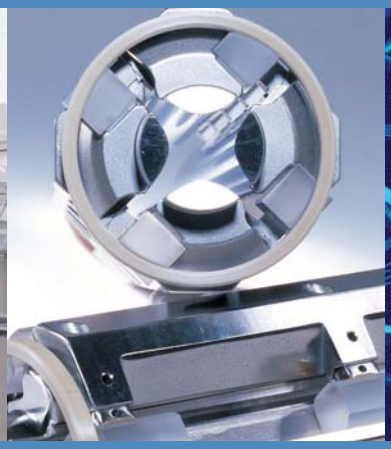
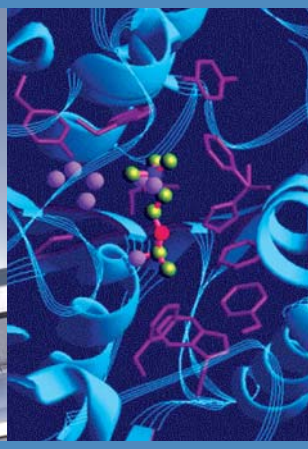
Finnigan™ Kiel IV Carbonate Device

Operating Manual

Revision A - 119 6820





Analyze • Detect • Measure • Control™

Thermo ELECTRON CORPORATION

Finnigan™ Kiel IV Carbonate Device

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Übereinstimmungserklärung gemäß EN 45014

Declaration of conformity according to EN 45014
Dichiarazione di conformità alla EN 45014

Name des Herstellers:
manufacturers name
nome produttore

Thermo Electron (Bremen) GmbH

Adresse des Herstellers:
manufacturers address
indirizzo produttore

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KIEL IV

Carbonate Device

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 55022 class B
EMV (Störfestigkeit): EMC (immunity) EMC (immunità)	EN 61000-3-2, -3; EN 61000-4-2, -3, -4, -5, -6, -11; EN 61000-6-2; EN 50204
Elektrische Sicherheit: electrical safety sicurezza elettrica	EN 61010-1
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This product complies with EMC directive 89/336/EEC and Low Voltage Directive 73/23/EEC.
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Bremen, Germany, 23. März 2005

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Read This First

Welcome to the Thermo Electron, Finnigan Kiel IV Carbonate Device system!

This *Finnigan Kiel IV Carbonate Device Operating Manual* describes how to setup and use your Kiel IV Carbonate Device. In addition, this manual describes principle hardware components.

It includes the following chapters:

- Chapter 1: "Preinstallation Requirements" summarizes requirements related to site, power, the reference sample and the various gases in use before operating your Finnigan Kiel IV Carbonate Device.

- Chapter 2: "Hardware Components" treats instrument layout, connections, vacuum system, valves and traps, oven and oven control, autosampler, Liquid Nitrogen Refill device, Reference Gas Refill, acid flow and pinch valve.

- Chapter 3: "Isodat 2.5" describes how to start Isodat 2.5 and subsequently how to create a Kiel IV Carbonate Device-related configuration.

  This chapter further denotes how to create a new Kiel IV Carbonate Device method and a new Kiel IV Carbonate Device sequence in Isodat 2.5's Acquisition Mode.

  Finally, it outlines interpretation of result files, time slicing and interfering masses.

- Chapter 4: "Basic Operations" describes several test routines as leak check, bakeout, autosampler operation, capillary matching, cleaning the acid valve, adjusting the liquid nitrogen refill sensor, pinch valve operation, troubleshooting, elementary handling of the Finnigan Kiel IV Carbonate Device, vial test, phosphoric acid preparation and sample vial handling.

- Chapter 5: "Measurement Procedures for Real Samples" deals with the measurement principle, sample placement into a vial, preparation of carbonates and IRMS and the measurement procedure itself. Furthermore, it outlines how the quality of result data is checked.

  The chapter comprises information about referencing vs. VPDB and about Reference Refill as well.

- Chapter 6: "Technical Information" outlines spare parts and consumables, the valve unit and valve replacement. It contains information about IAEA primary standards.

  Furthermore, advice is given for internal leak checking, maintenance and programming. Finally, this chapter contains schematics of compressed air supply, vacuum system and circuit diagrams.

Changes to the Manual

To suggest changes to this manual, please send your comments to:

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

Typographical Conventions

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

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

Admonitions

Admonitions contain information that is important, but not part of the main flow of text.

Admonitions 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 Name

The following headings appear in the left column of each page:

Second Level Topics

Third Level Topics

Fourth Level Topics

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, processor 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

The *Finnigan Kiel IV Carbonate Device Operating Manual* contains precautionary statements that can prevent personal injury, instrument damage, and loss of data if properly followed. Warning symbols which alert the user to check for hazardous conditions. These appear throughout the manual, where applicable, and are defined in Table i on page i-v.

Table i. Warning Symbols

Symbol	Description
	**General** This general symbol indicates that a hazard is present, which if not avoided, could result in injuries. The source of danger is described in the accompanying text. ▲
	**Cold Burns Hazard** Wear protective clothing. ▲
	**Electric Shock** High voltages capable of causing personal injury are used in the instrument. The instrument must be shut down and disconnected from line power before service or repair work is performed. ▲
	**Magnetic Field** Keep away from heart pacemakers, computers, credit cards, and any other magnetically sensitive device. ▲
	**Noxious** This symbol alerts to hazards resulting from noxious fumes. ▲
	**Hot Surface / Heat** Allow heated components to cool down before servicing them! ▲
	**Poisonous Gases** This symbols points to possible danger because of poisonous gases and vapors. ▲

Instrument-Specific Hazards

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 don't 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. Capacitors inside the instrument may still be charged even if the instrument is turned off. The superconducting magnet is still charged even if the instrument is turned off.

10. 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.

Contents

Figures

Tables

Chapter 1 Preinstallation Requirements

This chapter contains the following topics:

Site Requirements

The Finnigan Kiel IV Carbonate Device is attached to Thermo Electron isotope ratio mass spectrometers, e.g. a Finnigan DELTA V Plus or a Finnigan DELTA V Advantage, equipped with a Dual Inlet system.

It is placed stand-alone but must be arranged next to the IRMS within a maximum distance of 30 cm. The distance to walls may not be less than 60 cm. The space required is 900 mm width x 900 mm depth. Its height is 1900 mm, and it weighs approximately 100 kg (220 lb). See Figure 1-1.

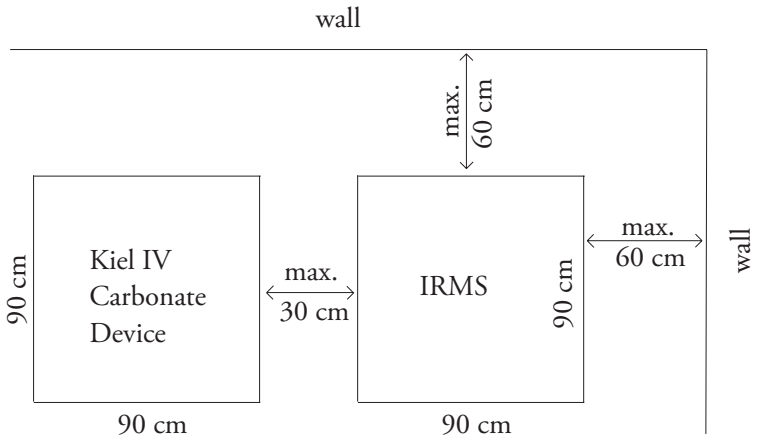


Figure 1-1. Kiel IV Carbonate Device - Site Requirements

Power Requirements

The Finnigan Kiel IV Carbonate Device will be supplied by the IRMS line distributor. The power consumption of the IRMS will increase by 1.2 kW.

Note It is absolutely necessary to run your instrument without disruptions of power supply! Thus, if your local area is susceptible to corrupted power or power disruptions, an uninterruptible power supply (UPS) should be installed in your laboratory. ▲

Gas Requirements

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

Warning All regulators should be oil- and grease-free and be specified for gases of high purity. The supply lines should terminate with 1/8“ male Swagelok® type connectors.
Thermo Electron (Bremen) recommends to use regulators with an outlet pressure range between 0 and 5 bar (that is, 0 and 73 psi). ▲

Warning All compressed air tubing and the air compressor should contain a water and oil trap. Water and oil may fill the compressed air supply and destroy the pneumatic valves! ▲

For operation, the Kiel IV Carbonate Device needs the gases summarized in Table 1-1.

Table 1-1. Kiel IV Carbonate Device - Gas Requirements

Gas	Comment
He, N_2	1 bar as sample vial vent gas
liquid N_2	For the liquid nitrogen-cooled trap provide approximately 0.5 l of liquid nitrogen per sample.
CO_2	Used as reference gas. See "Reference Refill" on page 5-22.
Ar	Sometimes, it may be necessary to check the unit for leaks. Therefore, use an argon tank.
compressed air	Supplied by the compressed air distributor of the IRMS. Should be in the range between 2.8 bar and 6 bar (that is, between 40 and 87 psi).

Further Requirements

- a laboratory to wash and prepare sample vials
- a fume hood, hot plate and stirrer to prepare phosphoric acid[1]
- contaminant-free weighing instruments[1]
- phosphorous pentoxide (500 g)[1]
- acetone p.a. for cleaning vials and weighing instruments[1]
- a suitable micro balance to verify the installation weight specifications[1]
- a liquid nitrogen tank (approximately 30 l per day)[1]

Reference Sample

To demonstrate the specified precision for small samples, it is required that the customer buys and supplies a sample of NBS-19 from the International Atomic Energy Agency or the National Bureau of Standards. Refer to "IAEA Primary Standards" on page 6-17.

[1]Keep available within installation distance.

Chapter 2 Hardware Components

This chapter provides information about the various hardware components of the Finnigan Kiel IV Carbonate Device. It contains the following topics:

Note For information about spare parts and part numbers, refer to Chapter 6: "Technical Information". ▲

Layout

This section describes the parts of the Finnigan Kiel IV Carbonate Device. Figure 2-1 shows the device in front view.

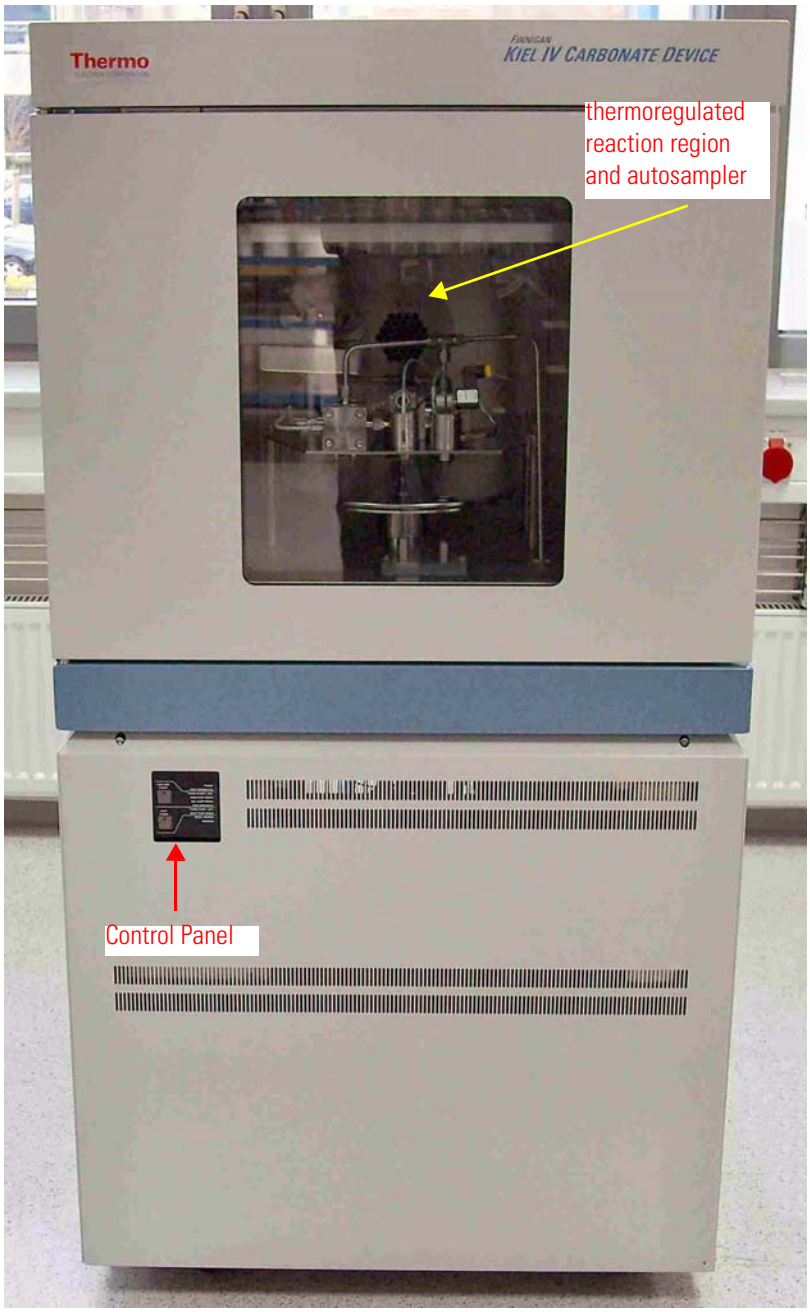


Figure 2-1. Finnigan Kiel IV Carbonate Device - Front View

Upper Section

Inside the heating cabinet, a round plate with holes can be found that holds sample vials. This is called the turret. Two pistons move the vials up or down in order to connect them to the vacuum system. For historical reasons, this connection port is called the acid valve. Phosphoric acid is stored in a borosilicate glass container and fed to the

acid valve via Viton tubing. A pinch valve controls the acid flow. Unused vials can be stored in two vial racks located in the upper part of the thermostated oven. See Figure 2-2.

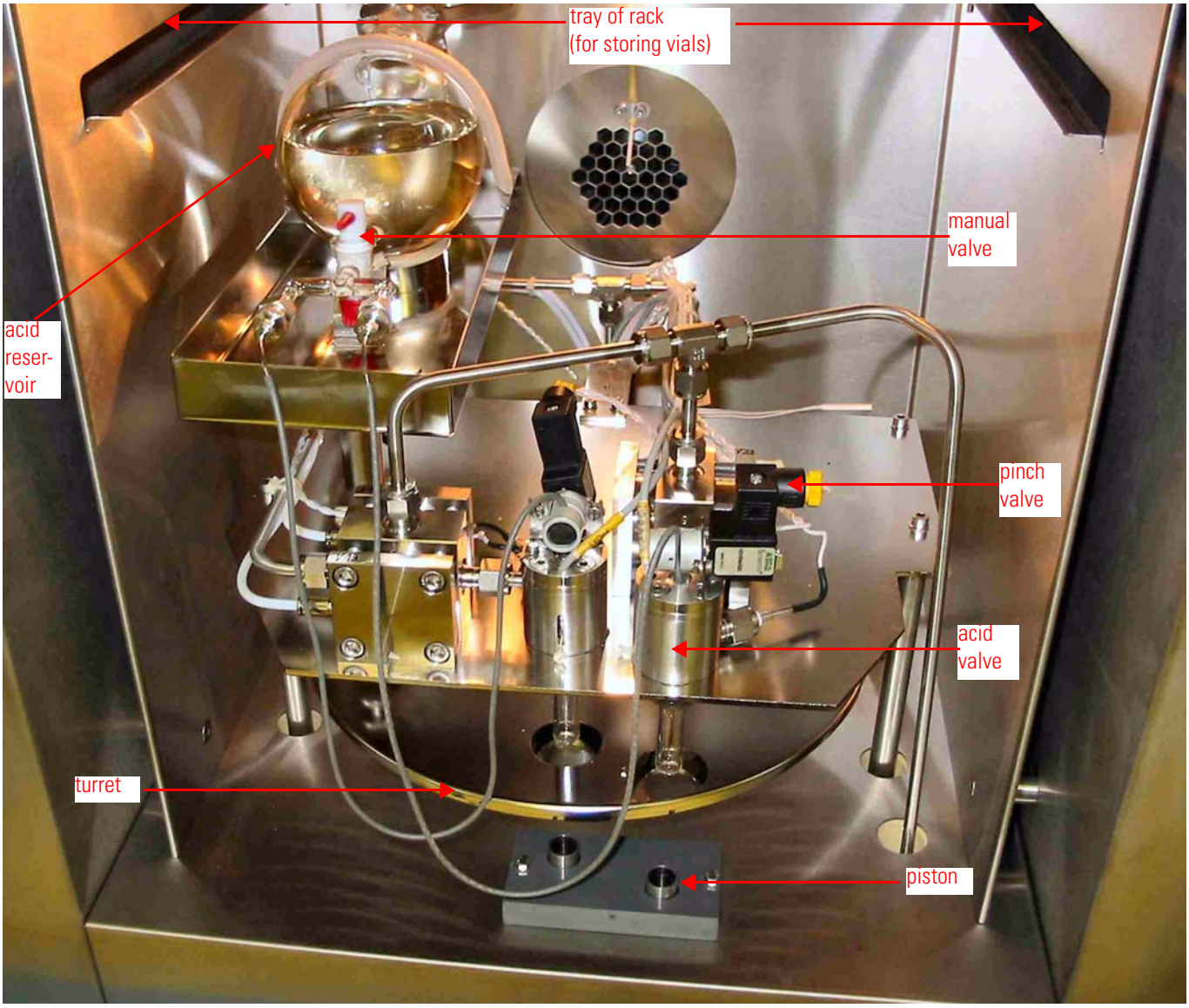


Figure 2-2. Heating Cabinet - Front View

Lower Section

After the grey side panels have been removed the lower cabinet becomes visible. See Figure 2-3 and Figure 2-5.

In the upper part of Figure 2-3, valve systems can be seen on the right side. They belong to trap 1 shown as **a**. In the middle of this picture the pneumatic levers for the pistons **c** are located, each with a position sensor **b**. Towards the back the turret motor **e** is barely visible. The sensor for the fill level of liquid nitrogen **d** in the dewar is located rightmost in this part of the cabinet.

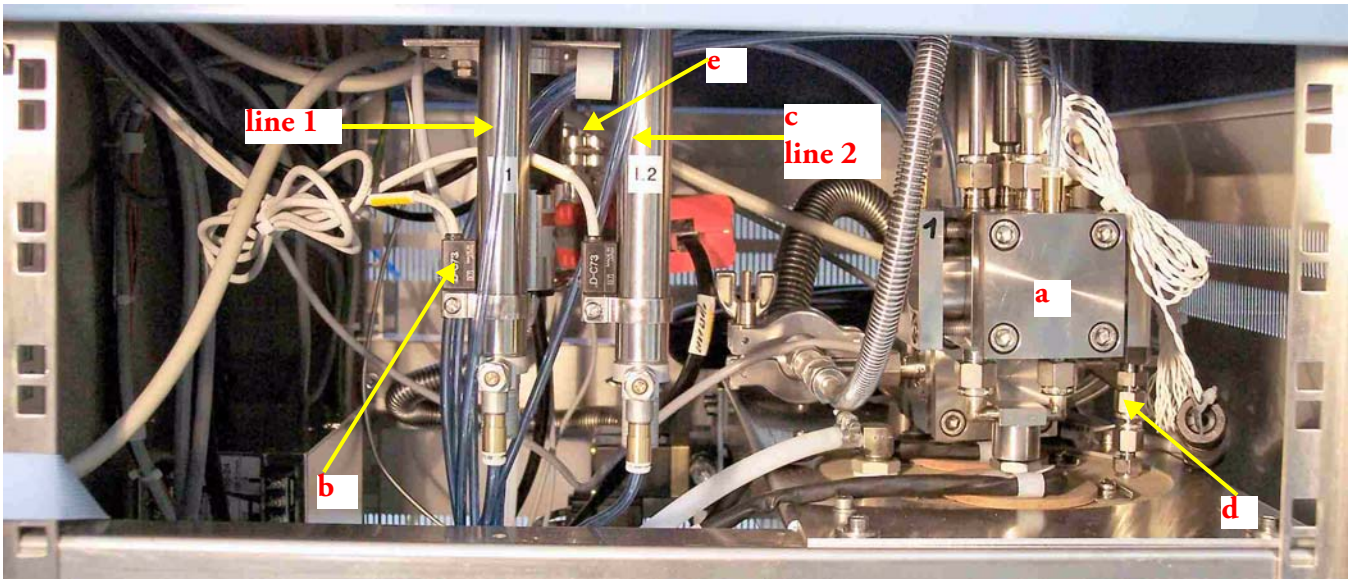


Figure 2-3. Front Panel - Upper Part

Figure 2-4 depicts trap 1 (**a**) and the sensor for the fill level of liquid nitrogen (**d**) in close-up view.

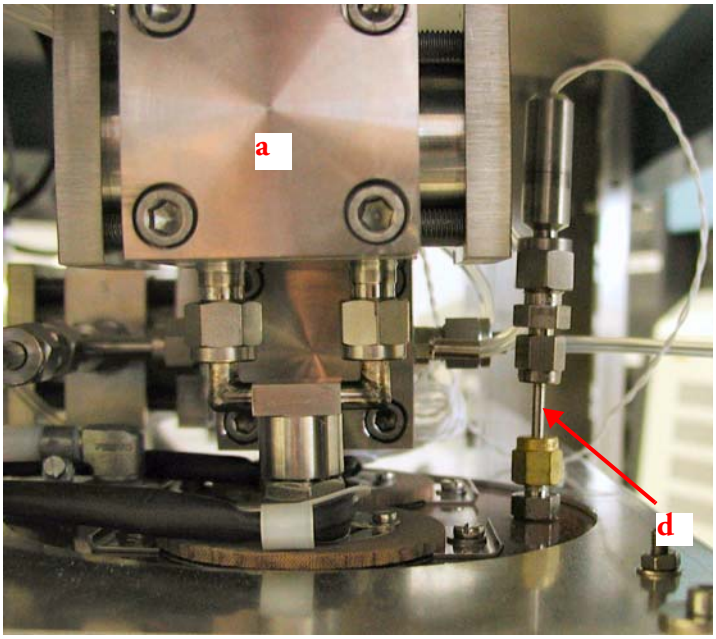


Figure 2-4. Close-Up View of Trap 1 and Sensor for Fill Level

The lower part of the cabinet contains the fore vacuum pumps and pneumatic control valves that switch on and off compressed air that in turn operates valves and the pneumatic levers for the pistons. A dewar located upon a lab boy can be found here as well. See Figure 2-5. The dewar is used to store a limited amount of liquid nitrogen that is required to operate the two traps.

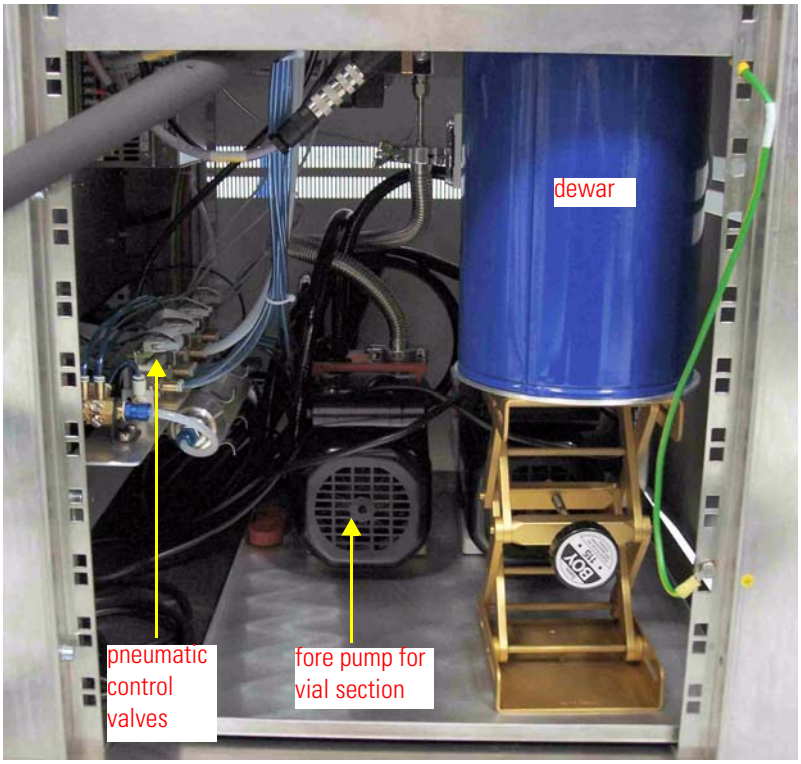
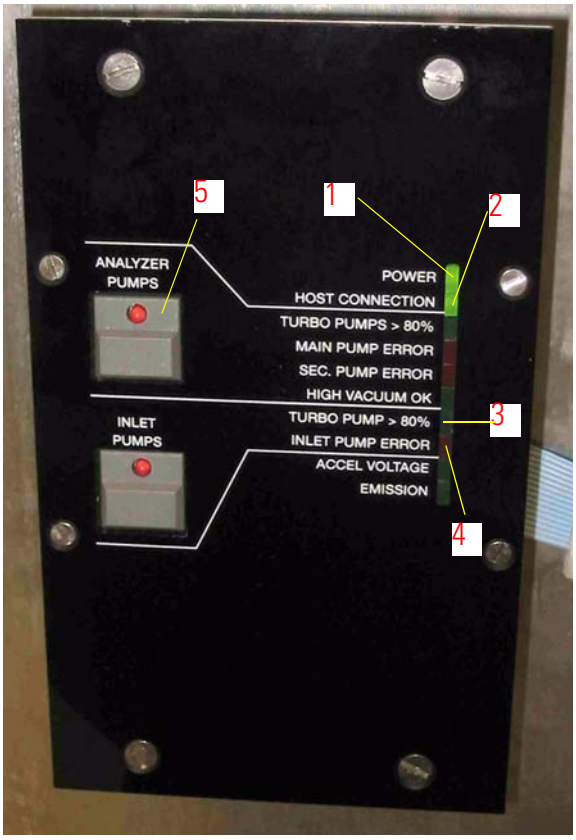


Figure 2-5. Front Panel - Lower Part



1 power indicator
2 host connection
3 status of turbo pump
4 error status of this pump
5 "Analyzer Pumps" switch (inoperable)

Figure 2-6. Control Panel in Close-Up View

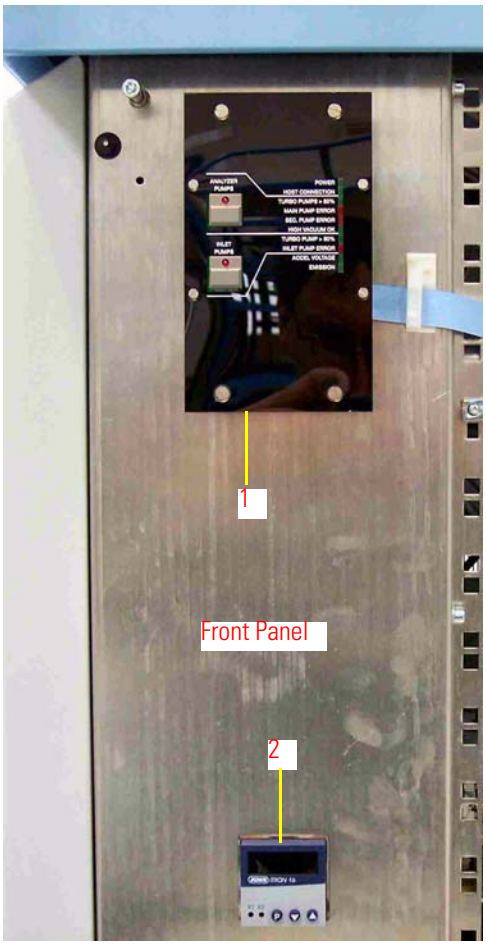
The front panel allows to:

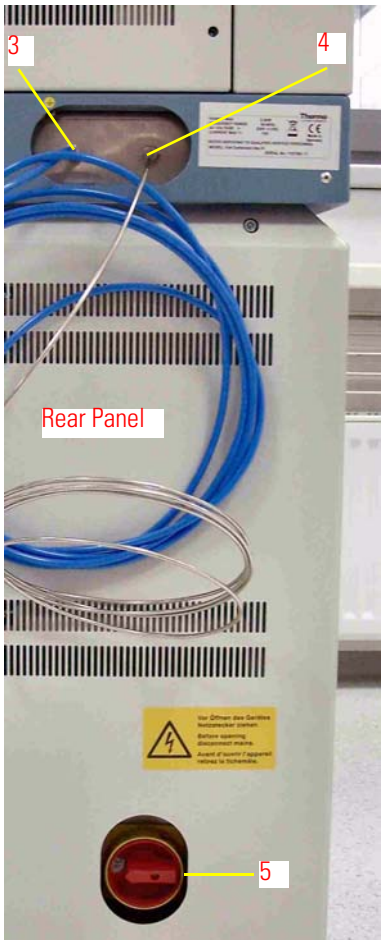
- control the oven temperature using the Jumo itron 16 temperature controller (**2** in Figure 2-7, left). For detailed instructions on how to use the oven controller, see "Oven and Oven Control" on page 2-27.

- switch on the vacuum system via the control panel (Figure 2-6 and **1** in Figure 2-7, left)

Note The **Analyzer Pumps** switch, **5** in Figure 2-6, is inoperable with Kiel IV Carbonate Device. ▲

On the rear panel (Figure 2-7, right) the main power switch **5** is located. The connection for vent gas **4** and compressed air **3** can be found here as well.

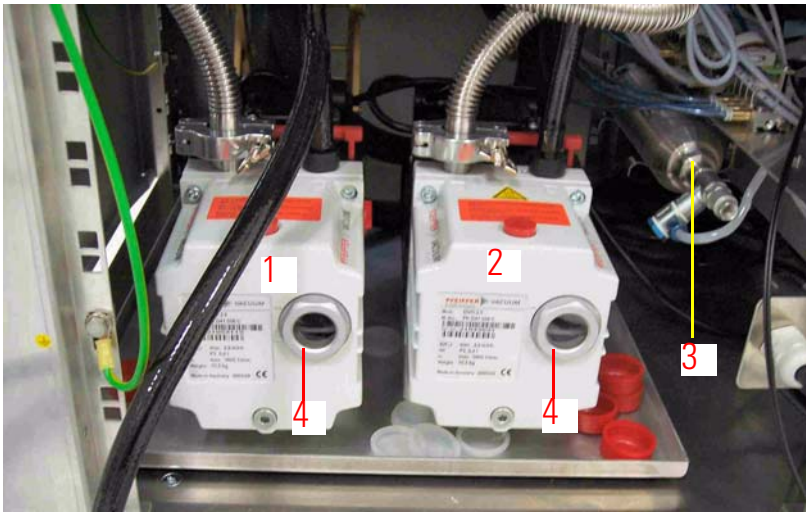




1 Control Panel
2 Jumo itron 16 temperature controller (used for oven control)
3 inlet for compressed air
4 inlet for He or N_2 (used to vent the vials)
5 main power switch

Figure 2-7. Parts of Front Panel and Rear Panel

Figure 2-8 shows the fore pumps located at the rear panel.



1 fore pump for turbo pump

2 fore pump for fore vacuum side of Kiel IV Carbonate Device

3 compressed air reservoir used during disconnection of vials

4 inspection glasses for checking oil levels of fore pumps

Figure 2-8. Fore Pumps at Rear Panel

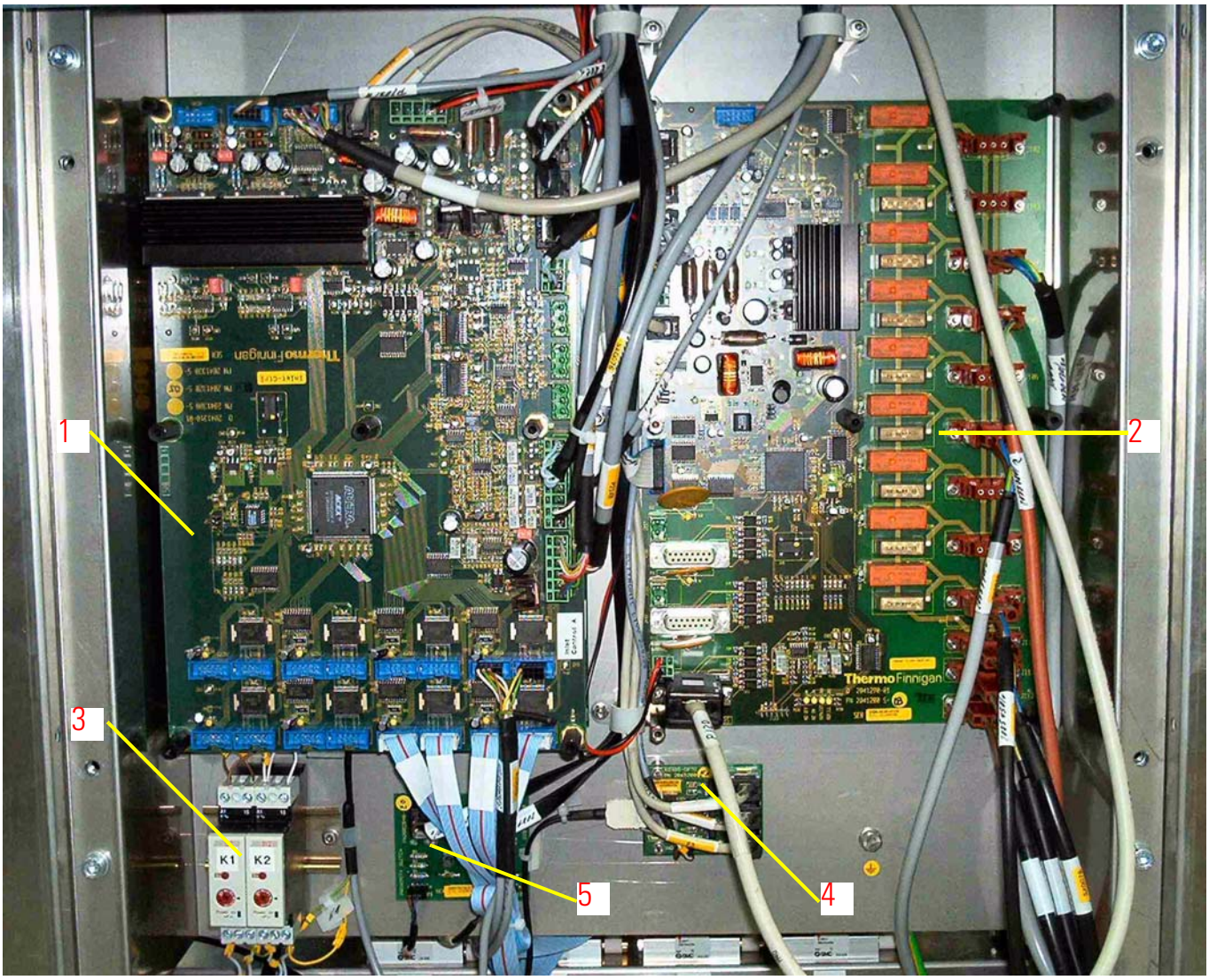


Figure 2-9. Electronics Cabinet

Behind the grey panel on the left side the electronics cabinet is located. See Figure 2-9. Access to the electronics parts is restricted to qualified service personnel only. The section is locked and additionally covered by a transparent pane.

1 shows Inlet Control boards (Figure 6-38, two of them are arranged in stacked order). **2** is the Power Distribution board. **3** depicts the safety switch-off for the acid valve (Figure 2-10). **4** is the fiberline to the serial bus interface (Figure 2-11). **5** shows the interface to connect the proximity switches to the Inlet Control board (Figure 2-12).

Figure 2-10. Safety Switch-Off for Acid Valve

The safety switch-off (monoflop) for the acid valve is shown in Figure 2-10. It has been factory-preset to 3 min. The purpose of these monostable relays is to limit the acid flow in case of a computer failure.

Caution A defective pinch valve causes acid to overflow the oven section of the Kiel IV Carbonate Device! Even in case of smallest problems with the pinch valve, stop working immediately and exchange it! ▲

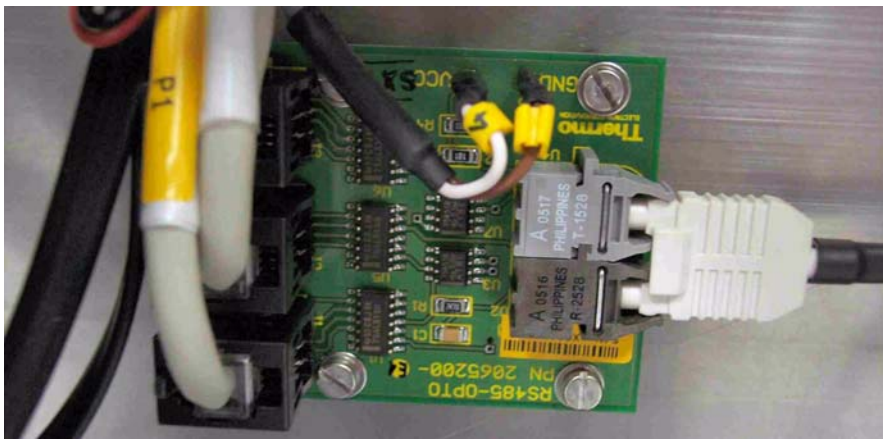


Figure 2-11. Fiberline to Serial Bus Interface

Figure 2-11 shows the fiberline to the serial bus interface.

Figure 2-12 displays the interface to connect the proximity switches to the Inlet Control board.

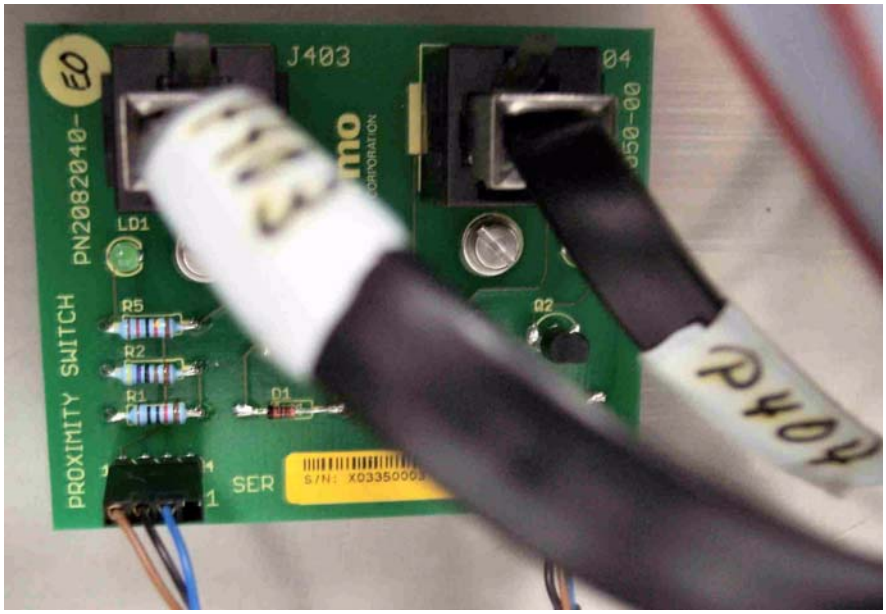


Figure 2-12. Interface Proximity Switches - Inlet Control Board

Caution Proximity switches can be operated up to a maximum temperature of 85 °C. ▲

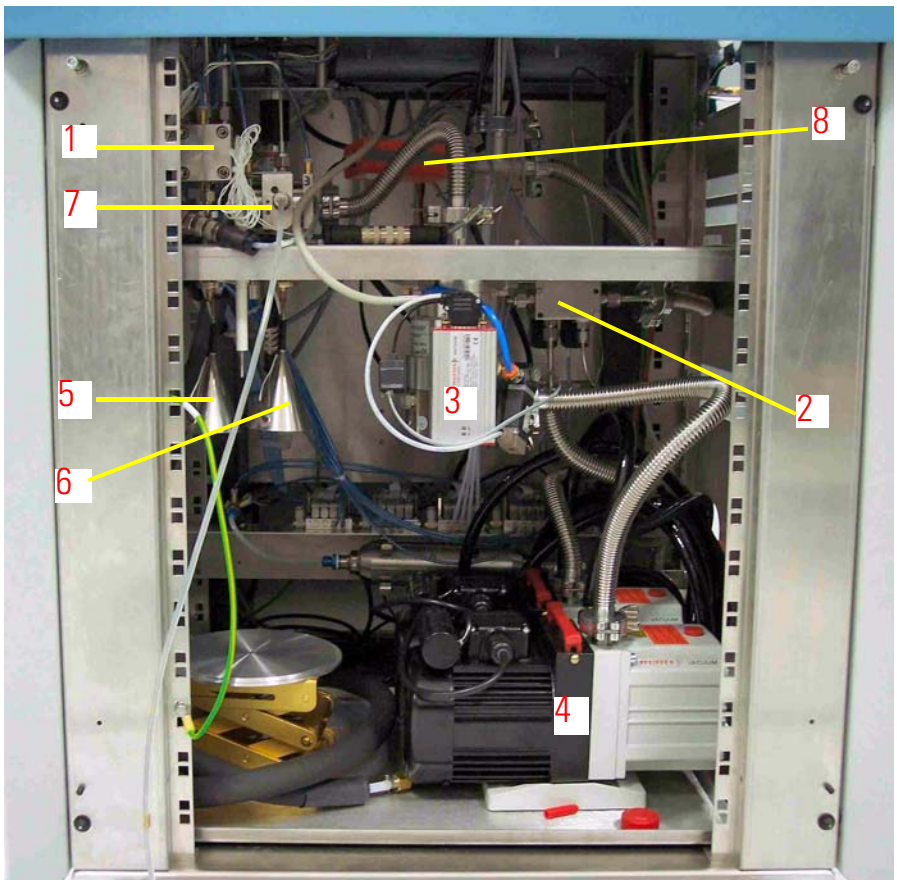


Figure 2-13. Parts within Right Panel

Figure 2-13 and Table 2-1 summarize some important parts to be seen behind the right panel.

Table 2-1. Important Parts within Right Panel

No.	Description
1	valve system of trap 1
2	vent valve (magnetic valve for fore vacuum connection, He/N_2 sample vial vent gas) It is closed when the pump is running. The pump controller keeps the valve closed. When the pump controller is switched off, the turbo pump acts as a generator and keeps the valve closed until pump speed decreases to less than 50 %.
3	turbo pump and its power supply (pump controller)
4	fore pump for backup of turbo pump
5	Autocool Unit for trap 1
6	Autocool Unit for trap 2
7	valve system of trap 2
8	Active Pirani Gauge (APG-M)

In the background of Figure 2-13 the fore vacuum gauge VM2 is located beneath the oven at the T piece. Figure 2-14 shows it in close-up view.

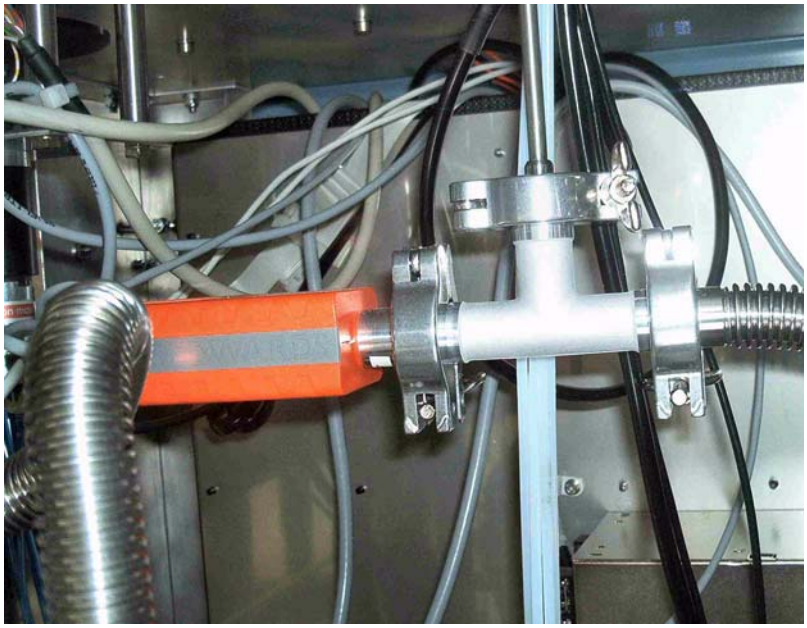


Figure 2-14. Position of VM2 Fore Vacuum Gauge

Additionally, Figure 2-15 shows V7 and V8 mounted on a distributor that connects to the fore pump, the vial vent gas and the oven section.

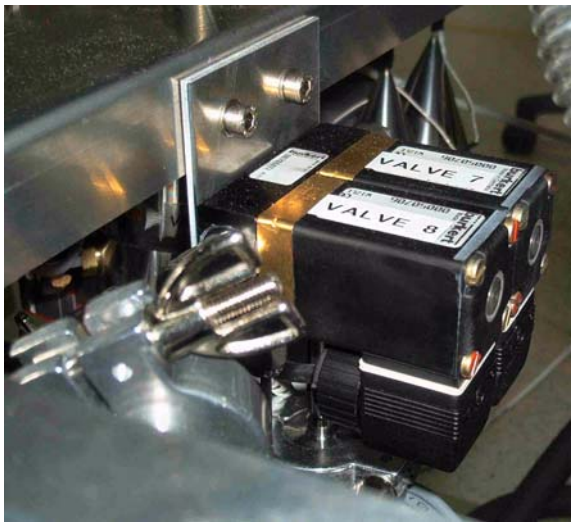


Figure 2-15. Valve 7 and Valve 8

Connections

This section provides information about how to connect the Kiel IV Carbonate Device to the IRMS and to the gas supply.

Connecting Kiel IV Carbonate Device to IRMS

To connect the Kiel IV Carbonate Device to the IRMS, proceed as follows:

1. Remove the side panels of the Kiel IV Carbonate Device.

2. Connect the compressed air connector which is located at the rear side of the Kiel IV Carbonate Device to the IRMS distributor. Use the quick release connection to connect the blue compressed air cable to the compressed air connectors of the IRMS. See Figure 2-5, right.

   As the IRMS has four connectors, four screws (wing unions for compressed air, quick release connections) are provided either with the Kiel IV Carbonate Device or with the IRMS itself.

3. Connect the auxiliary gas (e.g. He or N_2) to the connector at the rear side of the instrument. Set auxiliary gas pressure to less than 0.5 bar.

4. Connect the fiberline cable from this serial bus interface (Figure 2-11) to the rear panel connector of the IRMS.

Note If after switch-on the **Host Connection** LED is not on, interchange the grey and blue plugs of the optical fiber. ▲

5. Connect the mains cable to the appropriate connector of the IRMS.

6. Connect the fore vacuum exhaust to an appropriate vent.

7. Connect the reference refill tank capillary to the standard side of the IRMS (V22).

8. If not already active, start Isodat 2.5.

9. Open Instrument Control and close the Changeover Valve. See Chapter 6 of DELTA V Operating Manual.

10. Connect the stainless steel capillary from V3 and V4 (Microvolume of Kiel IV Carbonate Device) to the Changeover Valve of the IRMS by pulling it through the hole in the side panel of the IRMS.

11. Switch on **Inlet Pumps** at the front panel of the Finnigan Kiel IV Carbonate Device. After approximately 10 min, the green LED of the pump controller gets on, indicating that the vacuum system is operational.

12. Select the configuration for Kiel IV Carbonate Device and ensure that Isodat 2.5 can operate the valves. Refer to "Accessories Bar and its Components" on page 3-5 for instructions.

13. Perform a leak test.

14. Set trap 1 and trap 2 to 150 °C. Keep V1, V2, V3, V4 and V5 open. Set oven temperature to 70 °C (Standby mode).

15. Prepare phosphoric acid[1] and transfer it to the acid reservoir of the Kiel IV Carbonate Device. See Figure 2-58. Place it inside the oven:

    a. Take a 50 ml Luer-type syringe.

    b. Add a silicone tube.

    c. Put the syringe to the 1/16" tubing.

    d. Remove any air by sucking it away from the phosphoric acid tubing line using the syringe.

Note The Viton tubings and the 1/16"-1/4" straight connectors must be leak-tight. Neither sucking of air nor air release should occur during dropping. ▲

16. Connect the two black Viton tubes of the acid valves to each of the two acid glass ports. See Figure 2-16. Check the acid flow by opening V12 and V22, and open acid valve 1 or 2, respectively.

[1]For instructions about phosphoric acid preparation, see "Phosphoric Acid Preparation" on page 4-26.

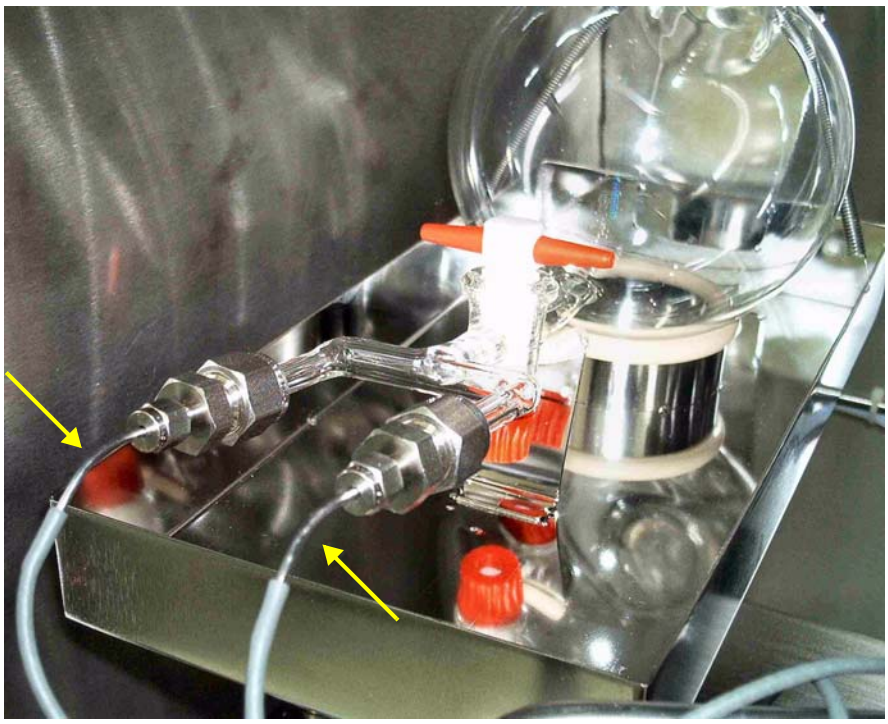


Figure 2-16. Connecting Viton Tubes of Acid Valves

17. Take a magazine and place vials at positions 1/1 and 2/1.

18. Insert the magazine into the oven and perform **Load Magazine**. Refer to "Load Magazine" on page 3-51.

19. Take the capillary heating transformer and connect the heating wires as shown in Figure 2-17 and Figure 2-18:

    a. Connect one 7.7 V input of capillary heating transformer (positive pole, e.g. **2** in Figure 2-18) to the brass contact in center of one capillary (e.g. **2** in Figure 2-17).

    b. Connect the other 7.7 V input of capillary heating transformer (positive pole, e.g. **3** in Figure 2-18) to the brass contact in center of the other capillary (e.g. **3** in Figure 2-17).

Note After the capillary has been wired make sure, the capillary (with or without insulation) has no contact to any plastic surface of tubes, housings, cables etc. to avoid melting or smoldering caused by a hot capillary. ▲

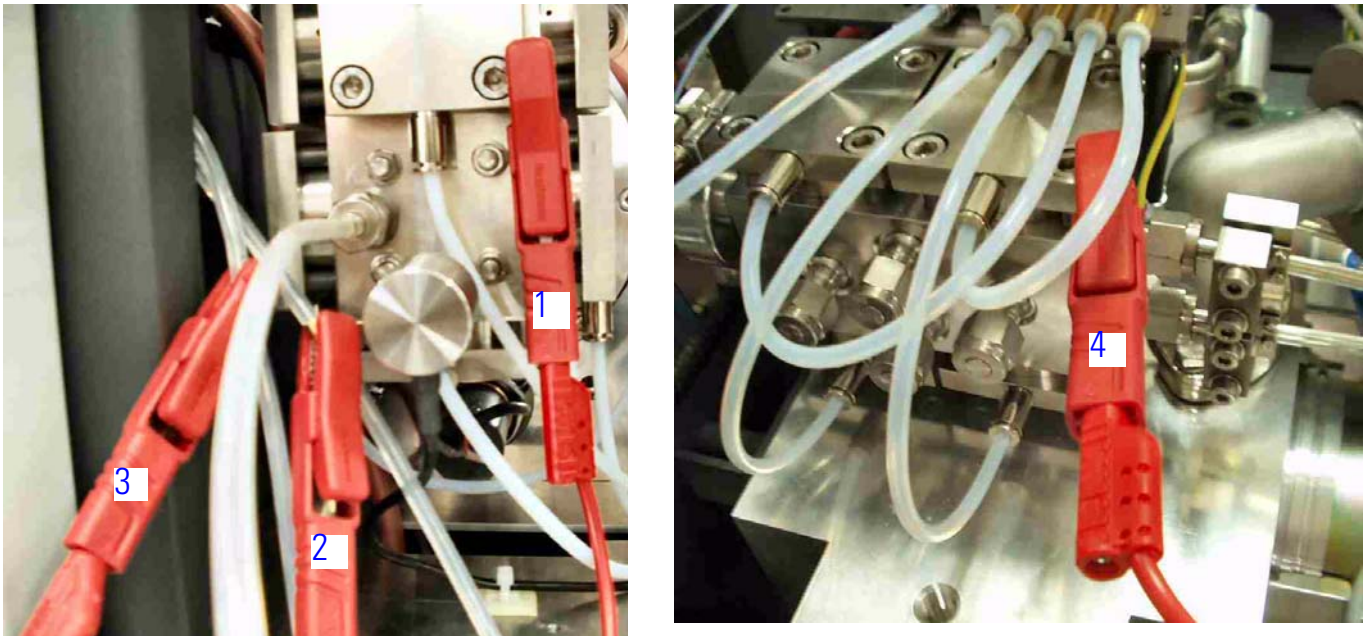
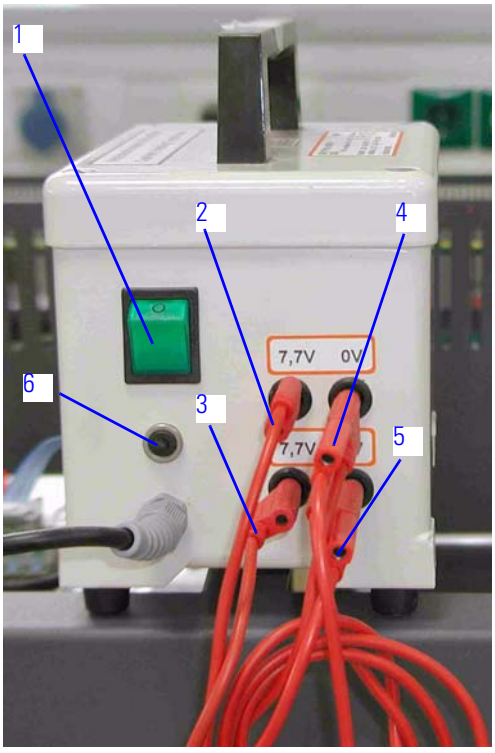


Figure 2-17. Fixing Alligator Crimps to Capillaries

20. Switch the capillary heating transformer on. Keep pumping for 12 h, that is over night. In the meantime, leave V1, V2, V3, V4, V5 and V9 open.



1 main switch (on/off)
2 input of 7.7 V (12 A)
3 input of 7.7 V (12 A)
4 input of 0 V
5 input of 0 V
6 automatic fuse
Press to reset

Figure 2-18. Capillary Heating Transformer

21. Perform a vial test. Refer to "Vial Test" on page 4-23.

22. Wait until the acid is warmed up to 70 °C. Open the manual valve of the acid reservoir shown in Figure 2-2.

23. Open V10 and V20 while the two vials are connected and V13, V23 and V7 are open. See Figure 4-22.

24. Look into the vials: in the beginning, acid drops may spray out due to air bubbles. After this initial period however, the acid should drop slowly into the vials. It may take some time until the first drop of acid appears, because acid must fill the Teflon tube first.

Note The Viton tubings and the 1/16"-1/4" straight connectors must be leak-tight. Neither sucking of air nor air release should occur during dropping. ▲

For instructions about matching sample capillary to standard capillary, see "Matching Sample Capillary to Standard Capillary" on page 4-9.

Vacuum System

The vacuum system of the Kiel IV Carbonate Device (see Figure 6-42) is located in the lower section. It consists of two different pump types:

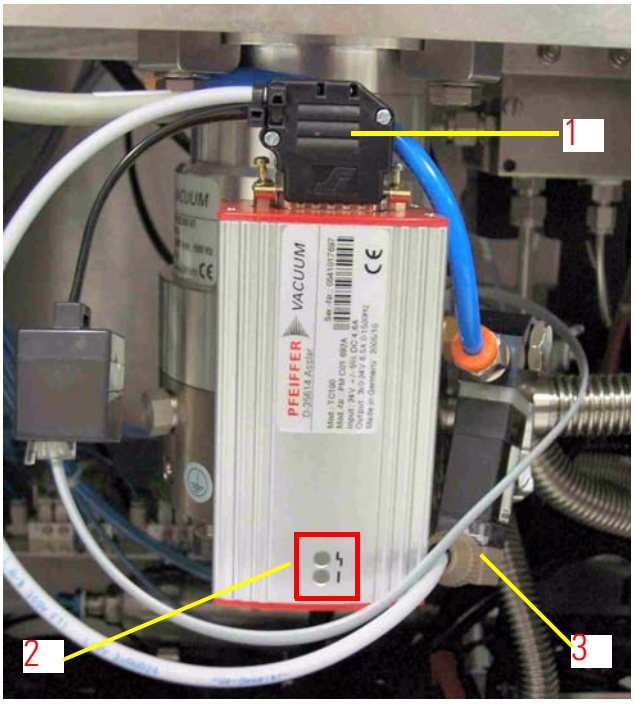
- A turbo pump (TMH 071 P, manufacurer: Pfeiffer, **3** in Figure 2-13 and Figure 2-19) is connected to the trapping section of the Kiel IV Carbonate Device , that is trap 1 and trap 2.

- A rotary vane pump (DUO 2.5, manufacurer: Pfeiffer, **1** in Figure 2-8) provides the fore vacuum for the turbo pump.

- A second rotary vane pump of the same type (DUO 2.5, manufacurer: Pfeiffer, **2** in Figure 2-8) is used during connection and disconnection of sample vials.

  The fore vacuum generated by this second fore pump of the Kiel IV Carbonate Device is monitored by an Active Pirani Gauge (**8** in Figure 2-13, APG-M, manufacturer: Edwards[1]) located in the lower cabinet.

[1]See Instruction Manual of BOC Edwards and www.bocedwards.com.

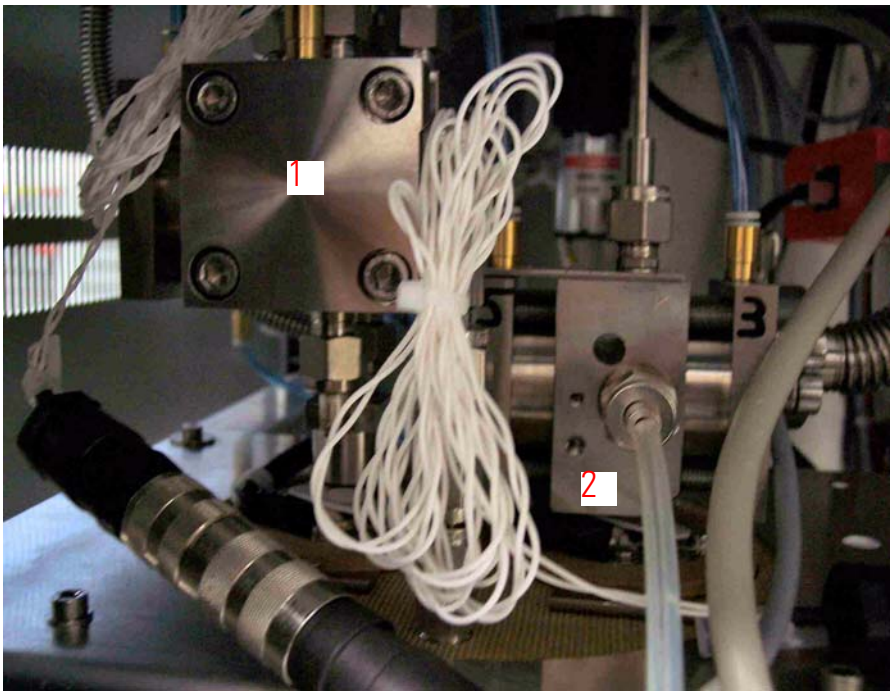


1 electrical connection to Power Distribution board
2 LEDs showing pump controller status
3 vent valve

Figure 2-19. Turbo Pump with Turbo Pump Controller

Valves and Traps

This section provides information about the valves and traps of the Kiel IV Carbonate Device. See Figure 2-20.



1 trap 1 assembly
2 trap 2 (Microvolume) assembly

Figure 2-20. Trap Arrangement

Pneumatic Valves

Layout

A cylinder on top is actuated by compressed air. Its gold-made plunger then presses a membrane underneath and thus tightens. Gas transfer is then impossible. When no compressed air is present, the cylinder is not actuated. Its plunger will not press, and a spring assembly resets the membrane and thus does not tighten. Gas transfer is possible.

Parts of a Pneumatic Valve

Figure 2-21 depicts the parts of a pneumatic valve.

1 sleeve
compressed air plunger moves within it

2 compressed air plunger

3 O ring seal; seals compressed air plunger against sleeve

4 guide sleeve, made of Pertinax
arranged above O ring seal

Figure 2-21. Parts of a Pneumatic Valve

Inserting a Pneumatic Valve

Figure 2-22 shows the pliers **1** to properly insert a pneumatic valve **2**. Hold the pneumatic valve tight by jamming it within the pliers (left in Figure 2-22). Then shove the outer sleeve above the pneumatic valve (right in Figure 2-22).

1 pliers to properly insert a pneumatic valve

2 pneumatic valve

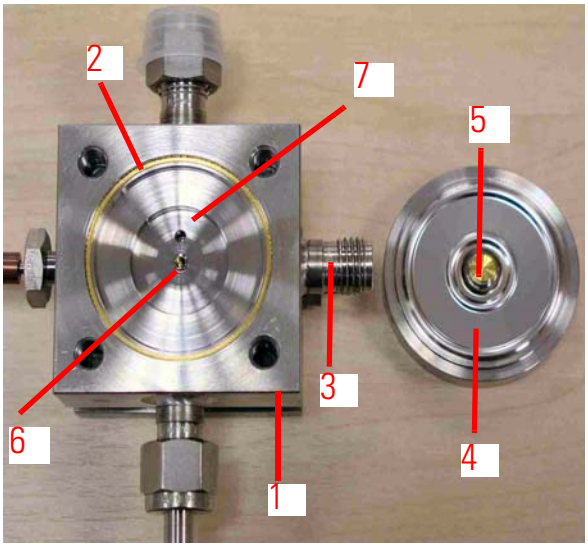
3 compressed air plunger

Figure 2-22. Pliers to Insert a Pneumatic Valve

Valves of Dual Inlet System

The Dual Inlet system is operated by pneumatic valves with a nominal closing pressure of 4 bar. Even though they are all made of stainless steel, after long-term operation they might be worn nevertheless. All the valves base upon the same construction principle. Figure 2-23 shows such a valve with its high-vacuum side opened. Open the pneumatic valve and grease the plunger without disassembling it.

Parts of a Valve



The stainless steel membrane 4 is turned down by 180° and then laid onto the gold-made gasket 2, that is with the plunger 5 oriented downwards.

1 valve block, made of stainless steel

2 gasket (gold), seals valve block against stainless steel membrane

3 Swagelok connector as gas inlet; laterally welded on the valve block

4 stainless steel membrane with valve plug that closes the valve. See also Figure 2-22.

5 plunger, made of gold; fits exactly to the knife edge

6 knife edge, located in center of valve block; also gas exhaust

7 hole, acting as gas inlet to the valve connected to 3 via an internal bore

Figure 2-23. Dual Inlet System Valve

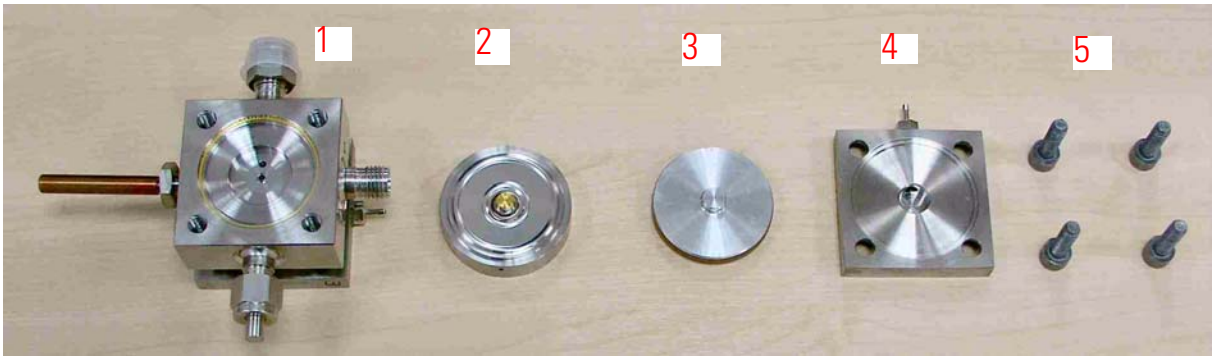


Figure 2-24. Parts of Dual Inlet System Valve

The parts of a Dual Inlet system valve are also made of stainless steel. They are depicted in Figure 2-24 and summarized in Table 2-2.

