2.0, start it by a double-click.

- Open the ***Configurator*** by a double-click.
  The Configurator window will appear.



- This box only appears when starting the system the very first time or after Reset of the IRMS.
- Select your particular ***IRMS***, e.g. Delta^{plus} XP
- Confirm by ***OK***.



- Look, whether the cups are ***Installed*** or ***Not Installed***  .
- Look at the ***Peak Center*** option of the cups  .
- Look at the ***Resistor*** values [Ω] of the cups  .
- Look at the ***Resistor 2*** values [Ω] of the cups  .

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

- In the ***Gas Configuration Editor***, check for your particular Configuration (e.g. ***CO2***) 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 (e.g. 3) is displayed together with the corresponding masses (e.g. m/z 44, m/z 45, m/z 46) below the grid.
- Finally, press the ***Save & Close*** button 

.
- The Configurator window will then appear.

3.2 Creating a GasBench Configuration

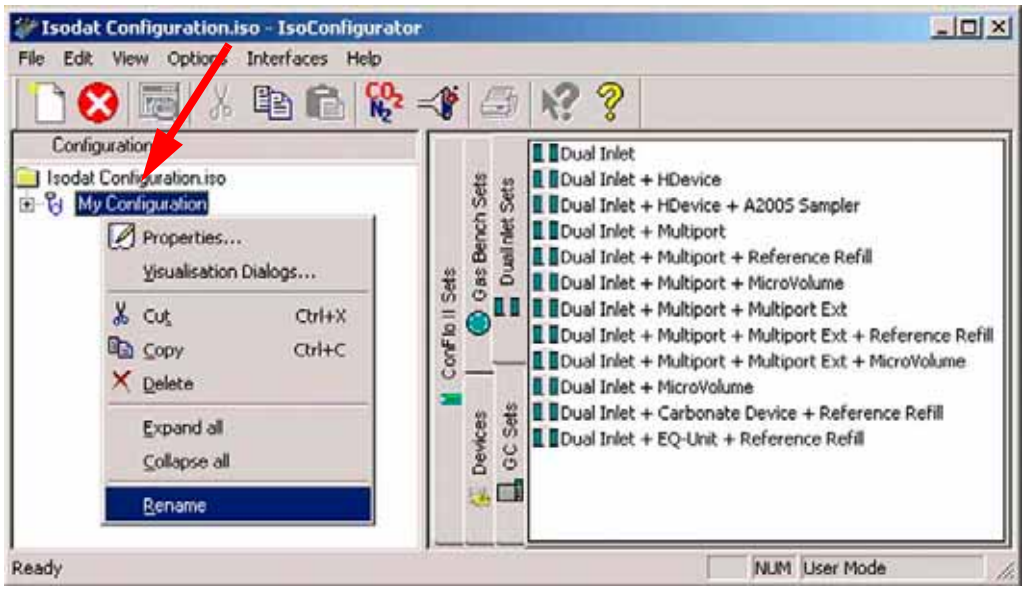
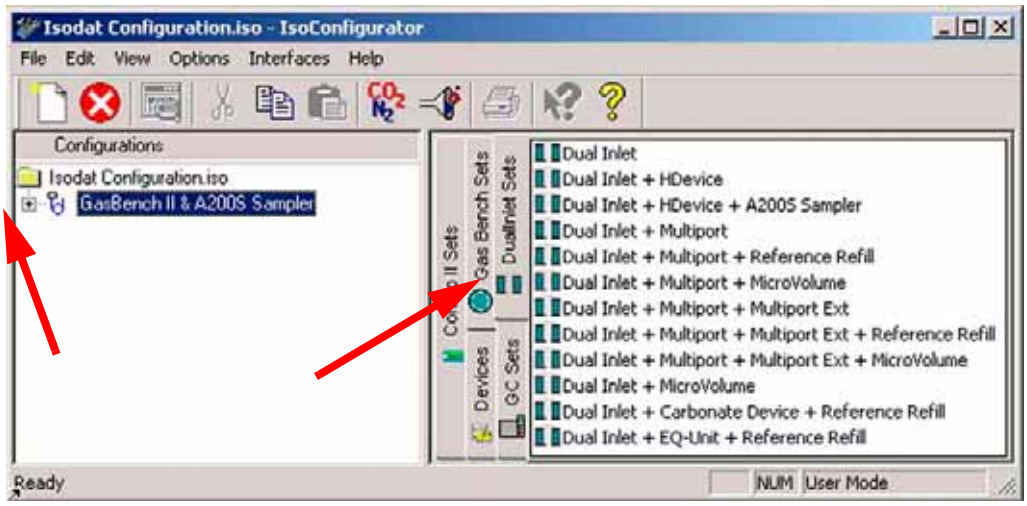


Figure 3-1. Configurator Window

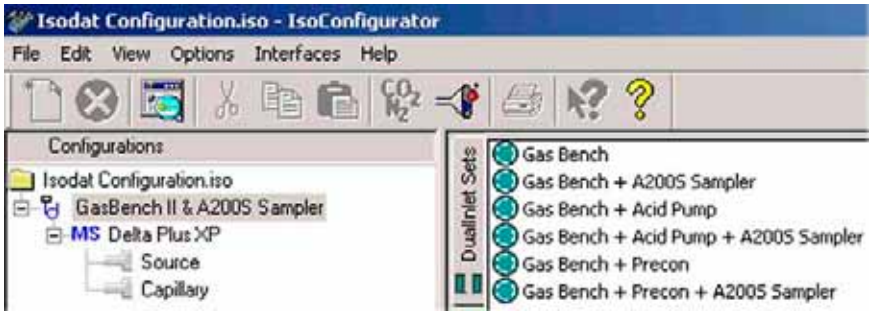
- Isodat 2.0 automatically creates a ***new*** Configuration, named ***My Configuration*** by default.
- To give it a significant name, ***right***-click on it and choose ***Rename***.
- Type a significant name, e.g. ***GasBench & A200S Sampler***.



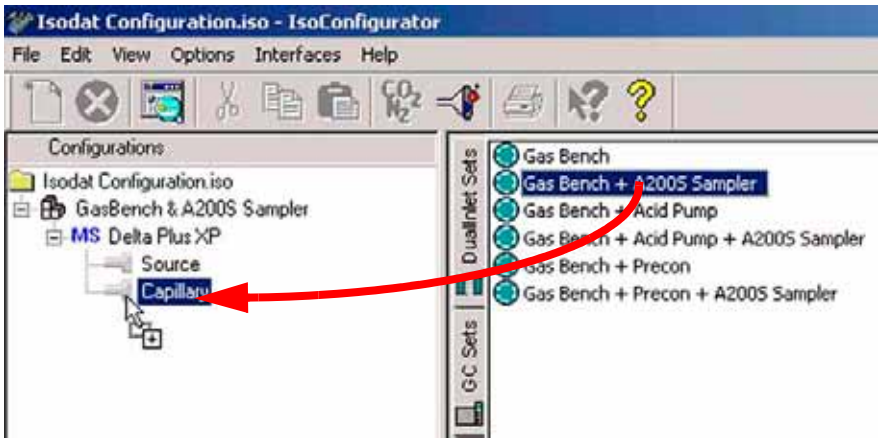
- Expand the tree of the new Configuration by clicking the signs.

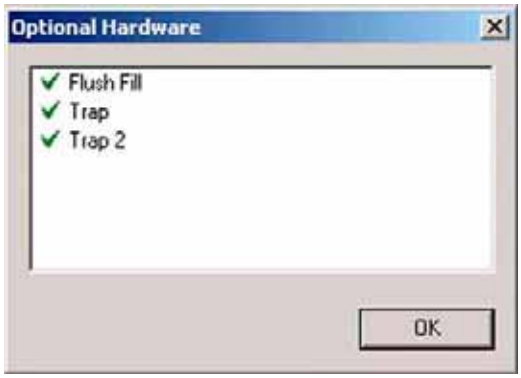
- Press the ***GasBench Sets*** tab 

.
The different GasBench Sets are shown in the right pane as shown below:



- Your selection should look similar to this example. ***Mark*** your particular GasBench Set on the right pane, e.g. ***GasBench + A200S Sampler***. For details refer to **Different GasBench II Methods** on page 3-31.
- ***Drag and drop*** it to ***Capillary*** port in the left pane.



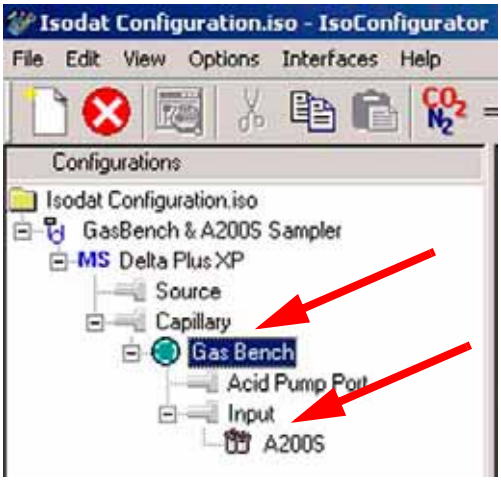


- Select or deselect optional ***hardware*** (that is Flush Fill, Trap or Trap 2.
- Confirm by ***OK***.

Figure 3-2. Optional Hardware - Flush Fill, Trap and Trap 2

Contrary to former times, Finnigan GasBench II now always contains a Flush Fill. Finnigan 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.



- GasBench II and A200S autosampler have been attached to Capillary port.
- Close the Configurator. All settings will be saved automatically.

3.3 Acquisition Mode

This section outlines Acquisition Mode. For detailed information, refer to:

- ISODAT NT Operating Manual, Part No. 109 2481
- ISODAT NT Operating Manual - Upgrade to Version 2.0, Part No. 115 49 90

- Start Isodat 2.0 by a double-click.

- Start Acquisition Mode.

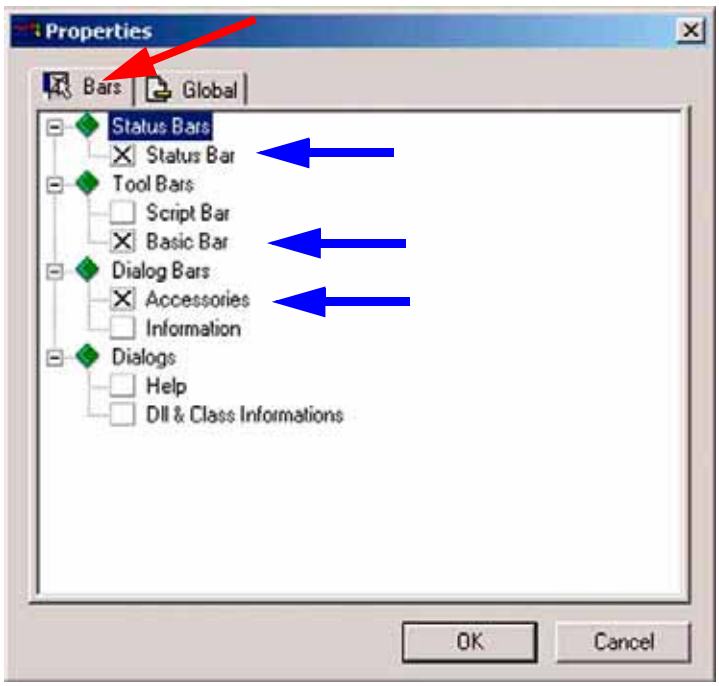
  You are now able to run any “Continuous Flow“ application which gives you full control over the automated measurement.

Note. It is recommended to check first, whether the following toolbars (that is dialog bars) are activated. Proceed as follows.

The Acquisition window appears.

- ***Right-click*** on the title bar in its upper left corner.

- Select ***Properties***.



- Click on the ***Bars*** tab.
- ***Mark*** the checkboxes of the bars you want to be displayed.
- Finally, confirm by ***OK***.

  The bars will appear in the Acquisition Mode window.

Figure 3-3. Properties Box

It is important to mark primarily the following bars:

- ***Status*** Bar
- ***Basic*** Bar
- ***Accessories*** Bar

The individual bars mentioned in the box above are described in detail in the ISODAT NT Operating Manual (Part No. 109 2481).

3.4 Accessories Bar

- To display the Accessories bar ***mark*** the corresponding checkbox in Figure 3-3 and confirm by ***OK***.
- It is important that you have already created a Configuration that contains GasBench II (e.g. ***GasBench II & A200S Sampler***, refer to **Creating a GasBench Configuration** on page 3-4).
- Select this Configuration at the Status Bar as shown below (see also bottom of Figure 3-4).

As defined in the Configurator, the selected configuration ***GasBench II & A200S*** will appear together its configured features.

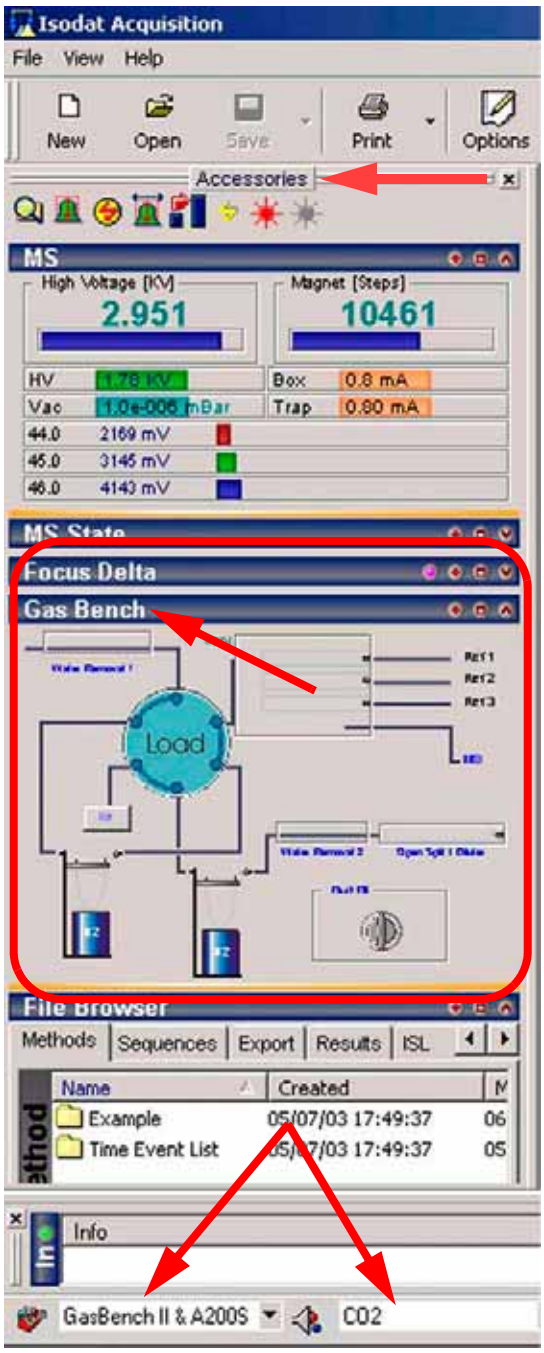
Troubleshooting - Error Messages

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 been found.

  It typically appears when the GasBench II connector has not been plugged into the IRMS.

- 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.



- The ***Accessories bar*** contains information about the:

  IRMS*

  MS State*

  Focus Delta*

  GasBench window*
  See **The GasBench Window** on page 3-11.

  File Browser*

- The ***Status Bar*** displays the actual ***Configuration*** (e.g. GasBench II & A200S) and the actual ***Gas Configuration***, e.g. CO2.*

Figure 3-4. The Accessories Bar Together with the Status Bar

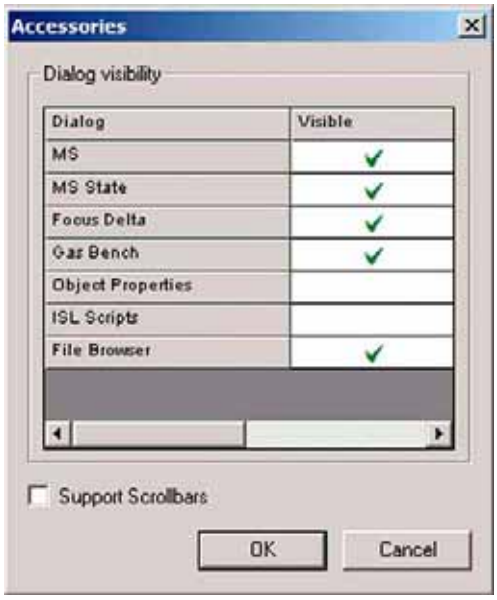
*For detailed information about the components of the Accessories bar, refer to ISODAT NT Operating Manual, Part No. 109 2481.

Changing Visibility of its Components

Change visibility of individual components of the Accessories bar as follows:

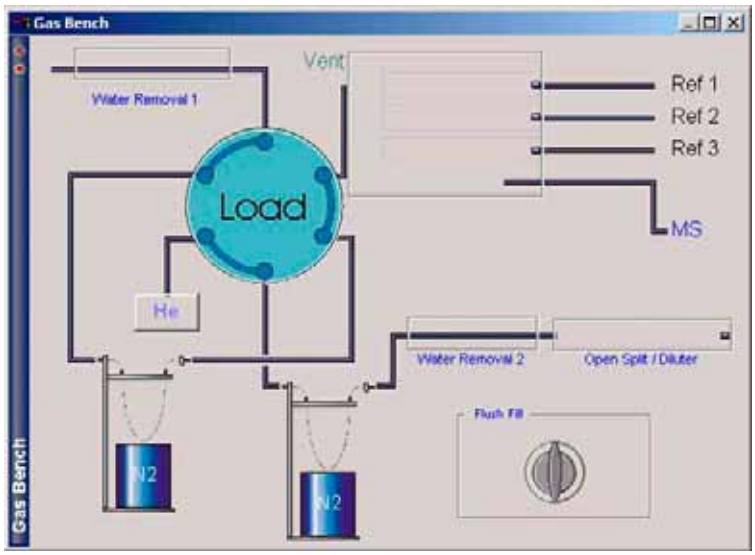
- ***Right-click*** on an arbitrary title bar (e.g. ***GasBench*** or ***Focus Delta***).

- Mark the ***Administrate Panels*** button.



- ***Mark*** the information to be displayed (additionally) on the Accessories bar, e.g. ***Focus Delta***.
- ***Unmark*** the information not to be displayed on the Accessories bar, e.g. ***ISL Scripts***.
- Finally, confirm by ***OK***.

The GasBench Window



The GasBench window (Figure 3-5) appears with any configuration containing a GasBench, no matter whether an autosampler or an acid pump or a PreCon device are additionally attached to it.

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

Figure 3-5. The GasBench Window

Click on a graphical object to operate the specific devices as there are:

- flush fill valve
- valco valve
- open split
- reference ports or traps

The Acid Pump Window

Note. 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 3-6).

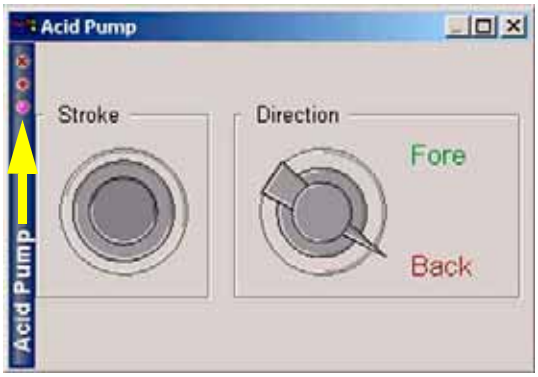
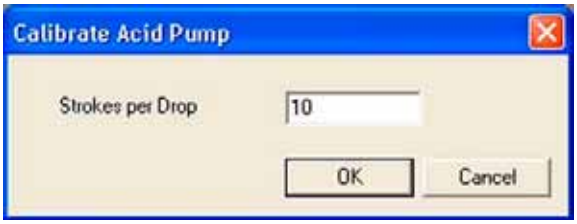


Figure 3-6. The Acid Pump Window

- The number of acid drops per stroke needs first to be adjusted at the acid pump itself (see **Acid Pump Adjustment** on page 6-5).
- Then, this number must be communicated to Isodat 2.0. Therefore, right-click somewhere into the Acid Pump window.

  Click on the appearing  button.



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

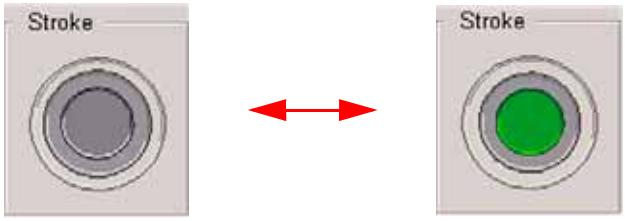


Figure 3-7. The Stroke Button

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 afterwards.

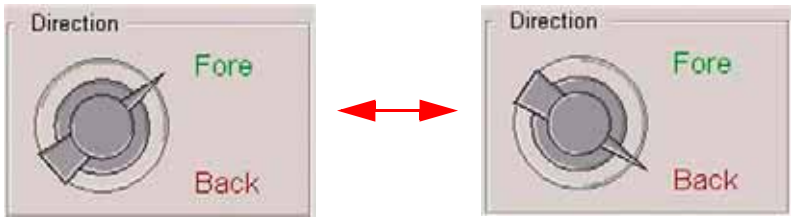


Figure 3-8. Positions of the Direction Button

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

Stroke button controls 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 saved in the Isodat 2.0 database using the ***Calibrate*** button. It appears after right-click on the acid pump window.

The File Browser

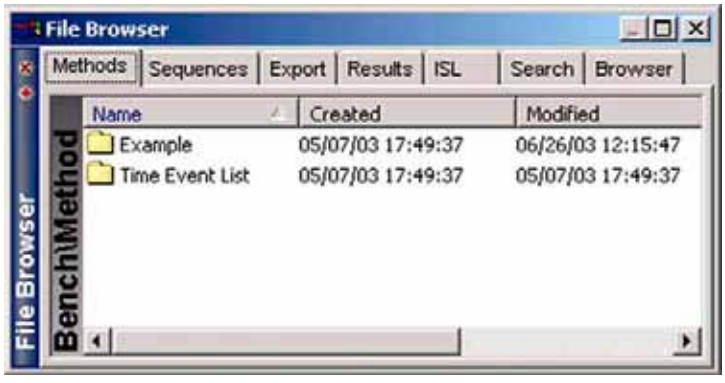


Figure 3-9. File Browser

The File Browser, also called File Browser bar, comprises six tabs:

Methods tab

Refer to **Creating a New Method** on page 3-17.

- Methods provide the complete description of a single measurement.
- Methods can be programmed or changed by the user.
- Different methods have been predefined in the ***Examples*** folder of the ***Methods*** tab. They cover all basic measurements.

Warning. Take them only as a guideline, but do not use them for measurements! For measurements, always create your own methods!

Sequences tab

Refer to **Creating a New Sequence** on page 3-34.

- Sequences contain the description of a sequence of single measurements (methods).
- Sequences 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).

Warning. Take them only as a guideline, but do not use them for measurements! For measurements, always create your own sequences!

Warning. You must create and save a new method and a new sequence on your own!

The predefined methods and sequences delivered by Thermo Electron (Bremen) 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 or sequence created on your own! Depending on your software version these examples may not work properly.

Export tab

- Edit voluminous amounts of GasBench II acquisition data for your own data systems using export templates (cf. LIMS).
- Refer to “Excel Export“ in ISODAT NT Operating Manual; Part No. 109 2481.
- Use ISODAT NT’s Result Workshop to select and display particular aspects of your acquisition data.
  Refer to “Result Workshop“ in ISODAT NT Operating Manual - Upgrade to Version 2.0; Part No. 115 4990.

Results tab

- Provides access to all previously acquired measurement results.
- Gives an overview of all results.
- Is empty prior to the first measurement.

> **Note.** To easily transfer and store data at your place of choice (e.g. on a drive where data security is guaranteed), change the result path by a right-click and then select **Set Path**. The basic path is automatically installed.
>
> For reasons of data security, we recommend you to frequently benefit from this feature.

From now on, all method, sequence and result files will be stored at a different location.

ISL tab

- Refer to ISODAT NT Operating Manual - Upgrade to Version 2.0; Part No. 115 4990.
- In the GasBench 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 (see **Creating a GasBench Configuration** on page 3-4). It is not necessary to change it.

Note. All acquisition scripts are usually named **acquisition.isl**, no matter to which application they belong (e.g. GasBench II or ConFlo III). However, they are stored in separate folders (that is in a GasBench II folder or in a ConFlo III folder).

Search tab

- Allows to find 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 to move files.

Browser tab

- If a Result Workshop document is open, this tab shows the objects that can be imported (e.g. methods, sequences, results).
- A file manager that allows to browse 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.

3.5 Creating a New Method

Isodat 2.0's ***Acquisition*** mode allows fully automated isotope ratio determination. All parameters relevant for data acquisition of a sample are stored in a ***method***. The following steps are needed to create a new method.

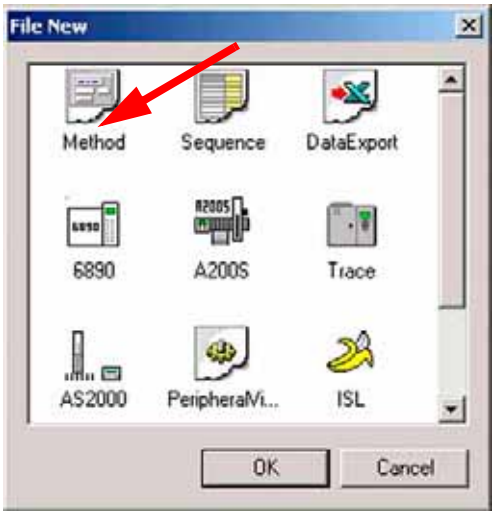
> **Note.** For an extensive description of the options of the method definition refer to ISODAT NT Operating Manual (Part No. 109 2481). In this section, only the entries that are specific for operating GasBench II will be described.

> **Warning.** You must create and save a new method on your own!
>
> The predefined methods delivered by Thermo Electron (Bremen) 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.

- Open the ***Acquisition*** mode.

- Select a ***Configuration*** for GasBench II applications, e.g. ***GasBench II & A200S***.
- Select the appropriate ***Gas Configuration*** for the intended measurement type, e.g. ***CO2***.

- Press the ***New*** button.

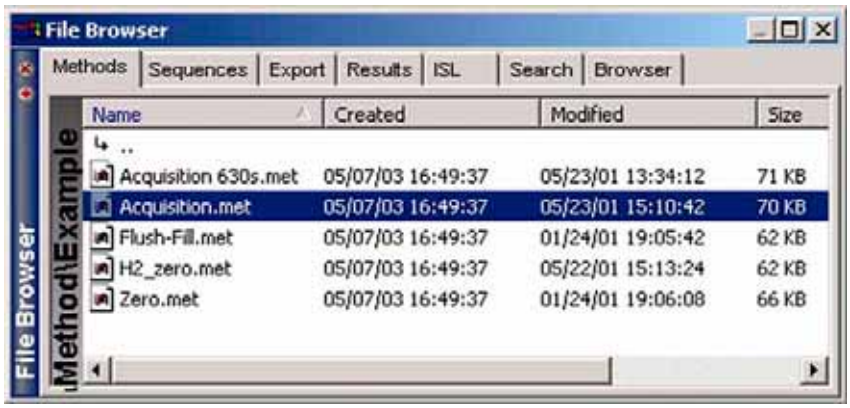


- To create a new method, mark ***Method***.
- Confirm by ***OK***.

The new method is organized in tab pages. Proceed with **Structure of GasBench Related Methods** on page 3-19, where they are described in detail.

Predefined Methods as Examples

For the sake of simplicity, predefined methods 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 methods to cover all kinds of measurements.



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

  Do not mix them up with the predefined methods in the folder ***Examples***!
- Double-click on your example method of choice, e.g. ***Acquisition.met***.

Figure 3-10. File Browser Displaying Predefined Methods for GasBench II

Instead of double-clicking on the example method of choice, drag and drop it to the ***Isodat Acquisition*** window right to the File Browser. The example method will be displayed. Proceed with **Structure of GasBench Related Methods** on page 3-19.

Select between the following example methods:

- Acquisition 630s.met — considerably faster than Acquisition.met; requires the column to be pre-heated to 70 ºC.
- Acquisition.met — lasts longer than 1400 s; no longer recommended, as it is an older version (first basis method of GasBench); used at ambient temperature.
- 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 (e.g. 10 or 100 pulses) 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 **Different GasBench II Methods** on page 3-31.

All GasBench methods are organized by the following tab pages:

- Instrument tab
- Time Events tab
- Component Names tab
- Evaluation tab*
- Peak Detection tab*
- Printout tab*

*In these tabs, the currently active gas configuration is indicated: e.g. Evaluation@***CO2*** alludes to ***CO2***, whereas Evaluation@***N2*** alludes to ***N2***.

Instrument tab

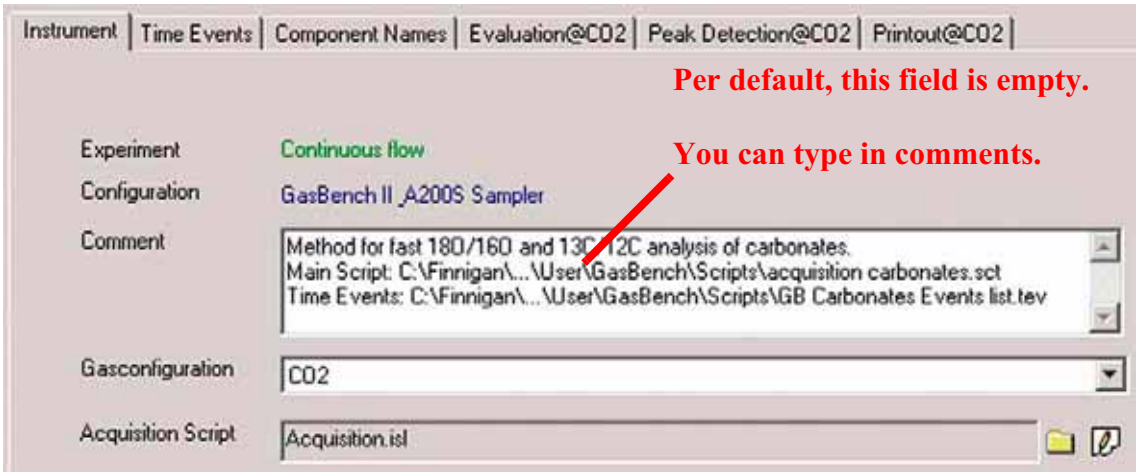


Figure 3-11. Instrument tab - Experiment Part

- At ***Comment***, you can type in general notes about Method, Acquisition Script, Time Events, etc.
- At ***Gas Configuration***, select the appropriate one, e.g. ***CO2***. Usually, the default entry can be accepted. Refer to the Status Bar in **Accessories Bar** on page 3-9.
- ***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 script press the button.

Warning. 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.

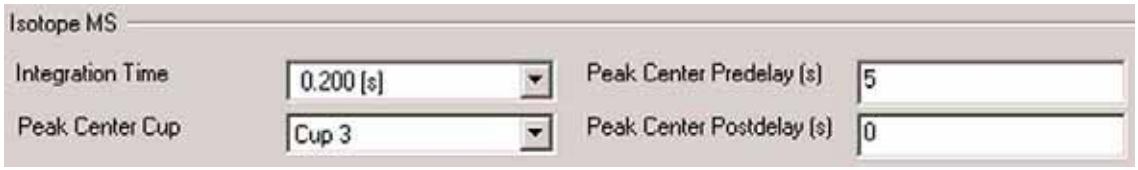


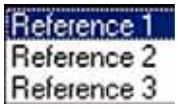
Figure 3-12. Instrument tab - Isotope MS Part

- ***Integration time*** is the time integrated to form a data point triplet, e.g. 0.200 s.
- Select the ***Peak Center Cup***, e.g. Cup 3 as narrow center cup in a triple collector.
- ***Peak Center Predelay*** is the time the system waits between activation of reference gas and start of peak center cycle, e.g. 20 s.

