KIEL CARBONATE DEVICE

OPERATING MANUAL

Issue 12/2002

Ident. No. 111 37 91

Thermo Finnigan

Übereinstimmungserklärung gemäß EN 45014
declaration of conformity according to EN 45014
Dichiarazione di conformità alla EN 45014

Name des Herstellers:
manufacturers name:
nome produttore:

Finnigan MAT GmbH

Adresse des Herstellers:
manufacturers address:
indirizzo produttore:

Barkhausenstraße 2
28197 Bremen
Germany

erklärt, daß das Produkt
declares that the following product
dichiara che il seguente prodotto

Wärmeschrank für Karbonatanlage

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

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

EN 50081-1, EN 55011 class B

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

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

Elektrische Sicherheit:
electrical safety:
sicurezza elettrica:

EN 61010-1

Ergänzende Informationen:
complementary information:
informazioni complementari:

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

Bremen, Germany, 30. July 1997

Der Entwicklungsleiter:
Head of Engineering:
Responsabile construzione:

A. Schröder

Thermo Finnigan MAT GmbH
Postfach 1401 62
28088 Bremen
Germany

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Reparatur-Begleitkarte*)
Repair-Covering Letter

Absender:
Despachter:

Geräte-Type:
Instrument Type:

Service-Nr.:
Service No

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

Festgestellte Mängel oder deren Auswirkung:
Established defect or its effect:

Bitte detaillierte Angaben machen / Please specify in detail

Ein Austauschteil haben wir erhalten unter Kommissions-Nr.:
An exchange part already received with commission no.:

Ja/Yes ☐ Nein/No ☐

Die Anlage ist außer Funktion
The system is out of function

Ja/Yes ☐ Nein/No ☐

Durch die nachfolgende Unterschrift bestätige(n) ich /wir, daß die o.g. Teile frei von gesundheitsschädlichen Stoffen sind, bzw. vor ihrer Einsendung an Thermo Finnigan MAT dekontaminiert wurden, falls die Teile mit giftigen Stoffen in Verbindung gekommen sind.

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

Datum / date

Unterschrift / signature

*) Bitte vollständig ausfüllen / Please fill in completely

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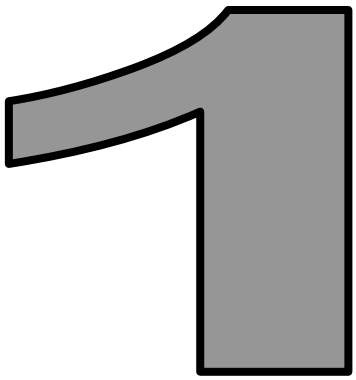
KIEL CARBONATE DEVICE



BASICS

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1.1. FOREWORD

It is assumed that the user is not only familiar with clean operating procedures and sample preparation but also has already had some working experience with IRMS, windows and ISODAT software.
Working with the *KIEL CARBONATE DEVICE* means to operate a complex system running many processes at the same time. Therefore the manual should be read prior working to become an overview about the system. It is recommended to read the text below and procedure seriously as well as to compare the Hardware-layout to the system.

This is a preliminary version of the *KIEL CARBONATE DEVICE* operating manual.

1.2. READ ME FIRST

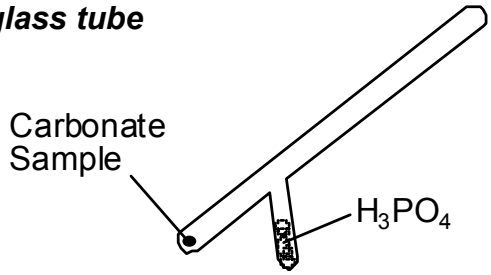
Basic Principle of the Kiel Carbonate Operation

Before starting any sample preparation with *KIEL CARBONATE DEVICE* and doing some measurements it is important to know briefly the operation procedure of the device. The *KIEL 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, following as T1) and finally sample trapping arrangement (Trap 2, following as T2).
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. In each hole can be placed a sample preparation vial, which is made of glass.
The vials at position 1 are called pump vials and are indicated as vial 1/1 and 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 magazine, containing vials with samples, is positioned inside the oven and the sequence is started all subsequent steps are fully automated and computer controlled.

1.3. INTRODUCTION (1/2)

For the measurement of stable carbon and oxygen isotopes in carbonates there are several methods and apparatus available. Isotope ratio determination of the above elements is usually carried out using carbon dioxide (CO_2) produced in the reaction between carbonates and phosphoric acid. The traditional method employs a glass tube with a side arm.

Fig: 1.1 Traditional glass tube



The carbonate samples are loaded in the end of glass tube. The side arm contains phosphoric acid. Reaction takes place after tilting the glass tube so to bring acid to sample. This method requires also a stable temperature e.g., 25 °C (or 50 °C to accelerate the reaction). The reaction time is between 2 hours for calcite (sample amount > 5 mg) and 48 hours for dolomite (sample amount > 10 mg). After the reaction 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 carbon dioxide gas for the isotope ratio determination must be isola-ted 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 apparatus which we describe below is acid on individual carbonate so-called *KIEL CARBO-NATE DEVICE*. The *KIEL CARBONATE DEVICE* is a fully automated preparation device for the precise and accurate determination of oxygen and carbon isotope ratios in carbonates, which have wide use in many fields of geology. One of the major applications is the esti-mation of ocean paleotemperatures from ^{18}O / ^{16}O ratios in marine microfossils. Ultimate precision and accuracy are a prerequisite for such work because a temperature difference of 1°C translates to a Δ ^{18}O difference of about 0,2 ‰. The *KIEL CARBONATE DEVICE* has been developed in close cooperation with leading academic researchers with the first unit introduced in 1982.

1.3. INTRODUCTION (2/2)

The *KIEL CARBONATE DEVICE* incorporates a number of design changes which enhance ease of use, diminish the trace metal content of the acid, and decrease both the cost of acquisition and operation, without changes to the underlying principles of operation. 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 minutes. Sample throughput of more than 10,000 samples per year is reported by a number of laboratories and can in fact be regarded as routine.

1.4. PROCEDURE (1/2)

The system consists of a thermostated reaction region, a trapping and gas cleaning sys-tem and an inlet system. 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, and allowing visual inspection of the sample and easy cleaning prior to re-use. In order to speed up the measurements, the sample containers are organised in two concentric rows, each with a separate reaction and measuring position. The reaction region also houses the reservoir of concentrated phosphoric acid, which is dispensed through two metal-free acid resistant dosing valves of all new design.

Once the sample containers are loaded and the sequence table is filled out, all subsequent steps are fully automated. Prior to reaction and measurement each container is evacuated. Only then a precisely controlled amount of acid is added to the sample under computer control. At no time is the acid in contact to a metal surface, except for a short final steel capillary and a platinum wire for droplet generation and counting. Because of these principle sources of contamination from the acid delivery system as well as possibilities for cross-contamination are minimised.

1.4. PROCEDURE (2/2)

It is thus possible to chemically characterise the trace element content of the carbonate sample by analysis of the spent acid, for example by ICP-OES or ICP-Mass Spectrometer. The CO_2 formed in the reaction of carbonate with acid is transferred into the new trapping and gas cleaning system; this consists of a temperature-controlled trap with associated valves, ultra high vacuum system, pressure readout and a micro- volume inlet system. With the temperature-controlled trap at LN_2 temperature, in a first step CO_2, is quantitatively removed from the reaction region, along with some water, and frozen into the trap. At a temperature of -90 °C the CO_2 is then transferred into the microvolume inlet system, while water is retained in the trap. This step of CO_2 transfer is at the heart of the Kiel performance, because it ensures identical performance with varying sample sizes: Since most precise results require similar pressure in both the 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. For this purpose a precision pressure transducer is mounted at the position of the trap. The data system then decides what portion of the available CO_2 needs to be transferred into the micro-volume inlet system in order to achieve the desired inlet pressure for measurement. If there is too much CO_2, a careful mechanism of consecutive gas expansions between two volumes takes place until the amount of CO_2 is just right to be transferred. This procedure is free of isotopic fractionation and assures maximum precision. It also eliminates any waiting times which otherwise would 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 micro-volume is warmed up and the CO_2 flows from the microvolume inlet into the changeover valve of the connected IRMS's dual inlet system. The *KIEL CARBONATE DEVICE* connects to changeover valve via a dedicated capillary. This design minimises the interaction of CO_2, with metal surfaces, a possible cause of memory and cross contamination. It does not compromise any other inlet system that might be connected to the IRMS. Since all valves are of unparalleled all-metal gold-sealed design and all gas lines are thoroughly pumped, it is guaranteed that there are no memory effects and no contamination.

1.5. EVENTS DURING A SAMPLE MEASUREMENT (1/2)

The following steps explain which action takes place during the measurement of carbonate samples: e.g. measurement started from vial 2/1 (vial 2 / line 1).

VM 1: Vacuum gauge of trap-region

VM 2: Vacuum gauge of the rotary pump

1 As soon as acquisition is user started the Carbonate unit is initialized.

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

3 Trap 1 (T1) and Trap 2 (T2) are heated out.

4 Oven temperature and stability are checked.

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

6 Vial 2/1 is connected to acid housing valve and checked by µ switch.

7 Rotary pump pumps out the vial 2/1 and corresponding lines.

8 Leak check is performed (VM 2 gauge indicates if a leak is present).

9 Vial 2/1 is pumped out by high vacuum if no leak is present.

10 Leak check is performed (VM 1 gauge indicates if a leak is present).

11 T1 is cooled down via liquid nitrogen.

12 As soon as T1 is cooled down acid is injected into the vial.

13 The reaction between acid and sample takes place;
the produced gases CO_2 and H_2O, are trapped by T1.

14 Non condensable gases are pumped out from T1.

15 T1 is heated and CO_2 is released while H_2O is still frozen.

16 CO_2 pressure is measured via VM1. (If the pressure is too high;
CO_2 is pumped out until an acceptable pressure is achieved).

17 Standard-gas pressure is pre-adjusted to the same value as sample pressure.

1.5. EVENTS DURING A SAMPLE MEASUREMENT (2/2)

18 T2 is cooled down to -196°C

19 CO_2 is transferred from T1 to T2.

20 T1 heated and H_2O is pumped out. T2 is heated in the meantime and CO_2 is released to IRMS.

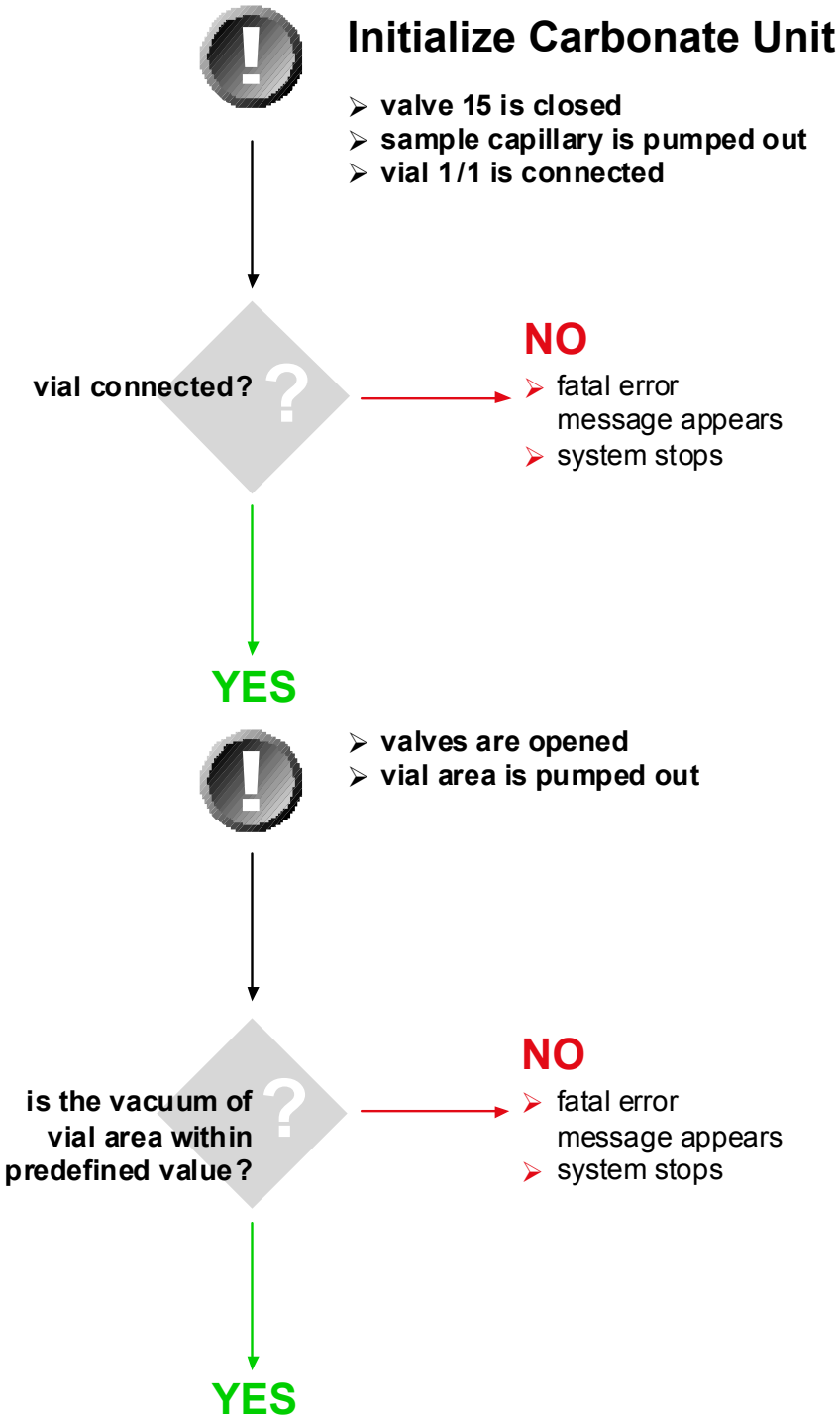
21 Vial 2/1 is removed and magazine moves to pump position.

22 Peak center is performed.

23 Standard-gas pressure is high-end adjusted to the same value as sample pressure. Data acquisition is started and the results are stored and / or printed.

NOTE: *For more information refer to page 1-7 ➢ 1-23 and 6-15 ➢ 6-19*

1.6 EVENTS DURING A SAMPLE MEASUREMENT (1/17)



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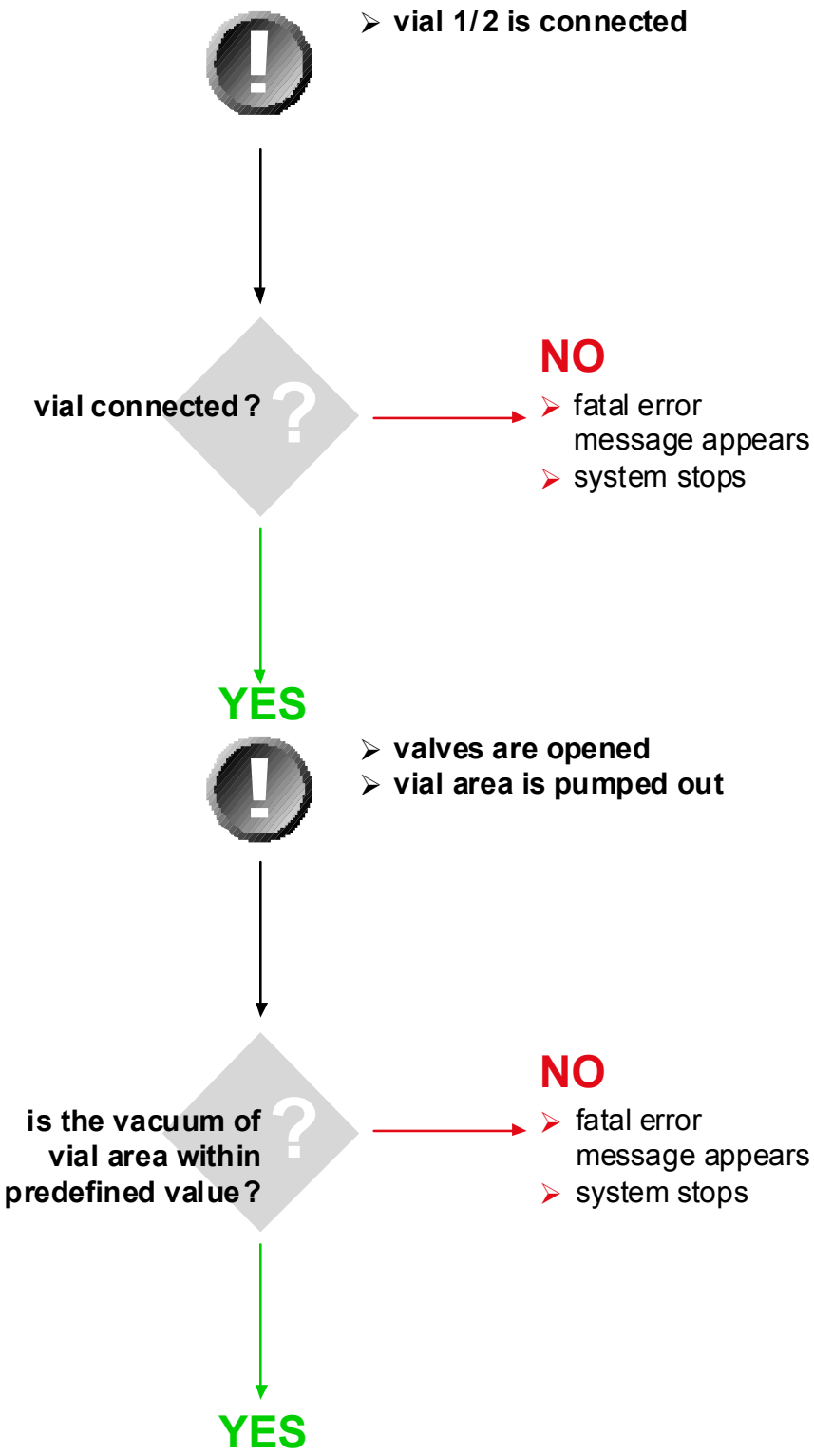
1.6 EVENTS DURING A SAMPLE MEASUREMENT (2/17)



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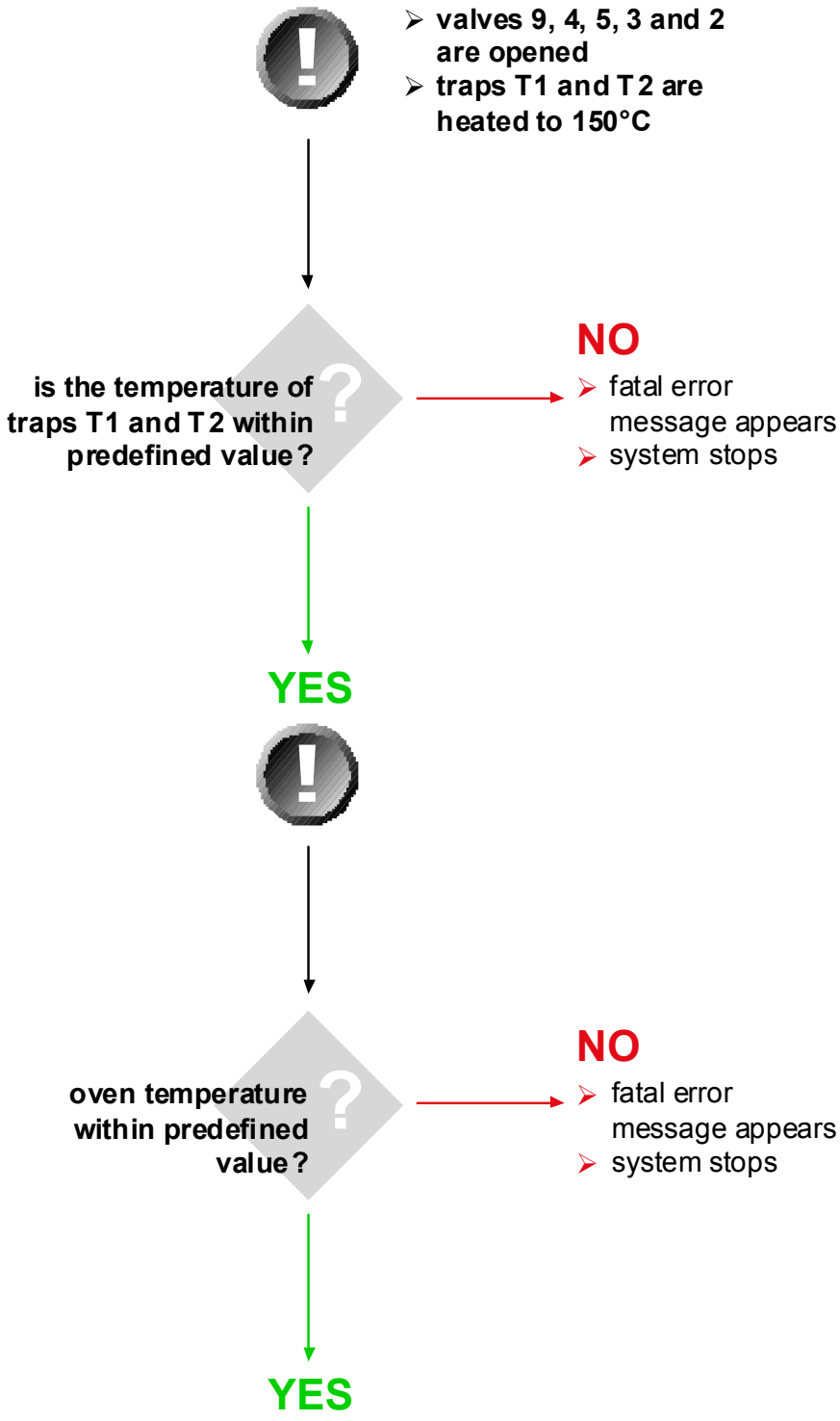
1.6 EVENTS DURING A SAMPLE MEASUREMENT (3/17)



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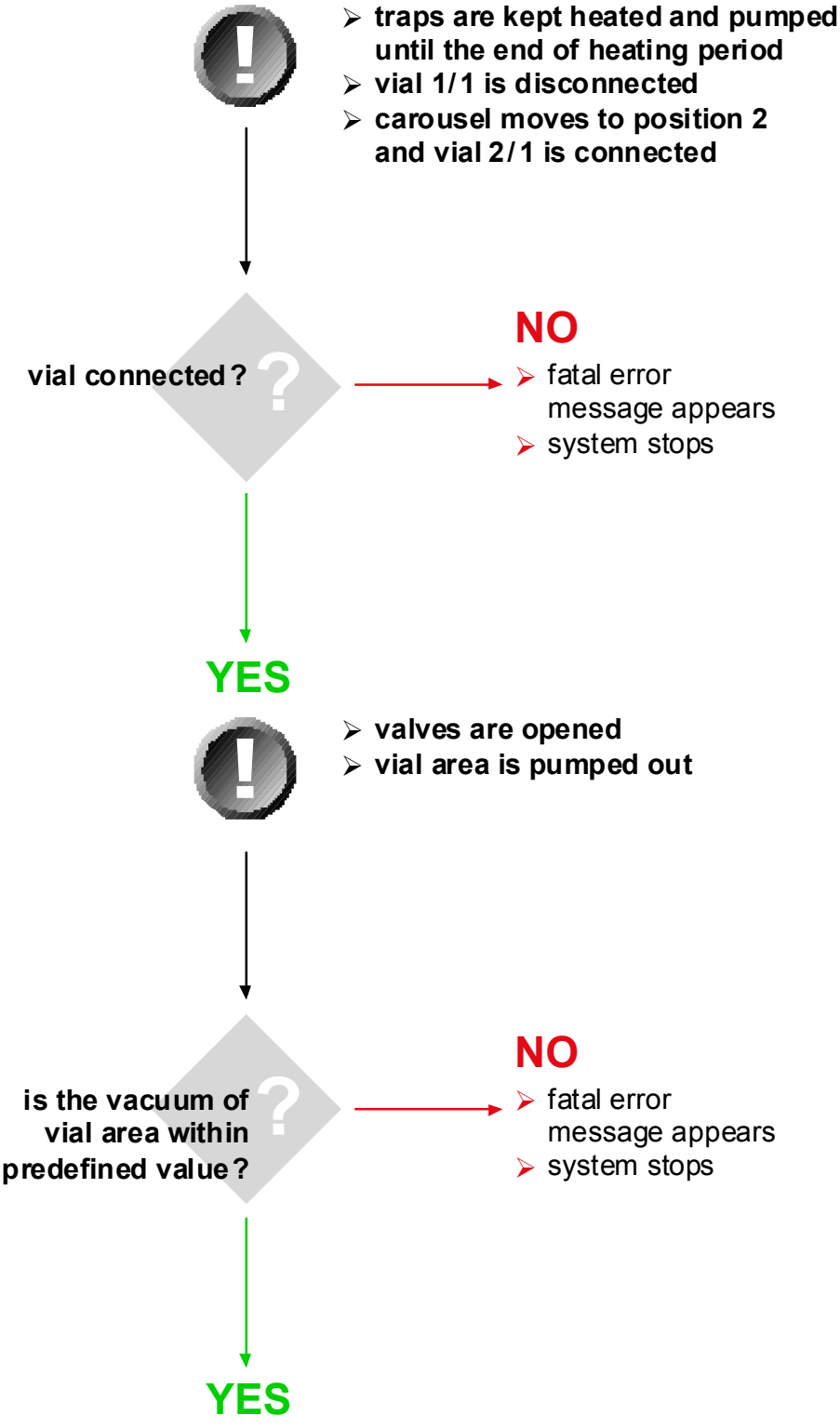
1.6 EVENTS DURING A SAMPLE MEASUREMENT (4/17)