Table 2-2. Parts of Dual Inlet System Valve*

No.	Description
1	valve block (made of stainless steel)
2	stainless steel membrane with valve plug that closes the valve (a sleeve not to be seen in Figure 2-24 is attached to its rear side)
3	actuator for compressed air (usually lying within rear side) Refer to "Pneumatic Valves" on page 2-18.
4	covering cap
5	Four screws to fasten covering cap

*See Figure 2-24.

Arrangement in Valve Blocks

Compressed air is either supplied by an optional compressor attached to the IRMS or by a user supplied pressure air line. The metal valves are equipped with gold gaskets and gold seats acting on knife edges. Up to six valves are machined into one monoblock, thus considerably reducing the volume in plumbing as well as possible leak of the installation.

This type of valve block is used throughout all inlet modules. For plumbing the valve blocks are fitted with special 1/4" Swagelok connectors. Compressed air is fed to the pneumatically operated valves by solenoid valves. These are controlled by dedicated electronics linked to the computer via a data bus.

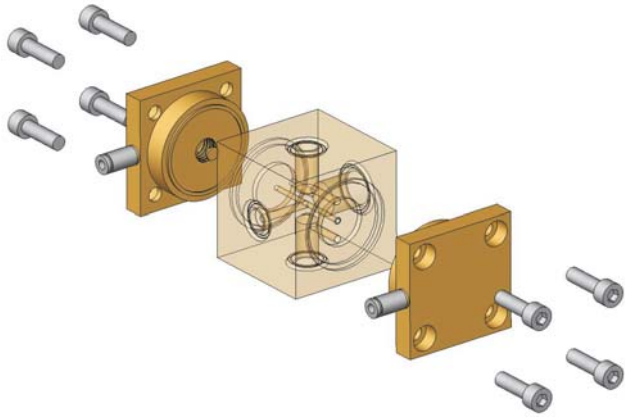
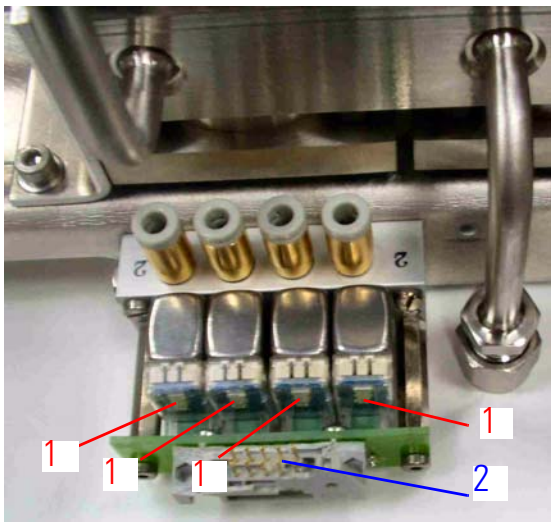


Figure 2-25. Double Valve Block

Manifold Block with Solenoid Valves

Four of the solenoid three-way valves are located on a manifold block. The solenoid valves are operated with a voltage of 24 V. The voltage is supplied by the Dual Inlet board.



1 four LEDs reveal individual switching status (on/off)

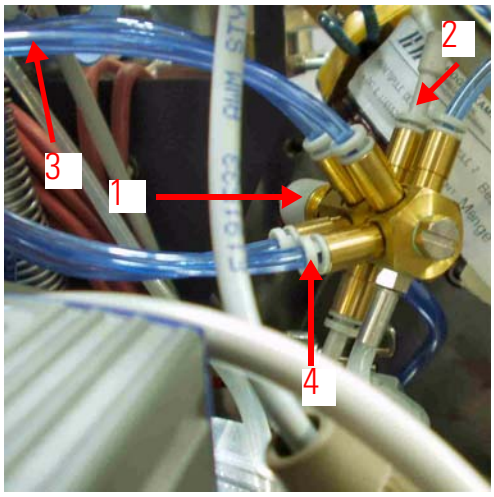
2 connector to Dual Inlet board

Figure 2-26. Manifold Block with Four Solenoid Valves

The solenoid valves are normally open (with the exception of TubeCracker, Part No. 108 2840). The working condition is signaled by a red LED located on the board. The actuators for compressed air transform a signal A into another signal B: they switch an electrical signal generated at the Dual Inlet board into a compressed air signal. Thereby, compressed air is provided which forcefully switches the actual valves.

Note In case of a power failure, all solenoid valves open automatically (with the exception of TubeCracker, where they close automatically). Thus, the pneumatic valves in the entire Dual Inlet system close avoiding its contamination. ▲

Compressed Air Distributor



1 connection where compressed air enters
2 blind plug
3 tubings
4 tubing connections

Figure 2-27. Compressed Air Distributor

The compressed air distributor, Figure 2-27, is part of the Dual Inlet system. Therefore, it is missing if no Dual Inlet system is available. The compressed air connections of the distributor are all equivalent ones. Compressed air enters at **1** in Figure 2-27 and is then distributed to all compressed air valves.

The number of compressed air valves of the system depends on which particular options for the Dual Inlet system are available. If only few compressed air valves must be connected to the compressed air distributor, one or more blind plugs **2** allow to close the unused connections tightly.

Trap 1

This trap consists of a trapping volume valve block and an Autocool Unit. See Figure 2-28. This trapping volume has two tubes, which are stuck into each other. The inner tube must be connected to trap 2. The other end is open and hangs inside the outer tube. See Figure 6-19. The outer tube is connected via valves 1 and 12 (22) to the carbonate preparation vial.

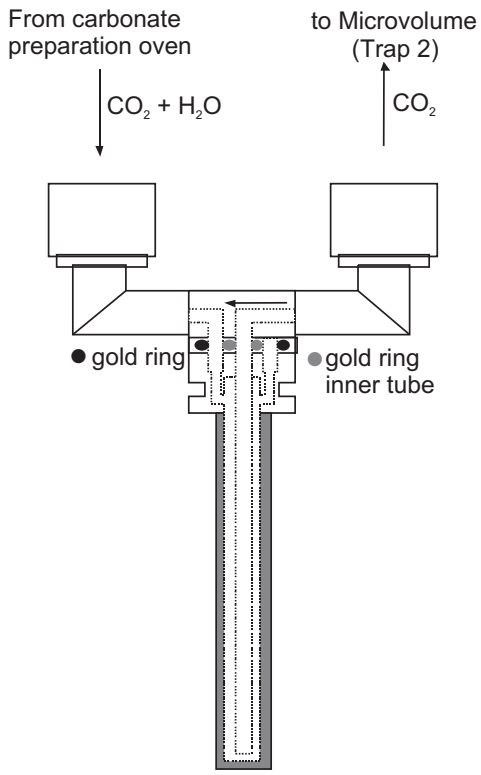


Figure 2-28. Schematic of Trap 1*

*The arrow points in counterflow direction.

By means of the Autocool Unit, temperature can be set individually, if required, within a range of about -196 °C to +150 °C. Before any analysis of carbonate the computer sets the trap to +150 °C in order to remove any impurities. After the cleaning procedure, the Autocool Unit cools the trap to -196 °C. As soon as acid drops into the vial which contains carbonate, the reaction takes place and CO_2, H_2O, N_2 and O_2 are present in different concentrations. Since the trapping volume is at -196 °C, the CO_2 and H_2O gases get frozen inside the outer tube. This means that they are isolated and separated from other produced gases.

After pumping O_2, N_2 as non-condensable gases, Autocool sets the trap temperature to -120 °C to -115 °C. At this temperature, CO_2 as gas in a vacuum is released into the inner tube for later use. The release temperature of -120 °C to -115 °C is extremely important. If temperature is too high, water can get trapped by trap 2. If temperature is too low, CO_2 might be retained. The punched arrow of the trap does not show the gas direction, but counterflow direction. It indicates the installation direction. See "Lower Section" on page 2-3.

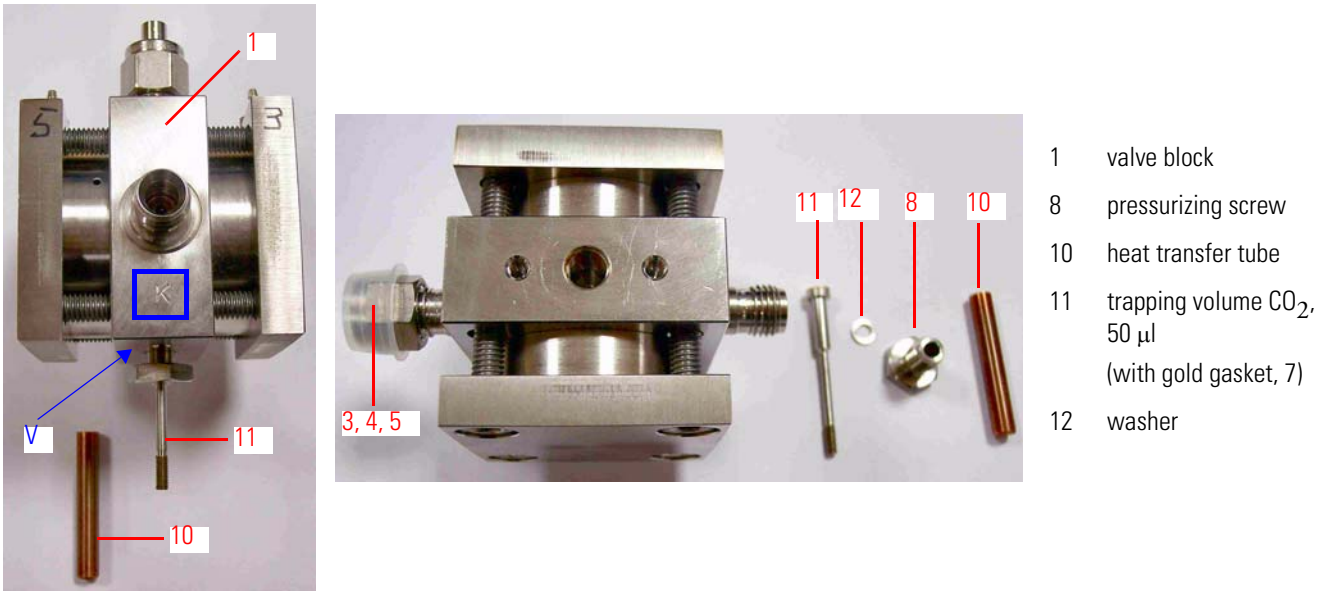
Note If the trap finger has to be exchanged, proper gold gaskets and flow direction of the inner and outer trapping volume must be guaranteed! Any scratch or the wrong direction influences trapping efficiency and incorrect CO_2 trapping, that is isotope fractionation. ▲

Microvolume (Trap 2)

In Dual Inlet mode, measurement is performed out of a volume for smallest amounts, the so-called “Microvolume”. Figure 2-29 shows the Microvolume and its parts[1]. It consists of a trapping volume, a valve block (valve 3 and 5), an Autocool Unit and a separate capillary. This capillay leads directly to the Changeover Valve of the IRMS.

1 reminds of a specially designed valve block. The trapping volume **2**, a drilled tube with a clamped gold seal on top, comprises a pre-set, included volume of 50 µl. Its lower part is cooled to the temperature of liquid nitrogen, e.g. -196 °C so that the gas to be measured will be frozen therein.

3 is a copper-made heat transfer tube that surrounds the trapping volume. The surface of the tube has been gold-plated. K indicates the connection for the stainless steel capillary. V on its rear side indicates the Swagelok socket for the vacuum connection.



1 valve block
8 pressurizing screw
10 heat transfer tube
11 trapping volume CO_2, 50 µl (with gold gasket, 7)
12 washer

Figure 2-29. Microvolume and its Parts*

*The numbers refer to Table 6-6.

The total volume in front of the capillary crimp including trapping volume and the capillary is around 145 µl. Due to the viscous flow conditions which require a pressure of at least 15 mbar for CO_2 gas in front of the capillary, a sample of 5 to 50 mbar/ml has to be concentrated to a small volume. The concentration in a Microvolume is performed by freezing CO_2 gas from trap 1 using liquid nitrogen and expanding it by subsequent heating. By means of the Autocool Unit, the temperature can be set individually within a range of about -190 °C and +150 °C, if required.

[1]“Microvolume” is a collective term for all the parts displayed in Figure 2-29.

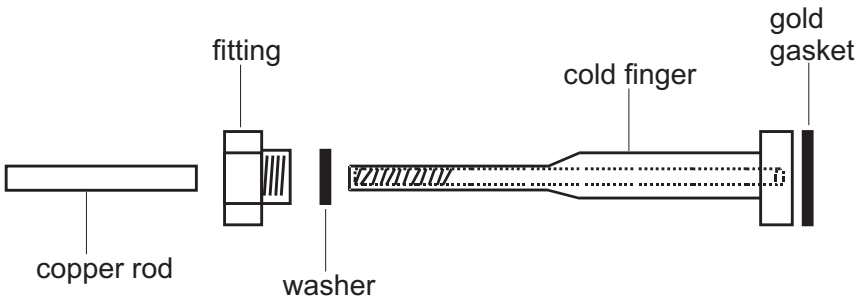


Figure 2-30. Microvolume Parts to be Inserted into Autocool Unit

Autocool Unit

Figure 2-31 shows the dismantled Autocool Unit. Under operating conditions, its funnel will be completely immersed into liquid nitrogen.

The funnel contains a heater to be turned on and off. If a current flows through it, bubbles will ascend into the tube and thus transport liquid nitrogen upwards to the cascade The transport direction of liquid nitrogen is indicated by the arrow in Figure 2-31.

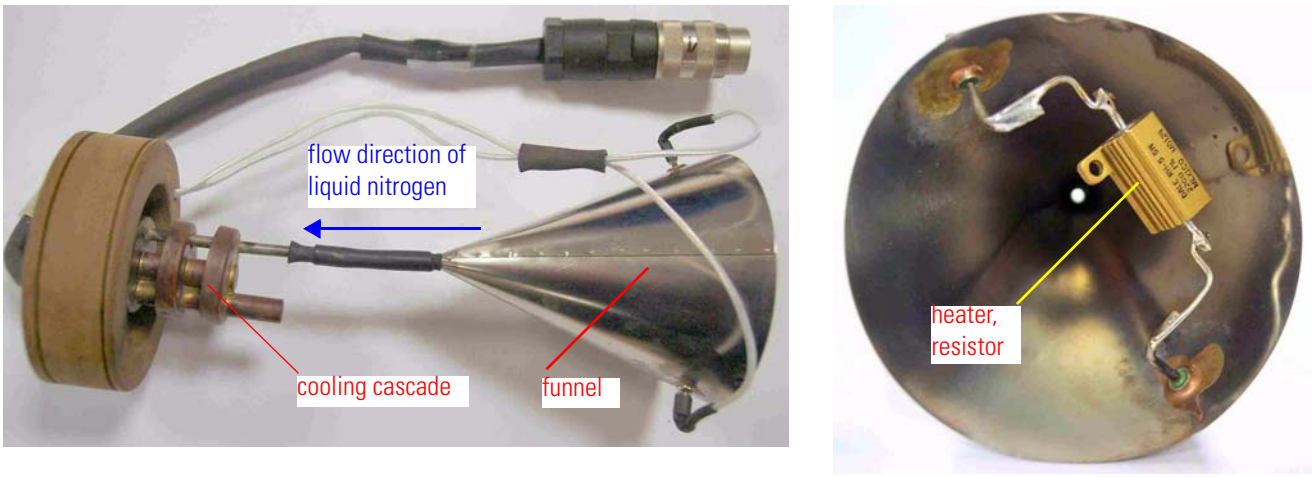


Figure 2-31. Autocool Unit and Interior of Funnel

The cascade with its three stages is depicted in Figure 2-32. Liquid nitrogen is transported towards the uppermost cascade and then drips through holes to the cascade below. Thereby, the unit is cooled to the temperature of liquid nitrogen, e.g. -196 °C.

As the cascade contains a heater and a temperature sensor, the temperature can be raised above this temperature and adjusted there very precisely within a wider range.

The biggest hole, **1** in Figure 2-32, takes up the heat transfer tube (**3** in Figure 2-29). Gilding its cupreus surface facilitates pulling it out of **1** after longer periods of operation for servicing or repair.

The heater cartridge fits into hole **2**. The smallest hole **3** contains a temperature sensor resistor (Pt 100).

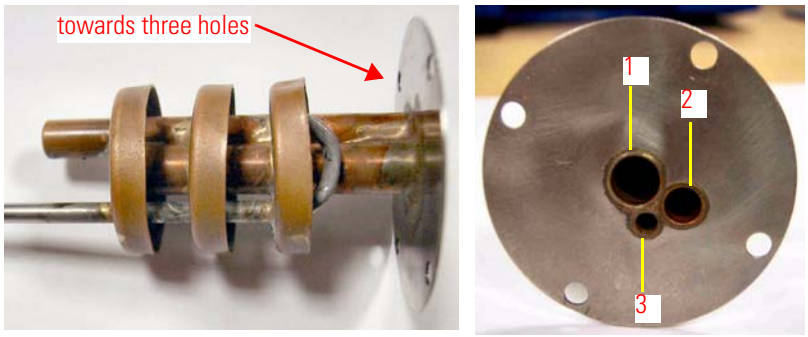


Figure 2-32. Cascade with Three Holes

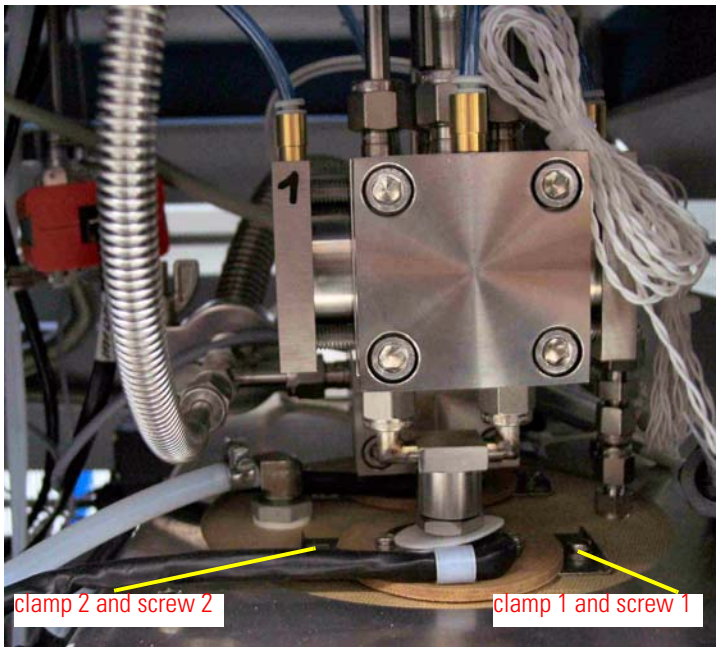


Figure 2-33. Mounting Instructions for Autocool Unit ontoTrap 1

In order to remove the cooling/heating cascade with funnel:

1. Loosen screws 1 and 2 in Figure 2-33 and the electronic connection to the electronic board. Trap numbers are indicated on the cable.

2. Push the clamp to the left (or right). Then, gently push down the Microvolume bar.

Warning Do not loose the Teflon 30 mm washer! It must be reattached at the same position. ▲

Warning Careless handling of liquid nitrogen might cause personal injury including frostbite. Wear protective clothing when operating this equipment including protective gloves and face shield. ▲

The temperature of the Autocool Unit which cools trap 1 or trap 2 can be set by a routine in Isodat 2.5's Instrument Control. If, e.g. the temperature level is set to -80 °C, the heater works against the temperature of the liquid nitrogen in order to keep the set temperature.

A temperature between -196 °C and +150 °C can be set. Trap 1 or trap 2 fit into a thermal contact attached to the lid of the dewar. The dewar contains liquid nitrogen up to a certain level. Fitted to the contact pipe are an electrical heater element, a temperature sensor and cascade arrangement of three small bowls. All parts of the assembly are made of a high thermal conductivity material and are placed in close thermal contact to each other. This achieves a quick changeover from one temperature to another.

To heat trap 1 or trap 2 to a defined temperature, the heater element is activated, and the temperature sensor controls the heating phase. To cool trap 1 or trap 2, another electrical heater element immersed in liquid nitrogen is activated and causes evaporation as well as agitation.

Above the latter heater element, a funnel-shaped hood of standpipe is positioned which leads to the uppermost bowl of the cascade. This arrangement enables about one drop of liquid nitrogen per second to be carried by the stream of evaporated nitrogen. Small holes in the bottom of the bowls enable a constant trickle of liquid nitrogen back into the dewar, and the continuos flow of liquid nitrogen rapidly cools down trap 1 or trap 2. By suitable balancing of the liquid nitrogen flow and heating trap 1 or trap 2, any temperature within the temperature range of ± 2 °C can be attained.

A dewar serves as reservoir for liquid nitrogen.

It is adjusted beneath the trap assembly using a "lab boy".

Figure 2-34. Dewar and "Lab Boy"

Oven and Oven Control

The Jumo itron 16 temperature controller allows to control the temperature of the oven. Notice its three keys indicated by the arrows in Figure 2-35.

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

Figure 2-35. Oven Control

Programming - Step 1

1. Press the P key and hold it for 2 s.
2. Pass through the menu until Y.0 is displayed.
3. Again, press the P key and hold it for 2 s.
4. Set the parameters according to Table 2-3.

Table 2-3. Parameters for Step 1 of Programming

Parameter	Value	Explanation
C111	003	temperature sensor, that is transducer type (e.g. NiCr-Ni, K)
C112	1	number of decimal places and temperature unit (e.g. 1 and °C)
C113	33	controller type (e.g. double setpoint)
C115	0	ramp function, that is ramp function is off
C116	0	outputs on fault, that is 0 % minimum output limiting Y.2 is effective
SP.L	0	lower setpoint limiting
SP.H	100	upper setpoint limiting
OFFS	0	process value correction

For details, refer to Jumo itron 16 temperature controller manual.

Programming - Step 2

1. Again, press the P key and hold it for 2 s.

2. Press the Arrow Up key and Arrow Down key to change values.

3. Set the parameters according to Table 2-4.

Table 2-4. Parameters for Step 2 of Programming

Parameter	Value	Explanation
Pb.1	0.4	proportional band 1
Pb.2	0.2	proportional band 2
d.t	2	derivative time [s]
r.t.	11	reset time [s]
CY.1	2.3	cycle time 1 [s]
CY.2	2.3	cycle time 2 [s]
db	0.0	contact spacing
HyS.1	1.0	differential 1
HyS.2	1.0	differential 2
Y.0	0	working point [%]
Y.1	85	maximum output [%]
Y.2	0	minimum output [%]
d.F	1.1	filter time constant [s]

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.

Tune Scan after Programming

Note After both programming steps have been finished, perform an Autotune. This requires to set the ramp function C115 to 0 before you press the Arrow Up key and the Arrow Down key simultaneously! During Autotune, the controller displays the setpoint value and "tune" alternating. ▲

Autosampler

Figure 2-36. Turret and Correct Vertical Placement of Vials

Installing and Removing Magazine

Caution Be careful not to destroy the acid dropper capillary and the drop counter spring during installation of the removable tray! ▲

The whole magazine turret consists of the magazine part containing the vials and a cover plate with two holes and a locator to install it inside the oven the specific way shown below. See Figure 2-36, Figure 2-37 and Figure 2-38.

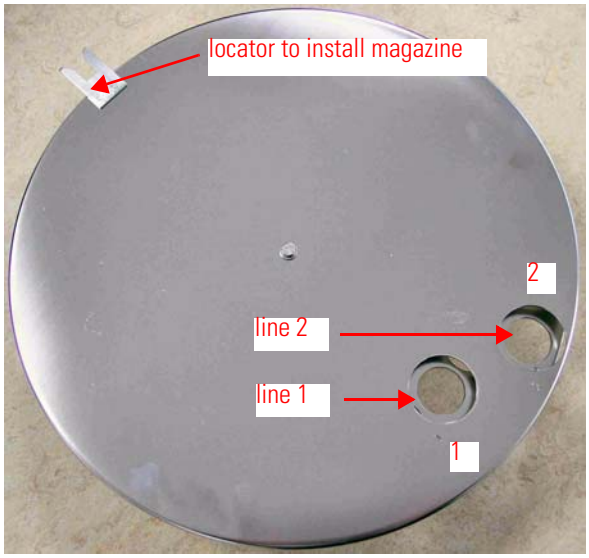


Figure 2-37. Turret and Lid for Line 1 and Line 2 Position

The turret can be removed from the oven to load/unload it with vials. For this purpose, a special stand comes with Kiel IV Carbonate Device.

Warning Be sure to put the stand in a safe place before you remove the hot turret from the oven! ▲

In order to remove the turret, stop any sequence and press **Take Magazine** in Instrument Control. After loading the turret, you can put it back to the oven. Then, press **Load Magazine** in Instrument Control.

Adjusting Magazine Position

To adjust the position of the vials in the magazine to the piston position, perform as follows:

1. Take away the cover of the magazine and place the magazine inside the oven.

2. Loosen the screws 1-4. Move the magazine. Tighten the screws.

3. Rotate the magazine until the vials are aligned to the piston.

4. Take away the magazine and tighten the screws 1-4 again.

5. Rotate the magazine several times.

6. Perform a **Take Magazine** procedure and a **Load Magazine** procedure to check positioning again.

   Moving the support rod can align the cover plate to the magazine. The support rod is fixed by two screws, which are located at one end.

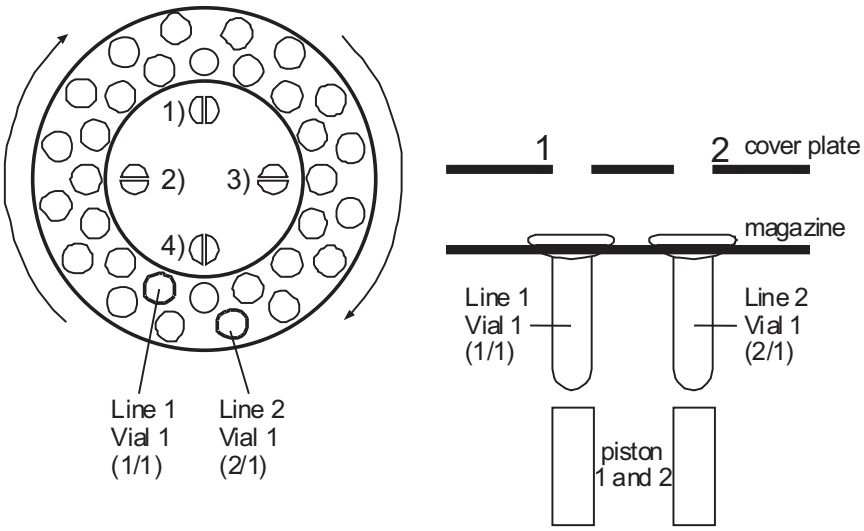


Figure 2-38. Magazine with Cover Plate and Vials

Adjusting Piston Speed

The speed of the piston to move the vials up- or downwards can be adjusted as follows (see Figure 2-39 and Figure 2-40):

- Turn the screw **clockwise** to **reduce** the speed of the piston movement and **counterclockwise** to **increase** it.
- The screw at the **upper** end of the piston is used to move the piston **down**wards! The screw at the **bottom** of the piston is used to move the piston **up**wards!

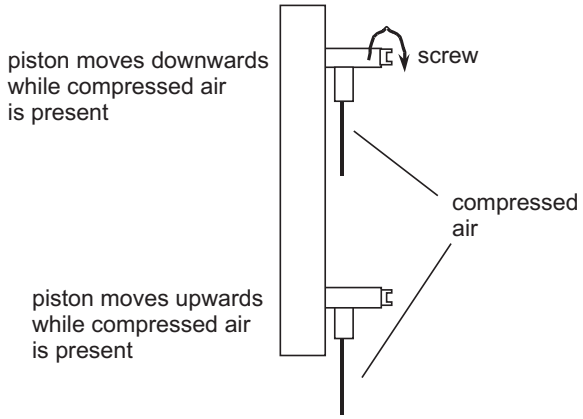
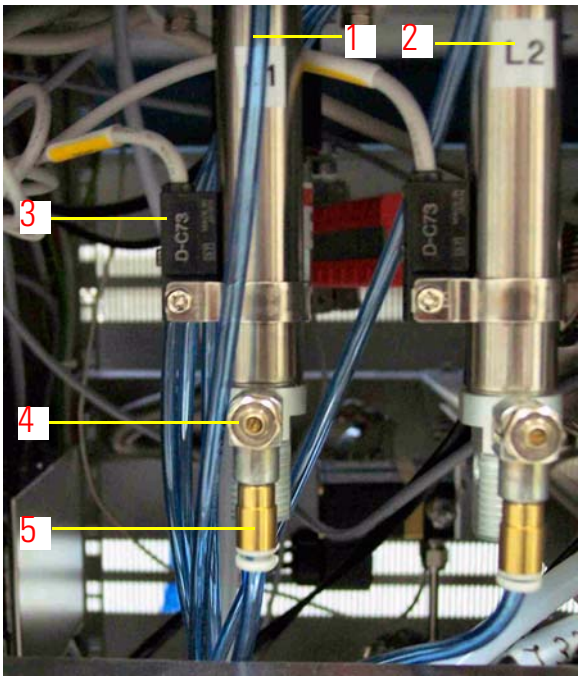


Figure 2-39. Piston Speed Adjustment



1 compressed air lever for piston line 1
2 compressed air lever for piston line 2
3 magnetic position sensor for piston with LED to indicate position
4 flow limiter
5 compressed air connection

Figure 2-40. Connections of Pneumatic Levers for Pistons

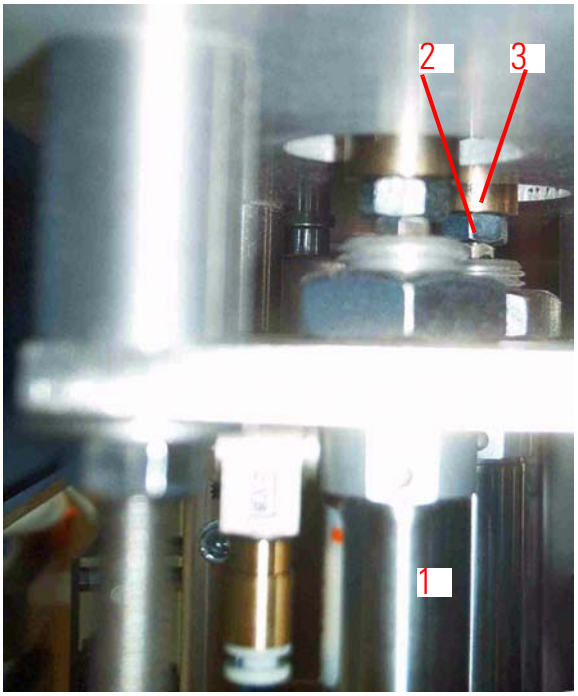
Figure 2-40 displays the connections of the pneumatic levers for the two pistons.

Adjusting Piston Height

Inside the piston, a spring assembly is located to ensure proper pressure when connecting vials. It may be necessary to adjust the overall height to ensure proper operation of the connect process.

For this purpose, the piston height can be adjusted. The piston itself is screwed into the piston compressed air lever and secured by a second nut. See Figure 2-41.

This position is difficult to access. The screw can be found on top of the pneumatic lever, at the bottom of the piston itself.



1 compressed air lever
2 safety nut
3 bottom of piston

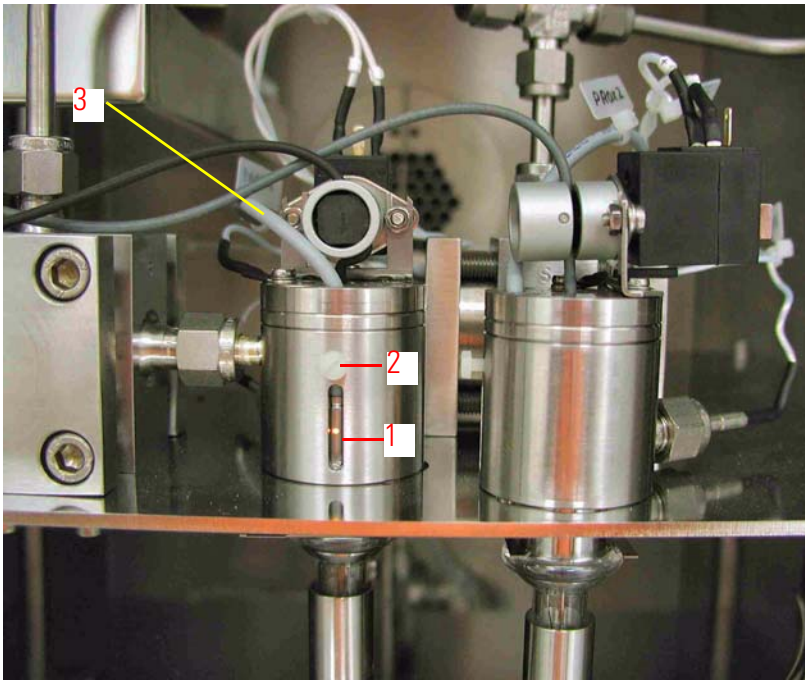
Figure 2-41. Adjusting Piston Height

A red PTFE vial bottom lever is located inside the piston. If phosphoric acid has spoiled into the piston, this lever can latch vials. This leads to a hardware failure.

Note In this case, remove the entire piston and clean it thoroughly, also on its inside. ▲

Proximity Switch

The proximity switch used to detect the presence of vials is located inside the acid valve. This switch is a rod which at one end contains a coil as shown. The electronic switch contains no mechanical parts. Once the piston moves the vial to the acid valve, the vial pushes a metal U-shape spring upwards close to proximity switch. See Figure 2-42. The induction of the coil changes, which means the vial is connected.



1 window to check sensor status
2 adjustment screw
3 electrical connection of sensor

Figure 2-42. Proximity Switch

Turret Motor

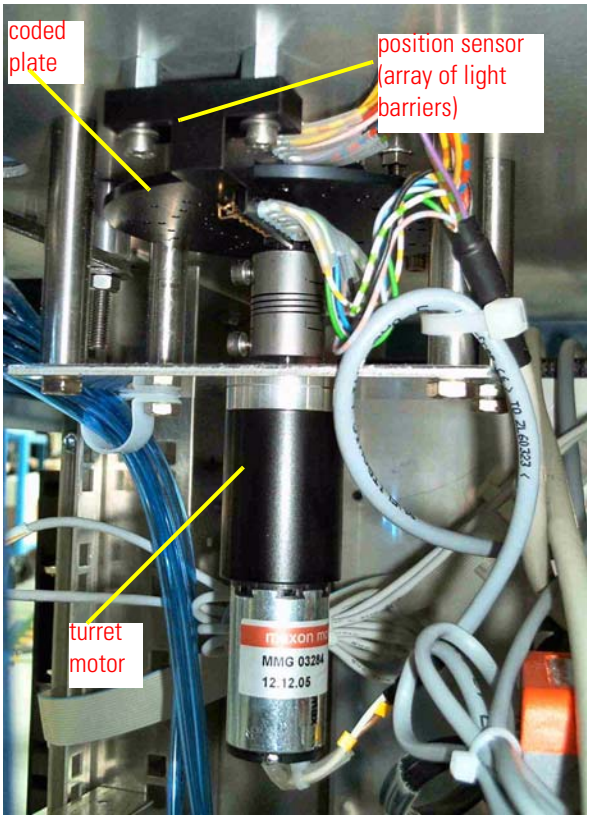
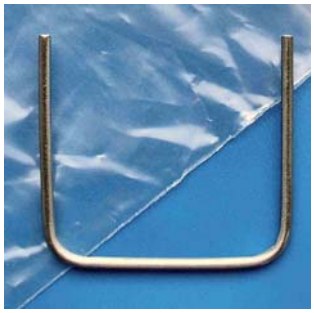


Figure 2-43. Turret Motor and Position Sensing Array

The motor to drive the turret is located beneath the oven, together with the position sensor for the autosampler section. The setup consists of an array of infrared light barriers and a plate with holes that is binary coded. Depending on the position of the rotating plate, more or less of the light barriers are closed resulting in a code that represents the position of the turret. See Figure 2-43.



In case the position sensor shown in Figure 2-43 has eventually shifted, use the tool (Part No. 115 7390) to readjust its position.

Figure 2-44. Tool to Readjust Array of Infrared Light Barriers

Liquid Nitrogen Refill Device

This section contains information to be read before operating the refill device. Read the manufacturer's handling instructions carefully as well.

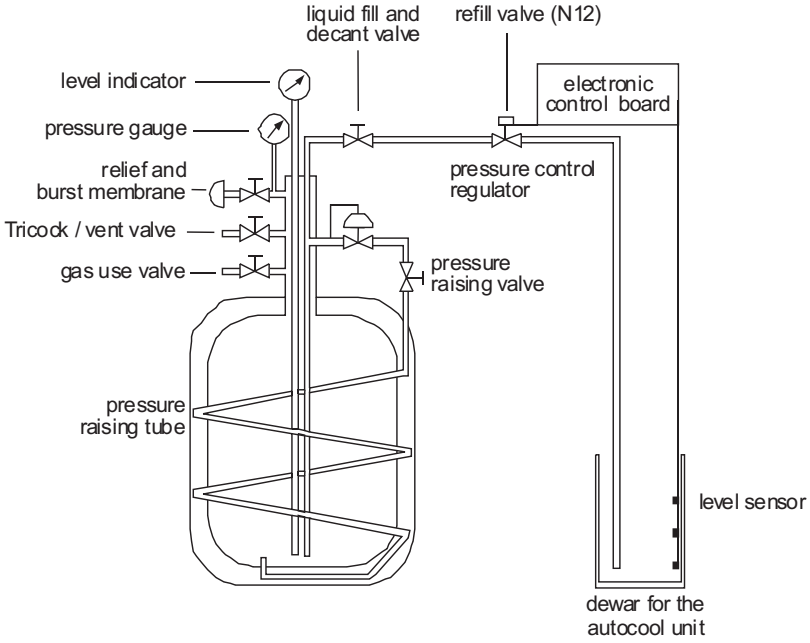
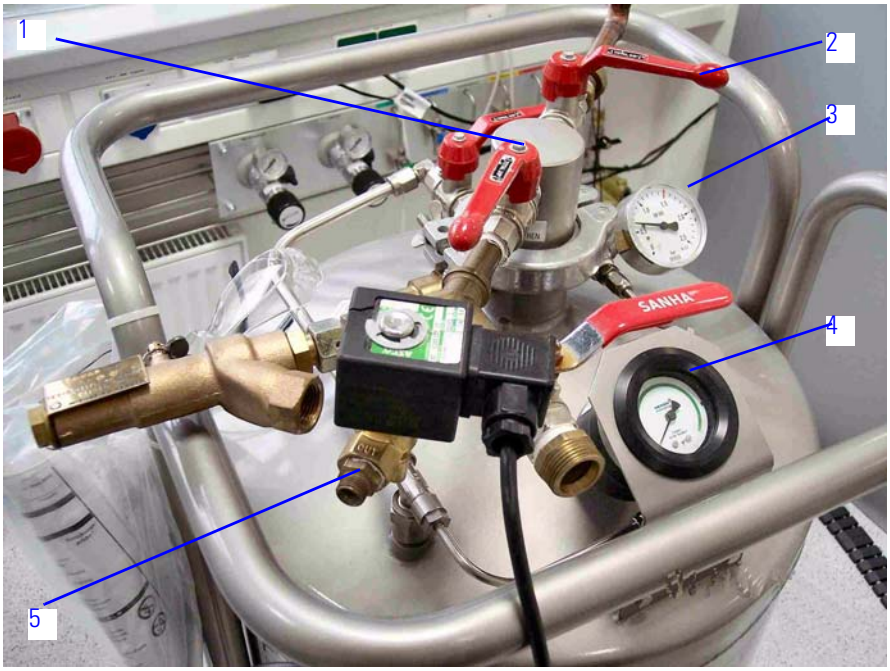


Figure 2-45. Schematic of a Standard Liquid Nitrogen Refill Device

Warning The refill device contains an extremely cold liquid. Careless handling might cause personal injury including frostbite. Wear protective clothing including protective gloves and a face shield. ▲

Warning Do not overfill or tilt the refill device and prevent spills. Use the refill device only in well-ventilated areas. Poor ventilation causes suffocation. Keep in mind: Safety first! ▲



1 liquid fill and decant valve
2 vent valve
3 pressure gauge
4 fill level display
5 connection to transfer tube
6 magnetic valve
for refill (open/close)
7 5 bar LN2 overpressure gauge
for overpressurized arm next to 6
8 central O ring seal
to close dewar

Figure 2-46. Magnetic Valve and Liquid Nitrogen Safety Unit

Figure 2-47. Example of a Liquid Nitrogen Refill Device

All liquid nitrogen reservoir tanks contain some kind of level indicator, a pressure gauge to read the internal pressure, safety pressure relieve valves and a mechanism to build up pressure. This mechanism can usually be switched off (pressure raising valve).

Furthermore, there are connections to decant the liquid phase or the gas phase, and usually there is a connection to vent the reservoir. Finally, there is a pressure regulator to adjust the reservoir pressure.

For proper operation of the refill device, a pressure of about 0.7-1.4 bar (10-20 psi) is required inside the tank to ensure liquid nitrogen flow, if the decant and refill valves are opened. For this purpose, all liquid nitrogen storage devices have a pressure raising valve and a pressure limiter.

Note If the central O ring seal, **8** in Figure 2-46, is not closed properly, the Kiel IV Carbonate Device will not operate, because no pressure raise is possible! ▲

Warning Note for Liquid Nitrogen Supply

Concerning the automatic refill device, you may have either a liquid nitrogen tank of your own or a tank delivered by Thermo Electron optionally (30 l or 90 l).

As a part of the tank, a **liquid fill and decant valve** (**1** in Figure 2-46) is also included. It is a **manual cutoff valve** to close and open the tank. During tank transport it must be closed. After the tank has been connected to the gas line, the valve must be opened to provide nitrogen for the entire system. Therefore, never close it during operation!

The **solenoid valve** (that is **magnetic valve**, **6** in Figure 2-46) is controlled by Isodat 2.5. Its status depends on the processes inside the device: when nitrogen is required, it will be opened allowing new nitrogen to flow along the tube. When no more nitrogen is needed, it will be automatically closed. The manual cutoff valve may still be open.

Warning The tube between solenoid valve and manual cutoff valve may never be closed! When liquid nitrogen inside the closed tube is warmed, pressure will increase considerably! ▲

Warning If the manual cutoff valve of the liquid nitrogen tank and the solenoid valve are closed simultaneously, the liquid nitrogen distributor as well as the gas line to the tank could burst and seriously injure operating staff! ▲

Therefore, together with the distributor a pressure control valve is delivered by Thermo Electron. This safety valve serves to reduce excess pressure and thereby prevents the tube from bursting. It must be installed by a technician. In case of an **upgrade**, perform as follows:

1. Unscrew the distributor's dummy plug.

2. Screw in the pressure control valve.

In case of a **new system**, the pressure control valve has already been screwed onto the distributor.

Warning Always mount the 5 bar safety valve between solenoid valve and manual cutoff valve! Never operate the instrument without safety valve, that is never unscrew it! In case the 5 bar safety valve is damaged, renew it immediately! ▲

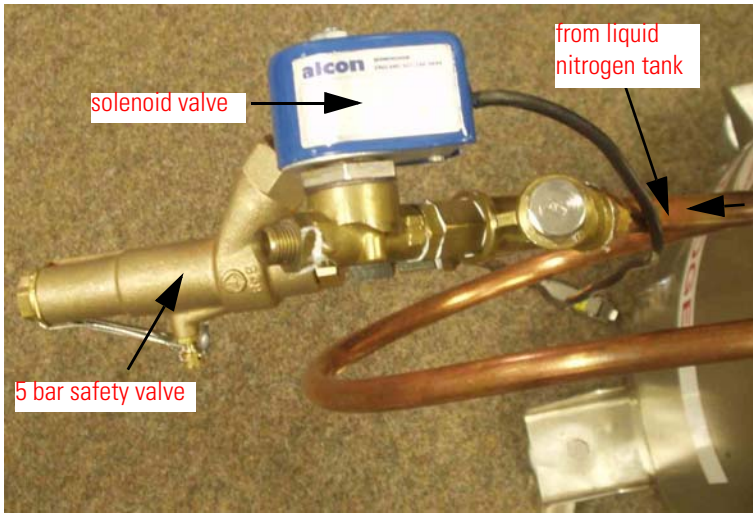


Figure 2-48. Valves and Distributor for Liquid Nitrogen (Top View)

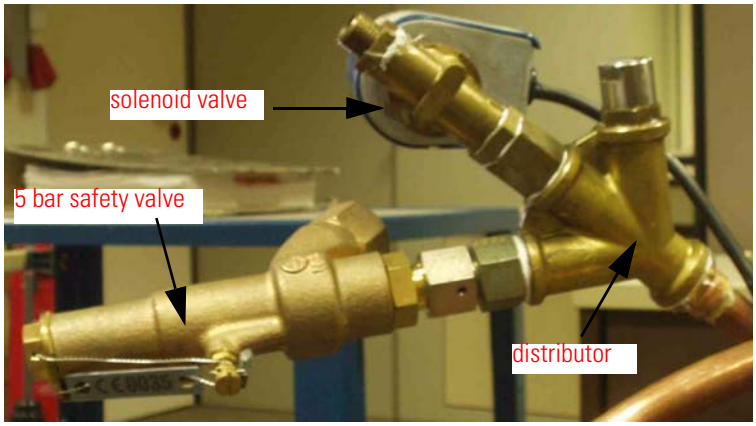


Figure 2-49. Valves and Distributor for Liquid Nitrogen (Side View)

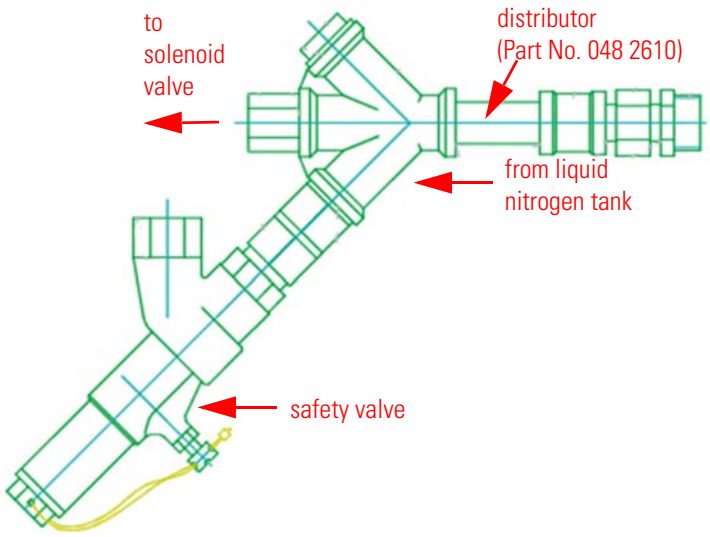


Figure 2-50. Valves and Distributor for Liquid Nitrogen

LN2 Transfer from Refill Device into Dewar

The refill device provides a constant level of liquid nitrogen in the dewar for the Autocool Unit. It is equipped with the necessary safety devices, valves and pressure gauges required to safely handle liquid nitrogen.

A solenoid-operated refill valve controls the transfer line to the dewar of the Autocool Unit. This refill valve must be directly connected to liquid fill and decant valve of the refill device. A level sensor installed in the dewar of the Autocool Unit activates the refill device.

The refill sensor used for liquid nitrogen refill can be found besides the trap assemblies. See Figure 2-51 and Figure 2-52.

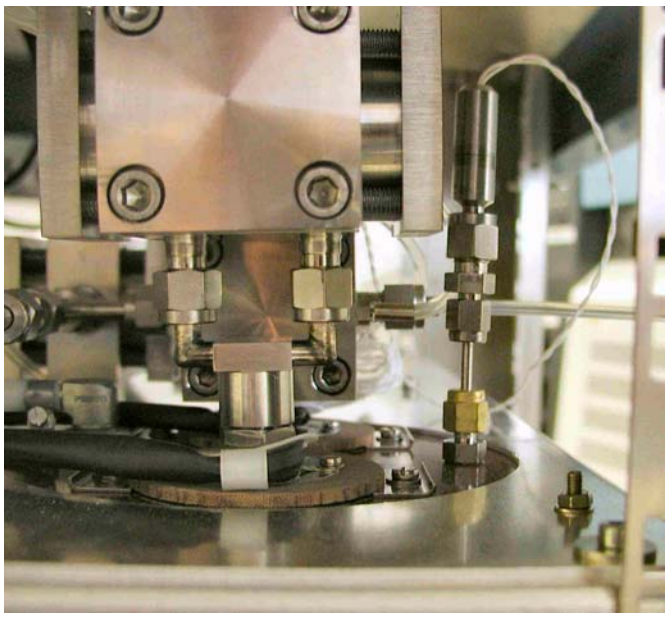


Figure 2-51. Position of Refill Sensor

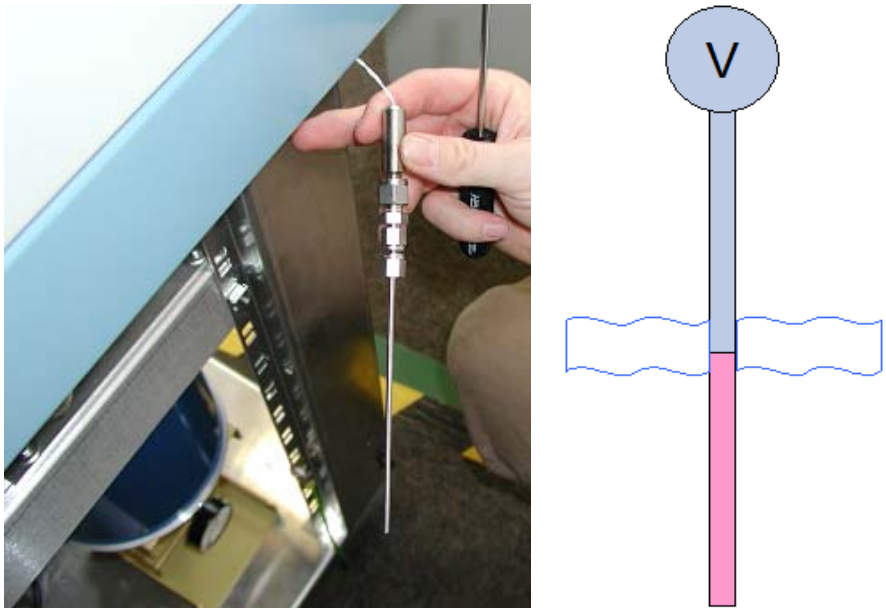


Figure 2-52. Liquid Nitrogen Refill Sensor

Functional Principle of Refill Sensor

The refill sensor is made up from a volume filled with silica gel, nickel wool and air that is connected leak-tight to a pressure gauge. If the volume is at room temperature, the inside of the tube is at atmospheric pressure. If the tube is emerged in liquid nitrogen, the nitrogen inside the tube will condense on the surface of the silica gel, and the pressure will drop below 10 mbar. This pressure change is recorded by the gauge and measured by Isodat 2.5.

Whenever the temperature of the traps is set to less than 20° C, the state of the sensor will be checked and, if necessary, liquid nitrogen refill will be initiated.

Possible Problems

- Liquid nitrogen is refilled only on request (via Isodat 2.5).
- If the sensor is defect or improperly adjusted, overflow may occur.
- If the sensor reacts too sensitive, cooling to temperature of liquid nitrogen is no longer possible. Change the sensor position by pulling it out of the dewar.
- Setting the -120 °C level seems to be problematic, if the sensor position is too high.

Reference Gas Refill

When working with the Finnigan Kiel IV Carbonate Device, a reference gas refill (synonymously called standard gas refill) is necessary to avoid running out of reference gas during measurements.

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. ▲

Warning CO_2 from a high pressure gas tank is not suitable! ▲

Reference refill provides the reference gas supply to the inlet system. See Figure 2-53 and Figure 2-54. It is a hardware option and consists of a metal tank of approximately 5 l with a manual valve connected via a capillary (see Figure 6-7) to one of the inlet ports on the standard side. With the reference refill selected, the standard side of the Dual Inlet system is completely pumped out before it is filled again for the next measurement.

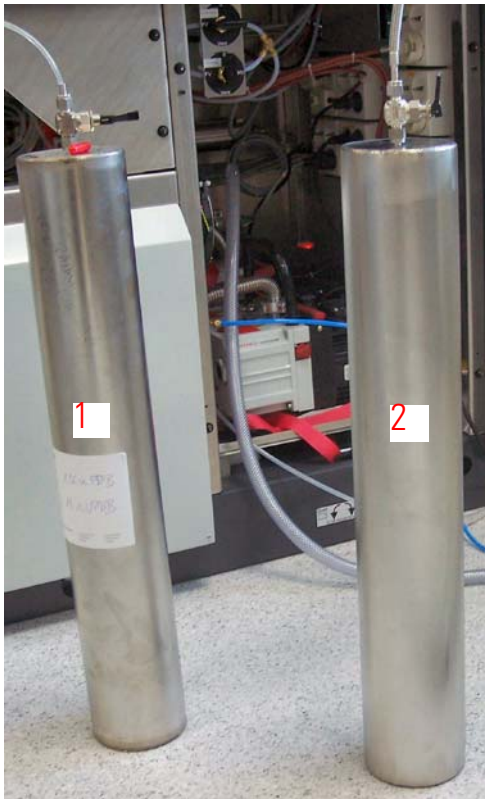


Figure 2-53. Reference Gas Refill Units

Figure 2-53 shows two reference gas refill units, the left one, **1** with a capillary for normal operation and the right one, **2** with a bigger tube (e.g. 1/4”) suitable for baking and refilling operation. Both capillary and tube are included in the Reference refill option.

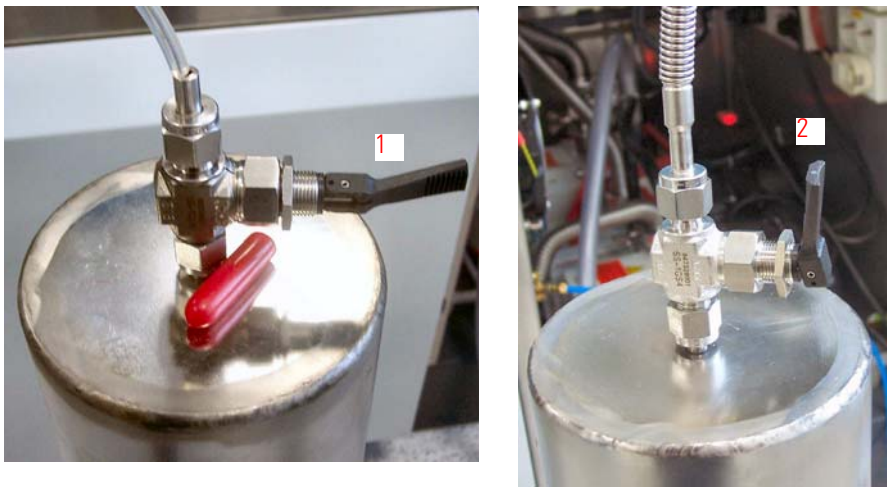


Figure 2-54. Manual Valves

Figure 2-54 shows manual valves. The left one, **1** denotes the manual valve to close the refill tank in open position. The right one, **2** denotes the manual valve in closed position. The reference refill parameters can be set at "Reference Refill" on page 3-23.

Filling Reference Refill Device from External Source

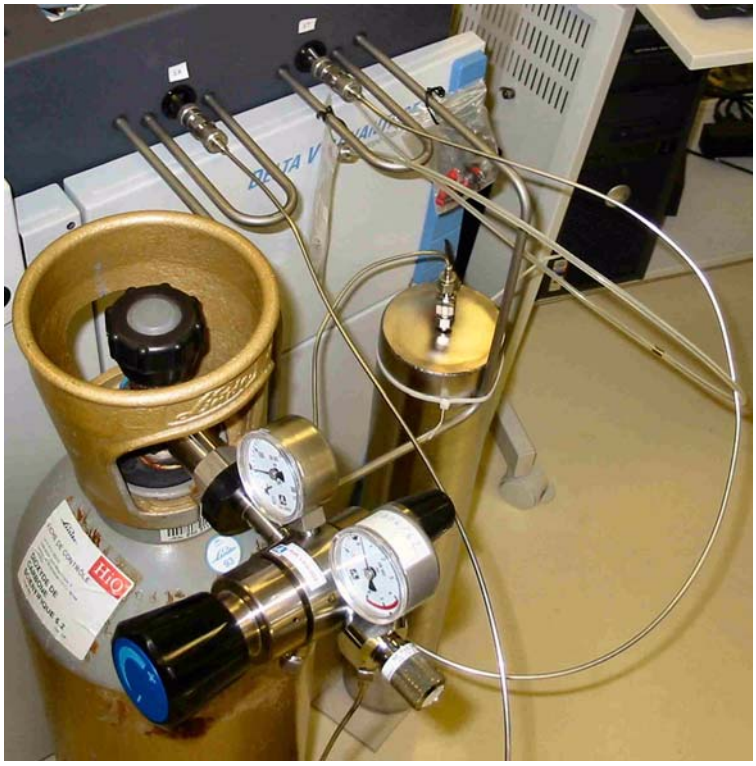


Figure 2-55. Filling Reference Refill Device from External Source - I

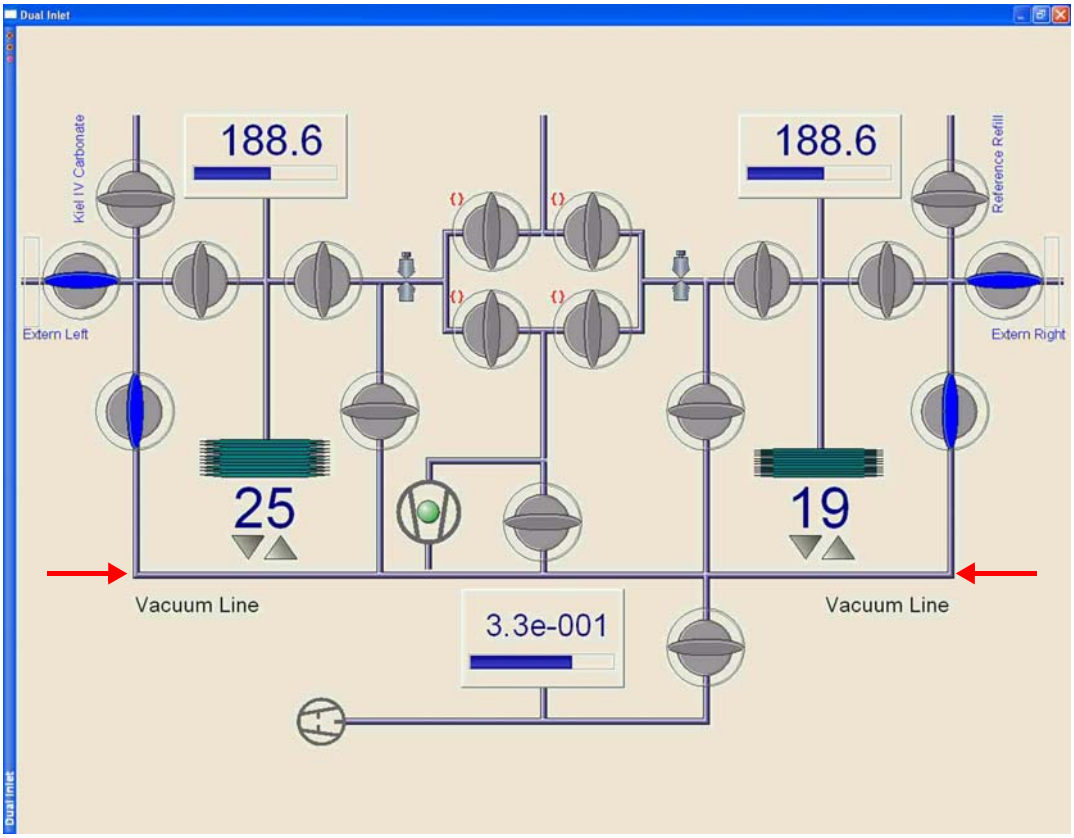


Figure 2-56. Filling Reference Refill Device from External Source - II

Whereas in Figure 2-55 the connections are outlined, Figure 2-56 shows the switching of the valves. To fill the Reference Refill Device from an external source, proceed as follows according to Figure 2-56:

1. Evacuate the Reference Refill device over night using the high vacuum pump.

2. If you fill from a high pressure tank with pressure regulator, adjust the manometer of the CO_2 tank to 0.6 bar. In order to avoid contamination, flush the manometer for about 5 min before connecting the line to the extern left.

3. Evacuate the entire vacuum line first using the fore vacuum pump and then using the high vacuum pump. See arrows in Figure 2-56.

4. Open the tank connection and allow gas from the tank to fill the Reference Refill device. Equilibrate for 15 min before breaking the connection. In order to obtain an ideal pressure of about 0.6 bar (8.5 psi) in the Reference Refill device, adjust about 0.6 bar (8.5 psi) at the pressure regulator of the CO_2 tank.

Acid Flow

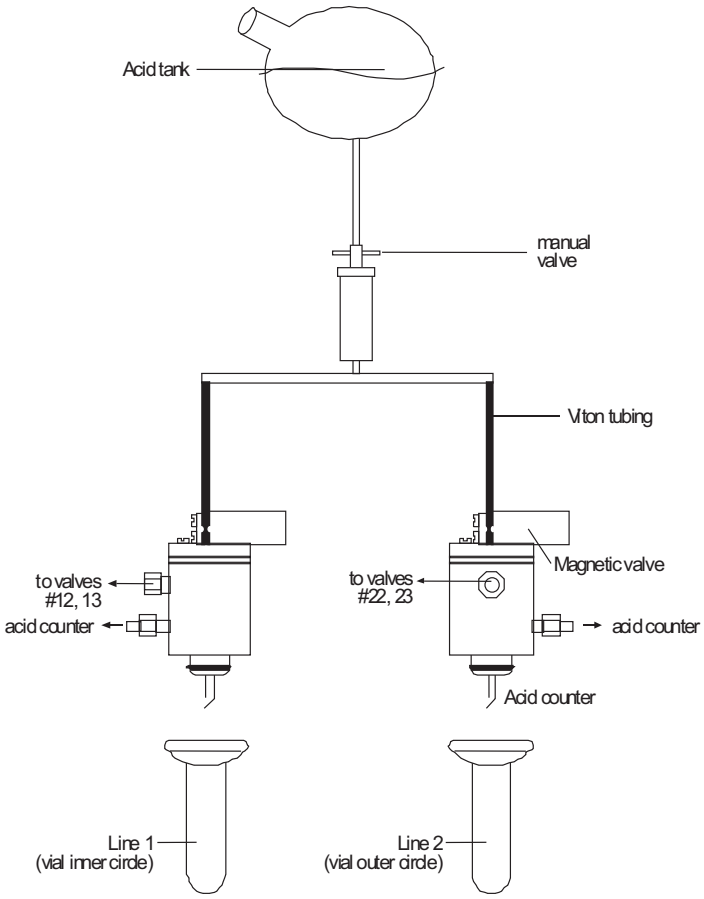


Figure 2-57. Schematic of Acid Flow

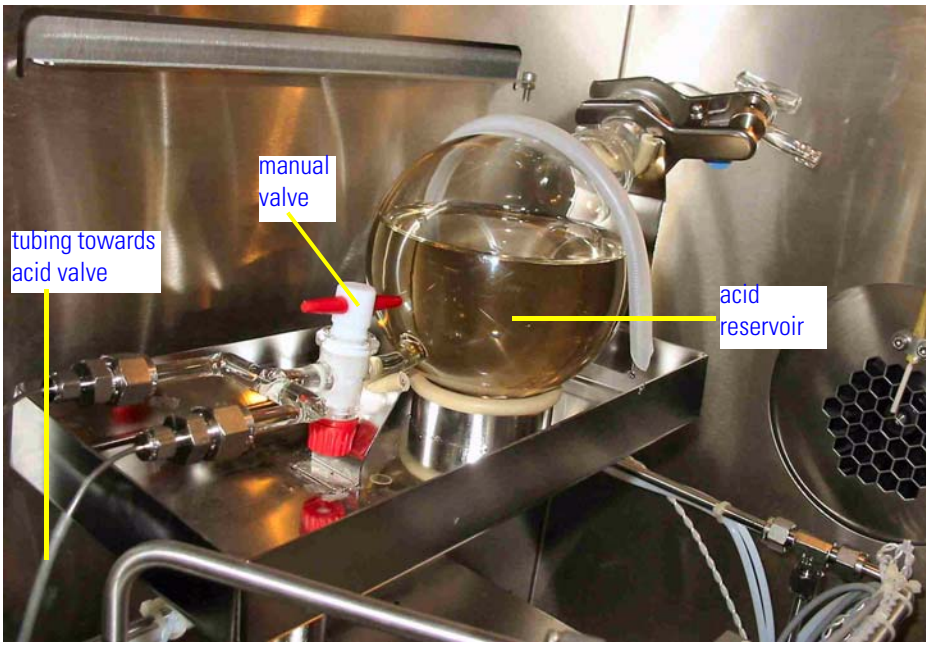
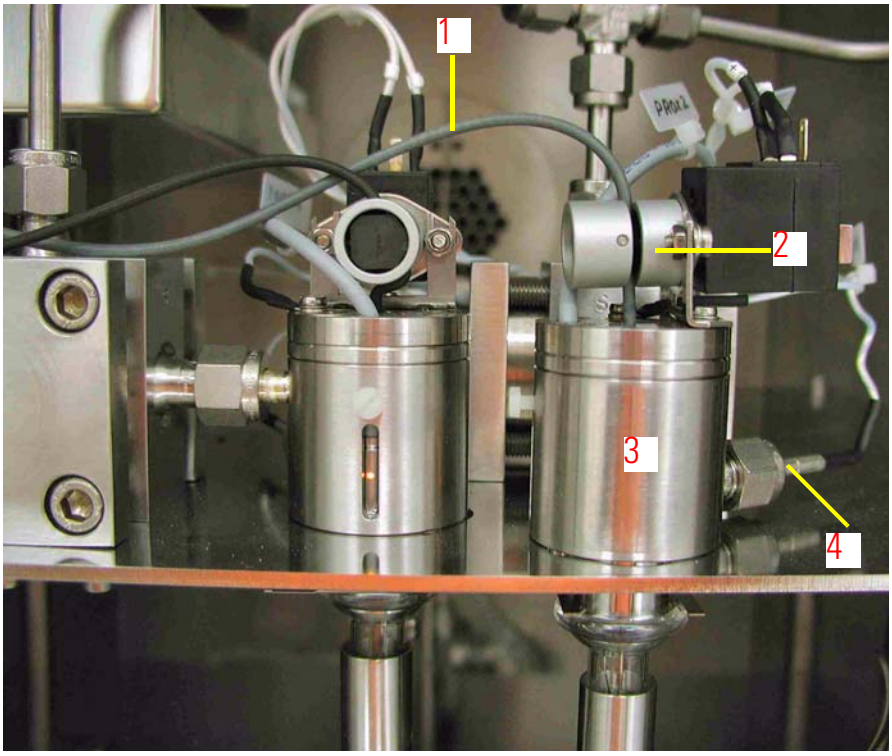


Figure 2-58. Acid Reservoir and Manual Valve

Figure 2-57 schematically shows the acid flow of the instrument. For its upper part, see also Figure 2-58. For its lower part, see also Figure 2-59.