Note. The retention time should be set to the **Reference Out** value of the respective reference gas pulse (in the Time Events list). This accomodates for the delay of 7 - 10 s associated with the gas passage through the capillary to the IRMS.

- ***Peak Center Postdelay*** is the time the system waits between end of peak center cycle and start of data acquisition, e.g. 5 s.

Figure 3-13. Instrument tab - Reference Device Part



- Select the ***Reference Port*** to connect the reference gas to, e.g. Reference 1.

  Choose between Reference 1, Reference 2 and Reference 3 as equivalent ports.

  Refer to **Connection Panel of Gas Bench II** on page 2-15.

- 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 e.g. 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.

- Mark the ***Use Scripts*** checkbox 

to start an ISL script.

Figure 3-14. Instrument tab - GasBench Part

- Transfer Time [s] is the 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.

> **Note.** If additional time is needed between piercing the vial and starting the measurement, transfer time should be increased.

- ***Enable Auto Dilution*** enables the action of the open split. The signal amplitude needed to activate the auto dilution is set at the Activation Amplitude window (in mV). Whenever a sample peak voltage exceeds this limit, the split will be activated.
- ***Extra Script*** refers to additional hardware of GasBench II, e.g. to traps which include the command scripts.

  Select an appropriate Extra Script by a click on the  button.

  To ***edit*** the Extra Script press the  button.

Time Events tab

The ***Time Events list*** controls all operations during data acquisition.

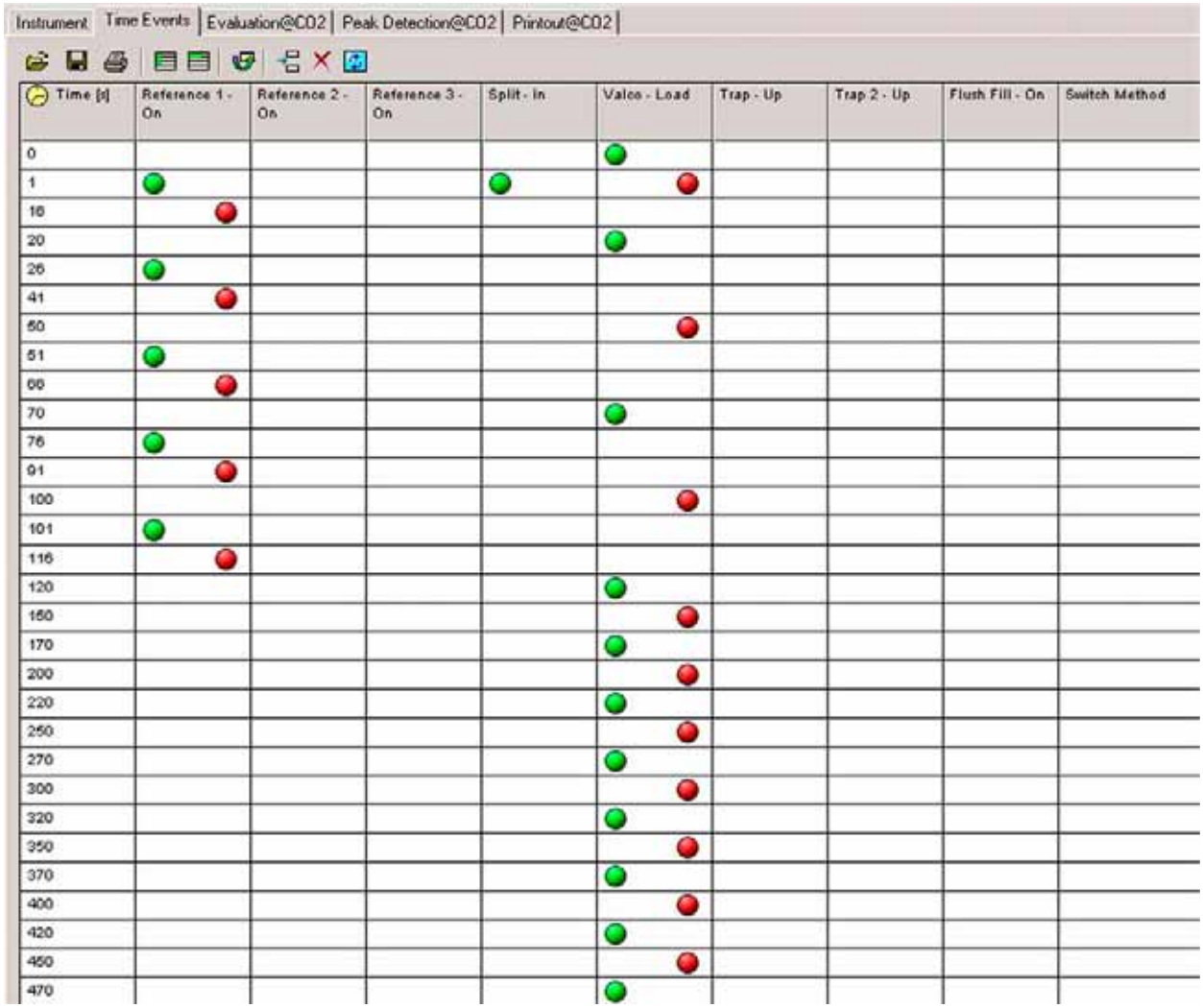


Figure 3-15. Time Events tab - Time Events List

- 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 .
- ***Insert lines*** using the right mouse button or click on .
- Edit the ***Time*** [s] at which the event will happen.
- ***Double-click*** on the field of a valve or use the space bar to set/toggle its status to active or inactive .

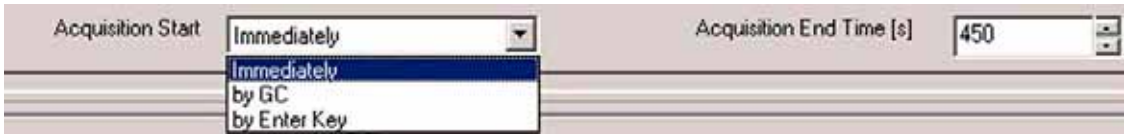


Figure 3-16. Time Events tab - Acquisition Start and Acquisition End Time

- Select the ***Acquisition Start***.
  The 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***.
- Edit the Acquisition End Time.
  The Acquisition End Time is the end time of data acquisition. After the 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 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 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.

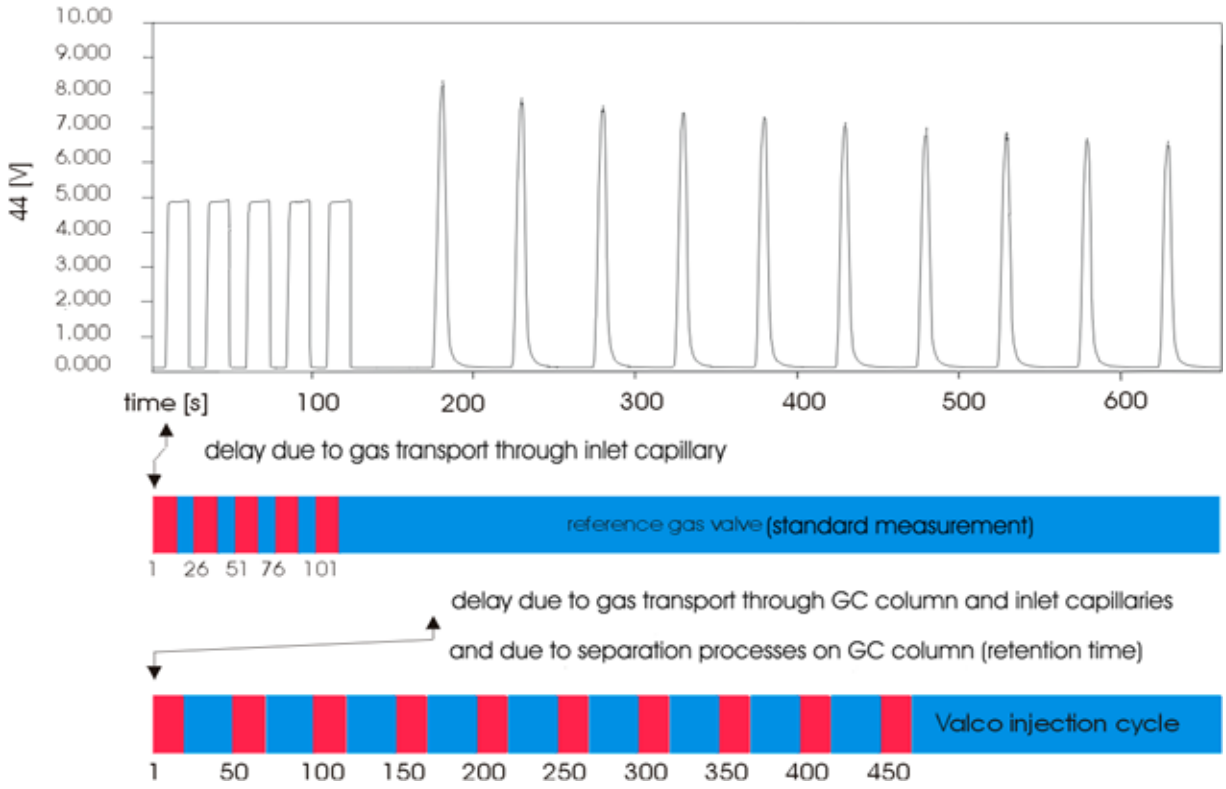


Figure 3-17. Timing Considerations

Component Names tab

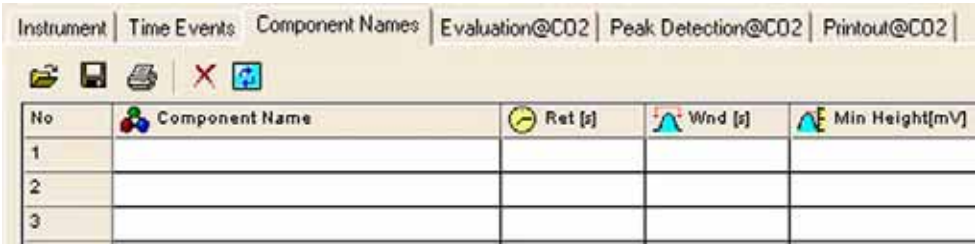


Figure 3-18. Component Names tab

- Hitherto, it is of no importance for GasBench applications, because only one sample gas is investigated.
- The 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 2.0 is supposed to find and designate each substance in the chromatogram.

Evaluation tab

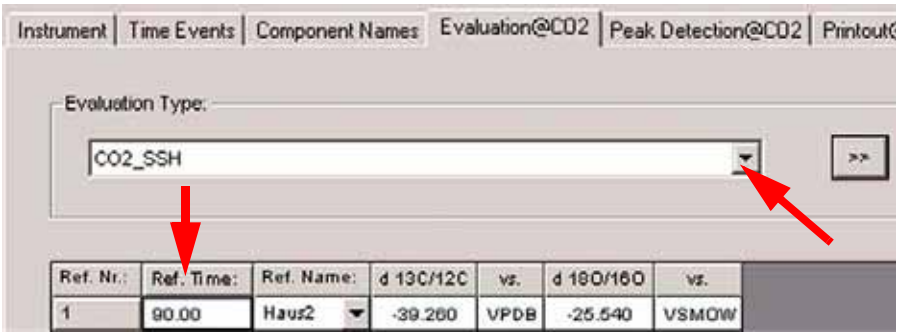
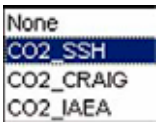


Figure 3-19. Evaluation tab



- At ***Evaluation Type***, select an appropriate ***i***on correction for CO_2 data evaluation from the list (that is None, SSH, Craig or IAEA).
- Press the >> button to add own scripts for ion corrections.

- Select a ***Ref. Name*** from your standard database, e.g. ***Haus2*** or edit the related δ values.
  In the latter case, ***User Defined*** will be shown at ***Ref. Name***.
- More standards can be added using the right mouse button.
- Enter the ***retention time*** in s (that is ***Ref. Time***, e.g. 90.00) of the standard peak(s) defined in the Time Events list, which are used for calculating the corresponding δ value(s). See Figure 3-15.
- 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.

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

Peak Detection tab

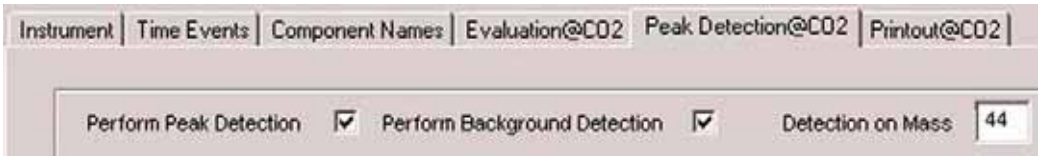


Figure 3-20. Peak Detection Tab - Peak Detection and Background Detection

- Mark the respective checkboxes, if you want to perform a ***peak*** detection or ***background*** detection, respectively.
- Type in the corresponding ***detection mass***, e.g. m/z 44 in case of CO_2.
- It is recommended to keep the defaults.

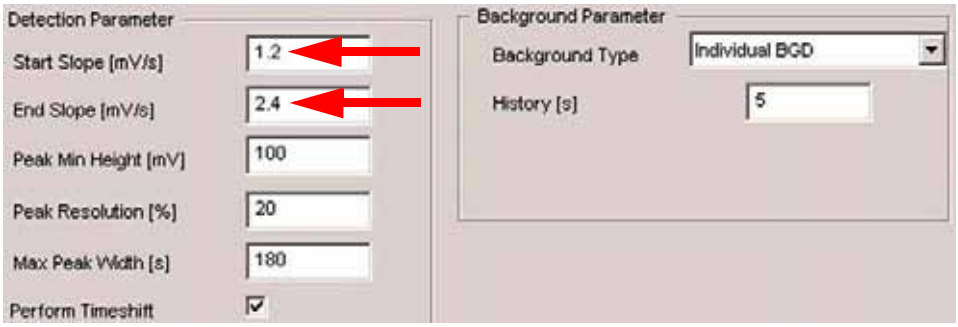


Figure 3-21. Peak Detection tab - Peak Detection Parameters

- Notice the ***peak detection parameters***, that is virtual parameters used in peak detection. Default values for Start Slope, End Slope, Peak Min Height and Background Type are shown above and can usually be accepted.
- S***tart slope*** [mV/s] and ***End slope*** [mV/s] are used to control the portion of the peak that is included in the integration. Lower values will result in capturing more of the peak slopes.

> **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.

- ***Peak Min Height*** [mV] limits the number of reported peaks as it allows to exclude small ones from evaluation.
- ***Peak Resolution*** [%]: overlapping peaks may not occur in GasBench applications! Overlapping peaks would indicate a gross error leading to a worthless measurement:
  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 only 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.

  Also, during the ten repetitions, one runs the risk of coincidence with the CO_2 peak, if the timing is wrong. This would also result in a massive shift of the δ value.

> **Note.** Therefore, clearly separated peaks are a crucial measure of precaution to be taken!

- ***Max Peak Width*** [s]: broader signals will not be recognized as peaks.
- ***Background Type***: it has been proven experimentally that the background type is important for GasBench 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***.

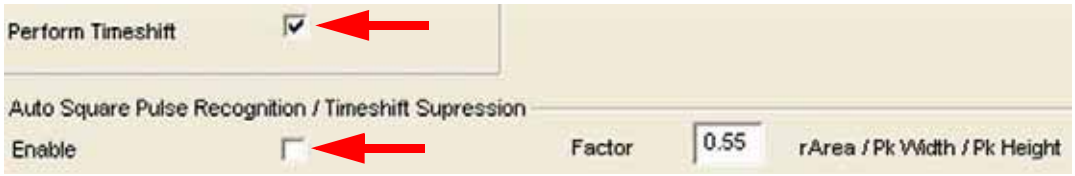


Figure 3-22. Peak Detection Tab - Auto Square Pulse Recognition / Timeshift Suppression

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:

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

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, which 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.

- Mark the ***Enable*** checkbox to automatically
  1. detect square peaks and
  2. suppress the timeshift correction of square peaks.
- If you unmark ***Enable*** and simultaneously mark ***Perform Timeshift***, timeshift correction will be enabled for all peaks.

  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.
- 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 (e.g. 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***.

Printout tab

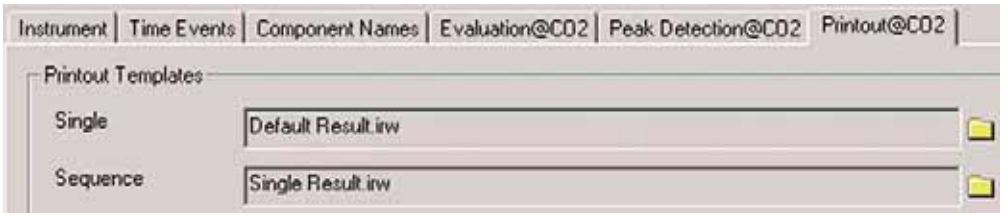


Figure 3-23. Printout tab

- In Printout tab, the use of printout templates is controlled.
  - ***Single*** selects a print template from the Result Workshop for an individual printout per sample.
  - ***Sequence*** selects a print template from the Result Workshop for a reduced printout per sample within a sequence summary.

Saving a Method

Warning. You must create and save a new method and a new sequence on your own!

The predefined methods and sequences delivered by Thermo Electron (Bremen) 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 or sequence created on your own! Depending on your software version these examples may not work properly.

After you met all your decisions throughout the method's tabs, you must save it. Proceed as follows:

Save command

- Click on the ***Save*** button to save a method (or sequence) previously created on your own.

Save As command

- Click on the arrow and

  choose ***Save as...*** to optionally choose a new name and folder for the currently active single document (e.g. method or sequence).

- Notice that the particular folder is shown that contains the currently active method.
- 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.
- Give the method a significant name, e.g. similar to the sequence it corresponds to. Keep the extension .met.
- Confirm by ***Save***.

Save All command

- Click on the arrow and

  choose ***Save All*** to save all currently active Isodat 2.0 documents (e.g. methods, sequences, result files, Result Workshop files).

  They will be stored without changing names and folders.

3.6 Different GasBench II Methods

Depending on the particular GasBench set chosen in the Configurator, different configurations will result as was depicted in **Creating a GasBench Configuration** on page 3-4.

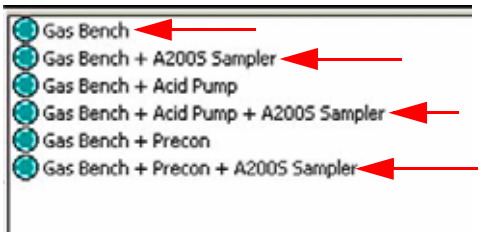


Figure 3-24. The GasBench Sets Chosen in the Configurator

Finnigan GasBench II can be used ***alone***. In this case, choose:

- ***GasBench***

In most cases, however, Finnigan GasBench II is used together with an ***autosampler***, that is the A200S sampler.

> **Note.** GC PAL and Combi PAL must be treated as A200S.

Thus, mostly choose between:

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

Different ***configurations*** will lead, in turn, to different corresponding ***methods***. The particularities in the tabs of the various possible methods will be described one by one now.

The GasBench Method

If you use Finnigan GasBench II alone and therefore chose the ***GasBench*** set in the Configurator (see Figure 3-24), the corresponding ***GasBench*** method results showing ***no*** particularity. See **Creating a New Method** on page 3-17.

The GasBench + A200S Sampler Method

If you use Finnigan GasBench II together with an A200S autosampler and therefore chose the ***GasBench*** set in the Configurator (see Figure 3-24), the corresponding ***GasBench*** method will result. See **Creating a New Method** on page 3-17.

The GasBench + Acid Pump + A200S Sampler Method

If you use Finnigan GasBench II in combination with an acid pump plus an A200S autosampler and therefore chose the ***GasBench + Acid Pump + A200S Sampler*** set in the Configurator (see Figure 3-24), the corresponding ***GasBench + Acid Pump + A200S autosampler*** method will result.

For basic information, refer to **Creating a New Method** on page 3-17.

Figure 3-25. Instrument tab - Acid Pump Part

As a particularity on the Instrument tab, note the Acid Pump box. The following parameters for acid pump control can be adjusted:

- ***Drop Count Forward*** number of drops pumped while the pump is in forward position (that is, releasing acid from the acid needle)
- ***Drop Count Backwards*** number of drops pumped while the pump is in backwards position (that is, retracting acid)
- ***Delay [s]*** waiting time between two strokes

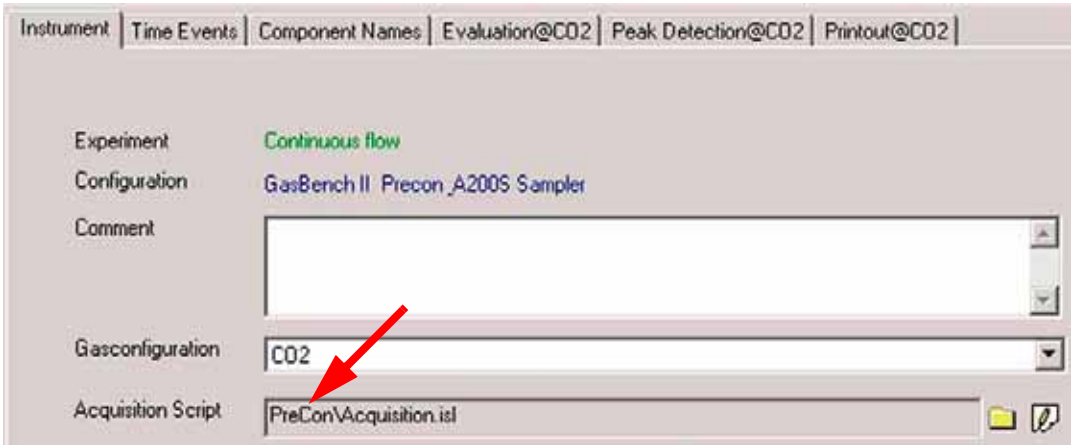
To ensure that no drop remains sticking, acid is first pumped in, before the acid pump is switched over in order to draw it back again. Due to the negative pressure, a drop sticking at the tip should thus be drawn backwards into the bulk volume.

The GasBench + PreCon + A200S Sampler Method

If you use Finnigan GasBench II in combination with a PreCon plus an A200S autosampler and therefore chose the ***GasBench + Precon + A200S Sampler*** set in the Configurator (see Figure 3-24), the corresponding ***GasBench + Precon + A200S autosampler*** method will result.

For basic information, refer to **Creating a New Method** on page 3-17.

As a particularity on the Instrument tab, note that the acquisition script acquisition.isl is stored in a special PreCon folder.



Furthermore, notice the PreCon box on the Instrument tab:

Figure 3-26. Instrument tab - PreCon Part

The script that controls PreCon is integrated. Specify its name and location. The folder \Finnigan\Isodat NT\Global\ISL\PreCon contains the following selection:

- 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.

The Time Events tab additionally contains entries for all the components in PreCon, e.g. valco valve and additional traps.

3.7 Creating a New Sequence

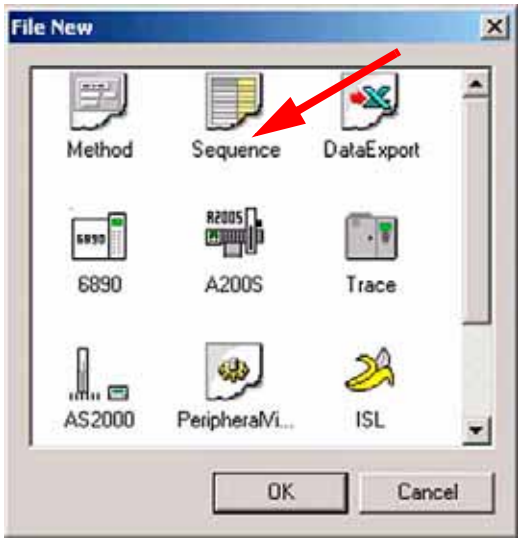
After creating and saving a ***method*** (see **Creating a New Method** on page 3-17), a ***sequence*** must now be created as follows.

Warning. As with methods, you must create and save a new sequence on your own!

The predefined sequences delivered by Thermo Electron (Bremen) in the **Examples** folder are only example files. They only show guidance through helpful default values, but must never be used for measurements!

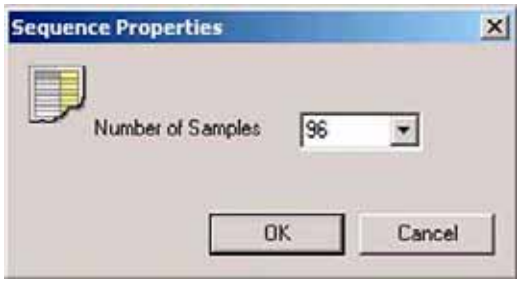
Never overwrite an example file with a sequence created on your own! Depending on your software version these examples may not work properly.

- Press the ***New*** button.



- To create a new sequence, mark ***Sequence***.

- Confirm by ***OK***.



- Specify the number of samples, e.g. 96.
- Confirm by ***OK***.

Note. In case of carbonates, 80 samples can be measured, leading to 88 lines. The first row can not be measured as it is not accessible by the acid needle without destroying the measurement needle.

The last row can not be measured as it is not accessible by the measurement needle without destroying the acid needle. In case of equilibrations, all 96 lines can be filled. See **Sample Trays** on page 2-7.

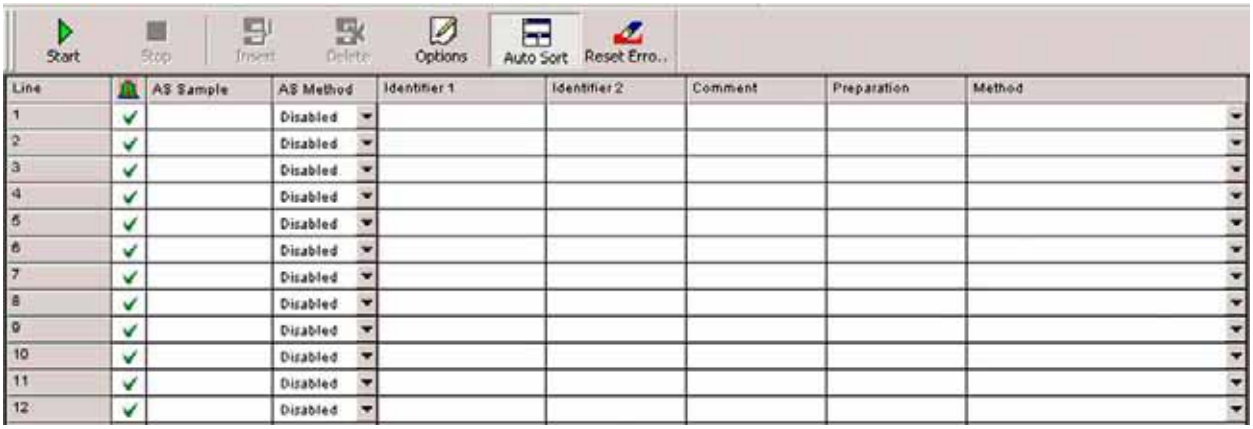


Figure 3-27. Sequence Grid (First 12 Lines)

The sequence grid contains all information about the individual samples bundled together in the sequence:

Line each line 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 position of the sample to be measured. The number between 1 and 96 corresponds to the sample's position in the tray. See **Sample Trays** on page 2-7, Figure 2-7 and Figure 2-11.

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).

Identifier1, 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 **Creating a New Method** on page 3-17 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 

.

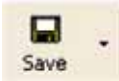
Saving a Sequence

As done with a method (see **Saving a Method** on page 3-29), after defining the new sequence you must save it before it will start. Proceed as follows:

Warning. 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!

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

Save Command

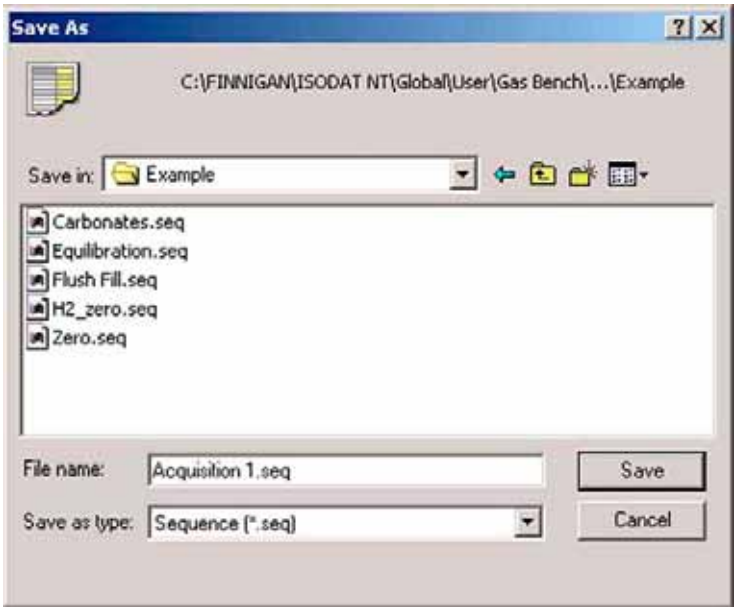


- Click the ***Save*** button to save a sequence created on your own.

Save As Command

- Click on the arrow and

  choose ***Save as...*** to optionally choose a new name and folder for the currently active sequence.



- Select a suitable folder.
  Create a new one, if you want e.g. to separate ***predefined*** sequences from those created on your ***own***.
- Give the sequence a significant name, e.g. similar to the method it corresponds to.
  Keep the extension .seq.
- Press the ***Save*** button.

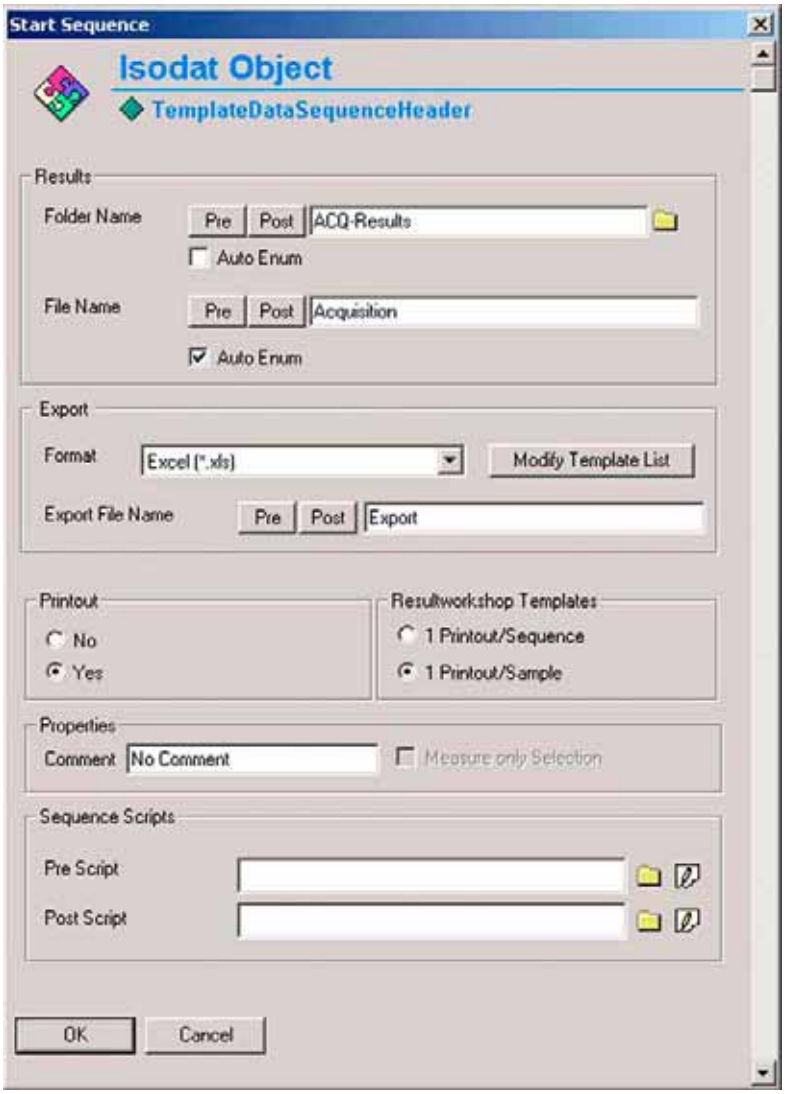
Save All Command

- Click on the arrow and

  choose ***Save All*** to save all currently active Isodat 2.0 documents (e.g. methods, sequences, result files, Result Workshop files).
  They will be stored without changing names and folders.