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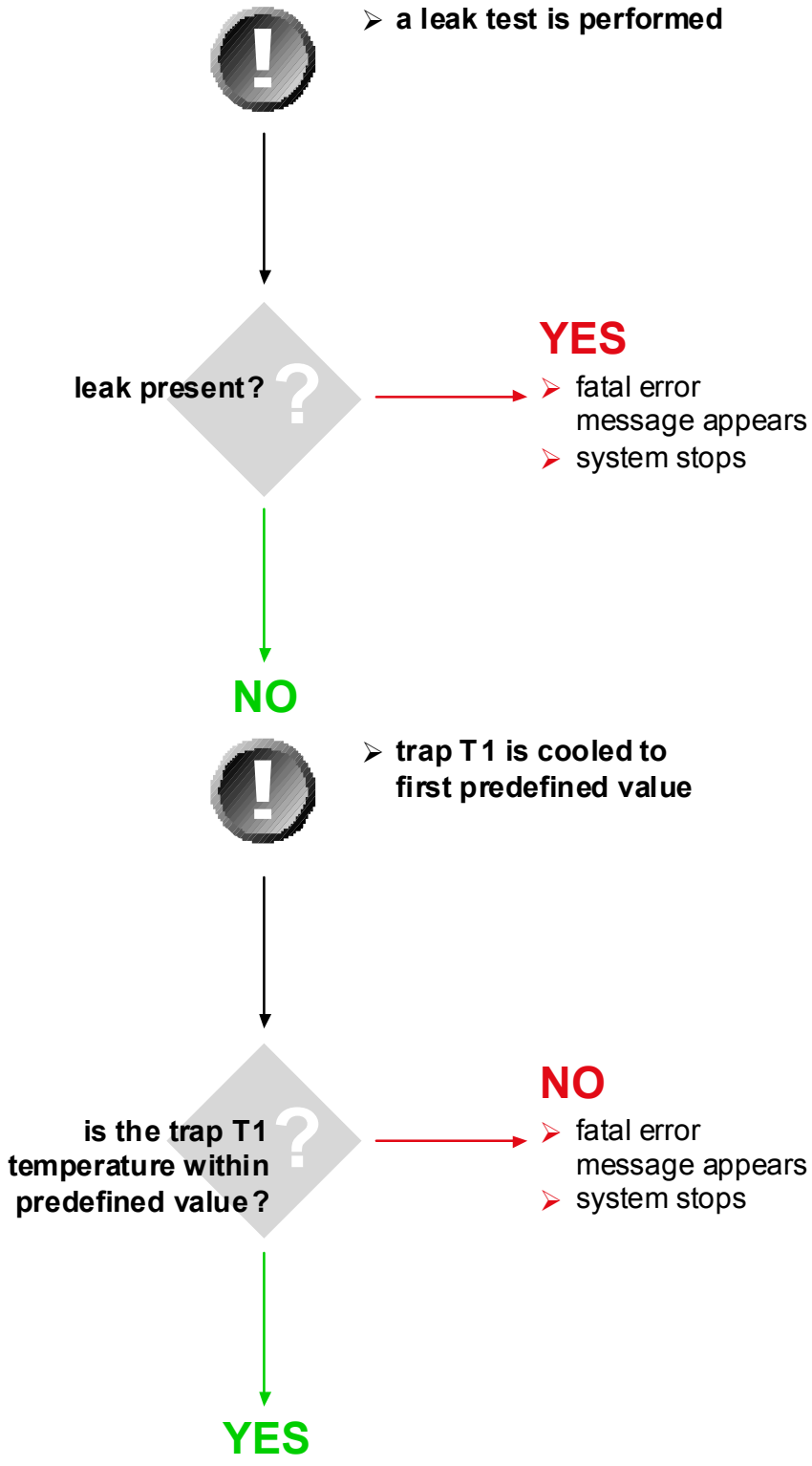

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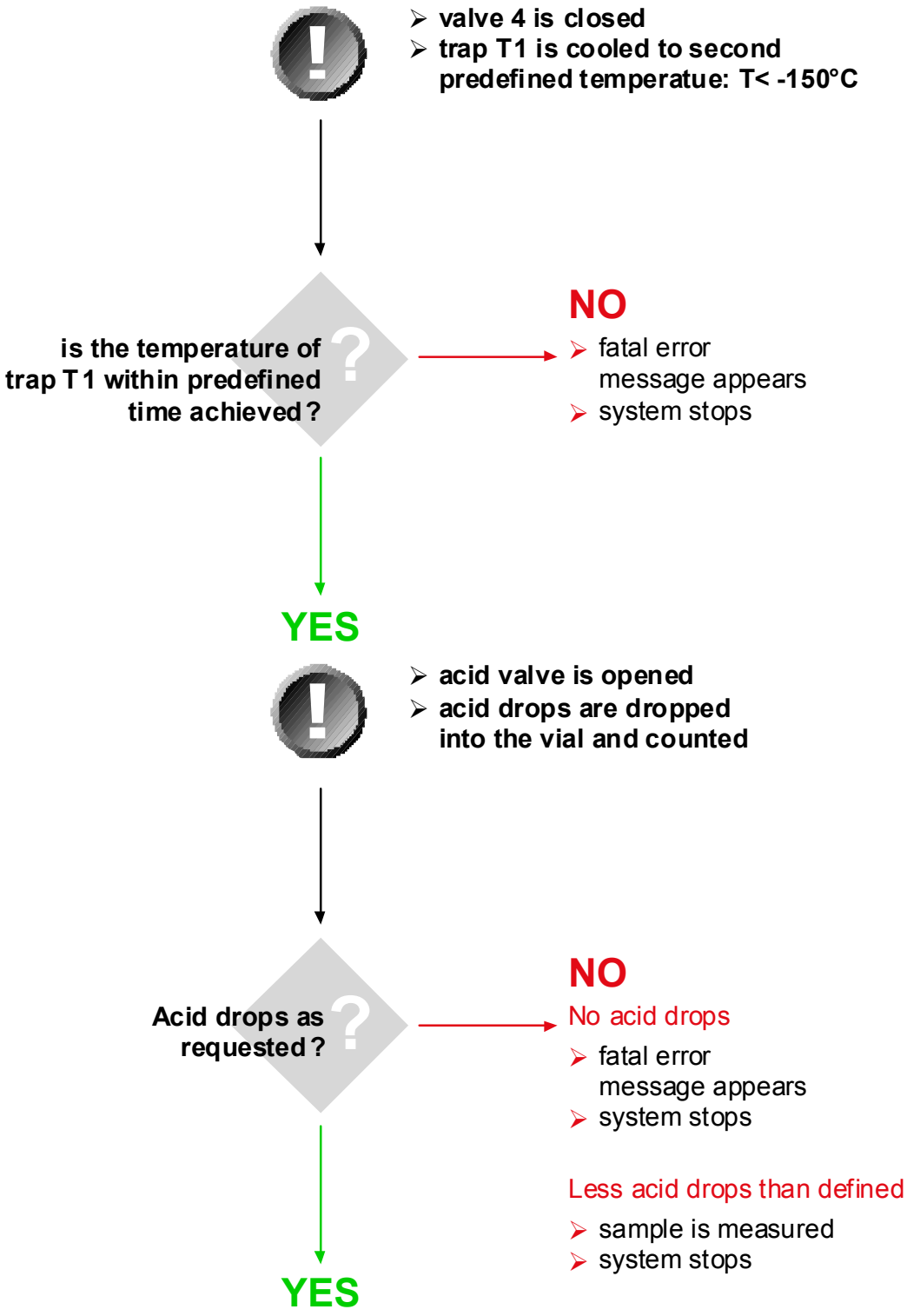

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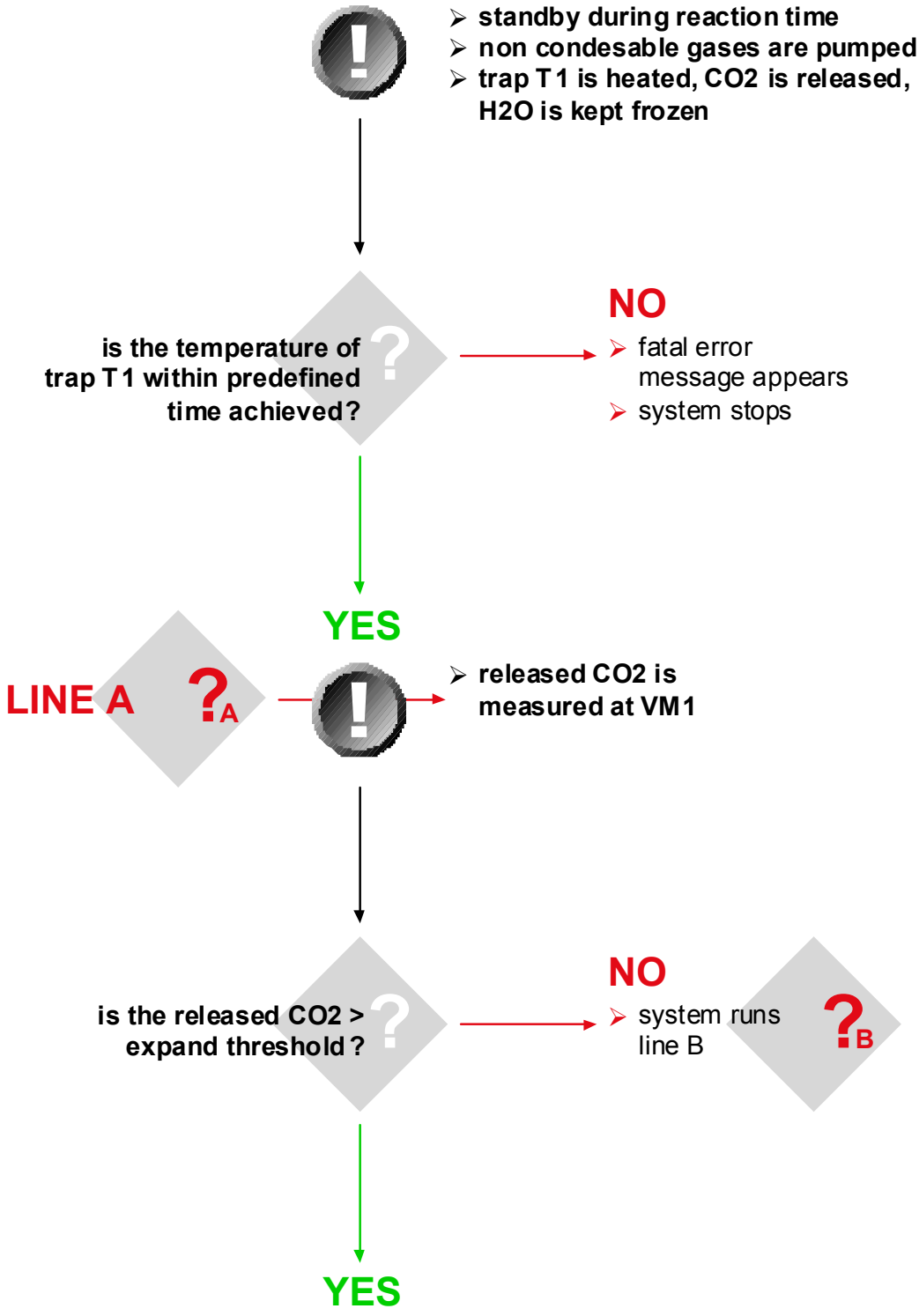
1.6 EVENTS DURING A SAMPLE MEASUREMENT (7/17)



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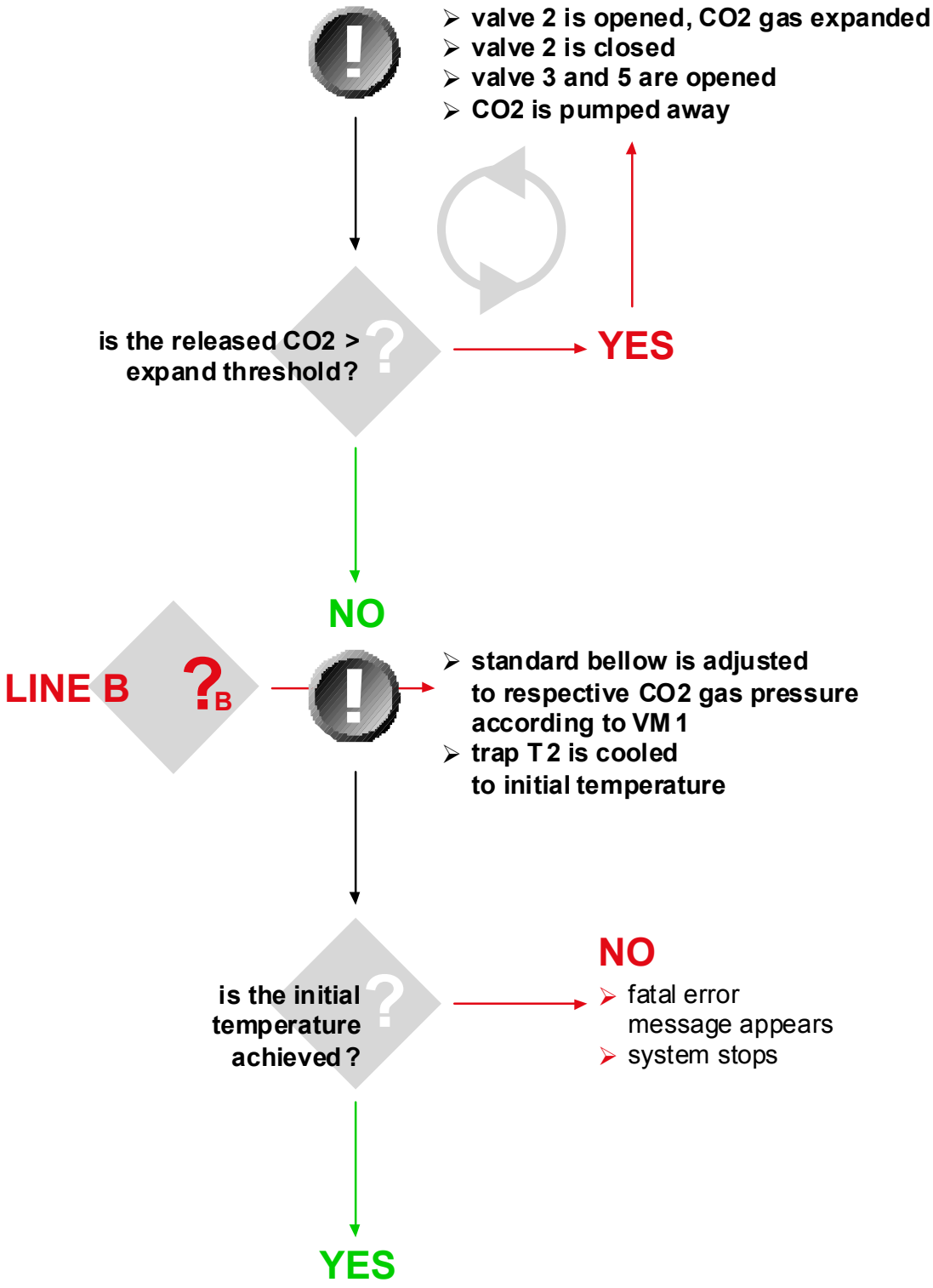
1.6 EVENTS DURING A SAMPLE MEASUREMENT (7/17)



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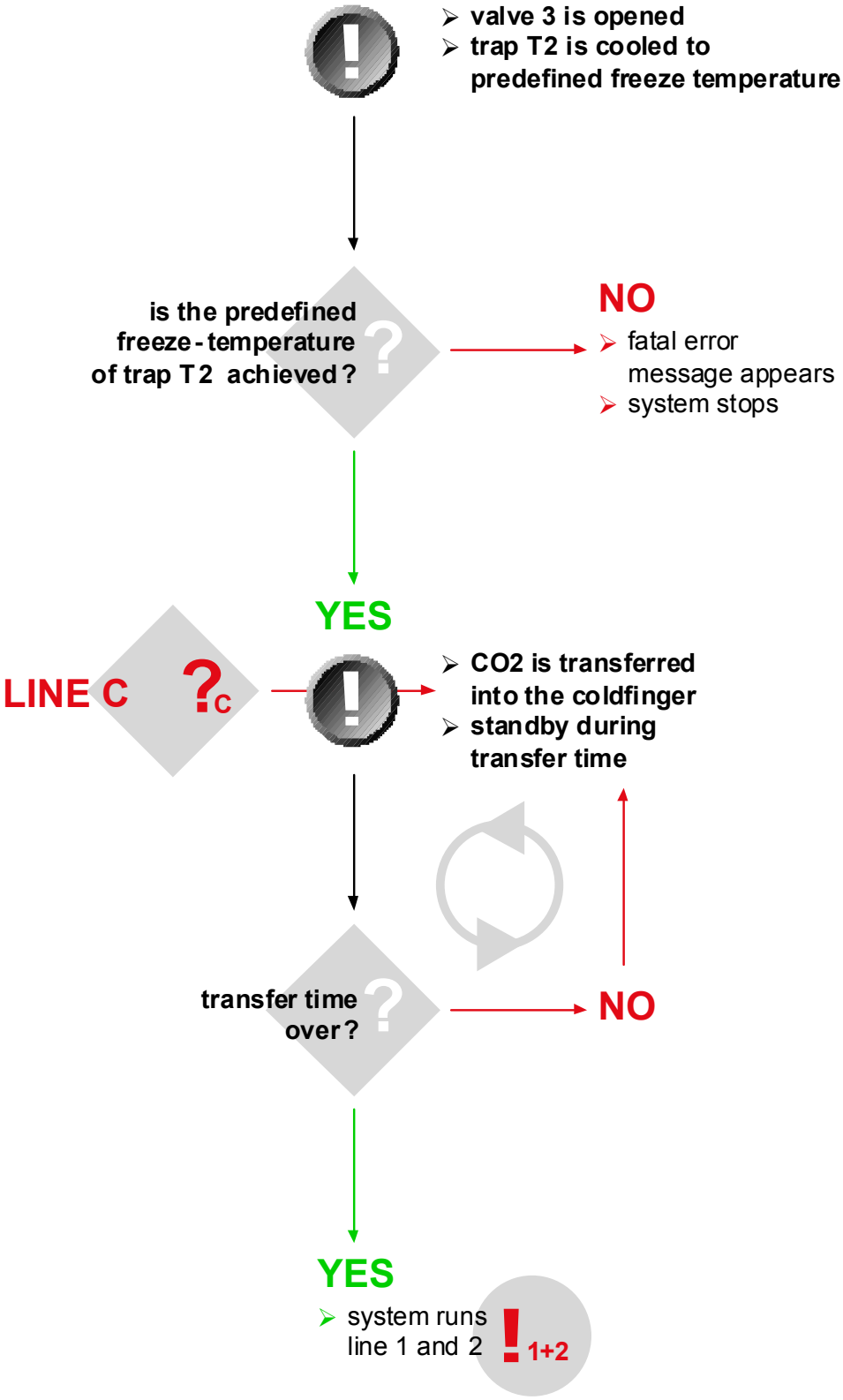
1.6 EVENTS DURING A SAMPLE MEASUREMENT (8/17)



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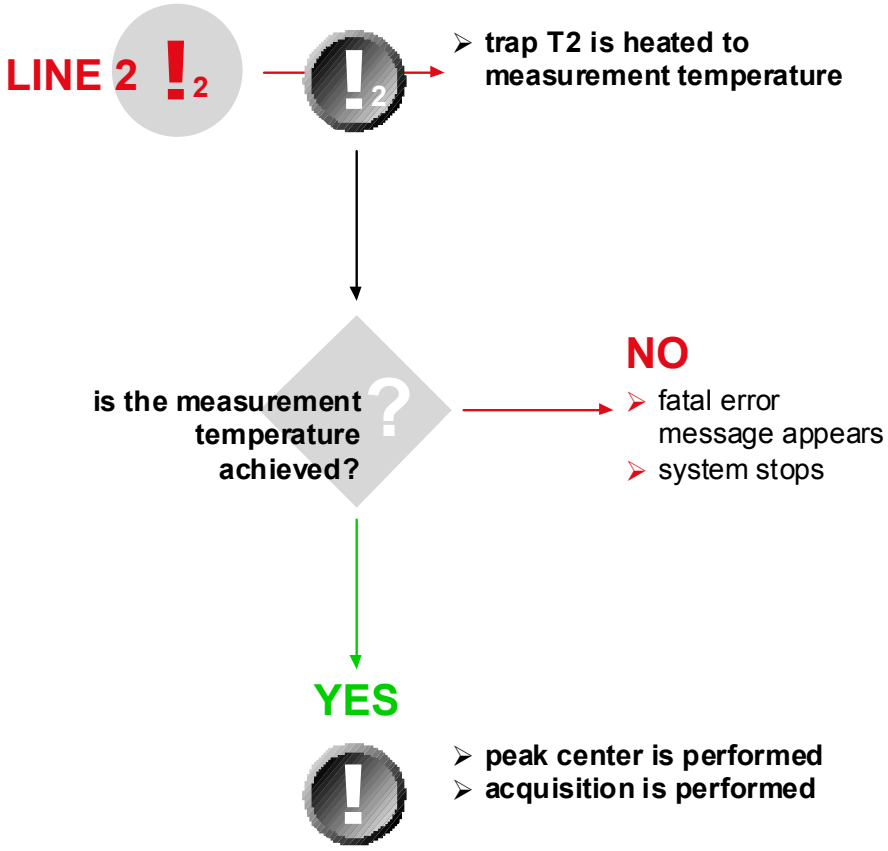
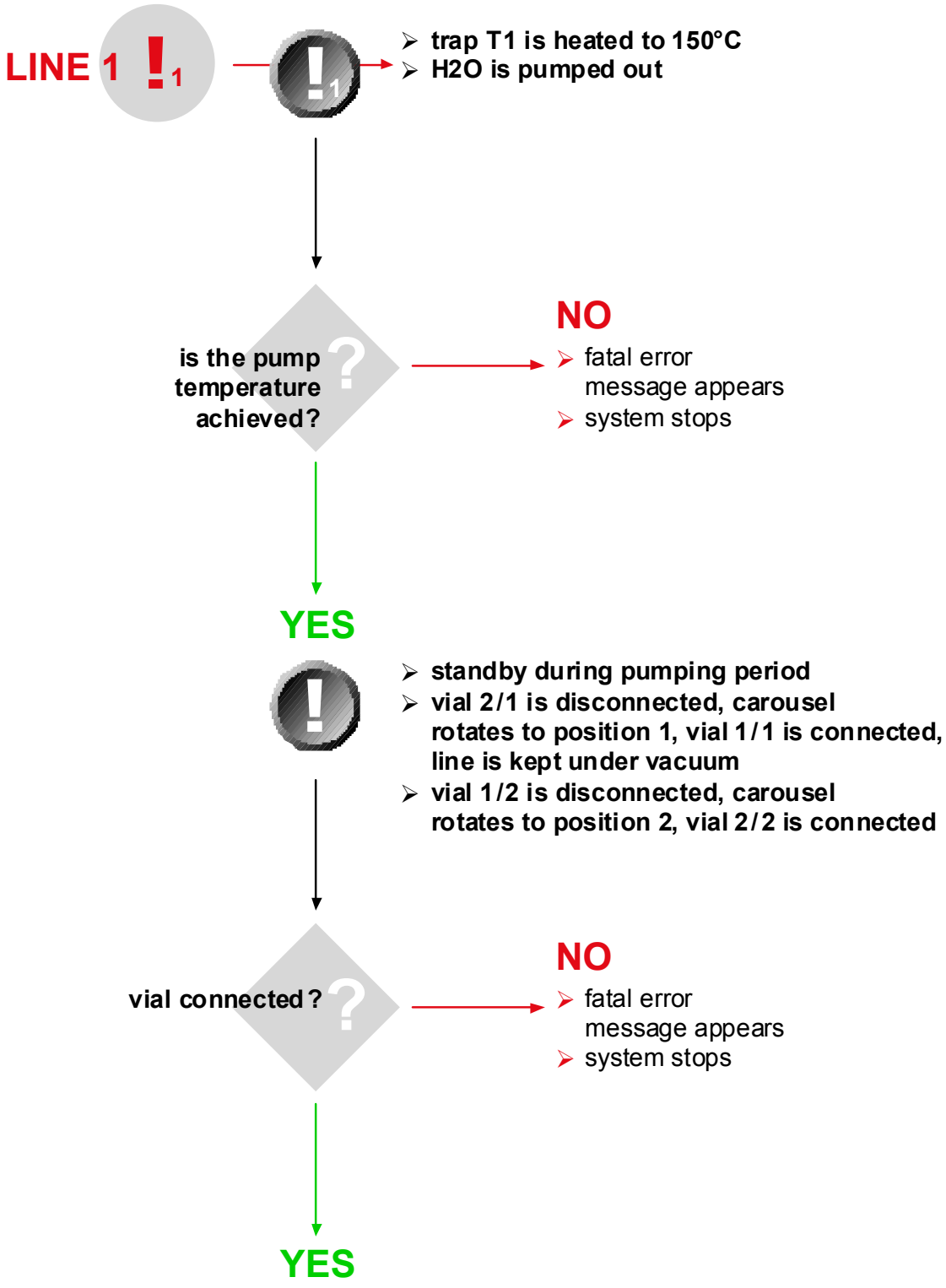
1.6 EVENTS DURING A SAMPLE MEASUREMENT (9/17)



The following action take place during the acquisition.
(See pages 1 - 17 ➢ 1 -23).