1 Viton tubing from reservoir
2 pinch valve
3 "acid valve"
4 drop counter connection

Figure 2-59. Pinch Valve and Drop Counters

Pinch Valve

The pinch valve is shown in Figure 2-60 (mounted), Figure 2-61 (disassembled), Figure 2-62 (with acid tubing) and Figure 2-63 (connected to acid valve).

1 drop counter assembly
2 drop counter electrical connection

Figure 2-60. Pinch Valve - Mounted

Figure 2-61. Pinch Valve - Disassembled

Figure 2-62. Feeding Acid Tubing into Pinch Valve

Figure 2-63. Mounting Pinch Valve upon Acid Valve

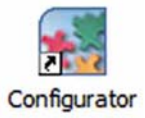
Chapter 3 Isodat 2.5

This chapter outlines the following topics:

Creating a Kiel IV Carbonate Device Configuration

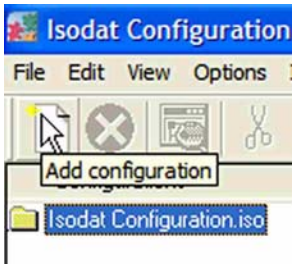
Note Do not create a Kiel III Carbonate configuration! ▲

To create a new Kiel IV Carbonate Device configuration:



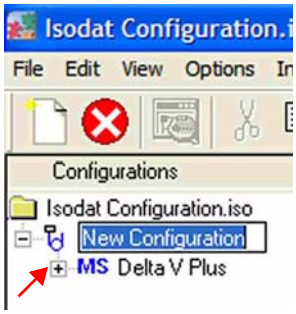
Start Isodat 2.5's Configurator.

Figure 3-1. Opening Configurator



Click the **Add Configuration** button.

Figure 3-2. Adding a New Configuration

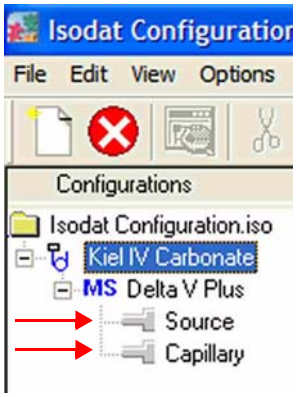


Replace **New Configuration** by a significant name, e.g. **Kiel IV Carbonate**.

The new configuration contains the IRMS you previously specified, e.g. Delta V Plus.

Click on its + symbol.

Figure 3-3. Renaming the New Configuration



The tree of the IRMS will be expanded. The ports **Source** and **Capillary** become visible.

Figure 3-4. Expanding Tree of IRMS

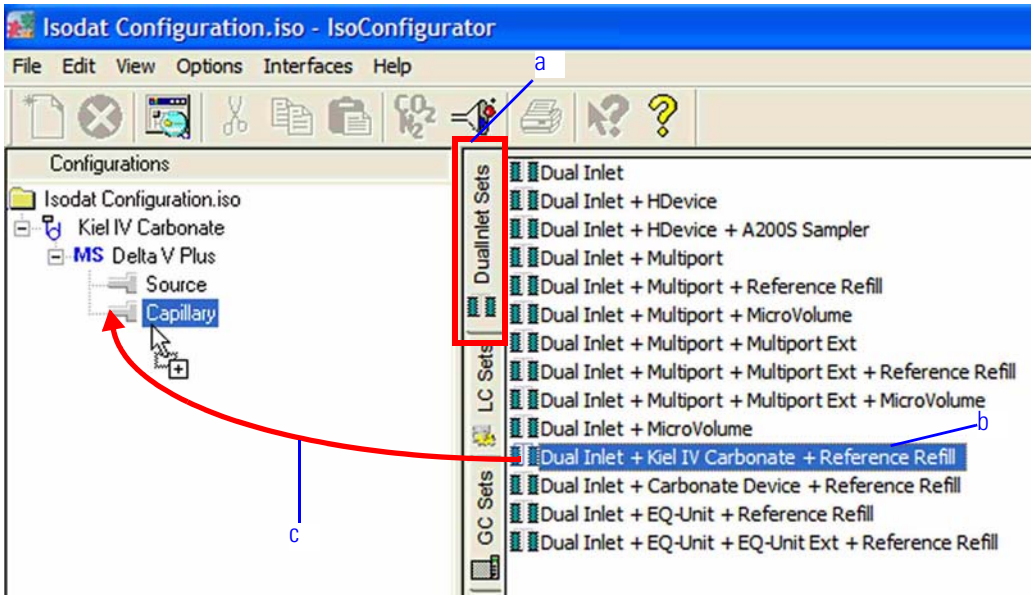
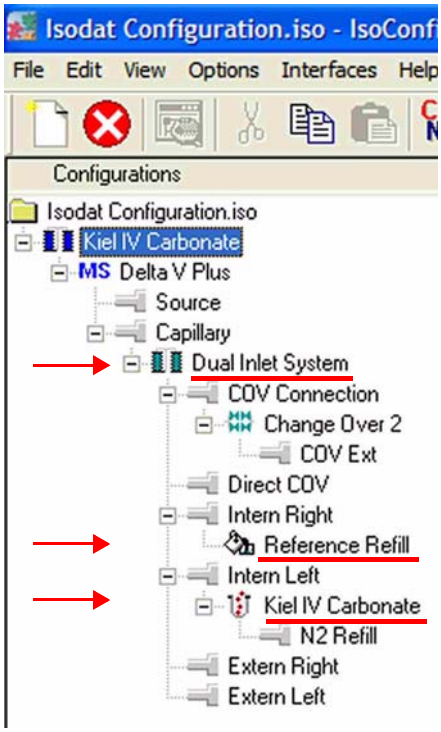


Figure 3-5. Appending Kiel IV Carbonate Set to IRMS

a. Click on the **Dual Inlet Sets** tab.

b. Among the Dual Inlet Sets in the right pane, mark the one that contains the Kiel IV Carbonate Device, that is **Dual Inlet+Kiel IV Carbonate+Reference Refill**.

c. Drag&drop it to **Capillary** port in the left pane.



The entire Kiel IV Carbonate Device has been appended to the capillary port.

Clicking on the + signs unfolds the tree showing the individual components of the device.

Close the Configurator. All settings will be saved automatically.

Figure 3-6. Kiel IV Carbonate Device Appended to Capillary Port

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 4991

Starting Acquisition Mode

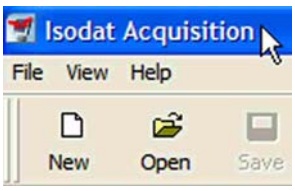
Start Isodat 2.5 by a double-click.

Start Acquisition Mode.

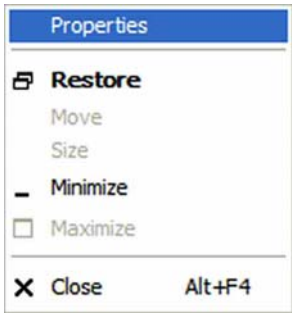
You are now able to run any application which gives you full control over the automated measurement.

Activating Toolbars

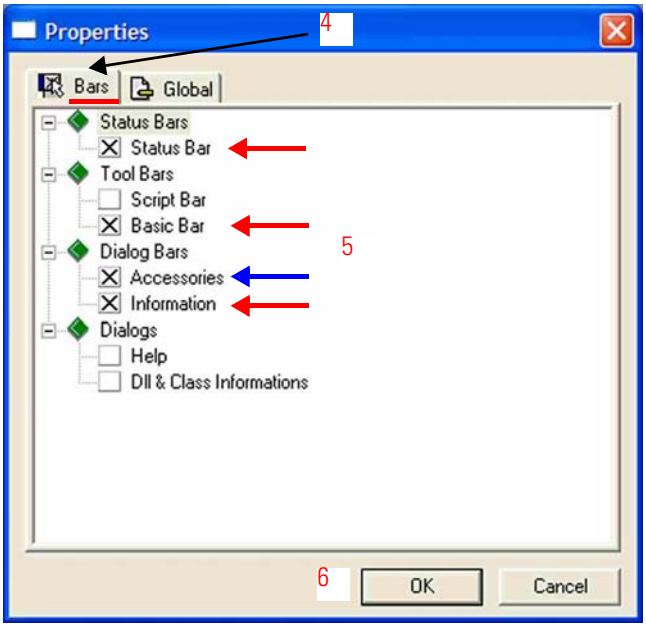
Note It is recommended to check first, whether the following toolbars (that is dialog bars) are activated. Proceed as follows. ▲



1. Move your cursor to the title bar **Isodat Acquisition**.
2. Right-click on it.



3. Select **Properties**.



4. Select the **Bars** tab.

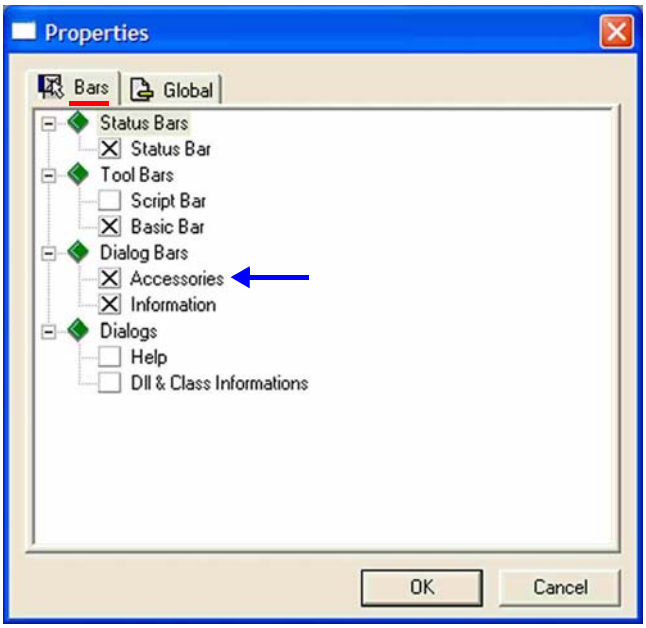
5. Select the toolbars to be displayed. We recommend to primarily select **Status** bar, **Basic** bar, **Accessories** bar and **Information** bar.

6. Confirm by ***OK***. The bars will appear in the **Acquisition** window

Figure 3-7. Visibility of Individual Toolbars*

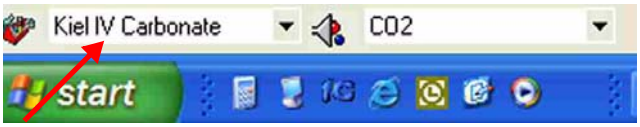
*The individual bars mentioned in Figure 3-7 are described in detail in the ISODAT *NT Operating Manual*, Part No. 109 2481.

Accessories Bar and its Components



1. In order to display the **Accessories** bar at all, mark the corresponding checkbox at **Bars** tab.

Note It is important that you have already created a configuration that contains the Kiel IV Carbonate Device, e.g. **Kiel IV Carbonate**. Refer to "Creating a Kiel IV Carbonate Device Configuration" on page 3-2. ▲



The **Status** bar displays

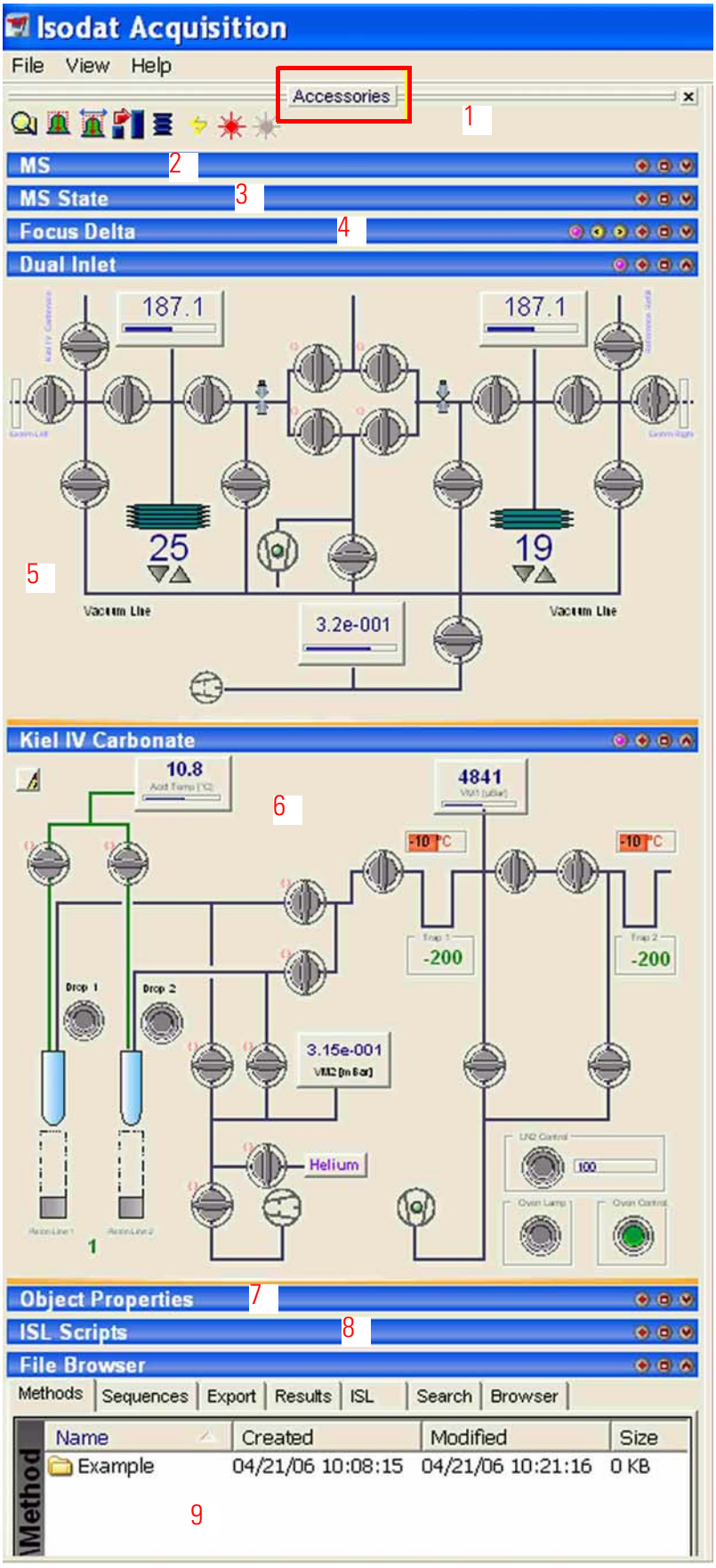
- the actual configuration (e.g. **Kiel IV Carbonate**)
- the actual Gas Configuration (e.g. **CO2**).

2. Select just this configuration.

Figure 3-8. Status Bar

The **Accessories** bar displays the selected configuration together with its configured features (as previously defined in the Configurator).
See Figure 3-9.

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



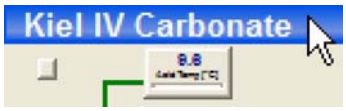
The **Accessories bar** contains information about:

1	Quick Access buttons
2	Readout of high voltage, magnet current and ion source pressure (MS)
3	MS State of heaters
4	Voltage settings in the ion source (Focus Delta)
5	Dual Inlet window See "Dual Inlet Window" on page 3-8.
6	Kiel IV Carbonate window See "Kiel IV Carbonate Window" on page 3-8.
7	Object Properties
8	A lot of running scripts are displayed (ISL Scripts)
9	File Browser

Figure 3-9. Components of Accessories Bar

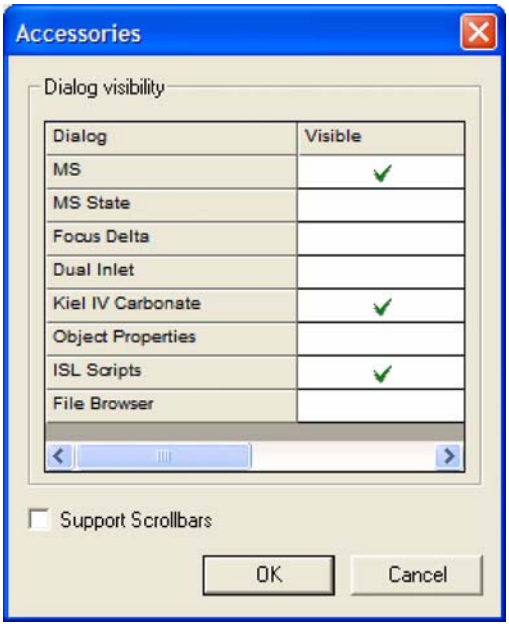
Changing Visibility of its Components

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



1. **Right-click** on an arbitrary title bar (e.g. **Kiel IV Carbonate**).

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



3. Mark the information to be displayed on the Accessories bar, e.g. Kiel IV Carbonate.

4. Unmark the information not to be displayed on the Accessories bar, e.g. ISL Scripts.

5. Confirm by **OK**.

Figure 3-10. Marking or Unmarking Accessories

Kiel IV Carbonate Window

The **Kiel IV Carbonate** window is shown as **6** in Figure 3-9. It will be discussed in detail at "Elementary Handling of Kiel IV Carbonate Device" on page 4-22.

Dual Inlet Window

The **Dual Inlet** window is shown in Figure 3-11 and as **5** in Figure 3-9.

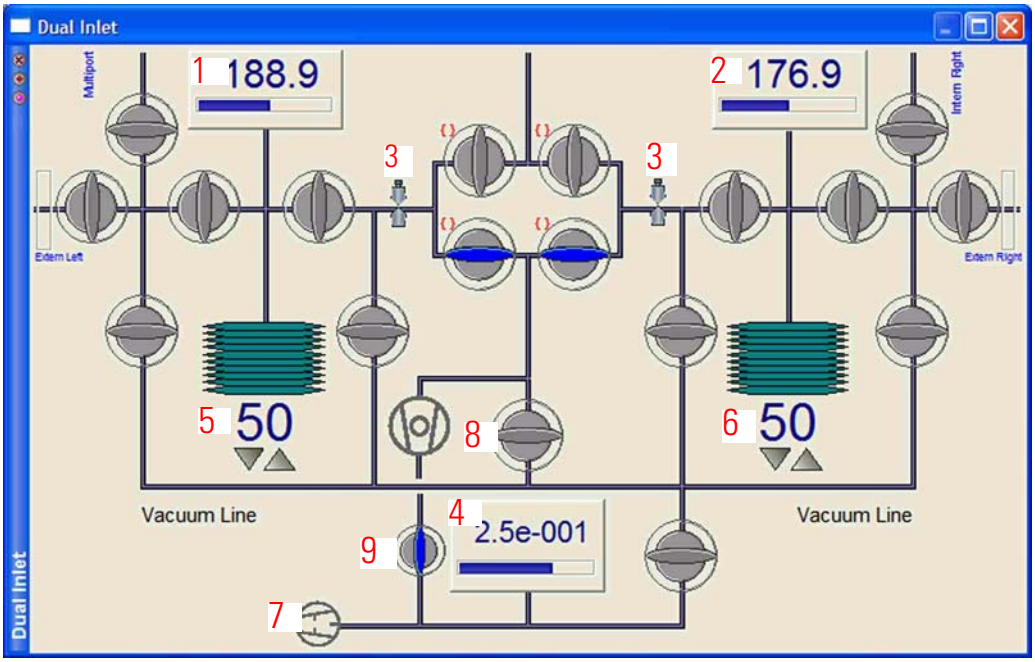


Figure 3-11. Dual Inlet Window

Table 3-1. Indications of Dual Inlet Window*

No.	Indication	Refer to
1	actual pressure of left side of Dual Inlet system (in mbar)	pressure transducer, 1 in Figure 4-2
2	actual pressure of right side of Dual Inlet system (in mbar)	pressure transducer, 1 in Figure 4-2
3	optical reminder of the crimp position of a capillary	
4	actual fore vacuum pressure in mbar measured by a Pirani gauge (as fore vacuum gauge of Dual Inlet system)	
5	volume proportion of left bellow (in %)	
6	volume proportion of right bellow (in %)	
7	Dual Inlet system fore pump	"Dual Inlet System Fore Pump" on page 2-30
8	Dual Inlet system turbo pump	"Dual Inlet System Turbo Pump" on page 2-27
9	Additional valve	"Additional Valve" on page 2-30

*Refer to Figure 3-11.

Operation of Changeover Valve

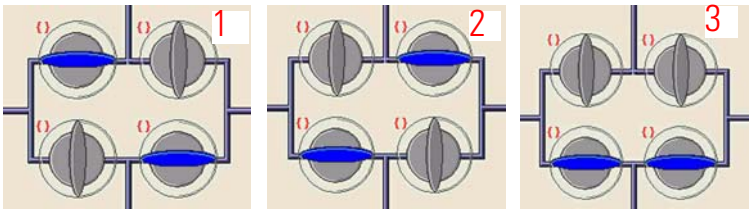


Figure 3-12. Switching Positions of Changeover Valve

Changeover Valve can be switched to three different positions described in Figure 3-12 and Table 3-2:

Table 3-2. Switching Positions of Changeover Valve

No.	Designation	Comment
1	Changeover Left	The left side capillary is opened to the ion source while the right side capillary is opened to Dual Inlet system turbo pump.
2	Changeover Right	The right side capillary is opened to the ion source while the left side capillary is opened to Dual Inlet system turbo pump.
3	Changeover Closed	Both capillaries are pumped by Dual Inlet system turbo pump.

Usually, the Changeover Valve is controlled by Isodat 2.5 in order to accomplish a Dual Inlet measurement. A flowchart of this basic measurement is shown in Figure 3-13.

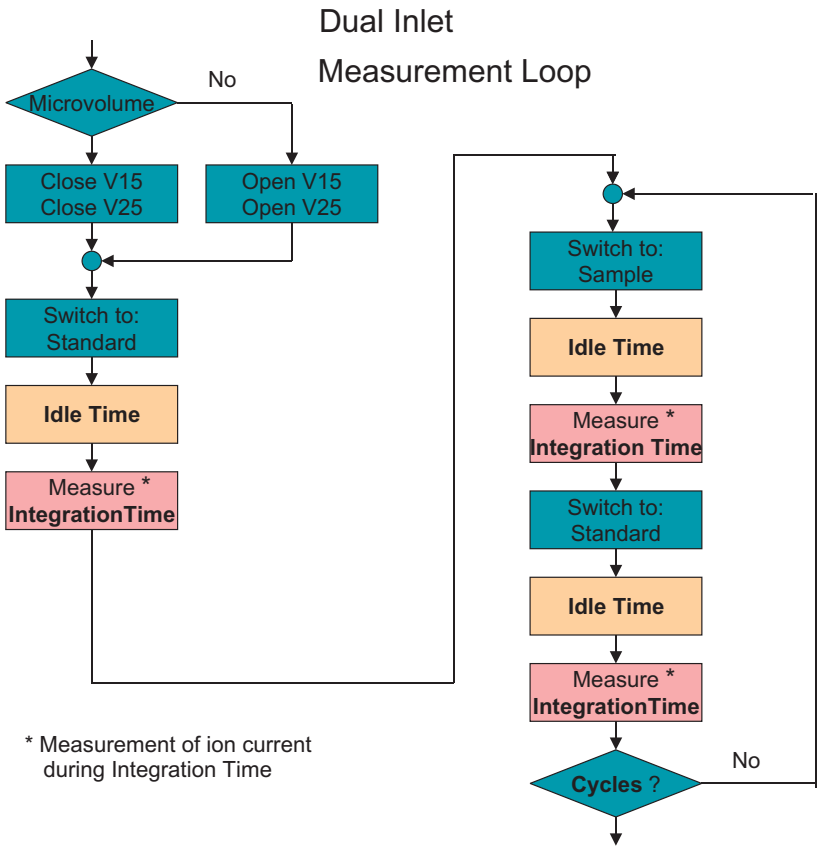


Figure 3-13. Dual Inlet Measurement Loop

Two important time constants can be adjusted in the Dual Inlet method:

- Idle time (Figure 3-14, is **Pre Delay** in Figure 3-13) and
- Integration time (Figure 3-15)

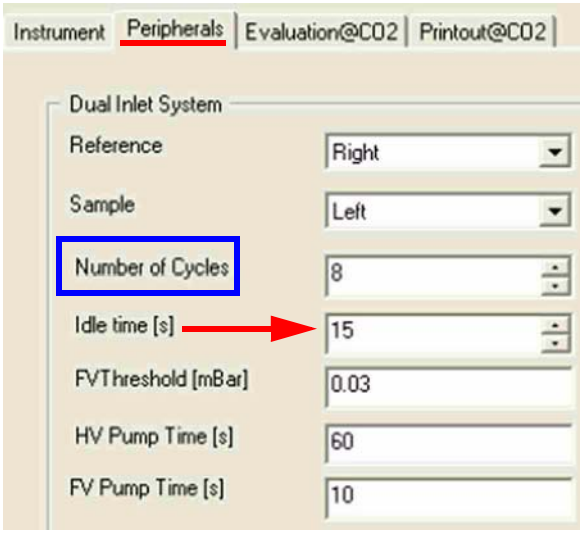


Figure 3-14. Setting Idle Time

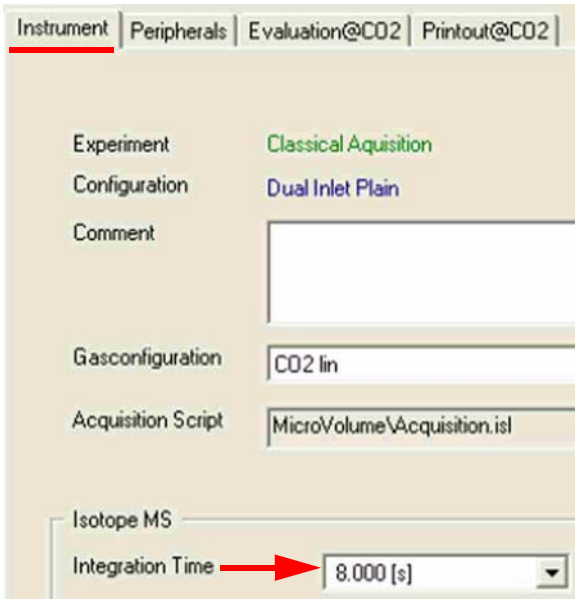


Figure 3-15. Setting Integration Time

Shot Noise Limits of Precision in Dual Inlet Measurements

Figure 3-16 displays how precision (one σ value) varies when integration time and amplitude are changed. Higher amplitudes and longer integration times result in enhanced measurement precision (that is low standard deviation of the n repetitions with n selected at **Number of Cycles** in Figure 3-14, e.g. n=8).

Thus, it can be used to select a reasonable integration time for a given measurement and to calculate the precision that can be expected.

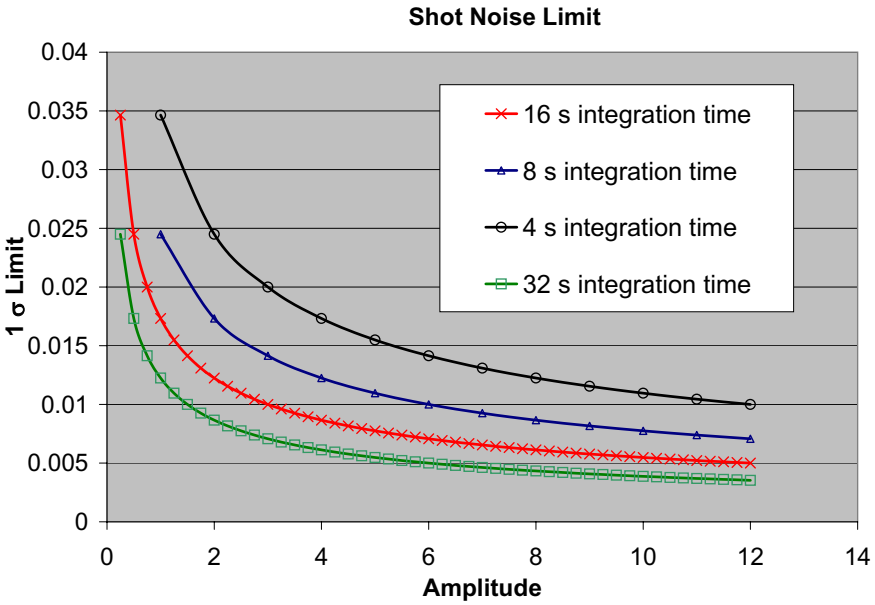


Figure 3-16. Shot Noise Limits of Precision

The diagram contains the results of a calculation for the shot noise (statistical noise) on a cup, taking into account the integration time, the resistor of the cup and the signal height in that cup. The sample calculation is taken out for the middle cup and thus is true for $\delta\ ^{13}C$. For $\delta\ ^{18}O$ roughly multiply the results by 1.4.

The same mathematics is used with the calculations that are contained on the **All Products** CD supplied by our marketing department.

When we talk about precision here, we call it "internal precision". This number is reported as "Standard Deviation" in the output grid. Standard deviation σ ("Std. deviation" column in Figure 3-76) is given by:

$$\sigma = \frac{1}{\sqrt{n-1}} \cdot \sqrt{\sum_{n} (\delta - \delta_{mean})^2}$$

where n denotes the number of repetitions.

Note This is not the number reported as "standard error" although in discussion both are often mixed up. ▲

The "Standard Error" is a number that is generally smaller because it takes into account the repetitions of the measurement (number of cycles - usually set to 8). The standard error is also reported in the output grid and represents the error in determining the average of a distribution (in

our case the average δ value of the n repetitions of individual measurements). Standard error σ_e ("Std. error" column in Figure 3-76) is related to standard deviation σ as follows:

$$\sigma_e = \frac{1}{\sqrt{n}} \cdot \sigma$$

File Browser

The File Browser, also called File Browser bar comprises several tabs. See **9** in Figure 3-9 and Figure 3-17.

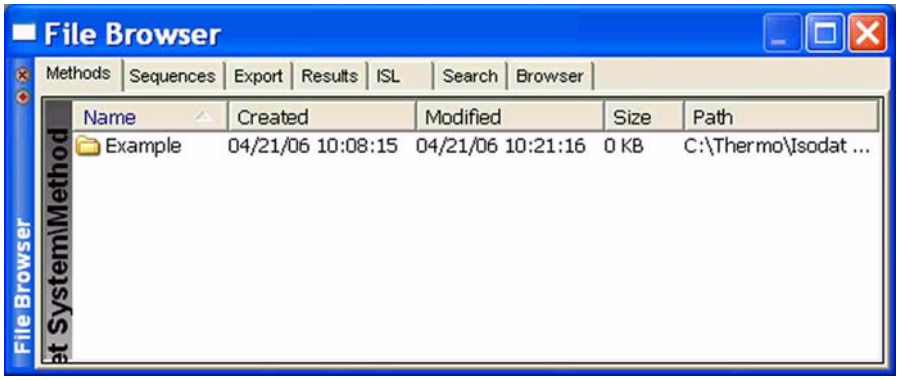


Figure 3-17. File Browser

Methods Tab

- Methods provide the complete description of a single measurement.
- Methods can be programmed or changed by the user.

Refer to "Creating a New Method" on page 3-20.

Caution Take the displayed methods only as a guideline. Do not use them for measurements! For measurements, always create your own methods! ▲

Sequences Tab

- 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).

Refer to "Creating a New Sequence" on page 3-31.

Caution Take the displayed sequences only as a guideline, but do not use them for measurements! For measurements, always create your own sequences! ▲

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

The predefined methods and sequences delivered by Thermo Electron 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 Kiel IV Carbonate Device 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 2.5's Result Workshop to select and display particular aspects of your acquisition data.

Refer to **Result Workshop** in ISOAT *NT Operating Manual - Upgrade to Version 2.0*; Part No. 115 4991.

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 using this feature frequently. ▲

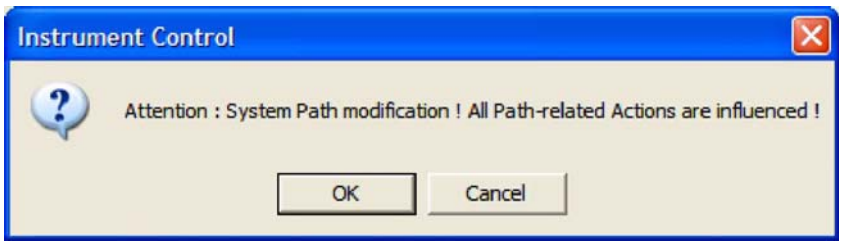


Figure 3-18. Modifying Result Path

From now on, all method, sequence and result files will be stored at a different location. See Figure 3-18.

ISL Tab Refer to ISODAT NT Operating Manual - Upgrade to Version 2.0; Part No. 115 4991.

Note All acquisition scripts are usually named **acquisition.isl**, no matter to which application they belong (e.g. GasBench II, ConFlo III or Kiel IV Carbonate Device).
However, they are stored in separate folders (e.g. in a particular Kiel IV Carbonate Device folder at C:\Thermo\Isodat NT\Global\ISL\Kiel IV Carbonate). ▲

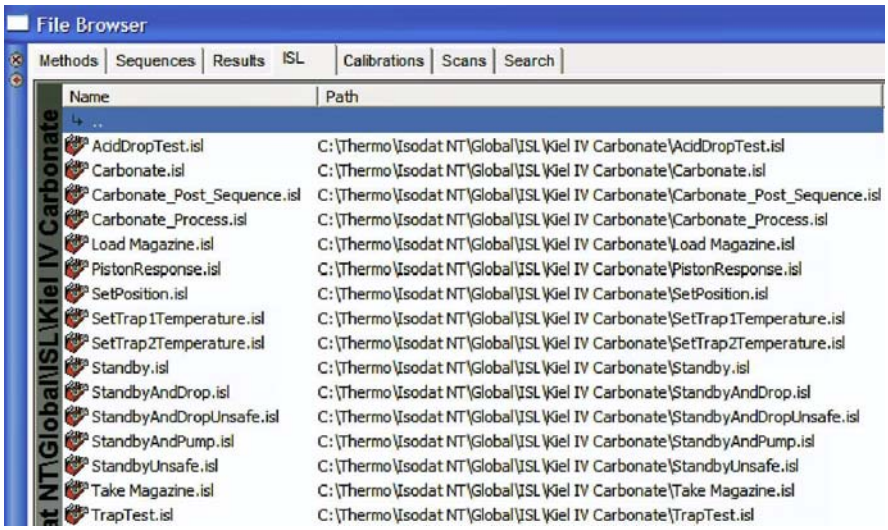


Figure 3-19. Location of ISL Scripts for Kiel IV Carbonate Device

Calibrations Tab
- shows the mass calibrations for the IRMS

Scans Tab
- Instrument scans can be saved here.

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 browsing to an arbitrary directory of your choice, even to a root of a harddisk drive.
- As with other file managers, files and folders can be created, moved or deleted.

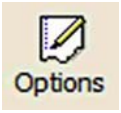
Info Window

In the **Info** window, information during the process of data acquisition appears online. It displays the content of the info log files as well.

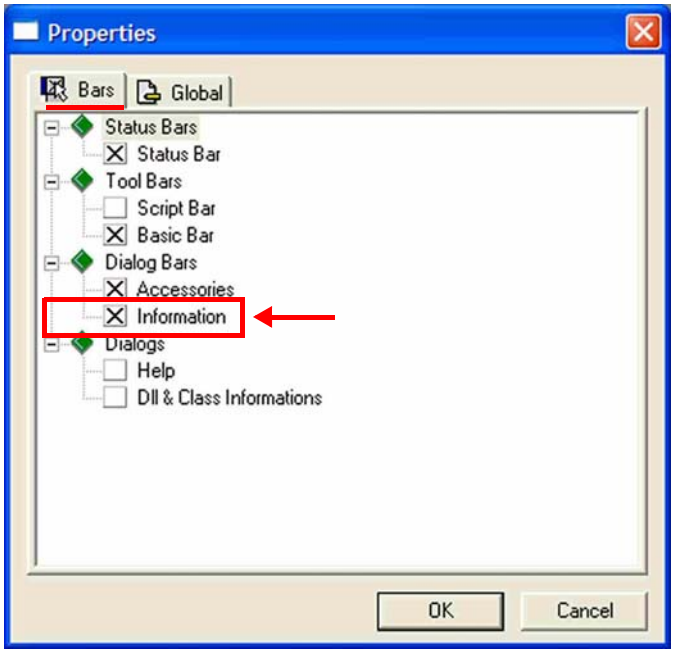
Activating Info Window

Ensure that the **Info** window will indeed be displayed as follows:

Open **Acquisition** mode.



Press **Options** button.

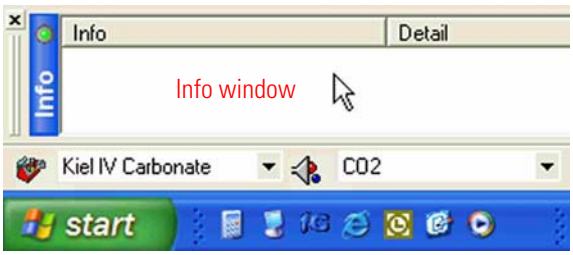


Choose **Bars** tab.

Mark **Information** checkbox.

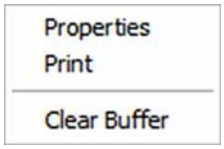
Confirm by **OK**.

After the **Info** window has been activated, it will appear beneath the **Accessories** bar. See Figure 3-20.



Right-click somewhere into the **Info** window.

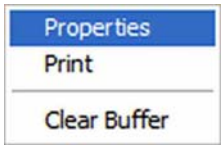
Figure 3-20. Info Window



Properties: Log file activation and filter handling for **Info** window
Print: Print online information.
Clear Buffer: Clear buffer of **Info** window.

Figure 3-21. Commands for Using Info Window

Properties Command



If you choose **Properties**, the window shown in Figure 3-22 will appear.

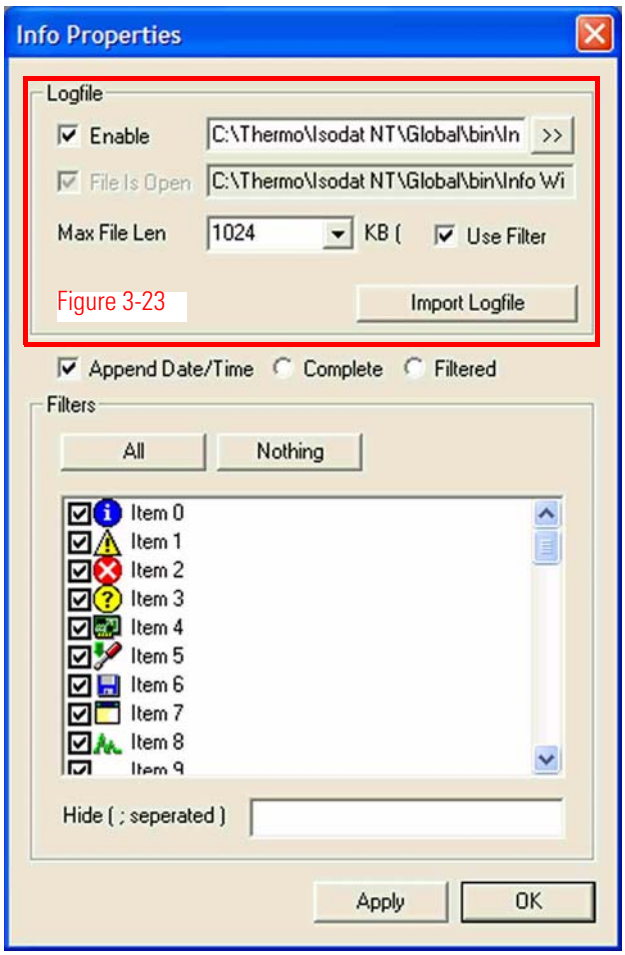


Figure 3-22. Info Properties Window

In general, all changes are effective globally, that is for all other Isodat 2.5 configurations.

Note During an acquisition, import and sharing of the log file are deactivated. A notation indicating a sharing violation appears. Importing a log file is only allowed during idle acquisition. Opening an ASCII log file in an appropriate program (e.g. MS Editor™) is only allowed, if Isodat 2.5 is entirely closed. ▲

Enabling Log File

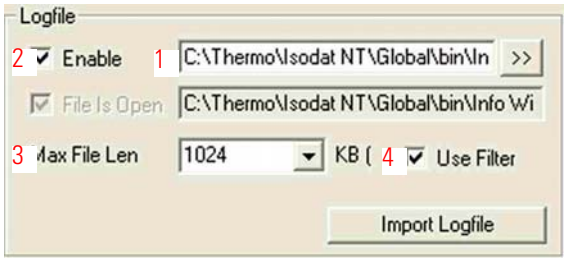


Figure 3-23. Enabling Log File*

* upper part of Figure 3-22

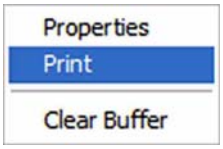
- A log file will be permanently saved at the assigned file location. Default is C:\Thermo\Global\bin\ Info Window Log Files\Workspace\Info.txt. See **1** in Figure 3-23.

- Choose the size of the log file at **3**.

Note The log file is stored in ASCII format. This allows to save huge amounts of information. Therefore, it is not necessary to activate the filter for the log file. See **4**. ▲

- Use the filter explained below for the online printout.

Print Command



Use this command to print the log file.

Then, select your printer and the printer settings you prefer.

Note During an acquisition, move the mouse pointer onto the **Acquisition** bar in order to reactivate the acquisition. ▲

Now, you can click the **Print** button to print the total current "online information" directly while the acquisition is running.

Offline View

Info	Detail
[02/10/06 13:37:48] 0 files saved.	
[02/10/06 13:37:48] Result Path	C:\Finnigan\Isodat NT\Global\User\Dual Inlet System\Results\ACQ-Results\
[02/10/06 13:37:51] Sample ISL Script 0	
[02/10/06 13:37:52] ResetRatioPlotControls	0
[02/10/06 13:37:53] Prepare Run - Start	
[02/10/06 13:37:53] Pump COV Sample Side 3 [Sec]	
[02/10/06 13:38:02] Set Trap 1 to 150 [°C]	
[02/10/06 13:38:02] Set Trap 2 to 150 [°C]	
[02/10/06 13:38:03] Set Trap 1 to 150 [°C]	
[02/10/06 13:38:54]	
[02/10/06 13:38:54] <Action Thread Done>	514.508
[02/10/06 13:38:54] The running Script 'Acquisition.isl' returns an Error - 'Script terminated by User'	
[02/10/06 13:38:54] Method	The running Script 'Acquisition.isl' returns an Error - 'Script terminated by User'
[02/10/06 13:38:54] Acquisition Warning !	
[02/10/06 13:38:56] Sequencer	Terminate Sequence !
[02/10/06 13:38:56] Sequencer	Sequence finished !

Figure 3-24. Offline View

Creating a New Method

Isodat 2.5's **Acquisition** mode allows fully automated isotope ratio determination of carbon (CO_2) and oxygen of carbonate samples. All parameters relevant for data acquisition of a sample are stored in a method.

Note For an extensive description of the options of the method definition, refer to ISODAT *NT Operating Manual* (Part No. 109 2481). This section describes only the entries that are specific for operating the Kiel IV Carbonate Device. ▲

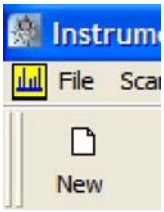
Caution You must create and save a new method on your own! The predefined methods delivered by Thermo Electron in the **Examples** folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! Never overwrite an example file with a method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

The following steps are needed to create a new method.

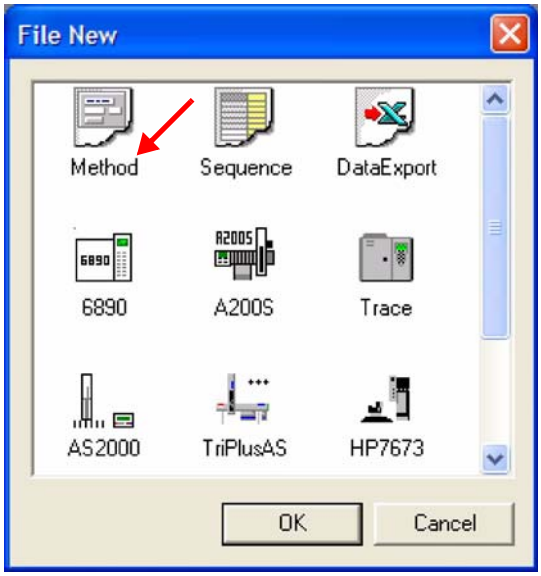
1. Open **Acquisition** mode.

2. Select a configuration for Kiel IV Carbonate Device applications, e.g. **Kiel IV Carbonate**.

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



4. Press the **New** button.



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

6. Confirm by **OK**.

7. Proceed with "Structure of Methods for Kiel IV Carbonate Device" on page 3-21.

Figure 3-25. Creating a New Method

Structure of Methods for Kiel IV Carbonate Device

All Kiel IV Carbonate Device methods are organized by the following tabs:

- **Instrument** tab
- **Peripherals** tab
- **Evaluation** tab
- **Printout** tab

Note In **Evaluation** tab and **Printout** tab, the currently active Gas Configuration is indicated. For example, Evaluation@CO2 alludes to CO2, whereas Evaluation@N2 alludes to N2. ▲

The following values are a guideline explaining the parameters for a CO_2 method using a Finnigan Kiel IV Carbonate Device and a Reference Refill.

As soon as a Kiel IV Carbonate Device configuration has been created, a predefined and stored method named **Kiel_Carbo.met** exists.

Instrument Tab

Experiment

Figure 3-26 shows the **Experiment** part of **Instrument** tab.

Figure 3-26. Instrument Tab - Experiment

Table 3-3. Instrument Tab - Experiment

No.	Parameter	Description
a	Comment	Per default, this field is empty. You can type in comments about Method, Acquisition Script, Time Events, etc.
b	Gasconfiguration	Select the appropriate entry, e.g. CO2. Usually, the default entry can be accepted. Refer to the Status bar in "Accessories Bar and its Components" on page 3-5.
c	Acquisition Script	Select an appropriate acquisition script by a click on the button. Acquisition.isl is the default entry and can usually be accepted. It controls the acquisition cycle. To edit the acquisition script, press the button.

Caution An acquisition script should only be edited by users trained on script editing, debugging and error tracking. Otherwise, potential errors within scripts, which are due to editing, may be hardly discovered afterwards. ▲

Isotope MS

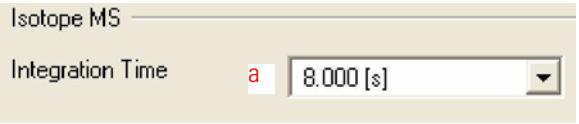


Figure 3-27. Instrument Tab - Isotope MS

Table 3-4. Instrument Tab - Isotope MS

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

Peak Center

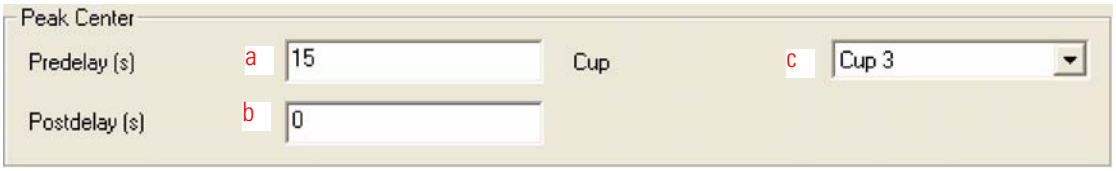


Figure 3-28. Instrument Tab - Peak Center

Table 3-5. Instrument Tab - Peak Center

No.	Parameter	Description
a	Predelay [s]	waiting time between activation of reference gas and start of peak center cycle
b	Postdelay [s]	waiting time between end of peak center cycle and start of data acquisition
c	Cup	Select the Peak Center cup, e.g. cup 3 as narrow center cup in a triple collector.

Reference Refill

Some important parameters concerning the vacuum in the Reference Refill can be preset according to Figure 3-29 and Table 3-6.

Figure 3-29. Instrument Tab - Reference Refill

Table 3-6. Instrument Tab - Reference Refill*

No.	Parameter	Description
a	Pump Overlay Time	capillary pump out time of Reference Refill tank
b	Refill Time	gas flow time from Reference Refill tank into inlet port of standard bellow
c	FV Threshold	minimum pressure of standard bellow including valves and tubes evacuated with fore pump before pumping with turbo pump
d	HV Pump Time	pump time of bellows - including valves and tubes - with turbo pump

*For further details, refer to "Reference Refill" on page 5-22.

Peripherals Tab

By means of the elements of **Peripherals** tab, you determine the properties of some peripheral options in the active method.

Dual Inlet System

Here, you determine some properties for the Dual Inlet system.

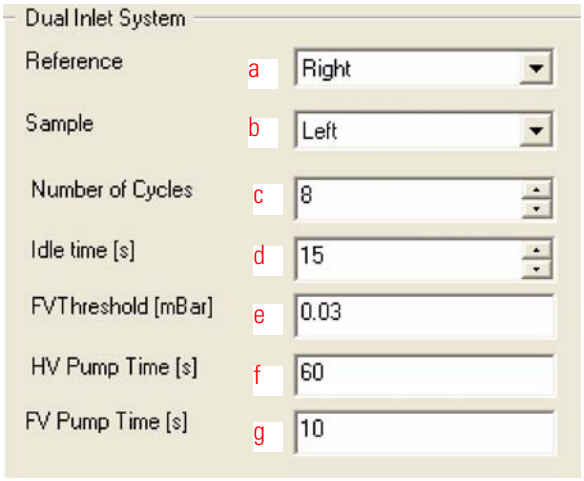


Figure 3-30. Peripherals Tab - Dual Inlet System

Table 3-7. Peripherals Tab - Dual Inlet System

No.	Parameter	Description
a	Reference	where the reference gas is available, that is in the left or right bellow
b	Sample	where the sample is available, that is in the left or right bellow
c	Number of Cycles	Measure e.g. 8 times sample and 8 times standard.
d	Idle Time [s]	waiting time after changing from sample to standard side and vice versa before integrating the ion intensities of m/z 44, m/z 45 and m/z 46
e	FV Threshold [mbar]	This value is used as a reference to the background vacuum reading of the Dual Inlet. The value will be checked prior to each measurement. Exceeding this value causes a fatal script error: a failure with pumps or leak exists. In this case, check the hardware!
f	HV Pump Time [s]	no function in this configuration
g	FV Pump Time [s]	no function in this configuration

Background

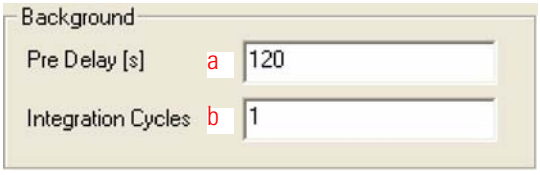


Figure 3-31. Peripherals Tab - Background

Table 3-8. Peripherals Tab - Background

No.	Parameter	Description
a	Pre Delay [s]	waiting time (after the Changeover Valves 31 and 33 have been closed) until the real mass spectrometer background will be measured

Table 3-8. Peripherals Tab - Background, continued

No.	Parameter	Description
b	Integration Cycles	number of repetitions of the background determination The integration time selected above is used each time.

Pressure Adjust

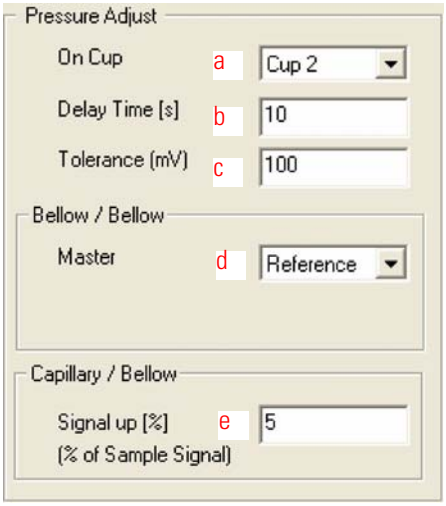


Figure 3-32. Peripherals Tab - Pressure Adjust

Table 3-9. Peripherals Tab - Pressure Adjust

No.	Parameter	Description
a	On Cup	Always select the cup where m/z 44 is measured.
b	Delay Time [s]	waiting time after changing from sample to standard gas (or vice versa) before matching standard bellow to sample ion intensity Prior to each press adjust determination, this time will elapse as a predelay. It appears as "Equlilibration Time" in the Info Window.
c	Tolerance [mV]	maximum acceptable ion intensity difference between sample and standard after matching (e.g. 50 mV meaning ± 25 mV) If tolerance is exceeded, the press adjust will be repeated.
d	Master	The standard bellow at the right side must be adjusted to the level of sample ion intensity minus signal up ± tolerance. For carbonate applications, always take sample (e.g. if left = 4200 mV, match the right bellow to 4200 mV - 100 mV ± 25 mV).
e	Signal Up [%]	Match the ion intensity of standard gas less than e.g. 100 mV before closing V 25 and starting the Dual Inlet acquisition. After V 25 is closed, the signal will increase. The exponential relationship to the pressure in the tubing before the crimp and V 25 is approximately considered to be a linear one.

Time Slicing

Figure 3-33. Peripherals Tab - Time Slicing

Table 3-10. Peripherals Tab - Time Slicing

No.	Parameter	Description
a	Slices	The single integration time specified in "Instrument" tab (see Figure 3-27) will be replaced by this number of individual integrations.
b	Slope Threshold	
c	Outlier Test	

Carbonate Device

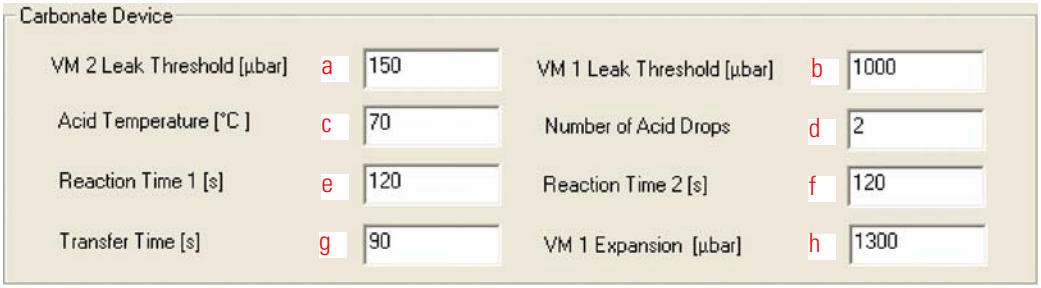


Figure 3-34. Peripherals Tab - Carbonate Device

Table 3-11. Peripherals Tab - Carbonate Device

No.	Parameter	Description
a	VM2 Leak Threshold [µbar]	After connecting the vial and pumping it (e.g. line 1, V 7 and V 13 open, V 12 closed), the pressure at the vacuum gauge VM2 must be below this threshold value. Otherwise, an error message will appear and preparation will start with the next sample.
b	VM1 Leak Threshold [µbar]	Maximum pressure rise accepted in any sample vial during leak test. If one of these vials shows a leak, the system skips this sample and starts the next preparation. Line 1 and line 2 are treated separately: here, the fourfold value is accepted. If one of these lines shows a leak, the system stops the whole sequence.
c	Acid Temperature [°C]	The oven temperature (controlled by the Jumo itron 16 temperature controller) must be set to this value. The temperature controller inside the heating cabinet (not the Pt 100 resistor of the Jumo itron 16) acts as the temperature set point!

Table 3-11. Peripherals Tab - Carbonate Device, continued

No.	Parameter	Description
d	Number of Acid Drops	Enter the desired number of acid drops per vial.
e	Reaction Time 1 [s]	Reaction time of carbonate. Time starts as soon as the last acid drop is injected.
f	Reaction Time 2 [s]	Pumpout time of non-condensable gases
g	Transfer Time [s]	CO_2 transfer time from trap 1 to trap 2
h	VM1 Expansion [µbar]	If the CO_2 gas pressure released from trap 1 exceeds this value, the gas will be systematically expanded and pumped until a pressure beneath this threshold is achieved.

Note Transfer time and CO_2 gas pumpout time are set at "Process Timing Tab" on page 3-47. ▲

Evaluation Tab

Cycle

Figure 3-35. Evaluation Tab - Cycle

Table 3-12. Evaluation Tab - Cycle

No.	Parameter	Description
a	Outlier Test	As outlier test, select "None" or "Sigma". The "Sigma" outlier is varying criteria of rejection according the gaussian normal distribution. It simply rejects the values outside a barrier of 1 to n times the standard deviation.

Note The Kiel III Carbonate Device can be used only with Isodat 2.0. This feature is used to import Dual Inlet measurement files that have been recorded with Isodat 2.0. ▲

Extended Parameters

Figure 3-36. Evaluation Tab - Extended Parameters

Table 3-13. Evaluation Tab - Extended Parameters

No.	Parameter	Description
a	Ion Correction Location	New ion corrections can be created by modifying predefined ones and saving them as new ones. They can be imported by Isodat 2.5. Use the folder C:\Thermo\Isodat NT\Global\ISL\Ion Correction for selecting the predefined and storing the new ion corrections.

Evaluation Type

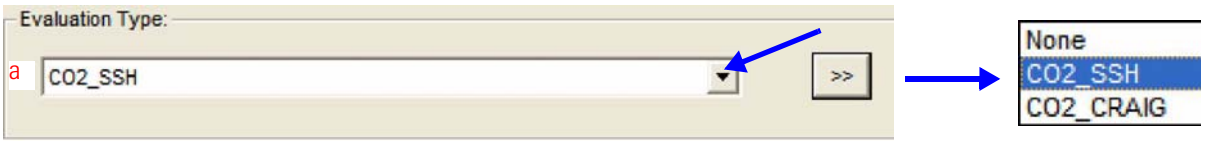


Figure 3-37. Evaluation Tab - Evaluation Type

Table 3-14. Evaluation Tab - Evaluation Type

No.	Parameter	Description
a	Evaluation Type	Select an appropriate ion correction for CO2 data evaluation from the list: "None", "CO2_SSH" (default) or "CO2_Craig". Press the >> button to add own scripts for ion corrections.

Standard Parameter

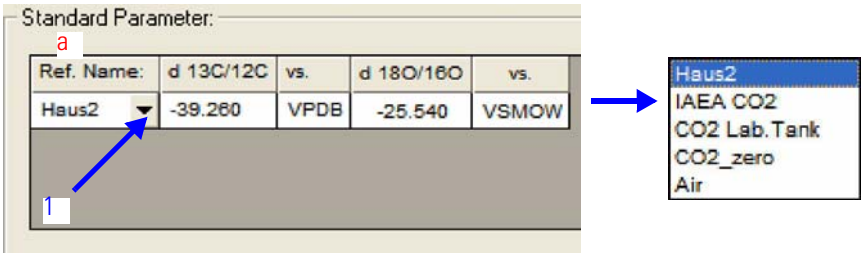


Figure 3-38. Evaluation Tab - Standard Parameter (I)

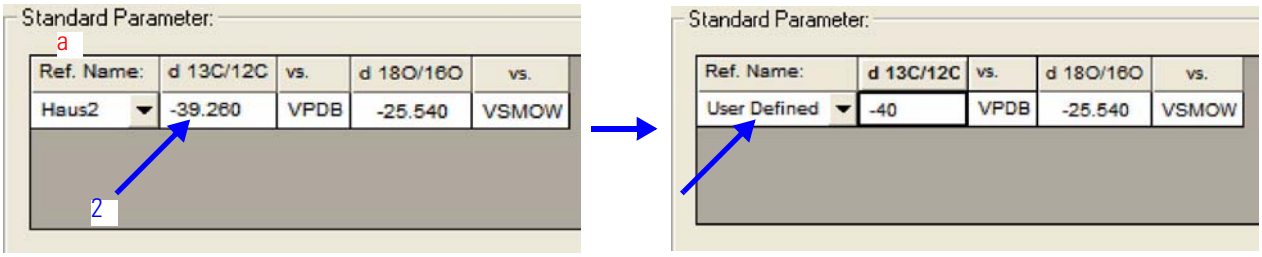


Figure 3-39. Evaluation Tab - Standard Parameter (II)

Table 3-15. Evaluation Tab - Standard Parameter

No.	Parameter	Description
a	Ref. Name	1. Select a Ref. Name from your standard database set in the Standard Editor, e.g. "Haus2" (Figure 3-38) or 2. Edit the related δ values (Figure 3-39). In this case, "User Defined" will be shown at "Ref. Name". 3. New standards can be created in the Standard Editor.

Note For correct reporting of sample δ values, the data entered in this field must resemble the true isotopic values of your reference gas. ▲

Printout Tab

In **Printout** tab, the use of printout templates is controlled. See Figure 3-40.

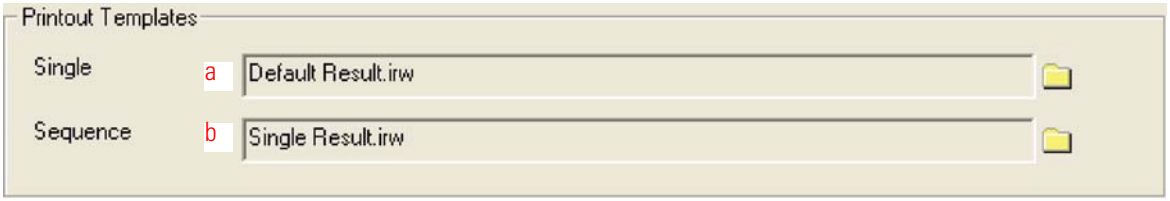


Figure 3-40. Printout Tab

Table 3-16. Printout Tab

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

Saving a Method

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

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

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

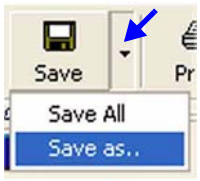
To save a method, proceed as follows:

1. Do one of the following:

Save Command

Click on the **Save** button to save a method 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 method (single document). See Figure 3-41.

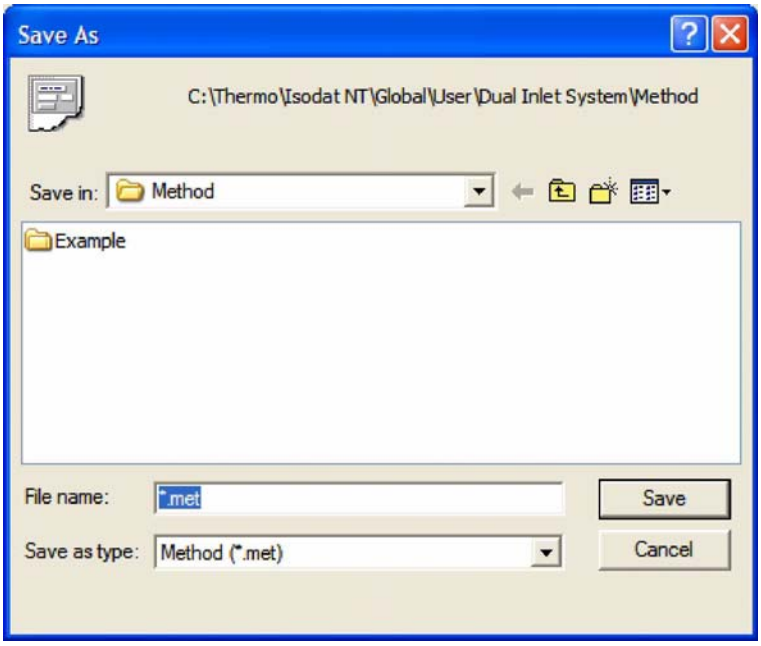
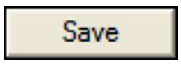


Figure 3-41. Saving a Method

Note Notice that the particular folder is shown that contains the currently active method. See Figure 3-41. ▲

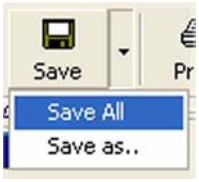
Caution Choose the folder above the **Example** folder, not the **Example** folder itself! This ensures not to mix or even overwrite the predefined example method with your own method. ▲

2. Give the method a significant name, e.g. similar to the sequence it corresponds to. Keep the extension .met.



3. Confirm by **Save**.

Save All Command



Click on the ▾ arrow and choose **Save All** to save all currently active Isodat 2.5 documents (e.g. methods, sequences, result files, Result Workshop files).

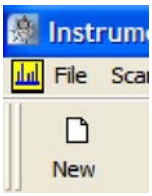
They will be stored without changing names and folders.