Starting a Sequence

- To start the sequence, finally press the ***Start*** button.
  The window below appears.



Results: Define full path for results storage.

Export: Define the format of measurement data to be exported: choose between None, Excel, Lotus, and ASCII. Name the export file.

Printout:

Decide, whether you want a printout. If so, choose between one printout per sample or per sequence.

Properties:

Type an arbitrary comment applied to all result files in this sequence.

Sequence Scripts:

Select an ISL script (*.isl) to be executed before and after the sequence.

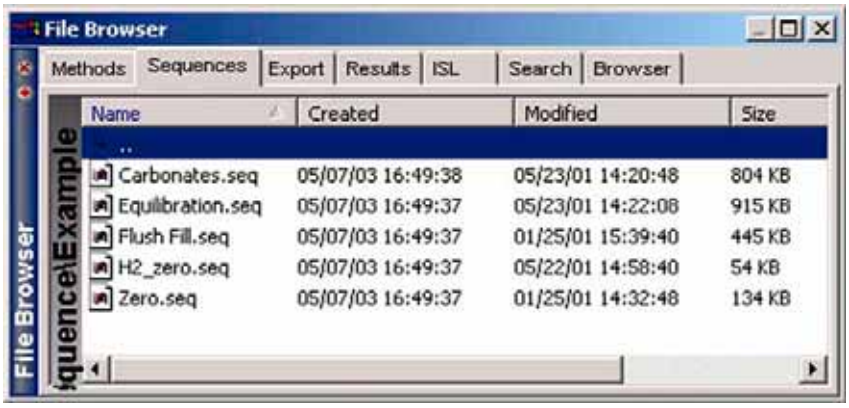
Finally, confirm by ***OK***.

Figure 3-28. Defining Parameters for Results Export, Printout and Sequence Scripts

- If an error message indicates low memory, close other applications.
- The measurement will be started.
  Refer to **Measurement Procedures for Real Samples** on page 5-1.

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.



- Click on File Browser's ***Sequences*** tab
- Select the location where your own GasBench II sequences are to be stored.

  Do not mix them up with the predefined sequences in the folder ***Examples***!
- Double-click on your example sequence of choice, e.g. ***Carbonates.seq***.

Figure 3-29. File Browser Displaying Predefined Sequences for GasBench II

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 following example sequences:

- ***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 (e.g. 10 or 100 pulses) 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:

- Zero.met ↔ Zero.seq;
- Flush Fill.met ↔ Flush Fill.seq;
- Acquisition 630s.met ↔ Carbonates.seq and Equilibration.seq;
- Acquisition.met ↔ Carbonates.seq and Equilibration.seq
  (as an older method, Acquisition.met is no longer recommended);
- H2_zero.met ↔ H2_zero.seq

3.8 Excel Export

Figure 3-30 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 following columns should be exported:

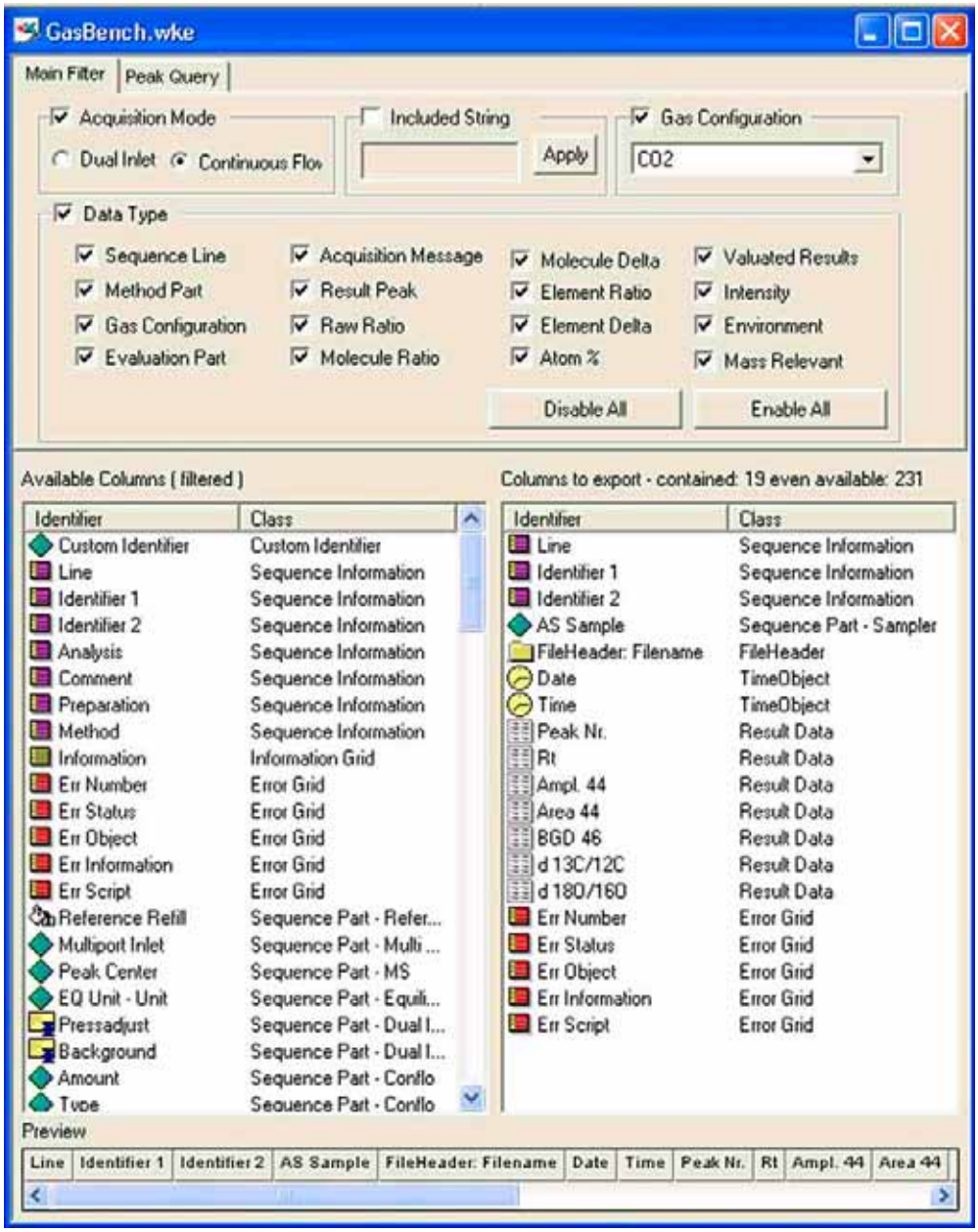


Figure 3-30. Excel Export Module Illustrating Basic GasBench II Output Parameters

3.9 Autosampler Programming

GC PAL Loader Software

All autosampler settings, positions and methods that include timing are entered directly into the autosampler's memory via the autosampler's panel. All changes of autosampler programming are effective immediately. To save a copy of the autosampler's memory contents, use the PAL loader software provided with your Combi PAL or GC PAL. This software package allows to read the autosampler's memory 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 Electron (Bremen) as PAL-GASBENCH V2.33 021031.sss.

Using GC PAL Loader Software

1. 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 2.0.
2. Start the loader software. Communication between computer and autosampler is now possible via COM Port.
3. Default installation location is: ***Program Files*** > ***PAL*** > ***Loader***. Notice the two subfolders ***Backup*** and ***Update***.
   Save the PAL-GASBENCH V2.33 021031.sss file in the subfolder ***Update***.
4. Open GC PAL loader software via ***Start*** > ***Programs*** > ***PAL System*** > ***PALLoader***.
5. Perform a backup of the ***default autosampler configuration***.
6. Wait until backup is complete.
7. On the Isodat 2.0 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 in our Customer Information System.
8. Copy these two files to the GC loader's update folder.
9. Press ***Update*** and select the file PAL-GASBENCH V2.33 021031.sss. Perform the update.
   The autosampler-related file PAL-GASBENCH V2.33 021031.sss will be installed automatically. This may last some minutes.

First Touch

- The autosampler's display shows four function keys, F1, F2, F3 and F4. See Figure 3-31.
- 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 is accessible.

Figure 3-31. Autosampler Display - General

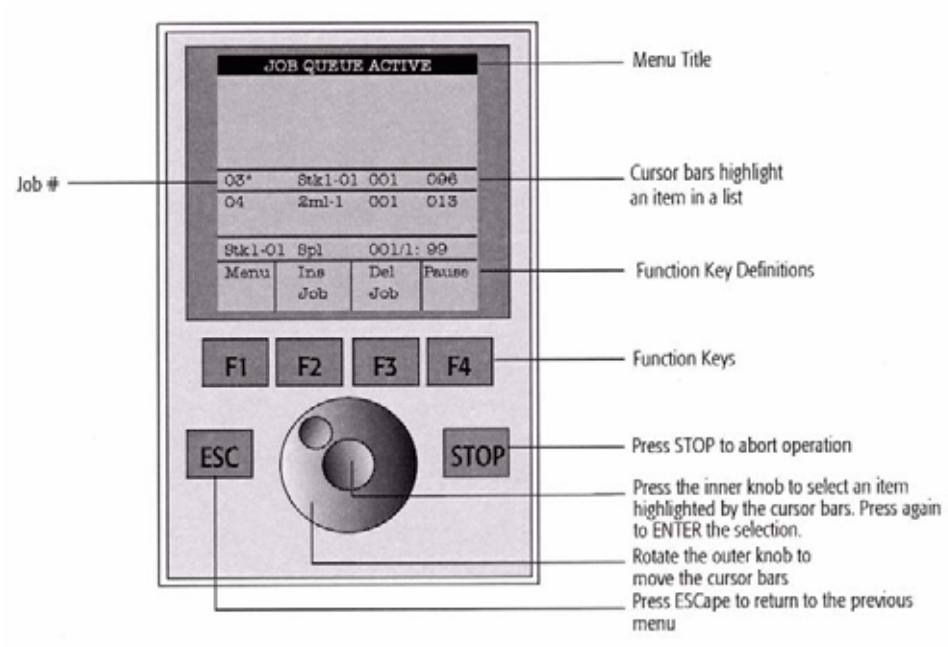


Figure 3-32 shows the meaning of the four function keys in the **Start** Menu:

- F1 Menu
- F2 Add Job
- F3 Delete Job
- F4 Start

Figure 3-32. Autosampler Display - Start Menu

- To find an individual parameter within the autosampler's memory, press the ***Menu*** button (***F1***) on the autosampler's panel.
- 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 below:

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

- ***ESC*** command: leads you back to the previous menu. Press it repeatedly to go back to the main menu.
- ***Home*** command: directly leads you back to the main menu (mostly F4).

- ***Stop*** command: stops the autosampler during operation. E.g. when a sequence is being performed in Isodat 2.0, 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**, can not 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 (e.g. 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

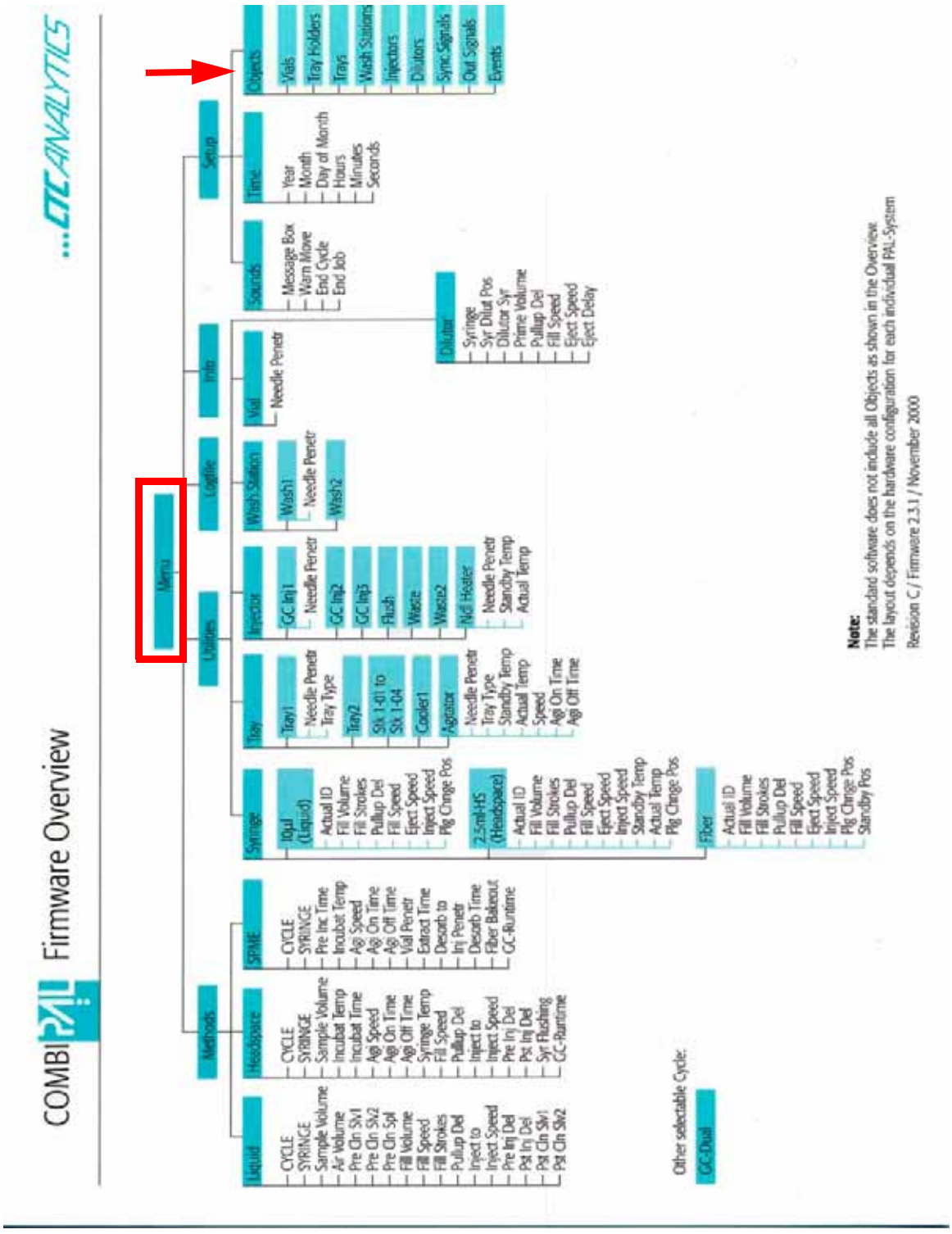


Figure 3-33. Adjustment Possibilities of Autosampler - Tree of Hardware Commands (Main Menu)

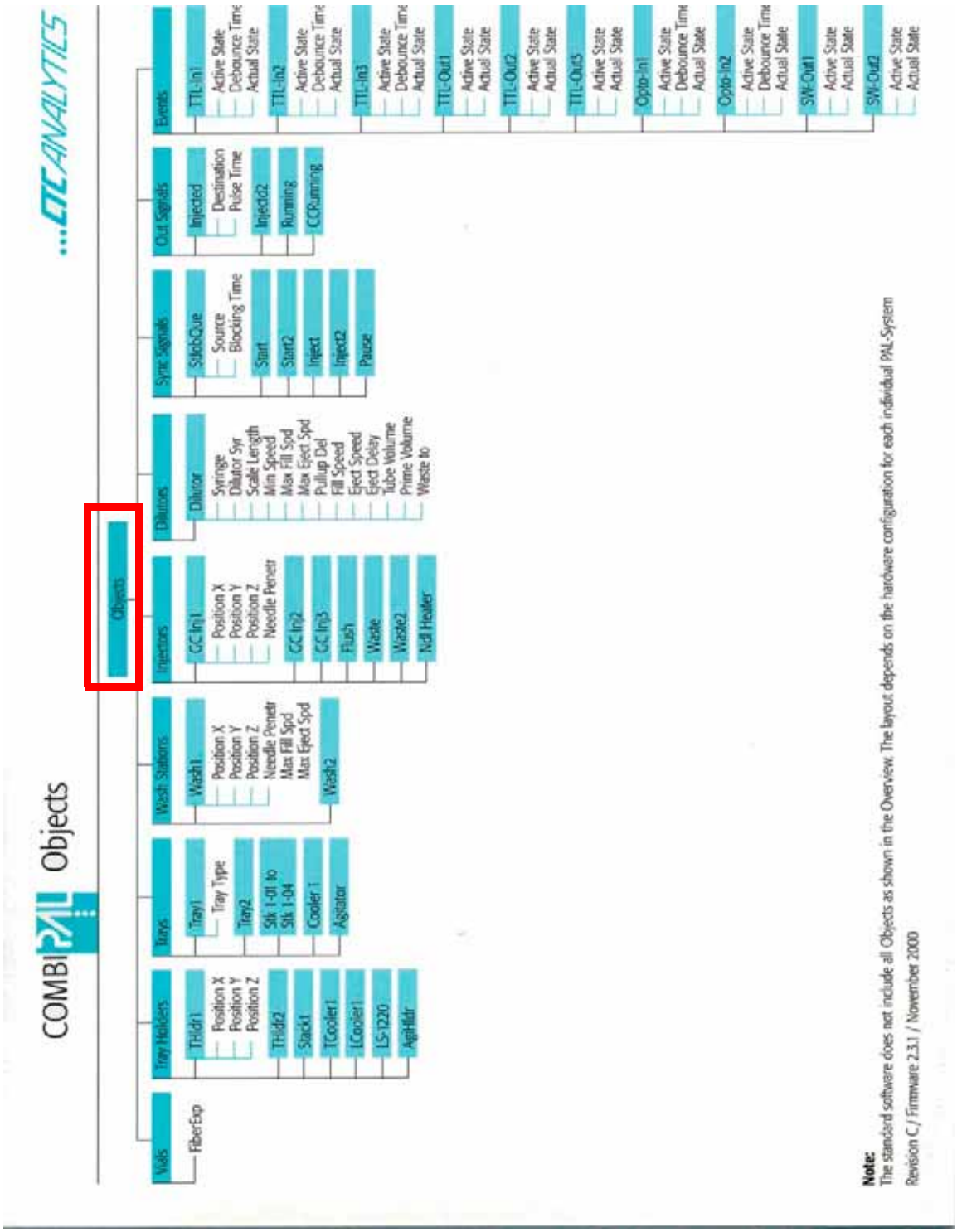


Figure 3-34. Adjustment Possibilities of Autosampler - Tree of Hardware Commands (Objects Submenu)

Figure 3-33 and Figure 3-34 have been taken from CTC Analytics PAL SYSTEM User Manual.

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 under Isodat 2.0. See **GC PAL Loader Software** on page 3-42.
>
> If preinstallation and configuration have already been performed, redirect into the autosampler's menu via **ESC**. See **First Touch** on page 3-43.

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

  Two tray holders will appear:

  Gas Bench tray holder (without numerical designation) and

  Gas Bench tray holder #2.

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

Example for Adjusting: 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 autosampler's compatibility mode, 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:

- ***A200S-7*** is used for flushing,
- ***A200S-8*** is used for carbonates and
- ***A200S-9*** is used for 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 formula:

$$\text{Time for one sample} = (\text{Fill strokes} + 1) \times \text{Pullup delay}$$

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

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
Vlv Cln Slv 1	0
Vlv Cln Slv 2	0

Testing the Autosampler

For a convienient test of the autosampler's communication independently of Isodat 2.0 perform as follows:

1. A "Hyperterminal" can be found in the ***Start*** Menu under:
   Start > ***Programs*** > ***Accessories*** > ***Communications*** > ***Hyperterminal***.
   Use the following settings:
   COM 1: 9600 baud, 1 stop bit, no parity
2. Type in the following command:

   #010000 (request status)

   The autosampler should respond with:

   #010001 (STANDBY) or

   #01w002 (READY), (BUSY, if w > 0)
3. Finally, order the sampler to Execute method M on Sample NNN in TRAY01: #99MNNN.

Chapter 4
Basic Operations

4.1 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. It should look more or less like Figure 4-1 or Figure 4-2, respectively.

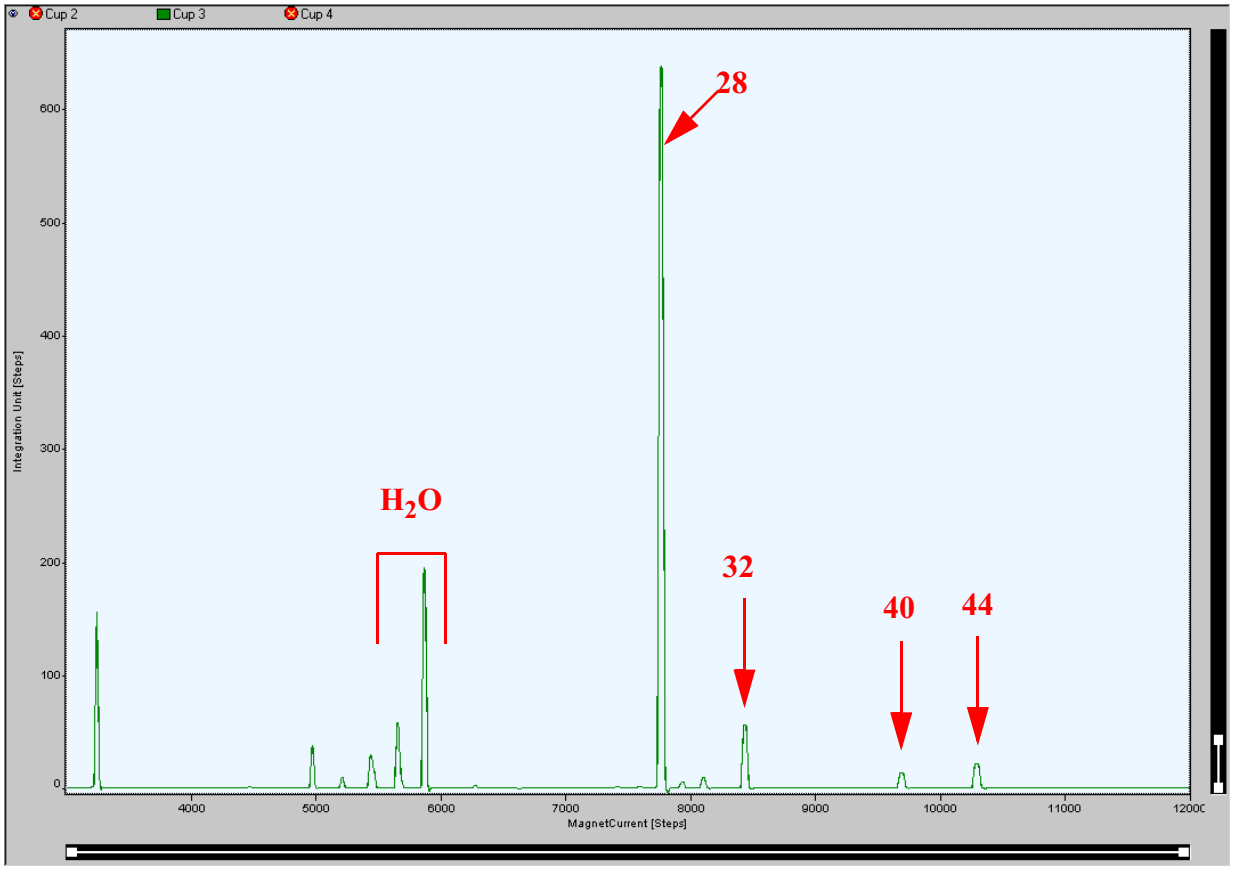


Figure 4-1. Mass Spectrum of Background Gas Composition (for Finnigan Delta^{Plus} XP)

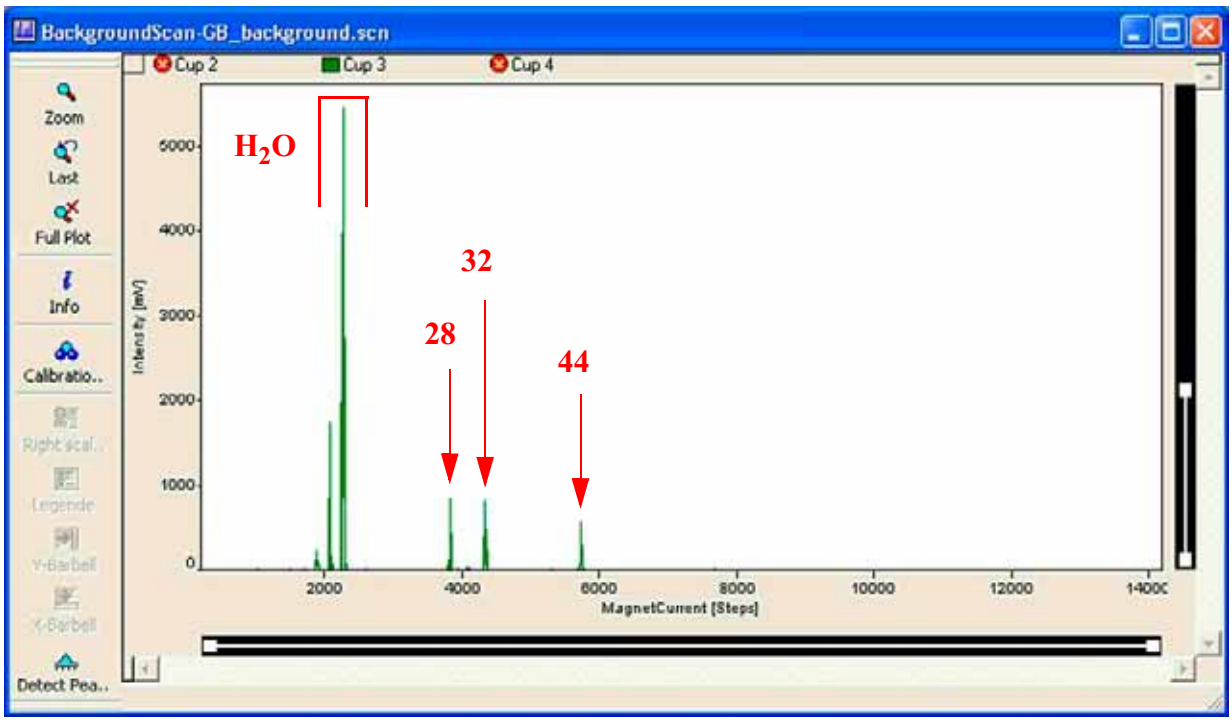


Figure 4-2. Mass Spectrum of Background Gas Composition (for Finnigan MAT 253)

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

- contains ions of m/z 16, m/z 17 and m/z 18.
- appears at magnet current values approximately between 5300 steps and 6000 steps.
- peak intensity should be maximal 1 V.
- intensity ratio of the three peaks is 1:2:4.

Air

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

CO_2

- contains ions of m/z 28 (CO) and m/z 44 (CO_2).
- appears around magnet current values of approximately 7800 steps and 10300 steps, respectively.
- 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, e.g. 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 hours. 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 (e.g. SNOOP®) which is applied to the connectors. Small bubbles appear when gas is leaking.

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

Warning. 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 8 port valve needs to be switched to introduce a portion of the gas stream into the IRMS.

Warning. 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.

4.2 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 sampling needle should be checked regularly before each run using a flow meter. Measure at the exhaust capillary at the valco switching valve, which is connected to port 7. Measure, while a closed bottle is attached to the measurement needle and while the valco 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. Since 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. During the 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.

4.3 Zero Enrichment Test (Standard On/Off Test)

Provided that GasBench II has no leak (see **Leak Check** on page 4-2), the Zero Enrichment test and Linearity test (see **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 2.0. 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 $\delta^{18}O$ and less than 0.06 ‰ for $\delta^{13}C$.

If this is obtained, you are ready to measure carbonates (see **Carbonates** on page 5-6), DIC (see **Dissolved Inorganic Carbon (DIC)** on page 5-20) or water equilibration (see **Water Equilibration (^{18}O)** on page 5-30 and **Water Equilibration (H/D)** on page 5-33).

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.
>
> See **Creating a GasBench Configuration** on page 3-4 and ISODAT NT Operation Manual - Upgrade to Version 2.0, Part No. 115 4990.

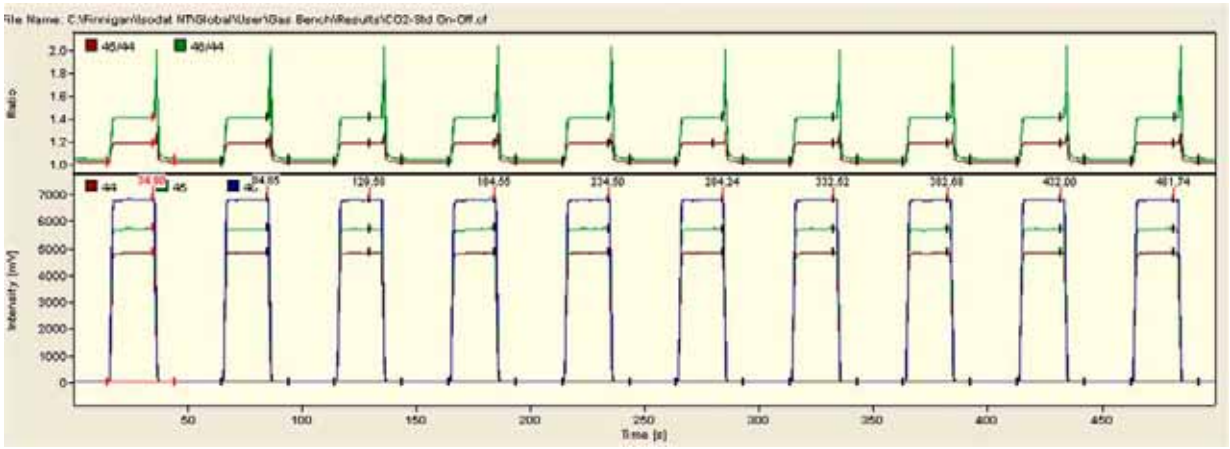


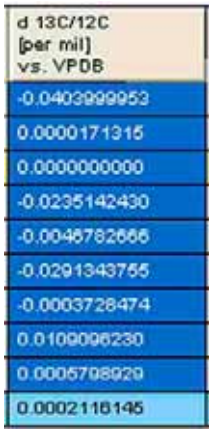
Figure 4-3. Zero Enrichment - Chromatogram

> **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



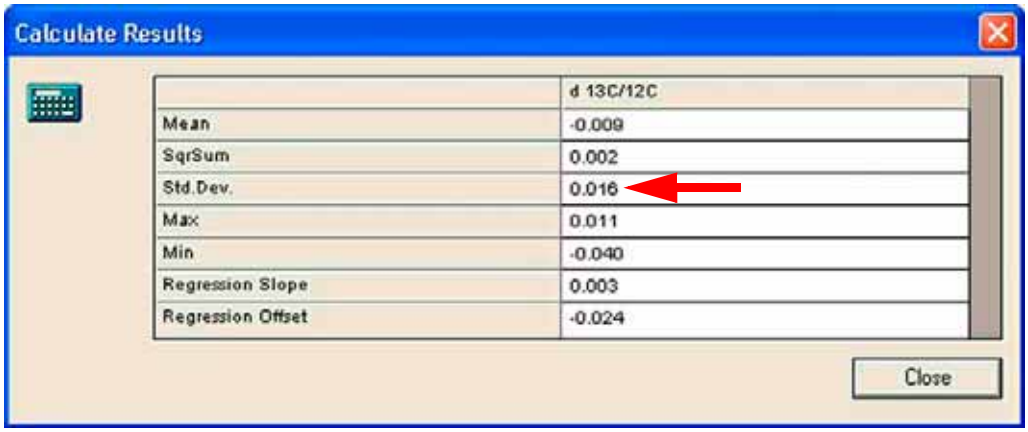
To obtain the standard deviation of all ten peaks,

- Click on the column header e.g. 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.