1.6 EVENTS DURING A SAMPLE MEASUREMENT (11/17)



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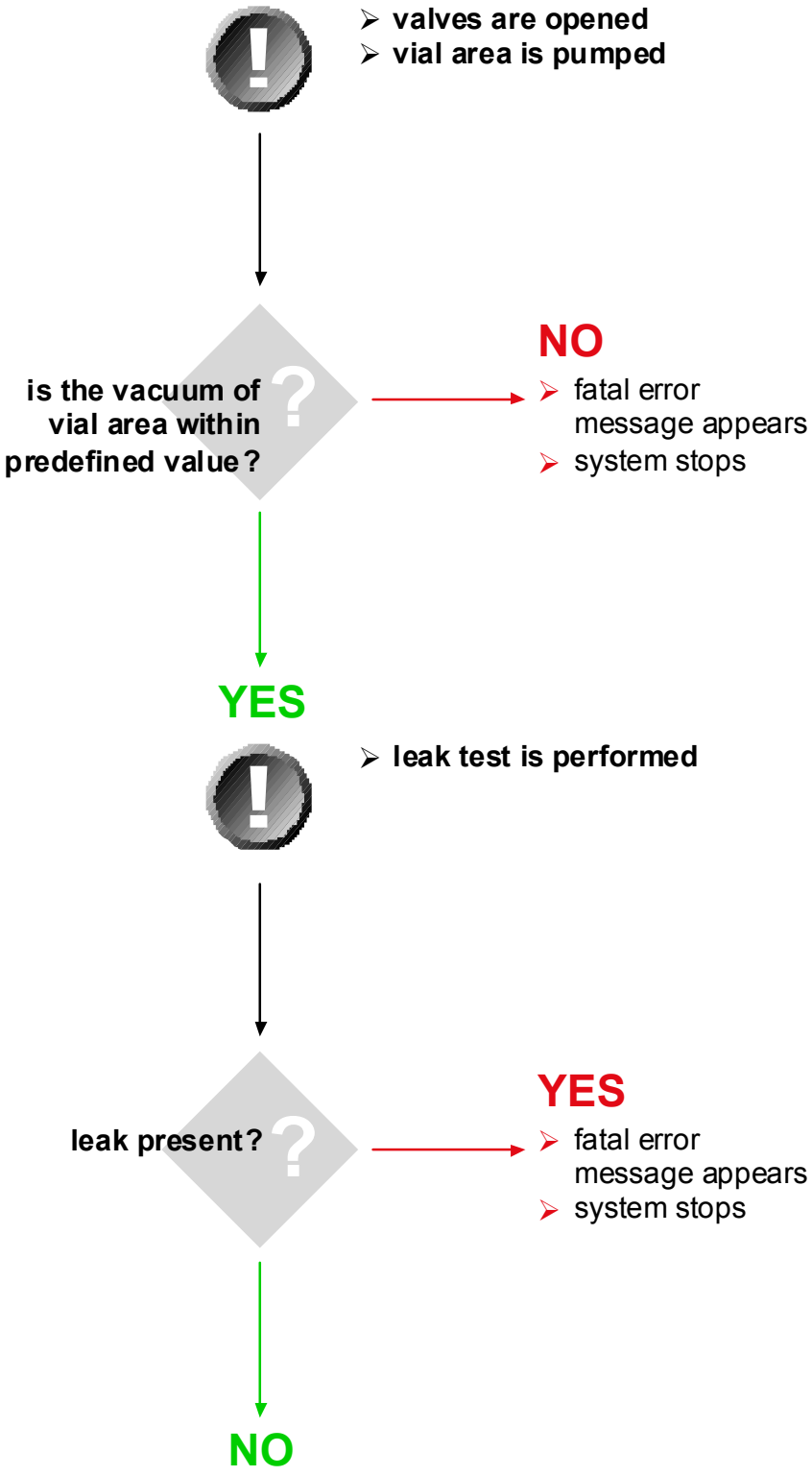

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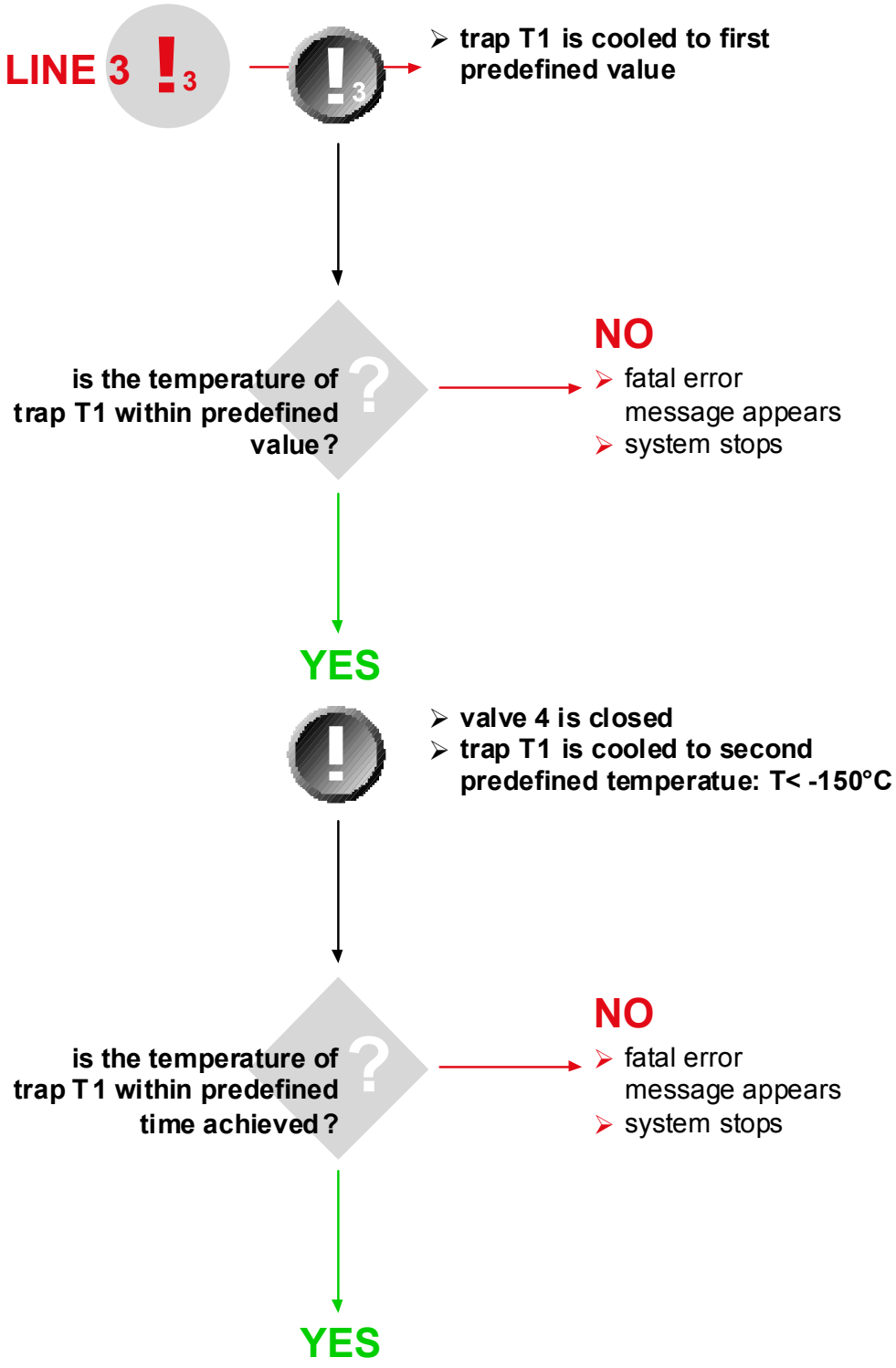
1.6 EVENTS DURING A SAMPLE MEASUREMENT (13/17)



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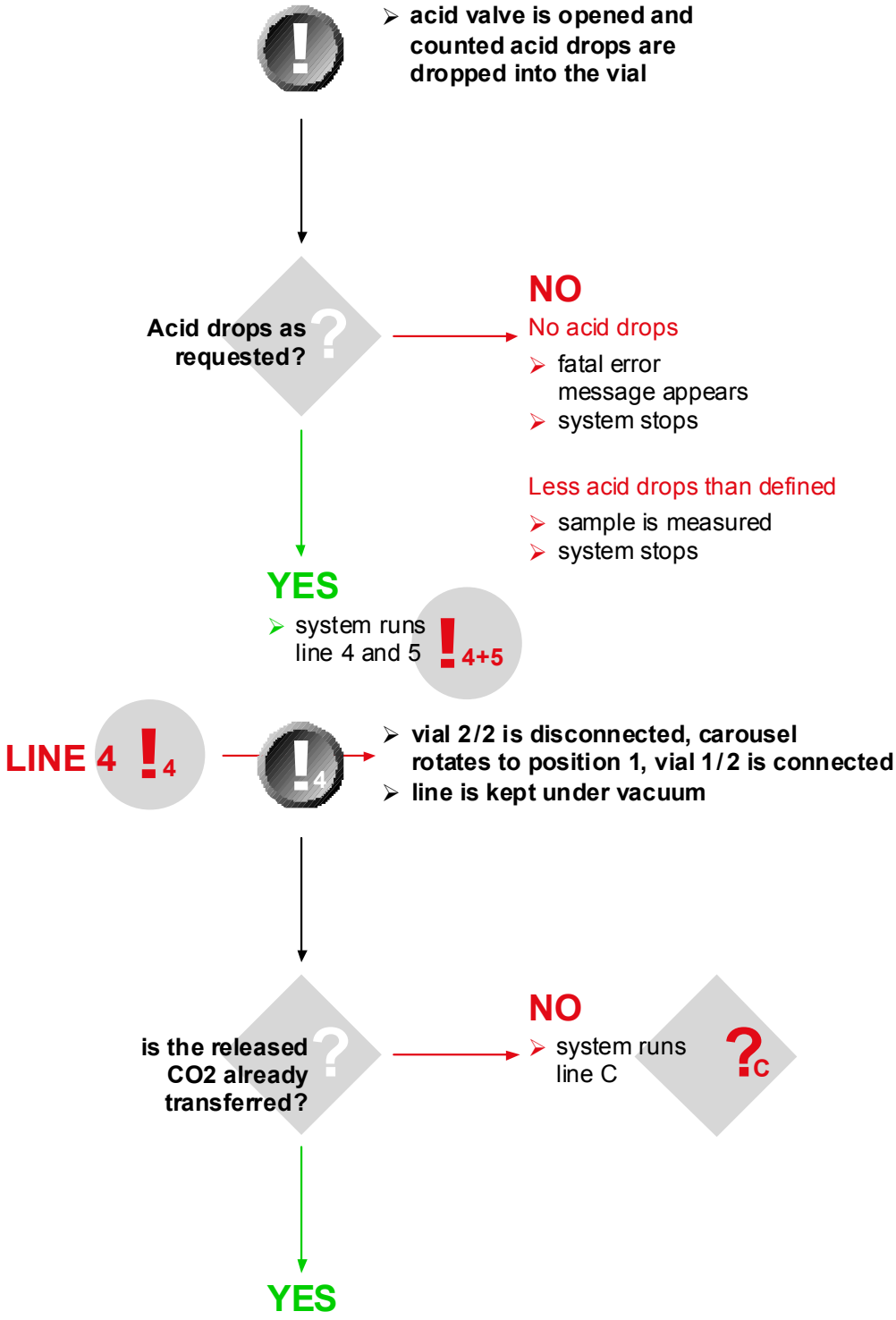
1.6 EVENTS DURING A SAMPLE MEASUREMENT (14/17)



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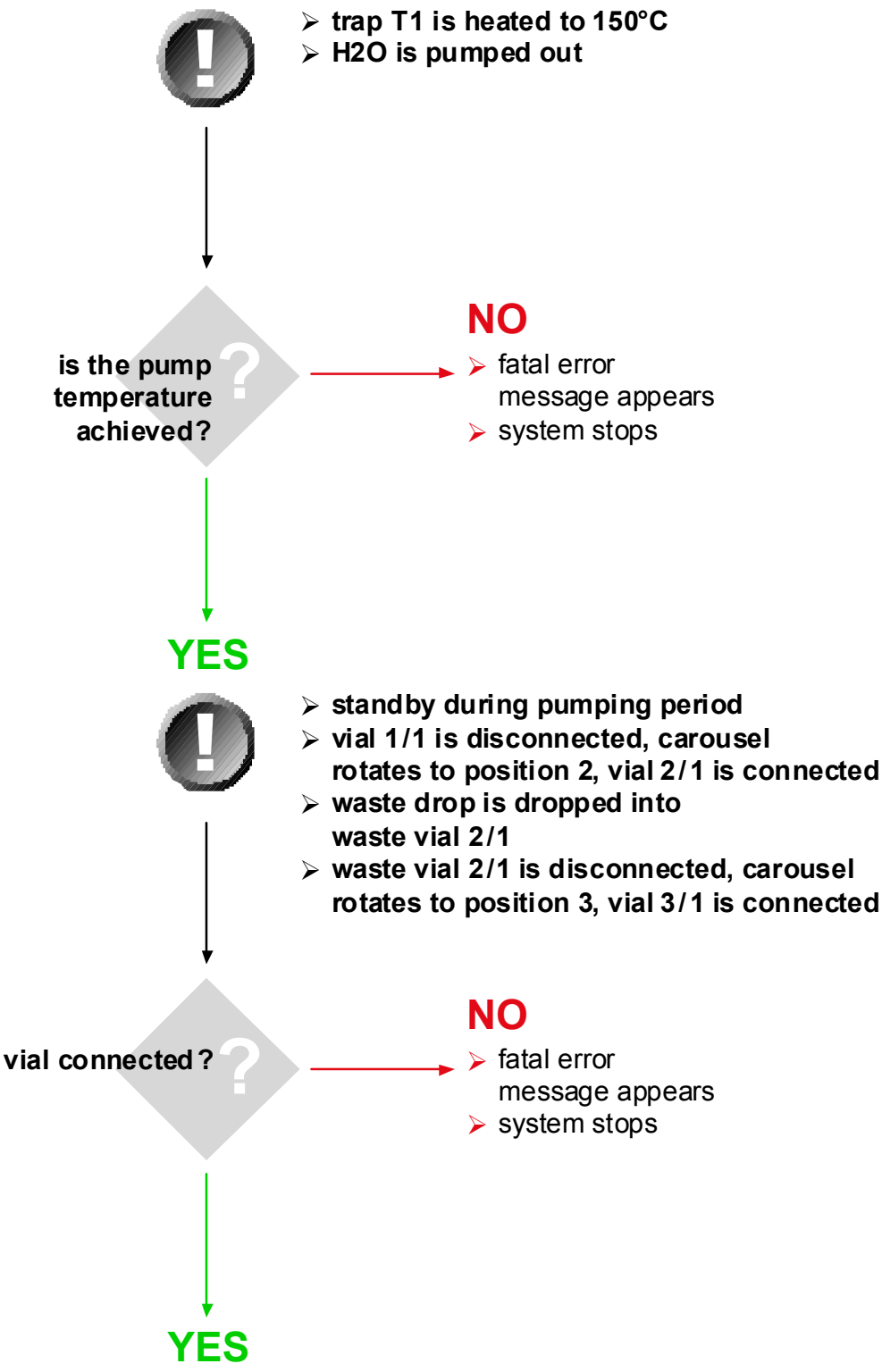
1.6 EVENTS DURING A SAMPLE MEASUREMENT (15/17)



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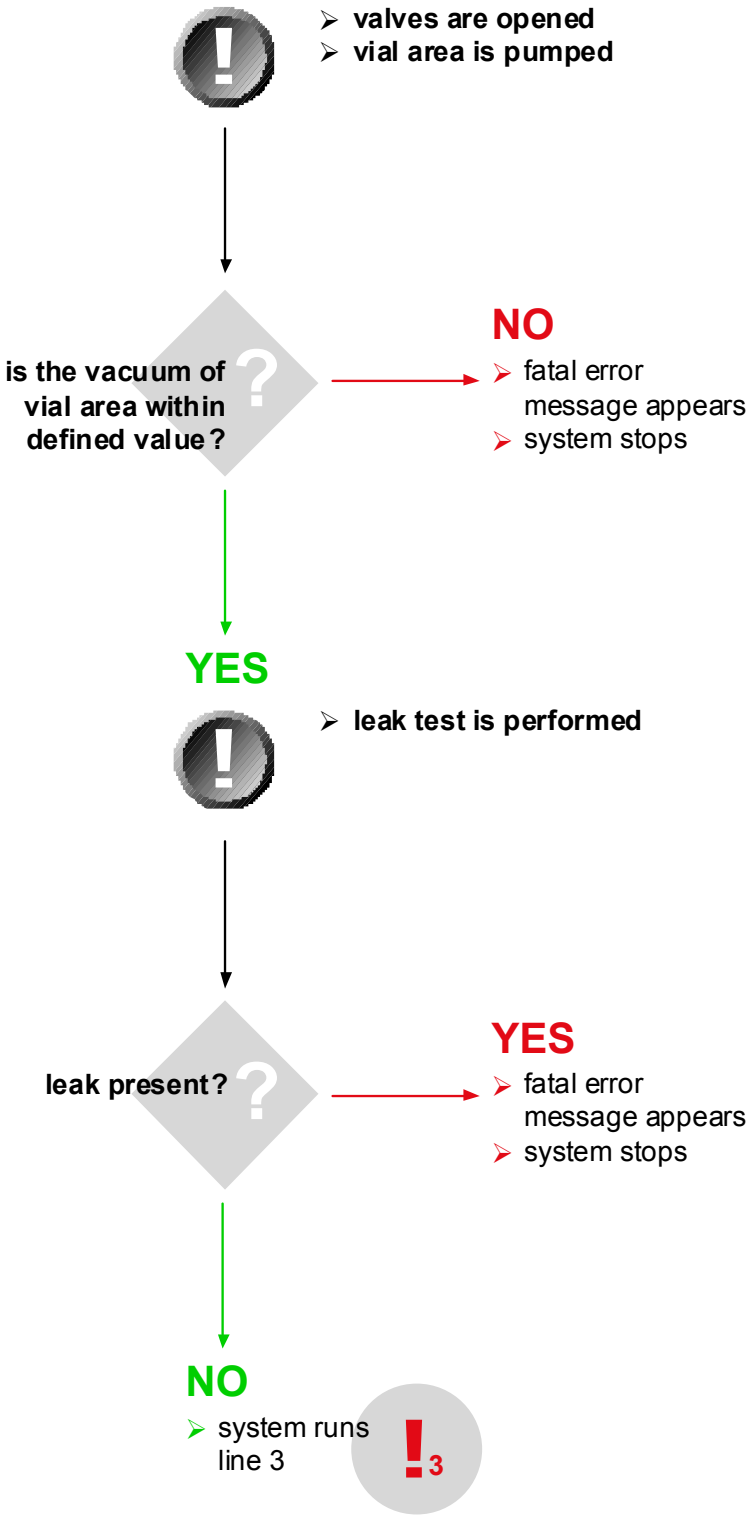