Creating a New Sequence

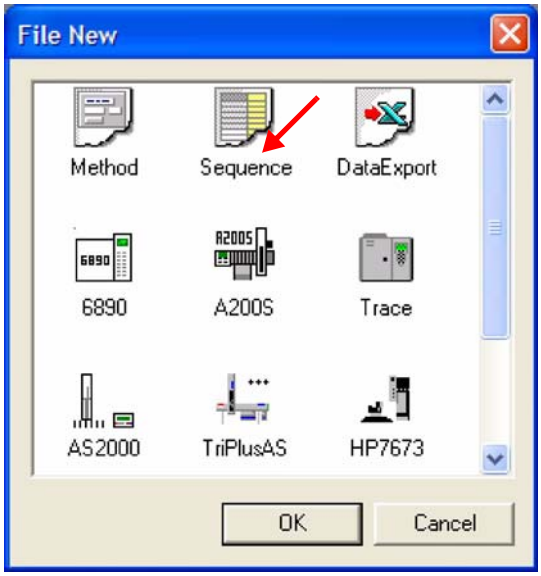
After creating and saving a method (see "Creating a New Method" on page 3-20), a sequence must now be created as follows.

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

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



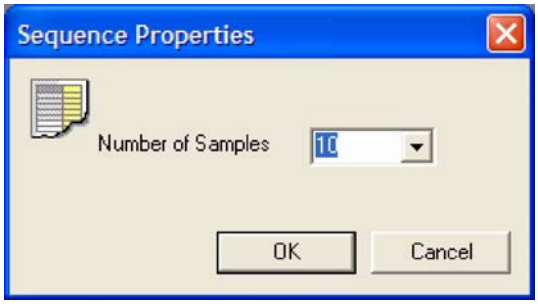
1. Press the **New** button.



2. Click on the **Sequence** icon.

3. Confirm by **OK**.

Figure 3-42. Creating a New Sequence



4. Specify the number of samples, e.g. 10.

5. Confirm by **OK**.

Figure 3-43. Selecting Number of Samples

The sequence grid, Figure 3-44, contains all information about the individual samples bundled together in the sequence. See Table 3-17.

Note Individual columns (e.g. **Line** or **Sample**) can be copied from example sequences. ▲

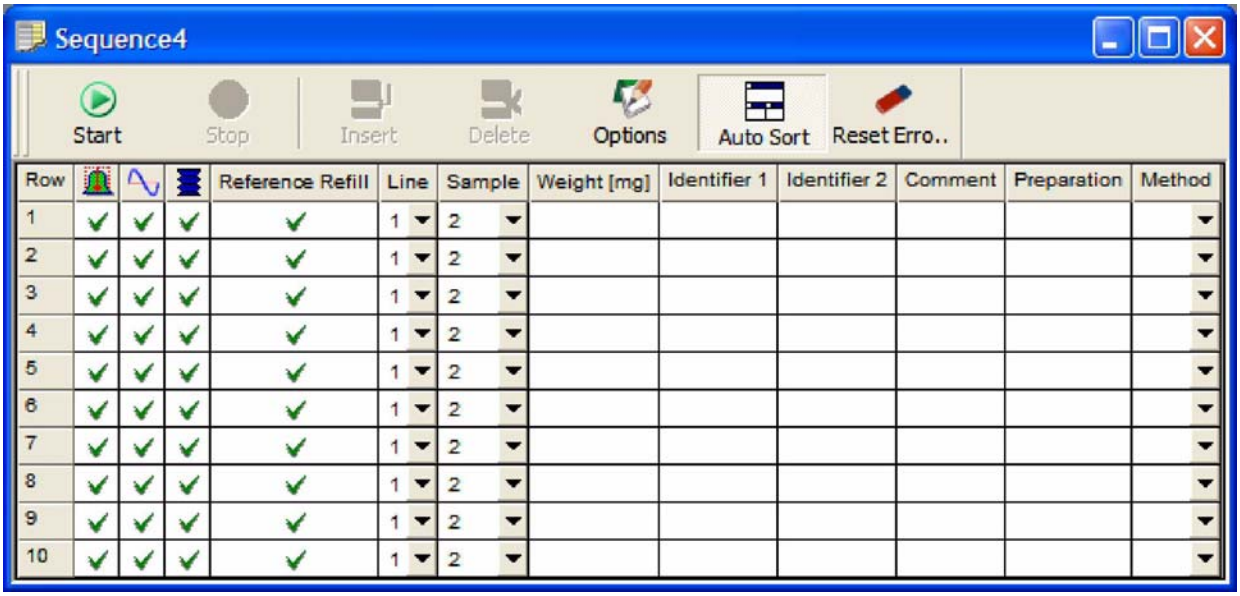


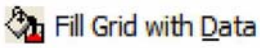
Figure 3-44. Sequence Grid

Table 3-17. Sequence Grid

Parameter	Icon	Description
Row		Each row refers to an individual sample.
Peak Center		Marking it ✓ allows performing a peak center procedure prior to measuring the particular sample. This ensures the peak to be in the middle of the cup. As this standard procedure is time-consuming, save a lot of time by omitting some peak centers. The device is sufficiently stable to operate during a certain time period without a peak center.

Table 3-17. Sequence Grid, continued

Parameter	Icon	Description
Background		Marking it ✔ allows performing a background scan. COV will be closed. The instrument is idle for "Background Pre Delay". See a in Figure 3-31. Then, the current in the three cups will be recorded.
Press Adjust		Marking it ✔ allows performing a press adjust prior to measurement. As press adjust is essential, always mark "Press Adjust"!
Reference Refill		Marking it ✔ allows performing a Reference Refill. Refer to "Reference Refill" on page 5-22. The frequency of the Reference Refill during a sequence depends on the sample amount to be analyzed, on the reference gas amount and on the fill level obtained during a given time period.
Line		Select line 1 or line 2 of the autosampler.
Sample		Select the position of the autosampler's turret.
Weight [mg]		optional, used for sample weight
Identifier 1, 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 at "Creating a New Method" on page 3-20 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 appear.



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:

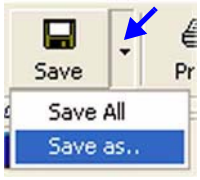
Caution The predefined sequences in the **Examples** folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! ▲

Caution 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 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 sequence (single document).

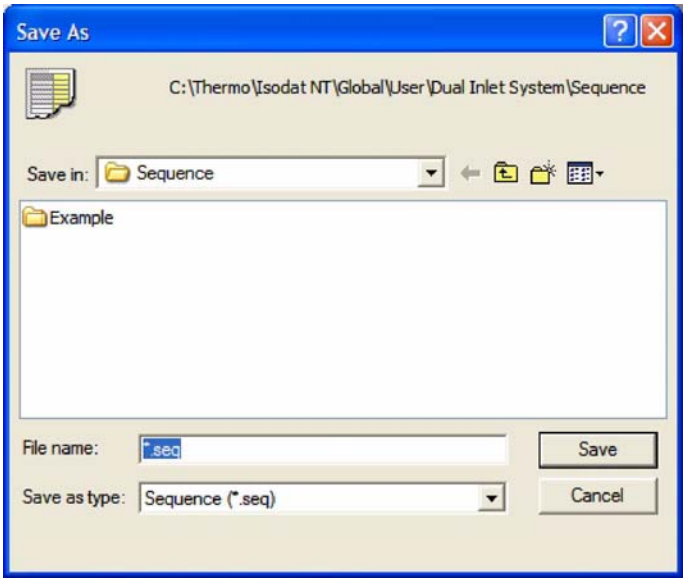
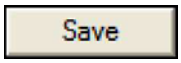


Figure 3-45. Saving a Sequence

Note Notice that the particular folder is shown that contains the currently active sequence. See Figure 3-45. ▲

Caution Choose the folder above the **Example** folder, not the **Example** folder itself! This ensures not to mix or even overwrite the predefined example sequence with your own sequence. ▲

6. Give the sequence a significant name, e.g. similar to the method it corresponds to. Keep the extension .seq.



7. Confirm by **Save**.

Save All Command

Click on the arrow and choose **Save All** to save all currently active Isodat 2.5 documents (e.g. methods, sequences, result files, Result Workshop files). They are stored without changing names and folders.

Starting a Sequence

To start the sequence, proceed as follows:

1. Press the **Start** button.

2. Define Parameters for Results Export, Printout and Sequence Scripts as follows. See Figure 3-46.

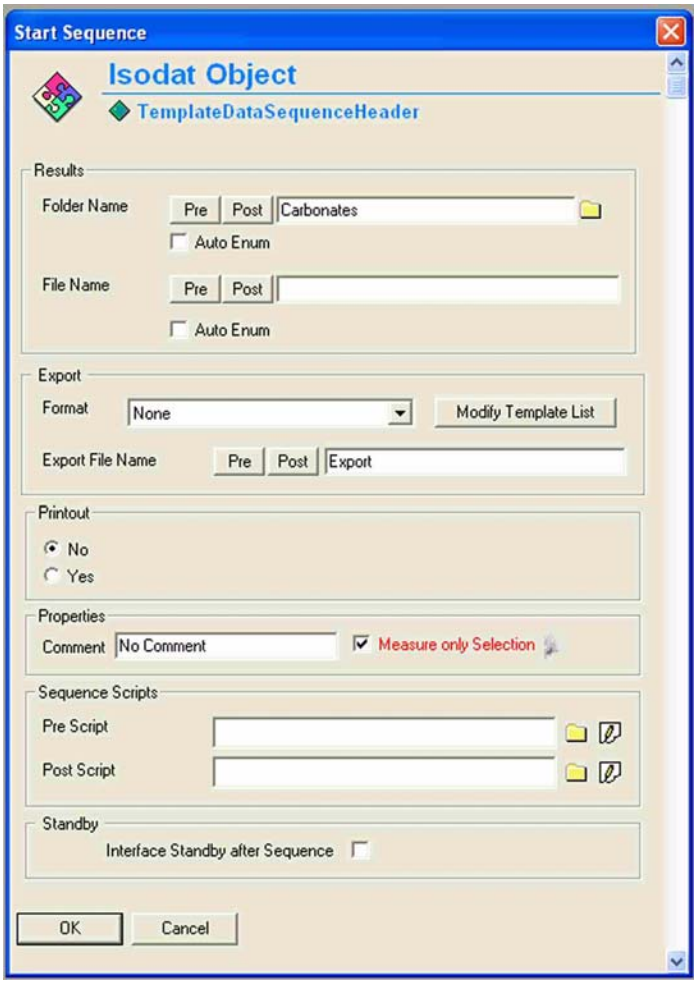


Figure 3-46. Defining Parameters for Handling Results

Results

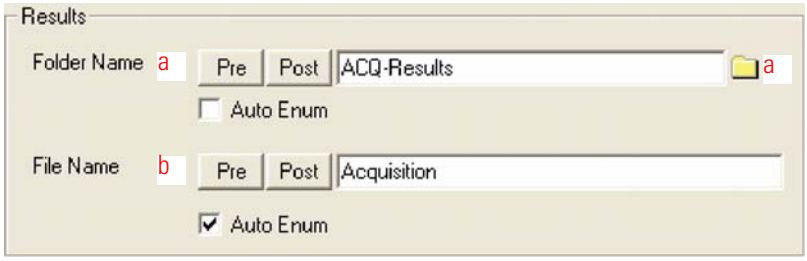


Figure 3-47. Defining Full Path for Results Storage

Table 3-18. Defining Full Path for Results Storage

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

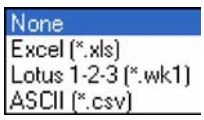
Use the **Pre** and **Post** buttons to automatically create meaningful folder names and file names (e.g. **ACQ-Results** as file folder and **Date** as a postfix will result in a folder **ACQ-Results_060725**, if the acquisition was started the 25th of july 2006).

Folder and path for storage of single result data will be set at the **Results** tab of the File Browser. If no entry is made at **Folder Name** (**a** in Figure 3-47), the result data will be stored directly at the **Results** tab without creating a particular folder.

Export

Figure 3-48. Defining Parameters for Results Export

Table 3-19. Defining Parameters for Results Export

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

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

Printout

Figure 3-49. Defining Parameters for Results Printout

Table 3-20. Defining Parameters for Results Printout

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

Properties

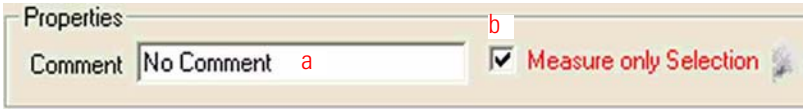


Figure 3-50. Properties Box - Comment

Table 3-21. Properties Box - Comment

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

Sequence Scripts

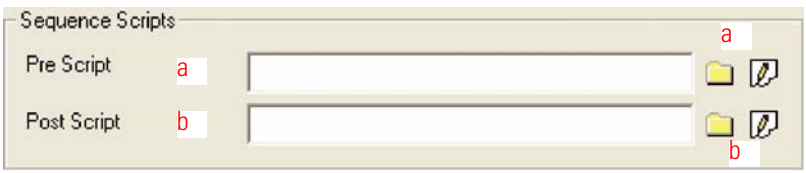


Figure 3-51. Selecting ISL Scripts to be Executed

Table 3-22. Selecting ISL Scripts to be Executed

No.	Parameter	Description
a	Pre Script	Select an ISL script (*.isl) to be executed before the sequence.
b	Post Script	Select an ISL script (*.isl) to be executed after the sequence. Useful for adding the "Standby & Drop" service script after a sequence

Standby

Figure 3-52. Standby

Table 3-23. Standby

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

3. Finally, confirm by **OK**. The measurement will be started.
   Refer to "Measurement Procedures for Real Samples" on page 5-1.

Standards

Standards can be set in

a. Isodat **Generic Editor** (recommended only for advanced users) or in

b. Isodat **Standard Editor**.

Using Generic Editor

Determination of Primary Standards

1. Browse to the folder **C:\Thermo\Isodat NT\Global\bin**.

2. Open the Isodat **Generic Editor** by a double-click on the file **IsodatEditor.exe**.

3. Click on its **Open** button.

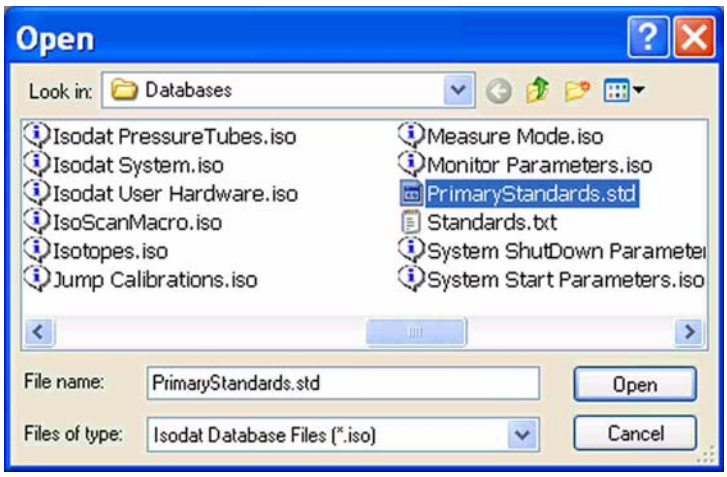


Figure 3-53. Selecting PrimaryStandards.std

4. Browse to the folder **C:\Thermo\Isodat NT\Global\Databases**.
   Select the file **PrimaryStandards.std**.
   Confirm by **Open**.
   The database containing the Primary Standards will be opened.

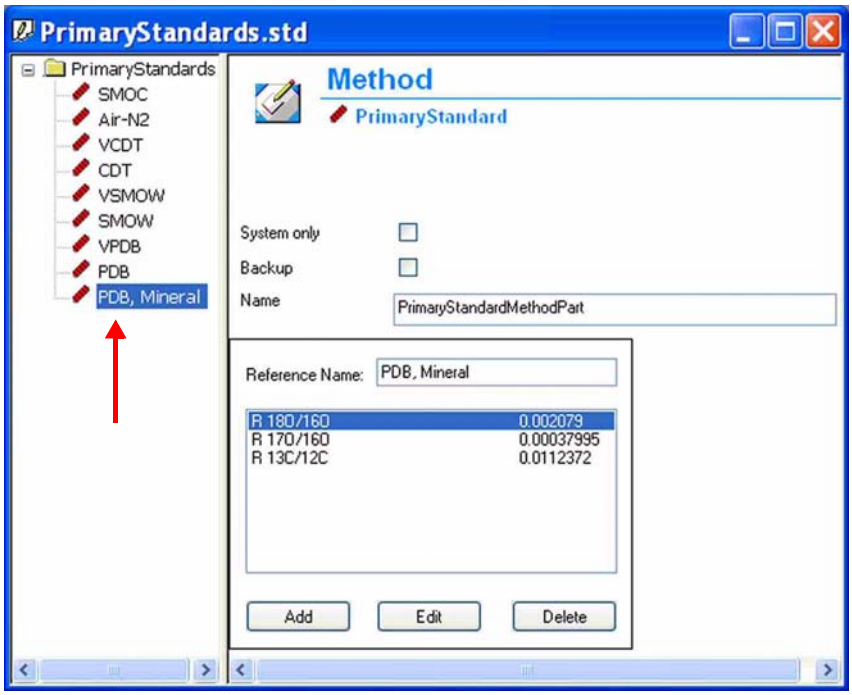


Figure 3-54. Opening Primary Standards Database

5. In the left pane, mark **PDB, Mineral**.
   The primary ratios will be shown.
   Check your primary ratios in the right pane.

Using Standard Editor

In **Acquisition Mode**, click on the arrow right to the **Editors** icon.

Select **Standard** Editor.

The Standard Editor will be opened as displayed in Figure 3-55. It is a database that contains the defined **Working** Standards.

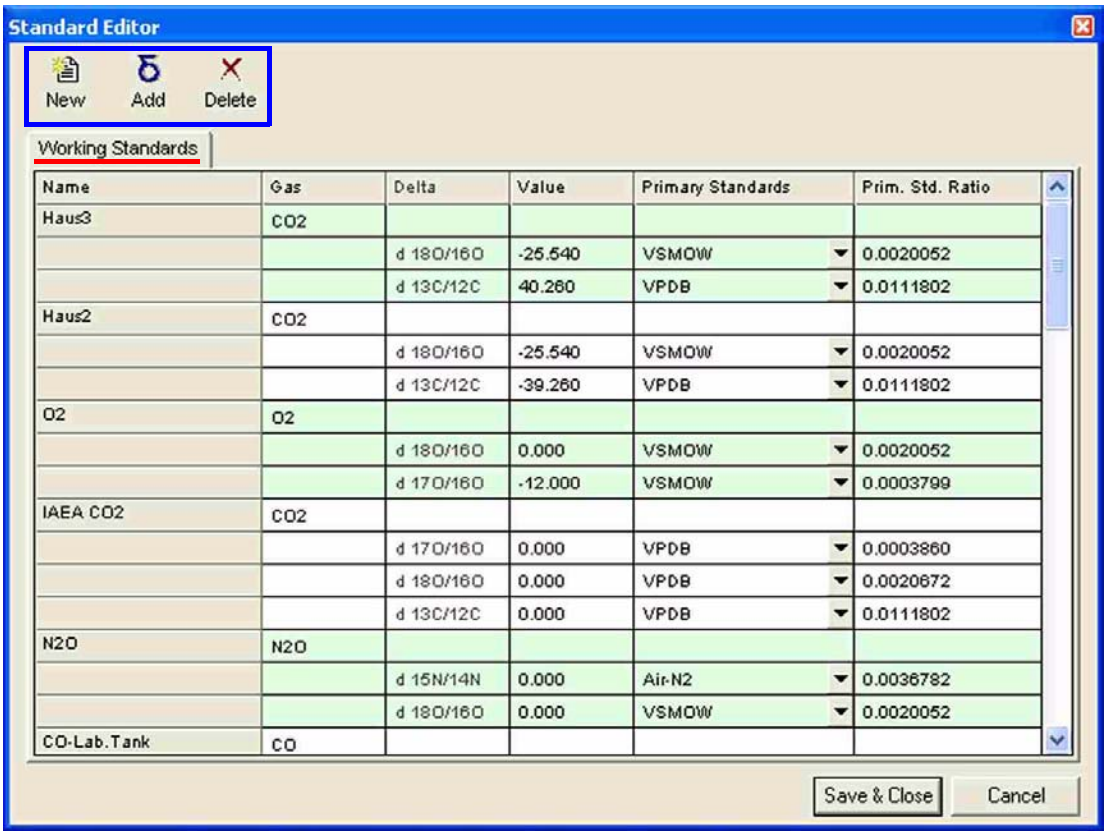


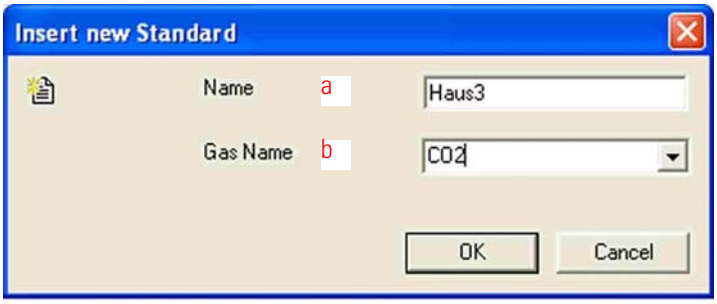
Figure 3-55. Opening Standard Editor

The Standard Editor contains a description of the referred isotopic standards. It allows to:

create new Working Standards that will be added to the database

add δ values that will be added to an existing Working Standard

delete individual δ values or entire Working Standards from the database



To create a new Working Standard:

a Type in a significant name for the standard.

b Type in the name of the gas or select it from the pulldown menu.

Figure 3-56. Creating New Standard

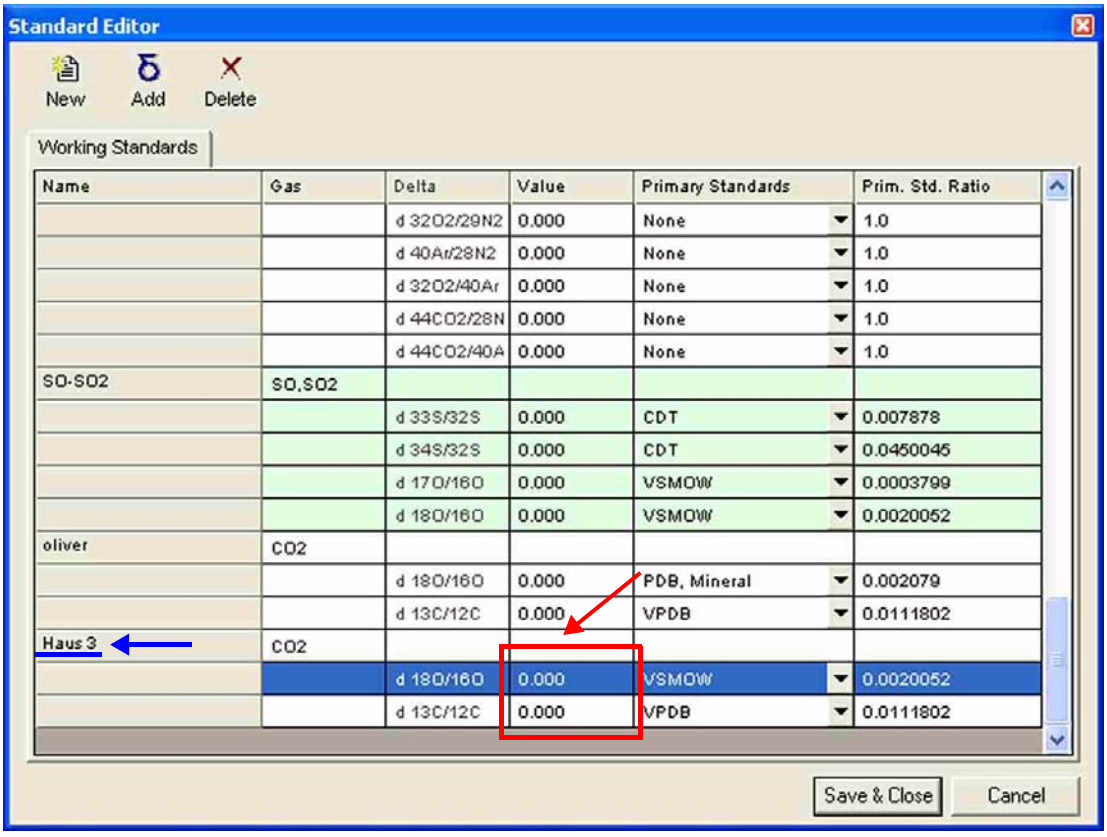


Figure 3-57. New Standard Appearing in Standard Editor

The new Working Standard has been included into the database and therefore appears in the Standard Editor. See Figure 3-57.

Note As based on Primary Standard Ratios, in the **Value** column of the new Working Standard, 0.000 is displayed. ▲

Primary Standards are based either upon calibrated international Standards (if available) or upon their relation to own Standards (if unavailable).

Note Primary Standard Ratios cannot be changed in Standard Editor! This is only possible in the database of the Primary Standards. ▲

To save your changes, finally click **Save & Close**.

Excel Export

Figure 3-58 shows a simple Excel Export template created for Kiel IV Carbonate Device using the Excel Export Editor. It can be used as an example for creating a customized export template.

Note In all cases, the following columns shown in Figure 3-58 should be exported. ▲

For more information about Excel Export, refer to ISODAT *NT Operating Manual - Upgrade to Version 2.0*; Part No. 115 4991.

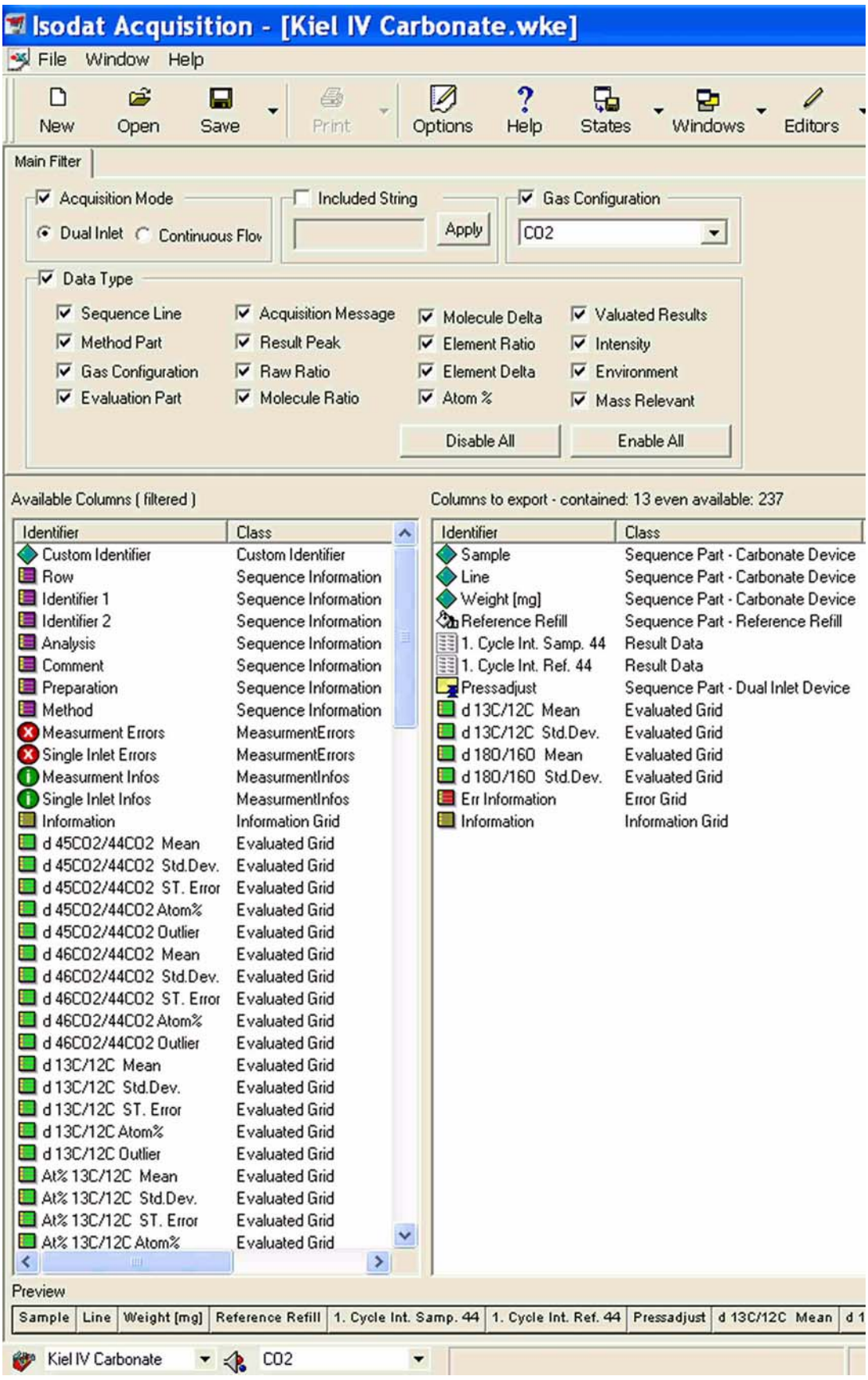
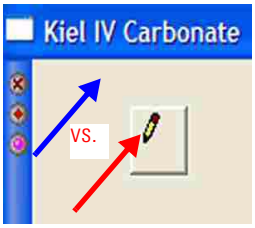


Figure 3-58. Excel Export Template

Dyn Externals

These hardware parameters are factory-set and are used in different parts of the process to perform carbonate analysis with the Finnigan Kiel IV Carbonate Device. Generally, it is possible to perform all kinds of carbonate analysis without changing these parameters. Since the unit can be connected to any Dual Inlet IRMS, we recommend to adjust the following parameters in order to optimize the individual application to be performed.

Two different groups of hardware parameters, **Dyn Externals** and **Service Scripts**, can be set in Kiel IV Carbonate window as follows.



- When **right**-clicking on a free spot within the device window, **Service Scripts** will be called. Refer to "Service Scripts" on page 3-49
- When **left**-clicking **directly** on the symbol, **Dyn Externals** will be called and can be edited. They are arranged in five tabs and will be discussed now.

Figure 3-59. Calling Dyn Externals vs. Service Scripts

Basic Functionality Tab

Basic Functionality tab deals with variables that control the connect/disconnect procedure. See Figure 3-60 and Table 3-24.

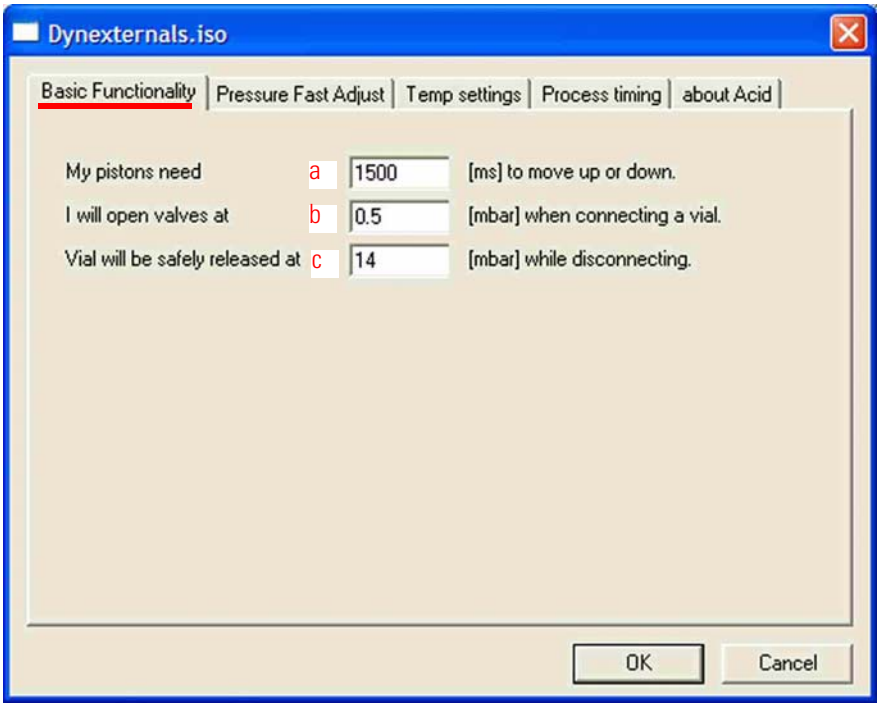


Figure 3-60. Basic Functionality Tab

Table 3-24. Parameters of Basic Functionality Tab

Parameter	Comment
a	delay time for piston movement
b	pressure threshold for fore vacuum section
c	pressure threshold for auxiliary gas (used, when vials are disconnected)

Pressure Fast Adjust Tab

Pressure Fast Adjust tab deals with signals for bellow adjustment. See Figure 3-61 and Table 3-25. Refer to "Reference Refill" on page 5-22 as well.

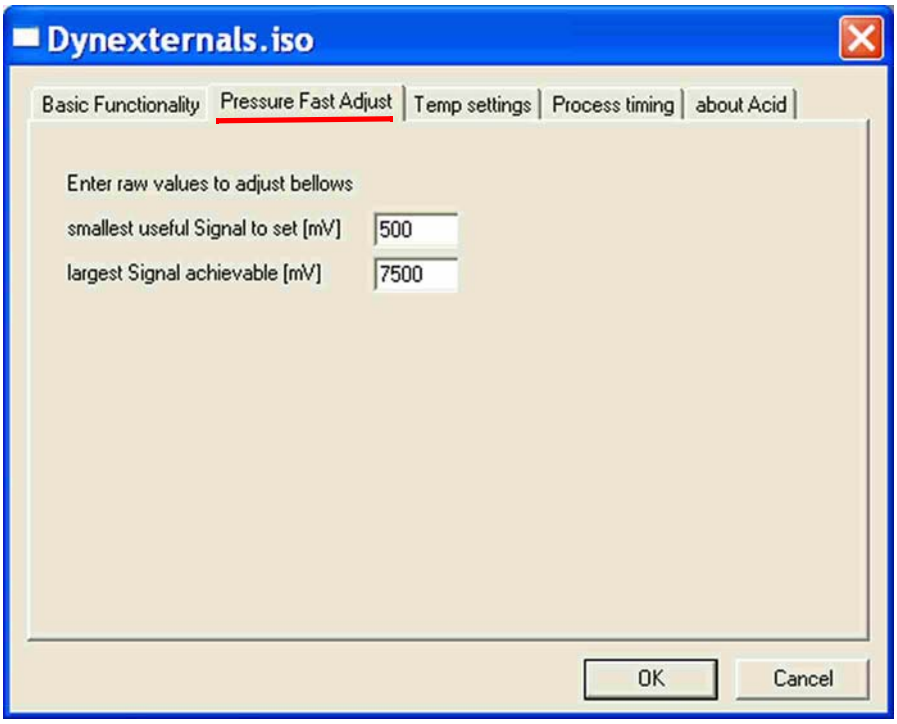


Figure 3-61. Pressure Fast Adjust Tab

Table 3-25. Parameters of Pressure Fast Adjust Tab

Parameter	Comment
Smallest Useful Signal to Set [mV]	minimum ion intensity acceptable to perform measurement (default: 500) corresponds to the signal after Reference Refill with bellow at 100 % and depends on refill time
Largest Signal Achievable [mV]	maximum ion intensity achievable with the current amount of gas in the bellow Default: 6500 for IRMS (Delta^{plus}, Delta^{plus} XL, MAT 252); preamplifier dynamic range: 10 V. If the ion intensity of m/z 44 exceeds this value, Isodat 2.5 waits for the signal to drop before an attempt to adjust pressures is made. Default 36000 for IRMS (Delta^{plus} XP, MAT 253); preamplifier dynamic range: 50 V. If the ion intensity of m/z 44 exceeds this value, Isodat 2.5 waits for the signal to drop before an attempt to adjust pressures is made.

Temp Settings Tab

Temp Settings tab is used to determine the temperatures for the traps. See Figure 3-62 and Table 3-26.

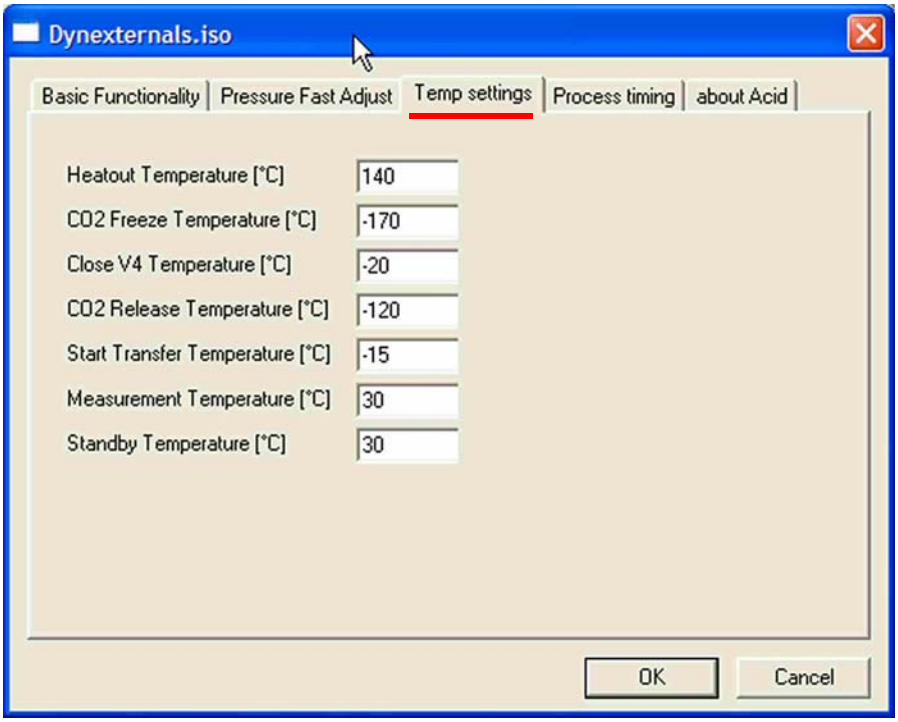


Figure 3-62. Temp Settings Tab

Table 3-26. Parameters of Temp Settings Tab

Parameter	Comment
Heatout Temperature [°C]	Temperature used during pumpout and cleaning cycles of the two traps (before and after each carbonate measurement in order to remove any impurities) Default: 150
CO_2 Freeze Temperature [°C]	must be set to -170 °C
Close V4 Temperature [°C]	initial pump out and cool temperature of trap 1. Default: -20 During leak test period, valves 12 (22), 1, 2, and 4 are open. If leak test is successful, Isodat 2.5 starts cooling trap 1 in order to trap the produced gases of the prepared carbonate. As soon as temperature of trap 1 reaches -20 °C, valve 4 is closed.
CO_2 Release Temperature [°C]	Default: -120 Be extremely careful in changing this value! If setting it to lower values, ensure that all gas is released during the equilibration time.
Start Transfer Temperature [°C]	initial temperature to transfer CO_2 gas from trap 1 to trap 2. As soon as trap temperature reaches -15 °C, valve 3 opens and transfer of CO_2 from trap 1 into trap 2 starts. Default: -15 It has no effect on isotope fractionation that the CO_2 expands into the crimped part of the capillary at -15 °C. At -120 °C, the CO_2 will be frozen into trap 2. The CO_2 loss through the crimping hole is negligible and conditioning of the capillary head is started.
Measurement Temperature [°C]	temperature of trap 2 just before starting an acquisition. Default: 30
Standby Temperature [°C]	at this temperature, traps 1 and 2 are set after finishing an acquisition. Default: 30

Process Timing Tab

Process Timing tab is used to set some time parameters for the traps. See Figure 3-63 and Table 3-27.

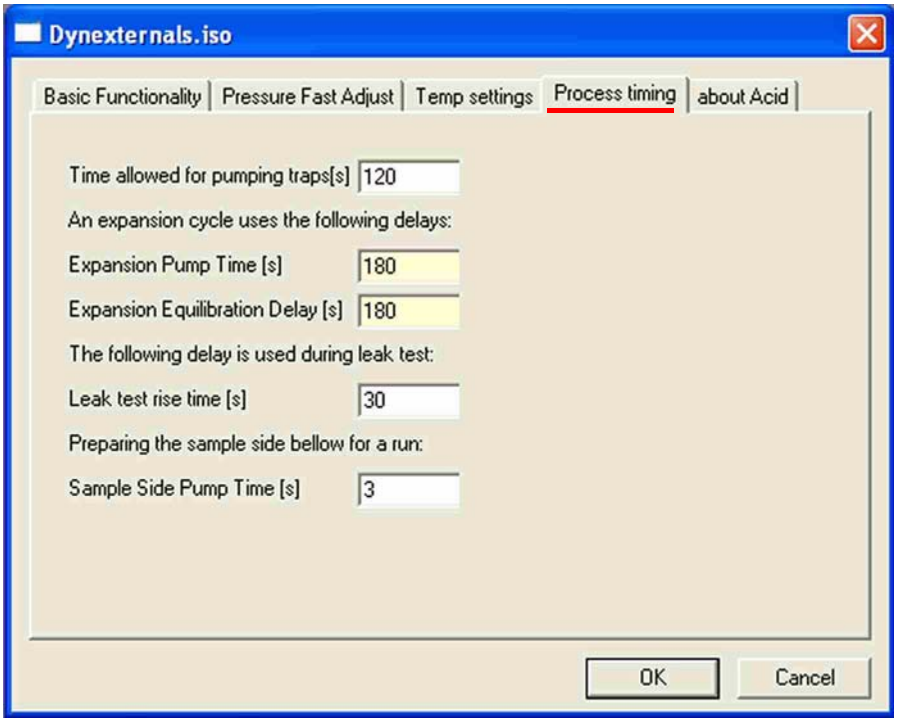


Figure 3-63. Process Timing Tab

Table 3-27. Parameters of Process Timing Tab

Parameter	Comment
Time allowed for pumping trap(s) [s]	pump time after setting the traps to pump temperature. Default: 120
Expansion Pump Time [s]	pump time during expansion cycles where part of the CO_2 is pumped away. Default: 180
Expansion Equilibration Delay [s]	waiting time after expansion of CO_2 gas before next action. Default: 180
Leak Test Rise Time [s]	will always be used to calculate the leak rate (in min^{-1}). Default: 30
Sample Side Pump Time [s]	pump time of the volume between valves 16, 15 and 32 of Dual Inlet system. Is used before each run. Default: 3

About Acid Tab

About Acid tab deals with parameters used in acid handling.

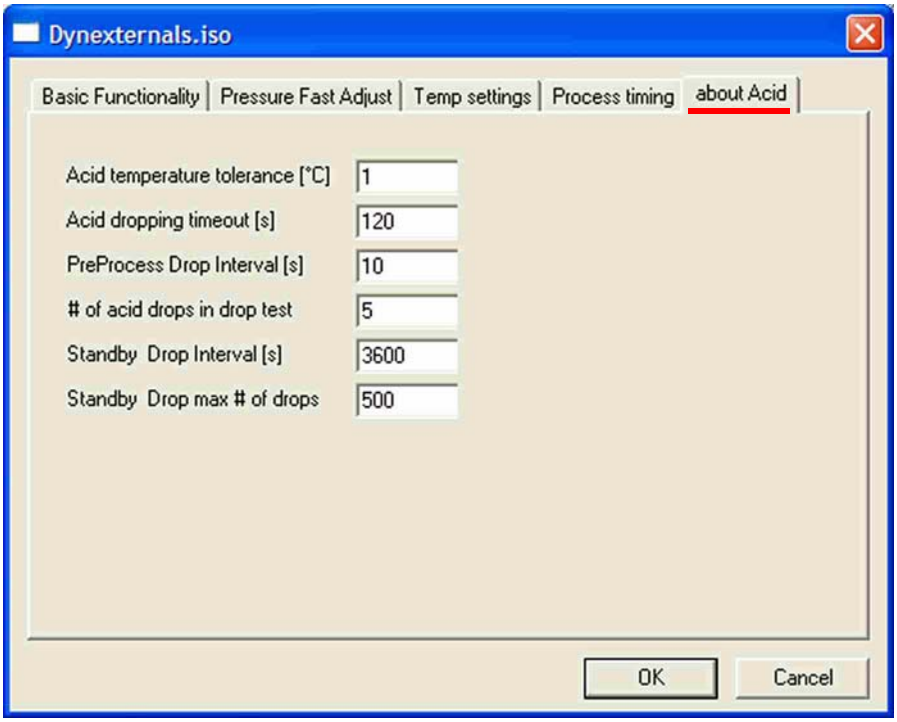
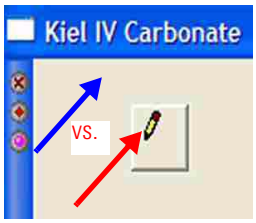


Figure 3-64. About Acid Tab

Table 3-28. Parameters of About Acid Tab

Parameter	Comment
Acid temperature tolerance [°C]	If oven temperature varies more than this value, acquisition stops. An error message will occur. Default: 1. Better is 3, because opening the door of the heating cabinet before the run is finished will lead to a fatal error. Using ±3 °C, this can be avoided.
Acid dropping timeout [s]	If no acid drop can be counted within this time (default: 120), the system stops indicating "fatal error". If at least one acid drop can be counted, the current sample will be measured. Afterwards, the system stops indicating a fatal error.
Pre process drop interval [s]	In order to avoid acid contamination due to rigid H_3PO_4/carbonate reaction (phosphoric acid might well up into the steel body of the acid valve), a delay time after each dropping can be applied. Default: 10
Number of acid drops in drop test	Number of drops during an Acid Drop Test. Default: 5. See Figure 3-69.
Standby drop interval [s]	If the system is in Standby and Drop mode (e.g. after finishing or stopping an acquisition), every interval time (default: 3600), one acid drop will be injected into the waste vials (2/1 and 2/2). During the remaining time, the system stays in pump mode.
Standby drop: maximum number of drops	Default: 500. E.g. after 100 drops, the 2.5 ml vial is half-full.

Service Scripts



- When **left**-clicking **directly** on the symbol, **Dyn Externals** will be called and can be edited. Refer to "Dyn Externals" on page 3-44.
- When **right**-clicking on a free spot within the device window, **Service Scripts** will be called. They will now be discussed.

Figure 3-65. Calling Dyn Externals vs. Service Scripts

The following five service scripts will be outlined:

Take Magazine

Load Magazine

Acid Drop Test

Standby and Drop

Standby and Pump

Figure 3-66. Available Service Scripts

Take Magazine

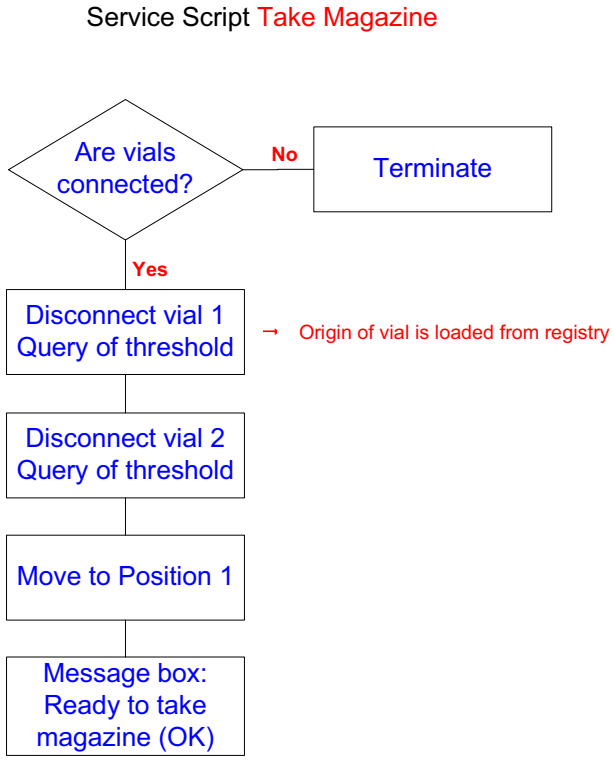
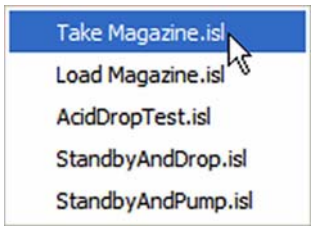
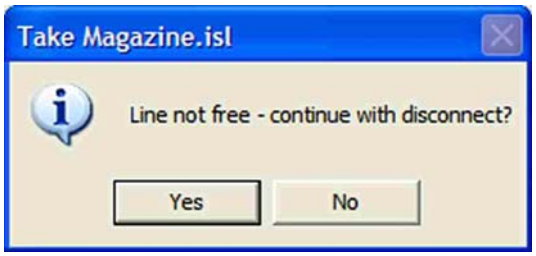


Figure 3-67. Service Script Take Magazine

To remove the magazine, proceed as follows:

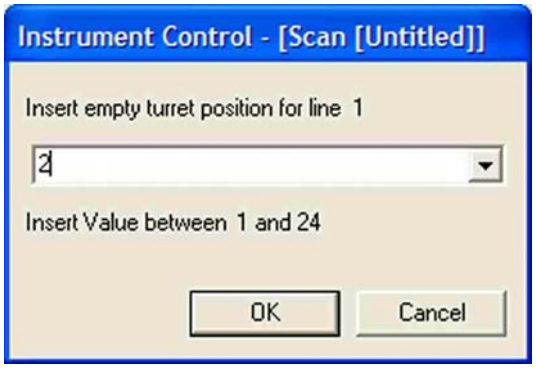


1. Select **Take Magazine**.



2. If vials are connected, the adjoining information appears.

3. Confirm by **Yes**.



If, for some reason, the original position of the vials actually connected to the acid valve is not stored in the registry, a request appears: **Check the turret, and name an empty position for the vials to put**.

4. Confirm by **OK**.

5. The magazine will be moved to the respective position and vials will be taken away from the acid housing

6. After moving to position 1 automatically, the message **Ready to take magazine. OK** will appear.

7. Open the oven door and take the magazine out of the oven very carefully.

8. Close the door to maintain the oven temperature constant.

Load Magazine

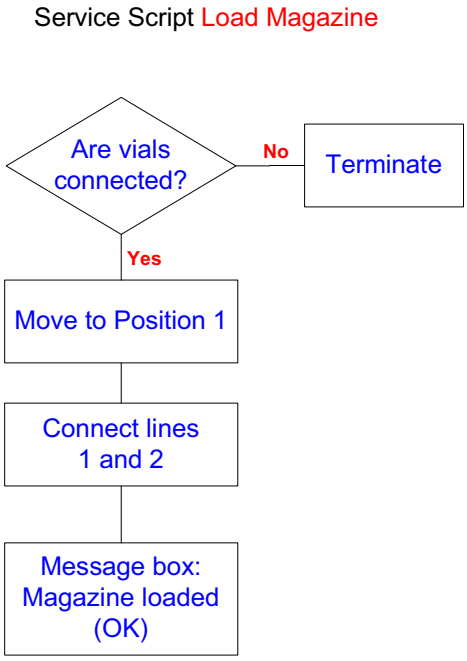


Figure 3-68. Service Script Load Magazine

After inserting the magazine into the oven, this test should be performed to keep the lines free from water and other impurities. The following actions take place:

1. The left piston moves up vial 1/1 (first vial/line one).

2. Valve 7 opens and the vial is pumped. The computer waits until the pressure in the vial, measured by the pressure meter VM2, is below the acceptable value. See Figure 3-60. Then, the piston moves down.

3. The right piston moves up vial 2/1 (second vial/line one).

4. Valve 7 opens and the vial is pumped. The computer waits until the pressure in the vial, measured by the pressure meter VM2, is below the acceptable value. See Figure 3-60. Then, the piston moves down.

5. Leave the valves 7, 13 and 23 open.

Note If no vial is available or the associated proximity switch gives no response, an error message appears. ▲

Acid Drop Test

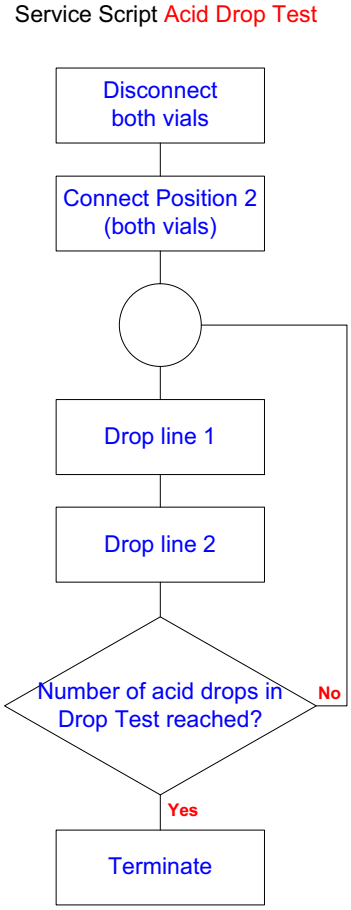


Figure 3-69. Service Script Acid Drop Test*

*See Table 3-28.

The Acid Drop Test checks the function of acid valves and counters. After connecting and measuring the VM2 value, valve 10 opens and injects one drop of acid to line 1. Then, valve 20 is opened, and one drop is injected to line 2.

Warning Do not perform the Acid Drop Test, if samples are loaded into the vial positions L1/P2 and L2/P2! ▲

This action is repeated until the requested number of drops is reached. See Table 3-28. To stop the action, select the properties again and click on **Stop Acid Drop Test**.

Note The vials 1/1 (vial one/line one) and 1/2 (vial one/line two) are so-called pump-position vials. This means that they are not sample prepared vials.They are used to keep the system clean and at vacuum. ▲

Standby & Drop

Service Script "Standby and Drop"

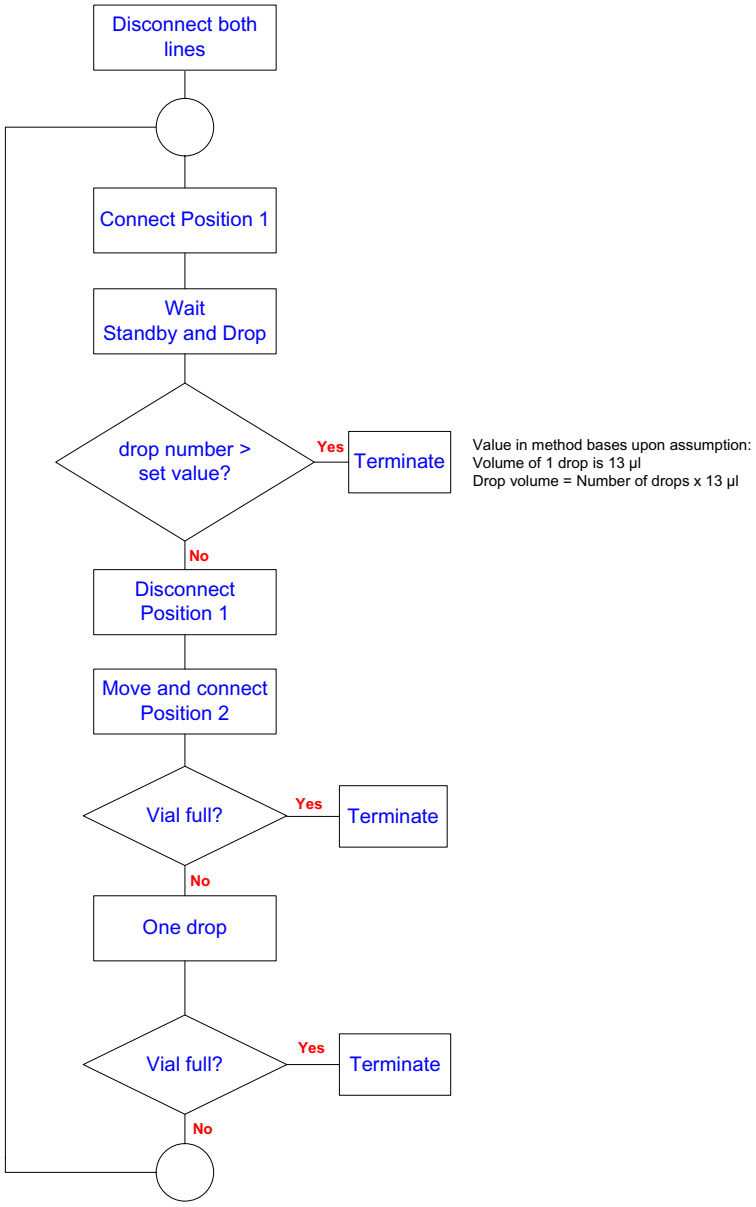
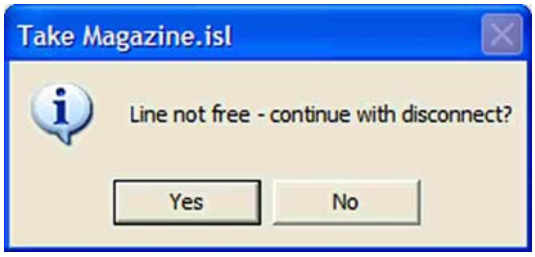


Figure 3-70. Service Script Standby and Drop

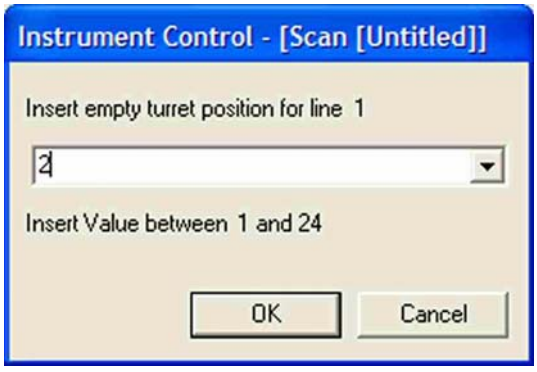
If the Kiel IV Carbonate Device is not used for more than 5 h, we recommend selecting the **Standby and Drop** function to keep the acid lines in flow. Otherwise, the acid may clog the lines or the magnetic valves 10 or 20 may squeeze the acid tubing. This function is placed as a postscript automatically after finishing an acquisition (see Figure 3-51). Standby and Drop can be performed manually as well.

Note Make sure that vials are available in position 1/1 (vial one/line one); 1/2 and 2/1 and 2/2 in the magazine prior to starting Standby and Drop. ▲



1. If vials are connected, the adjoining information appears.

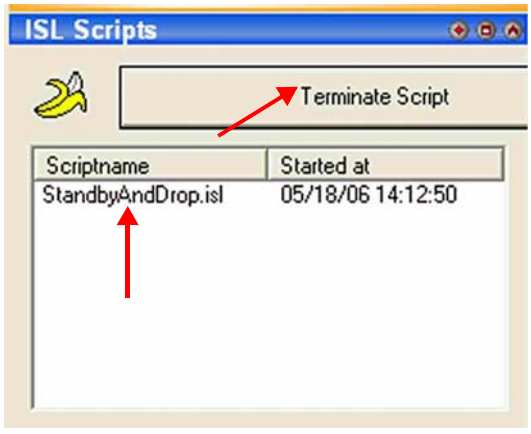
2. Confirm by **Yes**.



3. The pistons take the vials. The magazine moves to position one and loads the vials of position 1/1 and 2/1, and the valves 7, 13 and 23 are opened.

4. The pumping period is started. After a time defined by the user (Standby Drop Interval, see Figure 3-6 and Table 3-2), vial 1/1 is taken away, and the magazine moves to position 2. Vial 2/1 (vial two/line one) is connected and pumped. After pumping, acid is dropped and vial 2/1 is removed into the magazine.

5. The same procedure takes place for vial 2/2 (vial 2/line 2).

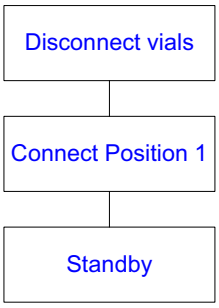


To stop the function, at **ISL Scripts** select the script **StandbyAndDrop.isl**.

Then, click **Terminate Script**.
This will terminate the executed script.

Standby and Pump

Service Script Standby and Pump



1. Insert at least two clean vials in position 1/1 and 2/1.
2. The script sets Kiel IV Carbonate Device in Standby mode, that is, it closes valves 12 and 22 and opens valves 1, 2, 3, 4 and 5.
3. Leave valves 7, 13, 23 open.
4. Bring the vials of position 1 to respective acid valve housing and keep pumping.

Figure 3-71. Service Script Standby and Pump

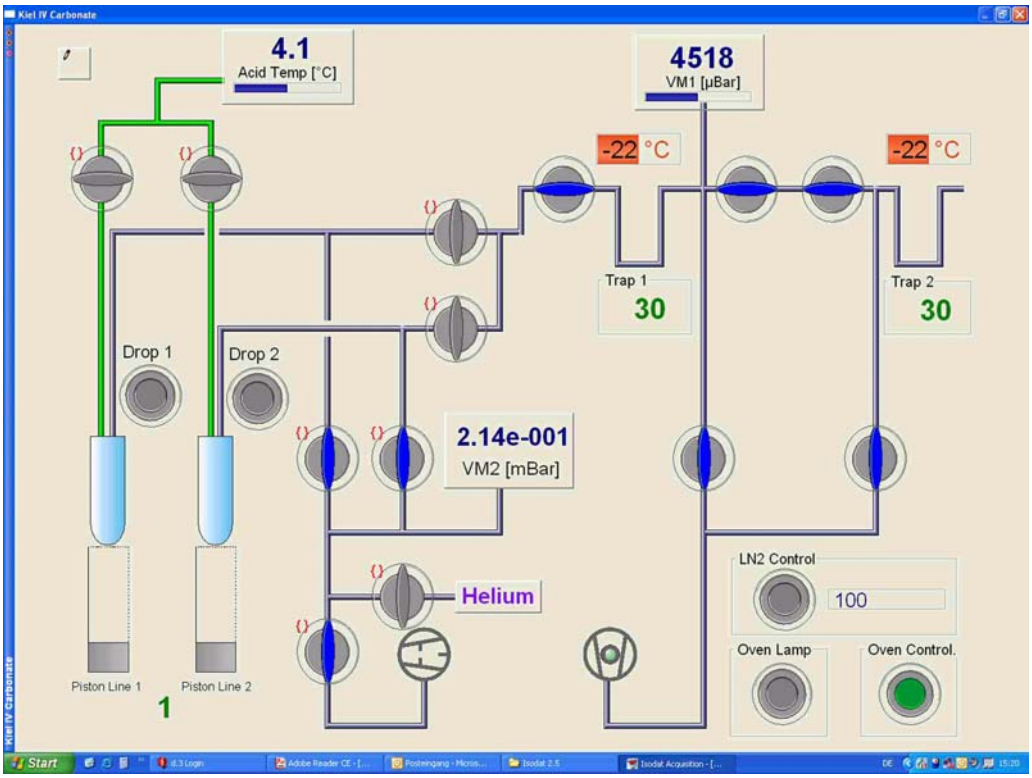


Figure 3-72. Kiel IV Carbonate Device in Standby Mode

Figure 3-72 shows the Kiel IV Carbonate Device in **Standby** mode.

Terminate

When **Terminate** appears within the above-mentioned service scripts, the process displayed in Figure 3-73 is executed.

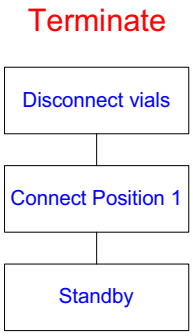


Figure 3-73. Actions during Terminate

Interpreting Results

Raw Tab

Raw <CO2> | Evaluated <CO2> | Grid - Errors | Grid - Infos | Sequence Line

	44 Sample [mV] 1	45 Sample [mV] 2	46 Sample [mV] 3	44 Reference [mV] 4	45 Reference [mV] 5	46 Reference [mV] 6	rR 45CO2/44 7	rR 46CO2/44 8	R 45CO2/44 9	R 46CO2/44 10	rd 45CO2/44 [per mil] vs. CO2 Lab Tank 11	rd 46CO2/44 [per mil] vs. CO2 Lab Tank 12
Pre				1859.576	2229.242	2625.168						
1	1833.946	2211.448	2620.630	1806.475	2165.569	2550.127	1.205841	1.428957	0.012060	0.004007	5.885	12.238
2	1786.200	2153.937	2552.424	1755.019	2103.892	2477.417	1.205876	1.428969	0.012060	0.004007	5.917	12.277
3	1739.410	2097.538	2485.593	1704.928	2043.912	2406.787	1.205890	1.428986	0.012060	0.004008	5.910	12.287
4	1693.851	2042.652	2420.460	1656.650	1985.975	2338.518	1.205921	1.428968	0.012060	0.004008	5.934	12.283
5	1649.445	1989.025	2356.944	1609.554	1929.494	2271.962	1.205875	1.428931	0.012060	0.004008	5.917	12.299
6	1606.289	1936.954	2295.258	1564.098	1874.989	2207.808	1.205856	1.428919	0.012060	0.004008	5.910	12.305
7	1564.147	1886.160	2234.942	1520.109	1822.236	2145.665	1.205871	1.428856	0.012060	0.004007	5.932	12.270
8	1523.382	1836.941	2176.869	1477.230	1770.858	2085.122	1.205830	1.428970	0.012060	0.004008	5.897	12.367

Figure 3-74. Raw Tab - Part I

d 45CO2/44 [per mil] vs. VPDB VSMOW 13	d 46CO2/44 [per mil] vs. VPDB VSMOW 14	d 13C/12C [per mil] vs. VPDB 15	d 18O/16O [per mil] vs. VSMOW 16	d 17O/16O vs. 17	AT% 13C/12C [%]	AT% 18O/16O [%]
6.299	-2.927	6.862	-2.945	6.296	1.113161	0.199531
6.330	-2.889	6.894	-2.907	6.316	1.113196	0.199538
6.323	-2.879	6.886	-2.898	6.321	1.113188	0.199540
6.348	-2.883	6.913	-2.901	6.319	1.113216	0.199539
6.330	-2.867	6.893	-2.886	6.327	1.113195	0.199542
6.324	-2.861	6.886	-2.880	6.330	1.113187	0.199544
6.345	-2.895	6.910	-2.914	6.313	1.113214	0.199537
6.311	-2.800	6.870	-2.818	6.363	1.113169	0.199556

Figure 3-75. Raw Tab - Part II

Individual Columns of Result File

Table 3-29 explains the individual columns of the result file shown in the **Raw** tab (Figure 3-74 and Figure 3-75).