- Right-click on the column header.

- Choose ***Calculate***.



Note. The standard deviation (of the e.g. 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 reference gas inlet ports:

- Check the dimensions of your fused silica reference gas capillary as shown in **Open Splits** on page 2-34.
- Check the distances of your reference gas capillaries as they should be set up in **Open Splits** on page 2-34. Use the GasBench window as a part of the Accessories window:

1. 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.
2. If 1a.) or 1b.) is out of order, the following checks can be performed:

Warning. Be careful not to cut any of the capillaries inside GasBench II!

   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.

Warning. 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.

Warning. Do not overtighten!

Check 1a.) and 1b.). If either of them is out of order, pass again through all steps 2a.) to 2f.).

4.4 Linearity Test

The mass spectrometers normally used together with GasBench II (that is Delta, Delta^{plus}, MAT 253) are not ideally linear. This means that the measured δ value depends on the actual peak height. With each IRMS, a certain slope is guaranteed, e.g. 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 and ^{18}O respectively. Determine the slope.

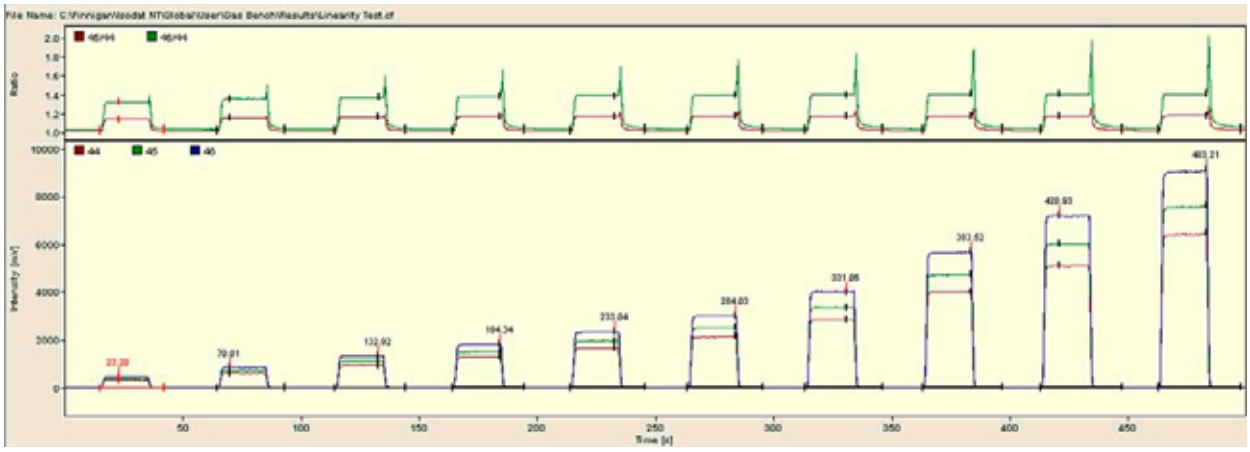


Figure 4-5. Linearity Test - Chromatogram

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	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

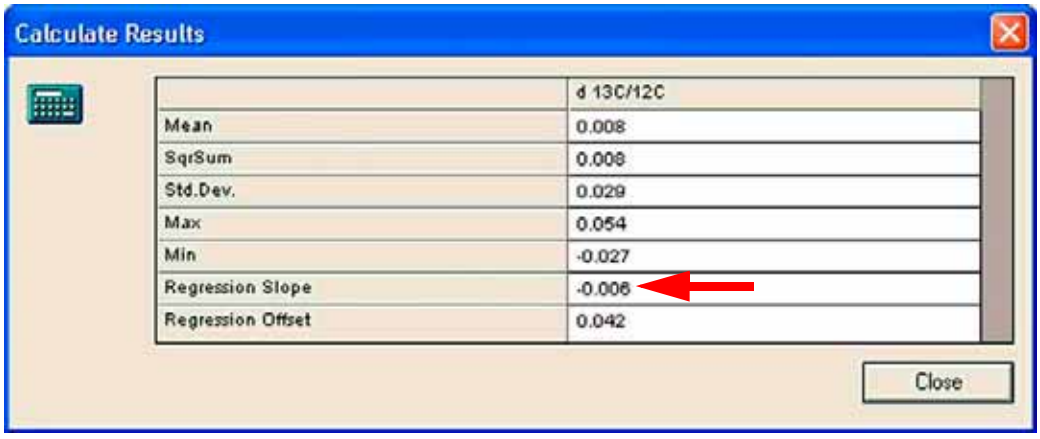
Figure 4-6. Linearity Test - Result Grid

To obtain the slope of all ten peaks,

- Click on the column header e.g. 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.

- Right-click on the column header.
- Choose ***Calculate***.



Note. The slope should be less than 0.05 ‰/V.

4.5 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, e.g. 500 ml.The following parameters can be optimized by this check:

- ***temperature and flow of GC column (PoraPlot Q)***
  GC temperature changes separation between peaks belonging to the same sample injection (aliquot). GC column flow shifts all GC peaks in time: higher flow means shorter retention time and vice versa.
- ***retention time and GC peak shapes (Δt_R N_2/CO_2)***
  Retention time depends on column type. Peak shapes tend to be tailed if the column is heavily used and needs recovering. Refer to **GC Oven** on page 2-26.
- ***time delay between METHOD / PROCESS (Δt loop injections)***
  Use this type of condition test when changing the timing 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.

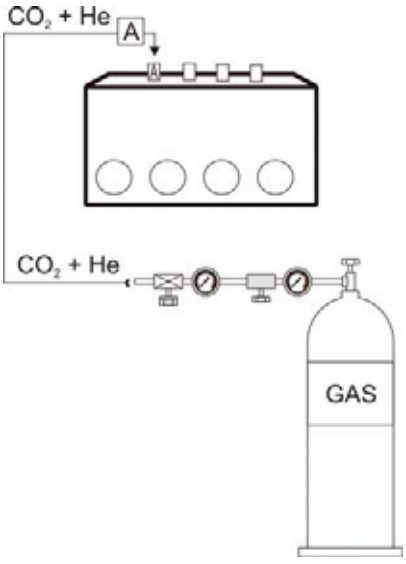


Figure 4-7. Basic Test for Sample Section (Autosampler and Bottles Excluded)

4.6 Starting an Automated Sequence

Before Starting an Automated Sequence

1. 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 8 port while a sample is connected.
2. 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 hours.
3. From time to time, check whether the water background of the IRMS is within acceptable limits, that is less than 3 V. See **Water** on page 4-3.

Preparing a Test Sample

The basic principle of the GasBench II technique is the measurement of any gas (e.g. CO_2) 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.

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 4-8.

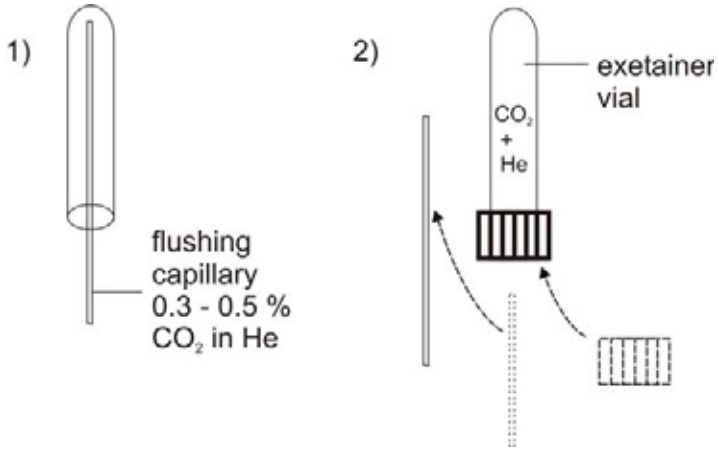


Figure 4-8. Flushing an Empty Exetainer for Preparation of a Test Sample

A more convenient way to fill the (He + CO_2) mixture into an exetainer vial is to use the flushing needle (refer to **Flush Needle** on page 2-18) 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 **Cleaning Procedure for Sample Vials** on page 5-5).

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

- ***A predefined sequence can be used for a measurement.***
  - Make sure that the IRMS is calibrated.
  - Make sure that the vials are prepared and placed in the tray.
  - Select an appropriate line in the sequence.
  - Press the ***Start*** button.
- ***The user must define a method for a measurement.***
  - The chapter **The File Browser** on page 3-13 gave an overview about what can be defined and seen by using the ***Method*** tab within the ***File Browser***.

> **Note.** For an extensive description of the options of the method definition refer to the ISODAT NT Operating Manual (Part No. 109 2481).
>
> In this section, only the entries that are specific for operating GasBench II will be described.

Method definition

The main visible procedure is

- perform a peak center before the acquisition.
- define CO_2 as a reference five times (duration: 20 s) and take the fifth as standard.

Ten loop switches for ten sample peaks on GC column

1 - 100 s	sampling line and valco 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. For detailed information about sequence editing and Combi PAL methods refer to the ISODAT NT Operating Manual (Part No. 109 2481), the ISODAT NT Operating Manual - Upgrade to Version 2.0 (Part No. 115 4990) and the Combi PAL Manual.

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 $\delta\ ^{18}O$.

4.7 Frequently Asked Questions

Note. 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.

1. A basic test must be performed, that is testing the IRMS alone.
2. Perform a zero enrichment test outlined in **Zero Enrichment Test (Standard On/Off Test)** on page 4-6.
3. Carry out a linearity test as described in **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 **Condition Test** on page 4-12.
5. Carry out a Zero Enrichment test with vial. The filling can be done manually or automatically.
6. Only if all the previous items are performed to specifications, carry out the measurement.

Chapter 5
Measurement Procedures for Real Samples

5.1 Introduction

General Remarks

Finnigan 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, i.e. CO_2, can either

- be part of the original gas sample (e.g. breathed air) 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 seconds. 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 and D/H from water samples),
- Global Change Research (^{13}C determination of dissolved inorganic carbon, DIC, from ocean water or fresh water) or
- Paleoclimatology (simultaneous ^{18}O and ^{13}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 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:

- 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

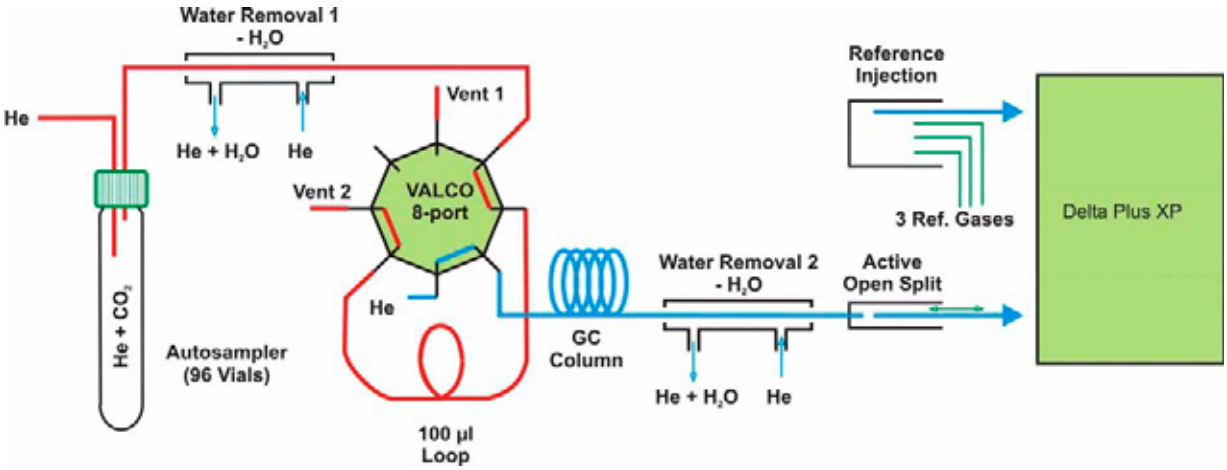


Figure 5-1. Schematic of GasBench II Components

LN2 is an abbreviation for liquid nitrogen. Gas flow of GasBench II in Load Mode. The sample loop is filled with the analytic mixture (refer to **Principle of Valco Eight Port Valve** on page 2-22).

> **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. Refer to **Instrument tab - Reference Device Part** on page 3-20).

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 switching valve or the mass spectrometer inlet valve. 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 ethanole 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 identic with 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 He or a mixture of He 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 He 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 only one 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, i.e. carbonate analysis.

Cleaning Procedure for Sample Vials

The sample vials used for carbonate measurements should be free of organic and inorganic contaminations before they are loaded with carbonate. To clean them perform the four steps described below:

1. Fill up the vials with warm diluted phosphoric acid (i.e. phosphoric acid plus warm distilled water) and leave them for eight hours.
2. Rinse the vials repeatedly with distilled water using a washing bottle.
3. Rinse the vials with acetone using a washing bottle, too. This helps to dry the vials faster.
4. Dry the vials in a drying chamber at 72 ºC for 2.5 hours. Cover them with aluminum foil to protect them against contamination.

5.2 Carbonates

Introduction

In order to measure carbonates, you need the carbonate option. In this chapter, simultaneous measurement of ^{13}C and ^{18}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-}.

Double Needle Setup

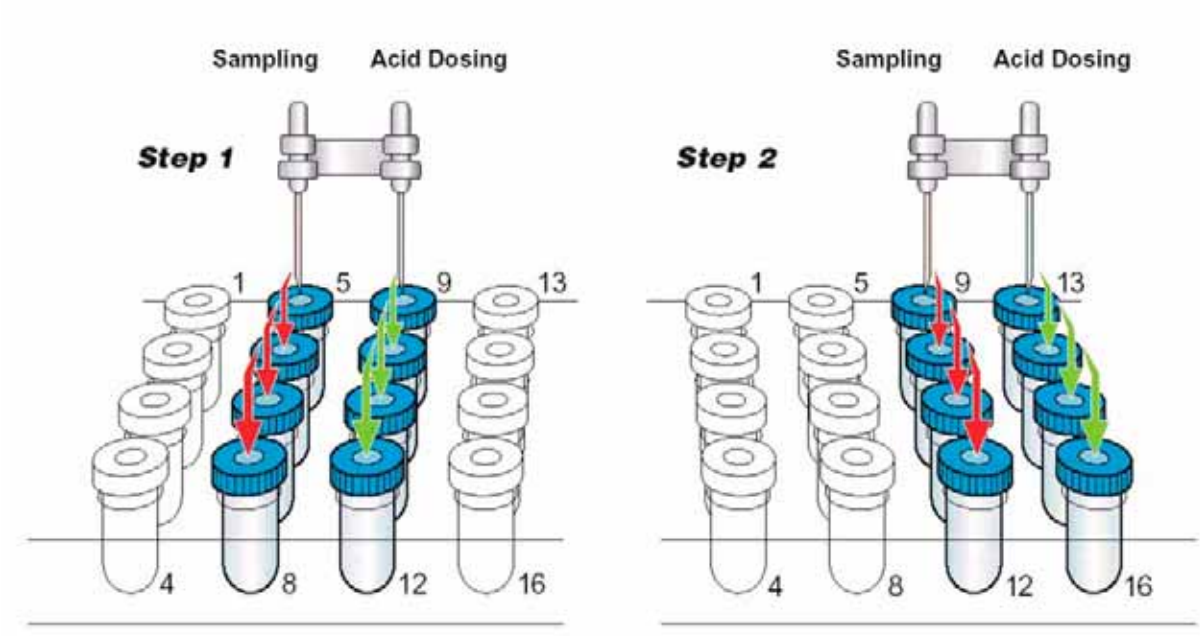


Figure 5-2. Defining the Sequence - Double Needle Setup

The double needle setup allows acid dosing to one sample while measuring another one (refer to Figure 5-2, Figure 5-6 and **Flush Needle** on page 2-18). While the right needle transports acid to a bottle filled with He, the left needle takes sample gas from the headspace.

Carbonates in Brief

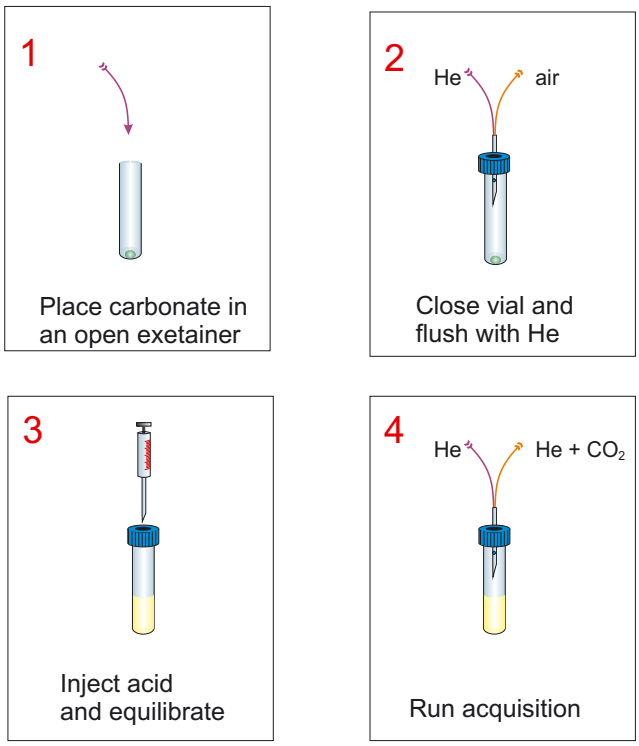


Figure 5-3. Sample Preparation for Carbonate Measurement

- 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.
- Place 50 - 600 µg of solid, carbonate-containing sample (e.g. dolomite, calcite, foraminifera) into a clean sample vial.
- Close the vial with a new cap and a new septum.
- Place the vials within the tray.
- Ensure that the rinsing/filling needle is properly mounted in the autosampler.
- Depending on your flushing needle setup, either choose the flush or double 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.
- Ensure that the sampling needle is properly mounted in the autosampler.

Note. It is strongly recommended to choose a double needle setup (that is measurement 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 autosampler's double needle holder.

- Start the analysis sequence with a double needle setup (refer to **Double 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:

1. Dosage of H_3PO_4 using our automatic device. Reaction between carbonate-containing sample and H_3PO_4 begins[1]. CO_2 will be released into the headspace.
2. Waiting about 1 hour for equilibration of the CO_2.
3. During measurement, helium enters the system, and a mixture of helium and CO_2 (as the sample gas) passes to GasBench II.

Note. The vials on the positions 1 - 9 are neither filled with carbonates nor with acid, but they will be flushed with He. 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, Figure 5-6, Figure 2-15 and **Creating a New Sequence** on page 3-34.

If everything operates successfully, 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 (i.e. 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

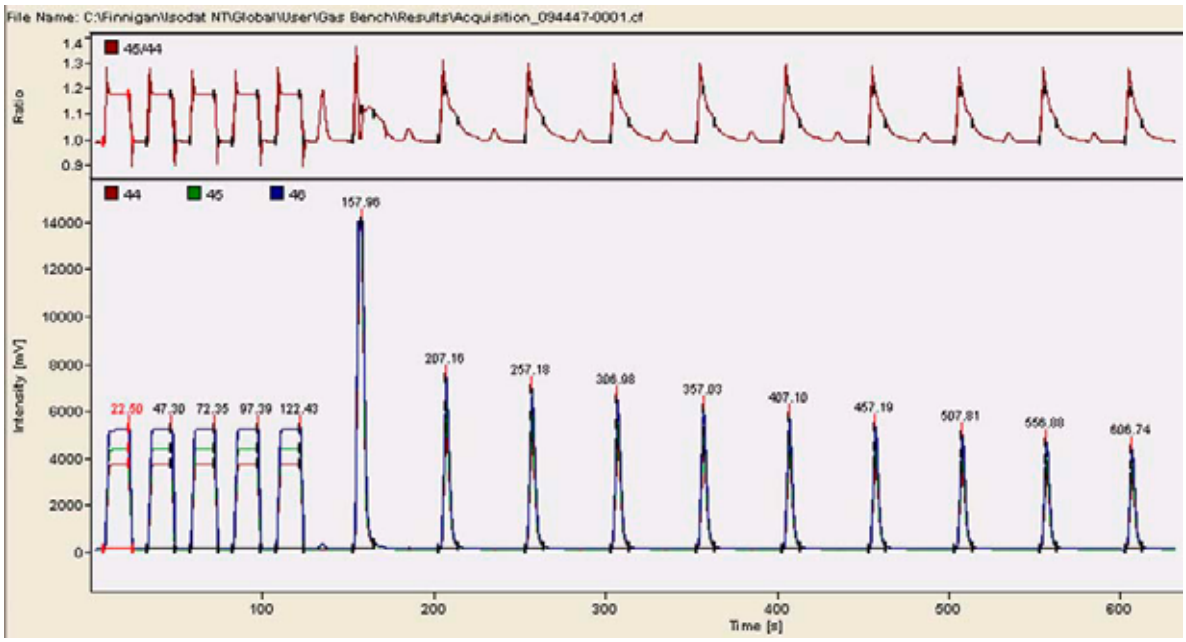


Figure 5-4. Carbonate Measurement - Chromatogram

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	-0.1
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

The arrow shows the overranged peak No. 6.

Figure 5-5. Carbonate Measurement - Result Grid

- 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/He 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, i.e. 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 He 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 section, **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 in section **Referencing versus VPDB** on page 5-13.

Figure 5-6 shows an uncorrected result, that is raw data from a series of measurements of the same sample.

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
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

Figure 5-6. Raw Data Example to Illustrate Linearity Correction

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 5-7 will be obtained.

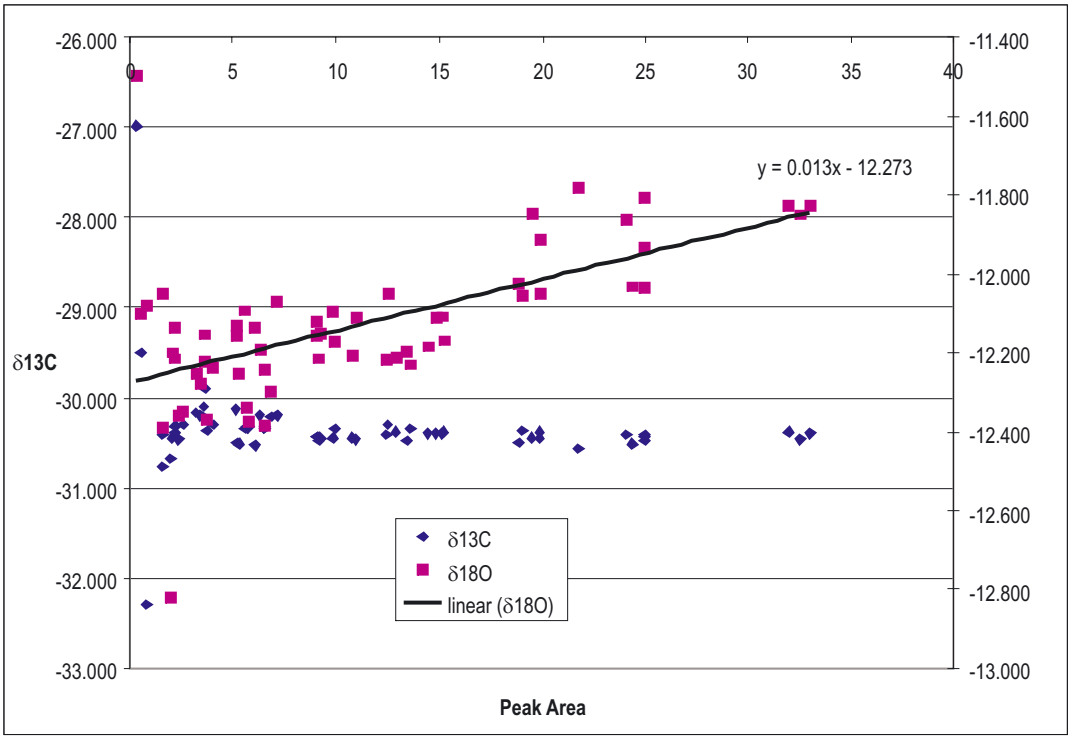


Figure 5-7. Measured δ Value versus Peak Area for a Set of Measurements (Same Sample but Different Sample Amounts)

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 and 0 ‰/Vs for ^{13}C in the example above), but depends on all of the the factors mentioned above. Therefore, 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, i.e. the slope, from reference samples (that is working standards) by plotting the measured δ value for ^{18}O and ^{13}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 see **Referencing versus 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 get a proper estimate for the slope, sample amount should vary. Furthermore, this procedure allows quality control during the entire data acquisition.

Referencing versus 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 7-6.

> **Note.** See **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 and ^{13}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:

- Determine the δ value of your working standard.
- Calibrate versus known standards supplied by IAEA or NBS.
- Use a primary standard to determine the δ value of the reference gas.
- With x meaning working standard and z denoting VPDB, the following equation is valid (refer to **Remark on the Strange Mathematics of Delta Values** on page 5-15):

$$\delta_z^x = \frac{\delta_y^x \cdot \delta_z^y}{1000} + \delta_y^x + \delta_z^y$$

and

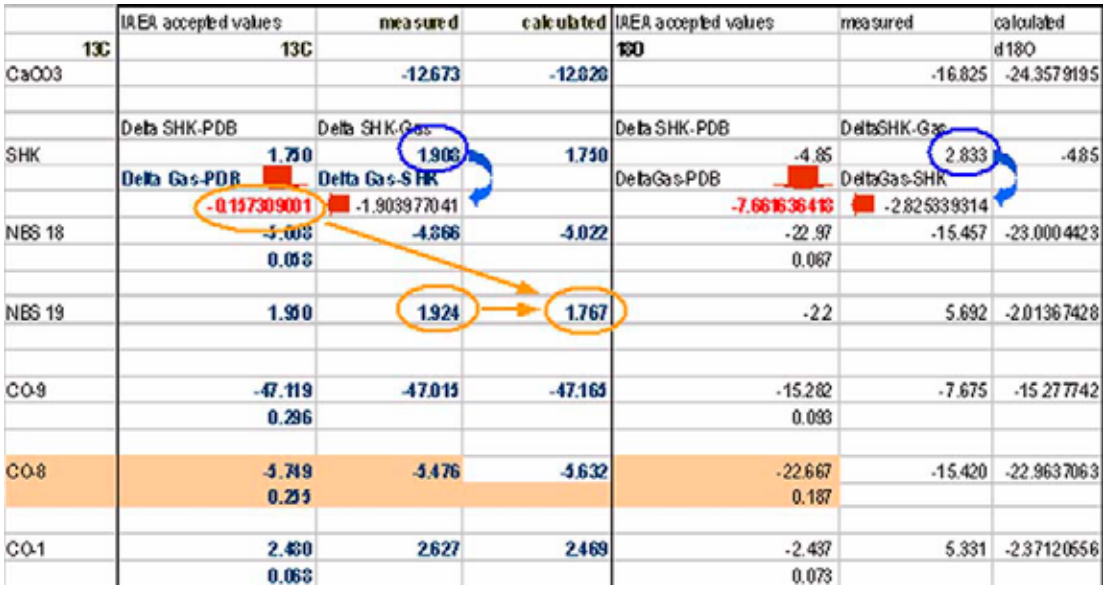
$$\delta_z^y \neq \delta_y^z$$

with:

x working standard

y gas

z absolute standard (that is VPDB)



	IAEA accepted values	measured	calculated	IAEA accepted values	measured	calculated
13C	13C			18O		d18O
CaCO3		-12.673	-12.820		-16.825	-24.3579195
	Delta SHK-PDB	Delta SHK-Gas		Delta SHK-PDB	DeltaSHK-Gas	
SHK	1.750	1.908	1.750	-4.85	2.833	-4.85
	Delta Gas-PDB	Delta Gas-SHK		DeltaGas-PDB	DeltaGas-SHK	
	-0.157309001	-1.903977041		-7.66163641	-2.825339314	
NBS 18	-5.008	-4.866	-5.022	-22.97	-15.457	-23.0004423
	0.053			0.067		
NBS 19	1.950	1.924	1.767	-2.2	5.692	-2.01367428
CO-9	-47.119	-47.015	-47.165	-15.282	-7.675	-15.277742
	0.296			0.093		
CO-8	-5.749	-5.476	-5.632	-22.667	-15.420	-22.9637063
	0.251			0.187		
CO-1	2.480	2.627	2.469	-2.437	5.331	-2.37120556
	0.063			0.073		

Figure 5-8. Calculation Example

Figure 5-8 is an example for obtaining δ values specified against VPDB starting from measured and corrected δ values.

1. Determine absolute δ value of 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 absolute δ value of 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. Ref. Gas to calculate 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:

$$\delta_{PDB}^{NBS\ 19} = 1.767$$

In this case, the result is incorrect.

Remark on the Strange Mathematics of Delta 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). See **Referencing versus VPDB** on page 5-13.

Phosphoric Acid Preparation

Phosphoric acid, H_3PO_4, is prepared from "Puranal" grade orthophosphoric acid (≥ 85 %) and "Puriss" grade phosphorous pentoxide or trade names of equivalent purity. Inside a fume cupboard, one “Winchester” (that is a 2.5 l package) of phosphoric acid is poured into a 5 l beaker that stands on a magnetic stirrer’s hotplate. Use a magnetic stir bar (PTFE).

Warning. Gloves and a face mask must be worn whenever handling P_2O_5! Goggles are not sufficient!

Note. A useful thermometer or stirring rod can be obtained by enclosing the thermometer in a large piece of heavy-walled Pyrex tubing with its bottom sealed off (that is shaped like a test tube).

Warning. Between the additions and during the final cooling stage the beaker is kept covered with cling film.

Adding Phosphorous Pentoxide

Warning. Take care during the initial stage of adding P_2O_5: the reaction can be vigorous as the powder contacts the relatively “wet” acid!

It normally takes about 2 kg of phosphorous pentoxide to obtain the required final specific gravity of greater than 1.92. This quantity of P_2O_5 is gradually added over a period of 2-3 hours while constantly stirring and heating to a temperature of around 80 ºC. The powder forms gelatinous lumps initially, but will gradually dissolve. The complete process can take 4-5 hours.