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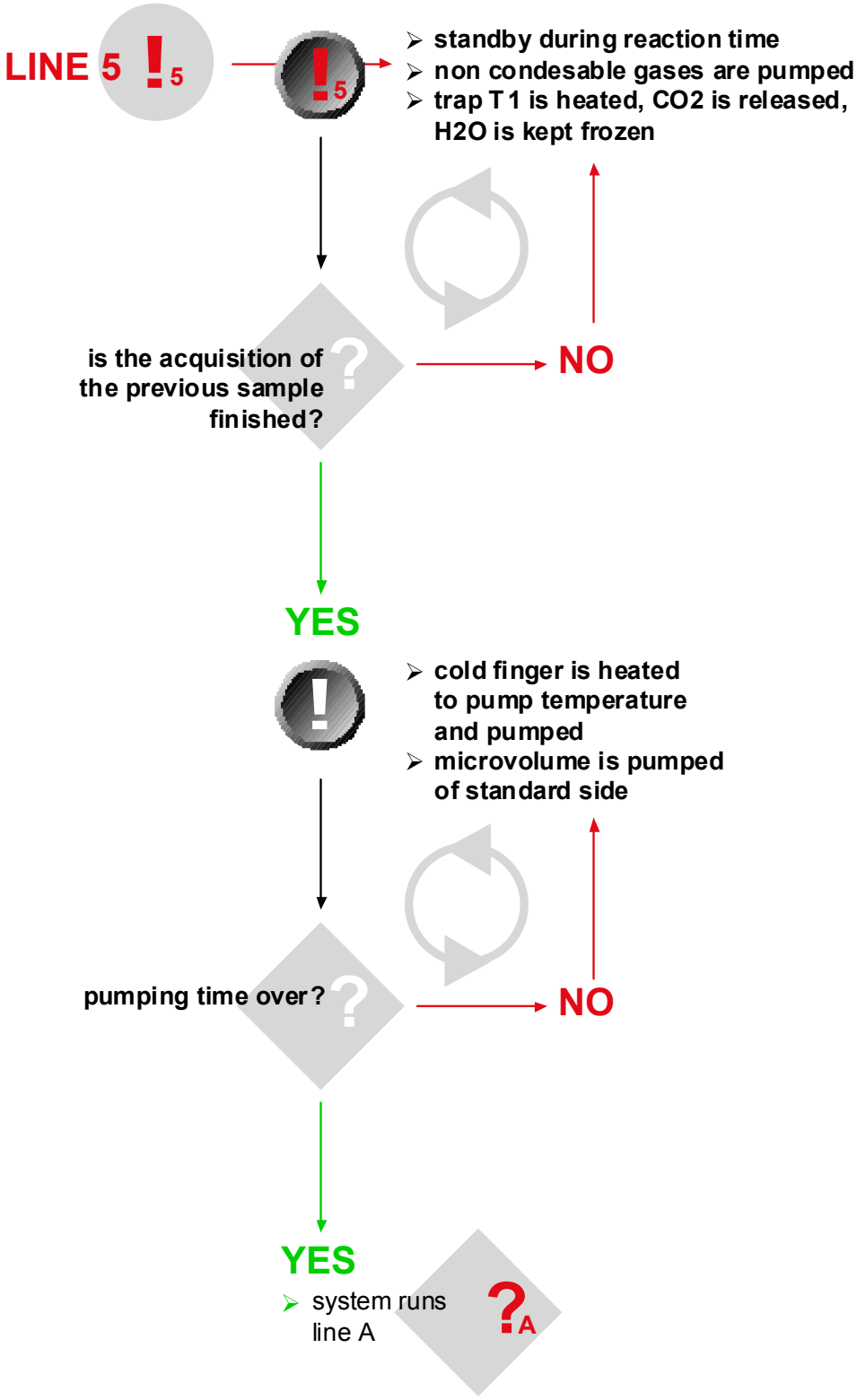
1.6 EVENTS DURING A SAMPLE MEASUREMENT (17/17)



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KIEL CARBONATE DEVICE

SOFTWARE

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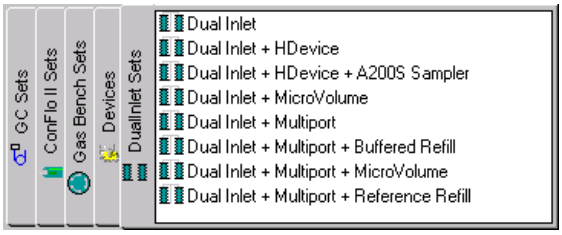
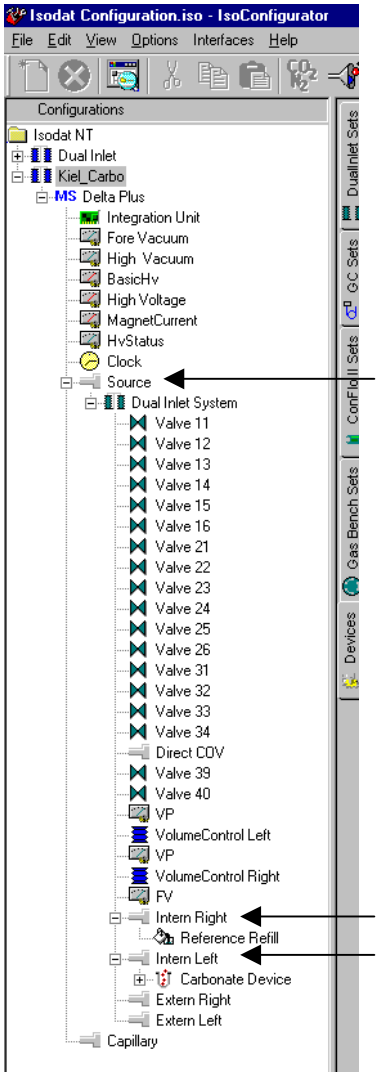
2.1. HOW TO INSTALL THE SOFTWARE FOR CARBONATE DEVICE OPERATION

Before operating the *KIEL CARBONATE DEVICE,* a configuration containing the dual inlet, *KIEL CARBONATE DEVICE* and optionally a reference refill needs to be created in the configurator. Generally the *KIEL CARBONATE DEVICE* configuration is preinstalled and available.

- For installation of IEEE board (GPIB-PCI, PCIIA) refer to Delta^{Plus} XP or MAT 253 manual
- To create a configuration proceed as follows:

  - Add a new configuration with the "Add Configuration" button
  - Give it a name, e.g. "Kiel Carbo"





- Select Dual Inlet and drag it to the source icon in the configuration.
- Open the complete tree structure of the Dual Inlet system to check for the attached hardware. (valves, volume control left / right).
- Select devices
  - Take Reference Refill and drag it into to the intern right icon.
  - Take Carbonate Device and drag it into the intern left icon.

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KIEL CARBONATE DEVICE

HARDWARE

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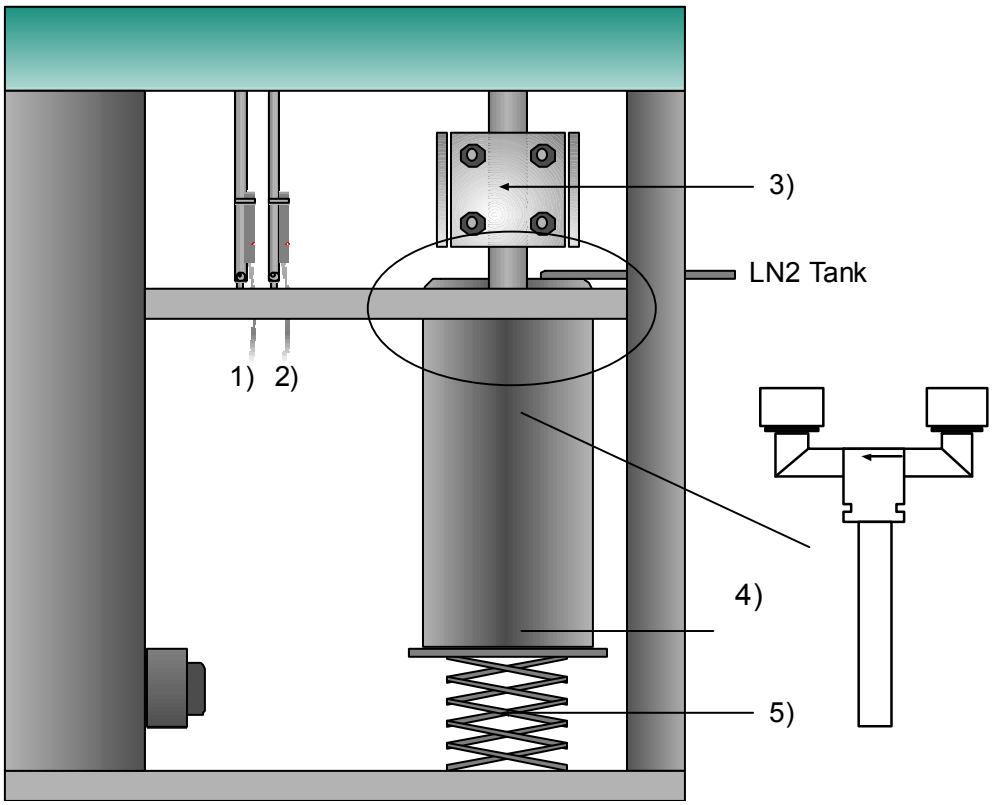
3.1 HARDWARE-LAYOUT LOWER SECTION (1/4)

Fig: 3.1 Front panel (open)



1 Piston for line 1 (lights are on when both pistons down)

2 Piston for line 2

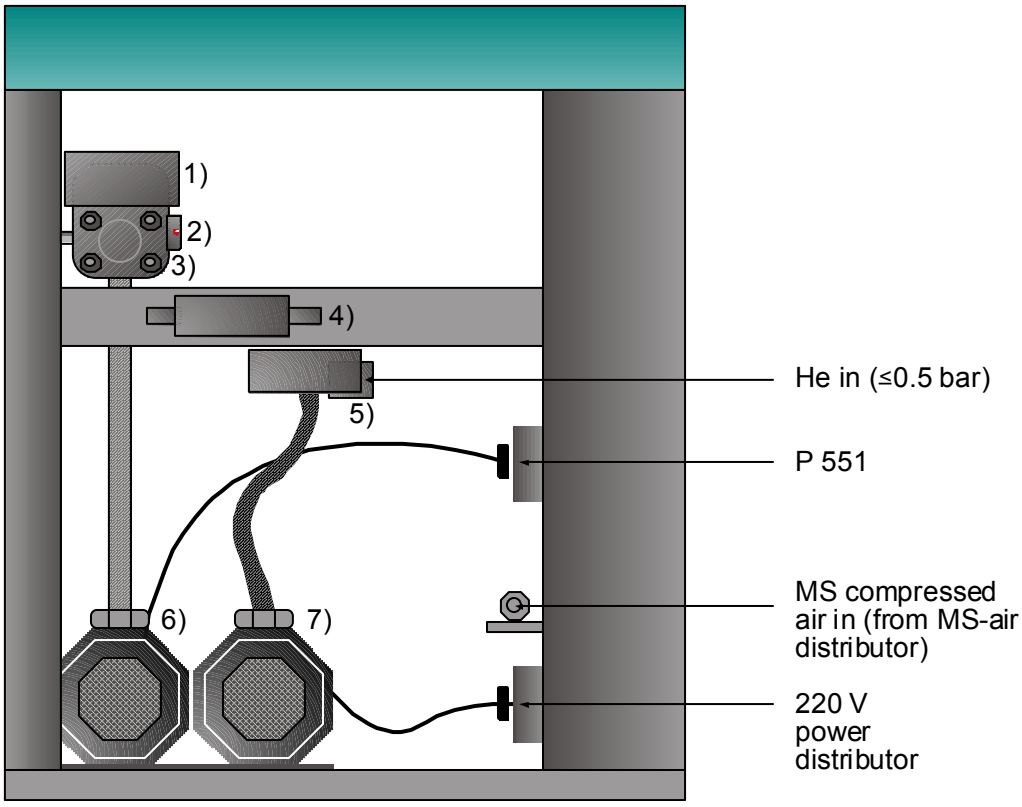
3 Pneumatic valves

4 Dewar for the auto-cool unit

5 Jack

3.2 HARDWARE LAYOUT LOWER SECTION (2/4)

Fig: 3.2 Rear panel (open):



1 Fan
2 *Venting valve
3 Turbo molecular pump
4 **Safety circuit valve
5 Valve combination
(v161 for valve 8 (aux. gas);
v160 for valve 7 (forevacuum))
6 Oil rotary pump for turbo pump
7 Oil rotary pump

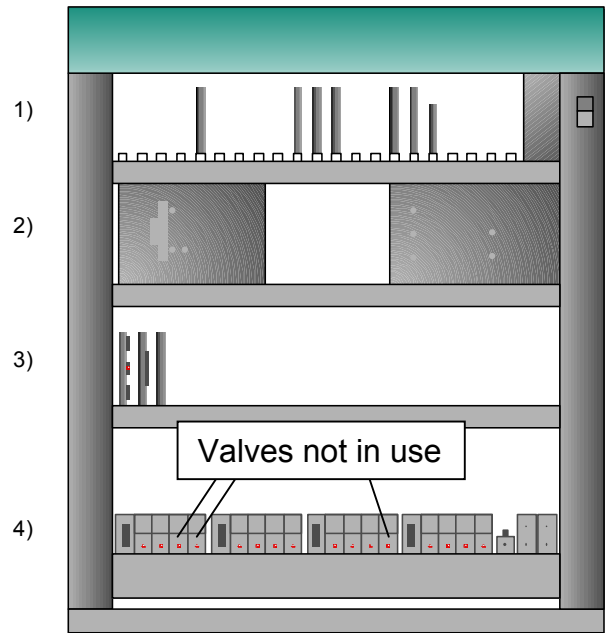
NOTE:

**** The venting valve is closed when the pump is running. The pump controller keeps the valve closed. If the pump controller is switched off the turbo pump works as a generator and keeps the valve closed until the pump speed decreases to < 50% of rotation / hour.***

*****The safety circuit closes the acid valves #10 and #20 after 5 minutes (factory set) if the acid counter or electronic for acid counter fails. To by-pass the safety circuit acid valves plug together the left and right plug.***

3.3 HARDWARE-LAYOUT LOWER SECTION (3/4)

Fig: 3.3 Left panel (open):



1) Electronic boards from left to right	2) From left to right	3) From left to right	4) Lights fomleft to right
Liquid nitrogen refill unit	Power supply (5V ± 20V)	Pump electronic	L1 piston left
(Bg. Nachfülleinrichtung)	(Netzteil)	Power supply 33V	L2 piston right
Adresscard	Power supply (E1 + 24V)	Safety pump	
Control unit trap 2	(Netzteil E1)	(Pumpensicherung K3)	valve 22
Control unit trap 1			valve 23
Driver →	S3 S4 S5 S6	S7	valve 12
MUX 16 carbonate			valve 13
(MUX 16 Karbonat)			
IEC BUS interface			valve 1
			valve 2
			valve 4
	Adress setting		valve 9
			valve 6
Approximate switch			valve 3
(Näherungsschalter)	S1	S2	valve 5

*Computer cannot move the magazine. Pull out board and put it back again.

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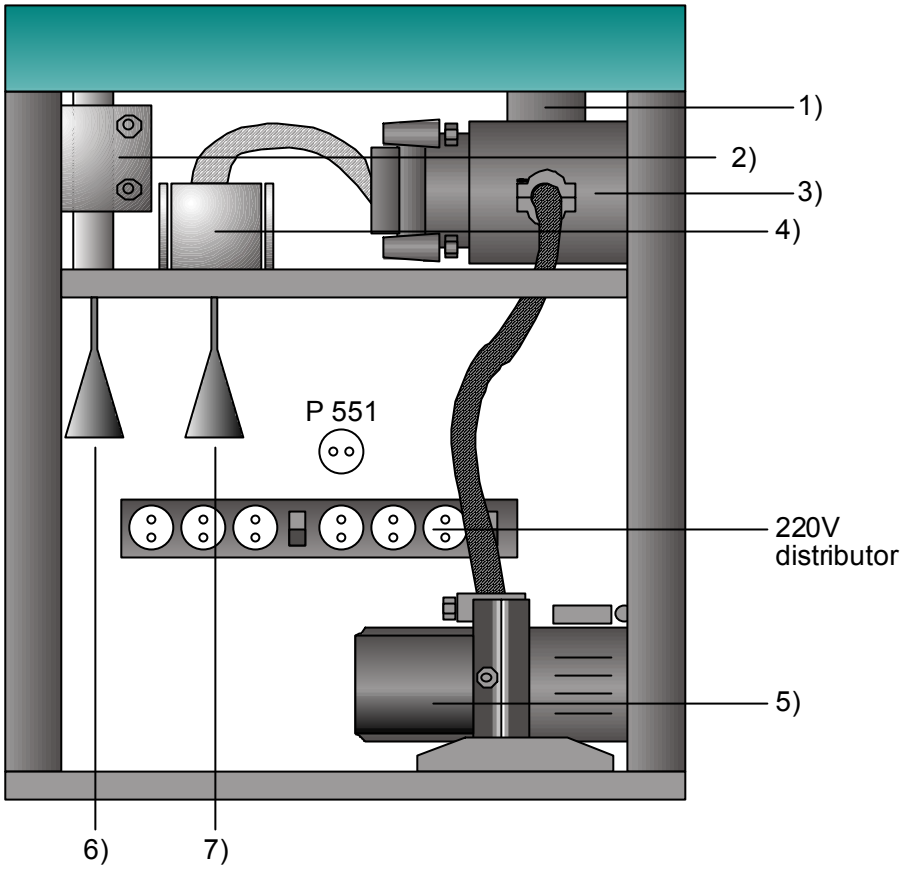
3.4 HARDWARE-LAYOUT LOWER SECTION (4/4)

Fig: 3.4 Right panel (open):



1 Fan

2 Valves for trap 1

3 Turbo molecular pump

4 Valves for trap 2

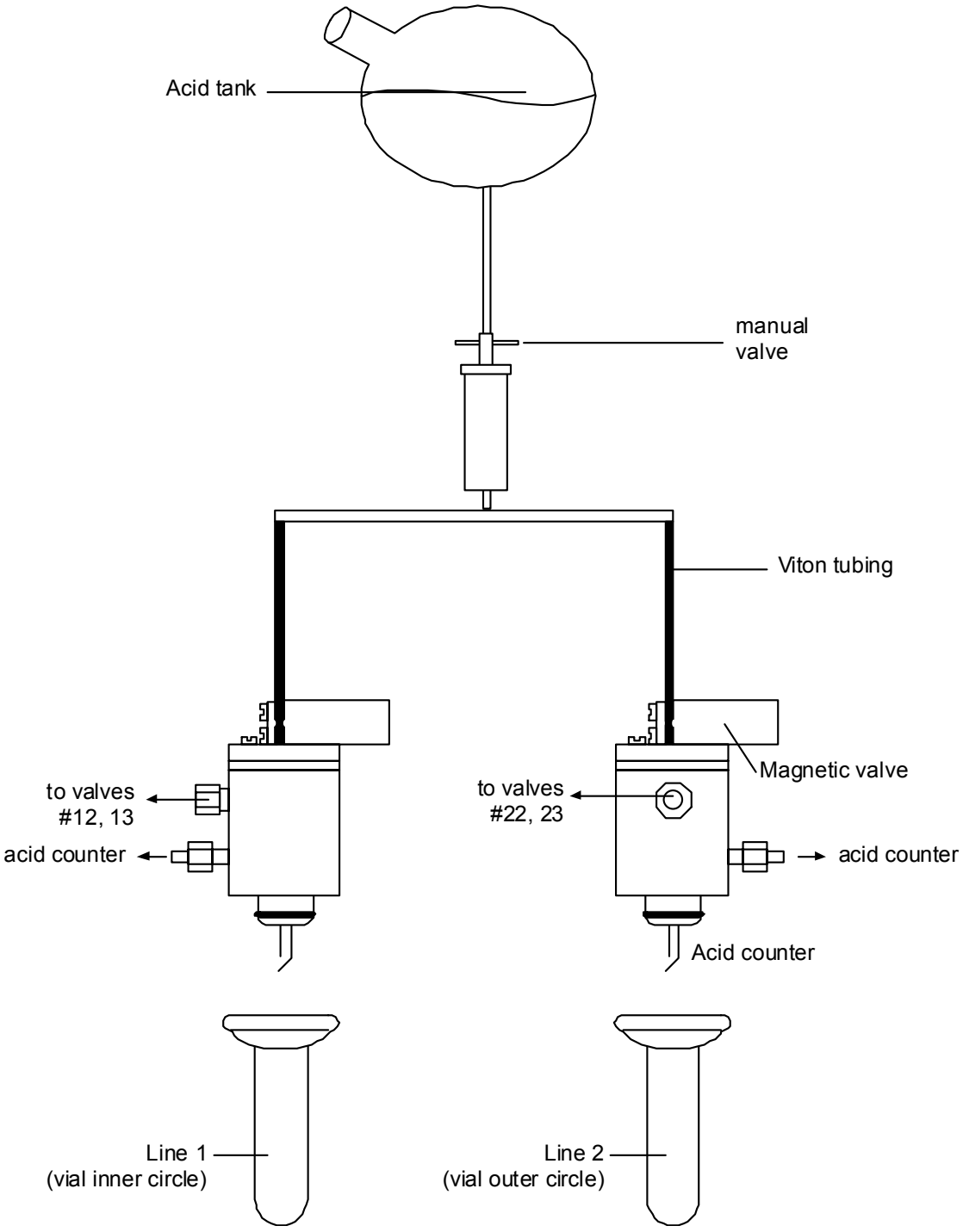
5 Rotary pump

6 Auto-cool unit for trap 1

7 Auto-cool unit for trap 2

3.5 ACID FLOW

Fig: 3.5 Acid flow schematic



3.6 INSTALLATION OF CARBONATE DEVICE TO IRMS (1/3)

- Remove the side panels of the Carbonate Device.
- Connect the compressed air of the Carbonate Device to the IRMS-distributor.
- Connect the aux. gas (e.g. He or N_2) on valve V161 (set the aux. gas ≤ 0.5 bar).
- Connect the green / yellow, earth wire to the chassis of IRMS.
- Connect the IEEE cable to the IRMS.
- Connect the vacuum tube of the turbo molecular pump to the fore vacuum pump and plug the fore vacuum pump into socket 551.
  (See Hardware-Layout lower section (rear panel)).
- Connect the vacuum tube of the other fore vacuum pump to valve combination V161 and V160 and plug it into J2. (see Hardware Layout lower section; rear panel)
- Connect the reference-refill-tank capillary at the standard side of the IRMS (V #22).

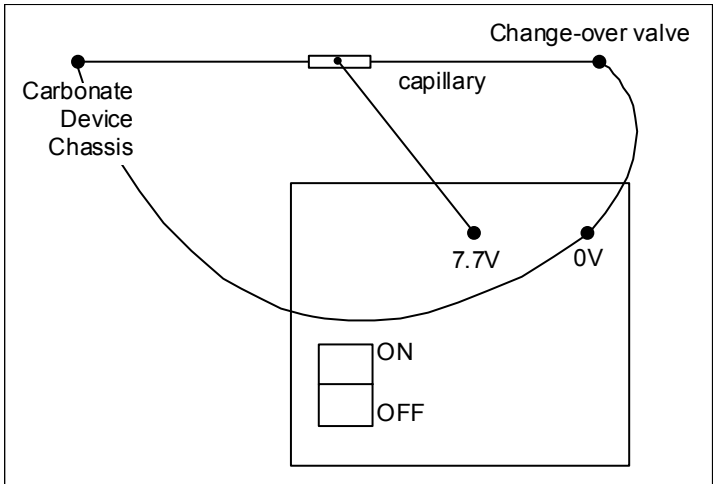
Warning: ***Before performing step 9, open instrument control and close the change over valves (#15, 31, 32, 33).***

- Connect the stainless-steel capillary from the valves #3 and 4 (micro volume of carbonate device) to the change-over valve of the IRMS by pulling it through the hole in the side panel of the MS.
- Plug in the main power-supply cable.
- Switch on both switches at Carbonate Device main distributor. Make sure by touching the fore vacuum pumps that they are operating. After approx. 1-3 min the green light of pump controller
  (see Hardware-Layout lower section; left panel, pos. 3) illuminates.
- Install Carbonate Device Software if necessary.
- Select the Carbonate Device Configuration and check that the software can operate the valves.

3.6 INSTALLATION OF CARBONATE DEVICE TO IRMS (2/3)

- Close valve 6 and open valve 9.
- Set T1 and T2 to 150 °C and keep valves 1,2, 3, 4, 5 and 9 open. Set the oven temperature to 70 °C.
- Prepare phosphoric acid and transfer it to the acid glass of *KIEL CARBONATE DEVICE*. Place it inside the oven.
- Connect the two black Viton tubes of acid valves to each of the two acid glass ports.
- Take a magazine and place vials at positions 1/1 and 2/1. Put the magazine inside the oven and perform the function Load Magazine.Take Capillary Heating Transformer (a device for the IRMS dual inlet) and connect the heating wires as shown below.
- Switch the heater on and keep pumping for 3-4 hours. Leave the valves #1, 2, 3, 4, 5 and 9 open during this action.