Table 3-29. Explanations of Columns of Result File

Number	Column	Explanation
1, 2, 3 4, 5, 6	Sample [mV] Reference [mV]	The signal readings during the given integration time (see Figure 3-27) are reported for all masses selected in the Gas Configuration and for sample and reference gas separately (columns 1-3 vs. columns 4-6). The values shown are corrected for background.
7, 8	rR	The signal values are used to create amplifier-corrected raw molecular ratios for all selected ratio traces (defined in Ratio Editor for the Ratio Group used in the Gas Configuration).
11 12	rd45CO2/44CO2 rd46CO2/44CO2	Amplifier-corrected elemental ratios. The molecular δ value for the reference gas selected in the method (see Figure 3-38) is calculated from the elemental isotopic composition given in the same location. This is done by utilizing a reverse ion correction based on the algorithm selected in the "Evaluation Type" entry of the selected method (see Figure 3-37).
13 14	d45CO2/44CO2 d46CO2/44CO2	With the molecular ratios between sample and reference and the known molecular ratio of the reference gas, the molecular δ value of the sample can now be calculated. Refer to "Excel Export" on page 3-42.
15 16 17	d13C/12C d18O/16O d17O/16O	From the derived molecular δ values, elemental isotopic compositions are calculated using the ion correction selected (see Figure 3-37) in the method.

Evaluated Tab

The **Evaluated** tab contains statistical information about the eight repetitions of a single measurement, e.g. their mean, standard deviation and standard error (that is, error of mean determination). Standard error depends on the number of repetitions whereas standard deviation does not. See columns in Figure 3-76.

The **Outlier** column reveals the number of outliers found during calculation of mean. The outliers found after running the outlier test will be highlighted red in the **Raw** tab. All outliers are then eliminated before a new, "corrected" mean, standard deviation and standard error will be calculated without them. These new, "corrected" values will finally be displayed in **Evaluated** tab.

Raw <CO2> | Evaluated <CO2> | Grid - Errors | Grid - Infos | Sequence Line

	Mean	Std. Deviation	Std. Error	Outlier
d 45CO2/44CO2	6.326	0.016	0.006	0
d 46CO2/44CO2	-2.875	0.036	0.013	0
d 13C/12C	6.889	0.018	0.006	0
d 18O/16O	-2.894	0.036	0.013	0
d 17O/16O	6.323	0.019	0.007	0

Figure 3-76. Evaluated Tab

δ_{mean} ("Mean" column in Figure 3-76) is given by:

$$\delta_{mean} = \frac{1}{n} \cdot \sum_{n} \delta$$

where n denotes the number of repetitions.

Standard deviation σ (“Std. deviation“ column in Figure 3-76) is given by:

$$\sigma = \frac{1}{\sqrt{n-1}} \cdot \sqrt{\sum_{n} (\delta - \delta_{mean})^2}$$

Standard error σ_e (“Std. error“ column in Figure 3-76) is related to standard deviation σ as follows:

$$\sigma_e = \frac{1}{\sqrt{n}} \cdot \sigma$$

Grid Errors Tab

If errors occur during sample measurement, the related error messages will be shown in **Grid Errors** tab, Figure 3-77.

Examples: Acid cannot be dropped, acid has run out, sample vials cannot be found, sample vials are not tight, liquid nitrogen has run out.

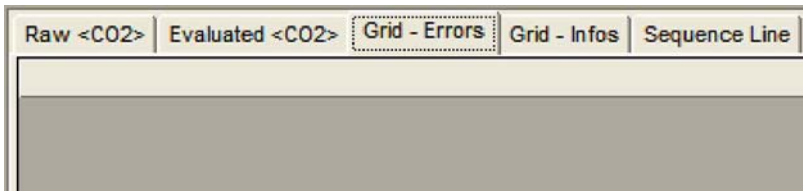


Figure 3-77. Grid Errors Tab

Grid Infos Tab

During the entire preparation process of the carbonate sample prior to measurement start, parameters are saved for informational purposes. They are summarized in **Grid Infos** tab. See Figure 3-78 and Table 3-30.

After their determination, measurement will start. The results of the measurement will finally be shown in Figure 3-74 and Figure 3-75.

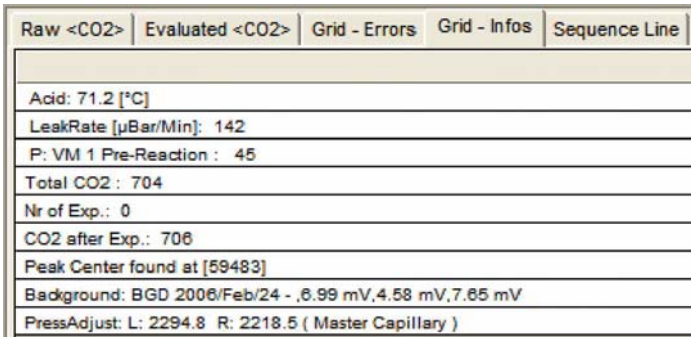


Figure 3-78. Grid Infos Tab

Table 3-30. Parameters of Grid Infos Tab

Parameter	Description
Acid [°C]	temperature of carbonate oven when acid is being dropped. Default: 72 °C
Leak Rate [µbar/min]	leak rate measured at sample vial after connecting it. Must be less than 400 µbar/min! Otherwise, sample preparation stops (no acid will be dropped. An error message will be displayed in "Grid Errors" tab). Maintenance: high leak rate indicates a) a leak in the line to V4 and V2 (both closed) b) density of H_3PO_4 is beneath the range 1.92-1.95 g*cm^{-3} due to water therein.
P VM1 Pre-Reaction [µbar]	pressure read off above trap 1 (VM1) after leak test, before acid will be dropped should be less than 100 µbar!
Total CO_2 [µbar]	overall amount of CO_2, measured above trap 1 prior to possible expansion and transfer to trap 2 (that is, Microvolume). Correlates to sample size: small samples yield a smaller value than larger ones (Figure 5-9).
Nr. of Exp.	number of expansion cycles performed. Correlates to sample size (larger gas amounts yield more expansions than smaller ones). Should be small. Above 70 µg of sample, an expansion will be performed. The parameter "VM1 Expansion [µbar]" in the "Peripherals" tab of the method defines the VM1 pressure that must be reached to start an expansion (the system automatically dilutes the sample). See h in Figure 3-34 and in Table 3-11.
CO_2 after Exp. [µbar]	CO_2 pressure after expansion, measured at VM1. Should correlate with sample signal
Peak Center found at [DAC steps]	If you previously marked "Peak Center" in the sequence grid, a peak center will be performed before the gas is measured. See Figure 3-44 and Table 3-17. After the Peak Center procedure, this high voltage-dependent value (in DAC steps) reveals, where the peak center has been found.* It can be converted into a high voltage value and should be the same for all measurements to be performed. DELTA V: 1 DAC step equals 21.9 mV MAT 253: 1 DAC step equals 6.55 mV
Background [mV]	If you previously marked "Background" in the sequence grid, the result of the background measurement† will be displayed here. See Figure 3-44 and Table 3-17. If no background is measured, the time and date of the last background determined will be reported. The value should be small. Default: each of the three values (for m/z 44, m/z 45 and m/z 46) must be less than 10 mV. Commonly, background is stable and will be used only in the beginning of a sequence.
Press Adjust	As press adjust is essential, always mark "Press Adjust" in the sequence grid! The result of the press adjust will be displayed here. See Figure 3-44 and Table 3-17.

*65535 DAC steps at 10 kV (in case of a MAT 253) or at 3.3 kV (in case of a DELTA IRMS)

†That is, no gas will be let into the ion source, changeover valve is closed.

Sequence Line Tab

In **Sequence Line** tab, the original content of the sequence line is displayed. See Figure 3-79.

Raw <CO2> | Evaluated <CO2> | Grid - Errors | Grid - Infos | Sequence Line

Row	Peak Center	Background	Pressadjust	Reference Refill	Line	Sample	Weight [mg]	Identifier 1	Identifier 2	Analysis	Comment	Preparation	Method
32	1	0	1	0	2	17		17/2		620			Carbo Kiel IV.met

Figure 3-79. Sequence Line Tab

Time Slicing

This feature has been introduced with Isodat 2.5. In Time Slicing mode, instead of a single, long integration, a series of shorter integrations will be performed. This is similar to run the IRMS in Continuous Flow mode. The number and duration of these integrations is determined by the number of time slices and the integration time selected in the method.

Raw Sample Tab

Raw Sample tab, Figure 3-80, presents the results of the individual integrations for the sample side. This corresponds to columns 1-3 in Figure 3-74.

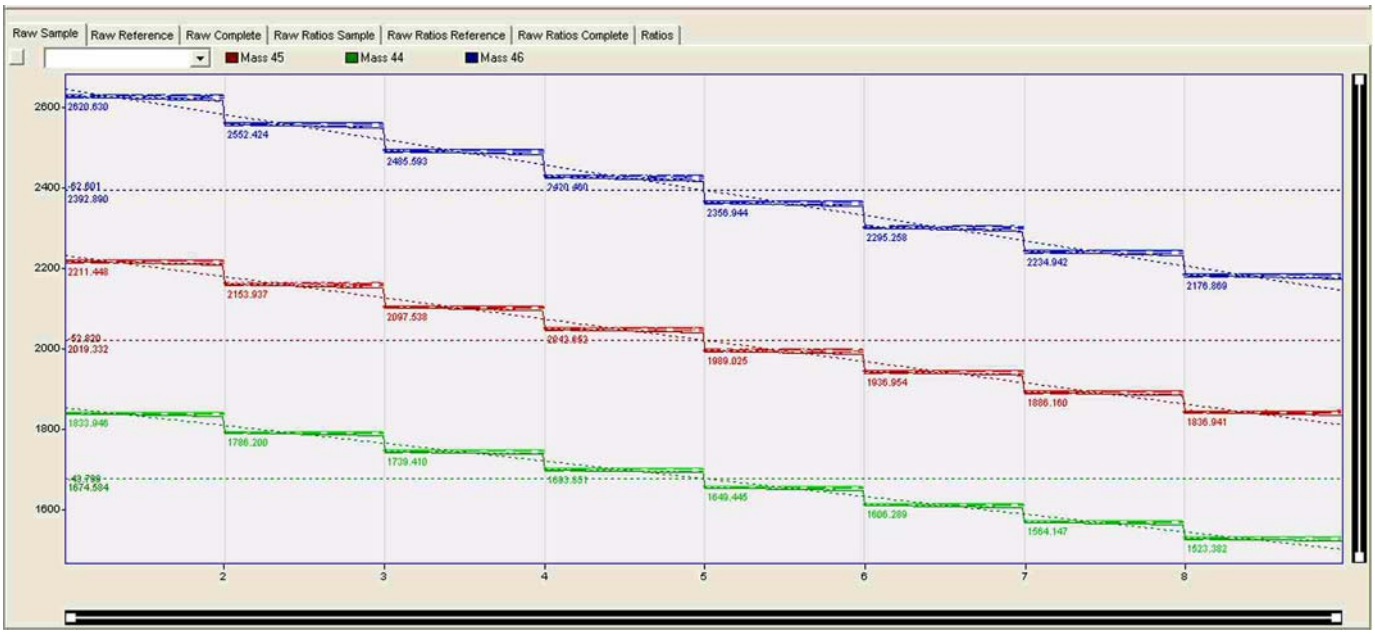


Figure 3-80. Raw Sample Tab

Raw Reference Tab

Raw Reference tab, Figure 3-81, presents the results of the individual integrations for the reference side. This corresponds to columns 4-6 in Figure 3-74.

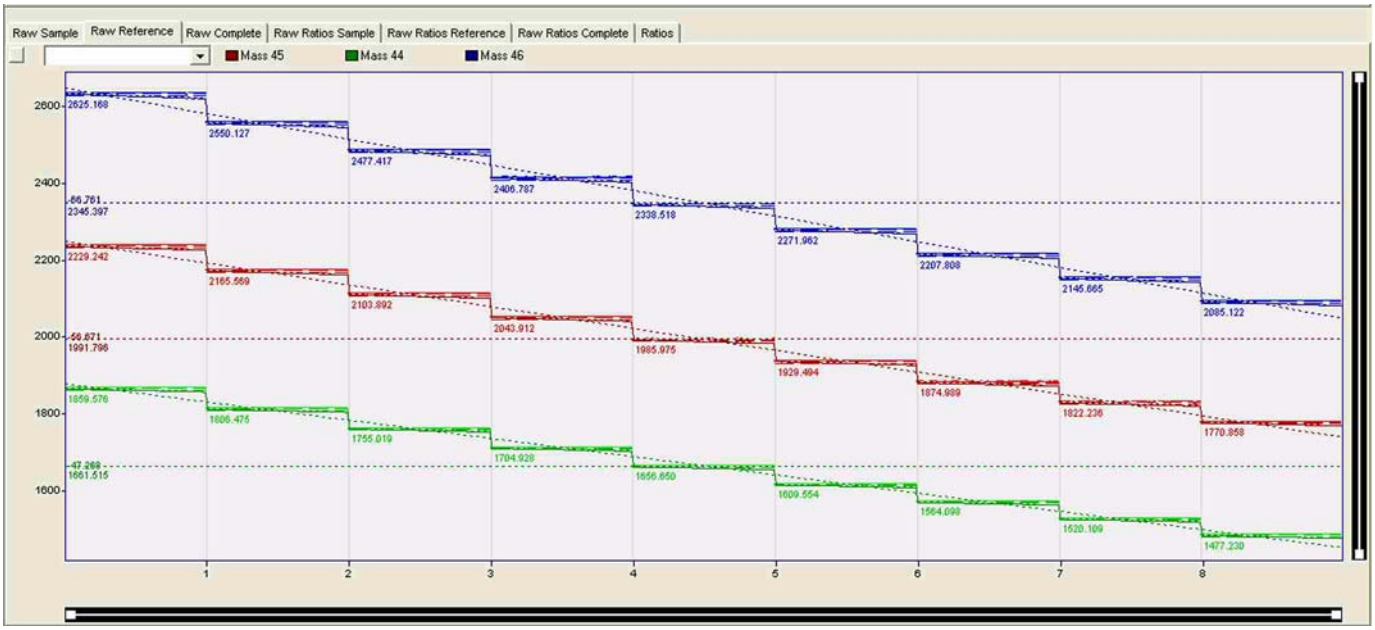


Figure 3-81. Raw Reference Tab

Raw Complete Tab

Raw Complete tab presents the results of the individual integrations for sample and reference combined. This corresponds to columns 1-6 in Figure 3-74.

Figure 3-82 nicely shows the signal decrease of sample and reference gas due to viscous CO_2 sample gas flow in the two different sample and reference gas capillaries.

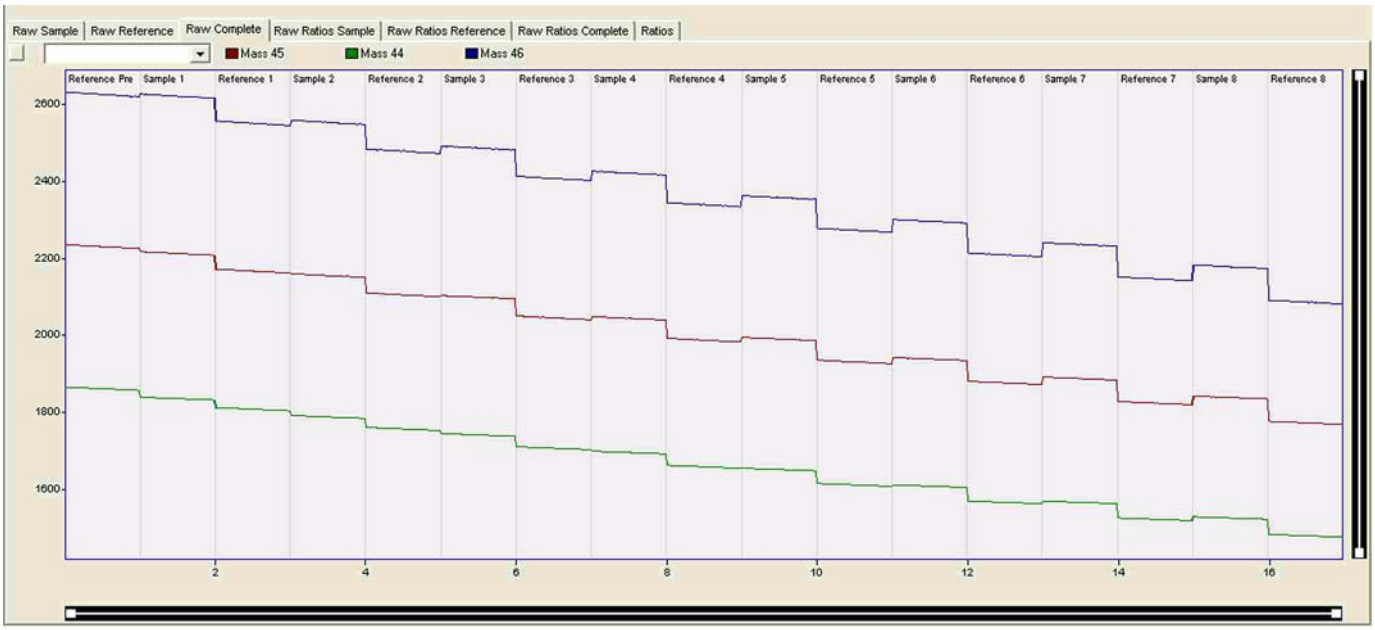


Figure 3-82. Raw Complete Tab

Raw Ratios Sample Tab

Raw Ratios Sample tab, Figure 3-83, displays the ratio of m/z 45 to m/z 44 and the ratio of m/z 46 to m/z 44 for the sample only.

Note If a Dual Inlet valve failure appears, the signal will not decrease constantly. ▲

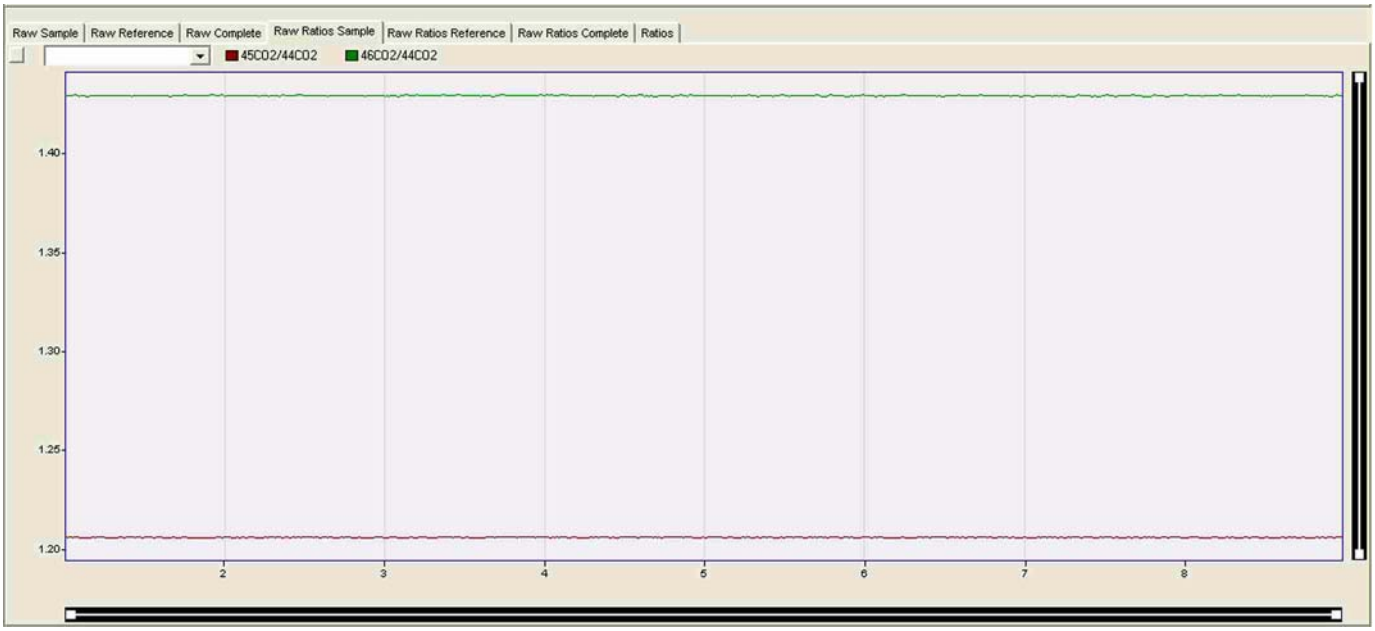


Figure 3-83. Raw Ratios Sample Tab

Raw Ratios Reference Tab

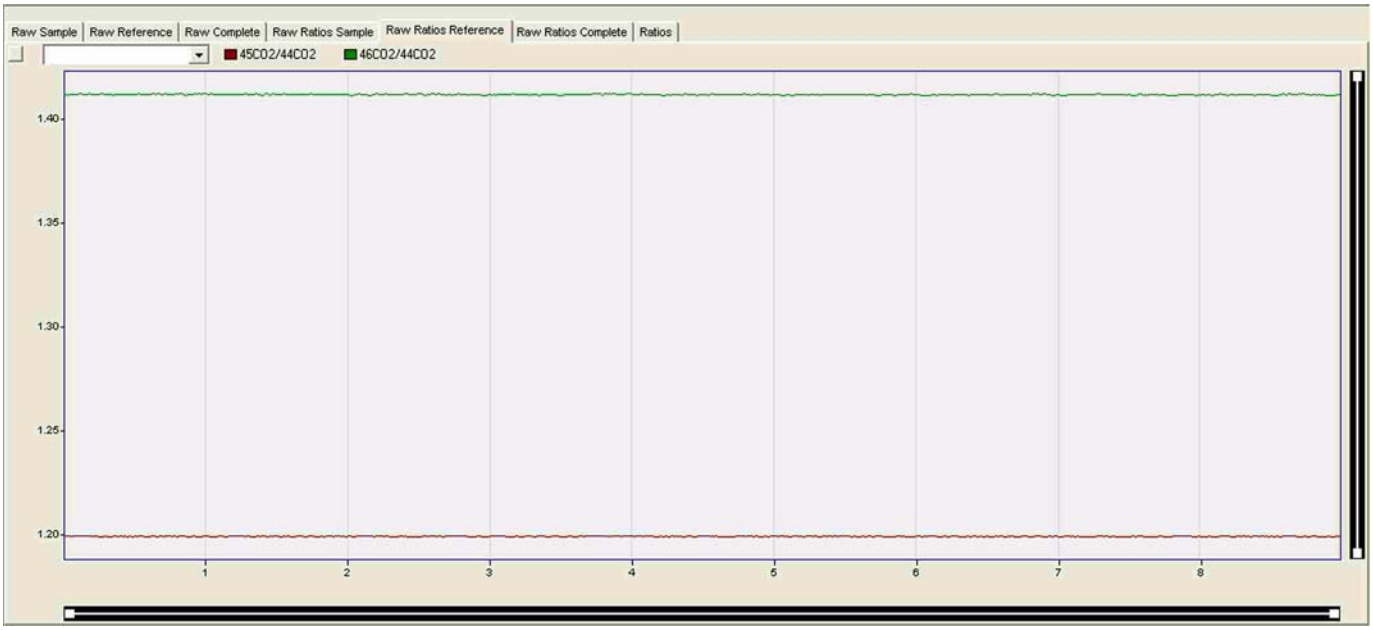


Figure 3-84. Raw Ratios Reference Tab

Raw Ratios Reference tab, Figure 3-84, displays the ratio of m/z 45 to m/z 44 and the ratio of m/z 46 to m/z 44 for the reference only.

Raw Ratios Complete Tab

Raw Ratios Complete tab, Figure 3-85, displays the ratio of m/z 45 to m/z 44 and the ratio of m/z 46 to m/z 44 for sample and reference. As failures become obvious here, it provides a tool for indication of a stable sample measurement.

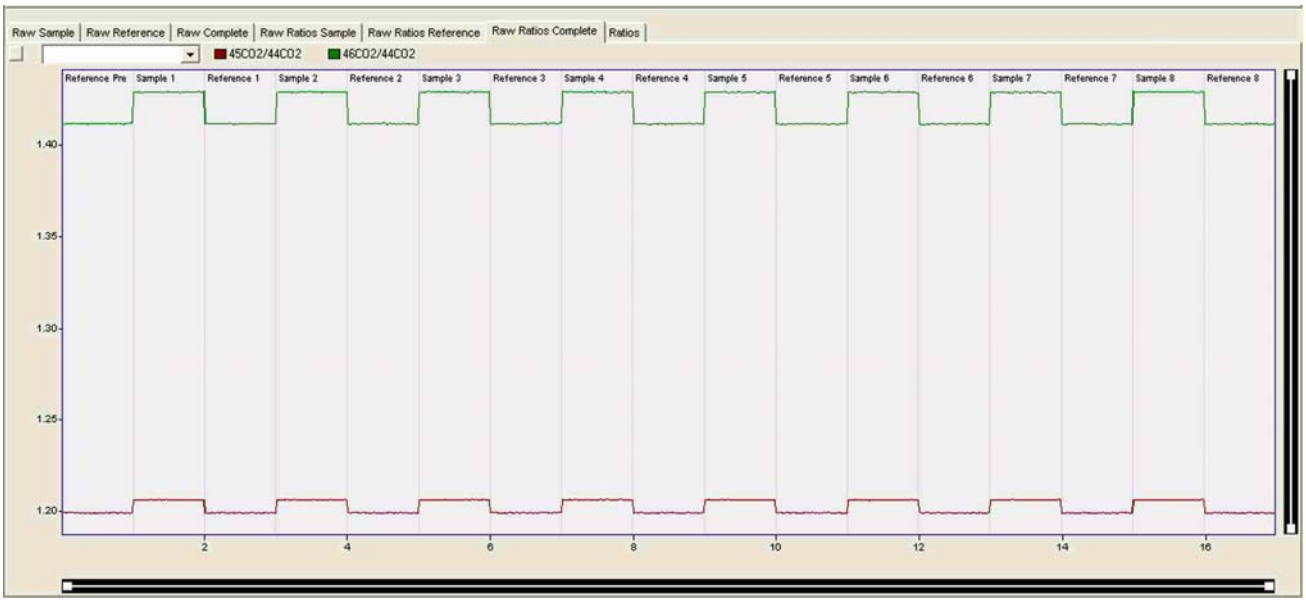


Figure 3-85. Raw Ratios Complete Tab

Ratios Tab

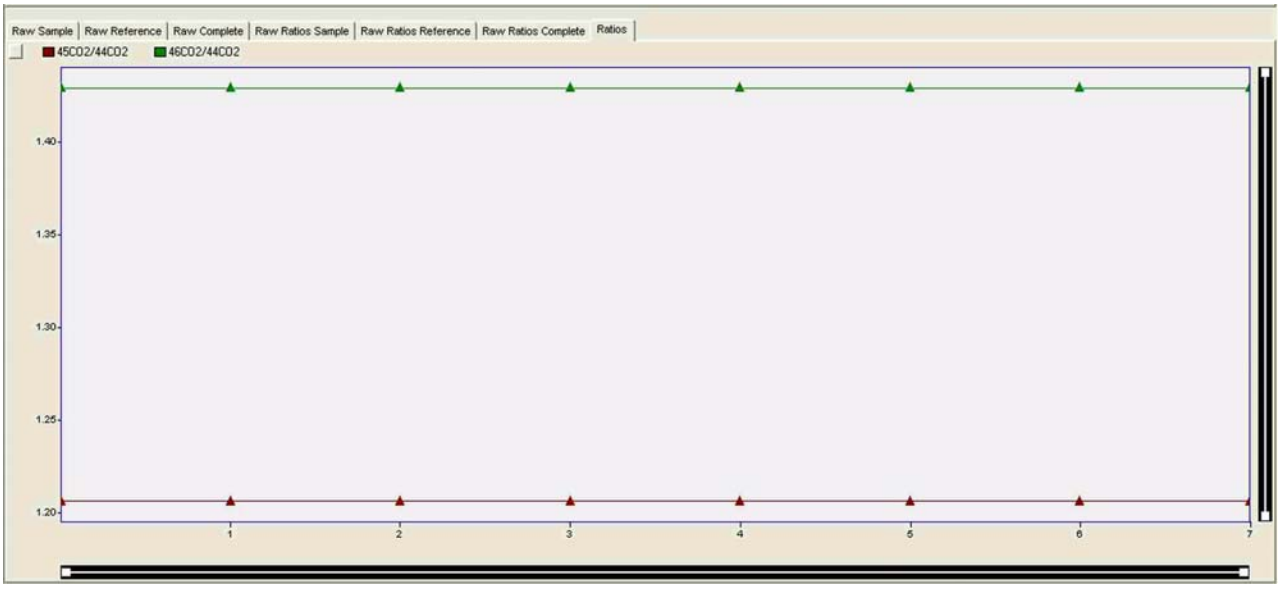


Figure 3-86. Ratios Tab

Ratios tab, Figure 3-86, corresponds to columns 7 and 8 in Figure 3-74. It contains the result after subsumption of all slices (the outliers have been mathematically eliminated).

Interfering Masses

Interfering masses can be implemented in acquisition scripts as follows:

1. In an arbitrary acquisition script, include the following line in the section after the comment “place your includes here”:

   Include "lib\InterferingMass_lib.isl".

   If you save a method that contains an acquisition script with this line and load it again, you will notice that a new tab has been added to the method tabs. If you click on this tab, the method page shown in Figure 3-87 will appear.

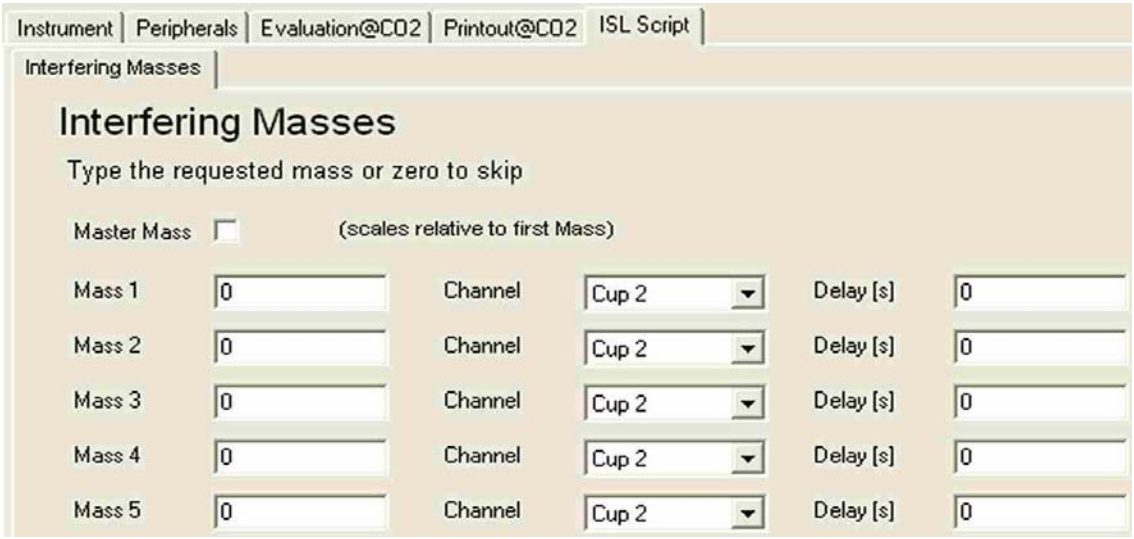


Figure 3-87. Interfering Masses Tab

Here, you can select up to five masses to be determined during execution of the interfering masses function. The result of each measurement (mass, cup and intensity) will be reported within the **Extended** tab of the result file.

2. But first, a call to this function needs to be implemented in the acquisition file. To do this, fill in the following line at an arbitrary position within the “main” section of the acquisition file:

   call DiMeasureInterferingMasses(2,2000)

The position of this 'function call' of course determines when the interfering masses will be measured during workflow. In the code example below, which is valid for the Kiel IV Carbonate Device, this point in time is immediately after the accomplishment of the sample measurement.

Code Example

```
main()
{ call InitScript();
_LoadDynExternals("Carbonate Device\Dynexternals.iso");
if (_GetSequenceInfo(IS_FIRST_SAMPLE_RUNNING,TRUE))
{


    _RegSetProfileNumber("TASK_LOCKING", "PREP_READY",0);
    _RegSetProfileNumber("TASK_LOCKING", "T1_FREE",1);
    _RegSetProfileNumber("TASK_LOCKING",
    "HVPUMP_FREE",1);
    _RegSetProfileNumber("TASK_LOCKING",
    "DROP_WHEN_STANDBY",0);
    _RegSetProfileNumber("TASK_LOCKING",
    "ACID_IN_SAMPLE",0);
    _RegSetProfileNumber("TASK_LOCKING",
    "SEQUENCE_ABORT_FATAL",1);
    _RegSetProfileNumber("TASK_LOCKING",
    "FIRST_PREPARATION_DONE",0);
    call PrepareRun();

}

    _StartFirstPreparation("\Carbonate Device\Instrument
    Control\PrepareSample.isl");

    string sSeqText=""; sSeqText=_GetSequenceText("Line","Empty");
    number nLine=_strtod(sSeqText);
    sSeqText=_GetSequenceText("Sample","Empty"); number
    nSample=_strtod(sSeqText);

    call MeasureOneSample(nLine,nSample);
    call DiMeasureInterferingMasses(2,2000);

}
```

3. In some cases, it will be necessary to control the Changeover Valve to measure the interfering masses while the COV is closed or in a specific position. To do this, include one of the following lines in your code immediately before calling the interfering masses function:

```
call ChangeOverLeft();
call ChangeOverRight();
call ChangeOverClose();
```

4. Finally, it is possible to call the interfering masses function several times during an acquisition script. The set of masses and cups selected will remain the same, but all results are reported as expected in additional lines of the **Extended** section.

Chapter 4 Basic Operations

This chapter contains the following topics:

Leak Check

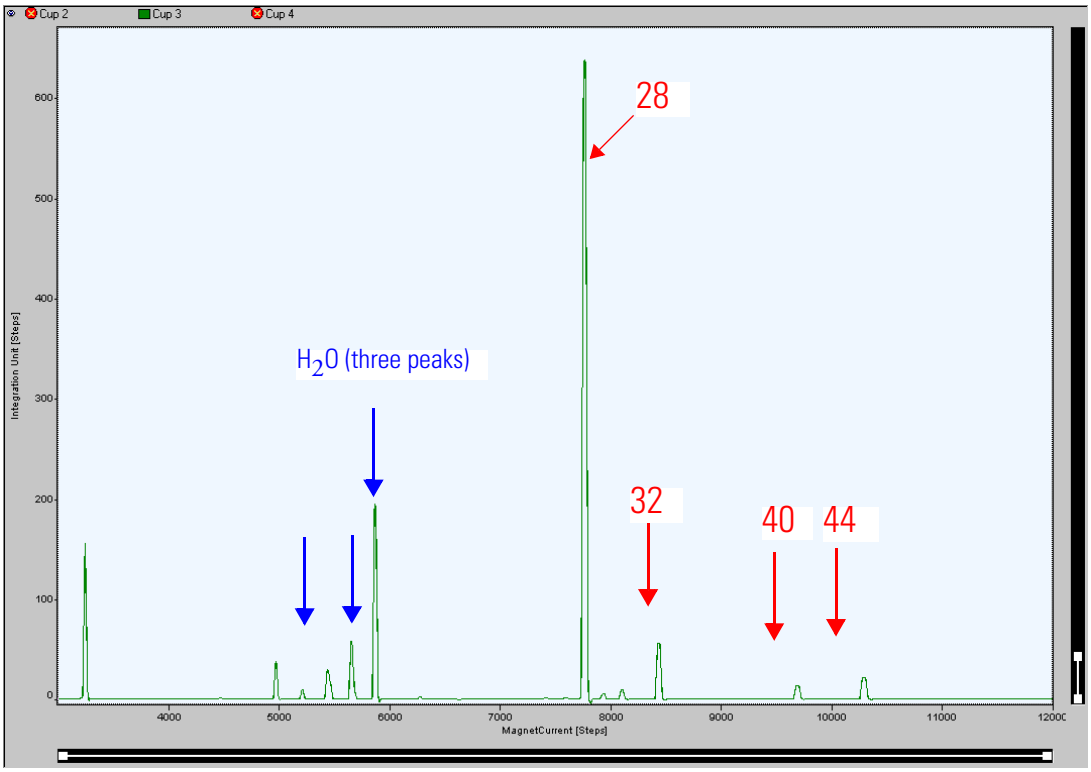


Figure 4-1. Mass Spectrum of Background Gas Composition*

*for Finnigan DELTA V

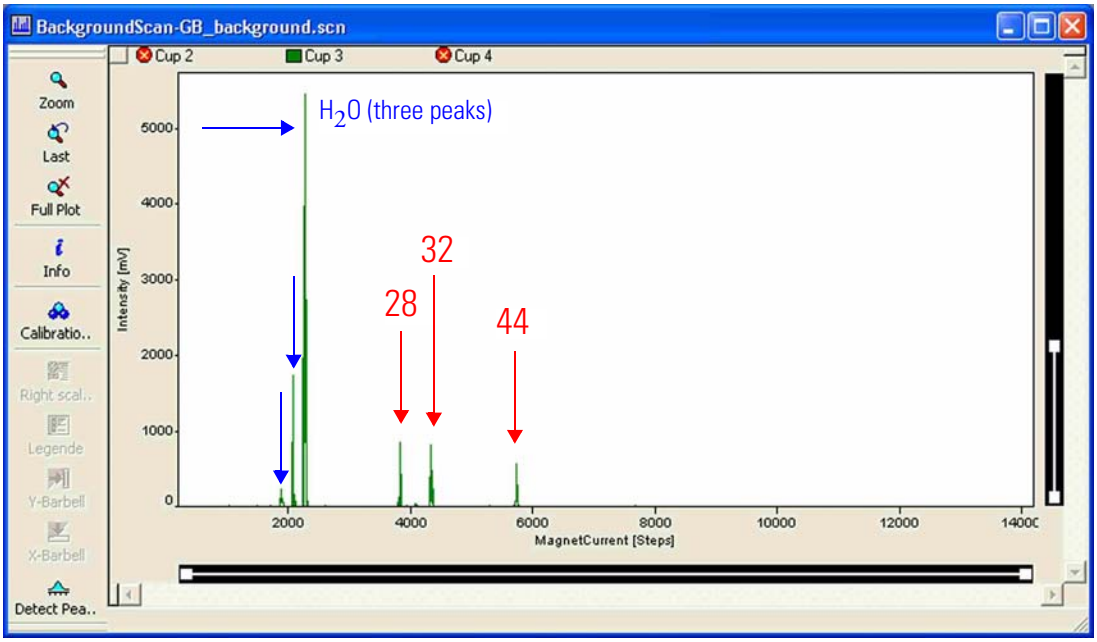


Figure 4-2. Mass Spectrum of Background Gas Composition*

*for Finnigan MAT 253

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.

The mass scan shows the composition of the background gas in the ion source region and informs about the amount of gases present. Try to identify the following patterns and compare them with the maximum values below (magnet step values for DELTA series):

Water

Water in the background gas is indicated by the following properties:

- 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 for DELTA series at 3 kV.
- Peak intensity after a couple of days of continuous operation should be max. 1 V for DELTA V and less than 500 mV for MAT 253.
- Intensity ratio of the three peaks is 1:2:4.
- CO_2 reference gas can be checked at normal sensitivity (e.g. 4 V gives a background level of m/z 18 as the normal background).
- If the m/z 18 signal of the CO_2 reference gas is too high, the CO_2 reference gas tank must be baked out and refilled again.

Air

Air in the background gas is indicated by the following properties:

- 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

CO_2 in the background gas is indicated by the following properties:

- 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 h. If a high water level is present in the ion source, usually some air is leaking into the IRMS 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 the Kiel IV Carbonate Device 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.

Dual Inlet Ar Signal

The Dual Inlet argon signal should be very small, that is less than 20 mV on m/z 46 as the center cup ($3*10^9$ Ω). When measuring small sample amounts (that is, about 10 µg), an argon background of less than 10 mV on the highest amplified cup is recommended. This is mandatory for all high vacuum lines.

Advanced Leak Checking Procedure

An advanced leak checking procedure that can be used to search for the smallest leaks is described in this section.

1. Make sure that the IRMS uses the **CO2** configuration.

2. Select m/z 40 in middle cup where the amplification is set to $3*10^{10}$.

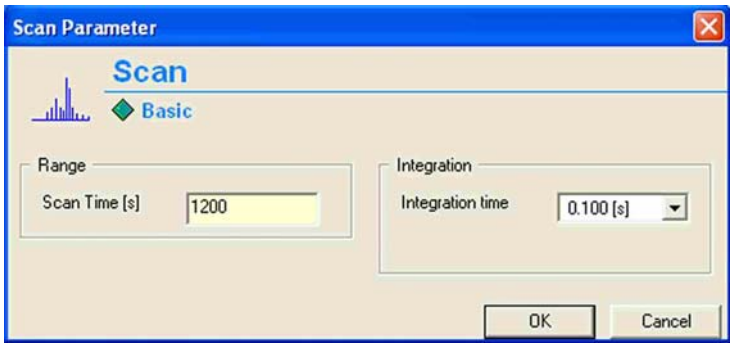


Figure 4-3. Scan Parameters during Leak Check

3. Switch on the **Tune Scan** option in Instrument Control and start an acquisition in order not to miss events. Use a reasonable big acquisition time, e.g. 1200 s and zoom the time axis to display a window of 100 s. See Figure 4-3.

4. Make sure that you can look at the screen while performing the following leak test.

5. Use a gentle flow of argon, so small that it is hardly detectable when directed towards the lips. Spray all fittings and flanges using a plastic syringe tip as gas outlet.

Note During this entire procedure, **no** raise in the actual argon level should be visible! To precisely locate a possible leak, it is required to use an argon flow as small as possible. ▲

6. Directly touch all fitting surfaces and welded connections and move the gas outlet slowly over them.

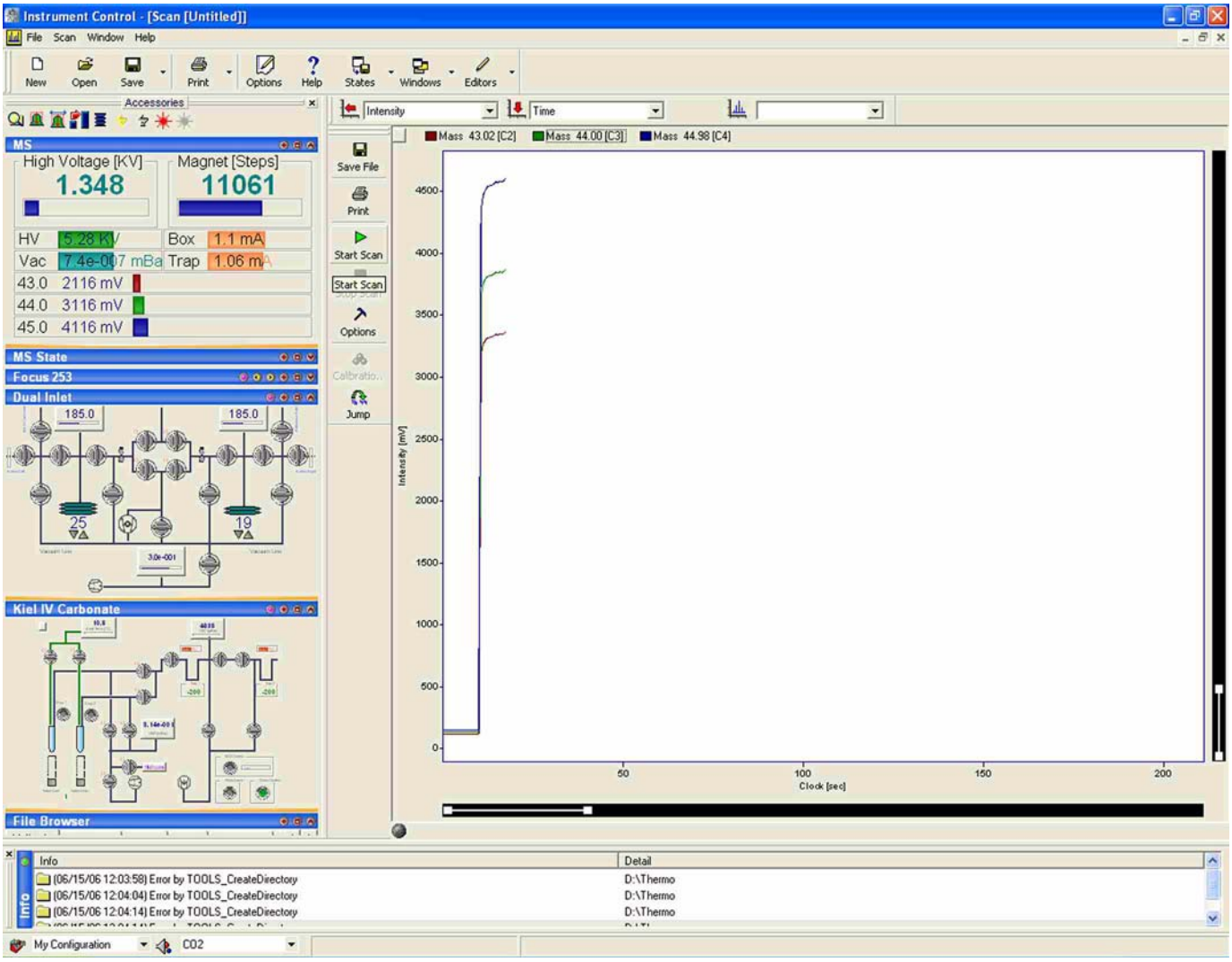


Figure 4-4. Instrument Control as Aid when Leak Checking

Note Using high flows during this procedure may produce false signals due to argon moving around the IRMS in an unpredictable way. See Figure 4-4. ▲

Use Instrument Control as an aid when checking for leaks by monitoring m/z 40: while spraying argon to the vicinity of a leak, it will be detected by a sharp rise of argon intensity. See Figure 4-4.

Bakeout of Kiel IV Carbonate Device

Upon installation and after some time, if precision deteriorates, the tubing of the Kiel IV Carbonate Device can be baked out in order to vacuum-clean the tubing. This procedure should be performed with the vacuum system switched on and the Kiel IV Carbonate Device in "Standby" valve position. The following steps are required:

1. Heating the **capillary** to the IRMS by using the designated 7 V capillary heating transformer (see Figure 2-18 and especially step 19 on page 2-14):

   a. Attach the middle steel point to 7 V.

   b. Put the grounding to both capillary ends. At 7 V, temperatures above 180 °C are obtained.

Note Bake out capillaries only, if all other parts are baked out at the same time. ▲

2. Heating the **valve blocks** associated with traps 1 and 2. This can be performed by using a heat gun capable of heating to a maximum of 120 °C. The grease and O ring seals in the valve blocks are suited for this temperature. From now on, both valve blocks of trap 1 and trap 2 can be heated by a heating cartridge[1].

3. Heating the **Micovolume** using an open flame. The tip of the Microvolume finger can be heated up to 600 °C using a suitable torch or a cigarette lighter.

Warning Be careful to heat only the finger and not the surrounding plastics or the valve block! ▲

[1]In former times, either a hair blower or heating bands (usable up to 450 °C) have been used instead of a heating cartridge. With these, it is easy to destroy the pneumatic part of the valve by uncontrolled heating. The valve contains an O ring seal and grease not suitable for temperatures above 150 °C!

4. Heating the **reference tank** before refilling with CO_2.

   a. Attach a 1/4” tubing to the Swagelok connector. See Figure 2-54.

   b. Attach the other end of the 1/4” tubing to the internal standard inlet. If internal standard inlet is not available, valve ports of internal sample inlet or external right or left inlet ports can be used.

   c. Bake out the reference tank using the heating bands over night, that is for 12 h.

   d. Open the manual valve (for those manual parts which cannot be heated using heating bands).

Operating the Autosampler

Connecting Vials

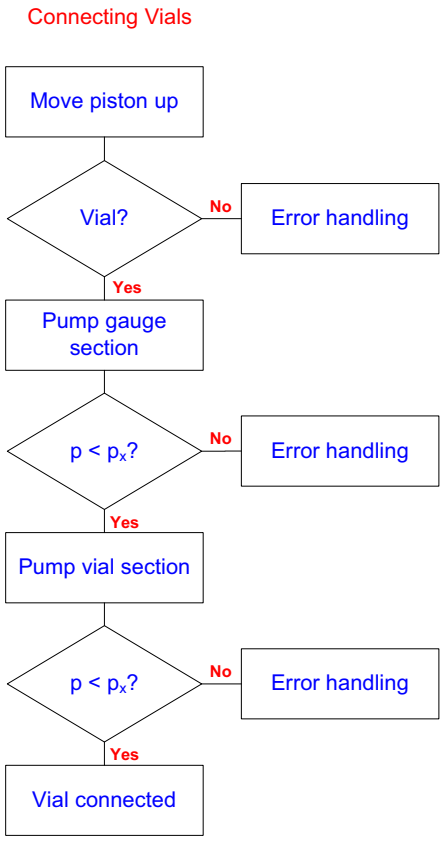


Figure 4-5. Connecting Vials

The connection of a vial to the acid valve (see Figure 4-5) is a straightforward process, if no errors occur. Two ISL Dyn Externals variables control this process.

The first one is a delay that should be set according to the movement speed of your piston (see Figure 3-60). The second is a pressure threshold, p_x in Figure 3-60. It is used to mark an upper level to the vacuum quality that you want to accept in the vial section of the Kiel IV Carbonate Device.

Correct function and positioning of the proximity switch in the acid valve that is used to detect the presence of a vial is important for proper operation of the connect algorithm as well. Refer to "Proximity Switch" on page 2-32.

Disconnecting Vials

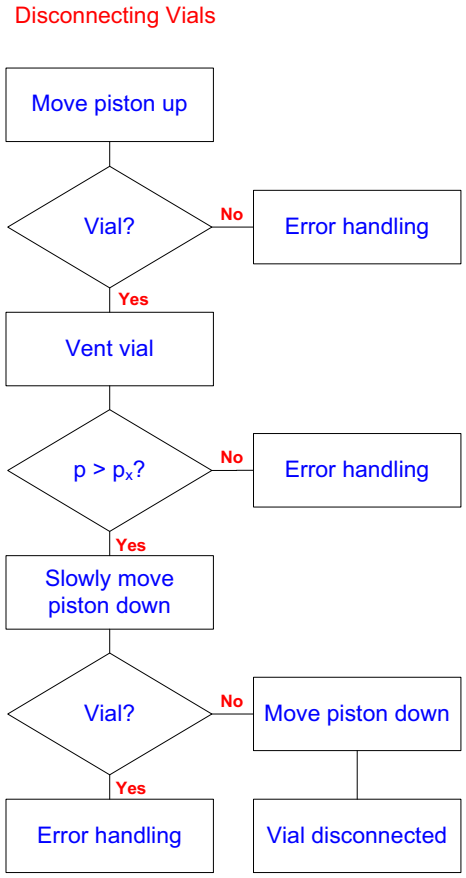


Figure 4-6. Disconnecting Vials

Disconnecting a vial (see Figure 4-6) requires the fore vacuum section of the Kiel IV Carbonate Device to be leaktight and the vent gas to have sufficient pressure.

The first point requires that the connect algorithm works properly. For the second point, it is necessary for the vent gas pressure to be approximately 0.5 bar. In this case, the gauge VM2 shows a pressure of approximately 14 mbar. After venting again, the pressure is checked with V12 and V22 closed. This level can be adjusted via the ISL hardware parameters (see **5** in Figure 3-60).

Matching Sample Capillary to Standard Capillary

This section describes how to match the sample flow from the Kiel IV Carbonate Device to the standard flow of the IRMS. As an example, see Figure 4-7. Flows must be matched to ensure equal voltage readings during the course of the measurement.

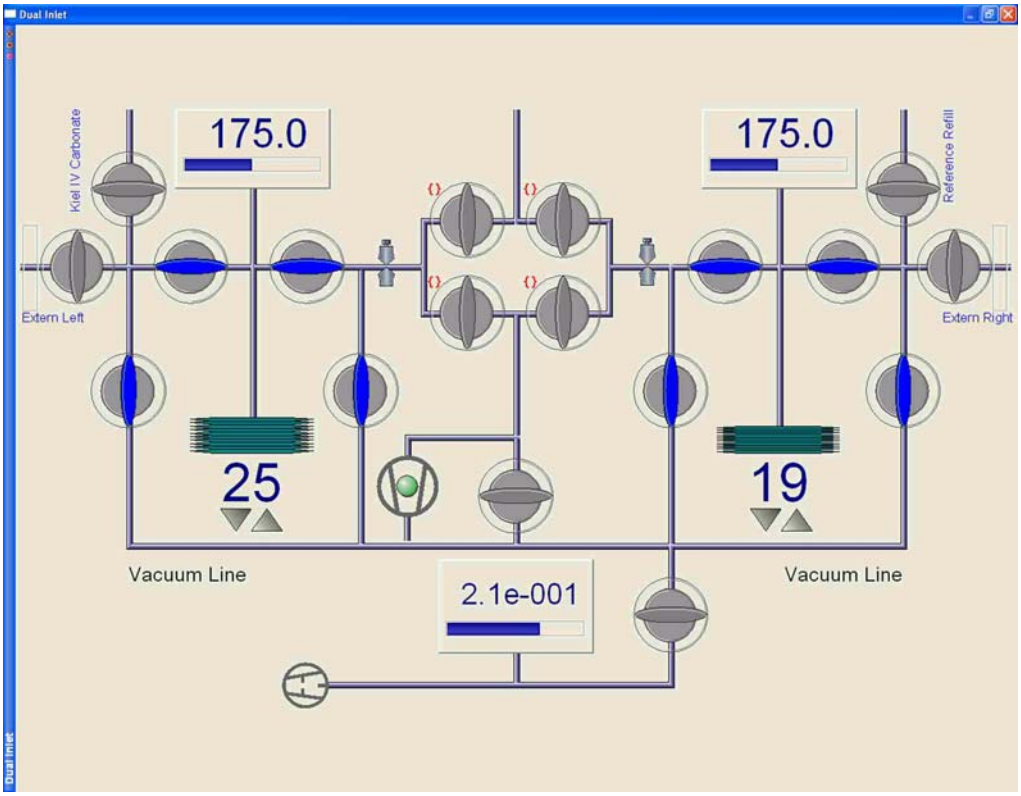


Figure 4-7. Matching Sample Capillary to Standard Capillary

The volume between V25, V26, V34 and V33 plus the capillary at the standard side of the IRMS has almost the same size as the volume between V3 and V5 plus Microvolume and the capillary of the Kiel IV Carbonate Device.

This means that matching the two signals from the two capillaries for an arbitrary pressure setting will result in an equal flow for both capillaries and, subsequently, for the parallel voltage drop for all possible signal heights.

The following procedure shows how to match the two capillaries:

1. Switch off the turbo pump of the Kiel IV Carbonate Device

Note In case of Kiel III Carbonate Device, the turbo pump can continue operating.

2. Close V1, V2, V3, V4 and V5 on the Kiel IV Carbonate Device.

Note In case of Kiel III Carbonate Device, V9 protects V4 from being vented. Therefore, only close V3, V5 and V9. Open V4.

3. Remove the flexible tubing which connects the valve combinations VC5 and VC3 (trap 1 and trap 2, respectively).

4. Connect an 1/8” stainless steel tube on the left sample port of the Dual Inlet (at V11). See arrow in Figure 4-8.

Figure 4-8. Connecting Transfer Tube to IRMS

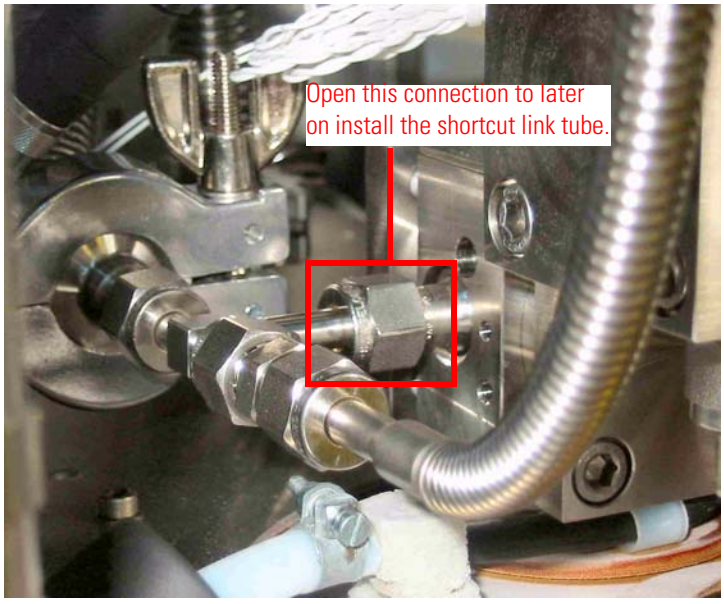


Figure 4-9. Connection for Installation of Shortcut Link Tube

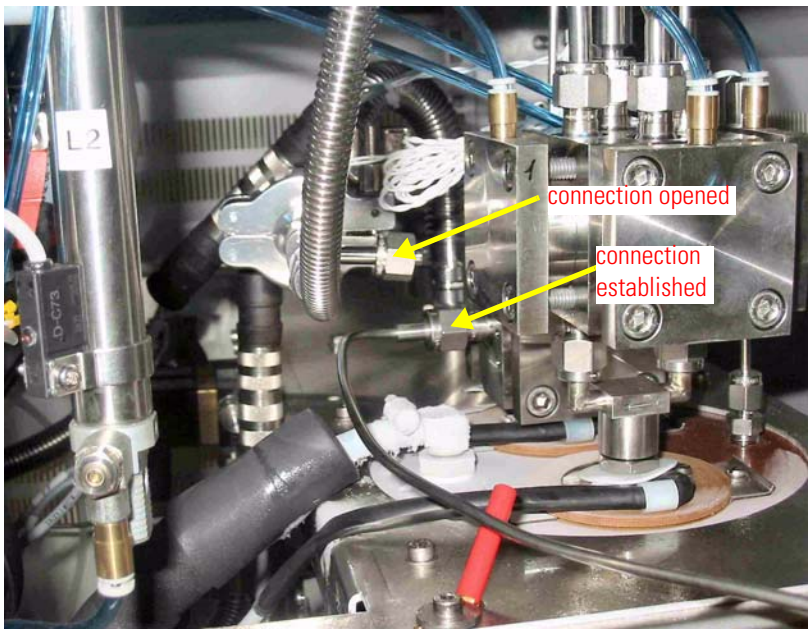


Figure 4-10. Connecting Transfer Tube to Kiel IV Carbonate Device

5. Connect the other side of the above tube to V5.
   See Figure 4-9 and Figure 4-10.

6. Now that the Microvolume (trap 2) of the Finnigan Kiel IV Carbonate Device is connected to the Dual Inlet, open both bellows to 100 %. Carefully pump all tubes including sample and reference of Dual Inlet.

7. Close V15 of sample side and let 50 mbar of CO_2 flow in at both sides of the bellows. V25, V24, V23, V13, V11, V14, V4, V2 and V3 are open.

8. Squeeze the carbonate capillary until an acceptable tolerance (that is, less than 50 mV) is reached. See Figure 6-7 and Figure 4-11.

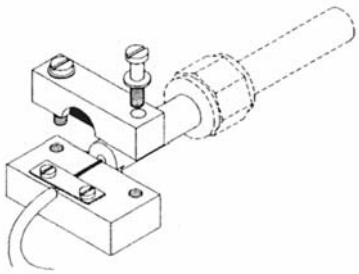


Figure 4-11. Crimping Device at the End of a Capillary

9. Match the signal intensity of the carbonate capillary to the signal intensity of the reference side (usually the right side, see Figure 4-12). Frequently check the result by switching the Changeover Valve to the respective side. Allow for signal settling times in the range of minutes.

10. After reference matching, the lines must be baked out including all tubings and the entire inlet system (IRMS and Kiel IV Carbonate Device).

Figure 4-12 illustrates the complete plumbing with the link tube to perform capillary matching.

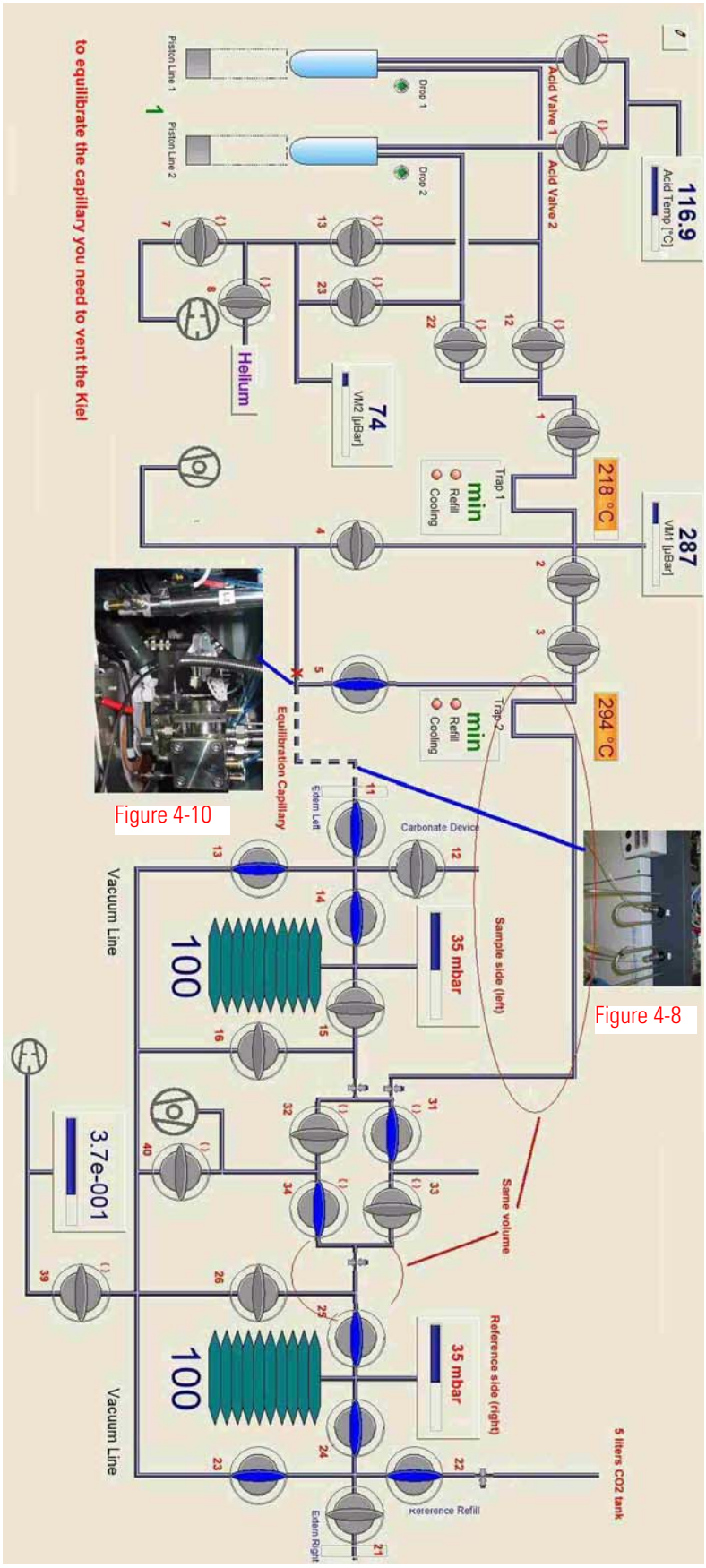


Figure 4-12. Vacuum Scheme of Kiel IV Carbonate Device

Cleaning Acid Valve

In order to clean the acid valve, it must first be **dismantled**. After the **cleaning** procedure, it must, of course, be **reassembled**.

Disassembling Acid Valve

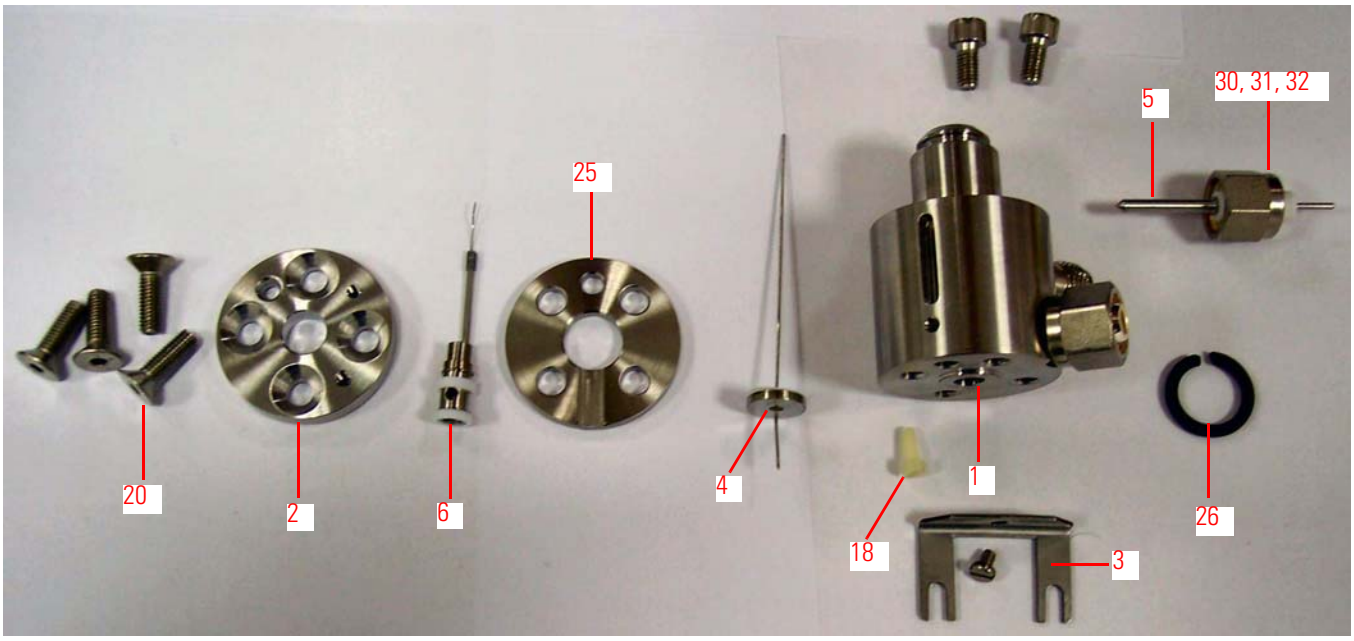


Figure 4-13. Parts of Acid Valve*

*For the numbers and a more detailed description, refer to "Acid Valve" on page 6-8 and to Table 6-3.