A few crystals of chromium dioxide, that is approximately 0.5 g, are added at the final dissolution stage. Heating and stirring continues until all phosphorous pentoxide has dissolved.

The stirrer hotplate is switched off allowing the acid to cool down to room temperature before checking specific gravity. If it is less than 1.92, the acid must be reheated and more P_2O_5 needs to be added. Finally, the acid which should be about 3 l after P_2O_5 addition, is stored in bottles until required. Use 'Parafilm' to seal the screw cap.

Common Pitfalls

Retention Times

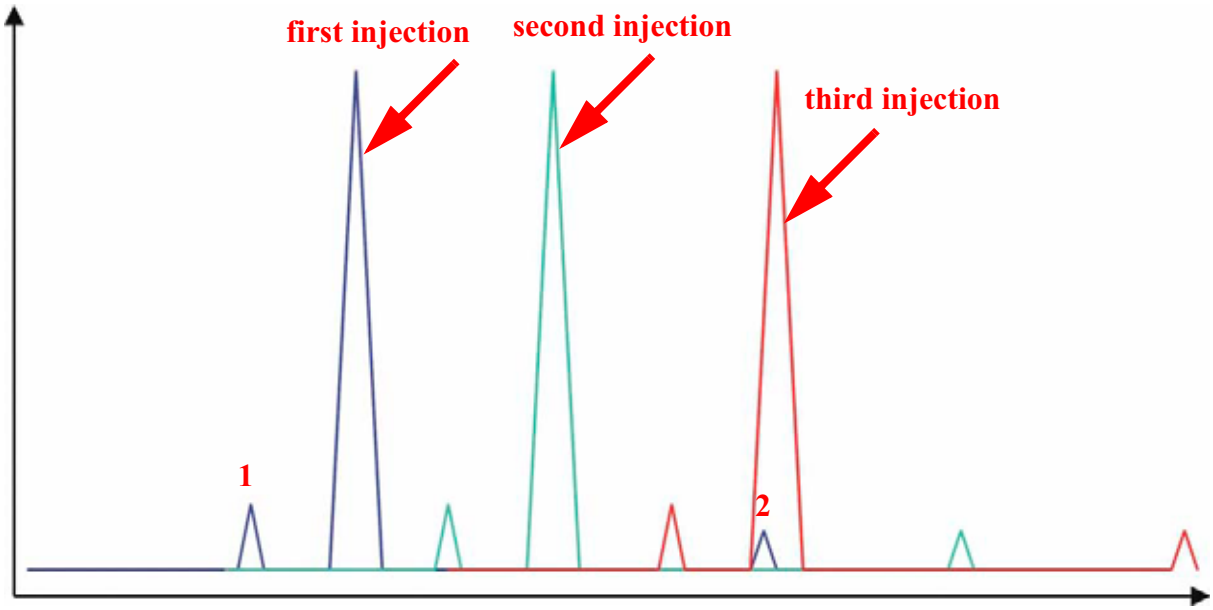


Figure 5-9. Upon Retention Times - Combining Chromatograms

1. Air peak precedes CO_2. See **1** in Figure 5-9.
2. Water peak may follow CO_2 but must not interfere with CO_2. See **2** in Figure 5-9.
3. Additional peaks, e.g. due to solvents, must not interfere with CO_2.

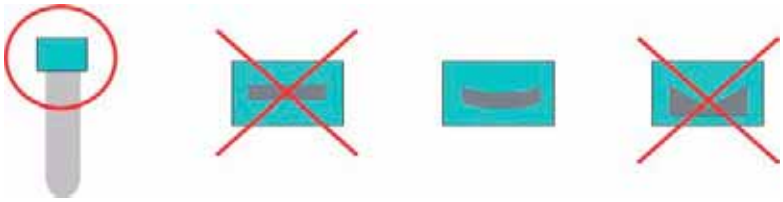
Wasting Acid

Due to improper adjustment of the acid pump, acid drops may be deposited on the septa. If so, acid can enter the measurement needle and travel towards the valco valve.

Warning. This must be avoided under all circumstances! Severe damage to water trap and valvo valve will result! Therefore, refer to **Acid Pump Adjustment** on page 6-5.

Handling Septa

Ensure that the sample vials are screwed down correctly in order to be really closed.



- left: will not be leaktight
- middle: fits correctly
- right: will develop fissures and tends to be cut by the needle

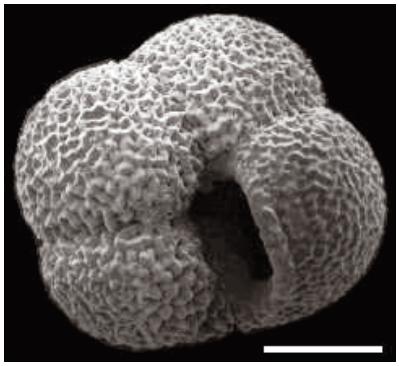
Figure 5-10. Correct Handling of Septa

Condensation of Water beneath the Septa

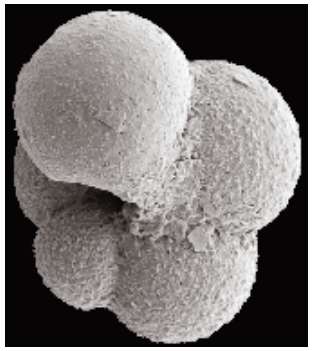
During equilibration, when tray temperature is only slightly above room temperature, water vapor condenses benath the septa. This effect is unavoidable and usually poses no problem. Once the septa have been punctured by the needle, these water droplets accumulate to one large drop. If now this particular 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.

Warning. Therefore, never measure equilibrated samples twice!

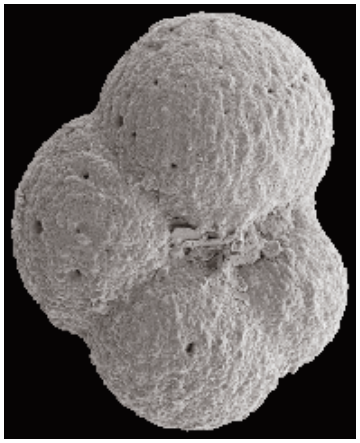
Neogloboquadrina Pachyderma (Ehrenberg, 1894)



Left-coiled specimen, umbilical view, scale bar 0.1 mm.



Right-coiled (dextral) specimen, umbilical view.



Left-coiled (sinistral) specimen, umbilical view.

Neogloboquadrina Pachyderma is the most abundant planktonic foraminifer of high latitudes. 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.

5.3 Dissolved Inorganic Carbon (DIC)

Dissolved Inorganic Carbon (DIC) in Brief

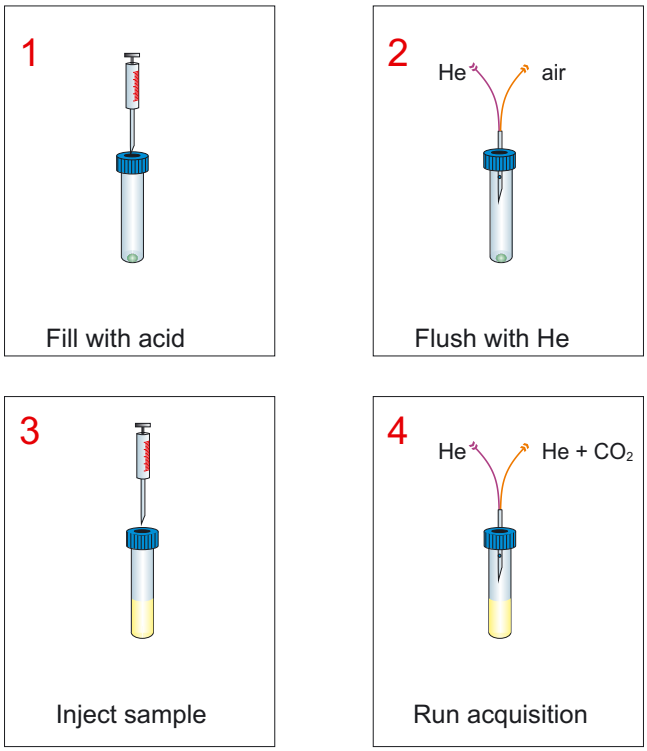
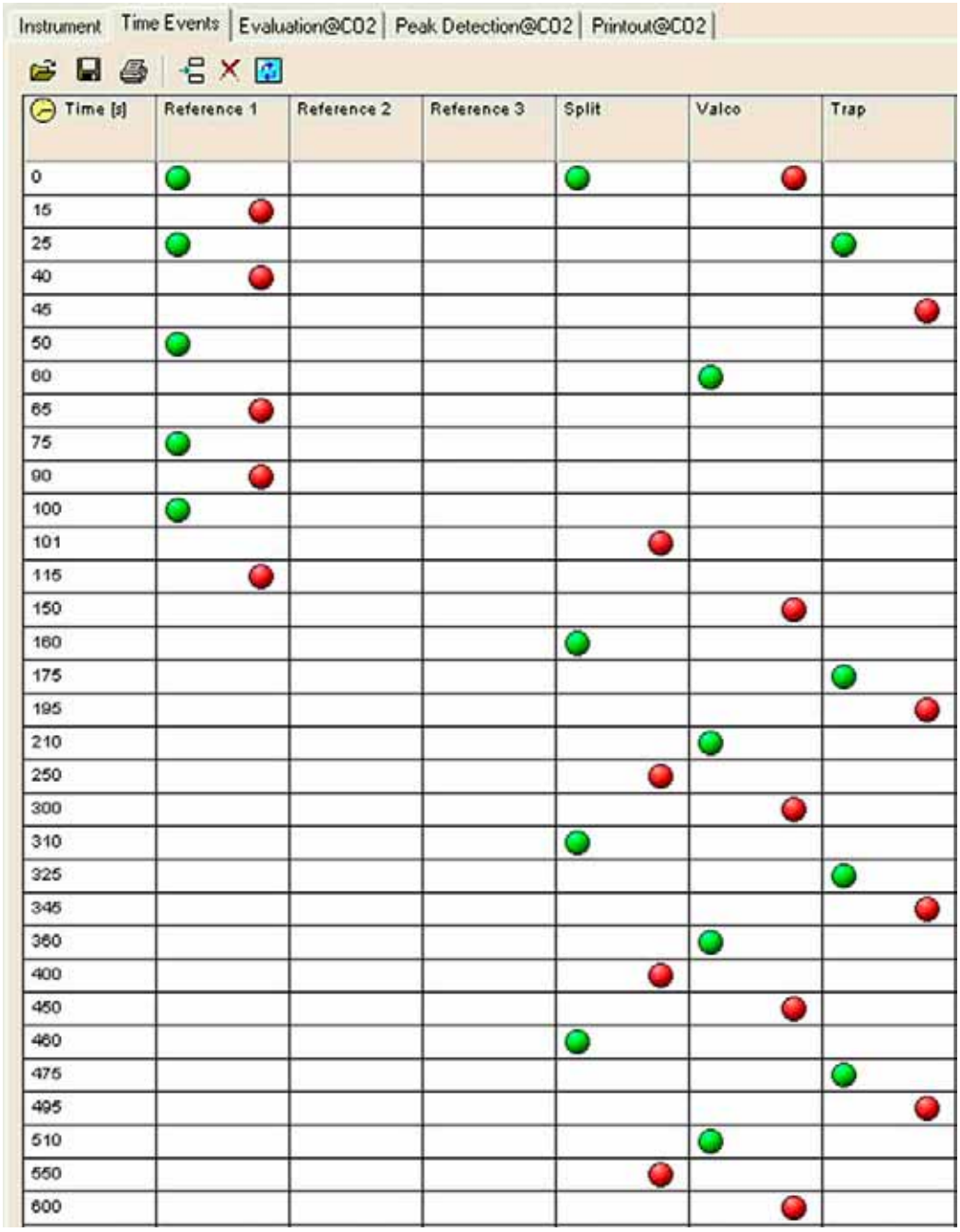


Figure 5-11. Sample Preparation for Dissolved Inorganic Carbon (DIC) Measurement

When real samples are collected, they must be poisoned using a saturated $HgCl_2$ solution to stop all biological activity.

Warning. 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.



Time [s]	Reference 1	Reference 2	Reference 3	Split	Valco	Trap
0	●			●	●	
15	●					
25	●					●
40	●					
45						●
50	●					
60					●	
65	●					
75	●					
90	●					
100	●					
101				●		
115	●					
150					●	
160				●		
175						●
195						●
210					●	
250				●		
300					●	
310				●		
325						●
345						●
360					●	
400				●		
450					●	
460				●		
475						●
495						●
510					●	
550				●		
600					●	

Figure 5-12. Dissolved Inorganic Carbon (DIC) Measurement - Time Events List (Partly)

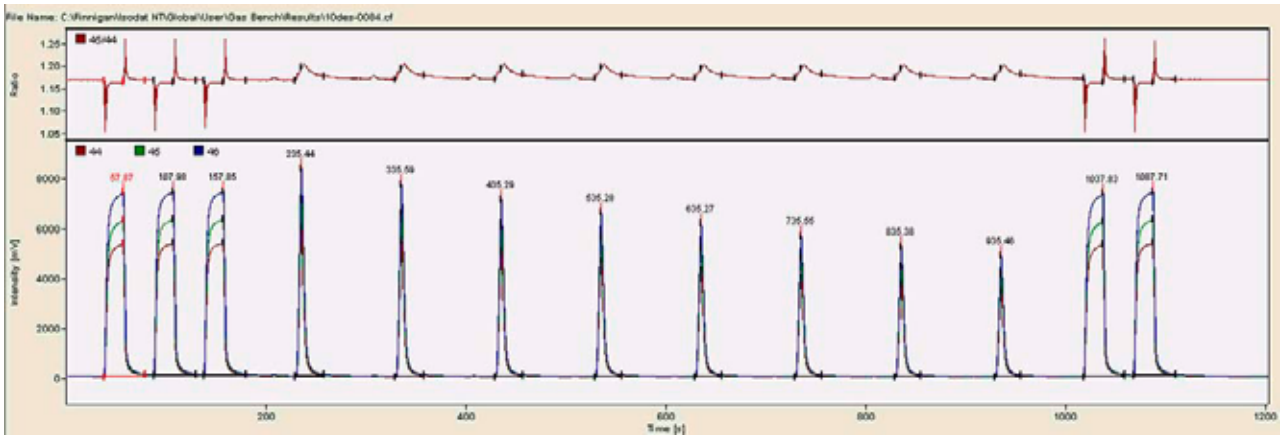


Figure 5-13. Dissolved Inorganic Carbon (DIC) Measurement - Chromatogram

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 5-14. Dissolved Inorganic Carbon (DIC) Measurement - Result Grid

- Almost no signal occurs on m/z 46 between the CO_2 peaks.
- Decreasing peak height indicates proper transport of sample/He mixture.

Warning. When filling a number of tubes from the same water standard, do not fill from sealed vessel with septum. A negative pressure will be created that could cause fractionation.

Warning. 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 ºC.

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, e.g. N_2. It is not dissolved in the water and thus the CO_2 content will not change.

1. Fill some drops of 98 % H_3PO_4 (about 30 µl) into an empty vial. See **Phosphoric Acid Preparation** on page 5-16 for its preparation.
2. Close the vial and place it in the tray.
3. Exchange the headspace (that is via the needle, He 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.

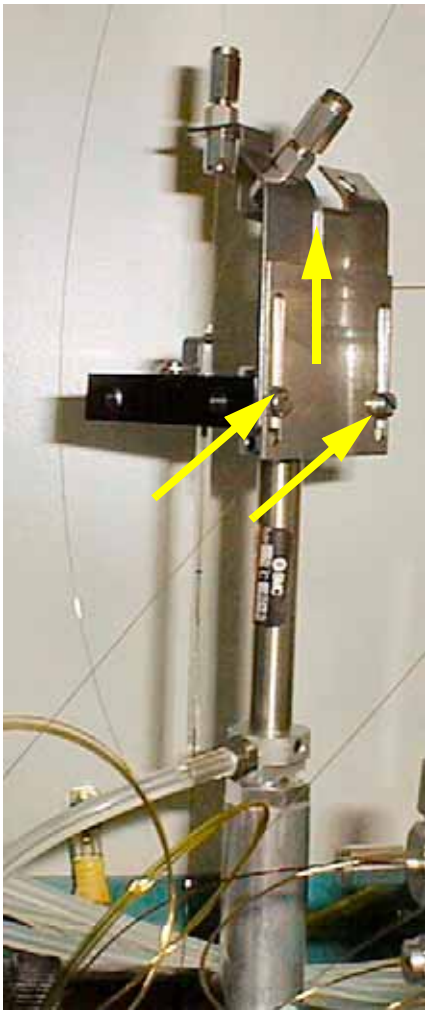
Note. A syringe must be used to prevent the sample from contacting and exchanging with ambient air.

5. Allow 18 hours to equilibrate.
6. Finally, the sample will be measured.

5.4 Breath Gas Analysis

Using the 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.



The modification can be obtained by

- loosening the two screws and
- moving fully upwards the small metal plate that limits the movement of the autodiluters pneumatic lever.

See arrows in Figure 5-15.

Figure 5-15. Adjusting the Open Split for Blanking

Additionally, the capillary feeding the split with helium needs to be retracted into the inner glass tube. See Figure 5-15 and Figure 5-16.

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.

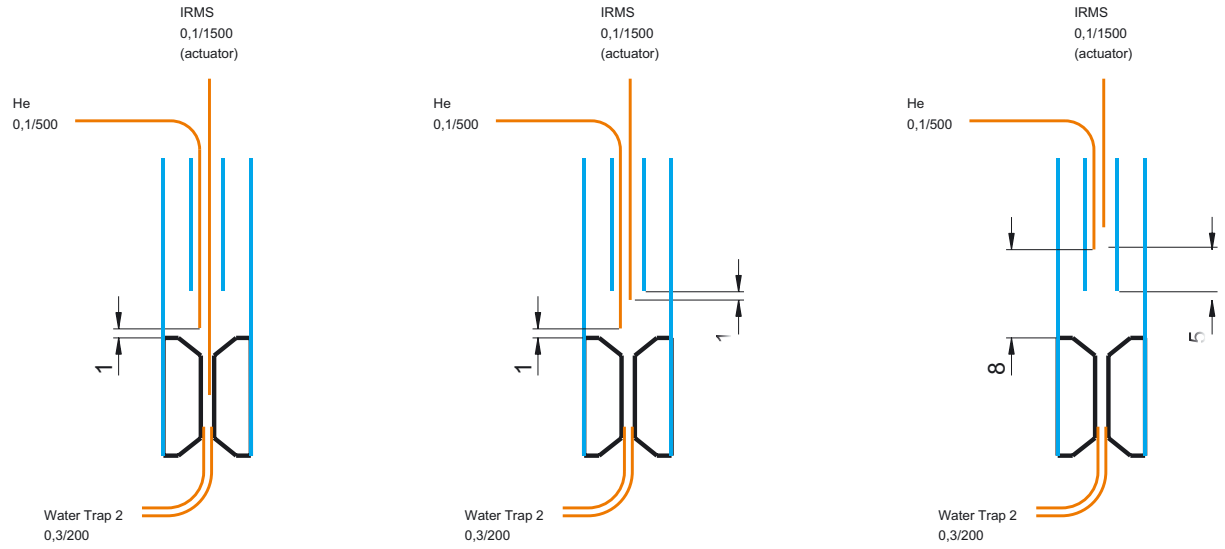


Figure 5-16. Principle of Blanking

- left side: no dilution
- middle: normal dilution
- right side: maximum dilution

Results of Blanking

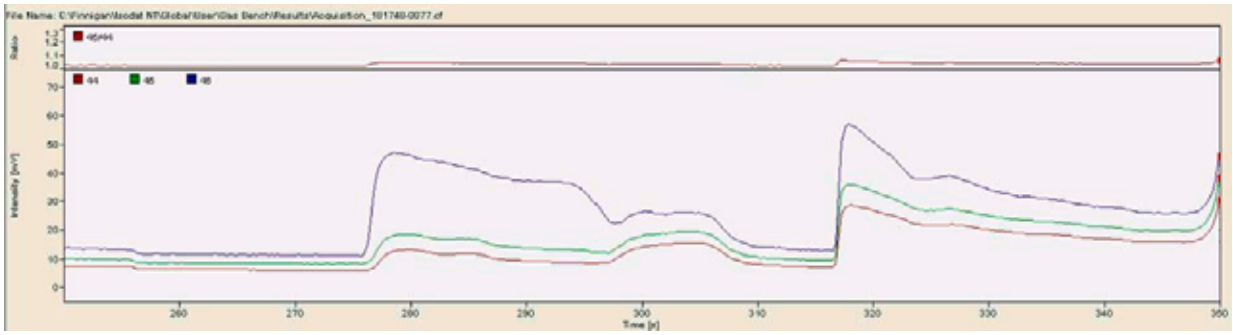


Figure 5-17. Blanking - Chromatogram

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 5-18. Blanking - Result Grid

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 **How to Change the Loop Size** on page 2-23 and proceed as follows:

- Fill empty sample vials with breath using a straw.
- Close them with fresh cap and septum. Place them in the sample tray.
- Perhaps, you should modify the method as with **CO_2 in Atmospheric Concentrations** on page 5-28.
- A sequence of its own is not necessary. Instead, use the Equilibration sequence ***Equilibration.seq*** to perform a measurement.

Results of Breath Gas Analysis

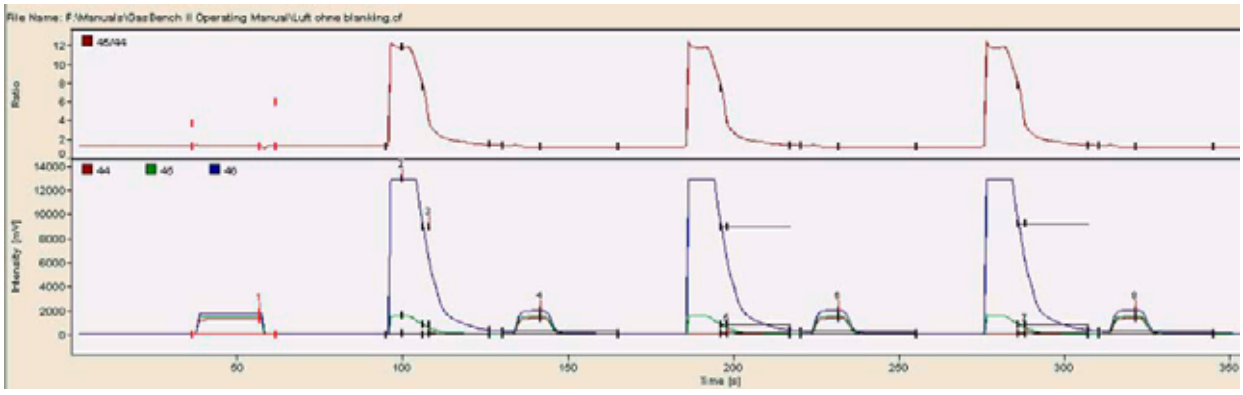


Figure 5-19. Chromatogram of Plain Analysis (without Blanking)

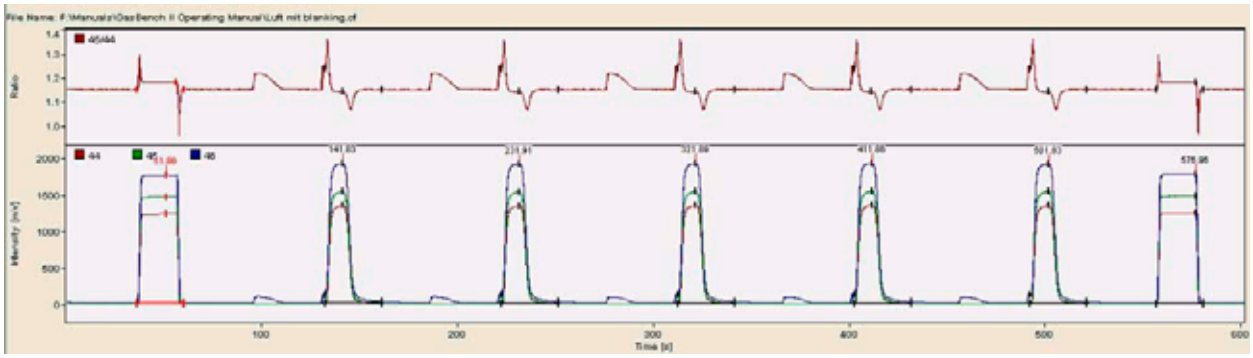


Figure 5-20. Chromatogram of Analysis (with Blanking Activated)

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 5-21. Result Grid of Analysis (with Blanking Activated)

> **Note.** Take into account the different ordinate scales when comparing Figure 5-19 and Figure 5-20.

5.5 CO_2 in Atmospheric Concentrations

Editing a Method

To measure CO_2 in atmospheric concentrations, use ***Acquisition 630s mod for air.met*** that has been delivered as a particular predefined method.

> **Note.** It differs only with respect to the Time Events List from Acquisition 630s.met used for carbonate measurements.

Select it from the File Browser's Methods tab. Then, double-click or drag and drop it into Isodat 2.0's Acquisition window. Refer to **Predefined Methods as Examples** on page 3-18 and **Creating a New Method** on page 3-17.

Time Events

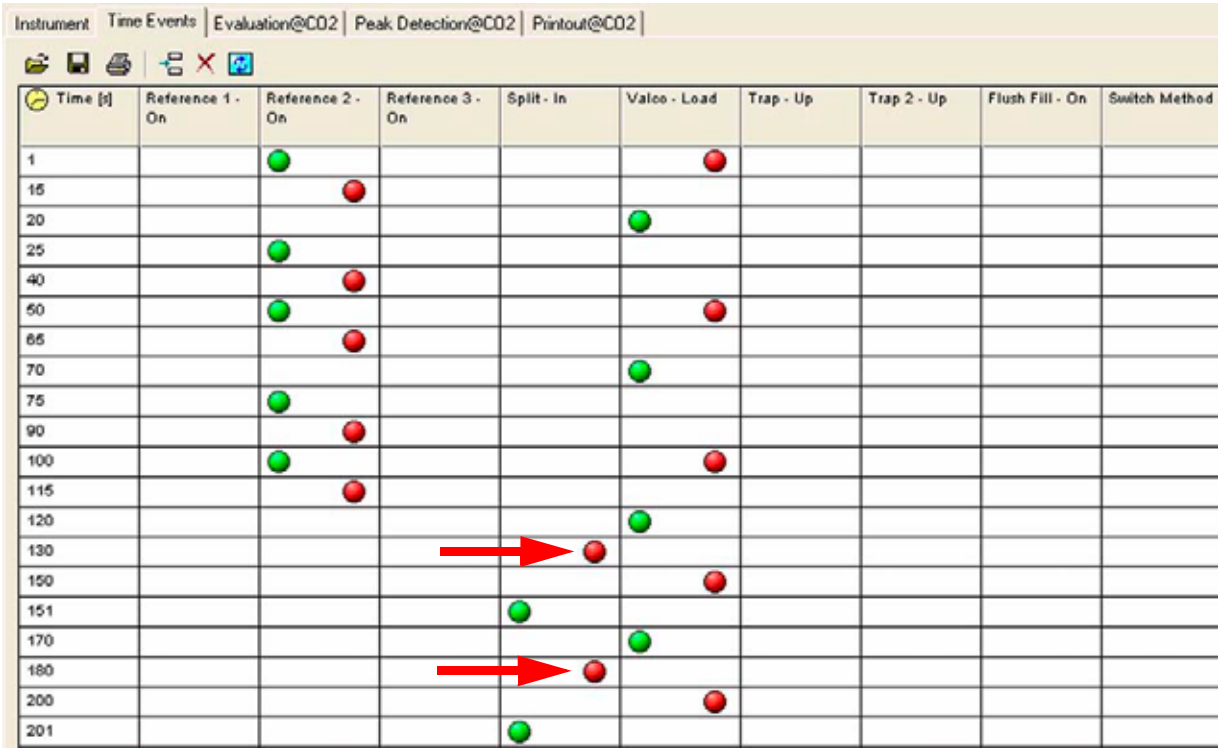


Figure 5-22. CO_2 in Atmospheric Concentrations - Time Events tab - Time Events List (Partly)

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, i.e. 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 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 5-23. CO_2 in Atmospheric Concentrations - Time Events tab - Acquisition

Results

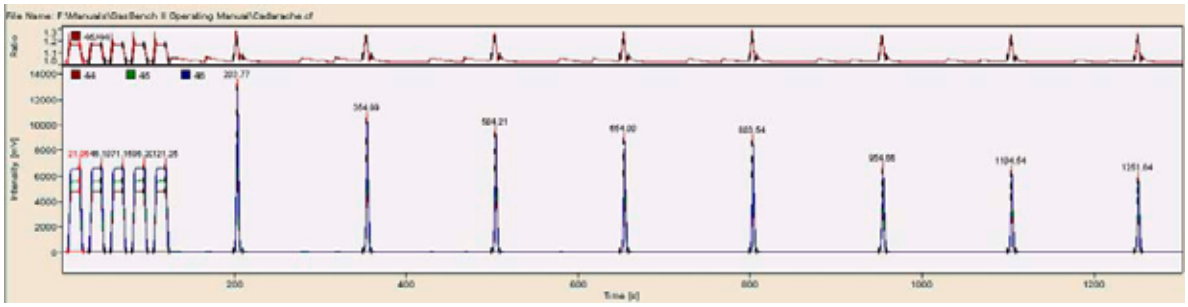


Figure 5-24. CO_2 in Atmospheric Concentrations - Chromatogram

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	6805	13.6	67.624	0.189	0.074
3	56.6	71.2	18.9	6801	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 5-25. CO_2 in Atmospheric Concentrations - Result Grid

5.6 Water Equilibration (^{18}O)

^{18}O Equilibration in Brief

- 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.
- Close the vial and place it into the autosampler tray.
- 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.
- Increase the pressure to result in a flow of the He/CO_2 mixture of approximately 100 ml/min - 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, i.e. 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.

- Ensure that the flush needle is properly mounted in the autosampler.
- Depending on your hardware, use the ***flush*** sequence or the ***double needle flush*** sequence to fill the vials automatically.
  Refer to **Creating a New Sequence** on page 3-34.
- Close the He/CO_2 mixture tank when the ***flush*** sequence is finished.
- Wait for approximately 18 h for proper equilibration.
- Start measurement sequence. See **Creating a New Sequence** on page 3-34.

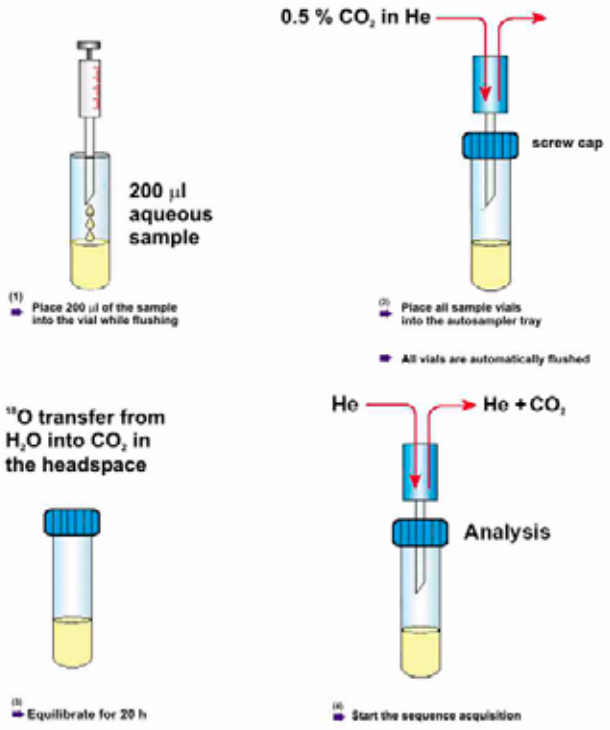


Figure 5-26. Sample Preparation for ^{18}O Equilibration

Sample Tray Temperature Control

For high precision ^{18}O equilibration, the temperature of the sample tray needs to be stabilized. Two operation modes are available:

- Passive Tray at room temperature, that is 24 °C

The thermal mass of the cast aluminum tray and its isolation allow to keep 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 (e.g. one reference sample for six unknown samples).