Fig: 3.6 Heating transformer



3.6 INSTALLATION OF CARBONATE DEVICE TO IRMS (3/3)

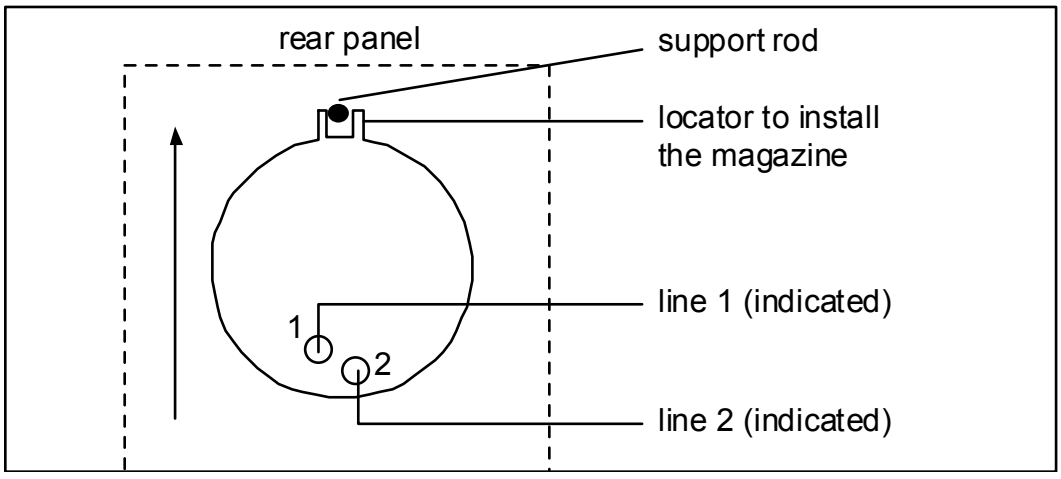
- Perform the vial test.
- Wait until the acid warms up to 70 °C. Open the valve of the acid glass.
- Open valves #10 and 20 (while the two vials are connected and the valves #13, 23 and 7 open).
- Watch inside the vials. The acid should drop slowly into the vials. (It may take some time until the first drop of acid comes because acid must fill the Teflon tube first).

NOTE: ***Procedure how to match the sample capillary to the standard capillary is written in chapter 05.***

3.7 HOW TO INSTALL THE MAGAZINE

The whole magazine 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:

Fig: 3.7 Installation of the magazine (schematic)



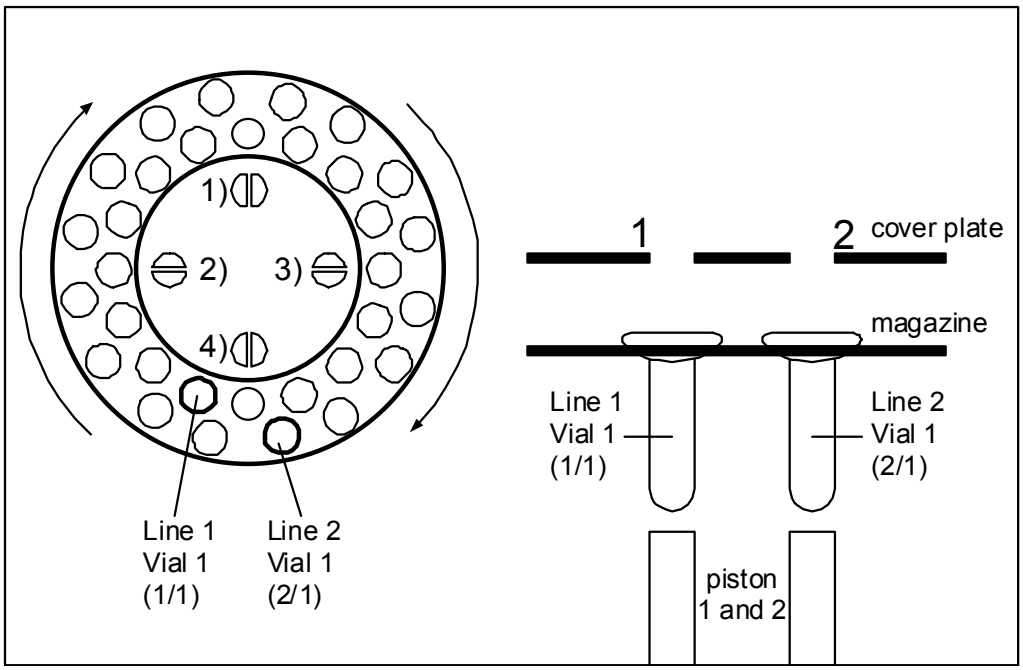
3.8 HOW TO ADJUST THE POSITION OF THE MAGAZINE

The position of the vials in magazine to the piston position can easily be adjusted by the following steps:

- Take away the cover of the magazine and place the magazine in the oven
- Loosen the screws (1 - 4). Move the magazine.
- Rotate the magazine till the vials look right to the piston
- Take away the magazine and tighten the screws (1 - 4)
- Rotate the magazine several times

Moving of the support rod can do the alignment of cover plate to magazine (the support rod is fixed with two screws, which are located at one end).

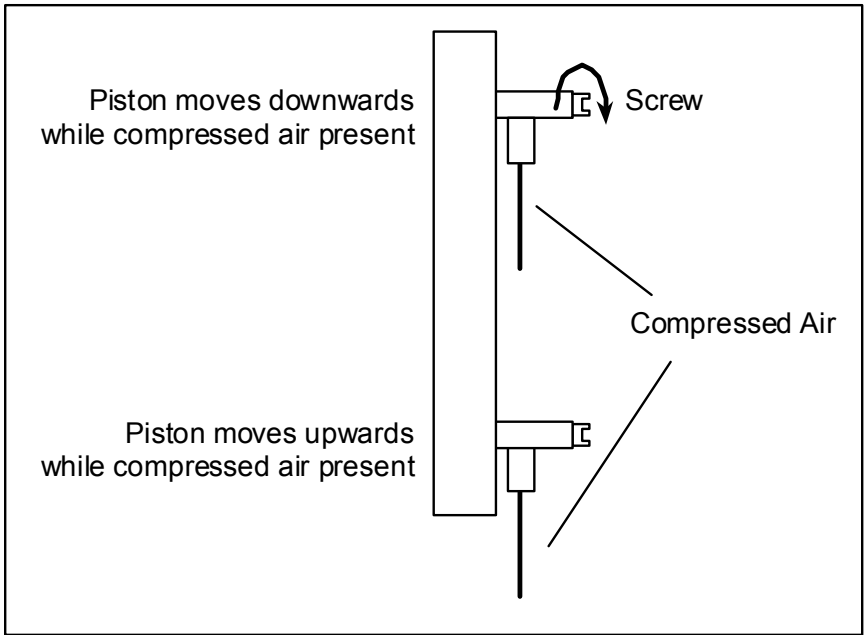
Fig: 3.8 Schematic of the magazine with cover plate and vials



3.9 HOW TO ADJUST PISTON SPEED

The speed of the piston to remove the vials up / downwards is adjustable. Turn the screw clockwise to reduce the speed of the piston movement upwards and vice versa.
The upper screw is to set the speed piston moves upwards.

Fig: 3.9 Piston speed adjustment

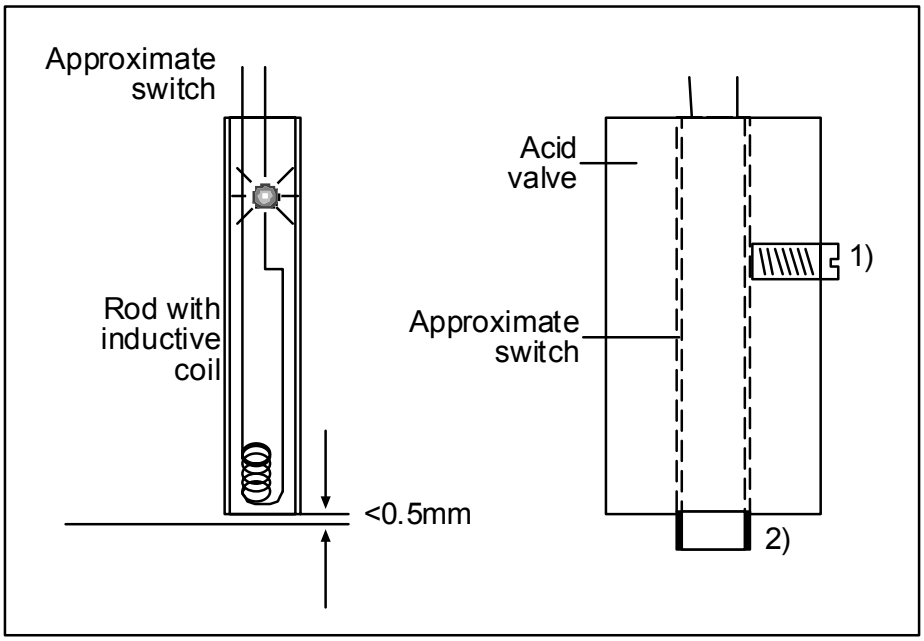


3.10 PROXIMITY SWITCH

The Proximity switch 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 up-wards close to proximity switch.
The induction of the coil changes, which means the vial is connected.

3.11 HOW TO TEST THE PROXIMITY SWITCH

- Loosen screw #1
- Take the rod carefully out of acid valve
- Bring the end of the rod close to the chassis of oven (e.g. acid valve platform)
- The light illuminates if the distance between the rod and ground is < 0.5 mm.



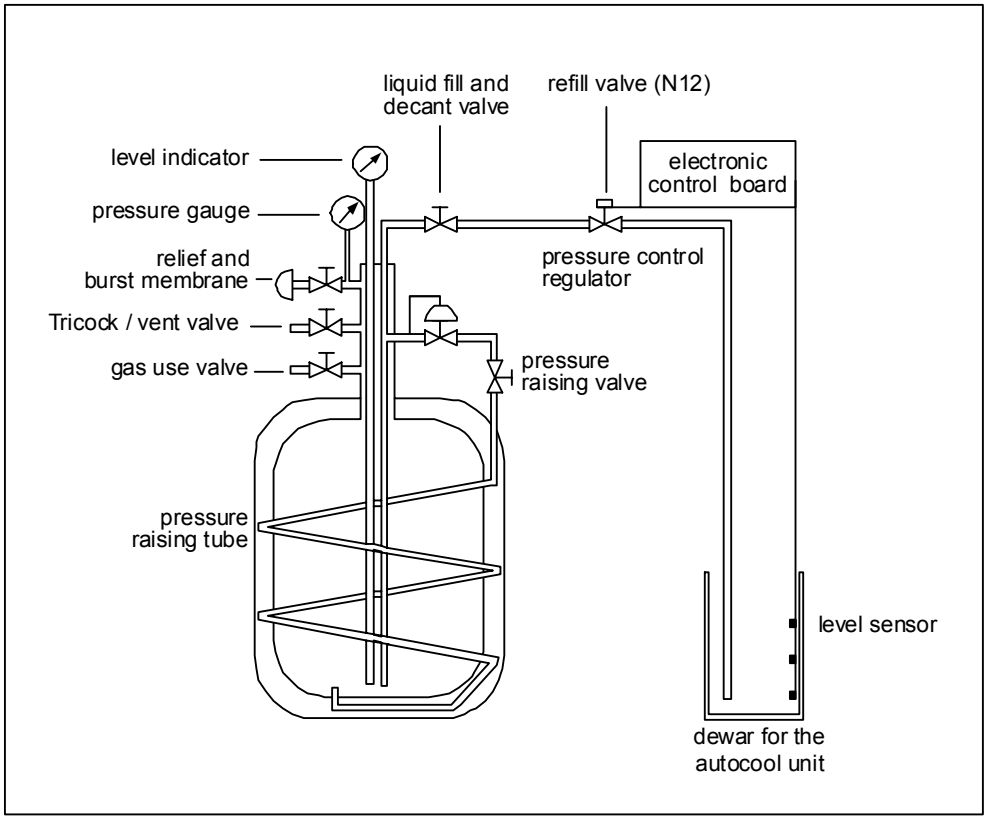
3.12 LIQUID NITROGEN TANK REFILL DEVICE (1/2)

Safety Warning:

before operating the refill device, please read these notes as well as the manufacturer's handling instructions carefully.

- The refill device contains extremely cold liquid gas and careless handling might cause personal injury including frostbite.
- Wear protective clothing when operating this equipment including protective gloves and face shield.
- 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!**

Fig: 3.12 Liquid Nitrogen Tank refill device



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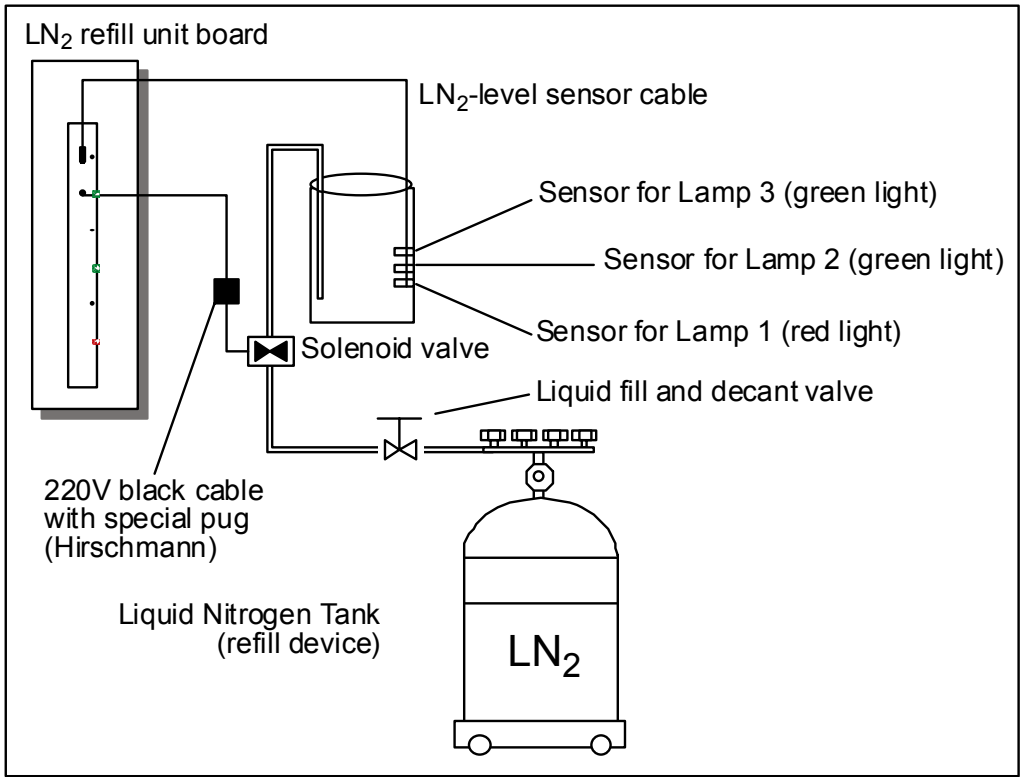
3.13 LIQUID NITROGEN TANK REFILL DEVICE (2/2)

Working Principle: The transfer of liquid nitrogen is effected by a build-up of pressure in the self-pressuring Dewar of refill device. The pressure builds- up by vaporization of liquid nitrogen in a coiled pressure raising tube located in the dewar's vacuum interspace when the gas vent valve is closed and the pressure-raising valve is opened. A pressure gauge monitors the pressure. A pressure of 5 psi should be sufficient to transfer liquid nitrogen. A pressure of 10 psi will transfer liquid about 10 L per minute. A higher pressure is not necessary and even wasteful. As soon as present pressure is reached, the pressure regulator installed in the circulation cuts the flow through the coiled pressure raising tube. The working pressure can be set to an optimum level with the pressure regulator. The blow-off valve is set to a limit of about 1.5 bar; an additional burst membrane prevents a build-up of dangerous pressure. The gas vent valve allows bleeding of excessive pressure, if necessary.

3.14 AUTO COOL REFILL DEVICE

The refill device provides a constant level of liquid nitrogen in the dewar for the auto cool unit. It is equipped with the necessary safety devices, valves pressure gauges required for a safe handling of liquid nitrogen.
A solenoid operated refill valve controls the transfer line to the dewar of the auto cool unit. The refill valve is directly connected to liquid fill and decants valve of the refill device.
A level sensor installed in the dewar of auto cool unit activates the refill device. The level sensor consists of three sensing thermistors, one each for the maximum, the intermediate and the minimum level. The electronic control board of the refill device evaluates the signals of the sensors and activates the refill solenoid valve to start or to end the liquid nitrogen transfer. This board is installed (see Hardware Layout Section: left panel).

Fig: 3.13 Liquid nitrogen tank and auto-cool



3.14 ELECTRONIC CONTROL BOARD REFILL UNIT (1/2)

Time in sec.	Lamp 1	Lamp 2	Lamp 3	µ volume temp.
0	start filling liquid nitrogen inside the dewar			
0	on	off	off	ambient (no LN_2)
120	on	off	off	-40°C
300	on	off	off	-90°C
390	off	off	off	-115°C
420	off	on	off	-140°C
450	off	on	on	-190°C

3.14 a WARNING NOTE FOR LIQUID NITROGEN SUPPLY

This paragraph concerns the following peripherals requiring the use of liquid nitrogen

- Kiel Carbonate device
- Micro volume (containing Auto cool)

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

As part of the tank a ***liquid fill and decant valve*** 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 (i.e. magnetic valve)*** is computer-controlled. 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.

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 Finnigan. 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*:

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 safety valve between solenoid valve and manual cutoff valve!***
Never operate the instrument without safety valve (i.e. never unscrew it)!

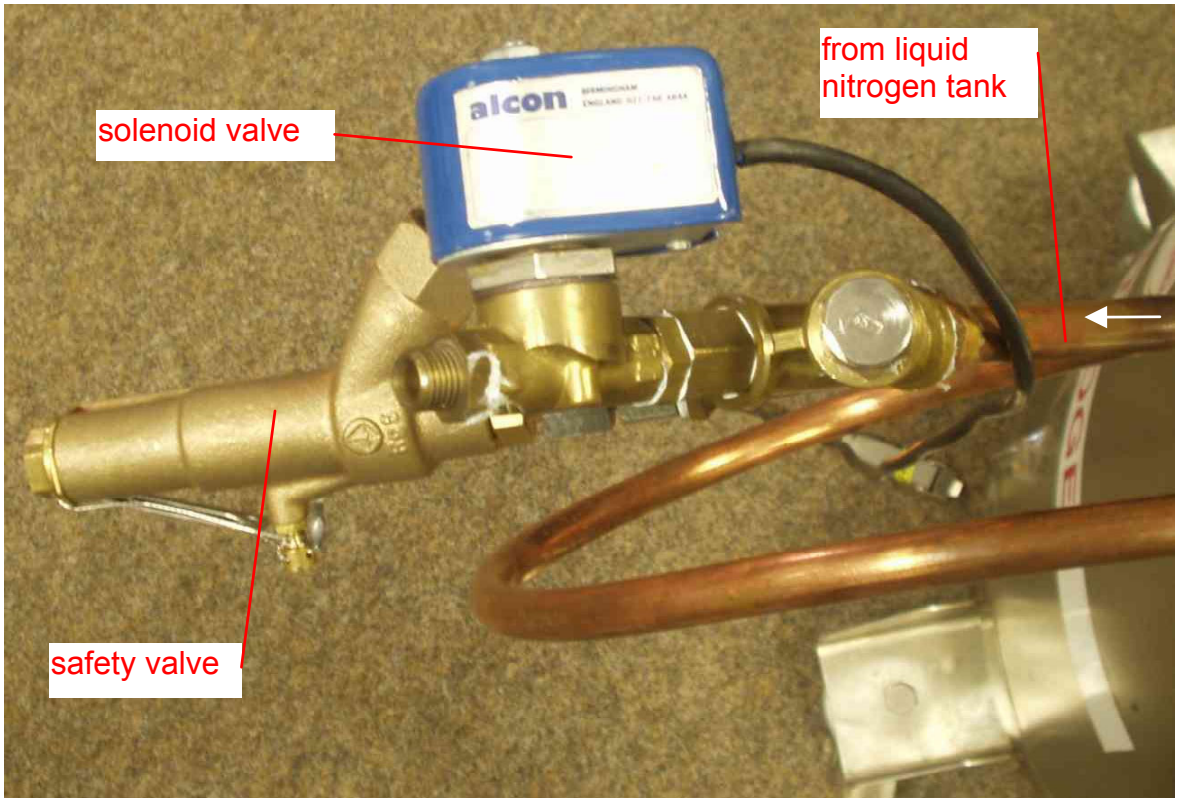


Fig. 3.14b–1 Valves and distributor for liquid nitrogen (top view)

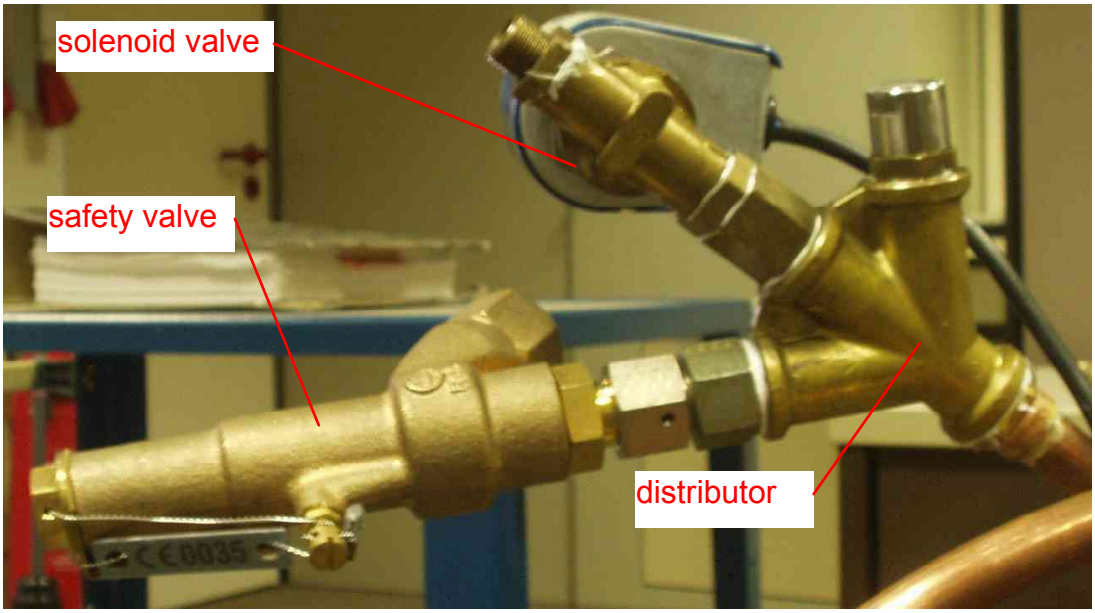


Fig. 3.14c–1 Valves and distributor for liquid nitrogen (side view)