Note At regular intervals, approximately every two or three months, the acid capillary might be clogged by crystallized acid. Disassembling and cleaning the acid valve avoids clogging. ▲

Always disassemble and clean the acid valve, if:

- a drop is indicated all along at trap 1 or trap 2 and therefore a "vial connect" failure appears either randomly or permanently.
- the leak rate is too high and therefore phosphoric acid gets inside the acid valve.

To disassemble the acid valve, proceed as follows:

1. Unmount the pinch valve by opening the two screws on each side. See Figure 4-14.

Figure 4-14. Acid Valve in Position

Warning Be sure to remove the valve together with the acid tubing in order not to spoil acid onto the pinch valve plunger! ▲

2. Remove the screw from the proximity sensor and pull out the sensor.

3. Remove the acid valve holder. See Figure 4-15.

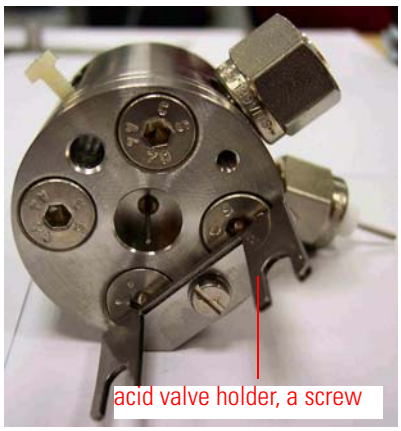


Figure 4-15. Acid Valve - I*

*View from above with pinch valve mounted

4. Mark the three parts of the acid valve so that they can be tightened in the same position later on.

5. Loosen the four screws and remove the upper part with the acid capillary. See Figure 4-16.

Figure 4-16. Acid Valve - II*

*View from above without pinch valve mounted

Note Always renew the Teflon gasket, **12** in Table 6-3. ▲

6. Remove the drop counter insert and electrical connection by opening the Swagelok connection at the electrical feedthrough. See Figure 4-17.

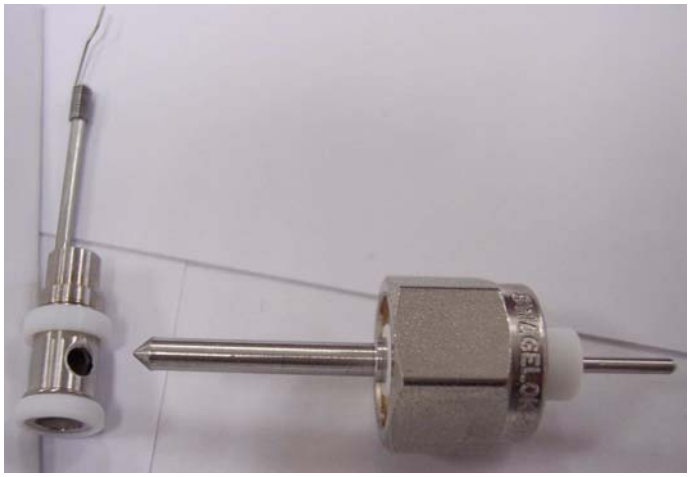


Figure 4-17. Drop Counter and Electrical Feedthrough

Caution Be careful not to destroy the acid dropper capillary and the drop counter spring during installation of the removable tray! ▲

7. Remove the spring plate from the bottom of the common mounting plate to get access to the screws that hold the acid valve in place. See Figure 4-18.

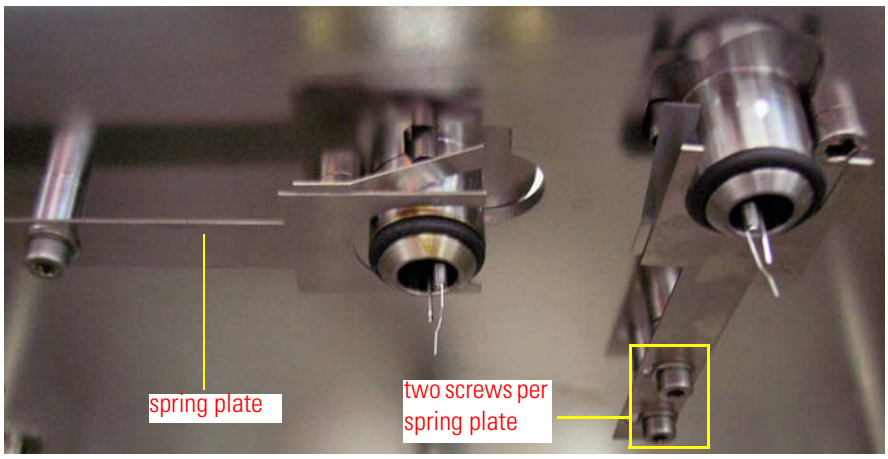


Figure 4-18. Mounted Spring Plate - Bottom View

8. Remove the bottom screws and the remaining Swagelok connection to the valve block in order to completely remove the acid valve. See Figure 4-19.

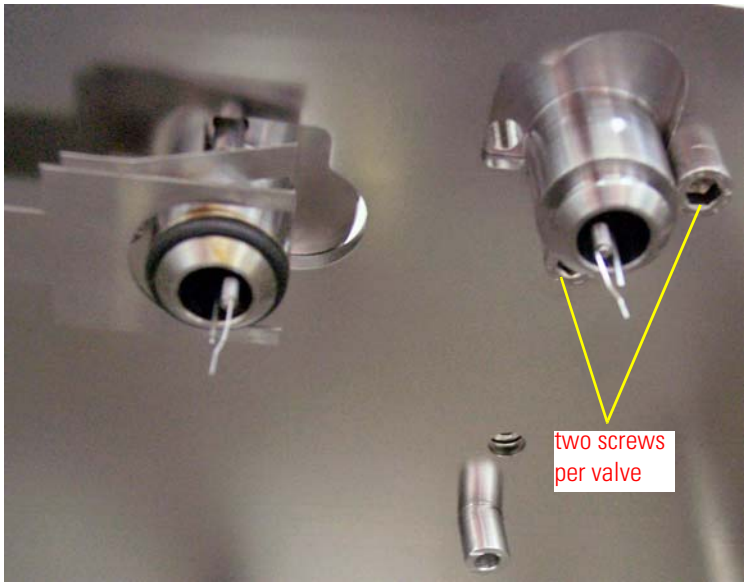


Figure 4-19. Mounted Valve - Bottom View

Note The Swagelok connection contains a removable stainless steel frit, Part No. 115 7670. See Figure 4-20. ▲

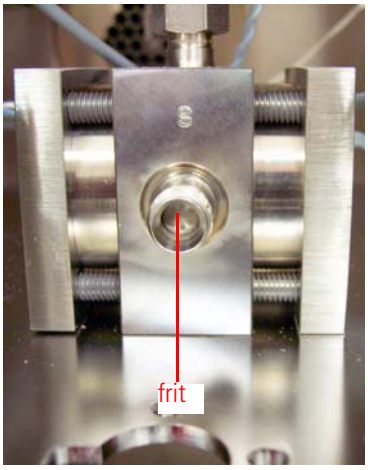


Figure 4-20. Valve Flange with Frit

All parts can be cleaned in deionized water and dried in acetone or in an oven at 70 °C.

Note Reassemble the acid valve in reverse order and thoroughly check for leaks! ▲

Note Use Apiezon H for sealing the Viton rings.
See www.apiezon.com. ▲

Brief and Superficial Cleaning Procedure

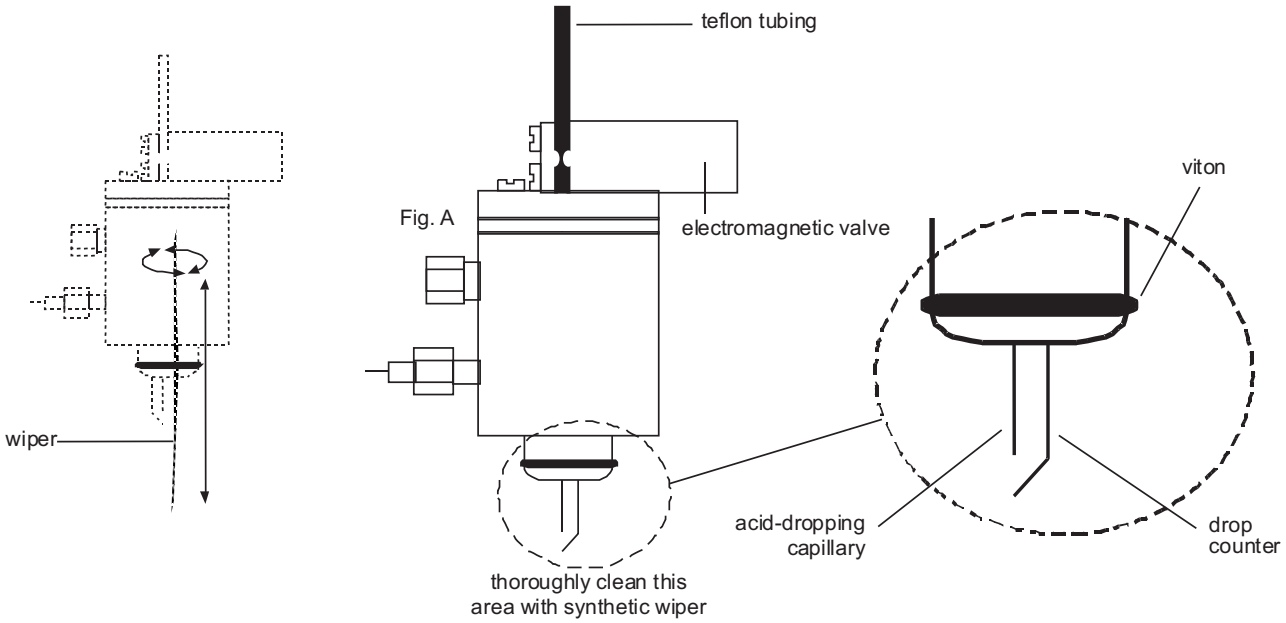


Figure 4-21. Cleaning Acid Valve

We recommend to clean the acid valve after every magazine that has been measured. Use a synthetic wiper.

Note The ends of the drop counter and the acid dropping capillary must be aligned. Otherwise, acid dropping stops (surface tension of the two wires or drops at the side wall of the vial). Dropping at the side wall will avoid acid reaction. ▲

To briefly and superficially clean the acid valve:

1. Use a lint-free wiper. Roll it up approximately as thick as a match.

2. Clean the inner part of the acid valve as shown at Fig. A in Figure 4-21.

3. Clean the Viton ring.

Thorough Cleaning Procedure

Note During the cleaning procedure, be careful not to lose any of the Teflon rings of the drop counter! ▲

1. Put all parts into a beaker containing deionized water and heat it above 80 °C for about 30 min.

2. Clean the parts twice or more times.

3. Put the parts into acetone for fast drying.

4. Put the parts into the heating cabinet for drying.

Reassembling Acid Valve

To reassemble the acid valve, first attach the acid capillary before installing the drop counter.

Note During reassembly, exchange the Teflon washer positioned beneath the first thick metal washer! ▲

Attaching Acid Capillary

1. Lay the metal body onto a table.

2. Put the acid capillary into the metal body.

3. Put the two thick metal washers which fix the dropping capillary.

4. Tighten all screws which fix the two washers and the drop counter.

Note The hole of the proximity switch must be in-line! ▲

Installing Drop Counter

1. The grounding ("shift") must be drawn inwards through the Teflon body.

2. Consequently, the wedged tip can be tightened with pressure into the small hole of the drop counter.

3. Put the drop counter into the full metal acid valve body from below.

Note The counter tip must be opposite to the grounding tip! This will avoid a short circuit to the full metal body of the acid valve. ▲

Adjusting Liquid Nitrogen Refill Sensor

If you encounter problems with setting temperatures below room temperature, the liquid nitrogen refill sensor must be adjusted. Before you actually touch the sensor itself:

1. Check that the liquid nitrogen tank is pressurized between 0.5 bar and 1.5 bar and that it contains liquid nitrogen. See Figure 2-47.

Note If the tank head pressure exceeds 1.5 bar, the consumption of liquid nitrogen during the liquid nitrogen refill process will increase dramatically. ▲

2. Check the electrical connection to the liquid nitrogen refill valve and the status of the manual valve in series with it.

3. Make sure that the resistor beneath the funnel can be heated and that no ice has been formed inside the capillary.

Note Frozen water will prevent the liquid nitrogen from rising into the cooling cascade! ▲

4. Only then, think of moving the sensor: move it carefully, only 1 mm at a time. If cooling is insufficient, move the sensor up. If heating is insufficient, move the sensor down.

Operating Pinch Valve

The pinch valve operates at 24 V. Without an impressed voltage, it will therefore be closed. The connection operates with grounding. The pinch valve controls the acid flow and operates with viscous H_3PO_4 up to 80 °C. The acid flow will be stopped at medium vacuum, that is approximately below $7\text{-}9*10^{-3}$ mbar.

Warning The supplied pinch valve is not acid-resistant. If any phosphoric acid is attached to the crimp of the pinch valve, the acid will degrade the pinch valve! The pinch valve must be immediately exchanged to avoid flooding the tubing of the Kiel IV Carbonate Device with acid! ▲

If no drop appears, the outer diameter of the Viton tubing is too wide. In this case, the tubing must be cut by a few centimeters. When the correct outer diameter is given, it will operate again. Open the acid valve using pliers. Now, phosphoric acid may flow through Viton tubing and acid valve.

Prior to a run a carbonate sequence, an acid drop test using carbonate-free position 2 test vials must be performed. Therefore, acid flow from the container through tubing and acid valve as well as vial connection and vial disconnection can be tested. If any of these tests fails, the underlying reason must be found and solved.

Acid flow can be stopped as a consequence of:

- improperly operating pinch valve
- crimped acid tubing because of too long idle time during closed pinch valve.
  Open the tube and avoid any phosphoric acid to drop on the crimp of the pinch valve. Cut or open the tubing using pliers in order to obtain acid flow. If no acid flows, the acid reservoir might be under vacuum or closed.
- a leak in the glass-to-tubing connectors.
  Close the straight connectors slowly and smoothly.

Troubleshooting

Note From time to time, take a look at the checklist shown below. It outlines the performance achievable by the system. Check all mentioned items. ▲

1. A basic test must be performed, that is testing the IRMS alone.

2. Only if all previous items are performed to specifications, carry out the measurement.

3. Finnigan Kiel IV Carbonate Device and IRMS must be free of leaks.

4. Bake out the transfer capillaries, traps and valves whenever possible to avoid contamination.

5. Check the drop counters for proper built-up of drops. Spraying of drops must be avoided!

6. Remove acid from O ring seals and drop counters using a lint-free cloth such as Kimwipes®.

7. Use new O ring seals on the acid valve.

Elementary Handling of Kiel IV Carbonate Device

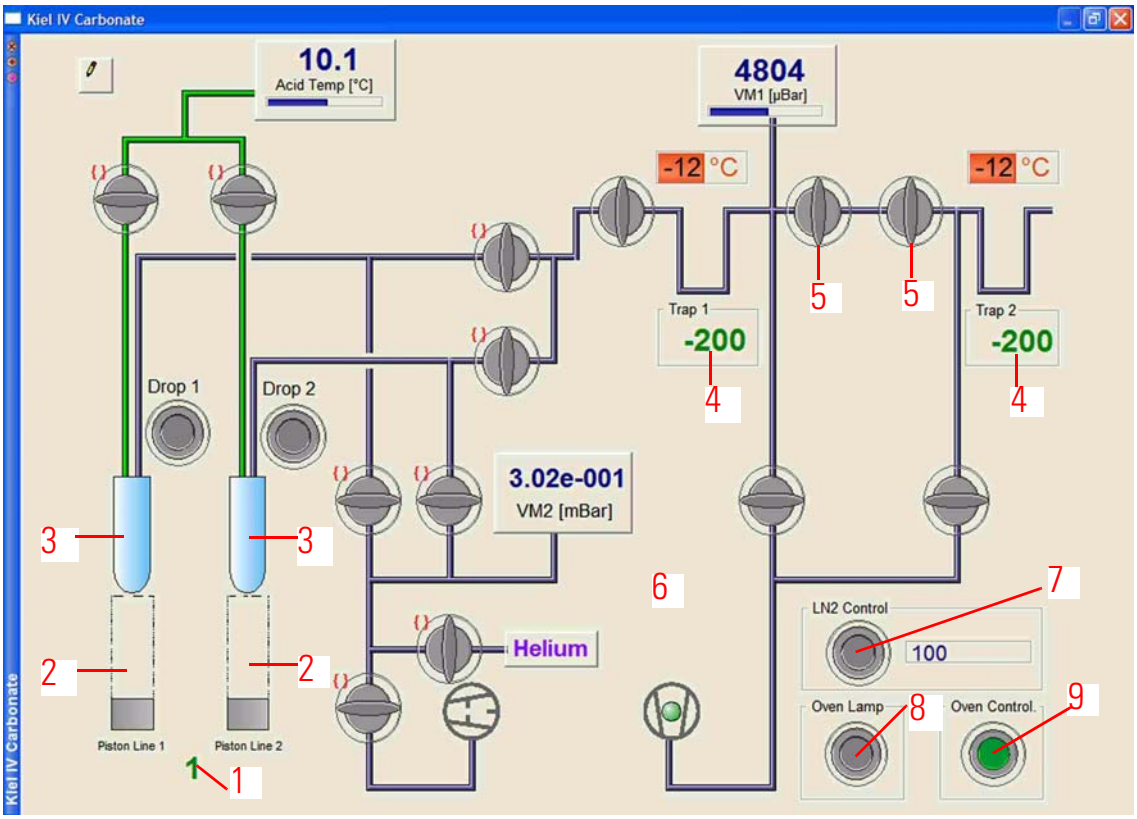


Figure 4-22. Kiel IV Carbonate Window

Figure 4-22 and Table 4-1 summarize basic operations to be executed via the **Kiel IV Carbonate** window.

It allows direct access to all Kiel IV Carbonate Device hardware components: autosampler turret control, trap temperature control, liquid nitrogen refill control, individual valves, vial connection and vial disconnection.

You can set or reset hardware components at any time, even during an acquisition. Click on a graphical object to operate the specific device.

Table 4-1. Basic Operations via Kiel IV Carbonate Window

No. in Figure 4-22	Comment
1	Move magazine to another position
2	Move piston up or down
3	Connect or disconnect vial. Use this button to check the connect algorithm and disconnect algorithm.
4	Set temperature of trap 1 or trap 2. Temperatures between -150 °C and 150 °C can be adjusted. Temperatures below -150 °C are not regulated.
5	Open or close valve. Refer to Figure 6-27 and Figure 6-42 for valve numbers.
6	Show available ISL scripts (via right-click somewhere)
7	Liquid nitrogen control. Press once to fill to 50 % fill level
8	Oven lamp (manual switch)
9	Oven control. Provides power to the Jumo itron 16 temperature controller. Refer to "Oven and Oven Control" on page 2-27.

Vial Test

Principle

The vial test monitors basic operations (connect/disconnect procedure on each position of the turret) and controls the usability of valves and vials for carbonate analysis.

A vial test method is a separate method without acid dropping and reduced timing. The leak rate will be reported for each vial. Thus, the vial test indicates, whether the individual vials ensure the needed quality.

We recommend performing a vial test when the Kiel IV Carbonate Device is set for first time of operation, after changing any hardware such as new pistons, magazine and after getting a new set of vials.

Performing a Vial Test

The vial test is performed as follows:

1. Take a magazine and place a vial into each position.

2. Insert the magazine into the oven.

3. Establish a vial test method as follows:

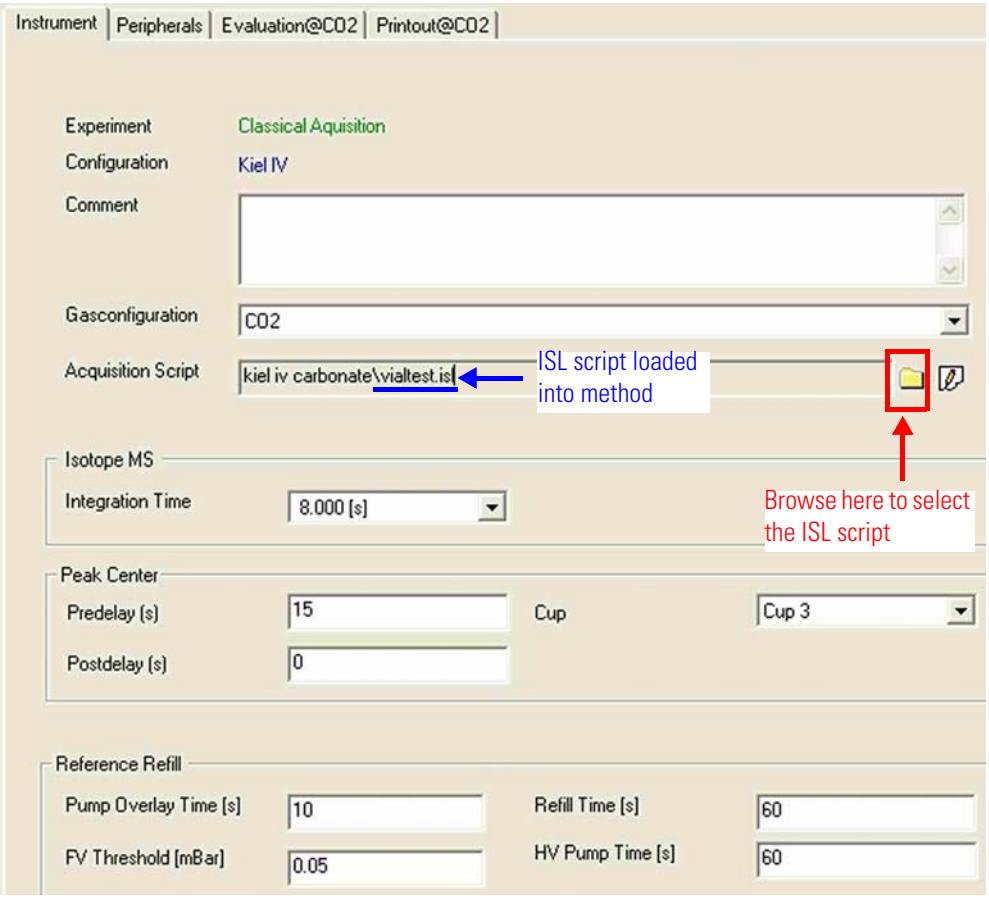


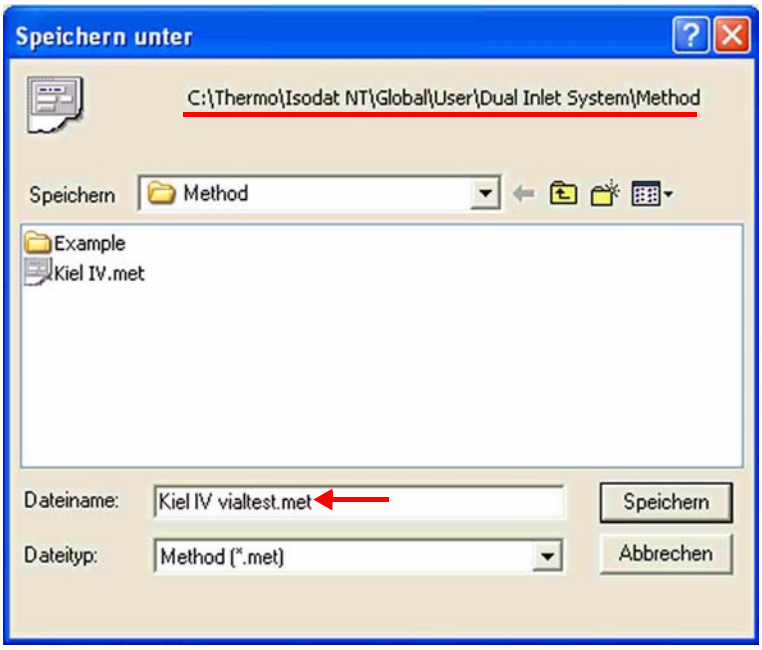
Figure 4-23. ISL Script is Loaded into Method

Browse to the folder **Kiel IV Carbonate** (see Figure 4-23).

Mark the ISL script **vialtest.isl**.

The ISL script will be loaded into the method (see Figure 4-23).

Figure 4-24. Selecting ISL Script for Vial Test



Save the method as a new method, e.g. as **Kiel IV vialtest.met**.

Figure 4-25. Saving Method as a New Vial Test Method

4. Use a new sequence to be run with the new method **Kiel IV vialtest.met** on each position (refer to "Creating a New Sequence" on page 3-31).
   During the connect/disconnect procedure, the following steps will be applied vial by vial:

   a. Take a vial and connect it to the acid valve.

   b. Measure the proximity switch, when the vial is connected. Refer to "Proximity Switch" on page 2-32.

   c. Open V7 and wait until the pressure at VM2 has fallen below 1000 mbar.

   d. Bring the piston down and measure the pressure at VM2. Refer to "Adjusting Piston Height" on page 2-32.

   e. Open V13 and wait until the pressure at VM2 has fallen below 200 mbar.

   f. When the vacuum is within an acceptable range (see **VM1 Leak Threshold** as **b** in Figure 3-34 and Table 3-11), continue with the next vial.

Possible Error Messages during Vial Test

During a vial test, the following error messages may occur:

- Vial is not connected.
- Vial is defective.

- Vial is missing.
- Connect procedure failed. In this case, test the connect/disconnect procedure and readjust the spring plate. See Figure 4-18.
- Proximity switch fails. See “Proximity Switch” on page 2-32.
- VM2 pressure is too high, that is a leak is present.
- Trap 1 and/or trap 2 are not operating properly.
  In this case, check the Autocool Unit (refer to “Autocool Unit” on page 2-24) and the liquid nitrogen dewar (refer to “LN2 Transfer from Refill Device into Dewar” on page 2-38).

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 hood, one “Winchester” (that is, a 2.5 l package) of phosphoric acid is poured into a 5 l beaker positioned on a magnetic stirrer’s hotplate. Use a magnetic stir bar (PTFE).

Warning Gloves and a face mask must be worn whenever handling phosphorous pentoxide! Goggles are not sufficient! ▲

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

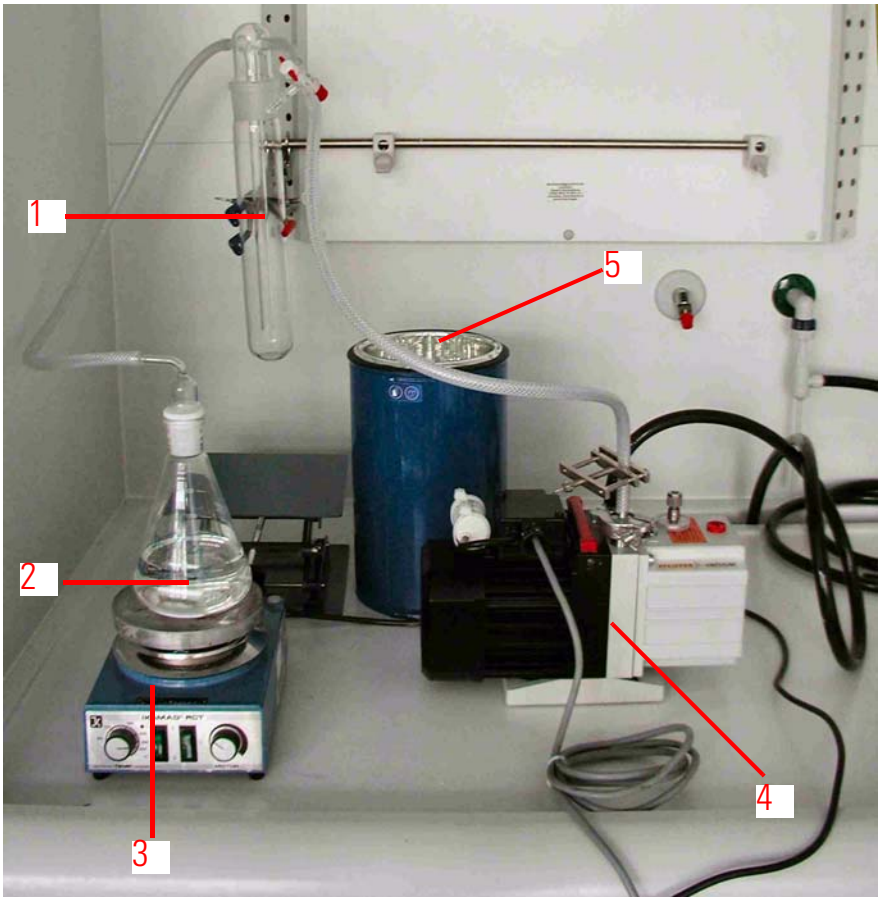
Note A useful thermometer or stirring rod can be obtained by enclosing the thermometer in a large piece of heavy-walled Pyrex tubing with its bottom sealed off (that is shaped like a test tube). ▲

Note An alternative way of phosphoric acid preparation has been described by J. Burman, O. Gustafsson, M. Segl and B. Schmitz: A simplified method of preparing phosphoric acid for stable isotope analyses of carbonates. Rapid Commun. Mass Spectrom. 2005, **19**, 3086-3088. ▲

Removing Water from Phosphoric Acid

Figure 4-26 shows the apparatus used to remove water and absorbed gases from phosphoric acid before phosphorous pentoxide is added. It avoids a rigid reaction with phosphorous pentoxide. Furthermore, the apparatus can be used to regularly dewater prepared 105 % H_3PO_4[1].

Note Procedures and considerations about water content of phosphoric acid have been described by E.A. Wachter and J.M. Hayes: Exchange of oxygen isotopes in carbon dioxide–phosphoric acid systems. Chem. Geol. (Isotope Geoscience Section) **52** 365–374 (1985). ▲



1 500 ml water trap
2 acid
3 hotplate and magnetic stirrer
4 vacuum pump
5 dewar for liquid nitrogen

Figure 4-26. Removing Water from Phosphoric Acid

Adding Phosphorous Pentoxide

It normally takes about 2 kg of phosphorous pentoxide to obtain the required final specific gravity of 1.92 g/cm^3 (or greater) at 25 °C. This quantity of phosphorous pentoxide is added gradually over a period of 2-3 h while constantly stirring and heating to a temperature of about 80 °C. The powder initially forms gelatinous lumps, but will gradually be dissolved. The complete process can take 4-5 h.

[1]The density of 105 % H_3PO_4 is 1.921 g/cm^3 at 25 °C. Refer to www.innophos.com.

If the phosporic acid supplied by Thermo Electron (Bremen), Part No. 111 2640, has been dewatered before, addition of approximately 30 g of phosphorous pentoxide is sufficient.

Warning Take care during the initial stage of adding phosphorous pentoxide: the reaction can be vigorous as the powder contacts the relatively "wet" acid! ▲

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

Figure 4-27. Checking Specific Gravity of Phosphoric Acid

Handling Sample Vials

Manual Cleaning of 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 steps described below:

1. Put the used vials into diluted phosphoric acid.

2. Repeatedly, rinse the vials with distilled water of high quality using a washing bottle (the quality of the destilled water is important).

3. Rinse the vials with acetone using a washing bottle, as well. This helps to dry the vials faster. Removal of dissolved inorganic carbon from the distilled water is also ensured.

4. Dry the vials in the Kiel IV Carbonate Device oven rack or in a drying chamber at 72 °C for 2.5 h. Cover them with aluminum foil to protect them against contamination. See Figure 4-28.

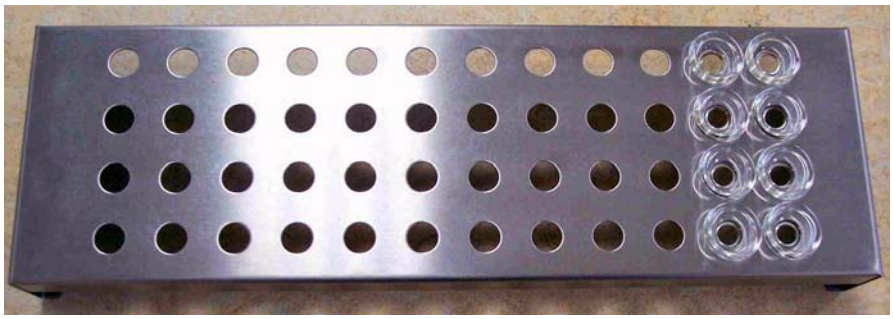


Figure 4-28. Oven Rack Containing Some Vials

Automatic Cleaning of Sample Vials

Used sample vials can be cleaned automatically in a laboratory dishwasher made of stainless steel. The dishwasher must be connected to deionized water of high quality. Commonly, the procedure outlined below is performed:

1. The vials are cleaned using an alkaline detergent at 85 °C.

2. An acidic neutralization using citric acid or acetic acid is performed.

3. A complete automated rinsing with deionized water of high quality at 85 °C is performed.
   If the dishwasher is only connected to normal deionized water, perform an extra manual cleaning using deionized water of high quality.

4. The drying procedure can be enhanced by rinsing the vials in acetone or methylchorine. This ensures removal of residual water that may contain acid-soluble minerals as well.

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

5. Dry the vials in the Kiel IV Carbonate Device oven rack or in a drying chamber at 72 °C for 2.5 h. Cover them with aluminum foil to protect them against contamination. See Figure 4-28.

Chapter 5 Measurement Procedures for Real Samples

This chapter treats the following topics:

Introduction

Before starting any sample preparation and performing measurements with the Finnigan Kiel IV Carbonate Device (Figure 5-1), it is important to get an overview of its operation procedure.

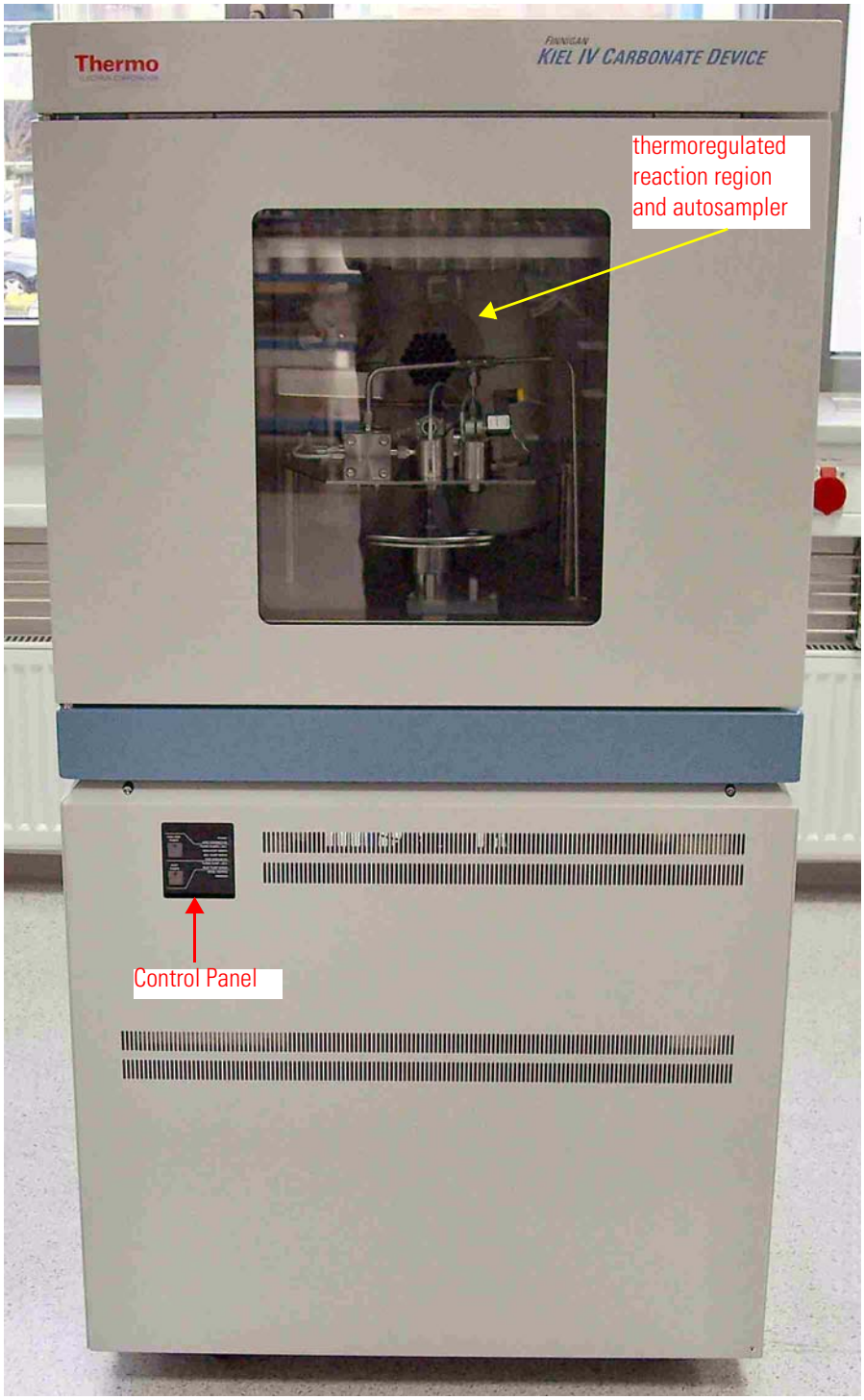


Figure 5-1. Finnigan Kiel IV Carbonate Device - Front View

It is assumed that the user is not only familiar with clean operating procedures and sample preparation, but also has working experience with IRMS, Microsoft Windows and Isodat 2.5.

Working with the Finnigan Kiel IV Carbonate Device means to operate a complex system running many processes at the same time. Therefore, to become an overview of the system, read this Operating Manual carefully prior to starting work. It is recommended to read the text below and procedure seriously as well as to compare the hardware layout to the system.

In this chapter, simultaneous measurement of ^{13}C and ^{18}O isotope ratios in calcite, aragonite (that is, mainly $CaCO_3$) or dolomite (that is, $CaMg(CO_3)_2$) will be covered. The latter is subject to a lot of discussion, and results should be treated carefully. The carbonate species reacts with phosphoric acid yielding CO_2 that carries an image of the isotopic value of the carbonate ion CO_3^{2-}.

Measurement Principle

Several methods and apparatus are available for the measurement of stable carbon and oxygen isotopes in carbonates. Isotope ratio determination of the above elements is usually carried out using CO_2 produced in the reaction between carbonates and phosphoric acid. The common method employs a glass tube with a side arm. See Figure 5-2.

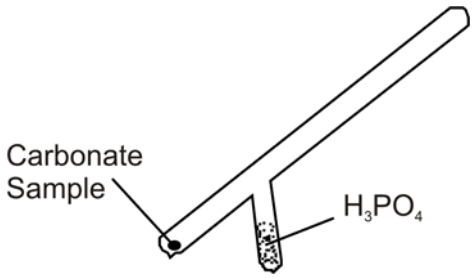


Figure 5-2. Common Glass Tube

The carbonate samples are loaded in the end of the glass tube. The side arm contains phosphoric acid. Reaction takes place after tilting the glass tube in order to bring acid to the sample. This method requires a stable temperature, e.g. 25 °C (or 50 °C to accelerate the reaction). The reaction time is between 2 h for calcite (sample amount above 5 mg) and 48 h for dolomite (sample amount above 10 mg).

After the reaction is finished, the glass tube contains CO_2, O_2, N_2, H_2O and even SO_2, if the sample is not pure $CaCO_3$. The CO_2 gas for the isotope ratio determination must be isolated and separated from other produced gases. This action takes place by trapping at different temperatures and pumping out O_2 and N_2 as non-condensable gases.

The Finnigan Kiel IV Carbonate Device is a fully automated preparation device for the precise and accurate determination of oxygen and carbon isotope ratios in carbonates, which are widely used in many fields of geology. One of the major applications is the estimation of ocean paleotemperatures from $^{18}O/^{16}O$ ratios in marine microfossils.

Ultimate precision and accuracy are prerequisites for such work, because a temperature difference of 1 °C leads to a $\delta^{18}O$ difference of about 0.2 ‰.

The Finnigan Kiel IV Carbonate Device has been developed in close cooperation with leading academic researchers with the first unit introduced in 1982. It incorporates a number of design changes which enhance ease of use, diminish the trace metal content of the acid and decrease both the costs of acquisition and operation, without changes to the underlying operation principles.

The system is designed for throughput at the highest level of precision and accuracy. Loading and exchanging the carousel are the only manual interactions with the system. Exchange of one autosampler carousel against a newly loaded one takes only minutes. Therefore, the system can run almost continuously in fully unattended operation. Each sample measurement takes about 15 min. Sample throughput of more than 10,000 samples per year is reported by a number of laboratories and can in fact be regarded as a routine.

Placing Sample into Vial

First Alternative

Most of the sample material used with the Kiel IV Carbonate Device is rather fragile in handling. Foraminifera and carbonate powders tend to charge electrostatically and stick to glass walls. Therefore, it is necessary to follow certain rules when loading this kind of samples into the sample vials (Part No. 075 4960). See Figure 5-3 and Figure 5-4.

We recommend using a small piece of weighing paper during weighing and in all filling steps. It can be folded to form a kind of boat.

Note The boat used for carbonate measurements should be clean and free of organic and inorganic contaminations. ▲

To place the sample into the vial, peform the following steps:

1. Carefully place the sample in the middle of the boat.
   See Figure 5-4 for correct sample placement.

2. Carefully lead the boat to the vial bottom in horizontal position.

3. Knock the vial in vertical position several times to ensure that all sample material is located at the bottom of the vial.

4. Take the boat out of the vial.

5. Use a new boat for each sample.

Note If weighing of the sample is required, weigh after step 1 and weigh the empty boat again after step 4. Often, parts of the sample material will not be released from the boat. ▲

Figure 5-3. Sample Vial - Part No. 075 4960

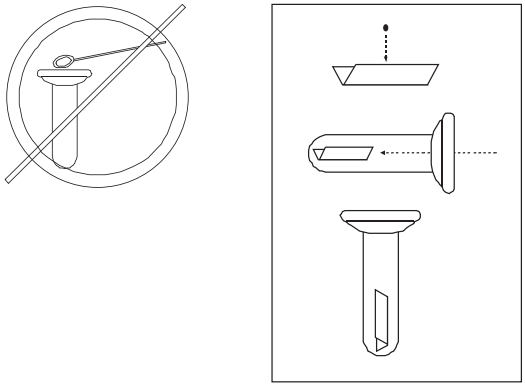


Figure 5-4. Correct Sample Placement

Second Alternative

Another possibility to place a sample of known weight into the sample vial is widely used in paleoclimatological research.

You need a grained standard with a closely selected grain size with known average weight (e.g. NBS-19; grain weight here is 7 µg). Further, you need a small brush where you remove all hairs but six or eight, and a mirror or a glass plate on a black surface and good lighting.

Place a small number of grains on the glass plate and pick up one grain using the brush. Move the brush into a sample vial and gently knock the brush at the glass wall. The grain will fall into the vial and stay there. Repeat this until a suitable number of grains is placed within the vial.

Then, knock the vial on your desk to force the grains to the bottom. Place the vial in the turret and continue with the next sample.

Preparing Carbonate and IRMS

1. Always use clean vials. Make sure that during sample preparation, no dust or other impurities fall into the vial.

2. Place the sample exactly at the bottom of the vial.

3. Do not leave the filled or clean vials outside the oven for a long time.

4. After placing the magazine within the oven make sure that the door is properly closed. Do not start the measurement immediately. Even if the oven shows the correct temperature, it takes at least 15 min until the vials are at the oven temperature.

5. Make sure that the oven temperature does not vary more than 0.5 °C within 15 min.

6. Make sure that clean vials without a sample are placed at position 1/1 and 2/1 (pump position).

7. In order to check the quality of your measurements or for calculation of your samples, place a few standard carbonates with known values in each 7^{th} or 9^{th} location.

8. If the Kiel IV Carbonate Device has not been used longer than 12 h, the first two measurements may not have the same precision as usual. Put more samples than necessary at this position.

9. Make sure that liquid nitrogen tank is properly filled and the manual valve (next to the magnet valve) is open. Take care that the liquid nitrogen filling tube is below the coil of the magnet valve.

10. Make sure that acid drop counter and O ring seal are clean. Refer to "Brief and Superficial Cleaning Procedure" on page 4-18.

11. Stay near the units at least during the first measurement and watch the measurement procedure.

12. Watch the liquid nitrogen refill unit during the first filling procedure of liquid nitrogen.

13. Define the sequence parameters. Finally, start the acquisition. Refer to "Starting a Sequence" on page 3-35.

Procedure

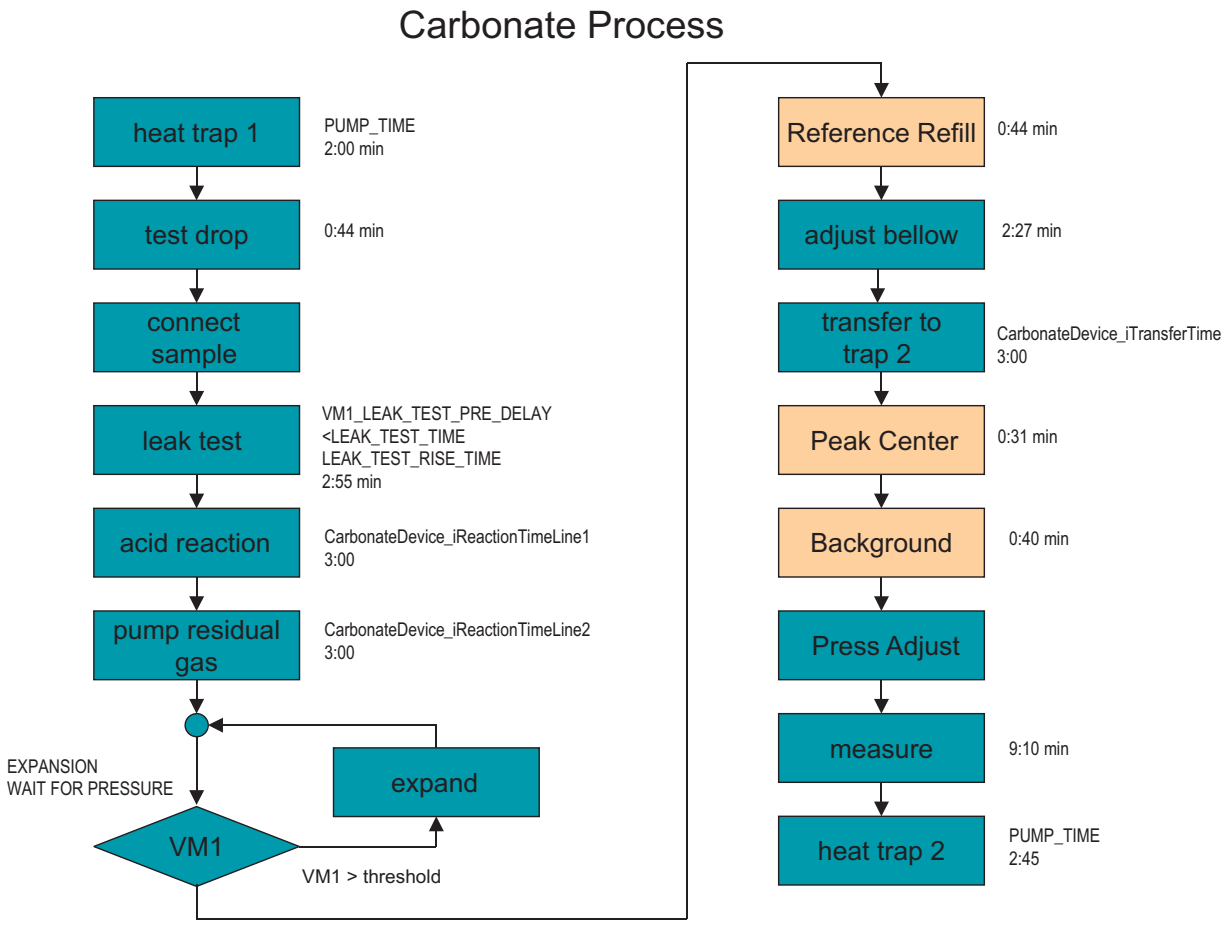


Figure 5-5. Flowchart of Carbonate Process Including Timing

The Finnigan Kiel IV Carbonate Device consists of a temperature controlled oven, an acid tank, pneumatic valves, an autosampler containing the glass vials (magazine), gas cleaning facilities (trap 1) and a sample trapping arrangement (trap 2).

The reaction region is housed in a precision temperature-controlled oven and consists of an autosampler with 48 sample vials or thimbles. The thimbles can be loaded with as little as 10 µg of sample. The vials are made of special glass, allowing visual inspection of the sample and easy cleaning prior to re-use.

The reaction region also houses the reservoir of concentrated phosphoric acid, which is dispensed through two metal-free, acid-resistant dosing valves of new design.

The sample preparation magazine is a round tray with 48 holes arranged in two concentric rows - each with 24 holes. The inner row is indicated as line 1, and the outer row as line 2. A glass-made sample preparation vial can be placed into each hole.

The vials at position 1 are called pump vials and are indicated as vial 1/1 and vial 1/2 (this means vial 1/line 1 and vial 1/line 2). These vials are not used for sample measurement.

The vials at position 2 (2/1 and 2/2) have two functions. Initially, they are sample preparation vials and, after the samples of these vials are measured, they are secondly used as waste vials.

Once the sample containers are loaded and the sequence grid is filled out, all subsequent steps are fully automated. Prior to reaction and measurement, each container is evacuated. Now, a leak test is performed. The steps of a leak test are denoted in Figure 5-6.

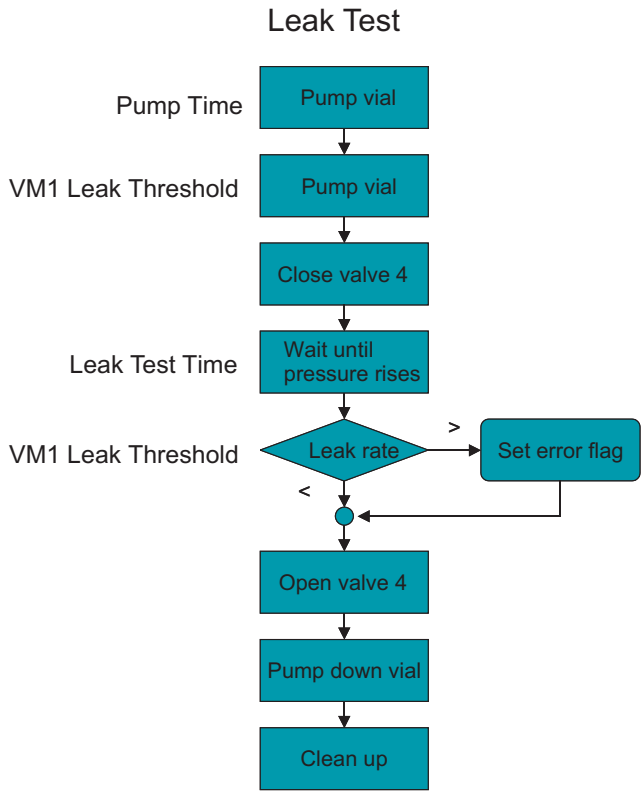


Figure 5-6. Leak Test

Only if no leak is present, a precisely controlled amount of acid is added to the sample. The acid is exposed to metal surfaces at no time, with the exception of a short final steel capillary and a steel wire for droplet generation and counting. Thereby, contaminations due to the acid delivery system as well as cross-contaminations are minimized.

Thus, it is possible to chemically characterize the trace element content of carbonate samples by analyzing the spent acid amount, e.g. by ICP-OES or ICP mass spectrometry.

The CO_2 formed in the reaction of carbonate with acid is transferred into the trapping and gas cleaning system. It consists of a temperature-controlled trap with associated valves, an ultra high vacuum system, a pressure readout and a Microvolume.

With the temperature-controlled trap at temperature of liquid nitrogen, in a first step, CO_2 is quantitatively removed from the reaction region (along with some water) and frozen within trap 1. The CO_2 is then transferred into the Microvolume (that is trap 2) at -90 °C, whereas water is retained within trap 1. See Figure 5-7.

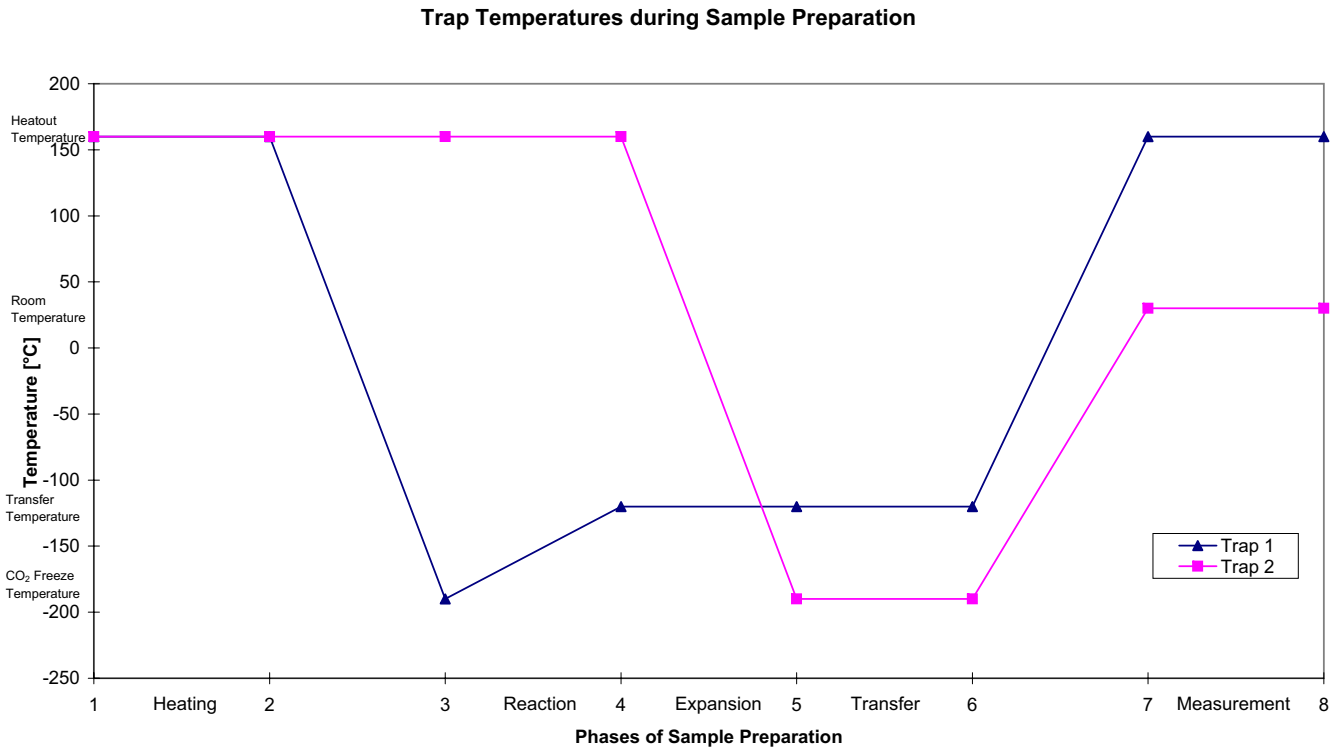


Figure 5-7. Trap Temperatures during Sample Preparation

This CO_2 transfer is the basic principle of the Kiel IV Carbonate Device, because it ensures identical performance with varying sample sizes. Since most precise results require similar pressures in both sample and reference line of the Dual Inlet system, the total amount of CO_2 available is first detected by reading the CO_2 pressure at the trap when at -90 °C. A precision pressure transducer is therefore mounted at the position of the trap. The data system then decides which portion of the available CO_2 must be transferred into the Microvolume in order to

achieve the inlet pressure desired for measurement. If there is too much CO_2, consecutive gas expansions between two volumes take place until the amount of CO_2 is just right to be transferred.

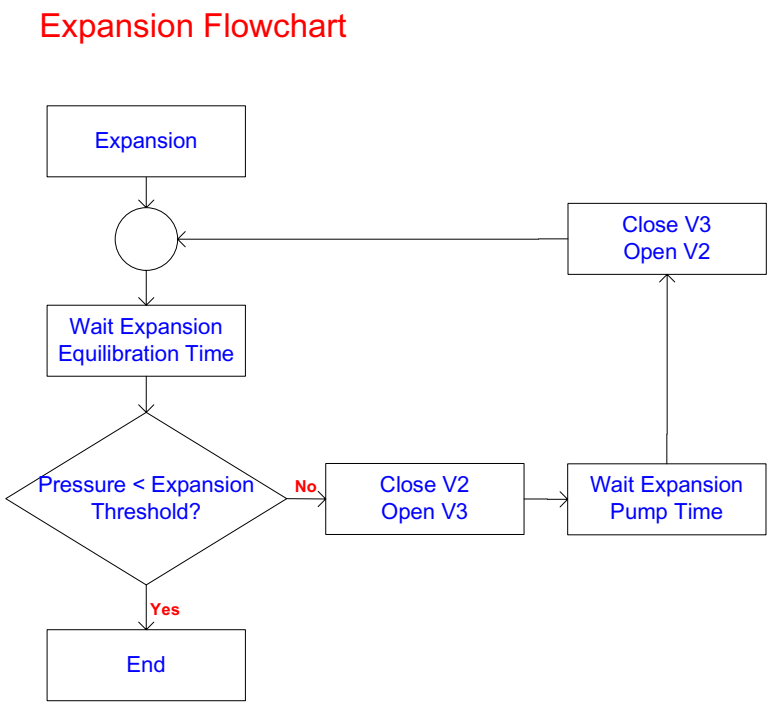


Figure 5-8. Expansion Flowchart

This procedure assures maximum precision and is free of isotope fractionation, if the associated times are chosen above 2 min. See Figure 3-63.

It also eliminates any waiting times which would otherwise be necessary to allow the inlet pressure to drop to the desired level. Following this, the water is removed from the gas cleaning and trapping system by baking the trap and pumping all valves and gas lines.

Simultaneously, the Microvolume is warmed up, and the CO_2 flows from the Microvolume into the Changeover Valve of the Dual Inlet system. The Finnigan Kiel IV Carbonate Device is connected to the Changeover Valve via a dedicated capillary. This design minimizes the interaction of CO_2 with metal surfaces, a cause of memory effects and cross-contamination. It does not compromize any other inlet system that might be connected to the IRMS. Since all the valves are of all-metal gold-sealed design and all gas lines are thoroughly pumped, memory effects and contaminations are excluded.

Note A gas tank that contains a liquid phase like CO_2 requires absolute temperature stability! ▲

At this point in time, the Dual Inlet press adjust takes place. It intends to match the sample signal to the signal from the reference bellow. Refer to Figure 3-32 and Table 3-9 for details on press adjust. Immediately after the press adjust the Dual Inlet measurement starts. See Figure 3-13.

Checking Quality of Result Data

The data present in the result document, and here especially the data collected in the **Grid Infos** tab, allow extended diagnostics on the collected data. Extract the information from the result document using an export template. Refer to **Excel Export** in *ISODAT NT Operating Manual*; Part No. 109 2481.

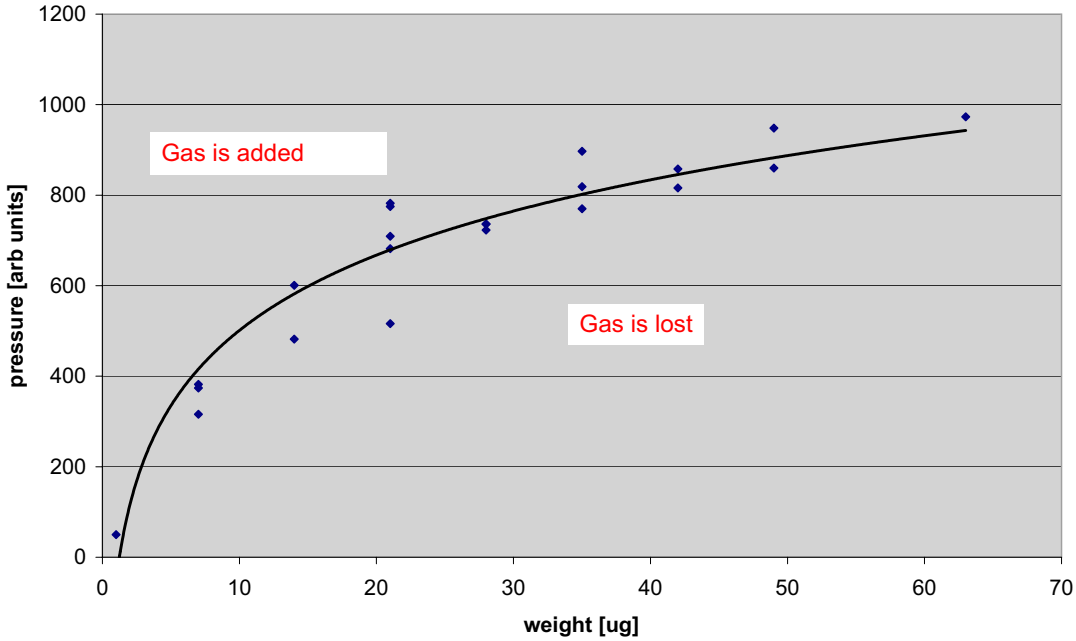


Figure 5-9. Pressure vs. Mass

Figure 5-9 shows a typical response curve for VM1. On the x-axis, the sample weight is denoted. In this special case, single grains of NBS-19 were counted and not actually weighed. This explains the pattern.

On the y-axis, the pressure displayed by VM1 for the respective sample is shown. The point close to 0/0 is faked to yield a nice regression curve for this example.

Use this plot type to check the completeness of reaction between carbonate sample and acid. This plot allows to judge the efficiency of trapping CO_2 in trap 1 as well. If any of the above parts of the preparation process fails, the gas amount (denoted by the VM1 pressure) will be smaller than expected for the sample weight used.

If, on the other hand, a leak is present, the displayed pressure at VM1 will be higher than expected. This allows to precisely check the dynamic behavior of the valves (V1, V2, V4, V12 or V22).

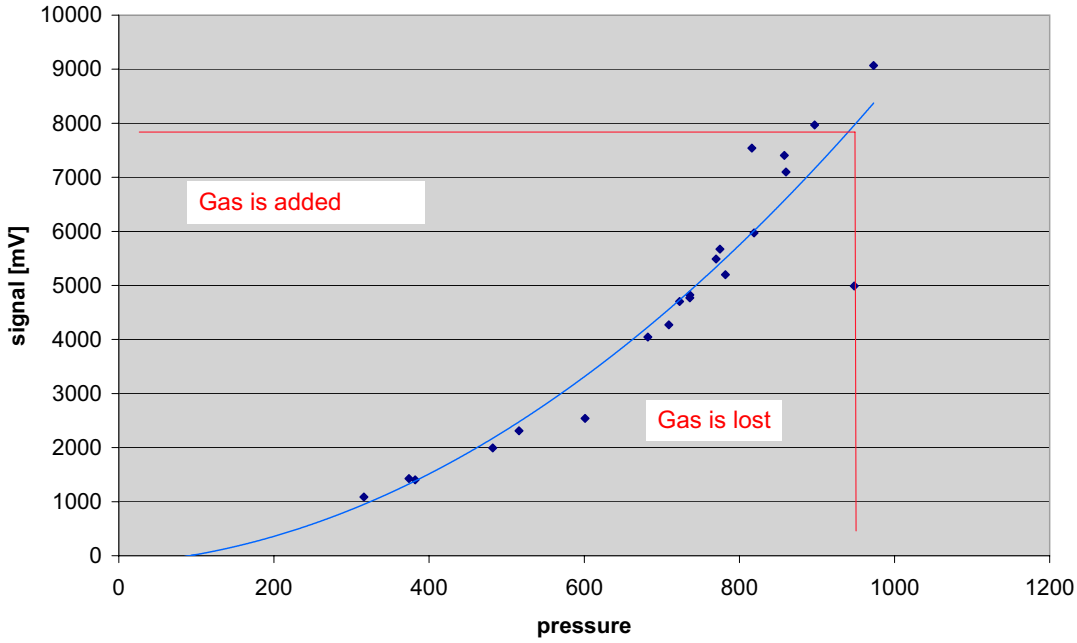


Figure 5-10. Signal vs. Pressure

Figure 5-10 explains the relation between the amount of gas measured in VM1 after expansion vs. the signal for m/z 44 achieved in the IRMS.

Use a plot like this to control complete gas transfer from trap 1 to the IRMS source. All points must be located along a quadratic correlation curve. Otherwise, severe problems in gas transfer are present.

Several reasons may contribute to gas loss in the section between valve V2 and the IRMS. Valve V5 is located closely to the liquid nitrogen dewar. During refill cycles, it may cool down and get stuck. In this case, you notice complete gas loss for a given sample.

Another possible reason for a virtual gas loss is the Press Adjust process. If the amount of reference gas available is to small to adjust for a given beam intensity, the algorithm may fail and decide to wait for the sample signal to drop to the reference level. Be sure to set a suitable value for the “largest signal achievable“ in the external parameters for the Kiel IV Carbonate Device. See Figure 3-61.