- Active temperature control at 32 °C

Ensure that room temperature is approximately 5 °C below the set tray temperature. Check the temperature stability over several hours. The controller read out 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 **Carbonates** on page 5-6 or using the simplified scheme given in **Water Equilibration (H/D)** on page 5-33.

Note. Refer to **Reference and intercomparison materials for stable isotopes of light elements**. In: **IAEA-TECDOC-825**, IAEA, ed., Vienna, 1995. See also Table 7-6.

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

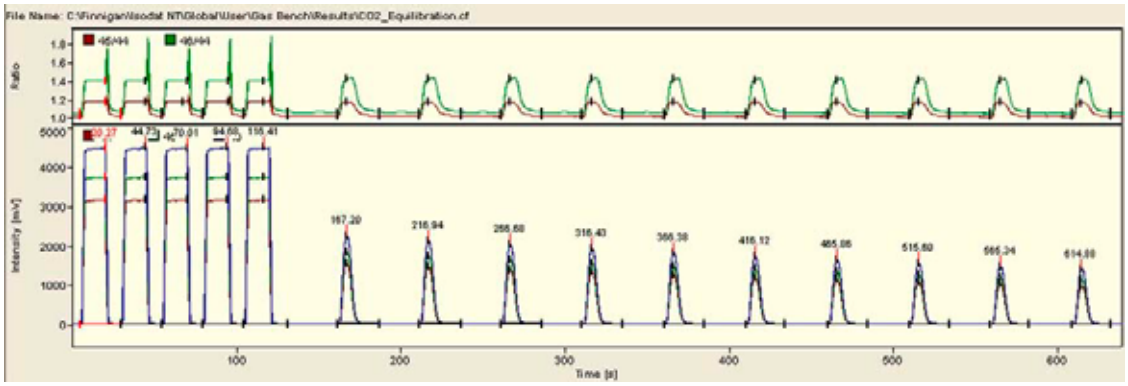


Figure 5-27. Water Equilibration (^{18}O) - Chromatogram

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	3169.949	9.261	9.853	13.342	45.741	0.0119844	-0.0404715422	-0.0247573364
2	44.7	25.1	3172.395	9.261	9.853	13.342	46.454	0.0119848	-0.0049359485	-0.0271250732
3	70.0	24.7	3162.652	9.261	9.853	13.342	46.106	0.0119846	-0.0193904556	-0.0185544341
4*	94.7	25.1	3175.371	9.261	9.853	13.342	46.452	0.0119849	0.0000000000	0.0000000000
5	116.4	27.0	3174.137	9.261	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	9.998	11.790	15.990	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	1.3767999590	25.1197961709
9	316.4	24.9	1328.000	9.621	11.475	15.481	7.964	0.0120099	1.3009169171	25.1052293560
10	366.4	24.2	1260.666	9.556	11.396	15.345	7.555	0.0120093	1.2616992999	25.0541139496
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 5-28. Water Equilibration (^{18}O) - Result Grid

5.7 Water Equilibration (H/D)

H/D Equilibration in Brief

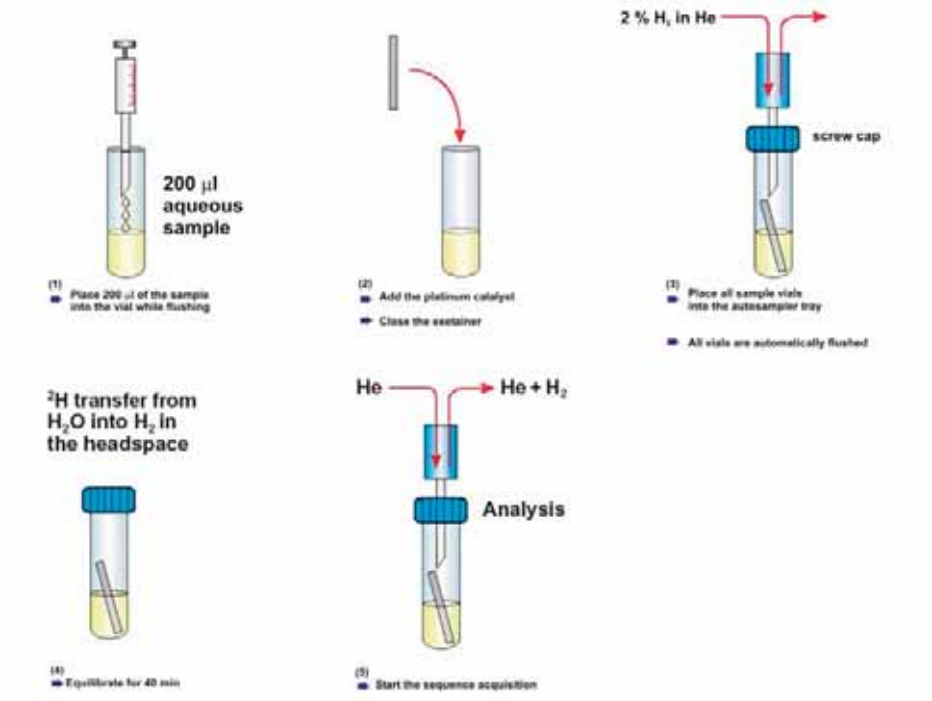


Figure 5-29. Sample Preparation for H/D Equilibration

In case of any hydrogen equilibration perform the following steps keeping the tray at room temperature (see **Sample Tray Temperature Control** on page 5-31):

- Insert the sample into the vials and insert the catalytic platinum sticks.
- Flush all samples with 2 % H_2 in He. Run a flushing sequence. See **Creating a New Sequence** on page 3-34. The equilibration is finished within 40 min. It is not necessary to wait additional time.
- 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 GasBench II.
- Run a mesurement sequence. See **Creating a New Sequence** on page 3-34.

Preparing an H/D Measurement

Preparing an H/D Method

When preparing a method for H/D equilibration choose ***Low pass filtered*** background. In case of H/D equilibration, this background algorithm yields better results than the ***Individual*** background algorithm recommended for CO_2 measurements.

H_3 Factor

For H_3 factor determination in detail refer to ISODAT NT Operating Manual, Part No. 109 2481. 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 H/D measurements. Instead, you must set the calibration manually by following the procedure given below:

- Switch the reference H_2 ***on***.
- Set Delta^{plus} XP to approximately 1000 magnet steps.
- Press the right mouse button on the magnet steps value.
- Select ***Pass to Gas Configuration***.
- Force the IRMS to jump to m/z 2 for instance by changing the Gas Configuration to ***CO2*** and back to ***H2***.
- Carefully adjust the magnet steps value to hit the peak center and repeat the last two steps.
- 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:

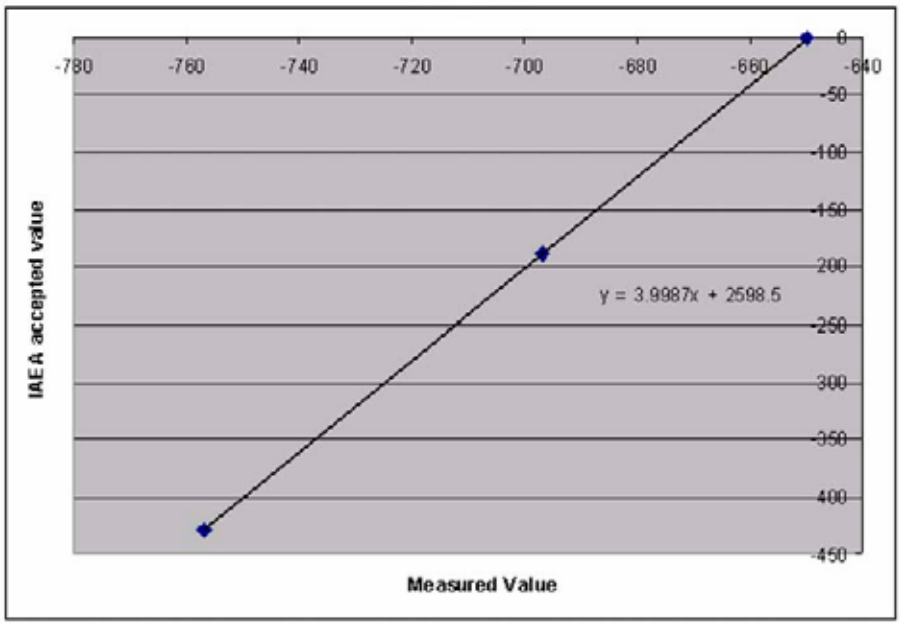
> **Note.** Refer to Nelson, S.T.: **A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods.** Rapid Communications in Mass Spectrometry **14**:1044-1046 (2000). John Wiley & Sons Ltd..

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 **Remark on the Strange Mathematics of Delta Values** on page 5-15.

Assume you measured the following values for the two primary standards VSMOW and SLAP and one sample GISP:

	measured value	accepted value (IAEA)
VSMOW	- 650	0
SLAP	- 757	- 428
GISP	- 697	- 189.73

Plot the measured δ values versus the accepted values (IAEA) as given in the example below:



Determine a trend line that fits the two primary standards, in this case:

accepted value (IAEA) = 3.99 · measured value + 2598.5

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. Since they have a significant mass difference to H_2^+ (Δ_m = 0.5 %), their presence leads to peak shape distortion. See Figure 5-30. Setting the electron energy below 100 eV considerably prevents He^{2+} formation.

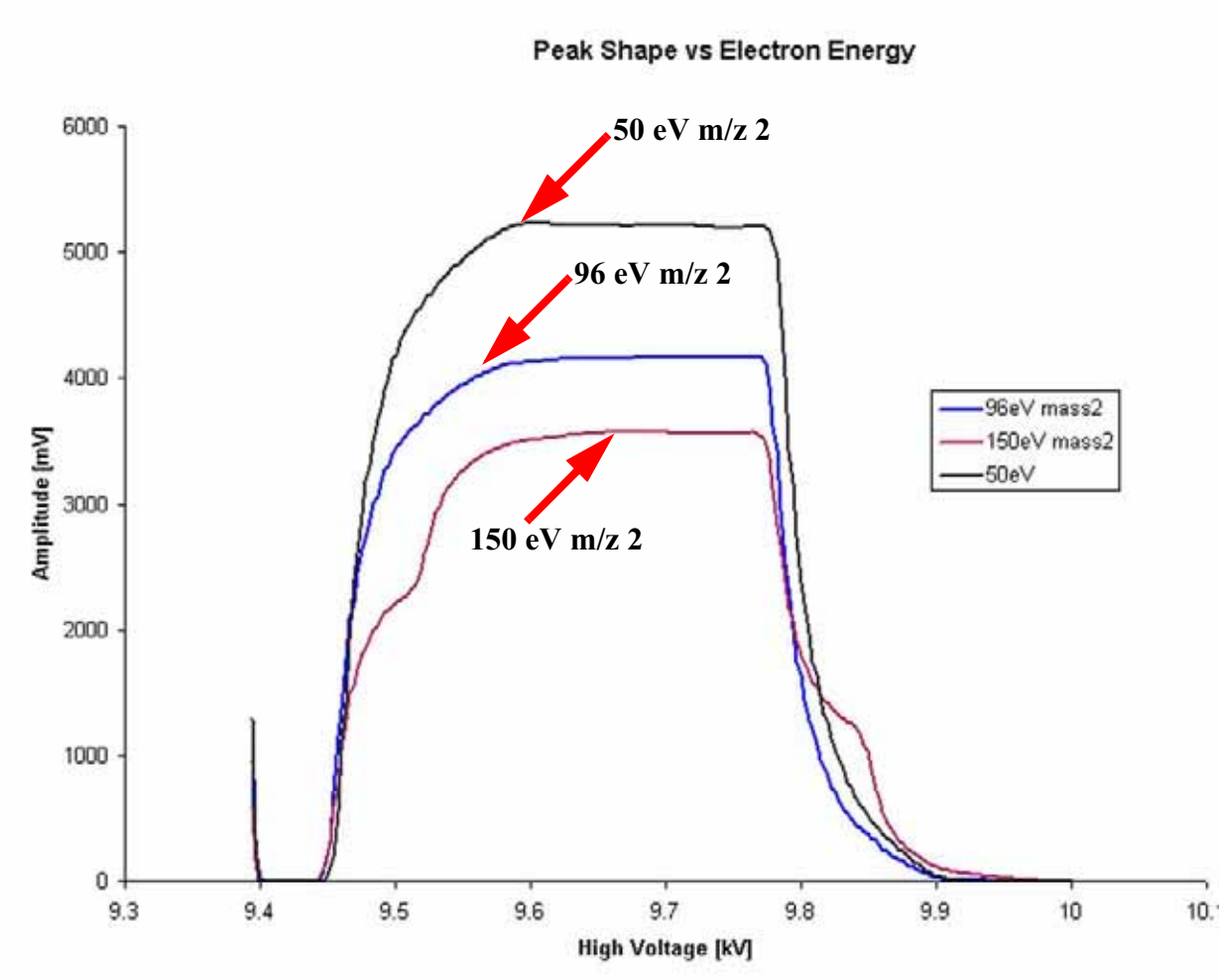


Figure 5-30. Peak Shape Scan for m/z 2 under Different Electron Energy Conditions

Determining the Optimal Setting of the Electron Energy

The following procedure should be performed to achieve the optimal setting:

- Perform a peak center with reference ***On***.
- Switch the reference ***Off***.
- Record the signal intensity on mass 2 versus the electron energy (see Figure 5-31).

The optimal setting is just below the appearance of the He^{2+} signal, where the sensitivity for H_2 is optimal.

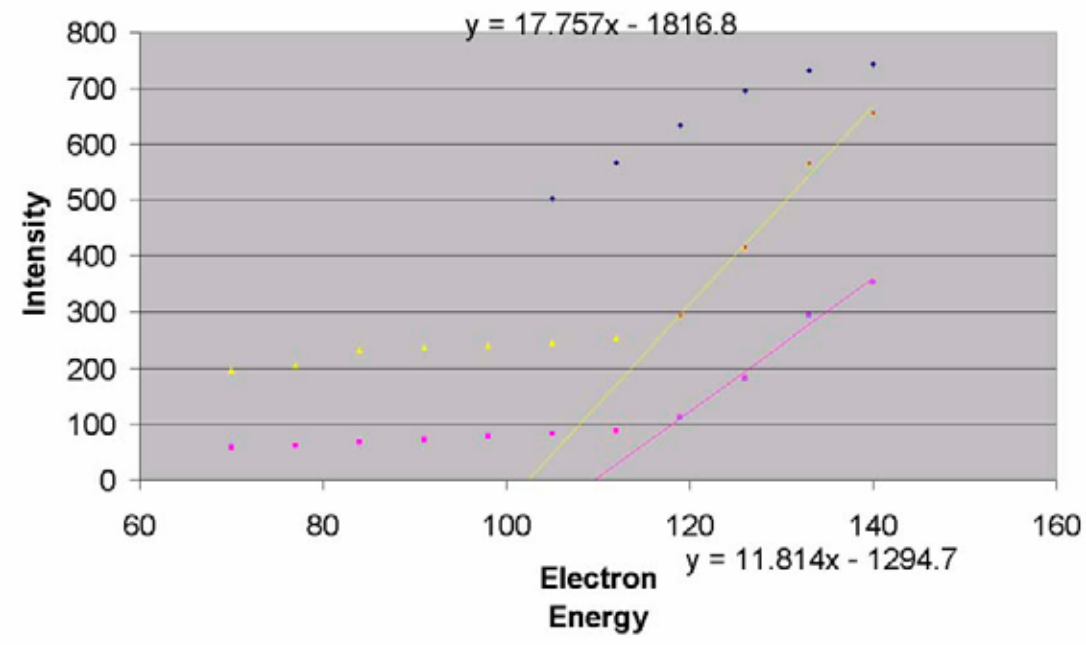


Figure 5-31. Signal Intensity on m/z 2 vs. Electron Energy

> **Note.** For further information, refer to Field, F.H. and Franklin, J.L.: **Electron Impact Phenomena**, pp. 244, 1957, Academic Press.

Results

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

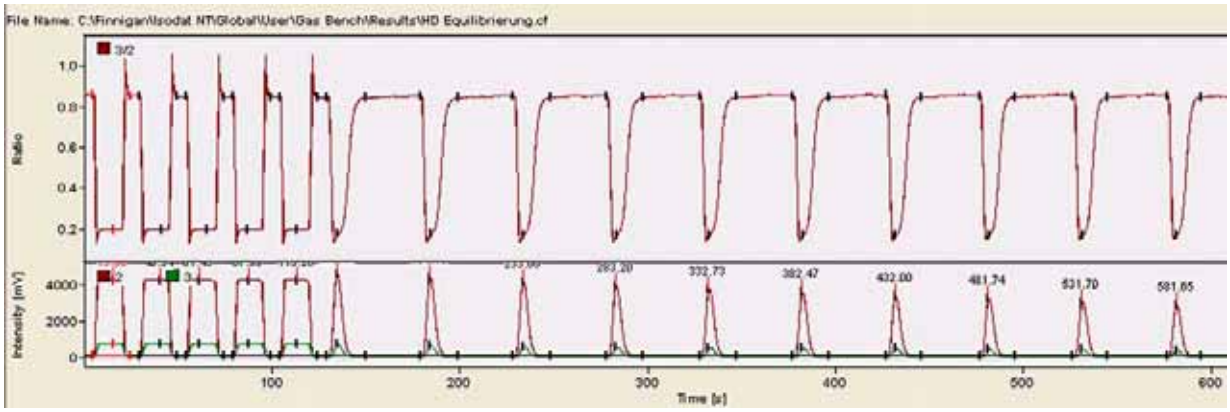


Figure 5-32. Water Equilibration (H/D) - Chromatogram

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	599.089	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 5-33. Water Equilibration (H/D) - Result Grid

Sample Amount Consideration 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 $\approx 5.357 * 10^{-4}$ 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 $CO_2 \approx 2.679 * 10^{-6}$ 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.

Chapter 6
Options

6.1 Carbonate Option

Components

The carbonate option (Part No. 113 2471) is used to measure δ ^{13}C and δ ^{18}O values simultaneously from carbonates. It allows for fully automated measurements of calcite, dolomite, foraminifera or bulk sediments and contains the following components:

Table 6-1. Carbonate Option (Part No. 113 2471) - Components

Quantity	Designation	Part No.
1	Acid pump with connections	113 7301
1	Pump head for acid pump	115 7620
1	Acid needle	113 7030
1 (500 g)	Phosphoric acid (PK500GR)	111 2640
1	Acid reservoir with tubing	113 7070
1	Double needle holder for autosampler (complete)	113 7080
1	Knurled nut, M8	111 9170
1	Hollow nut with drilled hole, 1/16”	113 7390
1 package*	Sample vials (borosilicate glass), washed	116 8790
1 sample	$CaCO_3$, as working standard	114 7090
1	Bulkhead connection (SERTO, 2 mm)	114 1450
2	O-ring (1.5 * 1.5)	114 1460
2	O-ring (2 * 1.5)	114 7070

*A package (sample vials made of borosilicate glass, washed) consists of 100 sample vials and 400 septa to hermetically close the vials.

Placement of the Components

- 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.
- Do not cut the tubing length. The small diameter tubing is for venting the reservoir. Place it beneath the cover of the tray.
- To ensure proper closing of the tray cover, a small cut must be made at the edge of the cover using a file.

- Connect the acid needle tubing to the acid pump (see Figure 6-4) and place the needle in the double needle holder on the right side. See Figure 2-18.
- Place the sampling needle in the left slot of the double needle holder.

Acid Pump

Figure 6-1 shows the switches that have been deactivated by Thermo Electron (Bremen) in the modified version. Direction and volume pumped per stroke are accessed externally via an additional device.

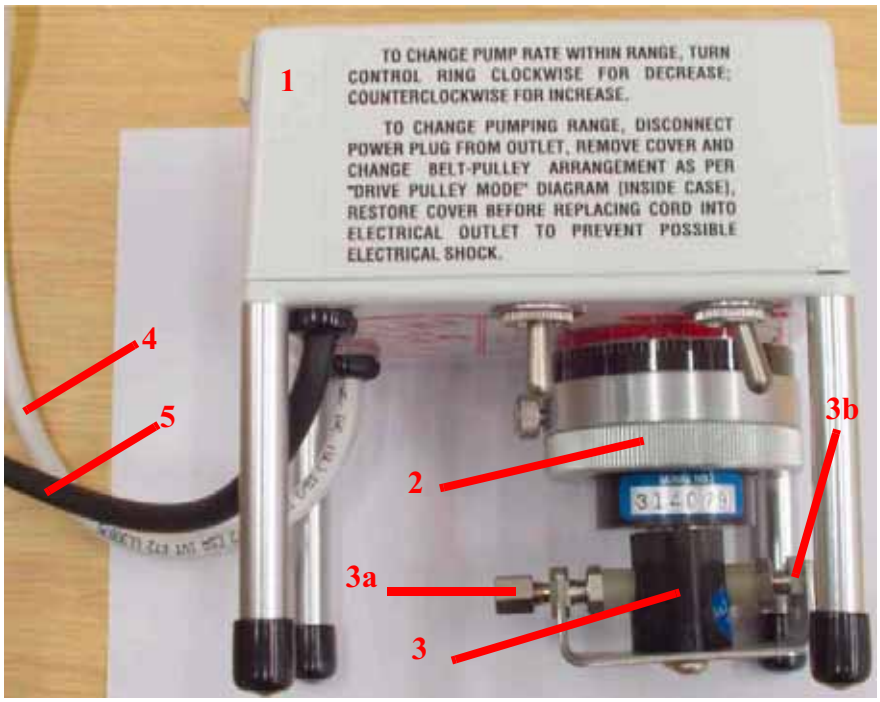


Figure 6-1. Acid Pump - Side View

1 control housing

2 adjusting screw

important, is 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 2.0.
See also **Instrument tab** on page 3-19.

3 head of pump (within a polypropylene housing)

shows the metric screw connections for the stainless steel pipes (**3a** and **3b**). Usually, the outlet **3b** is on the right and the inlet **3a** on the left. For the layout of these metric screw connections refer to 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.

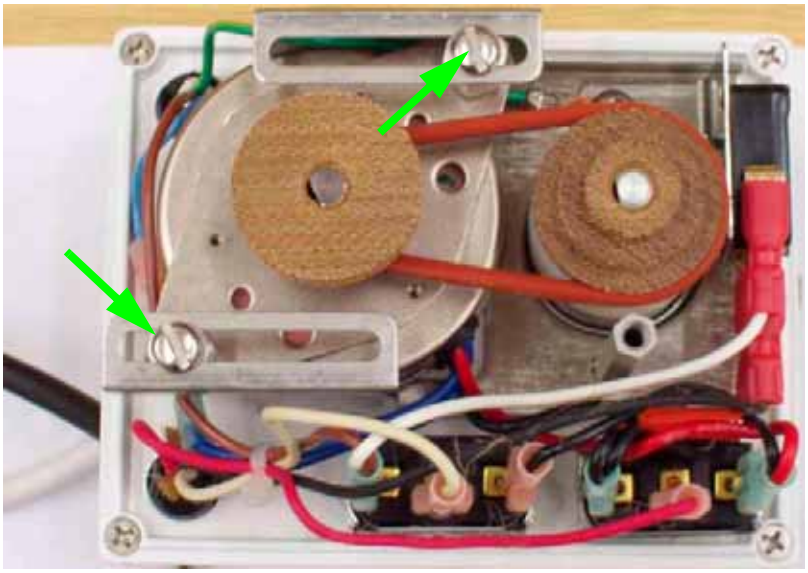


Figure 6-2. Acid Pump - Top View (Open)

The acid pump can be operated at three drive levels, i.e. at different rotational speeds, which are described inside the control housing. See **1** in Figure 6-1.

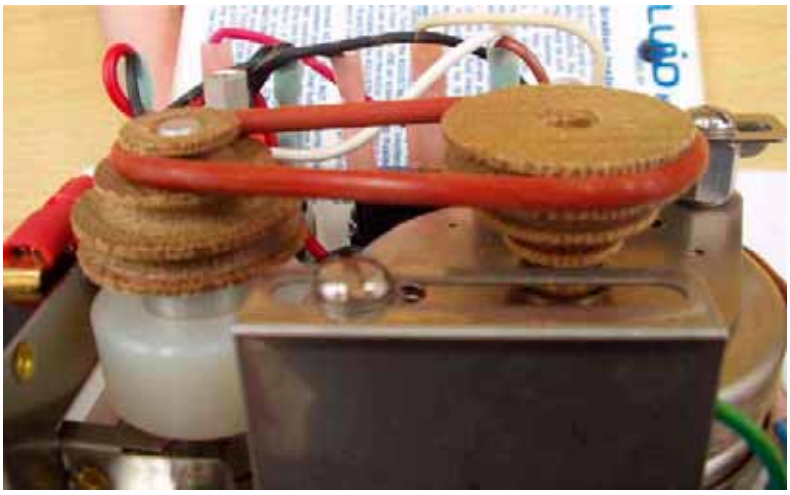


Figure 6-3. Acid Pump - Side View (Open)

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).

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.

Warning. Always pull the plug out of the socket before opening the control housing!

Acid Pump Adjustment

For proper function, the acid pump needs to be adjusted prior to operation.

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.

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.

Warning. 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 2.0, refer to Figure 3-6.

Connecting the Acid Needle

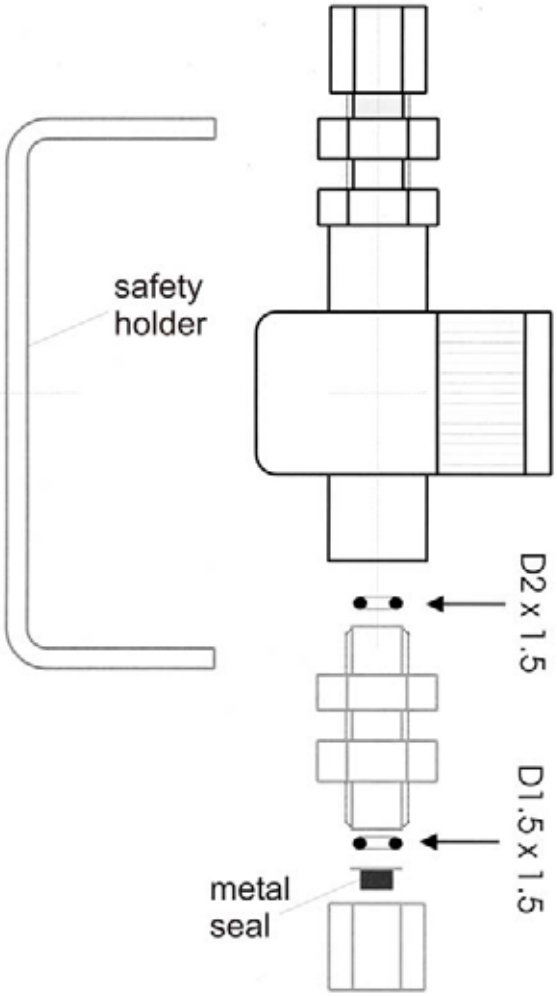


Figure 6-4 shows proper arrangement of O-rings in the bulkhead connectors to get a leaktight connection for acid needle and reservoir tubing.

Figure 6-4. Connecting the Acid Needle

6.2 Cryo Traps Option

Introduction

The basic problem to deal with is that a very small sample has to be analyzed from a relative big gas volume. The Finnigan cryo-option now renders this possible using the so-called GasBench II cryo-option. Two different types of the cryo-option can be delivered:

- ***single trap*** version (comprising only one trap)
- ***double trap*** version (comprising two traps)

Within the 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 double-trap version, 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 the proper timing, it is possible to collect these substances in the trap and yield high amplitudes from low concentrations.

Principle of Operation

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 switching valve. The complete scheme replaces the standard sample loop that comes with GasBench II.

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, 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 section will outline the cryo-option's double-trap version.

1. In a first step, the sample gas is carried through the measurement 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 on 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, see **How to Change the Loop Size** on page 2-23.

2. After switching valco 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 is achieved.

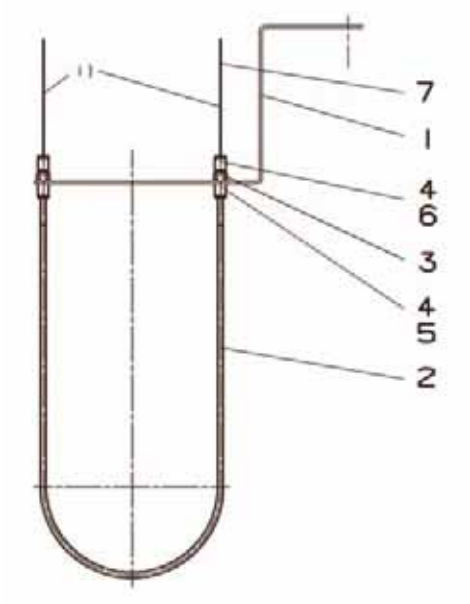


Figure 6-5. Trap Arrangement (Part No. 114 1260)

Table 6-2. Parts List for Trap Arrangement (Figure 6-5; Part No. 114 1260)

Position	Part No.	Designation	Quantity
1	114 1140	curved sheet metal	1
2	106 8330	trap subassembly[a]	1
3	106 8600	bulkhead connection, 1/16”, SGE	2
4	067 4930	nut, SSNE/16	4
5	067 4800	ferrule, 1/16”, GVF/16	2
6	056 6390	ferrule, 1/16”, GVF/005	2
7	100 4640	capillary, i.d. 0.32 mm, fused silica	5

[a]Trap subassembly comprises outer capillary tube, 1/16” * 0.8 mm, stainless steel, 600 mm (Part No. 060 5470) and nickel wire, d = 0.125 mm, 600 mm (Part No. 104 4070.)