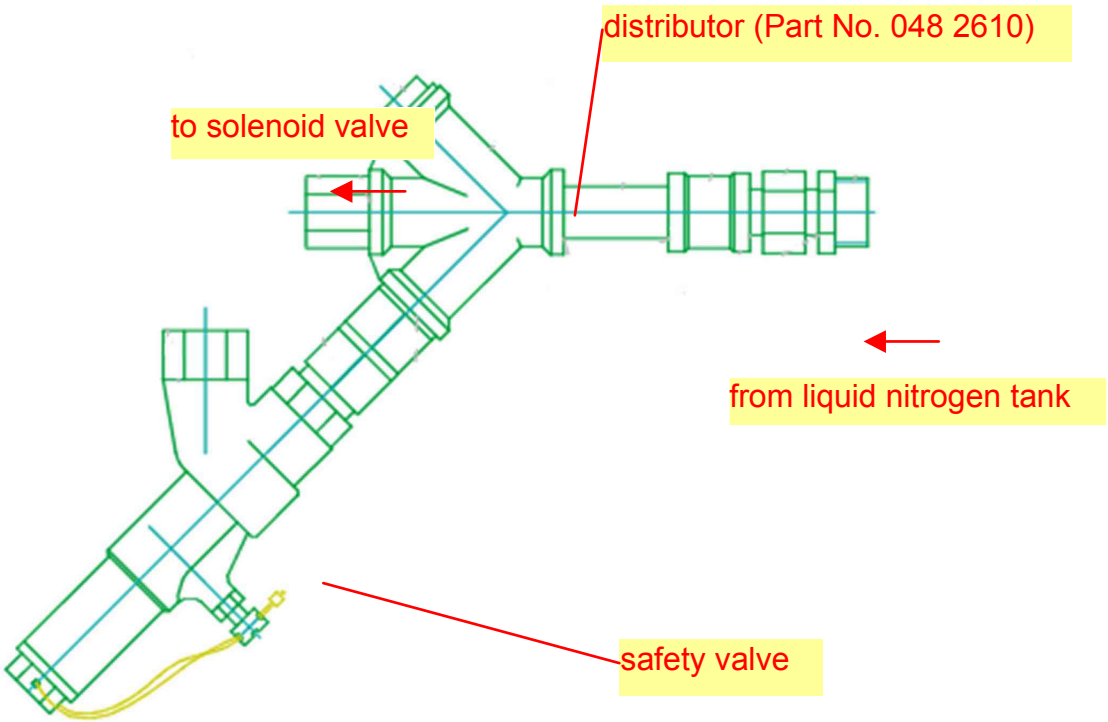


Fig. 3.14c–2 Schematic of valves and distributor for liquid nitrogen

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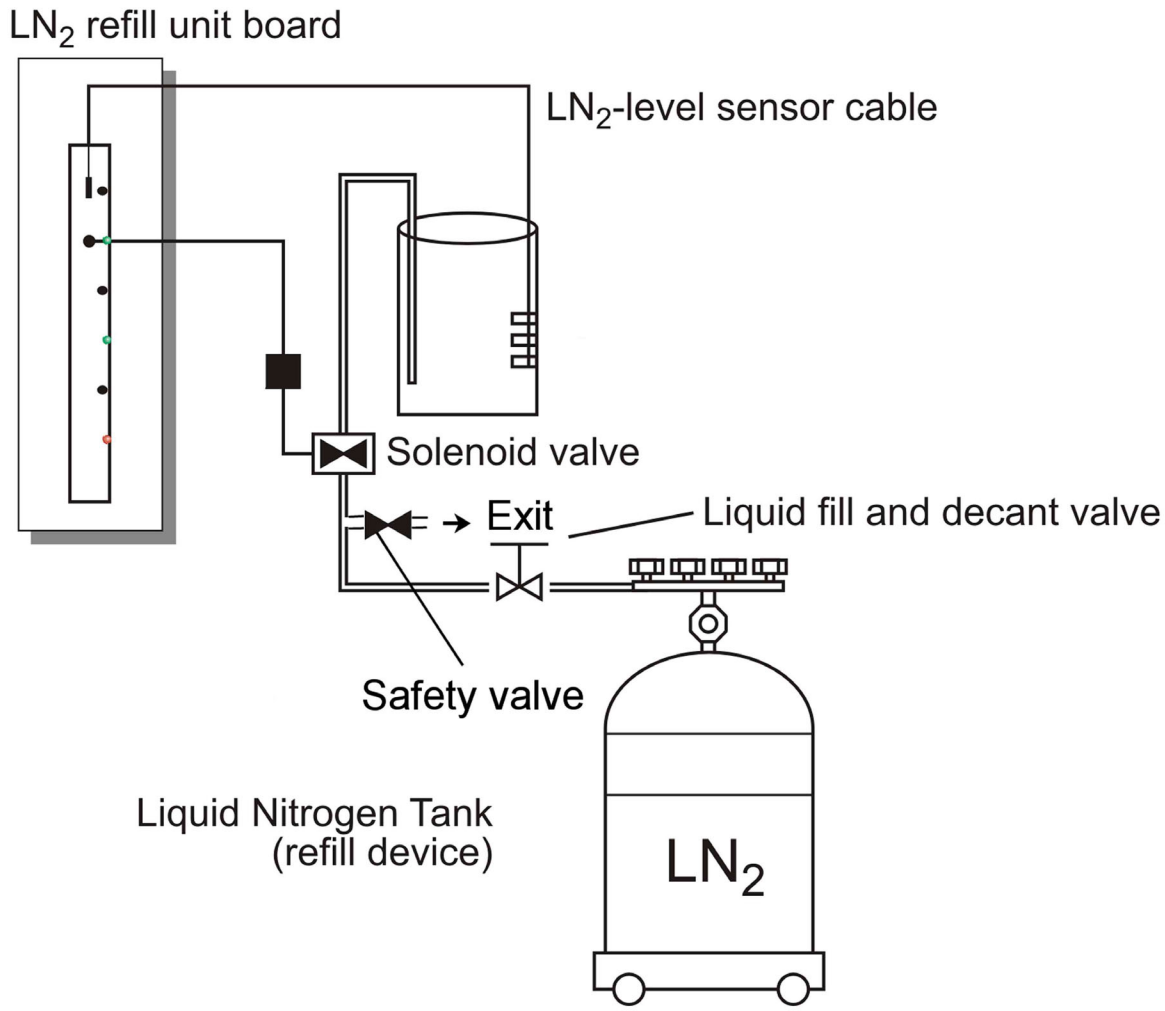

Fig. 3.14d–1 Schematic of valve positions

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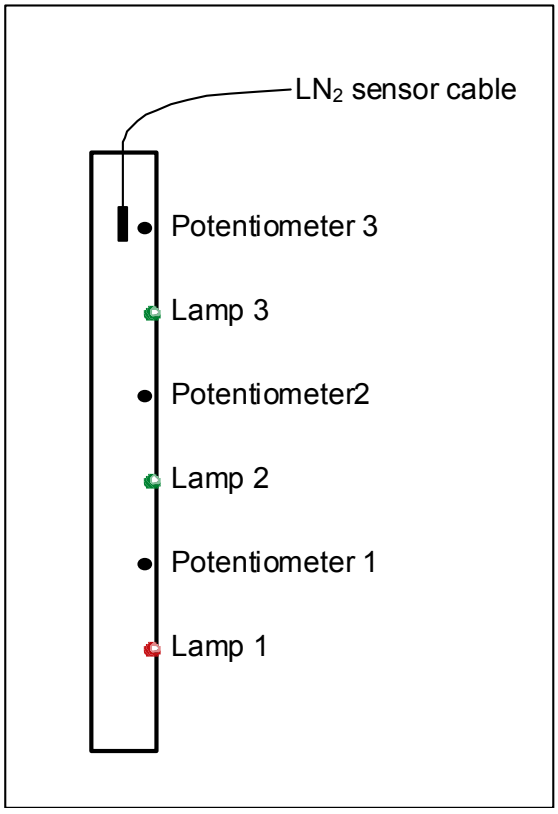
3.14 ELECTRONIC CONTROL BOARD REFILL UNIT (2/2)

(Hardware-layout lower section (left panel)).

The amount of the liquid nitrogen can easily be read out following the principle shown below:

Fig: 3.14 Electronic control



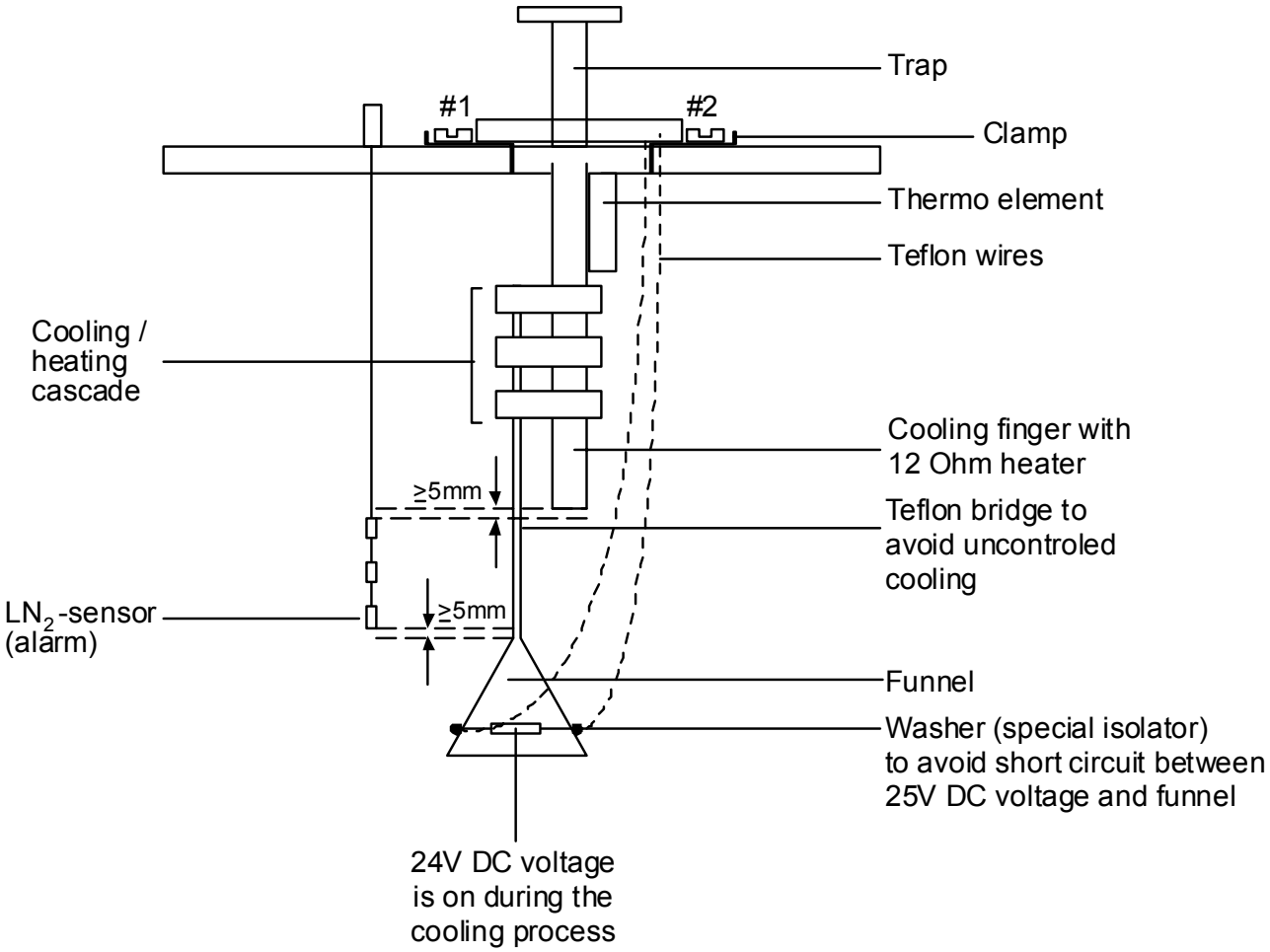
- **Lamp 3:**
  green light illuminates if the maximum level of liquid nitrogen inside the dewar is reached. During this time the solenoid valve on liquid nitrogen tank is closed.
  Lamp 1 = OFF
  Lamp 2 = ON
- **Potentiometer 3:**
  Has to be adjusted for the electronic setting of Lamp 3.

- **Lamp 2:**
  green light illuminates if at least the intermediate level of liquid nitrogen is reached.
  Lamp 1 = OFF
- **Potentiometer 2:**
  Has to be adjusted for the electronic setting of Lamp 2.

- **Lamp 1:**
  red light illuminates if no or not enough liquid nitrogen is inside the dewar.
  Lamp 2 = OFF
  Lamp 3 = OFF

- **Potentiometer 1:**
  Has to be adjusted for the electronic setting of Lamp 1.

3.15 AUTOCOOL DEVICE



NOTE:

- ***To remove the cooling / heating cascade with funnel loosen the screws #1 and #2***
- ***Push the clamp to the left (or right), then gently push down micro-volume bar***
- ***Careless handling of liquid nitrogen might cause personal injury including frostbite.***
- ***Wear protective clothing when operating this equipment including protective gloves and face shield.***

3.16 AUTO COOL UNIT (TRAP1 AND TRAP 2)

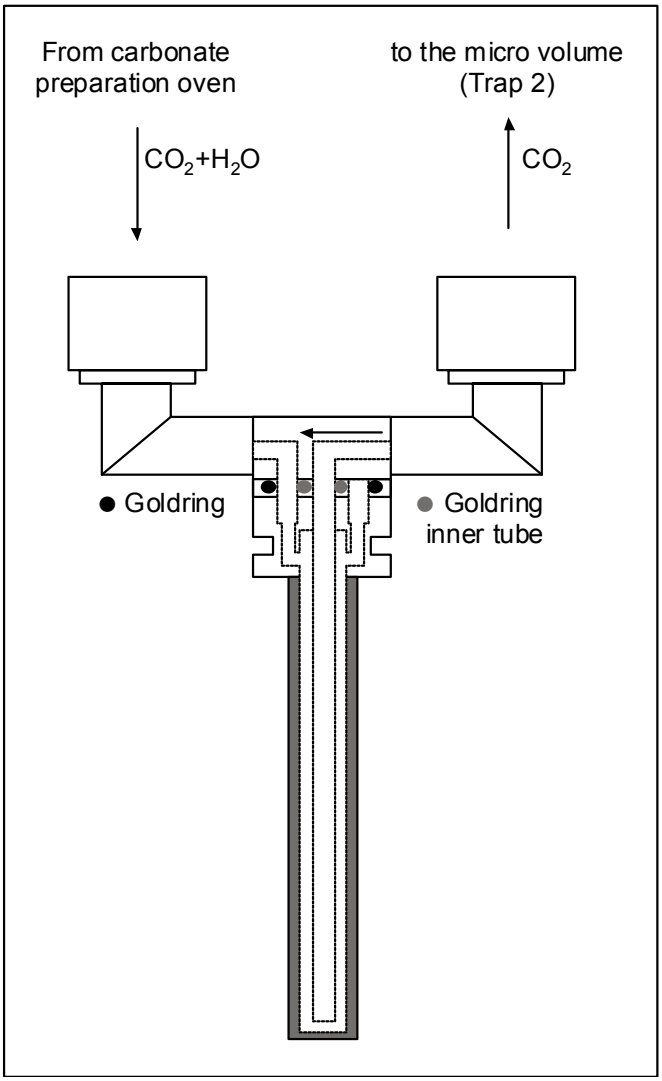
The temperature of the auto cool unit which cools the Trap 1 or Trap 2 can be set with ISODAT software routine in the instrument control mode. If, for instance, the temperature level is set to -80°C the heater works against the temperature of the liquid nitrogen in order to keep the set temperature. A temperature between -196°C and +150°C can be set. The Trap 1 or Trap 2 fits into a thermal contact attached to the lid of 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 3 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 the Trap 1 or Trap 2 to a defined temperature the heater element is activated and the temperature sensor controls the heating phase. To cool the Trap 1 or Trap 2 another electrical heater element immersed in liquid nitrogen is activated and causes evaporation as well as agitation.

Above the heater element a funnel-shaped hood of standpipe is positioned which leads to the uppermost bowl of the cascade arrangement of 3 bowls. This arrangement enables about one drop of liquid nitrogen per second to be carried by the stream of evaporated nitrogen. Small hole in the bottom of bowls enable a constant trickle of liquid nitrogen back into the dewar, and the continuos flow of liquid nitrogen rapidly cools down the Trap 1 or Trap 2. By suitable balancing of the liquid nitrogen flow and heating the Trap 1 or Trap 2 any temperature within the temperature range of ± 2°C can be attained.

3.17 TRAP 1

Fig: 3.15 Trap 1



This trap consists of a "special cold finger " valve block, and an auto cool unit. This "special cold finger" has two tubes, which are tucked one inside the other. The inner tube must be connected to trap 2 the other end is open hangs inside the outer tube. The outer tube is connected via valve 1 and 12 (22) to carbonate preparation vial. The valves of trap 1 are operated by computer or manually via monitor display. With the auto cool unit the 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 cleaning procedure the auto cool unit cools the trap to -196°C. As soon as the acid drops into the vial which contains carbonate the reaction takes place and CO_2, H_2O, N_2, O_2 become realized. Since the cold finger has -196°C the CO_2 and H_2O gases become 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, auto cool sets the trap temperature to -120°C to -115 °C. At this temperature CO_2 as gas is released within inner tube for later use. The release temperature -120°C to -115 °C is extremely important. If the temperature is too high water can get trapped by trap 2 if the temperature is too low CO_2 might be retained. The indication of the trap does not show the gas direction. It indicates the installation direction. (See Hardware Layout lower section; front panel).

3.18 MICRO VOLUME (TRAP 2)

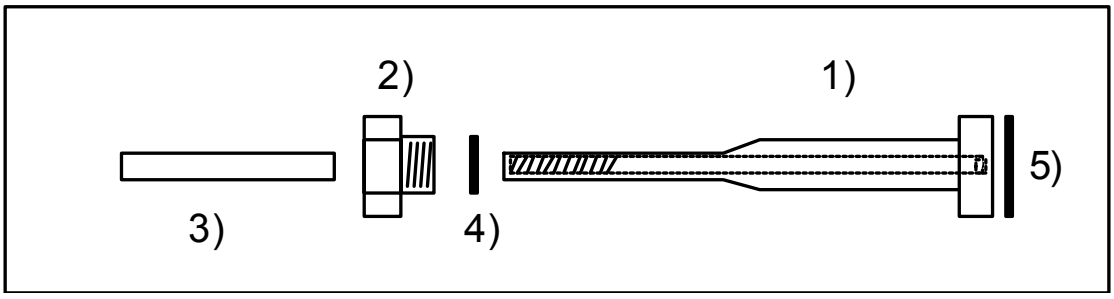
The micro volume consists of a cold finger, a valve block (valve 3 and 5), an autocool and a separate capillary. This capillay leads directly to change-over valve of the Mass Spectro-meter. Via valve #5 to the pump system of carbonate unit and via valve #3 to trap 1. The total volume in front of the capillary crimp including cold finger and the capillary is around 250 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 / µL has to be concen-trated to a small volume.

The cold finger volume can be reduced by inserting very clean small steel spheres. The concentration in a micro volume is performed by freezing CO_2 gas from trap1 using liquid nitrogen and expanding it by subsequent heating.

The valves of the micro volume are operated by computer during carbonate measurement or manually via monitor display.

With the auto cool unit the temperature can be set individually, if required, within a range of about -190°C and +150°C.

Fig: 3.16 Parts of a microvolume to be inserted into an autocool unit



1 "coldfinger"

2 fitting

3 copper rod

4 washer

5 gasket (gold)

KIEL CARBONATE DEVICE

SETUP

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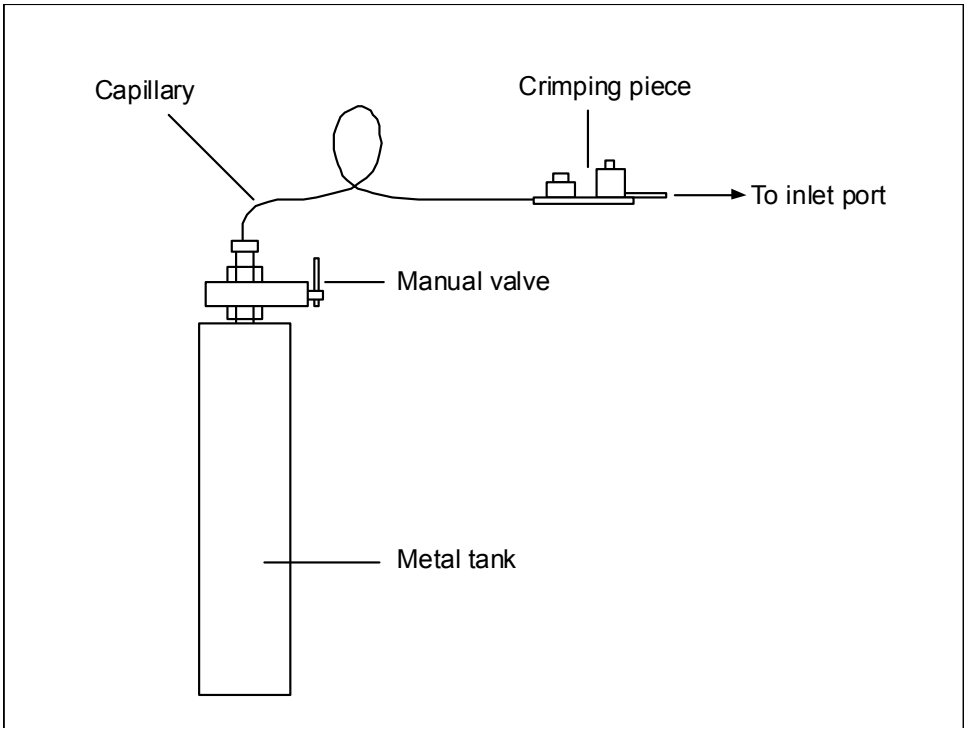
4.1 STANDARD REFILL (REFERENCE GAS REFILL)

When working with *KIEL CARBONATE DEVICE* a reference-gas refill is necessary in order to avoid running out of reference gas during measurements.
The standard refill (reference gas refill is a hardware option). It consists of a metal tank (contents approx. 5L) with a manual valve connected via a capillary 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.

Fig: 4.1 The reference refill



NOTE: ***The reference refill parameters can be set in method editor → instrument.***

4.2 PHOSPHORIC ACID PREPARATION

H_3PO_4 is prepared from "Puranal" grade orthophosphoric acid (min 85%) and "Puriss" grade phosphorous pentoxide or trade names of equivalent purity.
One "Winchester" of phosphoric acid is poured into a 51 beaker on a magnetic hotplate – stirrer inside a fume cupboard, using a PTFE spinbar.

WARNING:

- ***Gloves and face shield must be worn at all times while handling P_2O_5.***
- ***A useful thermometer/stirring rod can be provided by enclosing a thermometer in a large piece of heavy-walled Pyrex tubing with the bottom sealed off.***
- ***Between additions and during the final cooling stage the beaker is kept covered with cling film.***

4.3 ADDING THE PHOSPHOROUS PENTOXIDE

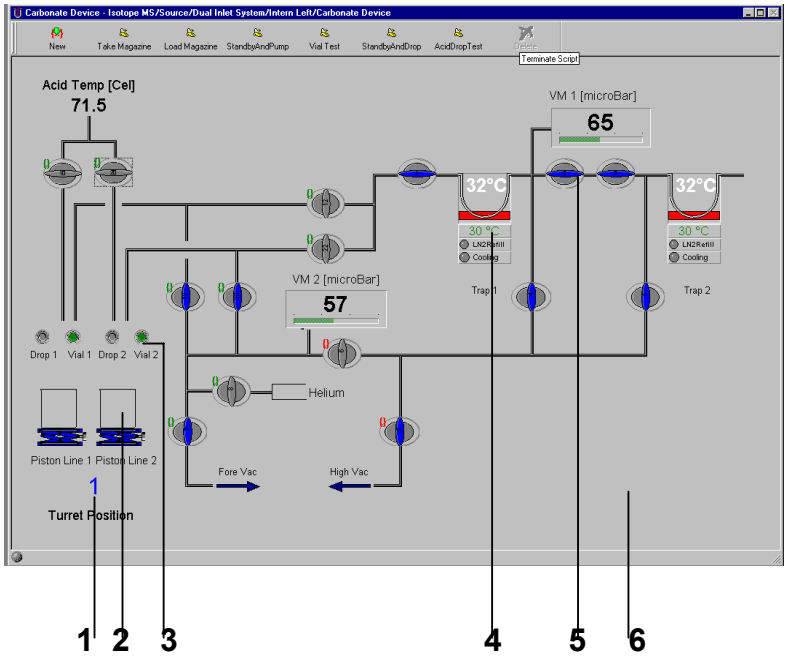
WARNING:

- ***Care must be taken during the initial stage of P_2O_5 addition as the reaction can be vigorous as the powder contacts the relatively 'wet' acid.***

It normally takes about 2kg of phosphorous pentoxide to obtain the required final specific gravity of greater than 1.92. This quantity of P_2O_5 is gradually added over a period of 2-3 hours with constant stirring and heating to a temperature of around 80 °C. The powder forms gelatinous lumps initially, but will gradually dissolve. The complete process can take 4-5 hours. A few crystals of chromium dioxide (0.5g approx.) are added at the final dissolution stage and the heating and stirring continued until all the phosphorous pentoxide has dissolved. The stirrer hotplate is switched off and the acid allowed cooling to room temperature before checking the specific gravity. If this is less than 1.92 then the acid must be reheated and more P_2O_5 added. Finally the acid, which should be about 31 after P_2O_5 addition is stored in bottles until required using "Parafilm" to seal the screw cap.