Figure 5-11 explains the relation between δ value and signal. Ideally, for both isotopes inspected, the correlation curve should be a line with no slope. The scatter of the data points around this curve should always be within the Standard Gaussian distribution.

Unfortunately, in reality the scatter increases below a certain sample size. For details, see the advertized specifications. The real correlation curve exhibits some general behavior:

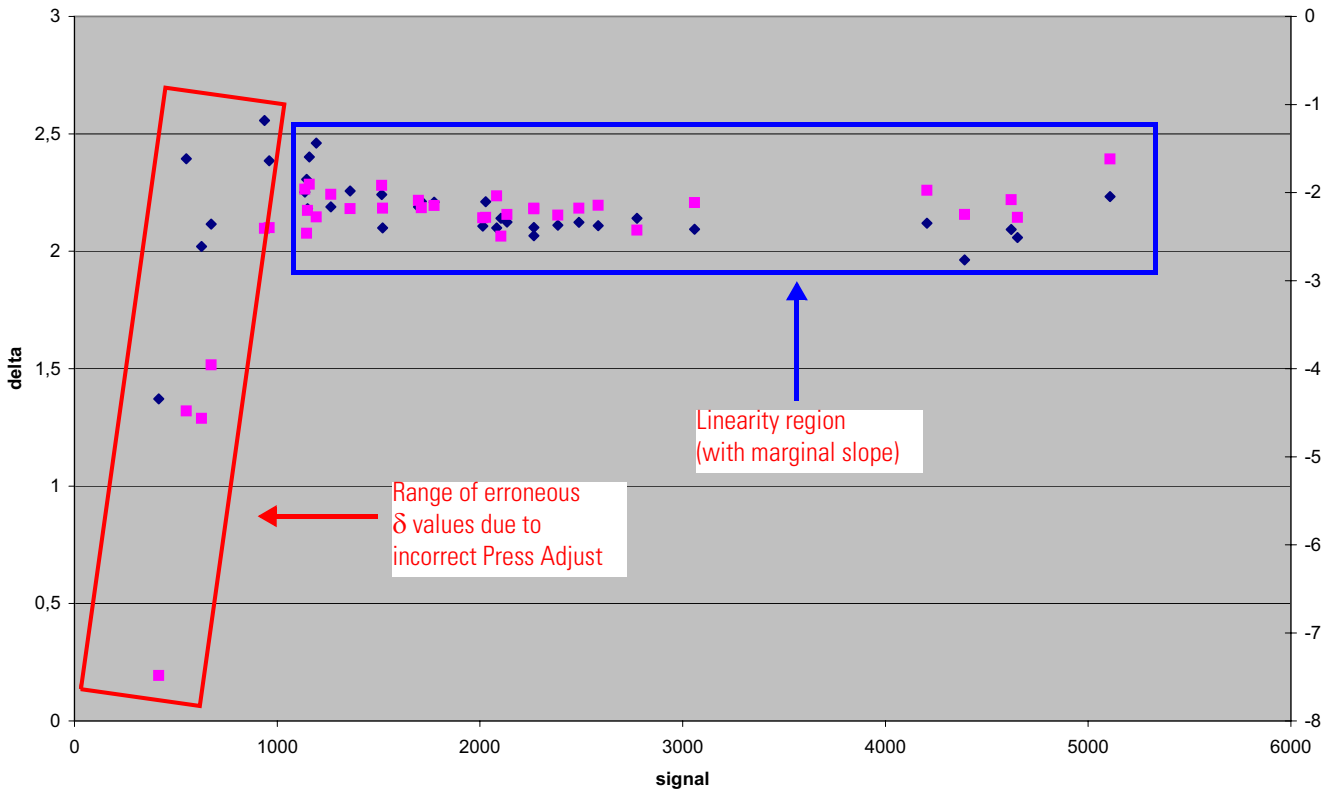


Figure 5-11. δ vs. Signal*

*Both the range of erroneous δ values and the linearity region are general properties, that is they occur in every carbonate measurement (^{13}C and ^{18}O).

Below a certain voltage, usually around 1.5 to 2 V, the δ value drops considerably below the real value. This lower limit of the lower range depends largely on the Press Adjust and Reference Refill parameters.

When using Reference Refill, the bellow is completely open (that is 100 %) and gas will be filled in during a certain time period. After the gas has been filled in, that is Reference Refill is finished, a certain pressure exists in the bellow corresponding to a certain signal height.

In case much gas was filled in, no smaller signal heights (that is smaller reference sample amounts) can be adjusted via the Press Adjust algorithm as the bellow is already completely open. Therefore, any smaller sample amounts will not have a correct Press Adjust.

The measurement will be carried out in spite of the incorrect Press Adjust and must consequently yield erroneous δ values. These are displayed in the left part of Figure 5-11.

This can be counterbalanced by filling a smaller gas amount into the bellow (that is less than 100 %) via a changed Reference Refill. Press Adjust is thus corrected via Reference Refill.

The linearity region (see right part of Figure 5-11) will always exhibit a marginal positive or negative slope about 0.01-0.02 ‰/V or even smaller. In case the standard devation within the linearity range is extremely small, this linearity error can be counterbalanced as well. This will add further precision and accuracy.

Referencing vs VPDB

All carbonate δ values must be referenced to the international standard VPDB (Vienna Pee Dee Belemnite), the successor of PDB as PDB is exhausted. However, VPDB with $\delta^{13}C = 0$ and $\delta^{18}O = 0$ as one would expect, does not exist. Instead, standards exist which are related to this virtual, that is unreal definition. See Table 6-26 on page 6-17.

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 5-16:

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

and

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

with:

x working standard
y gas
z absolute standard (that is VPDB)

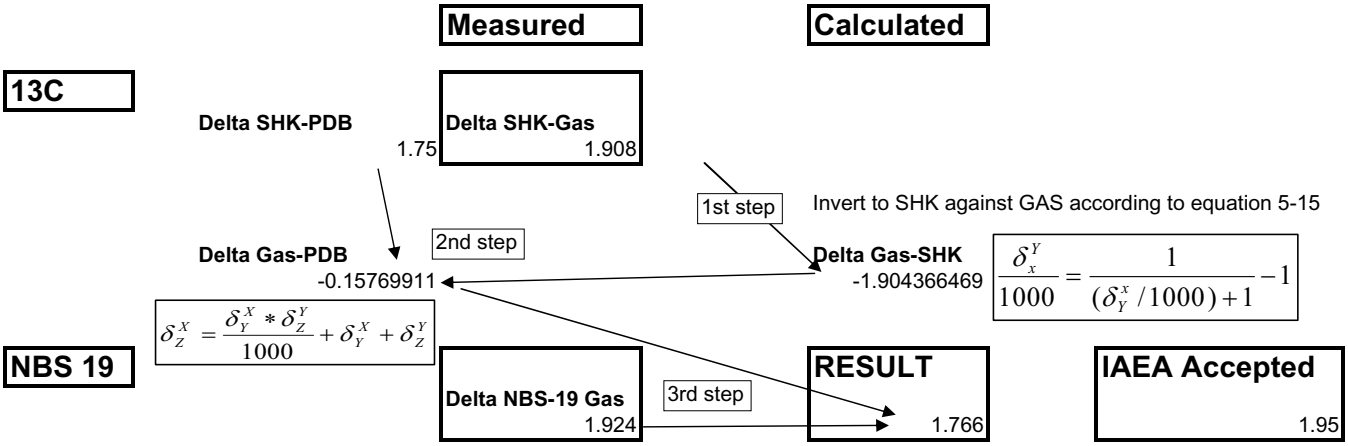


Figure 5-12. Calculation Example*

*SHK designates Solnhofen limestone.

Figure 5-12 depicts an example for obtaining δ values specified against VPDB starting from measured and corrected δ values.

1. Determine absolute δ value of the primary standard.
   In this example:

$$\delta_{PDB}^{SHK} = 1.750$$

2. Invert the measured value for primary standard versus gas used:

$$\delta_{Gas}^{SHK} = 1.908$$

Thus:

$$\delta_{SHK}^{Gas} = -1.903$$

3. Determine the absolute δ value of the gas used today with the aid of the equation:

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

Thus:

$$\delta_{PDB}^{Gas} = -0.157$$

4. Use this value and any measured sample δ vs. reference gas to calculate the δ value of sample vs. PDB with the aid of:

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

Thus:

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

In this case, the result is incorrect.

Remark on the Strange Mathematics of Delta Values

The δ definition:

$$\delta_y^x = \left(\frac{R_x}{R_y} - 1\right) \cdot 1000$$

with:

δ^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 δ^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 δ^x_y and δ^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 vs VPDB" on page 5-14.

Ion Correction

The isotopic composition of a compound A is expressed by its δ value, δ_A,

$$\delta_A = 10^3 \cdot \left(\frac{R_A}{R_{ST}} - 1\right)$$

Here, δ_A is given in ‰. R_A denotes the isotope ratio of compond A and R_{ST} the defined isotope ratio of a standard sample.

Examples

1. Carbon[1]

[1]As usual, the index SA refers to sample and the index ST to standard.

$$\delta^{13}C = 10^3 \cdot \frac{(^{13}C/^{12}C)_{SA} - (^{13}C/^{12}C)_{ST}}{(^{13}C/^{12}C)_{ST}}$$

2. Oxygen (measured as CO_2)[1]

$$\delta^{18}O = 10^3 \cdot \frac{(^{18}O/^{16}O)_{SA} - (^{18}O/^{16}O)_{ST}}{(^{18}O/^{16}O)_{ST}}$$

For CO_2, the IRMS measures the 45/44 and 46/44 ratios. M/z 45 comprises $^{13}C^{16}O_2$ as well as $^{12}C^{17}O^{16}O$ so that the 45/44 ratio is different from the ratio $^{13}C/^{12}C$ by a correction regarding the ratio $^{17}O/^{16}O$ in the sample or standard. Therefore,

$$R_{45} = \frac{^{13}C^{16}O_2 + ^{12}C^{17}O^{16}O}{^{12}C^{16}O_2} = \frac{^{13}C}{^{12}C} + 2 \cdot \frac{^{17}O}{^{16}O} = R_{13} + 2 \cdot R_{17}$$

In this equation, the definitions

$$R_{45} = \frac{\text{signal (m/z 45)}}{\text{signal (m/z 44)}}$$

and

$$R_{13} = \frac{\text{isotopic abundance (m/z 13)}}{\text{isotopic abundance (m/z 12)}}$$

(similarly for R_{17} etc.) are used.

Ion correction routines must be applied to the measured ratios in order to account for the additional ion species contributing to the measured ratios. Likewise, other ion species must be subtracted from the 46/44 ratio for oxygen in CO_2, the 65/64 and 66/64 ratios for sulfur, and the 34/32 ratio for elemental oxygen[1].

The ^{17}O correction applied in Isodat 2.5 follows the suggestions given by Santrock and coworkers[2] with:

[1]Refer to H. Craig: Isotopic standards for mass spectrometric analysis of carbon dioxide. Geochimica Cosmochimica Acta, **12** (1957) 113-140.

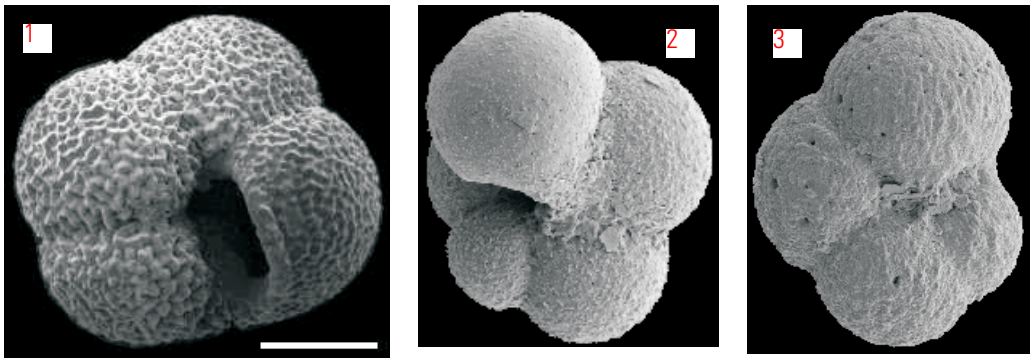
$$R_{17} = K \cdot R_{18}^{a}$$

using a = 0.516 and K = 0.0099235.

The δ values of the working standard against an international standard must be known.

Neogloboquadrina Pachyderma (Ehrenberg, 1894)

Neogloboquadrina Pachyderma is the most abundant planktonic foraminifer of high latitudes. As with any planktonic foraminifer, it avoids low-salinity and shallow waters. The left-coiled morphotype prevails at lowest temperatures and occurs throughout the Arctic Ocean.



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

2 Right-coiled (dextral) specimen, umbilical view

3 Left-coiled (sinistral) specimen, umbilical view

Figure 5-13. Neogloboquadrina Pachyderma

Events during Sample Measurement

To illustrate the primary steps, Figure 5-5 shows a flowchart of the events that belong to the measurement of one sample. The running software relies on multithreading to save precious time during a full run. Thus, preparation and measurement are separate functions that are interlocked by registry variables.

When following the sequence on screen, it is sometimes difficult to judge which step exactly takes place at this moment. Therefore, it is helpful that you familiarize with the output presented in the **Info** window. See Figure 5-14. Here, various information is presented in order to judge on the evolution of the measurement process. Also, if error messages appear, the previous informative “user infos“ can be used to judge on the origin of this specific error.

The sample printout shows the start of a sequence until the first sample preparation starts. Reported are beginning and end of subroutines (such as **Prepare Run**), orders to set trap temperatures and turret movements as well as vial connections and vial disconnections. See Figure 5-14.

[2]Refer to J. Santrock, S.A. Studley and J.M. Hayes: Isotopic analyses based on the mass spectrum of carbon dioxide. Analytical Chemistry, **57** (1985) 1444-1448.

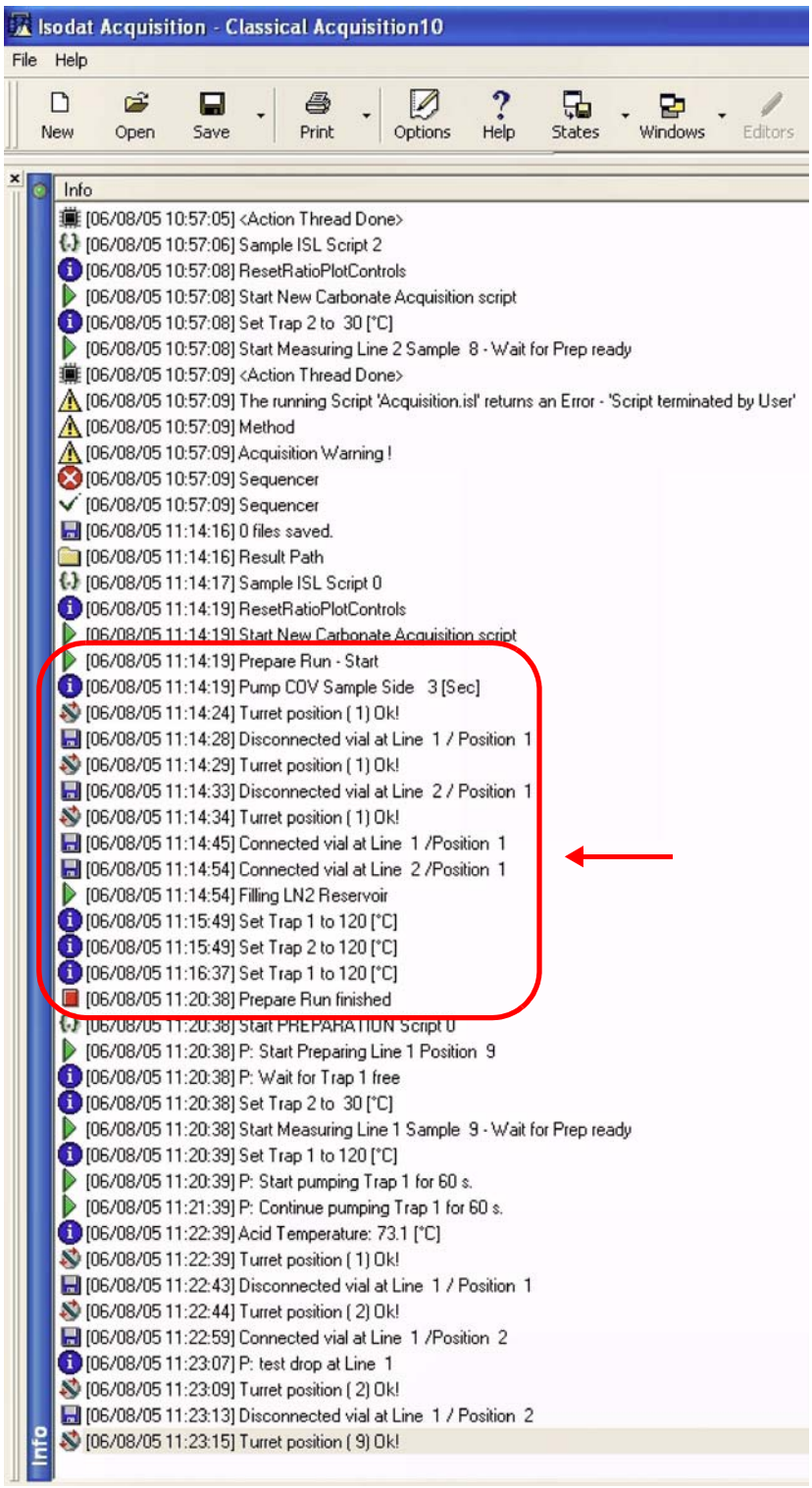


Figure 5-14. Evolution of Measurement Process in Info Window

Example Measurement started from vial 2/1 (vial 2/line 1)

VM1: vacuum gauge of trap region

VM2: vacuum gauge of rotary pump

1. As soon as the user starts the acquisition, the Kiel IV Carbonate Device will be initialized.

   a. Vial 1/1 (vial 1/line 1) and vial 1/2 (vial 1/line 2) are connected and pumped.

   b. Trap 1 and trap 2 are heated out.

2. Oven temperature and stability are checked.

3. Vial 1/1 is removed and magazine rotates to position 2.

4. Vial 2/1 is connected to acid valve housing.

5. Rotary pump evacuates vial 2/1 and the corresponding lines.

6. Vial 2/1 is evacuated to high vacuum, if no leak is present.

7. A leak check is performed. A leak rate is reported in the **Info** window and the result file.

8. Trap 1 is cooled down to -196 °C by liquid nitrogen.

9. The reaction between acid and sample takes place. The produced gases CO_2 and H_2O are trapped by trap 1.

10. Non-condensable gases are pumped out of trap 1.

11. Trap 1 is heated and CO_2 will be released, whereas H_2O is still frozen.

12. The CO_2 pressure is measured via VM1. If the pressure is too high, CO_2 will be pumped out until an acceptable pressure is achieved.

13. Trap 2 is cooled down to -196 °C by liquid nitrogen.

14. CO_2 is transferred from trap 1 to trap 2.

15. Trap 1 is heated and H_2O is pumped out. In the meantime, trap 2 is heated and CO_2 is released to the IRMS.

16. Vial 2/1 is removed and the magazine moves to the pump position.

17. A peak center is performed.

18. The reference gas pressure is high-end adjusted to the same value as the sample pressure.

19. Data acquisition starts, and the results are stored and/or printed.

Reference Refill

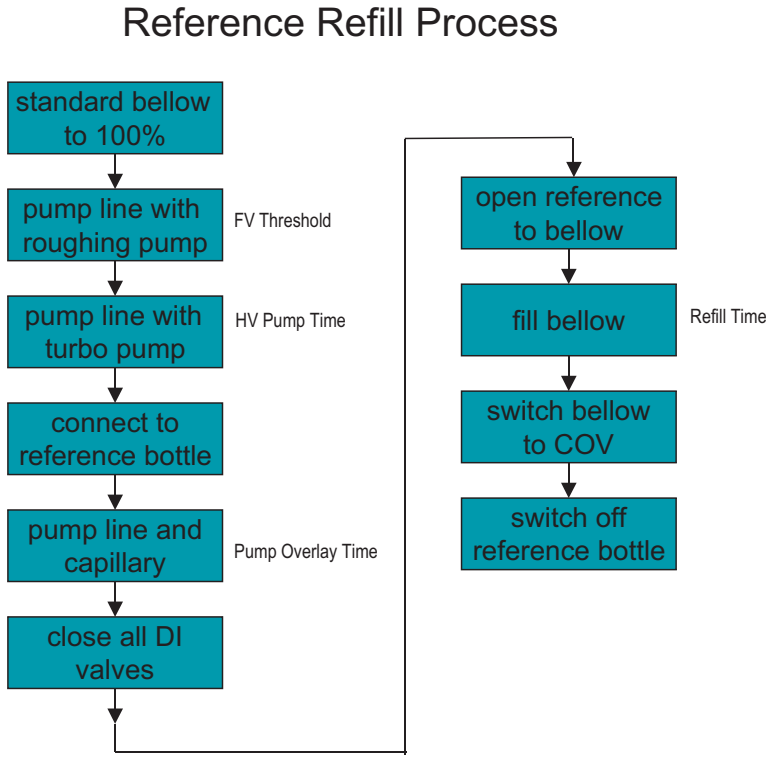


Figure 5-15. Reference Refill Process*

*Before each run, sample and standard side capillaries are pumped.

The Reference Refill process, Figure 5-15, is used to transfer a reference gas from a reservoir bottle (usually the Reference Gas Refill unit) into the right-hand reference bellow. This gas is then used during the following measurement cycles as the reference (or standard) gas.

The Reference Refill process consists of the three following steps:

1. Dual Inlet is prepared for the transfer by pumping away all residual gas from the respective bellow and its surroundings using the high vacuum pump. See Figure 5-16.

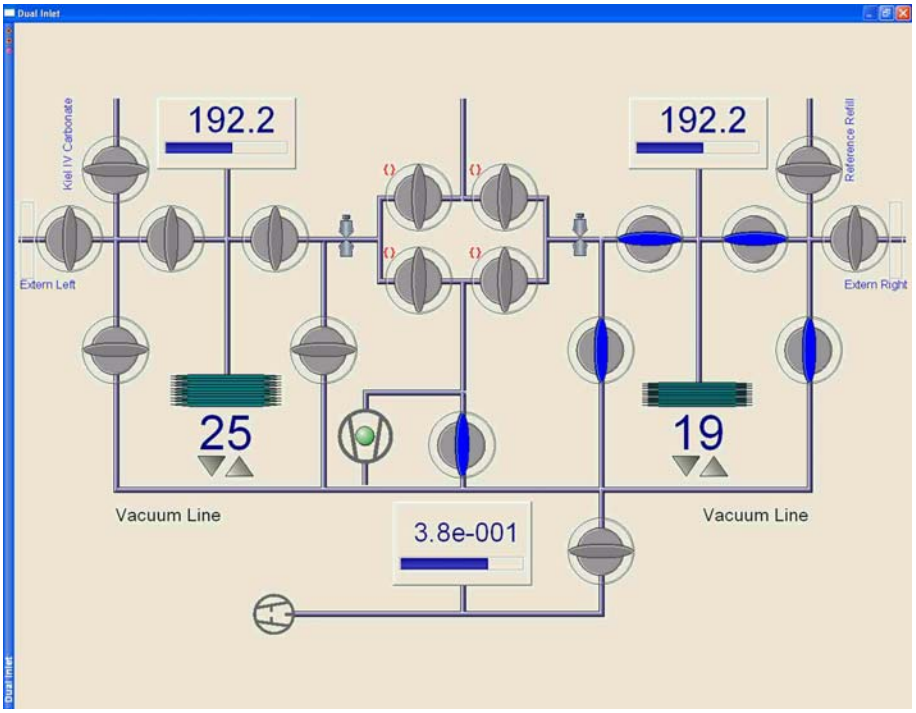


Figure 5-16. Reference Refill Process - Step 1

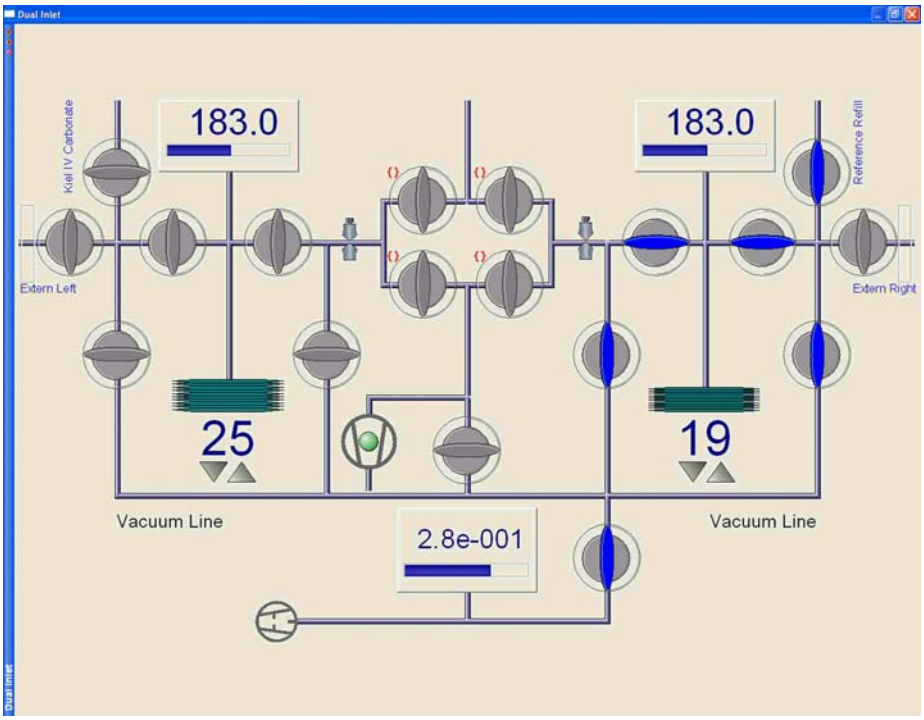


Figure 5-17. Reference Refill Process - Step 2

2. The bellow is connected to the fore vacuum pump again, and the valve to the reservoir (Refill unit) is opened. Gas accumulated behind this valve is pumped away for some time (**Pump Overlay Time**). See Figure 5-17.

3. The bellow is slowly filled with gas for some time (**Refill Time**). Laminar flow must be ensured during this period of time in order to avoid fractionation. See Figure 5-18.

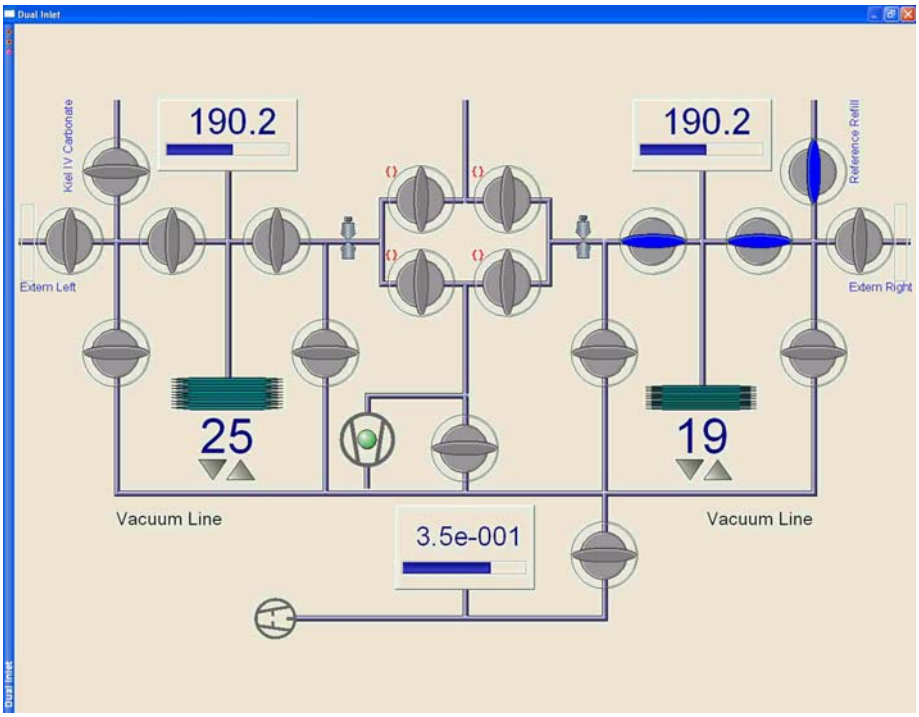


Figure 5-18. Reference Refill Process - Step 3

Selecting Correct Amount of Reference Gas

This section treats the reference refill algorithm. It assures that the correct amount of reference gas will be selected.

Selecting the correct amount of gas to fill the reference bellows is of utmost importance for the quality of the results of the individual measurements. This is because for each sample measurement it is required to perform a proper press adjust.

Consequently, adjust the parameter **Refill Time** in Figure 3-29 and Table 3-6 in such a way that after Reference Refill the amount of reference gas in the reference bellow yields a signal corresponding to the smallest sample signal that you want to measure.

Use plots like Figure 5-9 and Figure 5-10 to determine the sensitivity of your Kiel IV Carbonate Device and to decide how much signal corresponds to the smallest sample you want to analyze.

After this step, adjust the parameter **VM1 Expansion** (in Figure 3-34 and Table 3-11) according to this value and the compression of your bellow.

Example: If the smallest useful sample size results in a signal of 800 mV and the compression rate of your bellow is 10, then the expansion should take place above 8 V of signal. Or, if Figure 5-10 is the response curve of your IRMS, set **VM1 Expansion** to 950 µbar.

Chapter 6 Technical Information

Note This section is intended for use by trained Thermo Electron personnel only. Thermo Electron discourages use by and denies liability for the consequences of use by other than Thermo Electron personnel. ▲

This chapter contains the following topics:

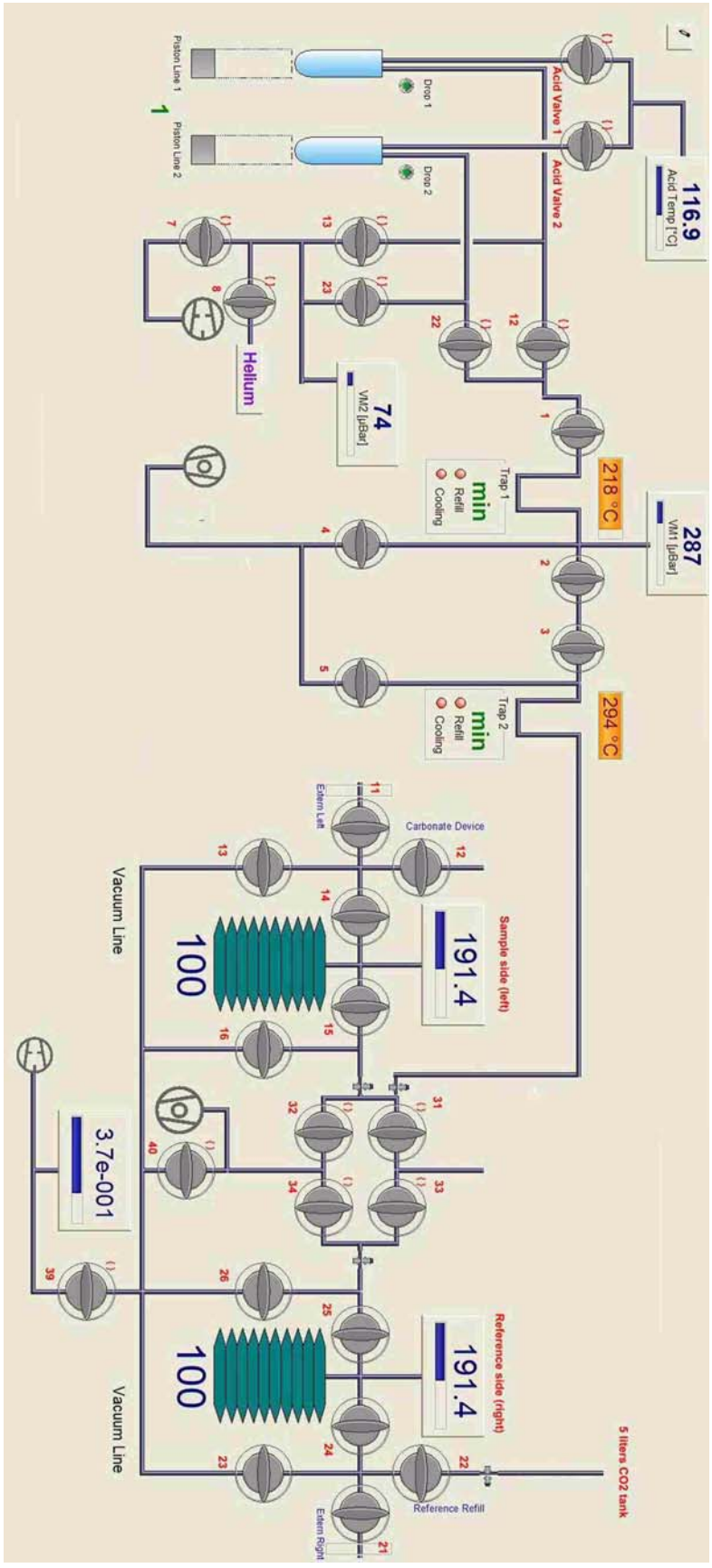


Figure 6-1. Vacuum Scheme of Device and Dual Inlet

Spare Parts and Consumables

Spare parts and consumables of the Finnigan Kiel IV Carbonate Device have been subsumed in a kit with Part No. 119 1160. Some of these are frequently used and shown in Table 6-1.

Table 6-1. Some Spare Parts and Consumables (Part No. 119 1160)

Position	Part No.	Designation	Quantity	Figure
1	059 8651	capillary for acid valve	2	Figure 6-2
2	109 4301	oil prevac. pump P 3 -3 ltrs	1	Figure 6-3
2	056 7830	flexible tubing (acid resistant)	0.5 m	Figure 6-4
3	017 2350	fiber reservoir TPH060/62/64	1	
3	059 8750	drop counter for acid valve*	2	Figure 4-17
4	115 3560	lamp for heating carbinet	2	
4	059 8671	gasket TEF 11.9x9x0.25 (pack of 3)	2	Figure 6-5
5	055 4440	O ring, 12.37x2.62 Viton	12	
6	054 5270	gasket gold o.d. 38xi.d. 36 5	2	Figure 6-6
7	067 1182	capillary tube, heatable	1	Figure 6-7
8	119 1170	pinch valve	1	Figure 6-8
9	065 3010	membrane, complete	2	Figure 6-9
10	065 3041	stamp Au, seal tip d=3 9	2	Figure 6-10
11	055 3140	jacket ring	2	Figure 6-11
12	115 7670	frit 1/4" o.d.x1/32", stainless steel	1	Figure 4-20
13	075 4960	sample vial, KS 19/9- 50 LG	24	Figure 6-12
14	106 9490	proximity switch, 4 mm	2	Figure 6-13

*6 in Figure 6-1.

Figure 6-2. Capillary for Acid Valve (Part No. 059 8651)

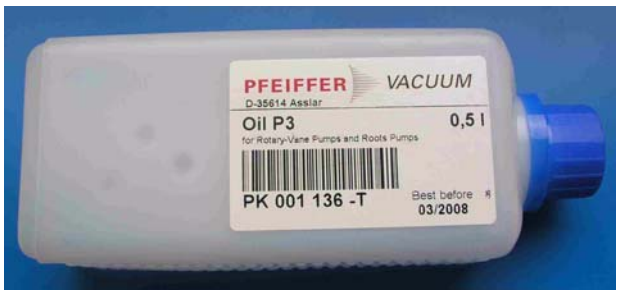


Figure 6-3. Oil for Fore Vacuum Pump (Part No. 109 4301)

Figure 6-4. Flexible Acid Resistant Tubing (Part No. 056 7830)

Figure 6-5. Teflon Gasket for Acid Valve (Part No. 059 8671)

Figure 6-6. Gold Gasket (Part No. 054 5270)

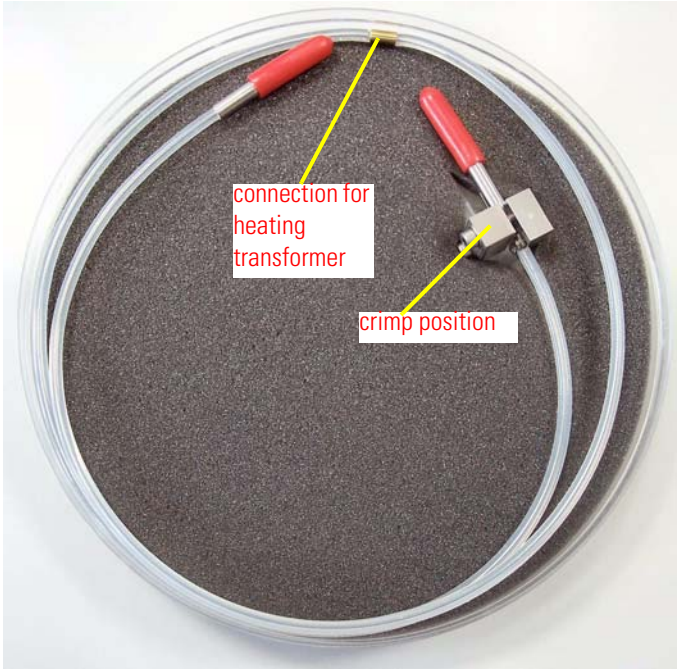


Figure 6-7. Heatable Capillary (Part No. 067 1182)

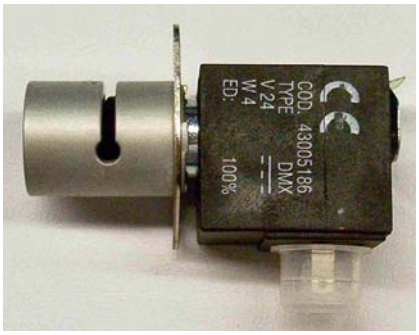


Figure 6-8. Pinch Valve (Part No. 119 1170)

Figure 6-9. Complete Membrane (Part No. 065 3010)

Figure 6-10. Gold Stamp (Part No. 065 3041)

Figure 6-11. Jacket Ring (Part No. 055 3140)

Figure 6-12. Sample Vial (Part No. 075 4960)

Figure 6-13. Proximity Switch (Part No. 106 9490)

Figure 6-14. Gold Gasket for Microvolume (Part No. 055 1010)

Figure 6-15. Copper Shim (Part No. 100 7730)

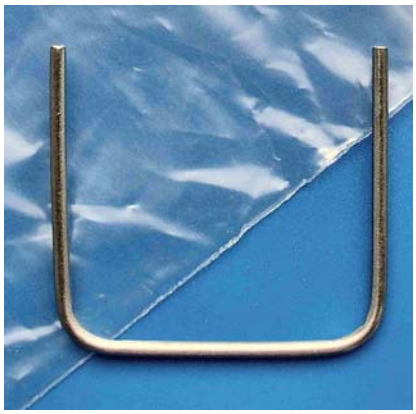


Figure 6-16. Tool to Adjust Turret Readout (Part No. 115 7390)

Installation Kit

The Installation Kit, Part No. 115 7800, comprises some important parts which are summarized in Table 6-2.

Table 6-2. Parts of Installation Kit (Part No. 115 7800)

Position	Part No.	Designation	Quantity
1	048 2610	distributor liquid nitrogen	1
4	114 5600	installation kit	1
5	114 7090	calcium carbonate	1
6	111 2640	ortho-phosphoric acid	500 g
7	111 3791	Finnigan Kiel IV Carbonate Device Operating Manual	1
8	041 4130	valve for liquid nitrogen	1

Acid Valve

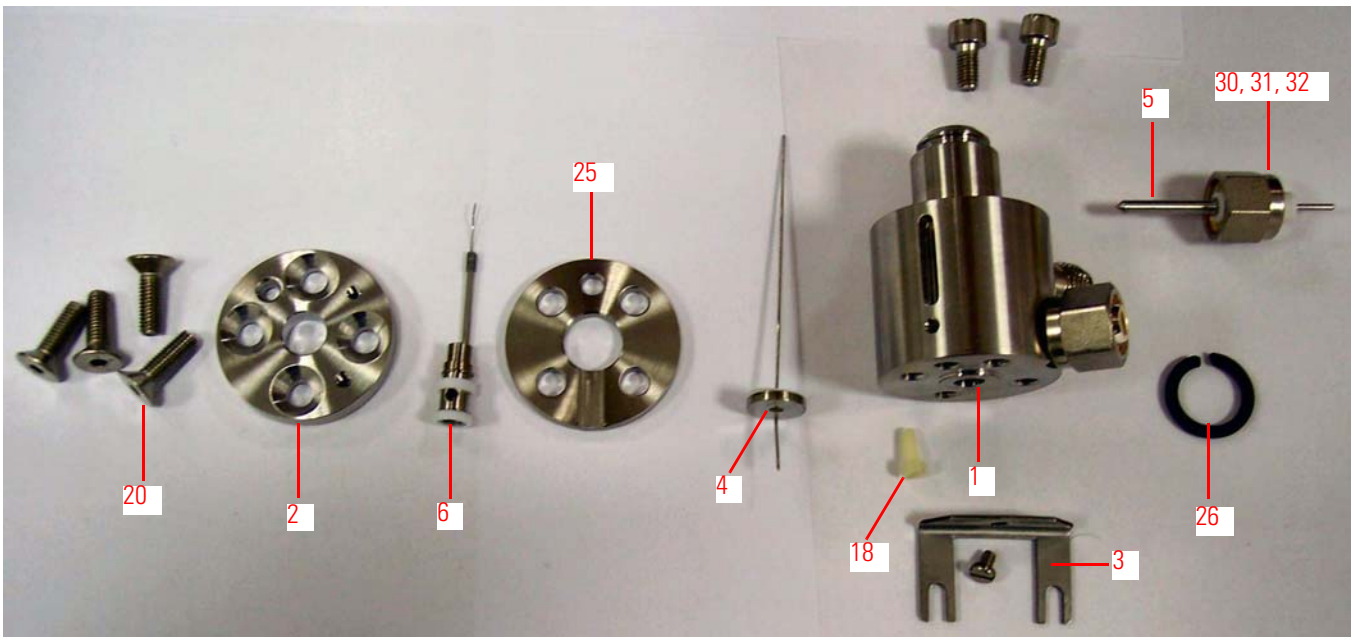


Figure 6-17. Parts of Acid Valve

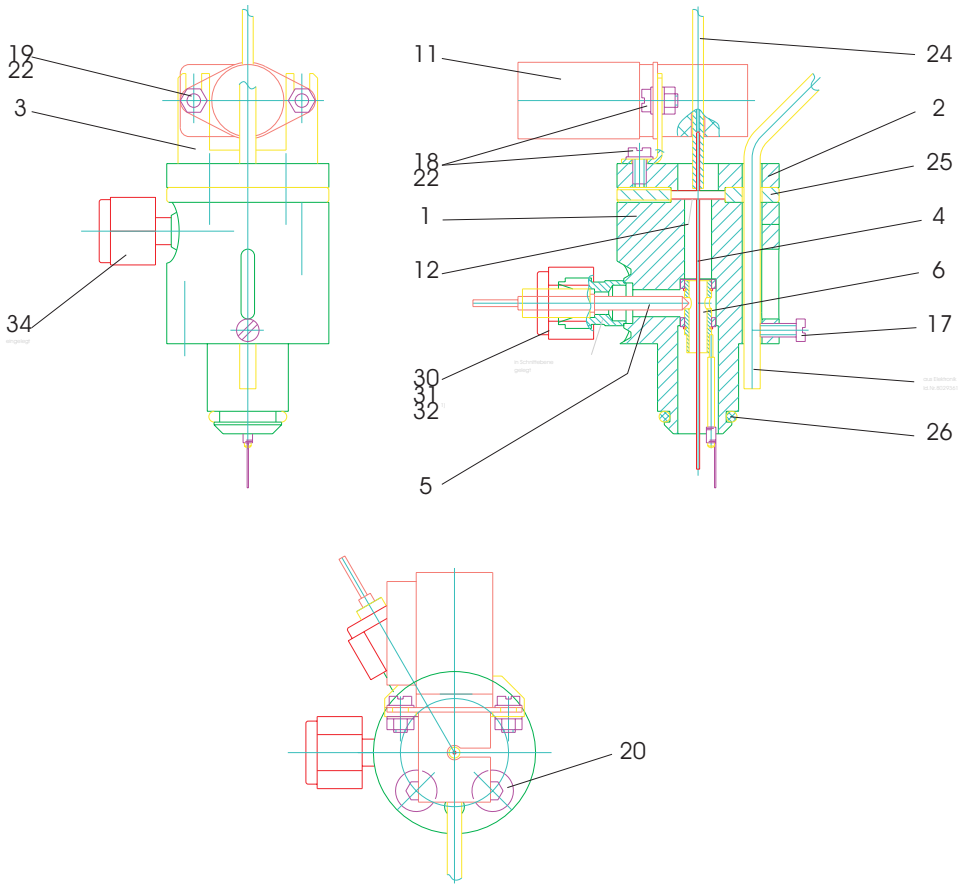


Figure 6-18. Acid Valve (Part No. 106 9450)

The acid valve, Part No. 106 9450, is shown in Figure 6-17 and Figure 6-18. Some important parts are summarized in Table 6-3.

Table 6-3. Parts of Acid Valve (Part No. 106 9450)

Position	Part No.	Designation	Quantity
1	106 9440	valve body for acid valve	1
2	106 0480	ring	1
3	115 7440	valve mount.	1
4	059 8651	capillary for acid valve	1
5	059 8700	contact pin for acid valve	1
6	059 8750	drop counter for acid valve	1
11	119 1170	pinch valve	1
12	059 8671	gasket, TEF, 11.9x9x0.25 (pack of 3)	1
17	045 3750	cylindrical screw, ISO 1207, M3x8, Nylon	1
18	045 0750	cylindrical screw, ISO 1207, M3x6, A4	3
19	046 0610	hexagonal nut, ISO 4032, M3, A4	2
20	115 7680	countersunk socket screw, ISO 10642, M5x16, A2	4
22	047 0210	disc, ISO 7092-3, A4	5
24	056 7830	flexible tubing, acid resistant	0.250 m
25	106 9460	distance ring, DN 6	1
26	055 4440	O ring, 12.37x2.62, Viton	1
30	052 1160	stainless nut, 1/4" o.d.	1
31	052 1330	front ferrule, Teflon, tube o.d. 1/ 4"	1
32	052 1340	back ferrule , Teflon, tube o.d. 1/ 4"	1
33	111 3460	mounting angle, acid valve	1
34	115 7670	frit, 1/4" o.d. x 1/32", stainless steel	1

Trapping Volume

The double-walled trapping volume, Part No. 100 7740, is shown in Figure 6-19. It comprises some important parts which are depicted in Figure 6-20 and summarized in Table 6-4.

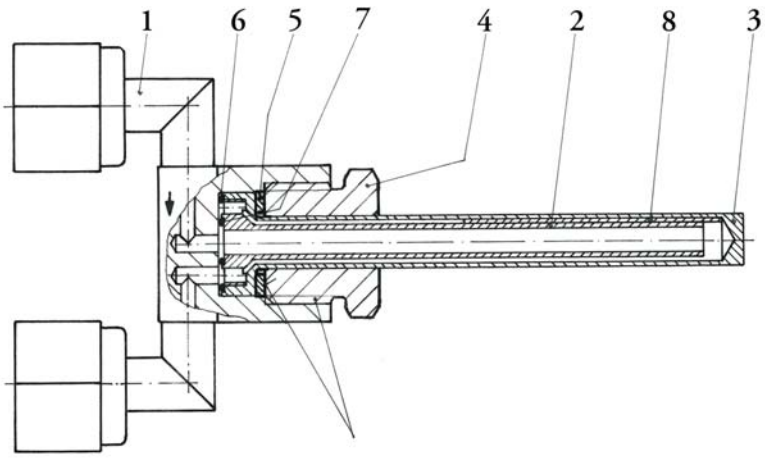


Figure 6-19. Trapping Volume (Part No. 100 7740)

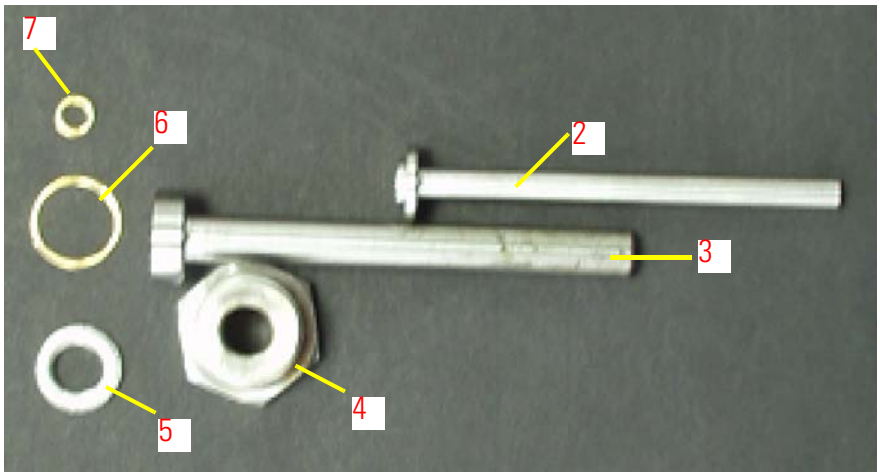


Figure 6-20. Important Parts of Trapping Volume*

*The numbers refer to Table 6-4.

Table 6-4. Parts of Trapping Volume (Part No. 100 7740)

Position	Part No.	Designation	Quantity
1	100 7700	distribution head	1
2	100 5520	inner tube	1
3	100 5530	outer tube	1
4	100 5540	mounting screw, M14x1.5	1
5	047 0850	disc, ISO 7092-6-A2	1
6	055 1240	gasket, gold, o.d. 11.5x i.d. 10	1
7	100 5570	gasket, gold, o.d. 5x i.d. 3.5	1
8	100 7730	copper shim, 0.5 mm	1

Cooling Unit

The cooling unit, Part No. 079 2400, is shown in Figure 6-21. It comprises some important parts which are summarized in Table 6-5.

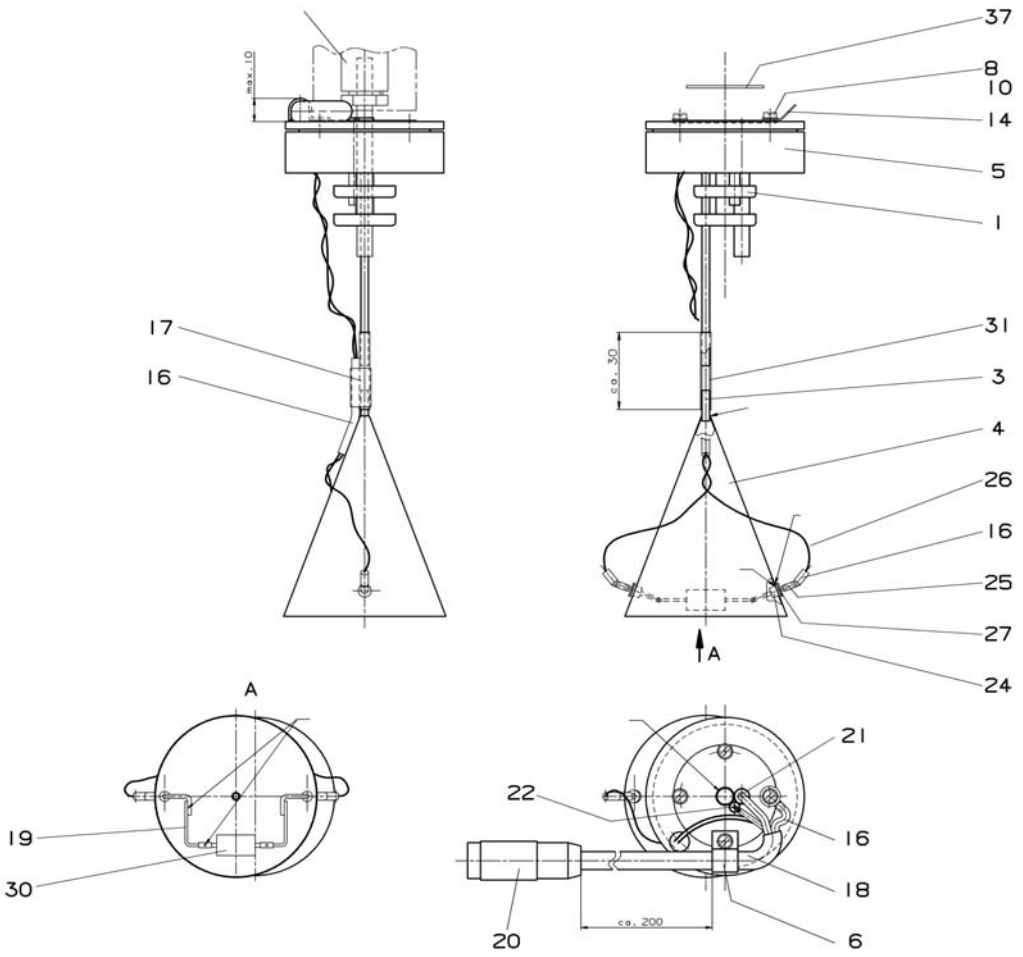


Figure 6-21. Cooling Unit (Part No. 079 2400)*

*Positions 7, 9, 11 and 37 are enclosed separately. See Table 6-5.

Table 6-5. Important Parts of Cooling Unit (Part No. 079 2400)*

Position	Part No.	Designation	Quantity
1	067 4300	cooling cascade	1
3	067 4390	tube	1
4	067 4400	funnel cooling unit	1
5	067 4410	lid	1
6	037 0650	clamp for cable, 6.4	1
7	050 4710	clamp for lid in cover	2
8	045 0760	cylindrical screw, ISO 1207, M3x8-A4	4
9	045 0790	cylindrical screw, ISO 1207, M4x8-A4	2
10	047 0210	disc, ISO 7092-3-A4	4

Table 6-5. Important Parts of Cooling Unit (Part No. 079 2400)*, continued

Position	Part No.	Designation	Quantity
11	047 0040	disc, ISO 7089-4-A4	2
14	033 0060	eyelet, 3A2, DIN 41496	1
16	034 1630	shrink tubing, 3.2 NF	0.1 m
17	034 2030	shrink tubing, 6.4 SW	2 cm
18	034 2040	shrink tubing, 9.5 SW	0.1 m
19	035 0610	wire, 1.0 E-CU	0.25 m
20	032 2230	plug, T 3475/2	1
21	038 5820	heating cartridge, 80 W, 24 V, 40 mm	1
22	006 5160	measuring resistor, Pt 100	1
24	046 7500	feedthrough	2
25	033 0740	socket contact	2
26	035 1410	Teflon cord, 0.6 NF	0.8 m
27	047 2950	disc, 2.2x5.5x0.5, VKF	2
30	075 1960	DR WID, 220 O 5 W	1
31	075 1970	tubing, 4.0x2.5, TEF	10 cm
37	102 8300	disc	1

*See Figure 6-21.

Microvolume

The Microvolume, Part No. 116 3150, is shown in Figure 6-22 and Figure 6-23 together with its important parts. These are summarized in Table 6-6. Refer to "Microvolume (Trap 2)" on page 2-23 as well.

Table 6-6. Important Parts of Microvolume (Part No. 116 3150)

Position	Part No.	Designation	Quantity
1	116 3160	valve block	1
2	065 3001	valve unit	2
3	079 2800	front ferrule, 1/4", Swagelok	3
4	079 2810	back ferrule, 1/4", Swagelok	3
5	052 1160	stainless nut, 1/4" o.d.	3
7	055 1010	gasket, gold, o.d. 6 25, i.d. 4 75	2
8	075 4460	pressurizing screw	1
10	041 2300	heat transfer tube	1
11	078 3330	trapping volume, CO_2	1
12	058 2330	washer	1
13	117 7150	pressurized air fitting, KQ2S	2

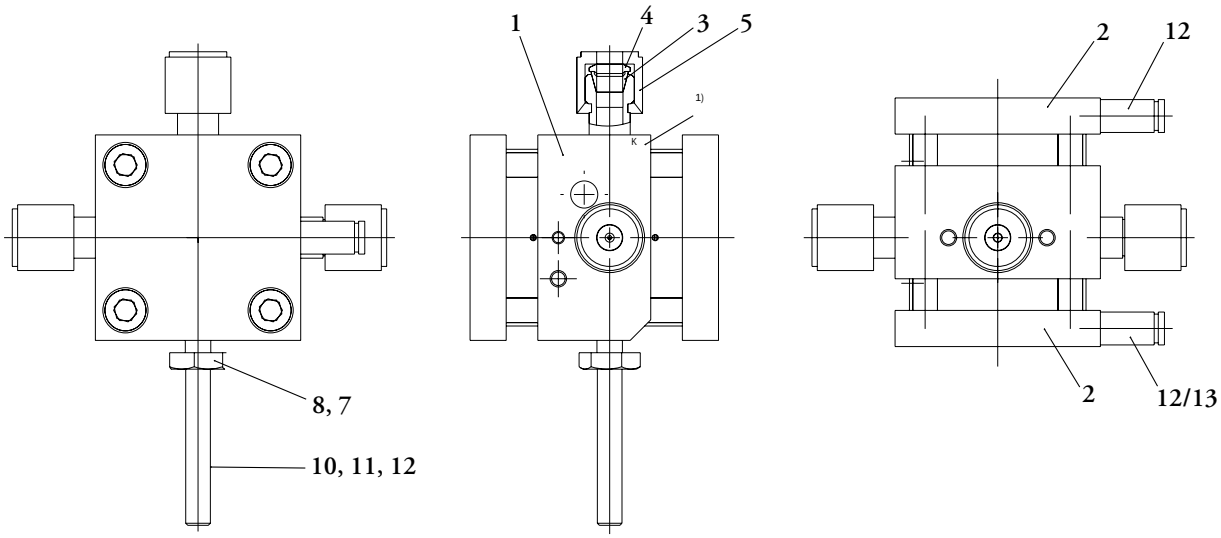
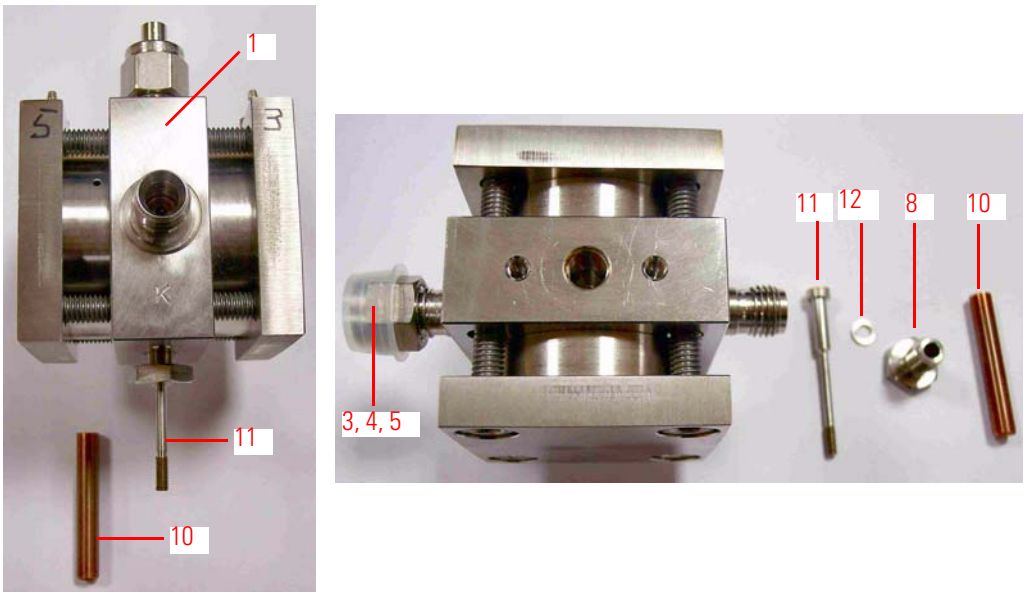


Figure 6-22. Microvolume (Part No. 116 3150)*

*The numbers refer to Table 6-6.



1	valve block
8	pressurizing screw
10	heat transfer tube
11	trapping volume CO_2, 50 µl (with gold gasket, 7)
12	washer

Figure 6-23. Microvolume and its Parts*

*The numbers refer to Table 6-6.

Valve Unit

The valve unit, Part No. 065 3001, is shown in Figure 6-24. Important parts of it have been summarized in Table 6-7.

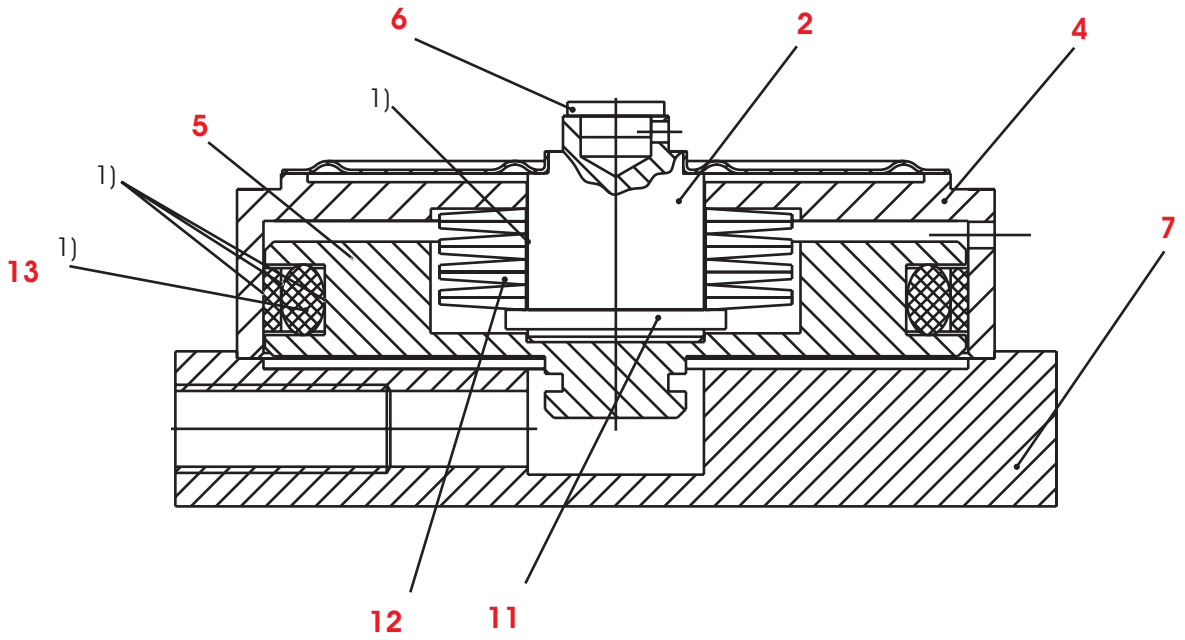


Figure 6-24. Valve Unit (Part No. 065 3001)*

*1) indicates parts that have been slightly greased with Li grease. Parts 2, 4, 11 and 12 are mounted.

Table 6-7. Important Parts of Valve Unit (Part No. 065 3001)

Position	Part No.	Designation	Quantity
2	065 3010	membrane, complete	1
4	065 3050	pressure unit	1
5	065 3030	piston	1
6	065 3041	stamp, gold, seal tip, d=39	1
7	065 3060	cover plate	1
10	045 3420	cylindrical screw, ISO4762, M6x20-A4	4
11	047 3430	guard ring, 10x1, DIN 471	1
12	043 1570	spring plate	8
13	055 3140	set of sealing rings	1
14	054 5270	gasket, gold, o.d. = 38xi.d. 36 5	1

Valve Replacement

Table 6-8. Parts Needed for Valve Replacement

Description	Part No.
membrane (complete)	065 3010
gold stamp	065 3041
gold gasket	054 5270

In order to rebuild one of the stainless steel valves inside the Kiel IV Carbonate Device oven, you need the parts listed in Table 6-8. Follow the steps below:

1. Detach the vial on the side where the valve is leaking. As this sets the rear side of the valve to atmospheric pressure, you can take it apart.

2. Open the valve. This closes the compressed air to the normally open valves.

3. Consider removing the acid reservoir (to avoid breakage)

4. Remove the upper oven shelf to get better access to the work area.

5. Remove the four Allen screws from the faceplate. We use a special, long T-handled 5 mm Allen wrench which has a ball on the end so the wrench can be used at many angles. See Figure 6-25.

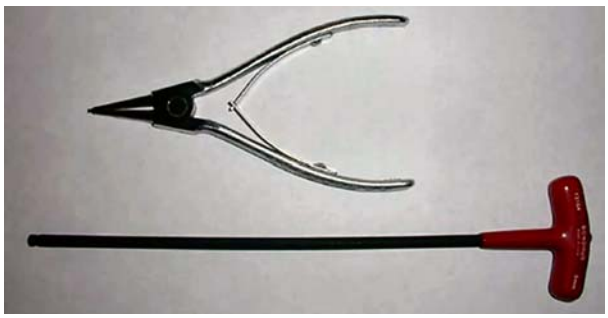


Figure 6-25. Tools for Valve Replacement

6. Pull the square faceplate away from the round piston assembly by hand. There is no need to disconnect the compressed air lines.

7. Rotate the piston assembly and find the air hole. Use the long tube which comes with “canned air” to blow the membrane assembly apart from the valve housing.

8. Place the membrane assembly with the set of compressed spring washers face up on a counter. Use the special tool, which looks like ‘needle nose pliers’, to remove the guard ring which frees the valve membrane from the membrane assembly. These pliers work opposite normal ones: when you squeeze the pliers they open the ring. The ends of the pliers fit into small holes in the guard ring.

Note Do not open the ring too far as it will stretch and have to be replaced. Remember that when you remove the ring, the compressed washers below will expand upwards. ▲

9. Remove the series of curved spring washers by simply lifting the valve housing off of the valve membrane, keeping the 'spring washer' unit intact. The valve membrane assembly will be left on the counter to be disposed of.