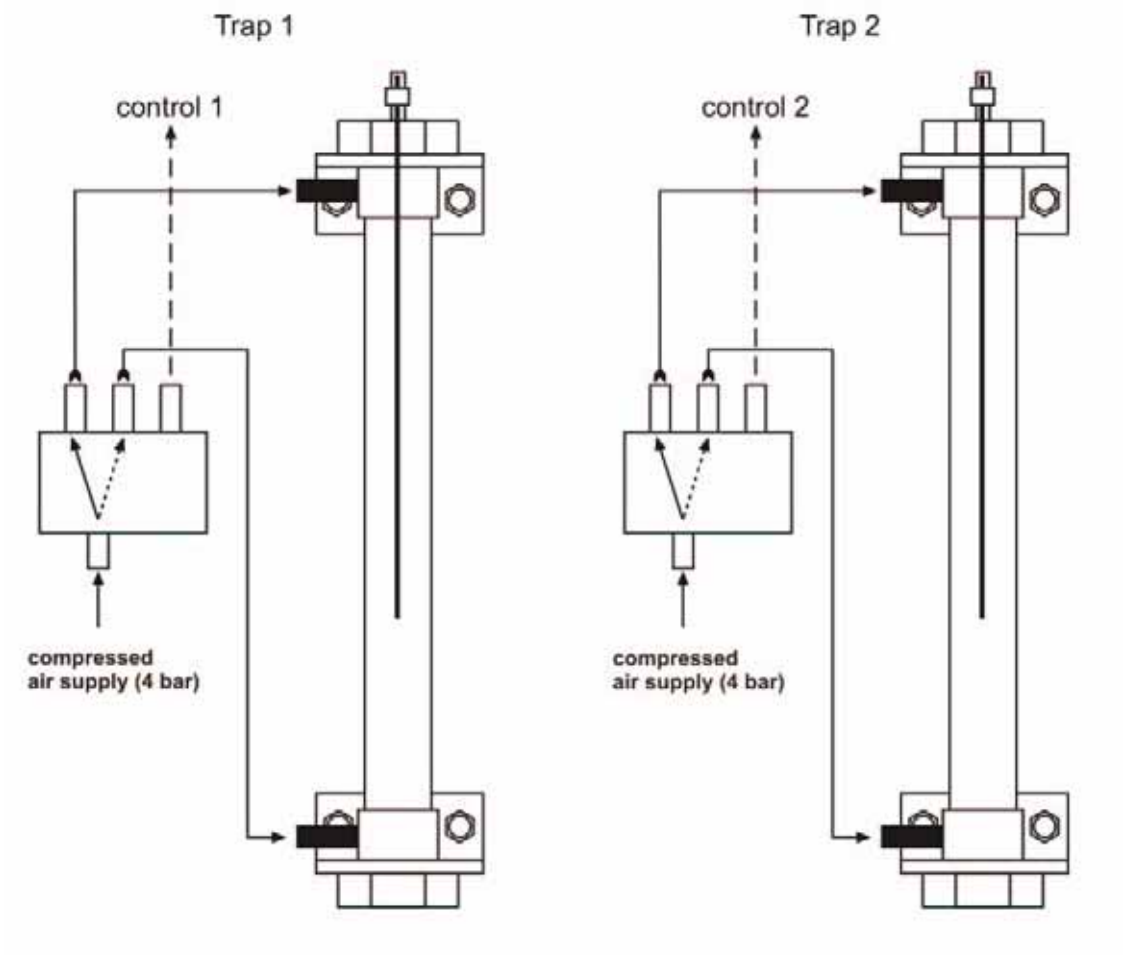


Figure 6-6. Compressed Air Schematic for Double Trap Arrangement

For connecting compressed air supply and control lines refer to Figure 7-7 and Figure 7-8. The compressed air supply should always be set to approximately 4 bar.

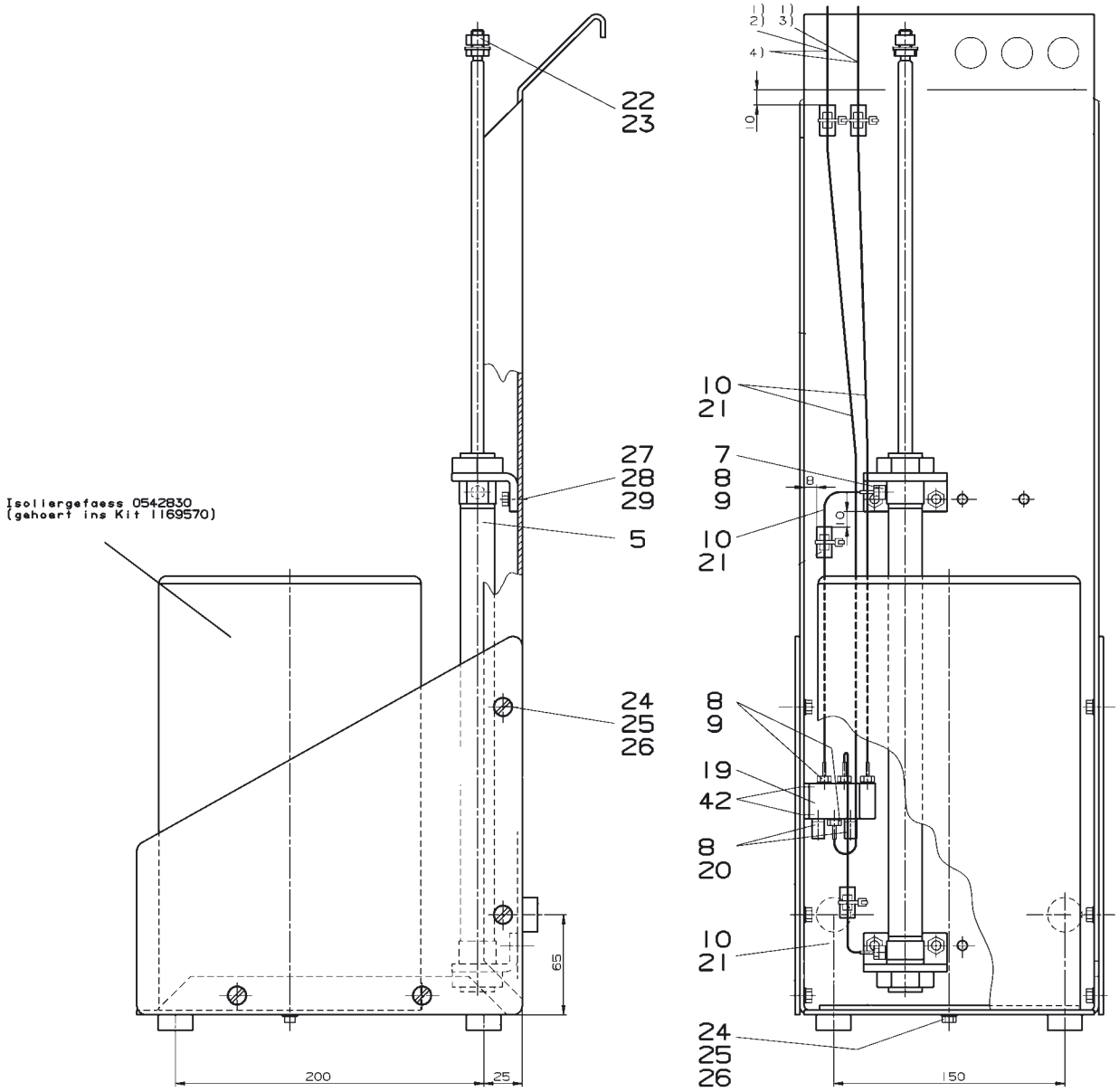


Figure 6-7. Cryo Trap Option - Version with One Trap (Part No. 112 1300)

Table 6-3. Parts List Referring to Figure 6-7 (Part No. 112 1300)

Position	Part No.	Designation	Quantity
5	111 6760	lift cylinder (C85KN, hub 250 mm)	1
7	052 4070	reducer (R1/8-M5)	2
8	050 5260	gasket, 8 * 5	10
9	070 3780	tubing nozzle	8

Table 6-3. Parts List Referring to Figure 6-7 (Part No. 112 1300)

Position	Part No.	Designation	Quantity
10	049 3621	wire end sleeve for compressed air tubing, AE 101	12
	116 9570	**installation kit for cryo trap option**	1
19	106 8510	valve (5/2 way)	1
20	052 1860	muffler, M5	2
21	101 5830	silicon tubing, 1.0 * 1.75NF	3
22	046 0560	nut, M8, DIN 934-1.4301	1
23	047 0070	disc, 8.4 DIN 125	1
24	045 1440	screw, M5 * 10 DIN 963	9
25	047 0050	disc, 5.3 DIN 125-1.4301	9
26	046 0590	nut, M5, DIN 934	9
27	113 0741	screw, M6 * 16, DIN 7991	4
28	047 0060	disc, 6.4, DIN 125	4
29	046 0520	nut, M6, DIN 934	4
42	045 4980	screw, M3 * 10 DIN 963	2

Connecting Cryo Trap

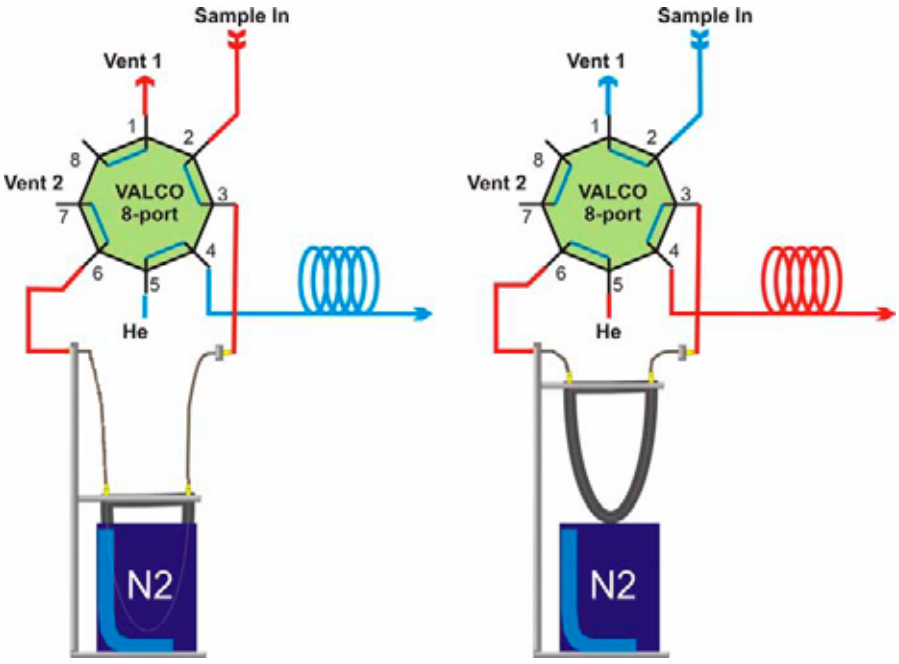


Figure 6-8. Fused Silica Trap Connection

Notes for GasBench II Trapping System

Installation Note

GasBench II can either be equipped with

- a ***single trap*** system or with
- a ***dual trap*** system.

The single trap system 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 (inner diameter: i.d. = 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 6-9 (single trap application) and Figure 6-10 (dual trap application).

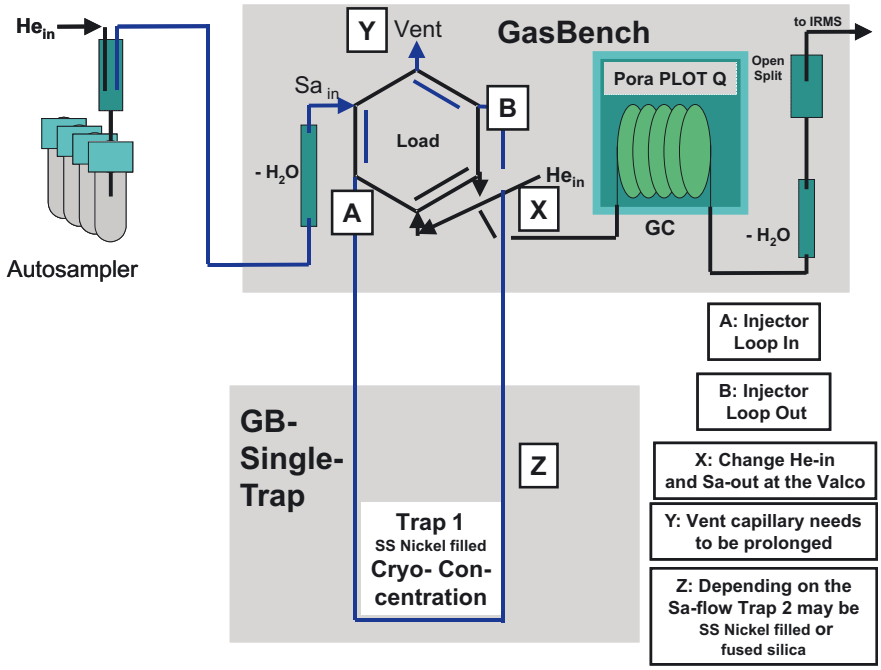


Figure 6-9. Single Trap Application

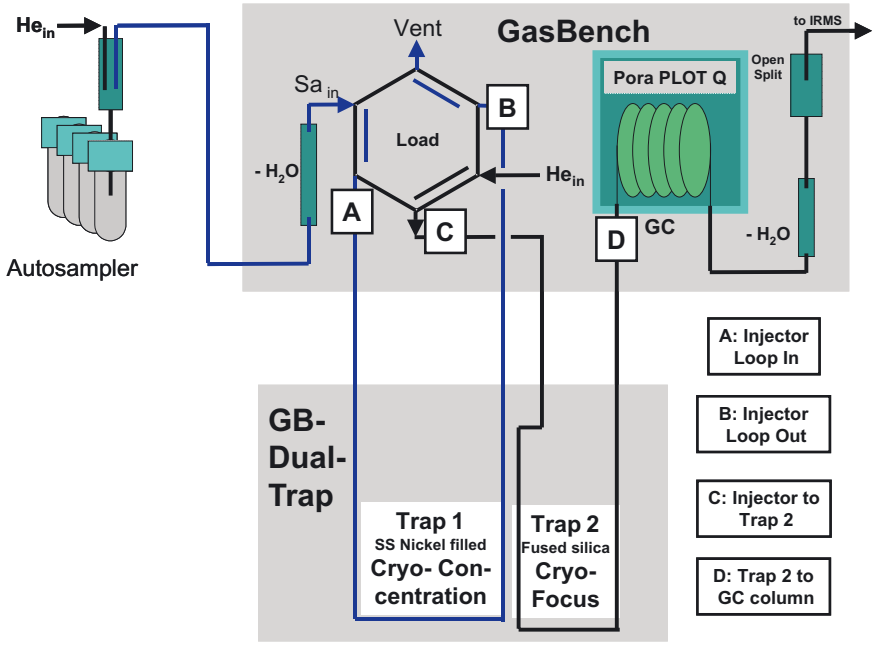


Figure 6-10. Dual Trap Application

Volumes of the Traps

1. i.d. 0.32 mm V = 80 µl/m
2. i.d. 1.0 mm V = 780 µl/m

General Notes

- Before releasing ferrules in the valco valve slowly reduce the He pressure in GasBench II to zero. Do not forget to 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 througputs through the trap are used during a long period of time).
- The cryogenic pre-concentration trap is a nickel-filled stainless steel trap (inner diameter: 1 mm) connected from valco port C to port D.
- An application for one trap is given in **CO_2 in Atmospheric Concentrations** on page 5-28.

- Before releasing the ferrule in the bulkhead union in front of the GC column slowly reduce the He pressure in GasBench II to zero. Do not forget to close the needle valve leading into the ion source before reducing the He pressure.

Trapping of N_2 at - 196 ºC

Liquid nitrogen can be adsorbed on silica gel or nickel surfaces at about - 196 ºC. 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.

Chapter 7
Technical Information

> **Note.** This section is intended for use by trained Thermo Electron (Bremen) personnel only. Thermo Electron (Bremen) discourages use by and denies liability for the consequences of use by other than Thermo Electron (Bremen) personnel.

7.1 Spare Parts and Consumables for GasBench II

Table 7-1 lists the ***spare parts and consumables*** for Finnigan GasBench II (available as kit with Part No. ***113 6810***) facilitating the selection of frequently used ones.

Table 7-1. Spare Parts and Consumables for GasBench II (Available as Kit with Part No. 113 6810)

Position	Quantity	Part No.	Designation
1	1	113 7030	acid needle
2	1	113 7120	needle holder (complete)
3	1	104 4110	reducing valve, ZRU1.5J, VICI
4	1	104 0430	t piece, ZX.5J, VICI
5	1	112 1170	bulkhead connection, VICI
6	5	104 0490	ferrule, ZF1V, VICI
7	2	900 0342	ferrule, Valco FS1.5
8	1	104 0480	ferrule, FS .5, VICI
8	5	106 0170	ferrule, 1/16”, GVF2/003
9	5	067 4790	ferrule, 1/ 8“-1/16”, TEF
9	5	100 6490	ferrule, 1/16”, GVF2/004
10	5	056 6390	ferrule, 1/16”, GVF/005
11	5	100 4850	ferrule, 1/16”, GVF/003
12	5	100 4640	capillary, 0.32 mm i.d., fused silica
13	2	067 4910	capillary, 0.10 mm i.d., fused silica
14	1	104 5480	capillary, 0.075 mm i.d., fused silica
15	2	054 3380	capillary, 0.05 mm i.d., fused silica
16	1	100 2605	water trap 1
17	1	074 3390	Nafion tubing, i.d. = 0.3 mm
18	1	104 1800	pipette
1	1	067 4570	micropipette, 100 µl
19	1	104 1730	outer glass tube at sample open split)
20	1	104 1860	inner glass tube as guide unit for capillaries of sample open split
21	400	116 8780	12 ml uncoated soda glass vial, RB
22	1	112 1070	single-use syringe, 1 ml, PK/100

Table 7-1. Spare Parts and Consumables for GasBench II (Available as Kit with Part No. 113 6810)

Position	Quantity	Part No.	Designation
23	1	112 1080	single-use cannula, PK/100
24	1	112 3380	test tube rack for 72 samples
25	2	113 7020	measurement needle
26	4	052 0910	ferrule, V. 1/16”, stainless steel
27	4	052 0940	ferrule, R. 1/16”, stainless steel
28	2	113 7390	hollow nut with hole, 1/16”
29	2	113 7080	needle holder
30	2	111 9170	knurled nut, M8
31	1	116 8790	sample vial, washed

7.2 Mechanical Parts

Table 7-1 summarizes important spare parts of the **outdated** version of GasBench II (Part No. 111 4260). Table 7-8 however, lists important spare parts of the **actual** version of GasBench II (Part No. 111 4262).

Table 7-2. Spare Parts for Gasbench II (Outdated; Part No. 111 4260)[a]

Position	Part No.	Designation	Quantity
13	100 2605	water trap GC-C III	2
14	111 3290	8 port Valco valve (VICI)	1
15	109 6570	reference open split	1
16	104 1760	sample open split	1
17	003 0960	fan (8550N, Papst)	1
18	003 1100	protective grating for fan	2
19	056 7350	coupling, 1/16” (B-100-61)	5
20	067 4552	JUMO itron 16 temperature controller	1
21	028 1310	relay (S0302-A210)	1
22	052 4391	manometer, 1/8, 0-2.5 bar	4
23	074 3360	coupling, 1/8” (RcX3M0-7-B)	4
24	067 4880	pressure reducer	4
25	049 3190	right-angle connection (B-100-2-2)	12
31	106 8510	valve (5/2 way)	1
32	108 3241	manifold standard, 4 station 10 PO	2
39	111 7410	ferrule, FS1.3 (Valco)	2
50	106 8410	distributor for compressed air (9 fold, M5)	1
51	052 1320	tubing connection, M5	3
52	050 5260	gasket, 8*5	17
53	070 3780	tubing nozzle	11
54	049 3621	wire end sleeve (AE 101)	32
55	101 5830	silicon tubing, 1.0*1.75 NF	3
56	069 1130	tubing, 4*1, PU 4	5
57	052 1860	muffler, M5	2
80	060 5470	capillary tube, 1/16”*0.8 mm	3
82	052 3460	t piece, 1/16” (B-100-3)	3
84	900 0342	ferrule, FS1.5 (Valco)	2

Table 7-2. Spare Parts for Gasbench II (Outdated; Part No. 111 4260)[a]

Position	Part No.	Designation	Quantity
85	104 8990	capillary, i.d. = 0.10 mm, fused silica	1
86	100 4640	capilllary, i.d. = 0.32 mm, fused silica	2.64 m
87	056 6390	ferrule, 1/16”, GVF/005	10
88	106 0170	ferrule, 1/16”, GVF2/003	8
89	067 4910	capillary, i.d. = 0.10 mm, fused silica	3
91	100 4850	ferrule, 1/16”, GVF/003	15
92	067 4930	nut, SSNE/16	17
93	111 2650	soap bubble counter, 10 ml	1
94	054 3380	capillary, i.d. = 0.05 mm, fused silica	7.50 m
95	104 5480	capillary, i.d. = 0.075 mm, fused silica	1
96	111 4290	line for gas supply (GZG)	4
98	111 4330	sample loop, 50 µl, Valco	1
99	111 4340	sample loop, 100 µl, Valco	1
100	111 4350	sample loop, 250 µl, Valco	1
101	111 4360	needle GasBench II	1
108	111 2870	column, open split GasBench II	1
109	111 6620	GC GasBench II	1
112	037 0650	clamp, 6.4	4
113	067 4651	coupling (complete), M5i-M5i	1
115	047 0070	disc, 8.4, DIN 125	1
116	052 1950	blind plug, M5	6
117	052 4070	reducer (R1/8-M5)	1
120	045 2450	threaded rod, M6-MS	4
123	033 1250	flat connection, 2*6.3 mm, M4	2
124	033 0820	flat connection	5
126	112 1170	bulkhead connector (VICI)	2
130	067 4790	ferrule, 1/ 8”-1/16”, TEF	4
134	048 0060	bolt, 2*10, DIN 7	3
141	112 7680	fastener gas supply, GBC	1
142	017 1911	capillary, FS Poraplot Q, 25 m	1
200	112 1060	installation kit GasBench II	1

[a]Table 7-2 refers to Figure 7-1, Figure 7-2 and Figure 7-8.

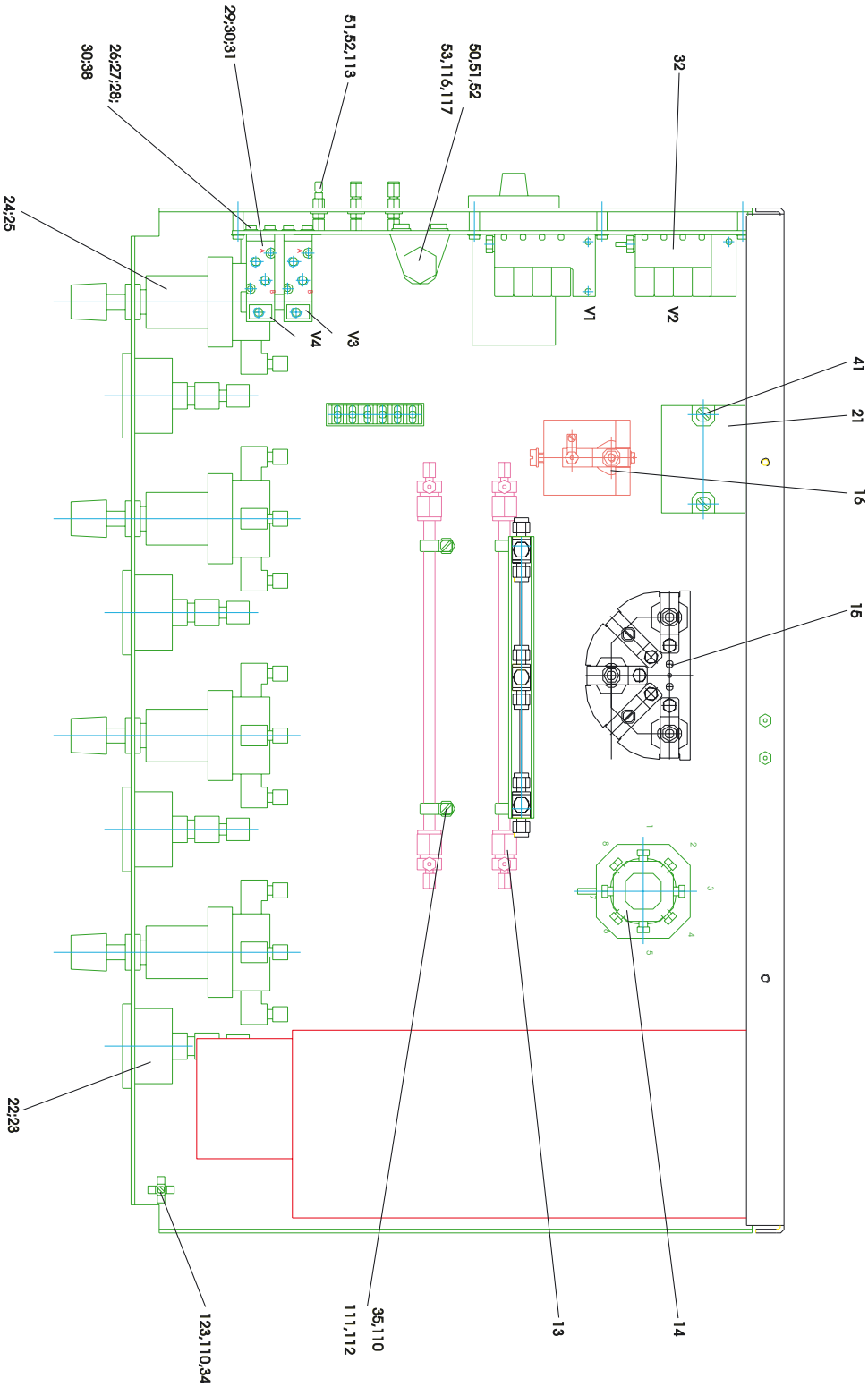


Figure 7-1. GasBench II - Top View (Part No. 111 4260; Outdated)

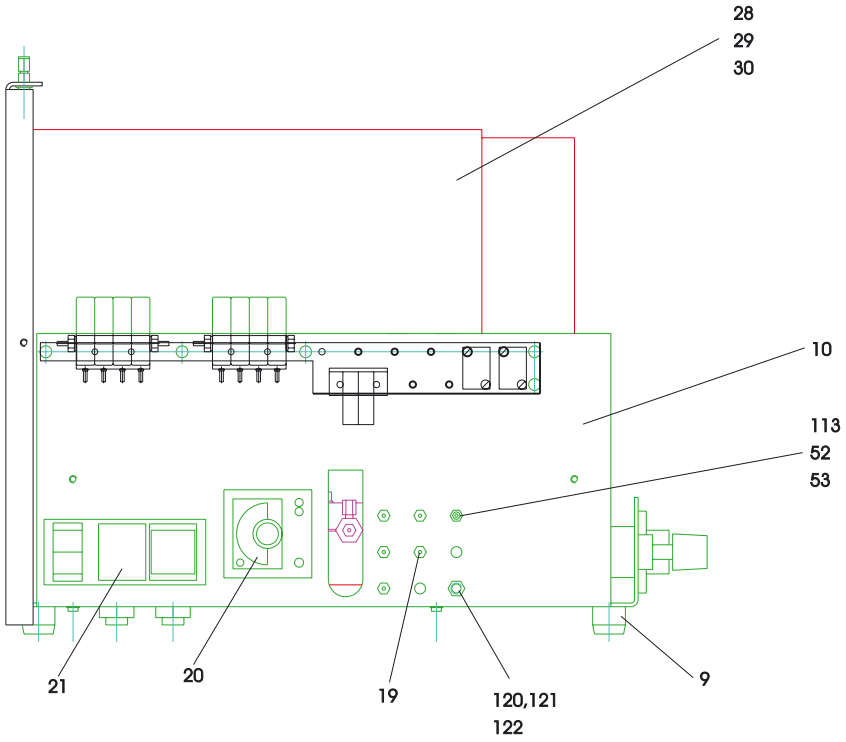


Figure 7-2. GasBench II - Side View (Outdated, Part No. 111 4260)

7.3 Plug and Measure Adapter

On the plug and measure adapter (pnm adapter, Part No. 205 2660), two addresses have already been adjusted by Thermo Electron (Bremen) via the two coding switches. See arrows in Figure 7-3:

pnm-ID First Device
S2 = 0
S1 = 8

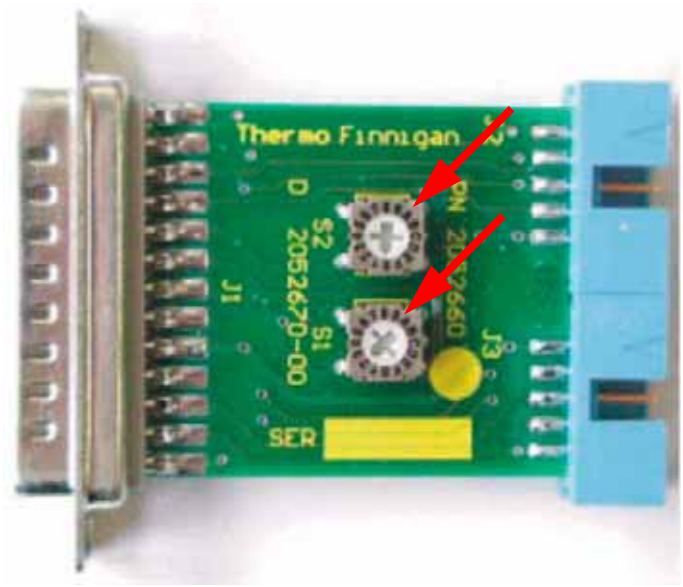


Figure 7-3. Plug and Measure Adapter (pnm Adapter)

7.4 Capillaries

Finnigan GasBench II contains two groups of capillaries:

1. Capillaries that connect two points in the gas flow scheme
   - usually of size i.d. = 0.32 mm
   - length not important.
2. 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 He each.

     Two capillaries, 0.1/250, 4 ml/min of He to water trap

     One capillary, 0.075/1000, for 0.5 ml/min to measurement needle

An exception is the column itself. It acts as its own flow restriction (1.5 ml/min).