4.4 INSTRUMENT CONTROL KIEL CARBONATE DEVICE

Fig: 4.2 Instrument control



1 Click here to move the magazine to another position

2 Click here to move the piston up or down

3 Click here to connect or disconnect the vial

4 Click here to set the temperature

5 Click here to open or close the valve

6 Click right mouse button here to see the *properties*:

- *Edit Hardware* (ISL Script Parameter)
- *Take Magazine*
- *Load Magazine*
- *Standby and Pump*
- *Vial Test*
- *Standby and Drop*
- *Acid Drop Test*

NOTE:

- ***Open or close the valves always by left mouse button.***
- ***Valves with red sign indication means these valves have a special safety key.***
- ***Valves with green indications means these valves have safety key if the user clicks them with the left mouse button by clicking them with the right button there is no safety at all.***

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4.5 TAKE MAGAZINE

Before removing the magazine out of oven select always the function "Take Magazine" and follow the instructions via computer dialogue. After clicking the property "Take Magazine" (see Instrument control, Carbonate Device) if vials are connected the following information appears: ***Line not free- continue with disconnect***

Yes ***No***

After pressing *Yes* magazine is moved to the respective position and vials are taken away from acid housing. After moving to position one automatically, the following message appears

Ready to take magazine

OK

Now open the oven door and take the magazine very carefully out of the oven and close the door to keep the oven temperature on a constant level.

4.6 LOAD MAGAZINE

After putting the magazine in the oven this function should be done in order to keep the lines free of water and other impurities. Following action takes place:

- The left piston moves the vial 1/1 (first vial / line one) up.
- Valve #7 opens waits until pressure meter VM2 value is under acceptable value then moves the piston down.
- After that opens valve 13 if VM2< 200 µbar.
- After that the right piston moves the vial 2/1 (second vial / line one) up.
- Valve #7 opens waits until pressure meter VM2 value is under acceptable value then moves the piston down.
- After that opens valve 23 if VM2< 200 µbar.
- Leave valves #7, 13, 23 open

NOTE: ***If no vial is available or the approximate switch gives no response an error message appears.***

4.7 STANDBY AND PUMP

To perform this function put at least two clean vials in position 1/1 and 2/1.

- Start the function via clicking the Standby properties.
- Close valve #6, 12, and 22. Open valves #1, 2, 3, 4, 5 and 6.
- Leave valves # 7, 13, 23 open.

Bring the vials of position 1 to respective acid valve housing and keep pumping.

4.8 STANDBY AND DROP

If the carbonate device is not used for more than 5 hours it is recommended to select Standby and Drop function to keep the acid lines in flow. Otherwise the acid may lock the lines or the magnetic valve #10 or #20 may squeeze the Teflon acid tube.
This function takes place automatically after finishing an acquisition.
Standby and drop can also be performed manually.

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 starting standby and drop.***

If the function is user-started and vials are connected, the message:

Line not free-continue with disconnect

Yes No

appears. Continue with *Yes*. 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 and the pumping period is started. After a user defined time (refer to ISL-script → Parameter → Standby and drop interval) the vial 1/1 is taken away and the magazine moves to position #2. The vial 2/1 (vial two / line one) is connected and pumped. After pumping acid is dropped and the vial 2/1 is removed into the magazine. The same procedure takes place for vial 2/2 (vial 2 / line 2). To stop the function selects the properties and click ***Stop < Standby And Drop>***

4.9 VIAL TEST

This test is recommended to perform when the 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. Touching the viton ring of the acid housing valve the surface must be equally flat and free of dust and other impurities to ensure a good vacuum. The test indicates if the vial ensures the needed quality.

To perform this test proceed as follows:

- Take a magazine and place in each position a vial
- Put the magazine in the oven
- Start the test via clicking the Vial Test properties.

Then the following steps should be performed:

- Take a vial connect to acid housing valve
- Measure the proximity switch if the vial is connected
- Open valve #7, wait to get VM2< 1000 µbar
- Bring the piston down, measure VM2
- Open 13, wait until VM2< 200 µbar
- If the vacuum within acceptable value continue with next vial

Error messages:

- Vial not connected
- No vial
- Proximity switch fails
- VM2 pressure to high, leak present

4.10 ACID DROP TEST

To test the function of acid valves and counters this test can be done. After connecting and measuring VM2 value valve 10 opens and injects one drop acid closing valve 10 opens 20 and injects one acid drop and repeats again. To stop the action select again the properties 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 under vacuum.***

KIEL CARBONATE DEVICE

TUNING

Issue 09/2002

Thermo Finnigan

5.1 MATCH THE SAMPLE CAPILLARY TO THE STANDARD CAPILLARY

How to match the sample flow from carbonate device to standard flow of IRMS

The volume between valves # 25, 26, 34 and 33 plus the capillary at the standard of the Mass Spectrometer has almost the same size as the volume between valves # 3 and 5 plus microvolume and the capillary of carbonate device. The gas flow from both capillaries to mass spectrometer must be the same and it is adjusted. The following procedure shows how to mach the two capillaries.

(see fig: 5.2)

- Close valves # 1, 2, 3, 4, 5, 6 and 9 on carbonate device.
- Remove the flexible which is connected between the valve combination VC5 and VC3.
- Connect 1/8 inch stainless steel tube (MAT part # 1060250) on the left side of dual inlet at valve # 11.
- Connect the other side of above tube V 4.
- Open the both bellows to 100% and pump carefully all tubes including left and right side of dual inlet.
- Close valve 15 of SA side and put 50 mbar CO_2 at both sides of bellows. Following valves are open # 25, 24, 23, 13, 11, 14, 4, 2 and 3.
- Match the carbonate capillary to standard by the signal intensity of mass m/z=44. Squeeze carbonate capillary until acceptable tolerance of < 50 mV is reached. (SS-capillary is elastic do not squeeze at one time wait a while until gas flow gets stabilised).

Fig: 5.1

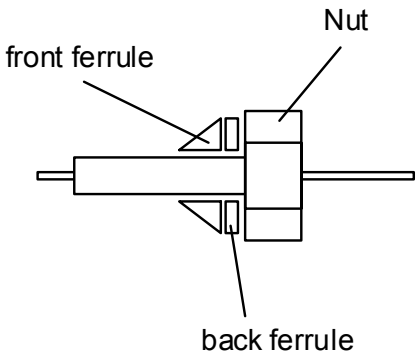

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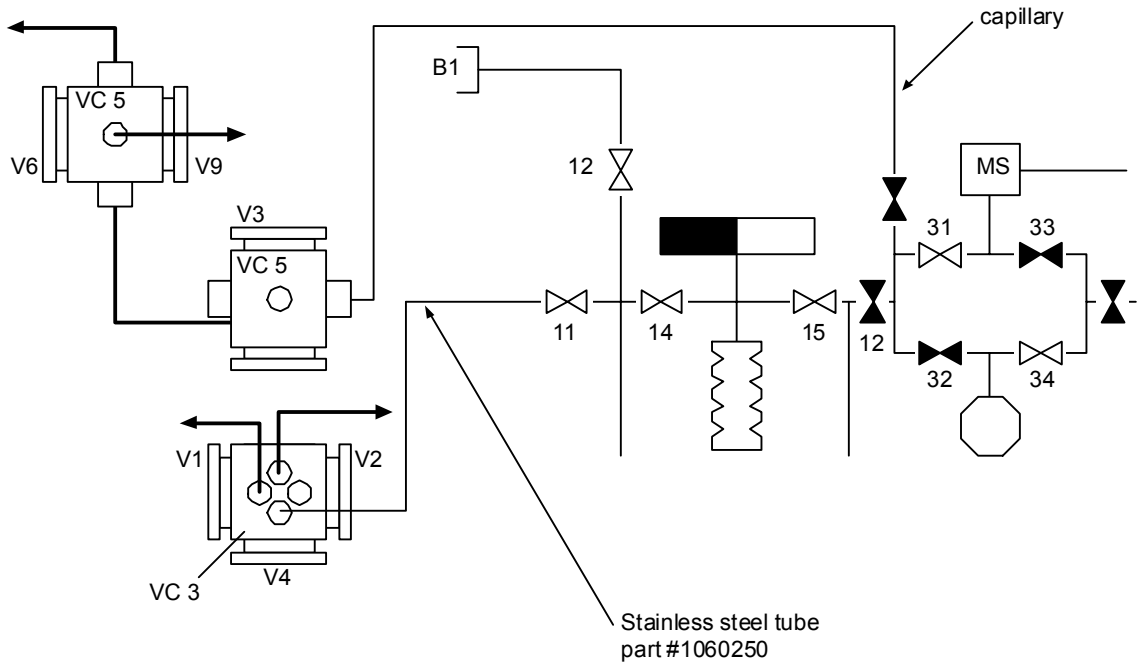
Fig: 5.2 Schematic of valves



5.2 MATCH THE SAMPLE VOLUME FROM *KIEL CARBONATE DEVICE* TO STD. VOLUME OF IRMS

In case that the volume at the sample side is smaller than standard side, the sample gas depletes faster than the standard gas - even if the gas flow is the same and vice versa. For CO_2 analysis via micro volume the same volume and the same gas flow is essential.

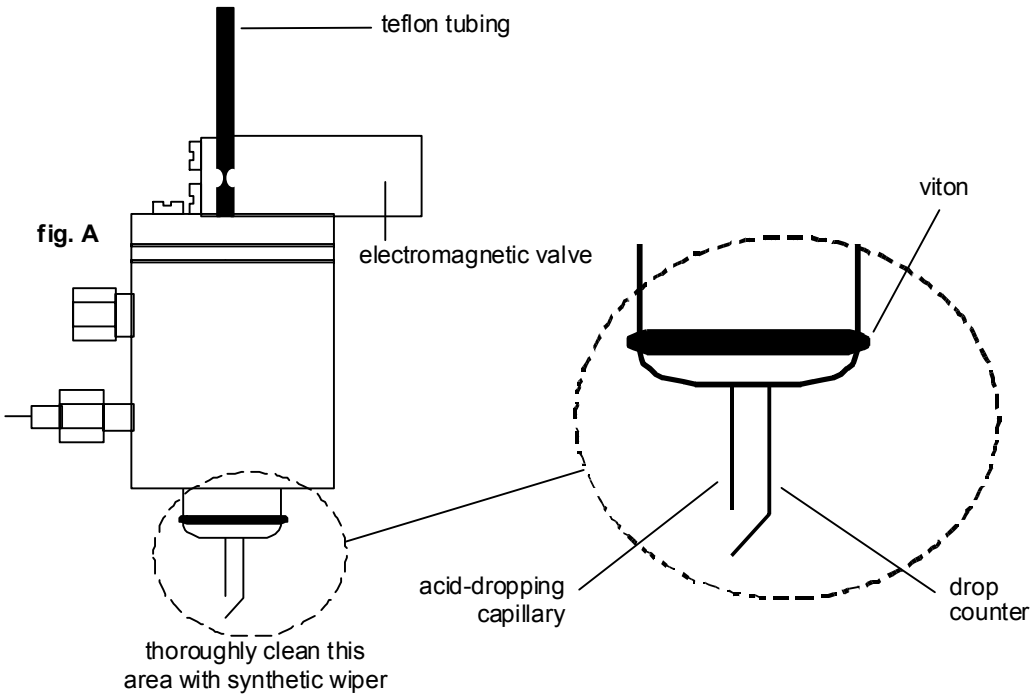
(see under Fig. 5.1)

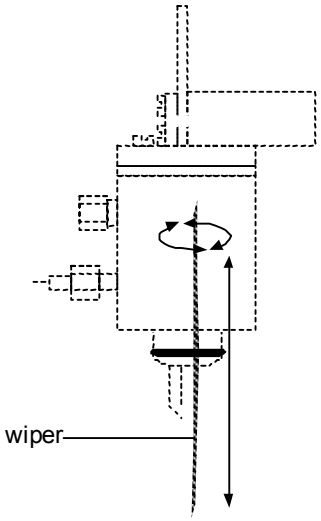
- Close valves # 31, 32, 15 and 16 on dual inlet
- Close valves # 3 and 5 on *KIEL CARBONATE DEVICE*
- Unscrew the capillary from the *KIEL CARBONATE DEVICE*
- Move the front and back ferrule to left in order to increase the volume.
- Screw the capillary to *KIEL CARBONATE DEVICE*
- Close valves # 3, 4, 9, 13 and 23 of *KIEL CARBONATE DEVICE*
- Open valves # 5, 6, 13 and 23 and wait until VM2 < 200 µbar
- Close valve # 6 and open valve # 9 and 32 (dual inlet)

5.3 HOW TO CLEAN THE ACID VALVE

It is recommended to clean the acid valve after every magazine measured, using a synthetic wiper:

Fig: 5.3 Acid valve





NOTE: ***The End of drop-counter and acid dropping capillary must align.***

The cleaning procedure can easily be performed following the steps written below:

- roll up the wiper approximately match thick
- clean the inner part of the acid valve as shown (fig.A)
- do not forget to clean the viton ring

5.4 HOW TO DISSEMBLE THE ACID VALVE

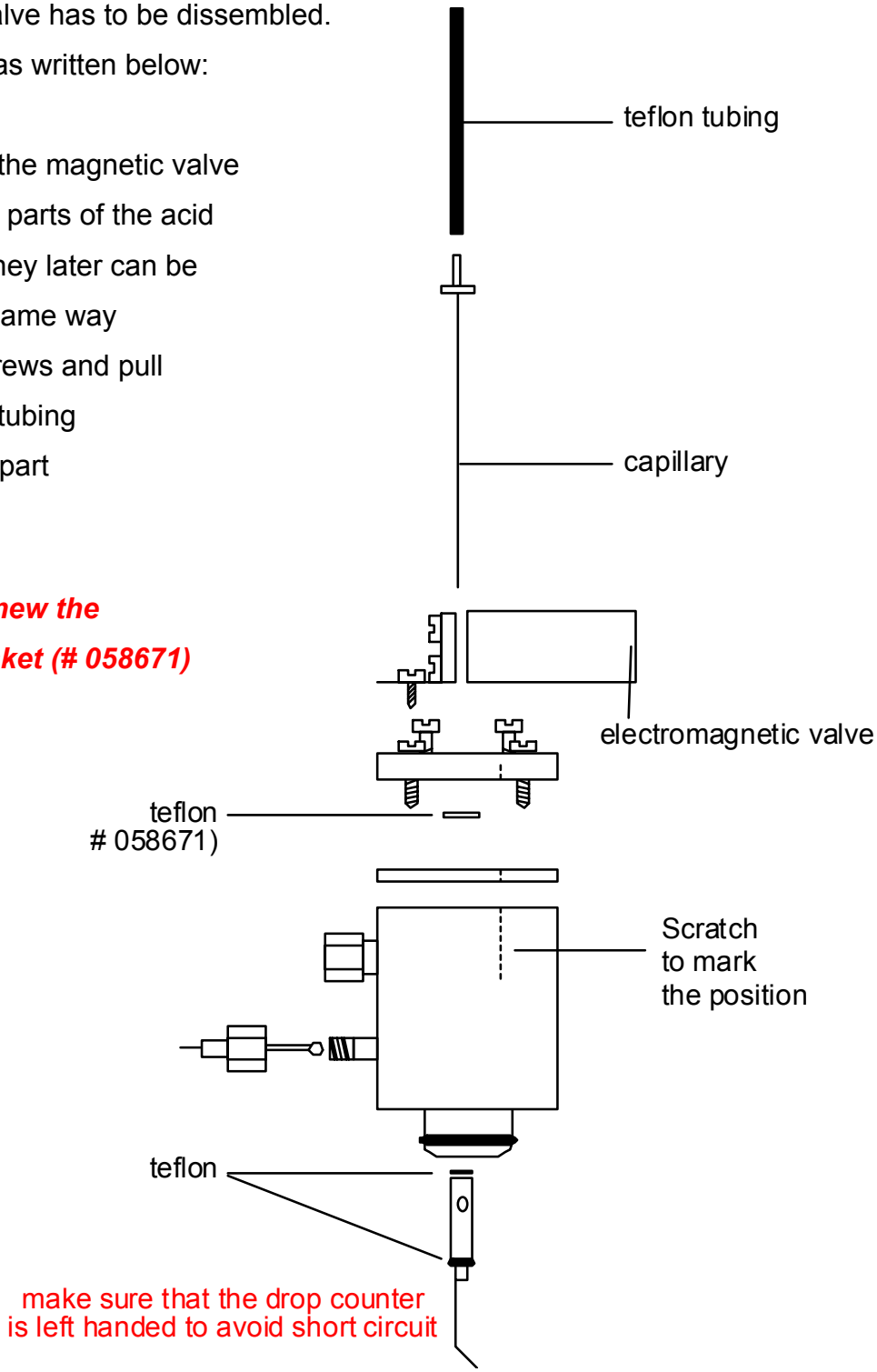
Fig: 5.4 Acid valve

Sometime the acid valve has to be dissembled.

In this case proceed as written below:

- First unmount the magnetic valve
- Mark the three parts of the acid valve so that they later can be tighten in the same way
- Loosen the screws and pull out the Teflon tubing and the upper part

NOTE: ***Always renew the Teflon gasket (# 058671)***



KIEL CARBONATE DEVICE

MEASUREMENT

Issue 09/2002

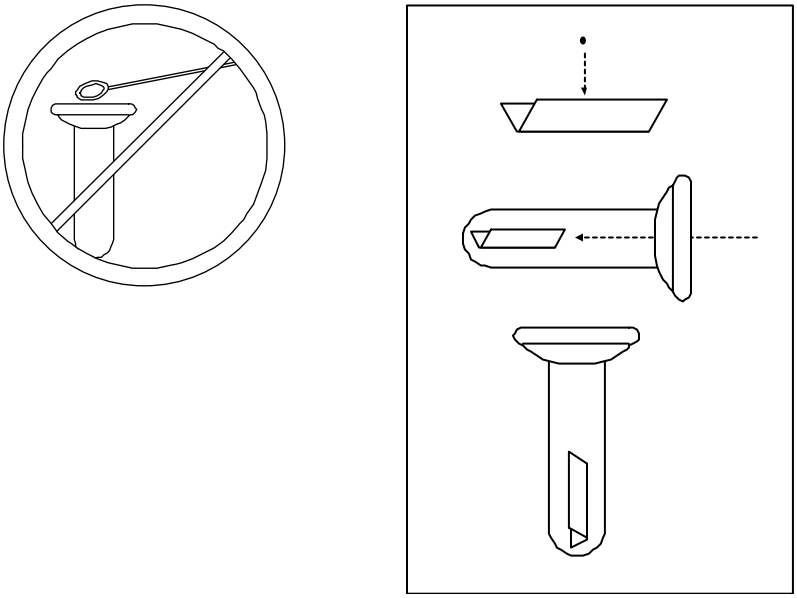
Thermo Finnigan

6.1 HOW TO PLACE THE SAMPLE IN THE VIAL

The boat used for carbonate measurements should be free of organic and inorganic material:

- Place the sample carefully in the middle of the boat
- Carefully lead the boat to the bottom of the vial in horizontal position
- Knock the vial in vertical position several times
- Take the boat out of the vial
- For each sample a new boat should be taken

Fig: 6.1 Correct sample placement



6.2 HOW TO CREATE A METHOD (1/6)

The ISODAT NT including Carbonate Device software allows fully automated isotope ratio determination of carbon and oxygen of carbonate samples. All parameters relevant for a data acquisition of a sample are stored in a Method. As soon as a Carbonate Device configuration is created a pre defined and stored Method under the name ‘’Kiel_Carbo.met’’ exists .
The following steps need to be performed to define a new **Method.**

- Open "Dual Inlet" module

- Select the configuration for Carbonate Device (e.g. Kiel_Carbo)
- Select the Gasconfiguration (CO_2)

- Select Method-Tab
- Create a new method

The new method is structured in Tab - pages: Instrument, Peripherals, Evaluation and Printout. The following values are a guideline explaining the parameters for a CO_2 method using *KIEL CARBONATE DEVICE* and reference refill.

6.2. HOW TO CREATE A METHOD (2/2)

The ISODAT NT including Carbonate Device software allows fully automated isotope ratio determination of carbon (CO_2) and oxygen of carbonate samples.
All parameters relevant for a data acquisition of a sample are stored in a **Method**

As soon as a Carbonate Device configuration is created a pre defined and stored **Method** under the name ‘’Kiel_Carbo.met’’ exists .
The following steps need to be performed to define a new **Method.**

- Open "Dual Inlet" module
- Select the configuration for Carbonate Device (e.g. Kiel_Carbo)
  - Select the Gasconfiguration
  - Create a new method

The new method is structured in Tab- pages: Instrument, Peripherals, Evaluation and Printout. The following values are a guideline explaining the parameters for a CO_2 method using *KIEL CARBONATE DEVICE* and reference refill.

6.2.1 INSTRUMENT TAB

- Select "CO_2-Gasconfiguration".
- The "Main Script" controls the acquisition cycle.

NOTE: ***It should only be edited by users trained on script editing.***

select *Peak Center Cup*: For example Cup 2 for a universal triple collector on a Delta^{Plus} (narrow cup for m/z 45).

Peak Center Pre Delay: Waiting time between activation of the reference gas and start of the peak center cycle (e.g. 5s).

Peak Center Post Delay: ➢ Waiting time between the end of the peak center cycle and the start of the data acquisition.

Integration time: ➢ The time needed to measure each individual ion intensity of masses 44, 45 and 46.

6.2.1.1 REFERENCE REFILL:

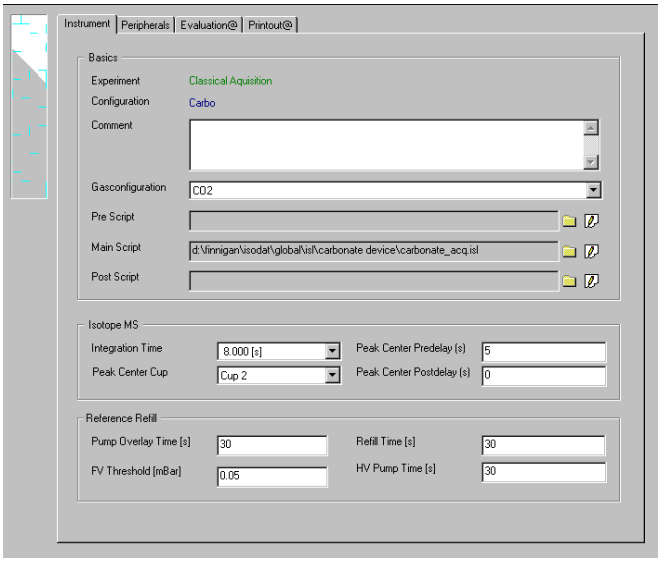
Pump Overlay Time: ➢ Capillary pump out time of Reference Refill tank.

Refill Time: ➢ Gas flow time from Reference Refill tank in to the inlet port of standard bellow .

FV Threshold: ➢ Minimum pressure of standard bellow including the valves and tubes evacuated with fore vacuum pump before to continue pumping with turbo molecular pump

HV- Pump Time: ➢ Pumping time of bellow including the valves and tubes with turbo molecular pump

Fig: 6.2 ***Instrument Tab***



6.2.2 PERIPHERALS-TAB

Dual Inlet System

Reference Left / Right: ➢ Where the standard gas is available (left / right bellow).

Number of Cycles: ➢ Measure e.g. 8 times sample and 8 times standard.

Idle Time: ➢ Waiting time after changing from sample to standard side and vice versa before integrating the ion intensities of masses 44, 45 and 46.