10. Gently place the new gold stamp into the new valve membrane. Push the gold stamp into the membrane using finger pressure only. Place the membrane assembly into a small vise and exert equal pressure on the gold stamp and the back of the valve membrane.

Caution Do not apply pressure to the edges of the stamp! Instead, apply firm even pressure to the middle of the stamp to avoid damaging the stamp edges. ▲

11. Insert the membrane assembly up through the valve housing, ensuring that the membrane post fits through the spring washers.

12. Using the plier tool, slightly open the guard ring and press down on the washers so the ring can fit into the groove of the membrane post.

Caution Be very careful while handling the attached gold stamp on the bottom! Do not scuff the edges! ▲

13. Clean the piston assembly housing and lightly grease the outer edge of the O ring seal inside. The valve will not work without some lubrication. Slide the piston assembly back into the housing

14. Dust off the valve block assembly and place the new gold O ring seal against the block body.

15. Place the piston assembly against the gold O ring seal and the valve block body.

16. Place the valve faceplate with the still attached compressed air line against the valve membrane assembly, making sure that the gold O ring seal does not slip. Reattach the four Allen screws as you would a car tire, rotating the tightening around each screw. Tighten

rather hard. The four Allen screws may need to be re-tightened after the assembly has been at vacuum.

17. Seat the new gold stamp by opening/closing the valve 20-30 times and check for leaks. Heat up the Kiel IV Carbonate Device oven to 70 °C to remove water before running samples.

Definitions

Table 6-9. Definitions

Term	Definition
faceplate	Square stainless steel plate to which compressed air is attached. It is attached to the valve block assembly by four Allen screws
valve block assembly	Part of valve left in oven when faceplate and piston assembly are removed
piston assembly	membrane assembly + piston housing
membrane assembly	valve membrane + gold stamp + spring washers + guard ring

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

Figure 6-26. IAEA Primary Standards

Calibrating vs. international standards requires users to have their own specimens of Primary Standards. Primary Standards are exclusively distributed by the IAEA via agencies in Europe and the US. The reference list shown in Figure 6-26 is taken from IAEA TECDOC 825, and the IAEA Analytical Quality Control Services Reference Materials Catalogue 2002-2003. It is very difficult to obtain homogeneity in both isotopes, ^{13}C and ^{18}O.

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). ▲

Note Also refer to Chapter 5.2 Environmental Level, pp. 55 in: IAEA Analytical Quality Control Services Reference Materials Catalogue 2002-2003. First edition, January 2002. Edited by Analytical Quality Control Services, International Atomic Energy Agency, P.O. Box 100, A-1400 Vienna. ▲

Checking for Internal Leaks

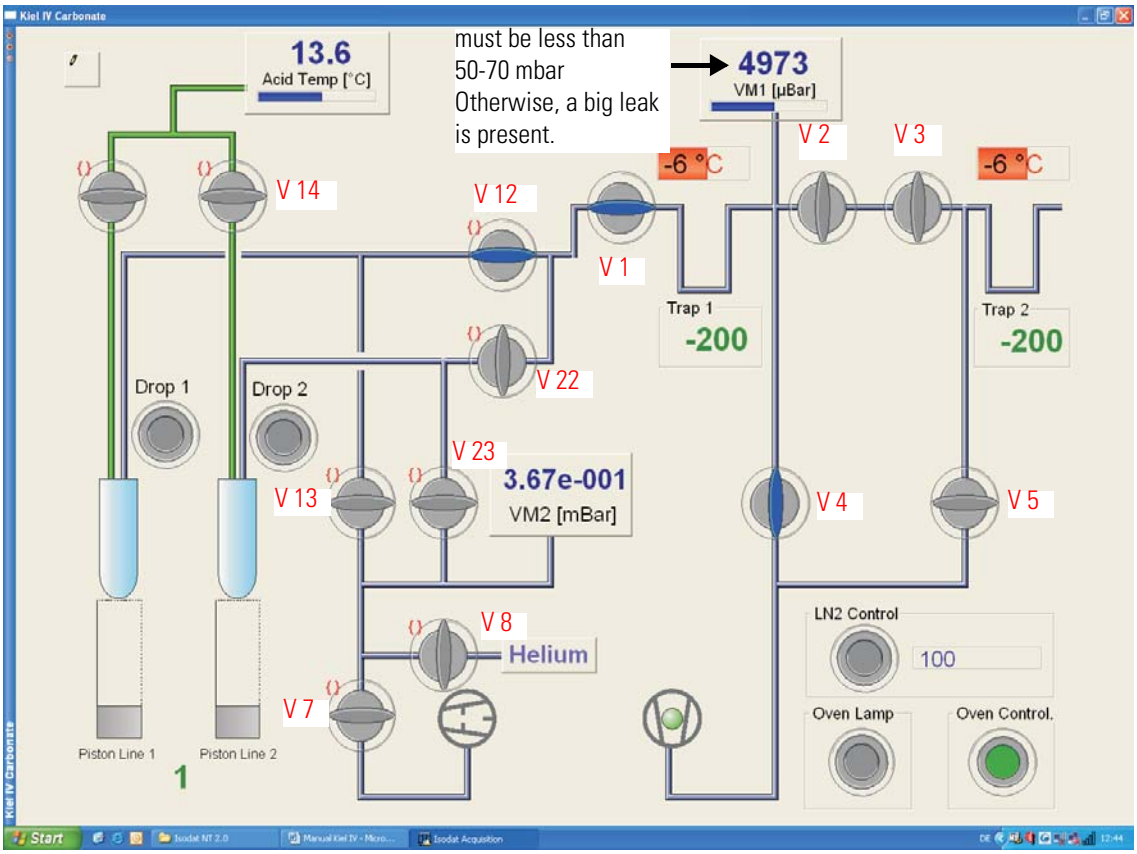


Figure 6-27. Checking VM1 Pressure Increase of Line 1

Note Pressure and temperature units are off-scale in Figure 6-27. ▲

Sources of a leak in order of probability:

- The vial rim is broken.
- The electrical feedthrough of the drop counter is not leaktight.
- The amount of phosphoric acid is too high in either of the acid drop vials (position 2).
- The Teflon washer of the drop counter is missing/not leaktight.
- The acid valve unit is dirty due to phosphoric acid accumulation. To clean it, see "Cleaning Acid Valve" on page 4-14.
- The Swagelok connections to the pneumatic valve unit (V12, V13 and V22, V23) are leaking.
- The pneumatic valve unit is not leaktight.

Note If the pneumatic valve unit is not leaktight, perform a leak test. ▲

In case of a leak, use the following procedure to resolve the problem.

Depending on the line that shows the problem, set the Kiel IV Carbonate Device valves to the positions shown in Figure 6-27. For a problem in line 1, open V12, V1 and V4. For a problem in line 2, open V22, V1 and V4.

If all parts operate properly, close all other valves. The pressure of VM1 should not exceed 50-70 mbar. See upper right corner in Figure 6-27.

High Vacuum Side

Leak Check of Pneumatic Valves

To check the pneumatic valves on the high vacuum side of the Kiel IV Carbonate Device for small leaks, proceed as follows (see Figure 6-27):

Note First, wait for 2 min. The VM1 pressure must not increase! ▲

Note After each step, check VM1 pressure. It must never increase! ▲

1. Pump the high vacuum side with V1, V2, V3, V4, V5 open. Disconnect one of the vials. Pump until VM1 pressure is at background level, that is below 50-70 mbar. See Figure 6-28.

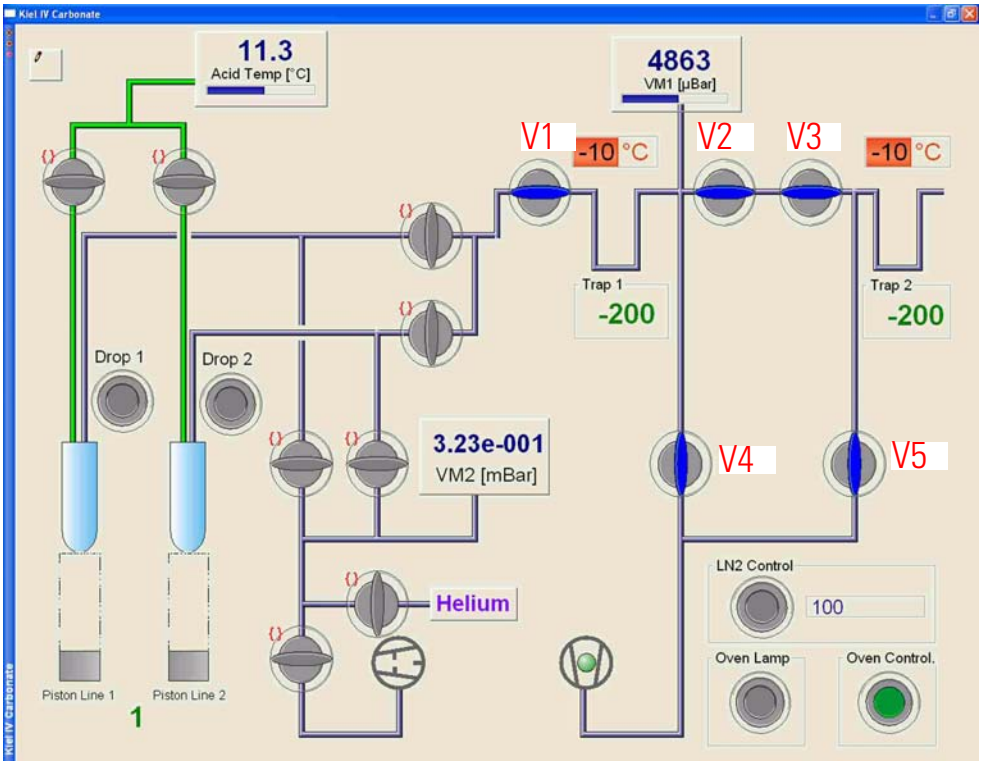


Figure 6-28. Leak Check of Pneumatic Valves - Step 1

2. Close all valves on the high vacuum side. See Figure 6-29.

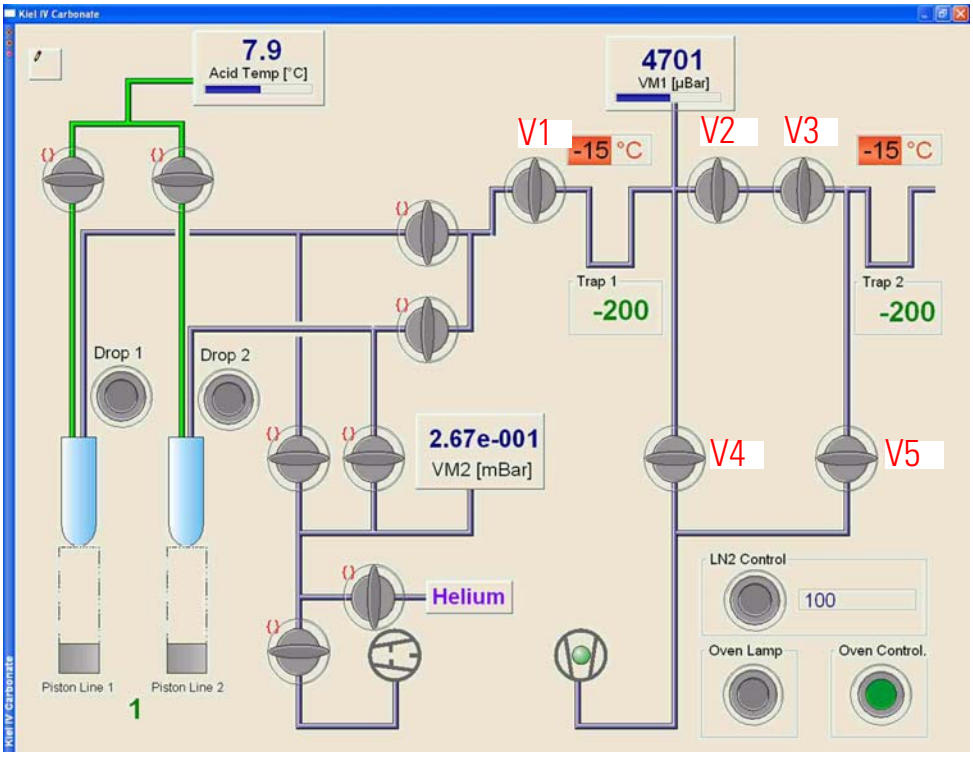


Figure 6-29. Leak Check of Pneumatic Valves - Step 2

3. To be able to open V12 or V22, lift the spring plate with one finger towards the proximity switch (Figure 4-18). Fill until V1 with air.

4. Close V12 or V22 (dependent on where the vial is not connected).

5. Open V1 and V2. Leave V4 and V5 closed. See Figure 6-30.

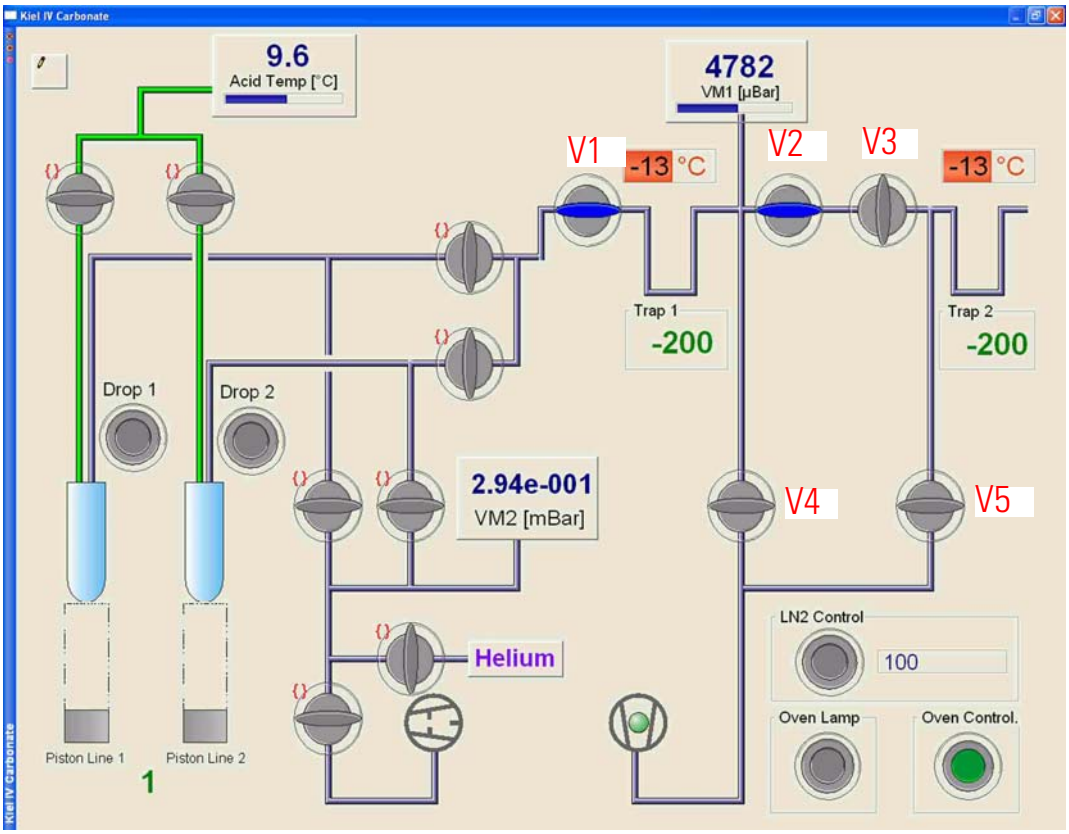


Figure 6-30. Leak Check of Pneumatic Valves - Step 5

6. Perform a **Tune Scan** on m/z 28 with COV sample side to the Kiel IV Carbonate Device open (V15, V16 closed). See Figure 6-31.

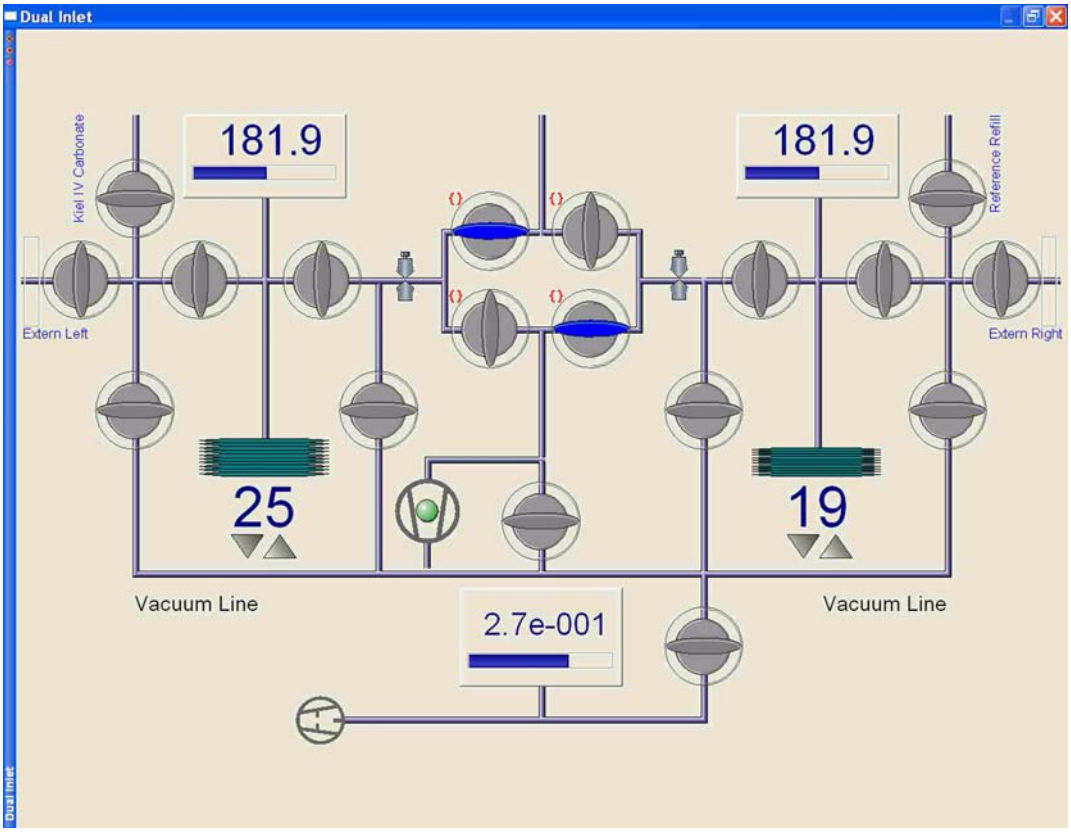


Figure 6-31. Leak Check of Pneumatic Valves - Step 6

To record m/z 28 from the Kiel IV Carbonate Device, the Dual Inlet system must be adjusted as shown in Figure 6-31.

A leak is possible between V3 pneumatic valve and the IRMS (that is, COV valve block, sample capillary, tubing from Changeover Valve to ion source inlet, needle valve).

Carbonate Side Leaks

Carbonate side leaks may occur at V3 pneumatic valve, at Microvolume or at the capillary connection to the Kiel IV Carbonate Device and the Changeover Valve (COV).

Checking V2

To check V2, proceed as follows:

Note First, wait for 2 min. The VM1 pressure must not increase! ▲

Note After each step, check VM1 pressure. It must never increase! ▲

1. Pump out the air in the lines from V2 to the IRMS via V5. See Figure 6-32.

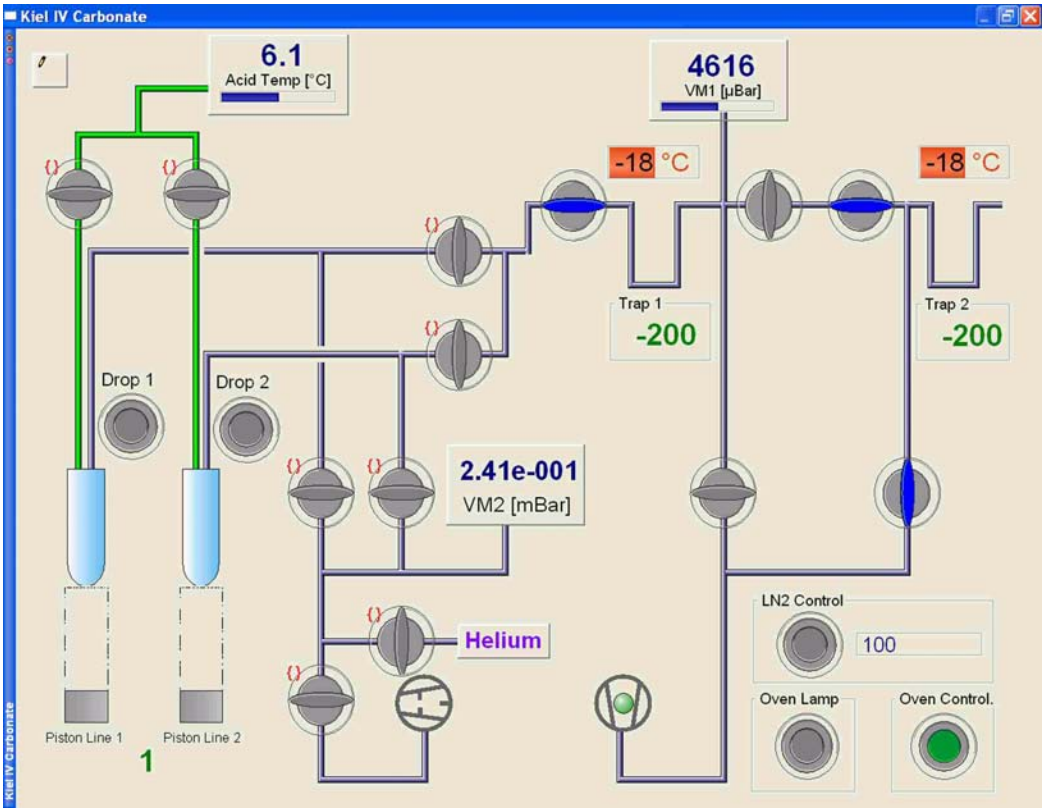


Figure 6-32. Checking V2 - Step 1

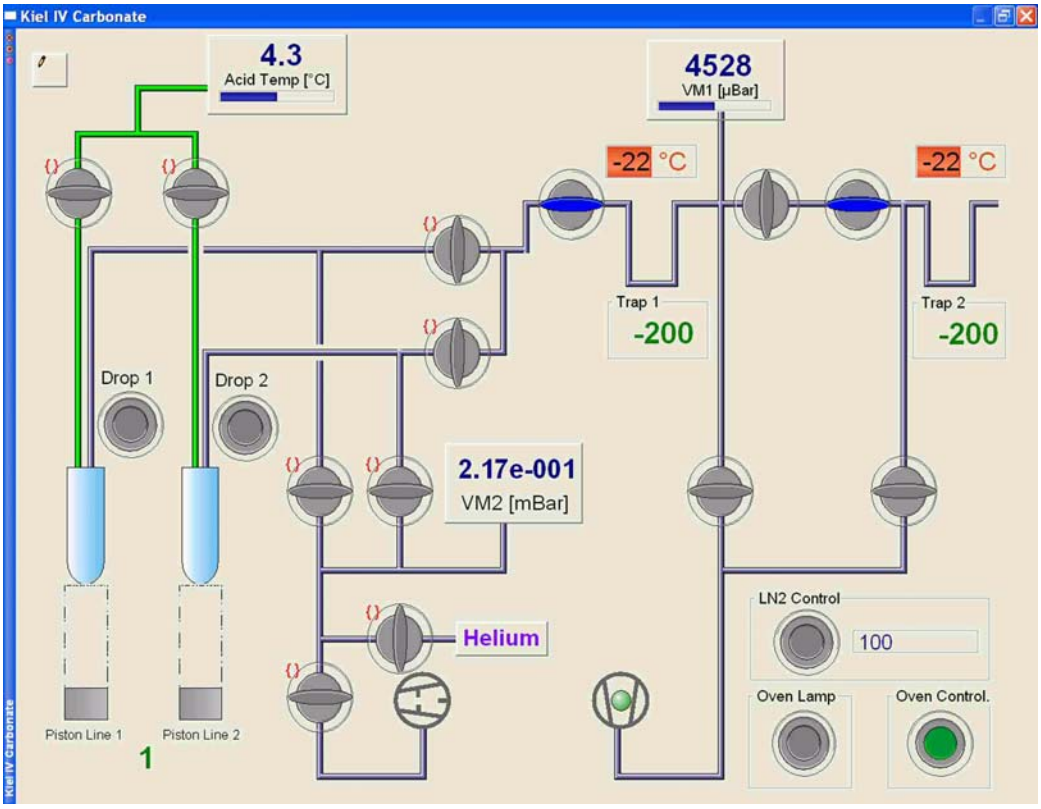


Figure 6-33. Checking V2 - Step 2

2. Close V5. See Figure 6-33. Observe VM1 pressure. If it does not rise, no leak is present. If it rises however, a leak is possible behind V2 at pneumatic valve unit or at the transfer tubing.

Checking V1

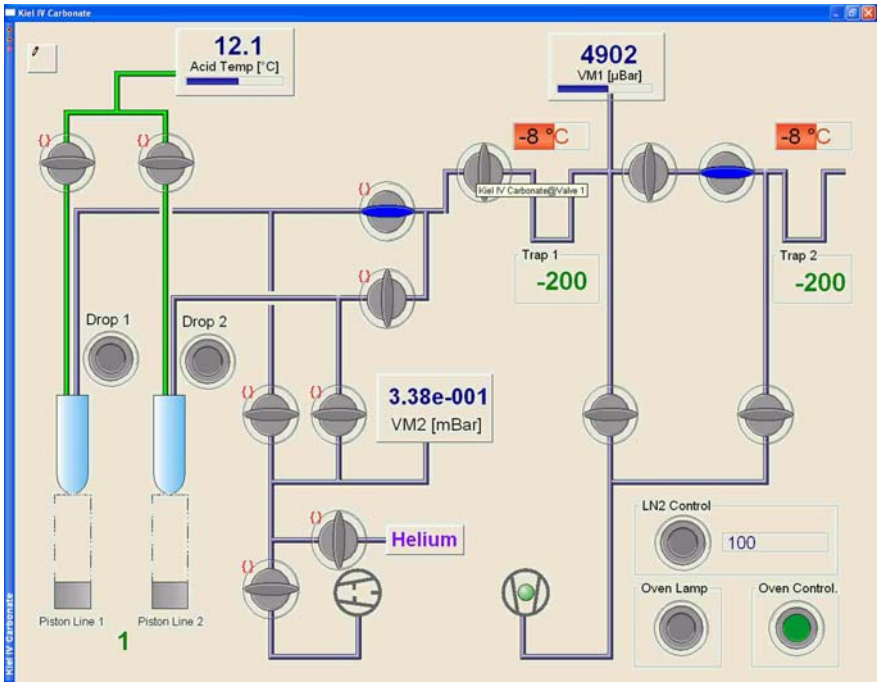


Figure 6-34. Checking V1 - Step 1

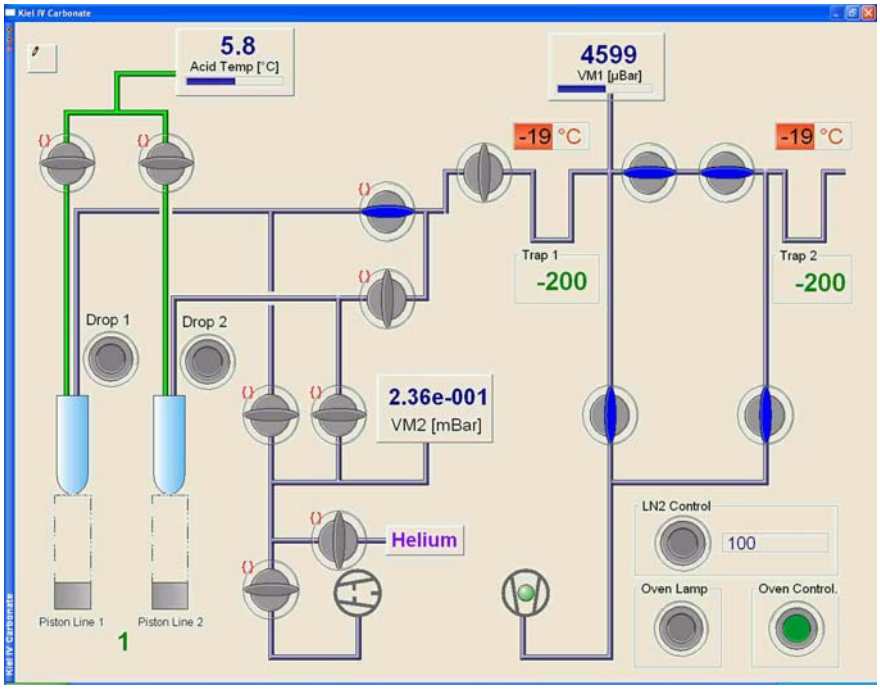


Figure 6-35. Checking V1 - Step 2

Note First, wait for 2 min. The VM1 pressure must not increase! ▲

Note After each step, check VM1 pressure. It must never increase! ▲

1. Close V1. See Figure 6-34.

2. Open V2, V3, V4 and V5. See Figure 6-35.

3. Close V4 and V5. See Figure 6-36.
   Observe VM1 pressure. If it does not rise, no leak is present. If it rises however, a leak is possible behind V1 at the four locations:

   - pneumatic valve unit or
   - transfer tubing or
   - VM1 connection or
   - water trap

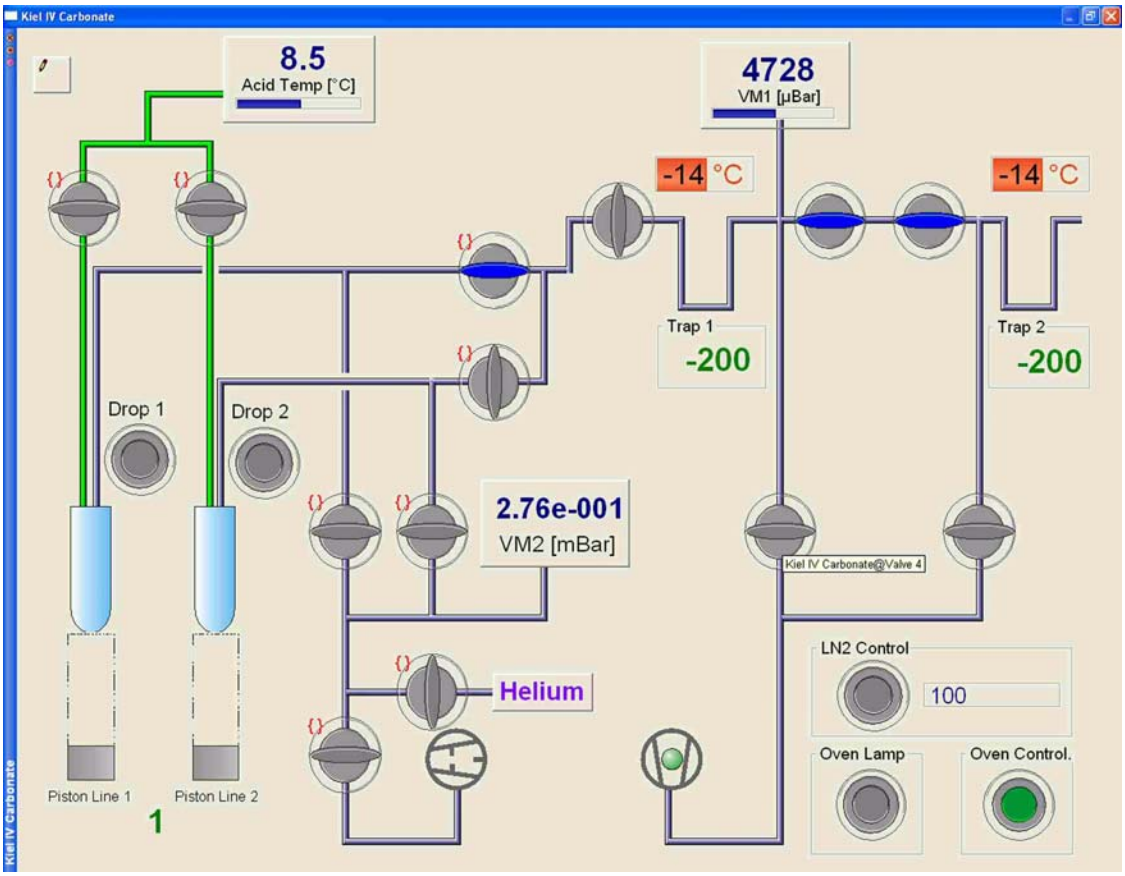


Figure 6-36. Checking V1 - Step 3

Maintenance

Turbo Pumps and Fore Pumps

Change the oil reservoir of the turbo pumps once a year. Check the oil level of the fore pumps frequently and exchange the complete oil once a year. Refer to manufacturer's manual.

O Ring Seals

Remove acid and any residuals from the O ring seals of the acid valve prior to starting a run. The O ring seals may be slightly greased using a high-vacuum grease, that is, Apiezon H.

Autocool Unit

Between runs, allow the Autocool Unit to heat up to room temperature by removing the dewar. This serves to completely remove frozen water. Discard the water that accumulates in the dewar.

Note If no liquid nitrogen is transported from the funnel into the cascade, the freezing temperature of -190 °C cannot be reached. Isodat 2.5 will then show a temperature error. As it can no longer be frozen, CO_2 is lost. During cooling, isotope fractionation occurs. ▲

Note If improper transport of liquid nitrogen between funnel and cascade occurs, ice droplets are clogging inside the funnel tubing. Release the liquid nitrogen dewar in order to let the ice melt and to release most of the frozen water. ▲

Note PTFE tubing connects the funnel to the cooling cascade. Due to PTFE chips sticking inside the tubing, transport of liquid nitrogen into the cascade is interrupted. File off the PTFE tubing in order to let the transport of liquid nitrogen work properly again. ▲

Note If temperatures above 120 °C cannot be obtained by the heating cartridge[1], it must be exchanged (it tends to age). As heating cartridges sometimes cannot be released, the Autocool Unit must be exchanged. At temperatures below 120 °C, it is impossible to heat out water from the trapping system. Isotope fractionation will lead to erroneous isotope ratios due to H_2O-CO_2 collisions within the ion source. ▲

Programming Information

Board Base Addresses

The board base addresses are summarized in Table 6-10.

[1] the 30 W heater, 2 in Figure 2-32

Table 6-10. Board Base Addresses

Usage	Code
Inlet Controller Internal	1
Inlet Controller External Options	2
Inlet Controller Kiel IV Carbonate Device primary	B
Data Logger MS	4
Inlet Controller Kiel IV Carbonate Device secondary	5
Source Control Gnd	6
Source Control HV	7
Power Distributor MS	8
Power Distributor Kiel IV Carbonate Device	9
PeriCon	C

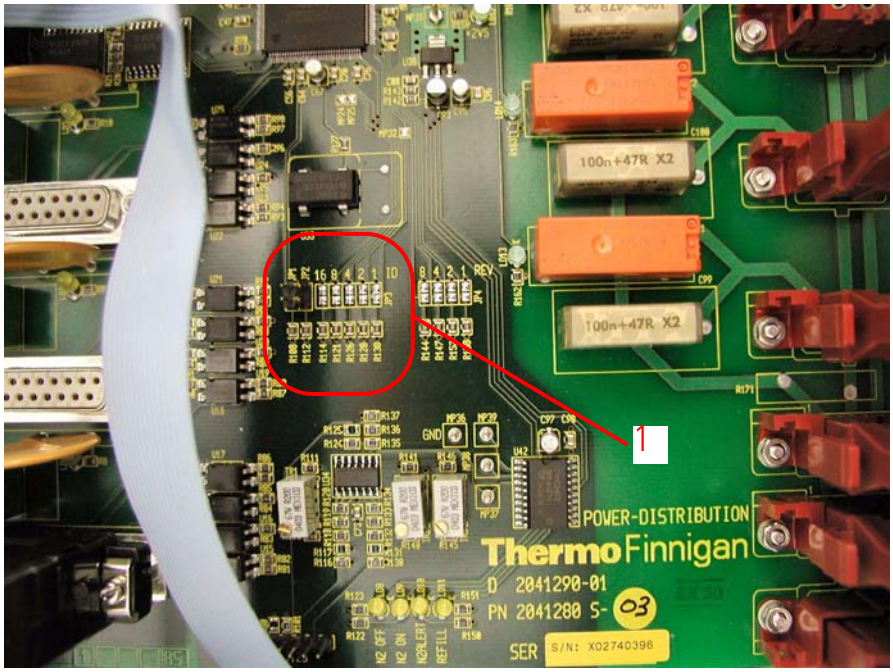


Figure 6-37. Adjusting Base Address of Power Distribution Board

Figure 6-37 depicts how to adjust the base address of the Power Distribution board. **1** denotes the address selection jumper.

Device Addresses

Table 6-11 summarizes the hardware addresses used within Kiel IV Carbonate Device (e.g. for plugs, contacts and pins).

Table 6-11. Device Addresses - Complete

Usage	Board	Jack	Pins	Logical Name in Isodat	Type of IO	Hex Address
Trap 1 temperature true value	IC 1			Get Trap 1 Temperature	ADC	0xB37
Acid true temperature	IC 1	J210		Get Acid Temperature	ADC	0xB37
Trap 2 temperature true value	IC 2	J214		Get Trap 2 Temperature	ADC	0x537
Position Sensing Array	IC 1	J204		Turrect Raw	DAC	0xB07
Motor torque setting				Turret torque	DAC	0xBFB
Turret Position				Turret position	DAC	0xBFF
Trap 1 temperature Set value	IC 1	J214		Set Trap 1 Temperature	DAC	0xB30
Trap 2 temperature Set value	IC 2	J214		Set Trap 2 Temperature	DAC	0x530
Proximity Switch Line 1	IC 2	J209		Bottle Line 1	DIO	0x507
Proximity Switch Line 2	IC 2	J208		Bottle Line 2	DIO	0x507
Drop Counter Line 1	IC 1	J215		Drop Line 1	DIO	0xB07
Drop Counter Line 2	IC 1	J215		Drop Line 2	DIO	0xB07
Piston Sensor Line 1	IC 1	J208		Piston Sensor 1	DIO	0xB07
Piston Sensor Line 2	IC 1	J207		Piston Sensor 2	DIO	0xB07
Motor control direction	IC 1				DIO	0xB00
Motor control enable	IC 1				DIO	0xB00
Motor control direction	IC 1				DIO	0xB00
Trap 1 Heater Disable	IC 1			Trap1 Heater Off	DIO	0xB00
Trap 2 Heater Disable	IC 2			Trap2 Heater Off	DIO	0x500
Valve 22	IC 1	J225	4	Valve 22	DIO	0xB28
Valve 23	IC 1	J225	5	Valve 23	DIO	0xB28
Valve 12	IC 1	J225	6	Valve 12	DIO	0xB28
Valve 13	IC 1	J225	7	Valve 13	DIO	0xB28
Piston Line 1 up	IC 1	J225	20	Piston Line 1 up	DIO	0xB28
Piston Line 2 up	IC 1	J225	21	Piston Line 2 up	DIO	0xB28
Piston Line 1 down	IC 1	J225	22	Piston Line 1 down	DIO	0xB28
Piston Line 2 down	IC 1	J225	23	Piston Line 2 down	DIO	0xB28
Pinch valve Line 1	IC 1	J217	4	Acid valve Line 1	DIO	0xB29
Pinch valve Line 2	IC 1	J217	5	Acid valve Line 2	DIO	0xB29
Valve 7	IC 1	J217	6	Valve 7	DIO	0xB29
Valve 8	IC 1	J217	7	Valve 8	DIO	0xB29
Valve 3	IC 1	J227	6	Valve 3	DIO	0xB2A
Valve 5	IC 1	J227	7	Valve 5	DIO	0xB2A
Valve 1	IC 1	J227	20	Valve 1	DIO	0xB2A
Valve 2	IC 1	J227	21	Valve 2	DIO	0xB2A
Valve 4	IC 1	J227	22	Valve 4	DIO	0xB2A

Table 6-11. Device Addresses - Complete, continued

Usage	Board	Jack	Pins	Logical Name in Isodat	Type of IO	Hex Address
Trap 2 cooling resistor	IC 2	J214			DIO	0x52E
Trap 1 cooling resistor	IC 1	J214			DIO	0xB02
Turbo pump Error	PD				DIO	0x902
Turbo pump 50%	PD				DIO	0x903
Control Refill Valve	PD			Refill Direct	DIO	0x901
LN2 Refill Unit Enable (LED)	PD			LN2 Refill Direct	DIO	0x901
Host Connection	PD			Host Connection	DIO	0x901
VM 1 pressure true value	IC 1	J215		VM 1	PM	0xB39
VM 2 pressure true value	IC 1	J215		VM 2	PM	0xB39
LN2 Level Sensor				LN 2 Pressure	PM	0x539

Table 6-12 shows DIO parameters as subset a of the device addresses.

Table 6-12. DIO Parameters

Usage	Opcode	Control Code	Address Code
Proximity Switch Line 1	1	10	0
Proximity Switch Line 2	1	11	0
Drop Counter Line 1	1	8	0
Drop Counter Line 2	1	9	0
Piston Sensor Line 1		11	
Piston Sensor Line 2		12	
Motor control direction		0	
Motor control enable		1	
Motor control direction		2	
Trap 1 Heater Disable	1	9	0
Trap 2 Heater Disable	1	9	0
Valve 22	1	0	
Valve 23	1	1	0
Valve 12	1	2	0
Valve 13	1	3	0
Piston Line 1 up	1	4	0
Piston Line 2 up	1	5	0
Piston Line 1 down	1	6	0
Piston Line 2 down	1	7	0
Pinch valve Line 1	1	0	0
Pinch valve Line 2	1	1	0
Valve 7	1	2	0

Table 6-12. DIO Parameters, continued

Usage	Opcode	Control Code	Address Code
Valve 8	1	3	0
Valve 3	1	2	0
Valve 5	1	3	0
Valve 1	1	4	0
Valve 2	1	5	0
Valve 4	1	6	0
Trap 2 cooling resistor		7	
Trap 1 cooling resistor		7	
Turbo pump Error		7	
Turbo pump 50%		9	
Control Refill Valve	1	4	0
LN2 Refill Unit Enable (LED)	1	12	0
Host Connection	1	0	0

Table 6-13 shows ADC parameters as subset a of the device addresses.

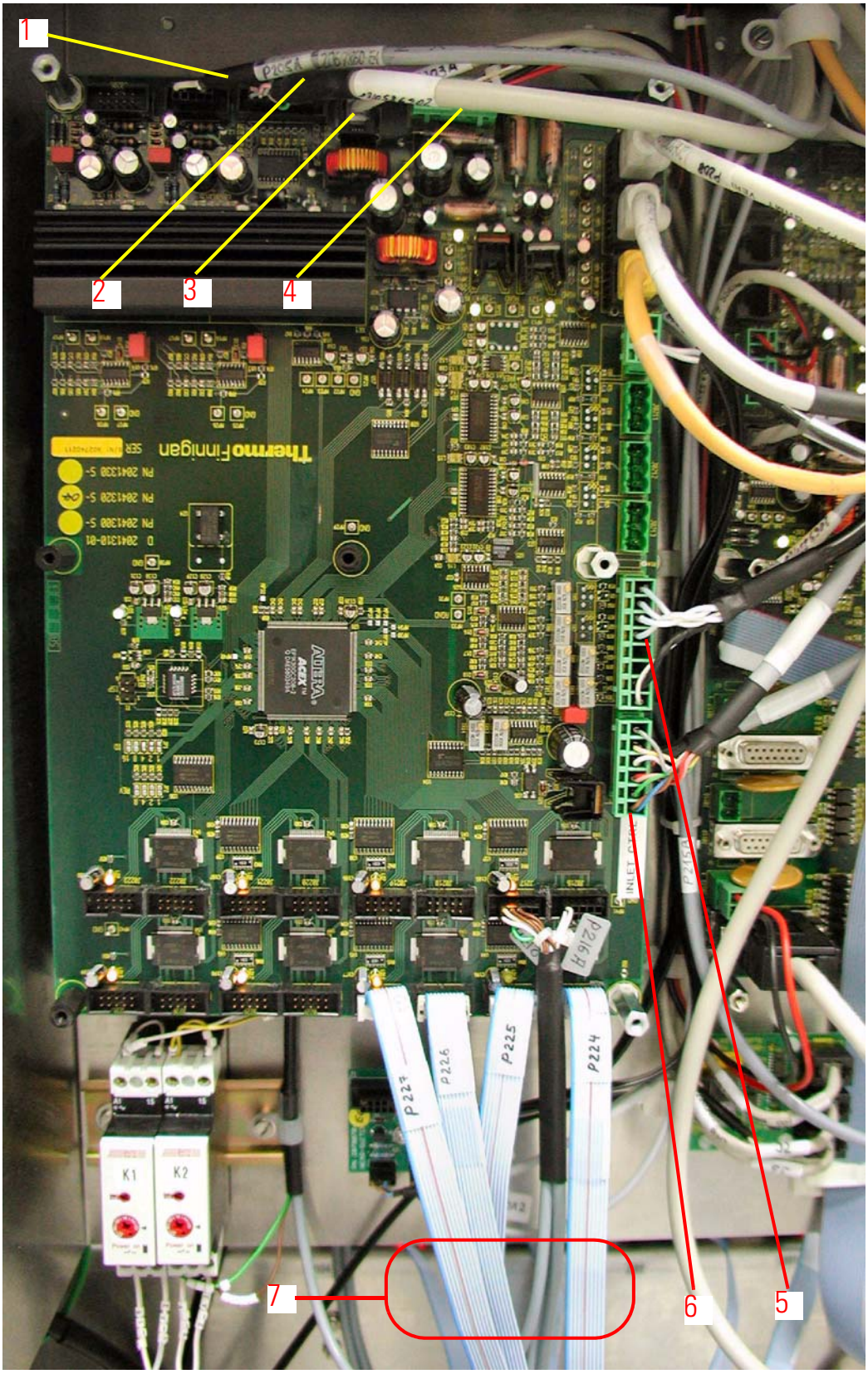
Table 6-13. ADC Parameters

Usage	Min.	Max.	Offset	Gradient 1	Gradient 2	Gradient 3	Log Calc.
Trap 1 temperature true value	0	4096	-200	0.0866699	0	0	
Acid true temperature	0	4096	-100	0.051	0	0	
Trap 2 temperature true value	0	4095	-200	0.0866699	0	0	
Trap 1 temperature Set value			-200	0.0866699	0	0	
Trap 2 temperature Set value			-200	0.0866699	0	0	
VM 1 pressure true value	0	4096	-532	1000	0	0	
VM 2 pressure true value	0	4096	-12.888	3.7087	-0.3733	0.0169	y
LN2 Level Sensor	0	4095	175.47	-0.188679	0	0	

Table 6-14 shows DAC parameters as subset a of the device addresses.

Table 6-14. DAC Parameters

Usage	Min.	Max.	Address Lo	Address Hi	Cut DAC Steps
Position Sensing Array	0	65535	0	0	0
Motor torque setting	0	65535	0	0	0
Turret Position	1	24	7	0	0
Trap 1 temperature Set value	0	4095	0	0	104
Trap 2 temperature Set value	0	4095	0	0	104



1 motor
2 trap
3 data in
4 power
5 drop counter and VM1
6 position sensor array
7 valves

Figure 6-38. Connections on Inlet Control Board

Figure 6-38 shows the connections on the Inlet Control board. More precisely, two identical boards are arranged in stacked order on top of each

other. The upper one has the board base address B, whereas the board base address of the lower one is 5 (see Table 6-10).

As a detail of Figure 6-38, Figure 6-39 shows where the sensitivity of the drop counters is adjusted.

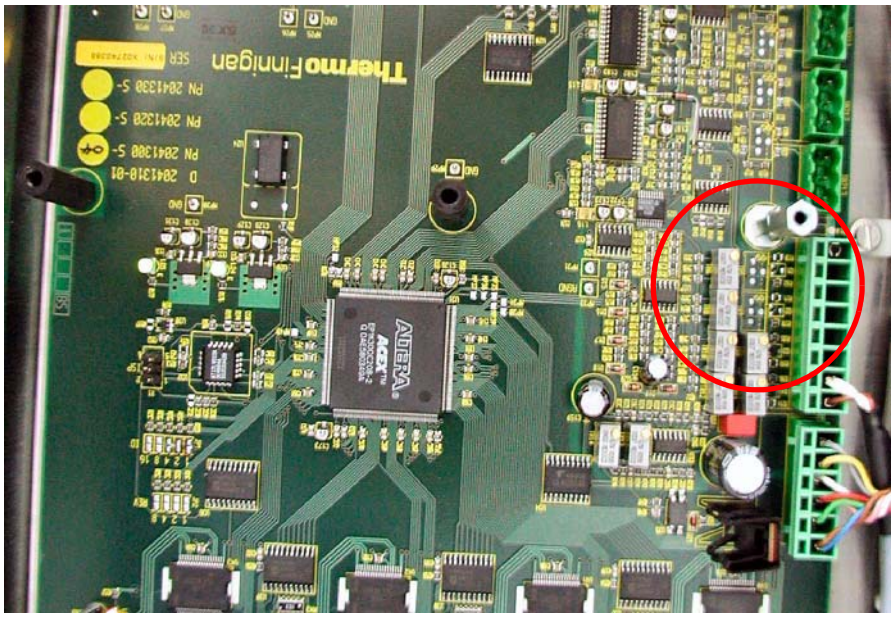


Figure 6-39. Adjusting Sensitivity of Drop Counters

Registry Use

LineX Sample Position

- Function **Disconnect** resets variable according to **Line** status to 0 when completed successfully.
- Function **Connect** sets respective variable to **Position** when completed successfully.

Note Manual connection/disconnection is not detected. ▲

Carousel Position

- controlled by function **MoveToPosition**
- not actively used with Kiel IV Carbonate Device since readout of position is always possible

Compressed Air Supply

The compressed air supply is shown in Figure 6-40 and Figure 6-41.

Figure 6-40. Compressed Air Supply

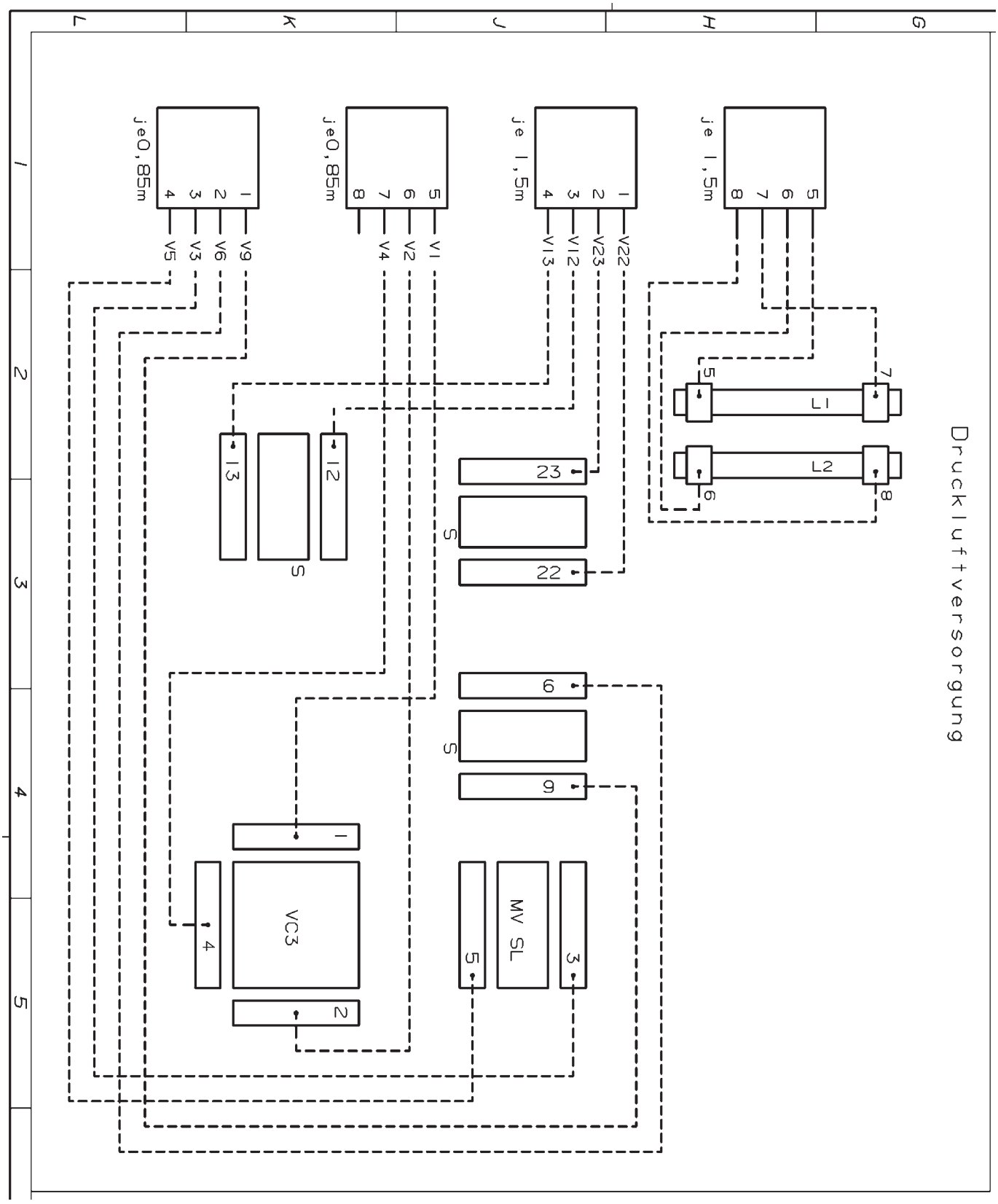


Figure 6-41. Compressed Air Supply - Schematic

Vacuum Schematic

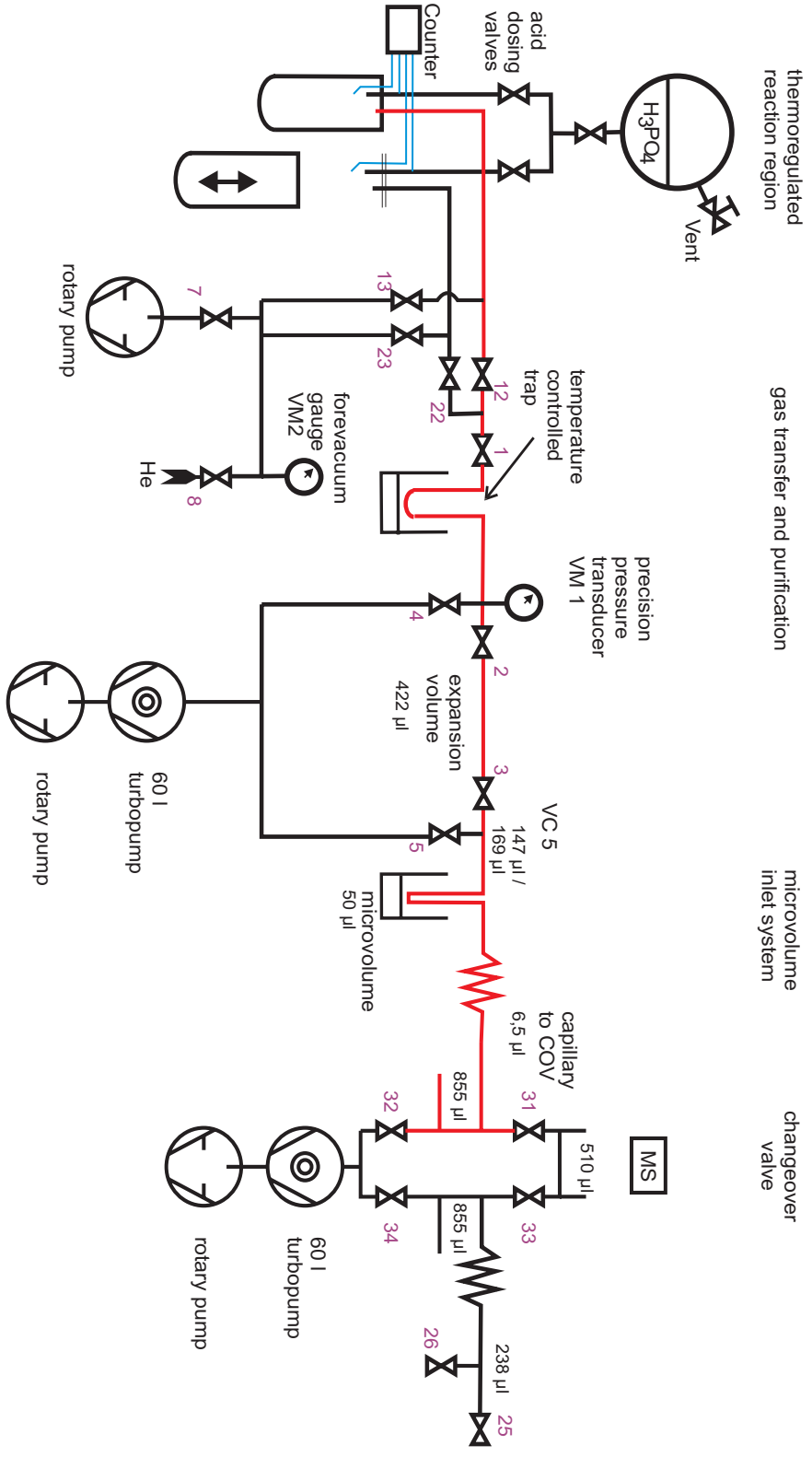


Figure 6-42. Kiel IV Carbonate Device - Vacuum Schematic

Circuit Diagrams

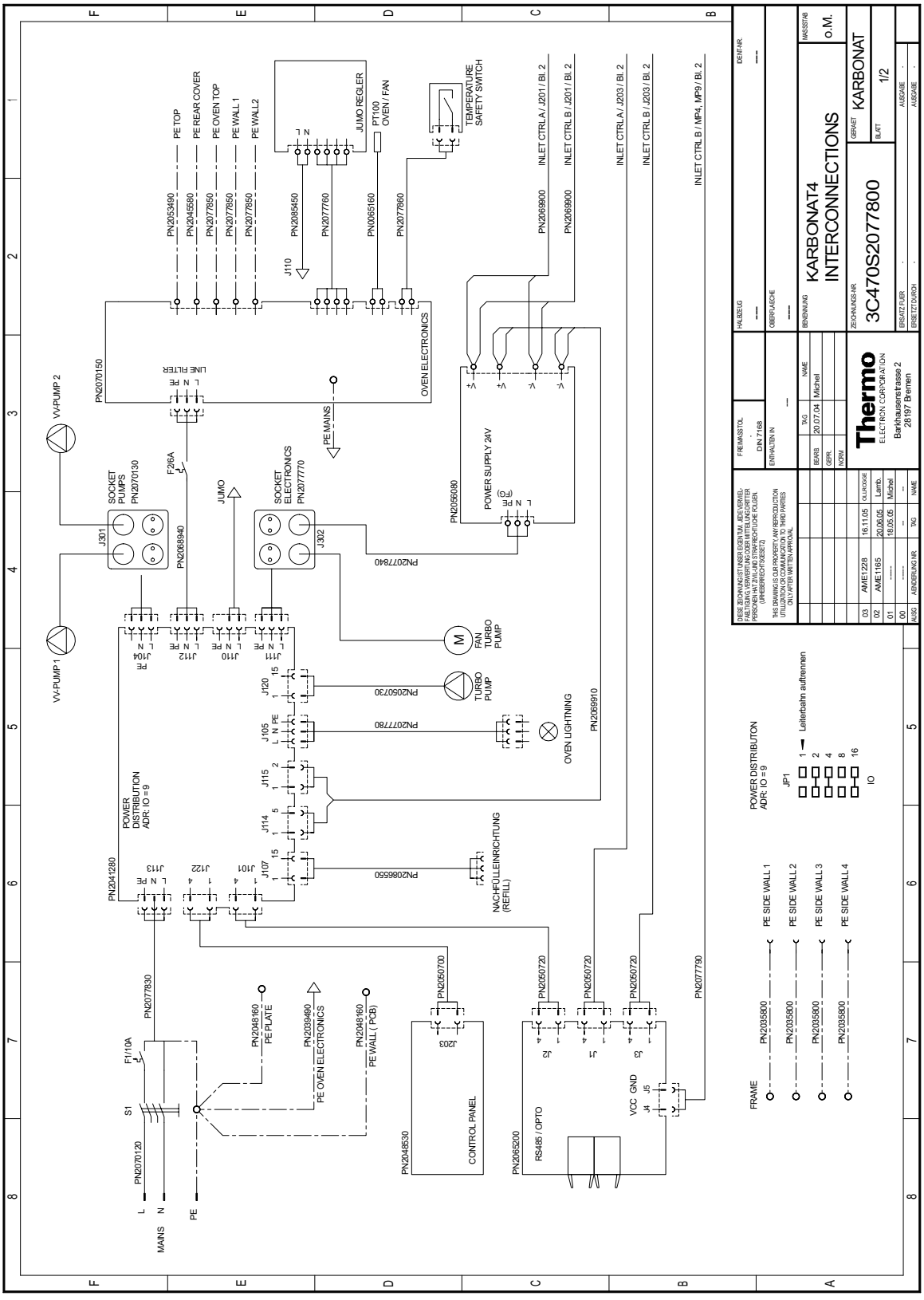


Figure 6-43. Circuit Diagram of Device - Control Logic

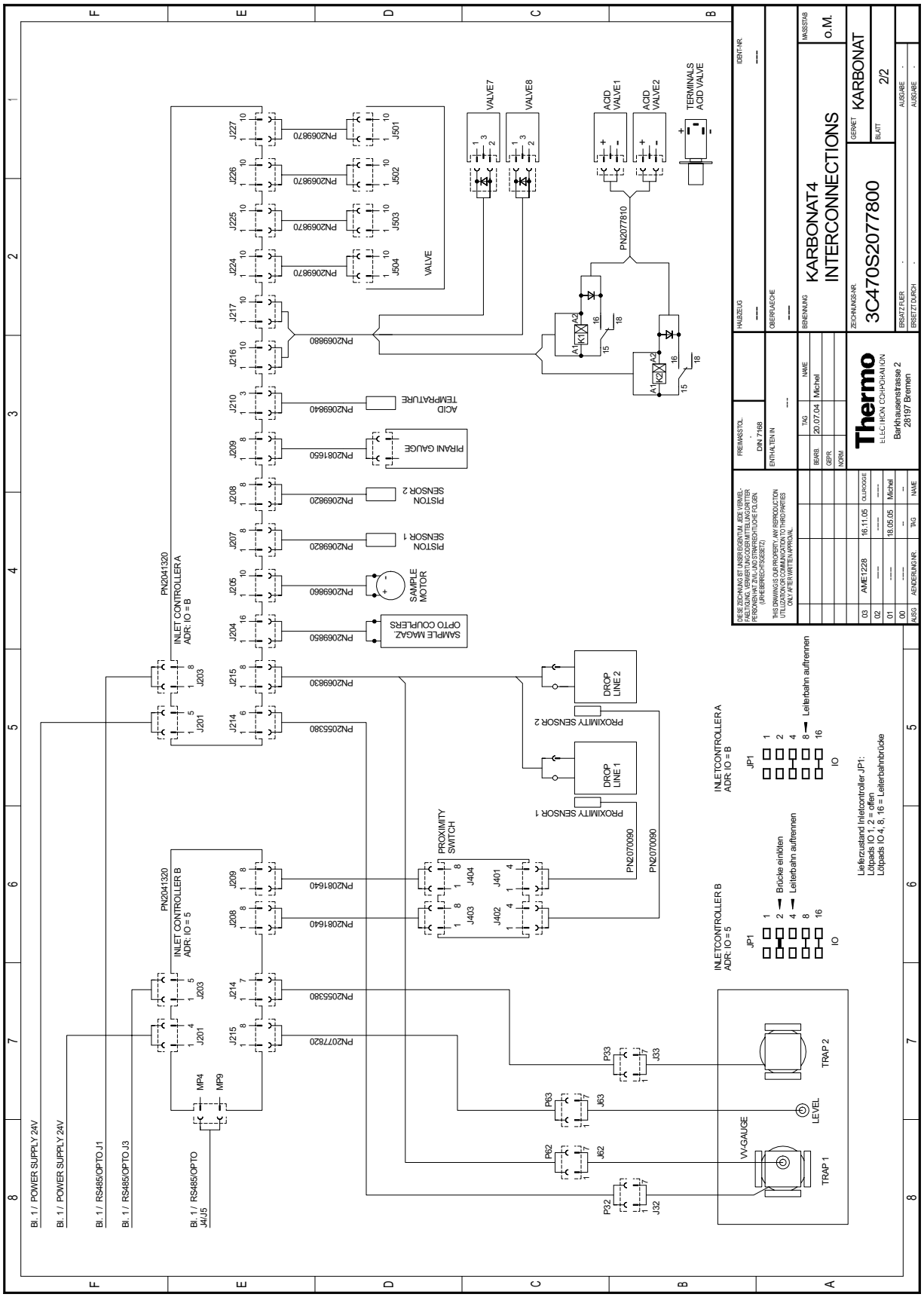


Figure 6-44. Circuit Diagram of Device - Mains Connections

Glossary

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

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 Gauss; 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™

ICP inductively coupled plasma

ICP-OES inductively coupled plasma optical emission spectroscopy

ID inside diameter

IEC International Electrotechnical Commission

IEEE Institute of Electrical and Electronics Engineers

in. inch

I/O input/output

IRMS isotope ratio mass spectrometer

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/MS liquid chromatograph / mass spectrometer

LED light-emitting diode

LHe liquid helium

LN2 liquid nitrogen

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

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

V volt

V ac volts alternating current

V dc volts direct current

vol volume

w width

W watt

Index

Numerics

A

B

C

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J

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L

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N

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