7.5 Water Traps

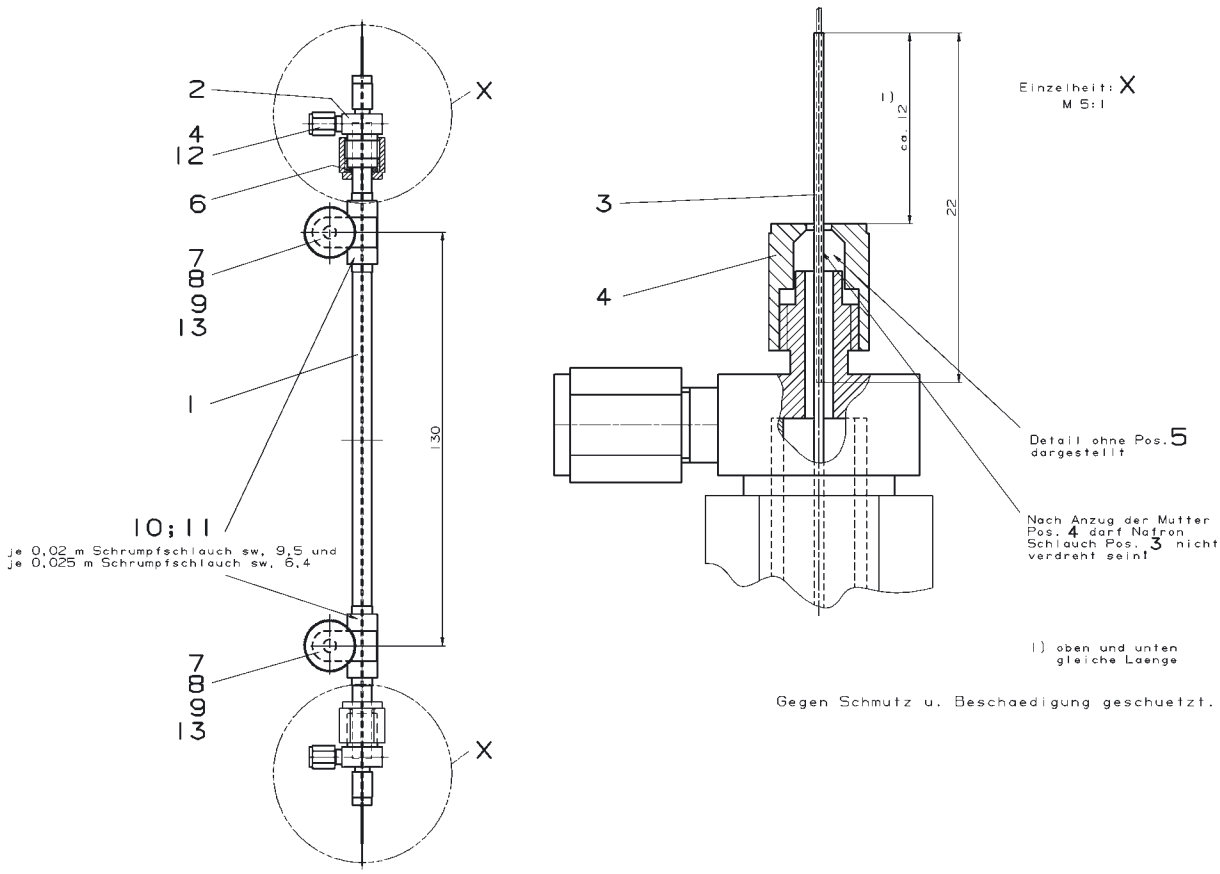


Figure 7-4. Schematic of Water Trap (Part No. 100 2605)

Table 7-3. Parts List Referring to Water Trap (Figure 7-4, Part No. 100 2605)

Position	Part No.	Quantity	Description
1	100 4651	1	glass tube
2	100 4620	2	t piece (1/16” * 1/16” * 1/4)
3	074 3390	0.25 m	Nafion tubing (i.d. = 0.3 mm)
4	067 4930	4	nut (SSNE/16)
5	056 6390	3	ferrule (1/16”, GVF/005)
6	065 2190	2	O ring (6.07 mm * 1.78 mm, Viton)
1	055 2180	2	O ring (6.07 mm * 1.78 mm, Viton)
7	053 5930	2	spacer bolt (M 4 * 25)
8	045 1740	2	knurled head screw (M 4*10, DIN 464)

Table 7-3. Parts List Referring to Water Trap (Figure 7-4, Part No. 100 2605)

Position	Part No.	Quantity	Description
9	111 6830	2	clamp
11	034 2040	0.09 m	shrinkable tubing (9.5 SW)
12	100 4850	1	ferrule (1/16”, GVF/003)
13	046 0220	2	nut M 4, DIN 934
14	047 0040	2	washer 4.3 DIN 125
2	100 4640	0.82 m	fused silica capillary (i.d. = 0.32 mm)

7.6 Reference Open Split

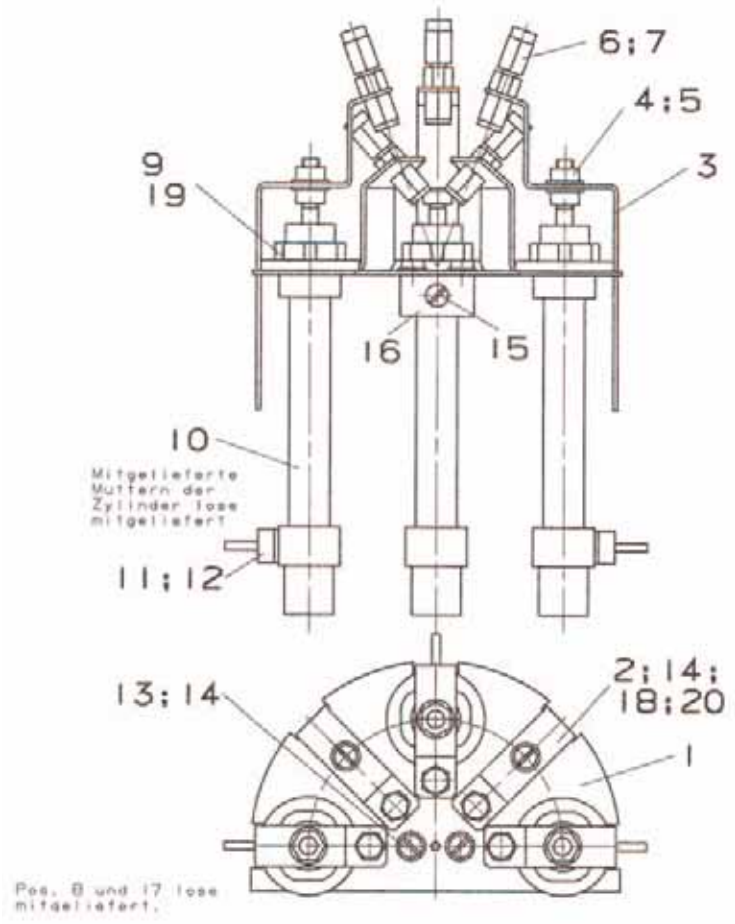


Figure 7-5. Reference Open Split (Part No. 109 6570)

Table 7-4. Parts List Referring to Reference Open Split (Figure 7-5, Part No. 109 6570)

Position	Part No.	Quantity	Designation
6	067 4590	5	screw connection (SSU 16/16)
7	067 4930	5	nut (SSNE/16)
10	067 4580	3	lift cylinder (8/25, SMC)
11	070 3780	3	tube nozzle
12	050 5260	3	gasket (8 * 5)
17	104 1800	1	pipette
1	067 4570	1	micropipette (100 µl)

7.7 Sample Open Split

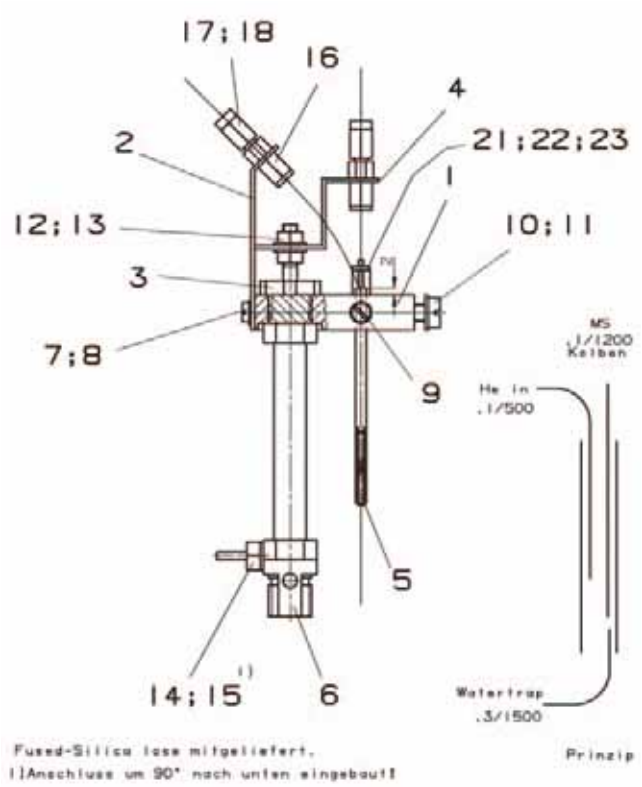


Figure 7-6. Sample Open Split (Part No. 104 1760)

Table 7-5. Parts List Referring to Sample Open Split (Figure 7-6, Part No. 104 1760)

Position	Part No.	Description	Quantity
5	104 1730	outer glass tube at sample open split	1
6	067 4580	lift cylinder (8/25, SMC)	1
14	070 3780	tube nozzle	1
15	050 5260	gasket (8 * 5)	1
16	067 4590	screw connection, SSU16/16	2
17	067 4930	nut, SSNE/16	2
18	100 4850	ferrule, 1/16” GVF/003	2
21	104 1860	inner glass tube as guide unit for capillaries of sample open split	1
2	104 1880	pipette	1
1	067 4900	micropipette, 20 µl	1
22	045 0710	screw M 2 * 6, DIN 84	1
23	047 0090	disc 2.5, DIN 125	1

7.8 IAEA Primary Standards

Table 7-6. IAEA Primary Standards

Name	Nature		Isotopic ratio	δ‰	Reference standard
V-SMOW	water	2H/1H	(155.761 ± 0.05) x 10e-6 (1) (155.751 ± 0.08) x 10e-6 (2) (155.601 ± 0.12) x 10e-6 (3)	0	V-SMOW
		18O/16O	(2005.20 ± 0.45) x 10e-6 (4)	0	V-SMOW
		I70/160	(379.91 ± 0.8) x 10e-6 (5)	0	V-SMOW
SLAP	water	2H/1H	(89.021 ± 0.05) x 10e-6 (1) (89.12 ± 0,07) x 10e-6 (2) (88.88 ± 0.18) x 10e-6 (3)	-428.0 (6)	V-SMOW
		18O/16O	(1893.91 ± 0.45) x 10e-6 (7)	-55.50 (6)	V-SMOW
NBS-19	calcite	13C/12C		1.95 (8)	V-PDB
		180/160		-2.20 (8)	V-PDB
				28.6 (9)	V-SMOW
			intercomparison materials		
GISP	water	2H		-189.73 ± 0.87	V-SMOW
		18O		-24.784 ± 0.075	V-SMOW
NBS-18	calcite	13C		-5.029 ± 0.049	V-PDB
		18O		-23.035 ± 0.172	V-PDB
IAEA-CO-1	calcite	13C		2.48 ± 0.025	V-PDB
		18O		-2.437 ± 0.073	V-PDB
IAEA-CO-8	calcite	13C		-5.749 ± 0.063	V-PDB
		18O		-22.667 ± 0.187	V-PDB
IAEA-CO-9	BaCO3	13C		-47.119 ± 0.149	V-PDB
		18O		-15.282 ± 0.093	V-PDB

Calibrating versus international standards requires users to have their own speimens of Primary Standards. Primary Standards are exclusively distributed by the IAEA via agencies in Europe and the US. The reference list is taken from IAEA TECDOC 825, and the IAEA Analytical Quality Control Services Reference Materials Catalogue 2002-2003.

Note. 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).
- 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.

7.9 Compressed Air Schematic

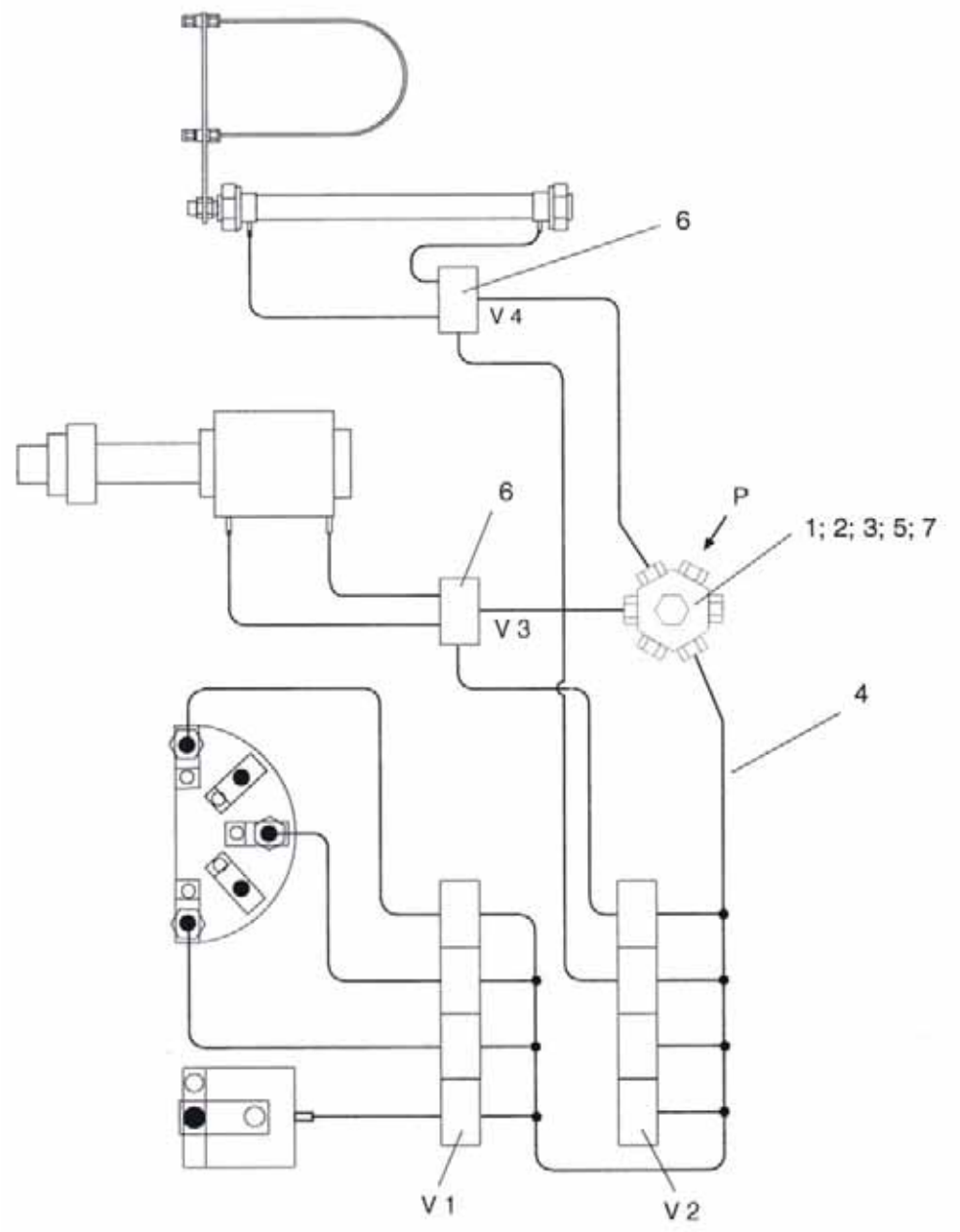


Figure 7-7. Compressed Air Schematic of GasBench II (Outdated, until 2002, Part No. 111 4260)

> **Note.** Pos. 5 is not shown above.

Table 7-7. Spare Parts Referring to Compressed Air Schematic, Outdated, Figure 7-7

Position	Quantity	Designation	Part No.
1	1	compressed air distributor (9-fold, M 5)	106 8410
2	1	connection	052 1320
3	9	gasket (8 * 5)	050 5260
4	3 m	silicon tubing (1.0 * 1.75 NF)	101 5830
5	5 m	tubing (4 * 1)	069 1130
6	2	muffler (M 5)	052 1860
7	11	tubing nozzle (over silicon tubing)	070 3780

Note. Finnigan GasBench II now allows using the third reference inlet for reference gases (see **Instrument tab - Reference Device Part** on page 3-20).

No more pressure regulator is required to adjust Flush Fill. Instead, use the pressure reducer of the reference gas tank (cf. **Optional Hardware - Flush Fill, Trap and Trap 2** on page 3-5).

As no additional pressure regulator is available when flushing with helium (e.g. when preparing carbonates), control the flush gas amount by timing.

Therefore, in the method's Time Events list, use the **Flush Fill - On** column to switch helium flow on and off (see **Time Events tab - Time Events List** on page 3-22).

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, refer to Figure 7-5 and to Figure 7-6.

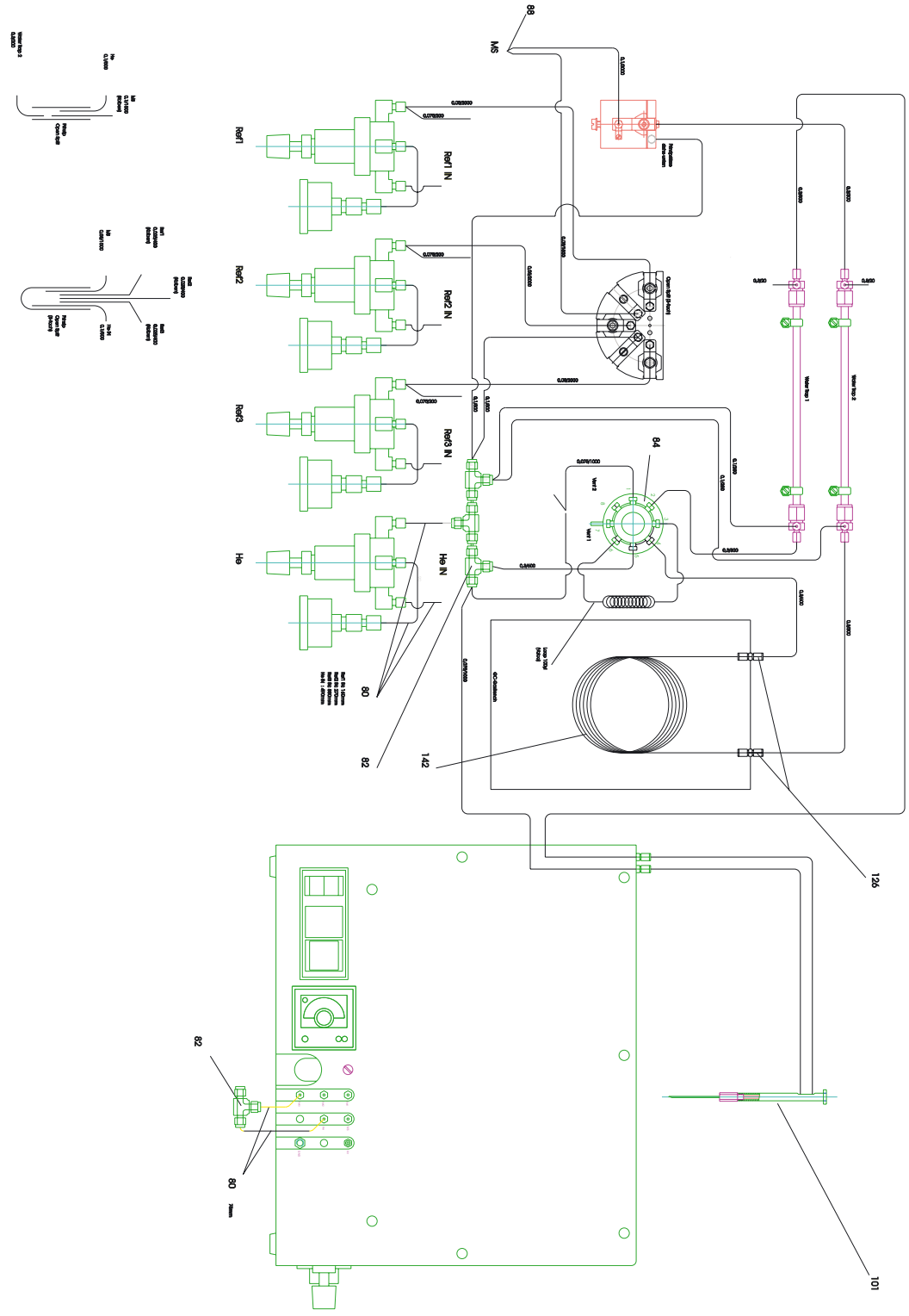


Figure 7-8. Tubing Scheme of GasBench II until Year 2002 (Outdated, Part No. 111 4260)

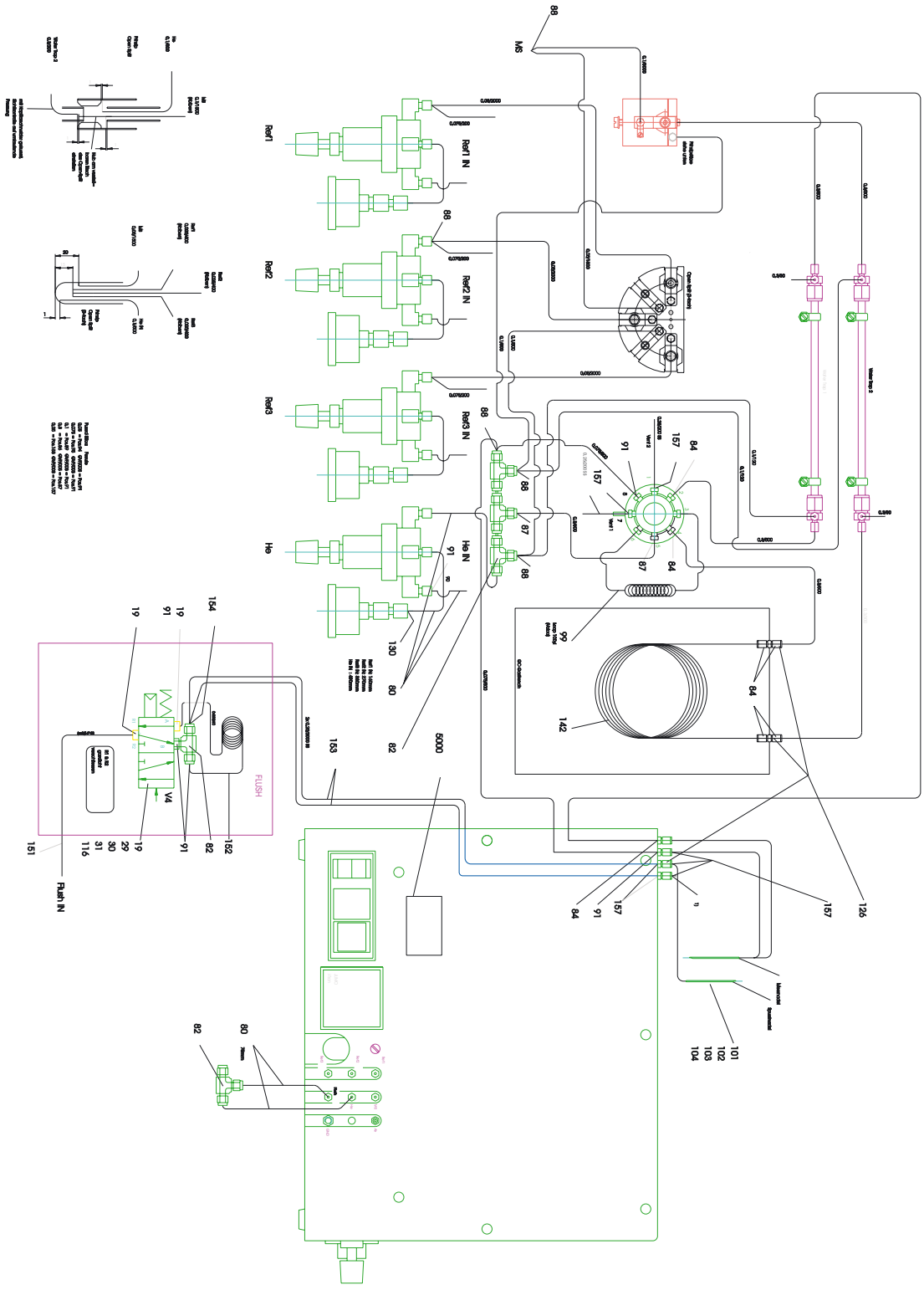


Figure 7-9. Tubing Scheme of GasBench II (Actual, Part No. 111 4262)

Table 7-8. Spare Parts for GasBench II (Actual, Part No. 111 4262), Figure 7-9

Position	Quantity	Designation	Part No.
1	3 m	capillary tube (1/16” * 0.8 mm)	060 5470
2	4	ferrule (1/8" - 1/16")	067 4790
3	3	t piece (1/16”)	052 3460
4	2	ferrule (FS 1.5, Valco)	900 0342
5	3.3 m	capillary (0.32 mm; fused silica)	100 4640
6	10	ferrule (1/16"; GVF/005)	056 6390
7	8	ferrule (1/16"; GVF2/003)	106 0170
8	3 m	capillary (0.10 mm; fused silica)	067 4910
9	1 m	capillary (0.10 mm; fused silica)	104 8990
10	15	ferrule (1/16"; GVF/003)	100 4850
11	17	nut (SSME/16)	067 4930
12	7.5 m	capillary (0.05 mm; fused silica)	054 3380
13	2 m	capillary (0.075 mm; fused silica)	104 5480
14	4	gas line (GZG)	111 4290
15	2	ferrule (FS 1.3; Valco)	111 7410
16	1	sample loop (50 µl; Valco)	111 4330
17	1	sample loop (100 µl; Valco)	111 4340
18	1	sample loop (250 µl; Valco)	111 4350
19	1	injection needle	111 4360
-	1	acid needle	113 7030
-	1	sample needle/flush needle	113 7020
-	1	double needle holder (complete)	113 7120
20	1	GC GasBench II	111 6620
21	1	column (1/16"; Poraplot Q)	017 1911
22	1	thermocouple (type K)	106 1390
23	1	ribbed radiator	106 1410

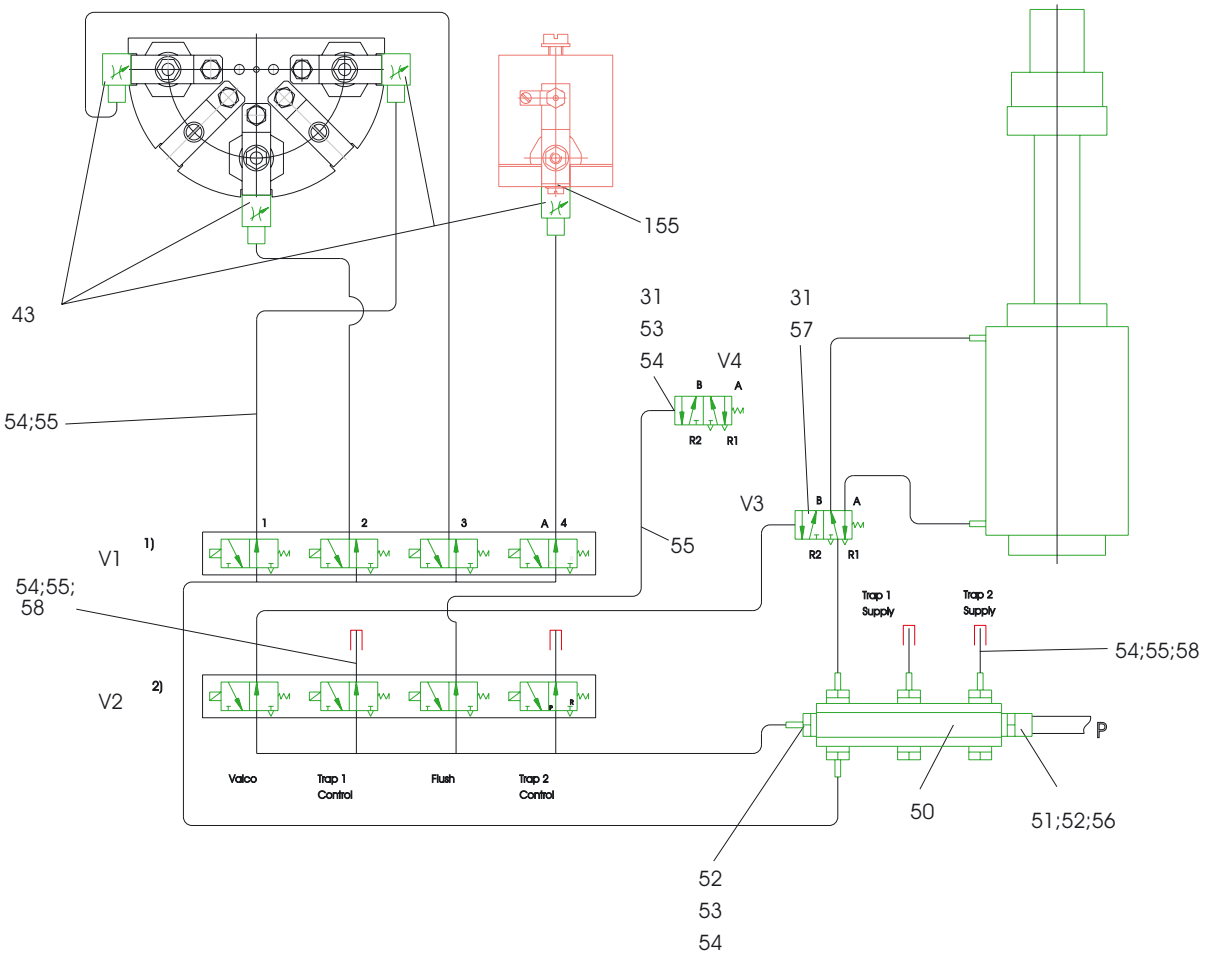
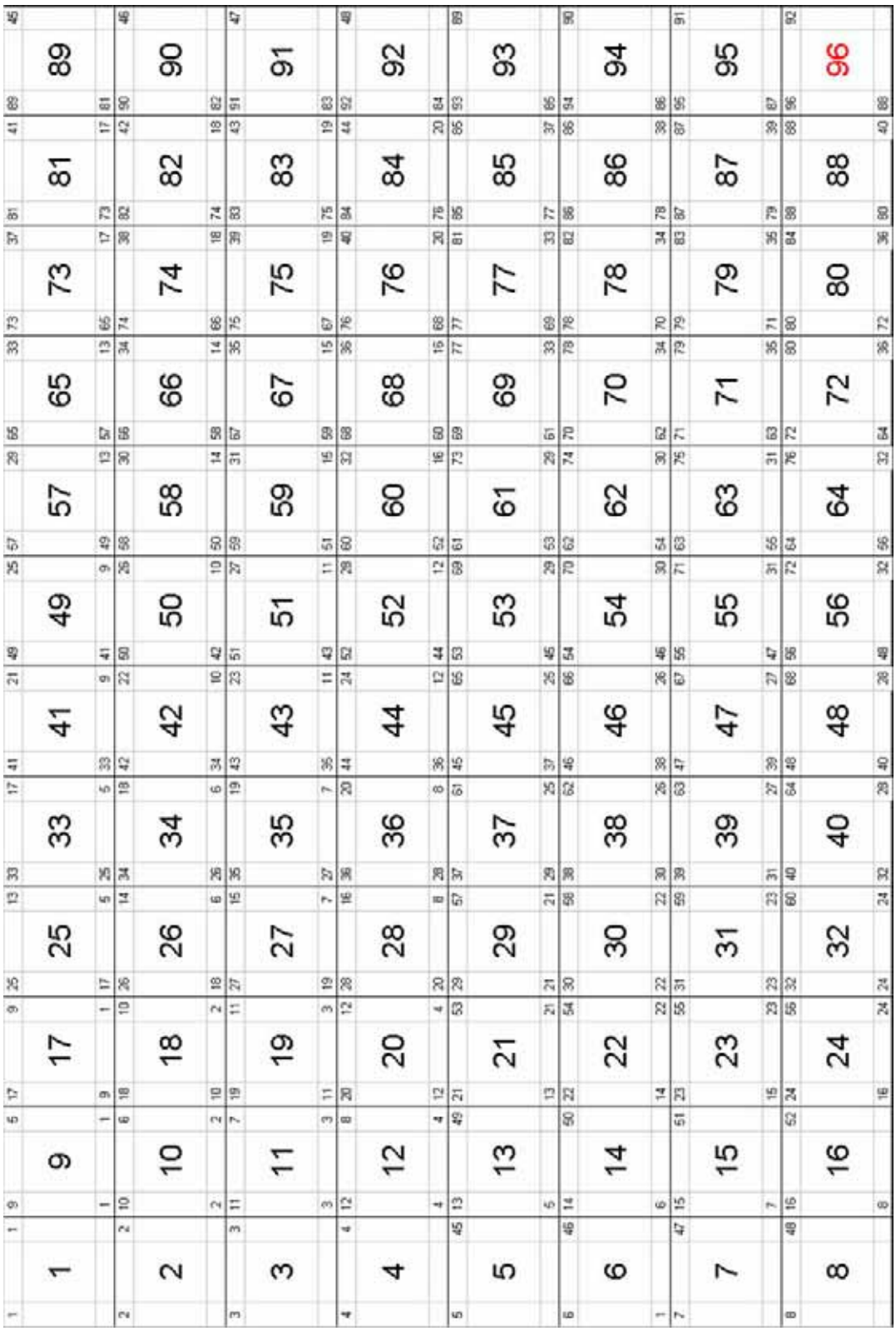


Figure 7-10. Compressed Air Schematic of GasBench II (Actual, Part No. 111 4262)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