FV threshold: ➢ No function in this Configuration.

HV Time: ➢ No function in this Configuration.

FV Pump: ➢ Time no function in this Configuration.

Background

Pre Delay: ➢ After closing the change over valves 31,33 wait e.g. 30 seconds until the real Mass Spectrometer background gets measured .

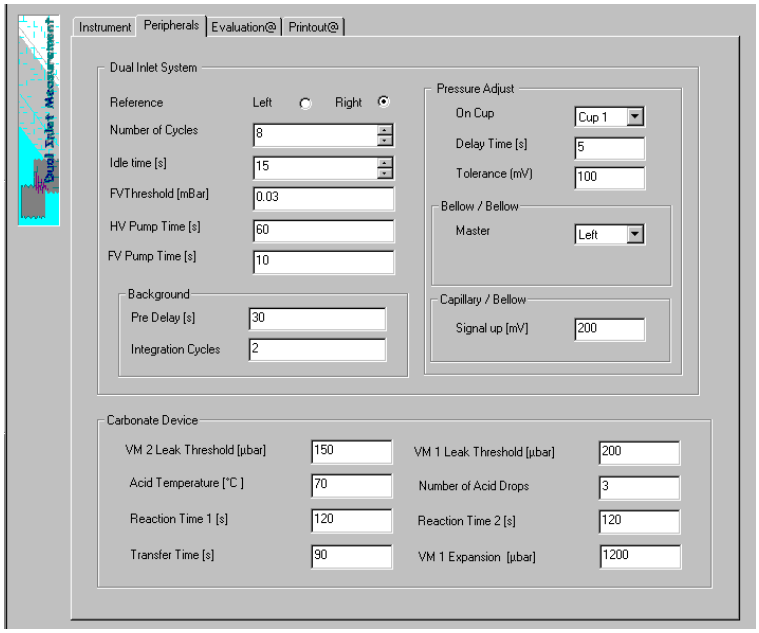
Integration Cycles: ➢ Measure e.g. 2 * Integration Time it means 16 Seconds.

Pressure Adjust

On Cup: ➢ Always select the cup where mass 44 is measured.

Delay Time: ➢ Waiting time after changing from sample to standard gas or vice versa before matching the standard bellow to sample ion intensity.

Fig: 6.3 Peripherals Tab



Pressure Adjust

Tolerance:

- Maximum acceptable ion intensity between sample and standard after matching (e.g. 50 mV meaning ± 25 mV).

Master (left):

- The standard bellow at the right side must be adjusted to the level of sample ion intensity minus signal up ± the tolerance.
  For carbonate application always take left (e.g. if *left* = 4200 mV, match the right bellow to 4200 mV - 100 mV ± 25 mV).

Capillary / Bellow

Signal Up:

- Match the ion intensity of standard gas less than e.g. 100 mV before closing the valve 25 and starting with acquisition.

Carbonate Device

VM2 Leak Threshold: ➢ After connecting the vial and pumping it with fore vacuum the vacuum gauge VM2 must be at least 150 micro bar otherwise an error message is given.

VM1 Leak Threshold: ➢ The pressure of vial including all preparation line pumped with high vacuum measured with gauge VM1 must be at least 200 micro bar otherwise an error message is given.

Acid Temperature: ➢ Oven temperature (programmed by microprocessor) must be set to this value.

Reaction time 1: ➢ Reaction time of carbonate. Time starts as soon as the 1st acid drop is injected.

Reaction time 2: ➢ Pump out time of non-condensable gases.

Transfer time: ➢ CO_2 transfer time from trap 1 to trap 2

VM1 Expansion: ➢ If the CO_2 gas pressure released from trap 1 is more than this value, the gas is systematically expanded and pumped until a pressure beneath this threshold is achieved.

6.2.3 EVALUATION @- TAB

Ion Correction Type

➢ Select ion correction type

Outlier Test

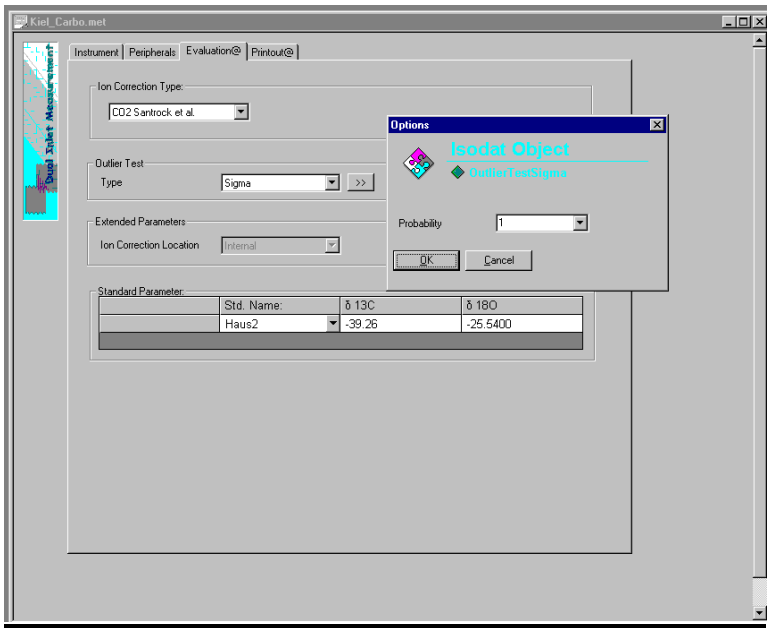
Type: Sigma

➢ The sigma outlier is varying criteria of rejection according GAUSS. It simply rejects the values outside a barrier of 1 to n times the standard deviation.

Standard Parameter

➢ Select a standard name (predefined in standard table) or edit the delta values (user defined) These values are isotope ratio of ^{13}C and ^{18}O of your standard gas (in this method gas in the right side of bellow: see Peripherals, Dual Inlet System, Reference).

Fig: 6.4 Evaluation @-Tab



6.2.4 PRINTOUT @- TAB:

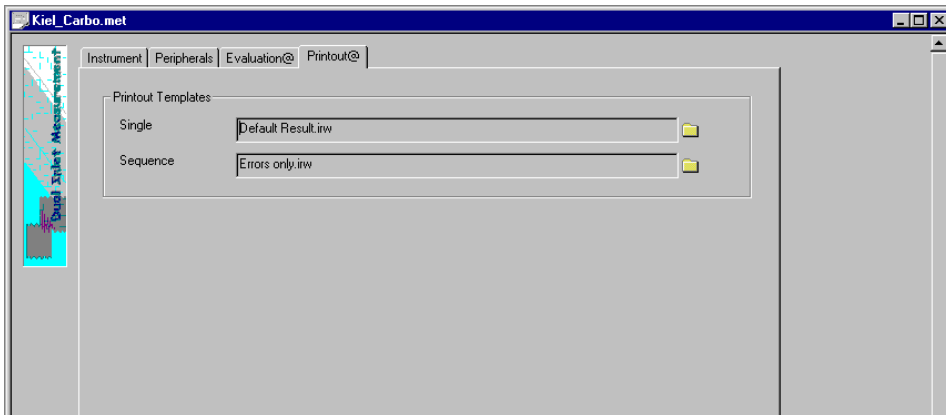
Single:

- Single print select a print template from the Result Workshop for an individual printout per sample.

Sequence:

- Sequence Print select a print template from the Result Workshop for a reduced print per sample within a sequence summary.

Fig: 6.5 Printout @-Tab



6.3 HOW TO PERFORM PRESSURE PRE-ADJUST

Each dual inlet acquisition requires a good and precise matching between sample gas and standard gas.
Since the amount of sample gas is limited and generally is less than 1 micro mol carbon-dioxide, it is necessary to match the standard gas as quick as possible to sample amount.

The Pressure Pre Adjust procedure operates as follows:
Once the CO_2 gas is released from trap 1 -and just before trapping in trap 2- the software measures the CO_2 gas pressure via VM1 manometer. According to this pressure the computer calculates the ion intensity of mass 44 and adjusts by changing the bellow volume on the standard side the same ion intensity.

The Pressure Pre Adjust parameters are factory set. Nevertheless a second adjustment during the installation of *KIEL CARBONATE DEVICE,* can be applied users laboratory (after changing hardware of IRMS like ion source filament, capillary, micro volume etc).

Proceed as follows to perform Pressure Pre Adjust parameters:

- Put e.g. 40 µg carbonates in a vial and perform an automatic acquisition.
- Note the VM1 pressure just before sample gets trapped from trap 2.
- Measure ion intensity of mass 44 as soon as the gas enters the mass spectrometer.
- Put the values of VM1 and ion intensity in "Hardware ISL Script Parameter / Pressure Pre Adjust" in line "Pressure 1" and "Signal 1".
- Do the same procedure with e.g. 80 µg.
- Put the values of VM1 and ion intensity in "Hardware ISL Script Parameter / Pressure Pre Adjust" in line "Pressure 2" and "Signal 2".

6.4 HARDWARE ISL SCRIPT PARAMETER

These hardware parameters are factory set and are a part of process to do carbonate analysis with Kiel Carbonate Device. Generally it is possible to do all kinds of carbonate analyses without changing the factory set parameters. Since the unit can be connected to any dual inlet IRMS we recommend to change the following parameters to optimize the specific application performed.
The following hardware parameter can be set in Instrument Control Carbonate Device:

6.4.1 PRESSURE PRE ADJUST-TAB (see How to perform Pressure Pre Adjust)

Pressure 1 (µBar):
- 300
- The VM1 pressure with e.g. 40 µg carbonate

Signal 1 (mVolt):
- 3000
- Ion intensity of above carbonate amount

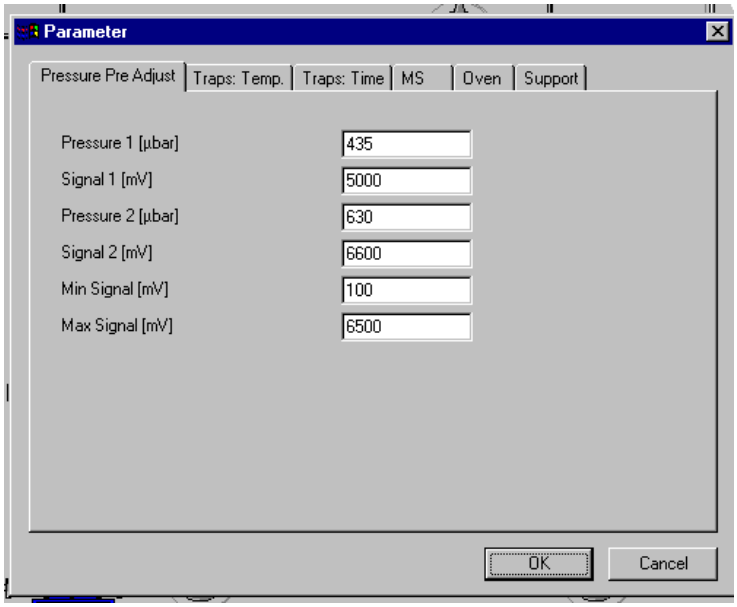
Pressure 2 (µBar):
- 700
- The VM1 pressure with e.g. 85 µg carbonate

Signal 2 (mVolt):
- 7000
- Ion intensity of above carbonate amount

Min. Signal (mVolt):
- Minimum acceptable ion intensity to perform measurement

Max. Signal (mVolt):
- Put 6500 for IRMS (Delta^{PLUS}, Delta^{PLUS} XL, MAT 252) (Preamplifier dynamic range 10V). In case ion intensity of mass 44 is higher than this value software waits until above settlement is reached.
- Put 36000 for IRMS (DELTA XP, MAT 253) (Preamplifier dynamic range 50V). In case ion intensity of mass 44 is higher than this value software waits until above settlement is reached.

Fig: 6.6 ***Pressure Preadjust Tab***



6.4.2. TRAPS: TEMP.- TAB

Pump Temperature (°C):

- 150
- Heat and pump out temperature of traps 1 and 2 before and after each carbonate measurement in order to remove any impurities.

Close V4 Temperature °C:

- -20
- Initial pump out and cool temperature of trap 1.
- During leak test period the valves # 12 (22), 1, 2, and 4 are open. If the leak test is successful the software starts to cool trap 1 in order to trap the produced gasses of prepared carbonate. As soon as the trap1 temperature reaches -20°C valve 4 gets closes.

Start Transfer Temperature (°C):

- -15
- Initial temperature to transfer CO_2 gas from trap 1 to trap 2. I.e. as soon as the trap temperature is -15 °C valve 3 opens and starts transfer of CO_2 from trap 1 into trap 2.

Measure Temperature (°C):

- 30
- Trap 2 temperature just before starting an acquisition.

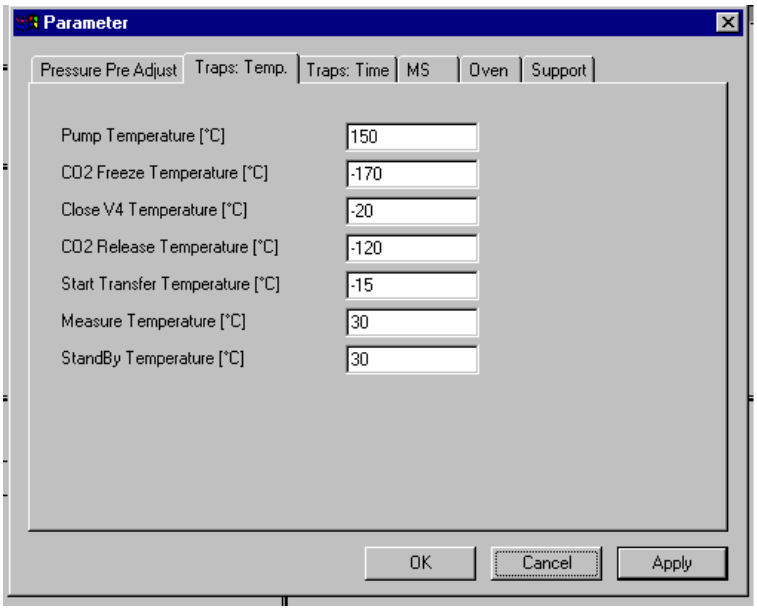
Standby Temperature (°C):

- 30
- At this temperature traps 1 and 2 are set after finishing an acquisition set.

Pump time (sec):

- 120
- This is the pumping time after setting the traps to pump temperature.

Fig: 6.7 ***Traps: Temperature-Tab***



6.4.3 TRAPS: TIME- TAB

Expansion Pump Time (sec):

- 60
- This is pumping time of a part of CO_2 gas if the pressure according VM1 is higher than defined.

Expansion equilibration Time (sec):

- 60
- Waiting time after expansion of CO_2 gas before next action.

6.4.4 MS- TAB

Sample Side Pump Time (sec):

- 3
- Pumping time of the volume between valve 16, 15 and 32 of dual inlet.

6.4.5 Oven- Tab:

Acid Temperature Tolerance (°C):

- 1
- If the oven temperature changes more than ± above value the acquisition stops and gives an error message.

Leak test Time (sec):

- 120
- If within this time the pressure of VM1 in sample preparation line is not reached the acquisition will skip this line and gives an error message. Lines 1/1, 1/2, 2/1 and 2/2 are excepted. If one these lines shows a leak the system stops with FATAL error.

Acid Dropping Time (sec):

- 30
- If within this time no acid drop can be counted the system stops with FATAL error. If at least 1 acid drop could be counted in this case the current sample will be measure and then the system stops with FATAL error.

6.4.6 SUPPORT- TAB:

Standby Drop Interval (sec):

- 3600
- If the system is in Standby and Drop mode (e.g. after finishing or stopping an acquisition). Every interval time (in this example 3600) one acid drop will be injected into waste vials (2/1 and 2/2). The time remaining the system stays in pump mode.

Drop Test: Number of Drops:

- 5
- Number of drops during an Acid Drop Test (refer to "Instrument control" Carbonate Device)

LN_2 switch off Temperature (°C):

- -150
- As soon as trap 1 temperature ≤ -150°C the solenoid valve of the liquid nitrogen tank is closed automatically to avoid an overflow of liquid nitrogen.

Cooling Setpoint (°C):

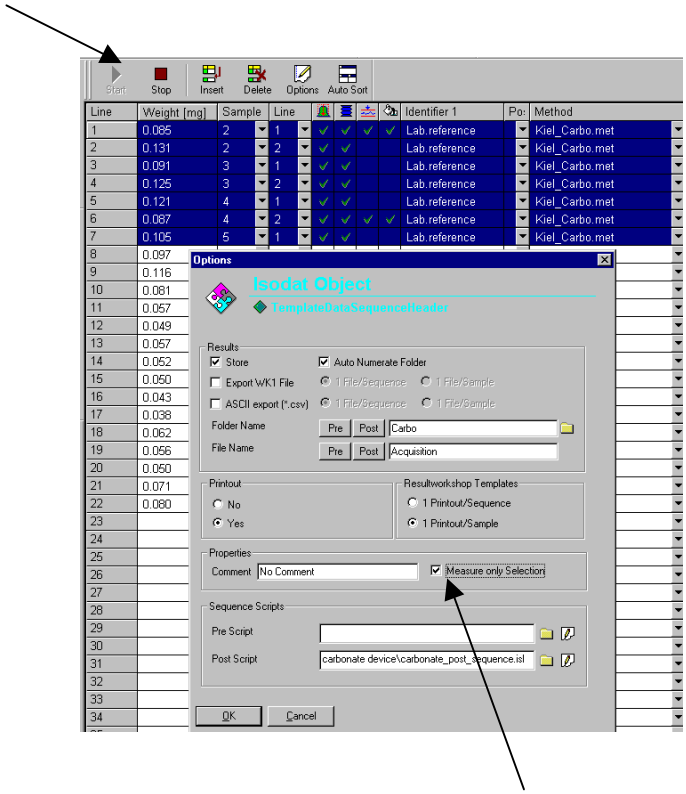
- 23
- Below this temperature (ambient temp.), the traps must be cooled by liquid nitrogen.

6.5 PREPARE THE CARBONATE AND IRMS FOR SAMPLE MEASUREMENTS

- Always take clean vials and make sure, that during the sample preparation no dust or other impurity falls inside the vial.
- Place the sample exactly at the bottom of vial.
- Do not leave the filled or clean vials for a long time outside of oven.
- After placing the magazine inside the oven make sure that the door is properly closed and do not start the measurement immediately. Even if the oven shows the right temperature it takes at least 15 min until the vials are at the oven temperature.
- Make sure that the oven temperature does not change more than 0.5 °C within 15 minutes.
- Make sure that at position 1/1 and 2/1 (pump position) clean vials without sample a are placed.
- Place a few standard carbonates with known values in each 7^{th} or 9^{th} location in order to test the quality of your measurements or for calculation of your samples.
- In case the carbonate unit was not used for more than 12 hours it may be, that the first two measurements do not have the same precision as usual. Put at these position more sample than necessary.
- Make sure that liquid nitrogen tank is properly filled and the manual valve (next to magnet valve) is open. Take care that the liquid nitrogen filling tube is under the coil of magnet valve.
- Make sure that the acid drop counter and O-ring are clean (see how to clean acid drop counter).
- Stay at least during the first measurement near the units and watch the measurement procedure.
- Watch the lights on liquid nitrogen refill unit during the first filling procedure of liquid nitrogen and make sure that the lights and liquid nitrogen level operates according the description on page 3-13.
- Put enough gas in the standard bellow. If there is a reference refill unit connected to standard side of IRMS check the valve is open.

- Fill the sequence table with sample name, wt, …
- A background measurement should be performed at least each 7-8 samples.
- Reference refill should be performed at least each 6-8 samples.
- For each measurement / magazine a specific file-folder to be used.
- Start the acquisition.

Press here to start



Click here if only specific (marked) vials should be measured (e.g. 1-7).

- Define results to store or export.
- Result files should be titled like e.g. Carbo Define Printout

Post Script:

- if "standby and drop"- mode is desired after end of acquisition put: device\carbonate_post_sequence_isl

- Press "OK" to start the acquisition

6.6 EXAMPLE OF A MEASUREMENT PROCEDURE (1/2)

The following steps explain which action takes place during the measurement of carbonate samples: e.g. measurement started from vial 2/1 (vial 2 / line 1). The parameters are pre-defined by the user via peripherals parameter (→ PP) and Hardware, ISL script parameter (→ HSP).

PP: Peripherals parameter (see method)
HSP: Hardware, ISL script parameter
VM 1: Vacuum gauge of trap-region
VM 2: Vacuum gauge of the oil rotary pump

- When acquisition is user started the Carbonate unit is initialized.
  Vial 1/1 (vial 1 / line 1) and vial 1/2 (vial 1 / line 2) are connected,
  checked by µ switch and pumped.
  - Valves # 1, 2, 3, 4, 5 and 9 are opened.
- Pressure is measured by VM1 and compared with “leak check threshold (→ PP)”.
- Trap 1 and Trap 2 are heated out at 150°C (→ HSP); e.g. 120 sec (→ HSP).
- Oven temperature, e.g. 70°C (→ PP), and its tolerance ± 1 °C (→ HSP) is checked.
- Vial 1/1 is removed and magazine rotates to position 2.
- Vial 2/1 is connected to acid housing valve and checked by µ switch.
- Rotary pump pumps out the vial 2/1 and corresponding lines.
- Leak check is performed (VM 2 gauge indicates if leak is present);
  leak test threshold (→ PP).
  - Valves # 1, 2, 3, 4, 5 and 9 as 7, 13 and 23 are open.
- Vial 2/1 is pumped out by high vacuum:
  - Valves # 2, 3, 5 and 13 are closed.
  - Valves # 4, 7, 9, 12 and 23 are open.
- Leak check is performed (VM 1 gauge indicates if leak is present);
  leak test threshold (→ PP). Time: 120 sec (→ HSP).

PP: Peripherals parameter (see method)

HSP: Hardware, ISL script parameter

VM 1: Vacuum gauge of trap-region

VM 2: Vacuum gauge of the oil rotary pump

- Trap 1 (T1) is cooled down to -170°C (→ HSP).

  At T< -50°C (→ HSP).
  - Valve # 4 is closed.
- As soon as T1 is cooled down acid is injected into the vial.

  Number of acid drops (→ PP).
- The reaction between acid and sample takes place: reaction 1 (→ PP);

  the produced gases as CO_2 and H_2O are trapped by T1.
- Non condensable gases are pumped out T1: reaction 2 (→ PP).
  - Valve # 4 is open.
- T1 is heated and CO_2 is released while H_2O is still frozen.
  - Valve # 4 is closed.
  - Valve # 2 is open.
- CO_2 pressure is measured via VM1: expansion threshold (→ PP).

  (If the pressure is too high: CO_2 is pumped out until acceptable value is achieved: pumping time (→ HSP).
- Standard-gas pressure is pre-adjusted to the same value as sample pressure: pressure pre-adjust (→ HSP).
- Trap 2 (T2) is cooled down via liquid nitrogen to -170°C (→ HSP).
  - Valve # 3 opens at -15 °C (→ HSP).
- CO_2 is transferred from T1 to T2.

PP: Peripherals parameter (see method)

HSP: Hardware, ISL script parameter

VM 1: Vacuum gauge of trap-region

VM 2: Vacuum gauge of the oil rotary pump

- T1 is heated and H_2O is pumped out to 150°C (→ HSP).
  - Valve # 4 open.

    T2 is heated to measure temperature of 30°C (→ HSP).

    CO_2 is released to IRMS.
  - Valve # 3 closed.
- Vial 2/1 is removed and magazine moves to pump position.
- Peak center is performed.
- Standard-gas pressure is high-end adjusted to the same value as sample pressure.
- Data acquisition is started and the results are stored and / or printed.
- Vial 2/2 is connected during the acquisition of sample 2/1 and the procedure is repeated from step 7) on.

Note: ***If vials 1/1, 2/1 as well as 2/1 and 2/2 indicate a leak the acquisition is stopped and FATAL error message appears.***
In case of another vial showing a leak the measurement is continued with the following vial.

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