High Temperature Conversion

Elemental Analyzer (TC / EA)

OPERATING MANUAL

Issue 9/2003

Ident. No. 112 76 01

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

Thermo chemical elemental analyzer TC/EA

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

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

EN 50082-2, EN 61000-4-2, -3, -4, -5, -6, 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, 16. Dezember 1998

Der Entwicklungsleiter:
Head of Engineering:
Responsabile construzione:

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.

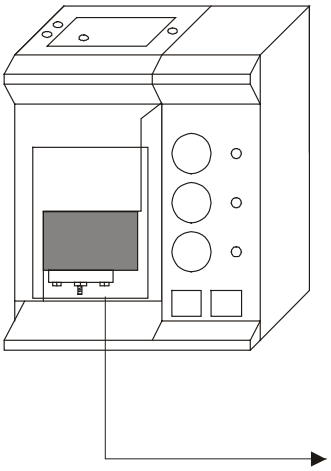
By signing this document I am/ we are certifying that the a. m. parts are free from hazardous materials. In case the parts have been used for the analysis of hazardous substances I/we attest that the parts have been decontaminated before sending them to Thermo Finnigan MAT.

_____
Datum / date

_____
Unterschrift / signature

*) Bitte vollständig ausfüllen / Please fill in completely

LOCKING PIN



The spiral heating system is locked during transportation by a locking pin.

The pin has to be removed as follows:

Remove the front cover plate by lifting.
Unscrew the screw No.1.
Unscrew the screws No.2 alternately.
Pull out the locking pin carefully.

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ABOUT THIS MANUAL

This Manual starts with an overview about TC/EA. Major aspects of how to set up the system prior to starting any application are described. An explanation of the different applications follows providing detailed information illustrated by numerous examples. For technical information refer to chapter 11.

NOTE: Thermo Finnigan denies liability for errors and omissions within this Manual.

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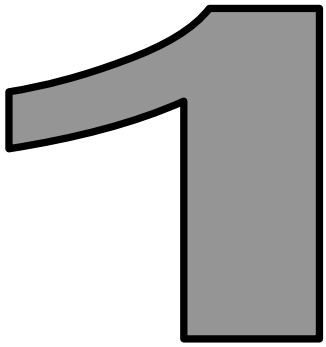

PRECAUTIONS

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PRECAUTIONS

1 Power requirements

- Mains connection: plug the cable into a 220V/230V socket only!
- Never touch the plug with wet hands!

2 Make sure that the TC/EA is not exposed to direct sunlight.

3 Make sure that the cooling system of the TC/EA is not impaired.

4 To avoid damage to the internal circuits and to the external surface keep the system away from heat (i.e. radiators, etc.).

5 Enough space at the rear panel of the TC/EA is needed for proper ventilation.

6 Avoid using aerosol sprays near the system. This can cause sudden ignition of the spray.

7 Do not clean the TC/EA with either paint thinner or alcohol or other organic solvents.

8 Do not place any objects - especially liquids - upon the TC/EA.

9 Place the system on a flat, solid surface that can carry at least 150 kg.

10 Do not put any objects upon the main power supply cable.

INSTALLATION REQUIREMENTS

The TC/EA can be connected to any current Thermo Finnigan MAT IRMS equipped for Continuous Flow application.

POWER:	***230 V, single phase, 8A***
DIMENSIONS:	***45 X 70 X 50 cm (WxDxH)***
WEIGHT:	***50 kg***

The specifications are subject to change without notification.

MAINTENANCE MEASURES FOR TC / EA (1/2)

Due to our knowledge arising from almost 100 TC/EA devices in the field and to feedback from our users during the last three years, we inform about maintenance measures. They may facilitate proper work, may be helpful to keep your device in good order and increase the life time of the TC/EA reactor and the furnace heater.

As the life time of the furnace heater is limited, do not heat it to higher temperatures than necessary!

This implies in detail:

- to measure:
  - ***oxygen*** of ***organic*** samples at 1325 °C - 1350 °C
  - ***oxygen*** of ***inorganic*** samples at 1450 °C
  - ***hydrogen*** of ***organic*** samples at 1400 °C
  - ***hydrogen*** of ***inorganic*** samples at 1450 °C
  - ***water*** (sample amount: 0.5 µl) at 1400 °C
- to cool down the furnace:
  - If you do not want to perform any analysis ***for about one day*** (e.g. over night), cool down the furnace to 600 °C and set the column to 150 °C.
    Cooling speed of furnace: 300 °C per hour.

MAINTENANCE MEASURES FOR TC / EA (2/2)

- If you do not want to perform any analysis ***for more than one week***, cool down both furnace and column to ambient temperatures.
  Cooling speed of furnace: 300 °C per hour.

- If the TC/EA has not been in use ***for a long time*** or if it was ***off***, heat the column to 300 °C over night. Heat the furnace to the desired temperature using a speed of 300 °C per hour.

- Always watch the background of the masses 28 and 40. If the values exceed those given in the TC/EA Operating Manual by at least 20 %, perform a leak test. A small leak will crack the ceramic tube and after a while the glassy carbon reactor, too.

- After 70 to 100 measurements cool down the reactor to 500 °C and take the graphite crucible out of the reactor using a special tool, which can be delivered on request. After cleaning insert it again.

- If you want to send back the furnace, fix the heater using a special holder, which was delivered with TC/EA. To handle it properly, read the “Unpacking” page, which precedes Chapter 1 in the TC/EA Manual.

- In case of a new or replaced furnace, set the heating transformer to initial voltage (see “Transformer” page in the TC/EA Manual).

TRANSFORMER

The reactor heating stops at a lower temperature than selected, because the resistor value increases over time. Therefore, a higher voltage setting becomes necessary.

NOTE: A new reactor heater has a resistor of approximately 3.0 Ω.
After six months of operation, the resistor is about 8 - 9 Ω.

For a new setting proceed as follows:

- Switch “OFF” main power supply.
- Remove the left side panel.
- Move wire (B) to the next higher value (see fig. S 6).

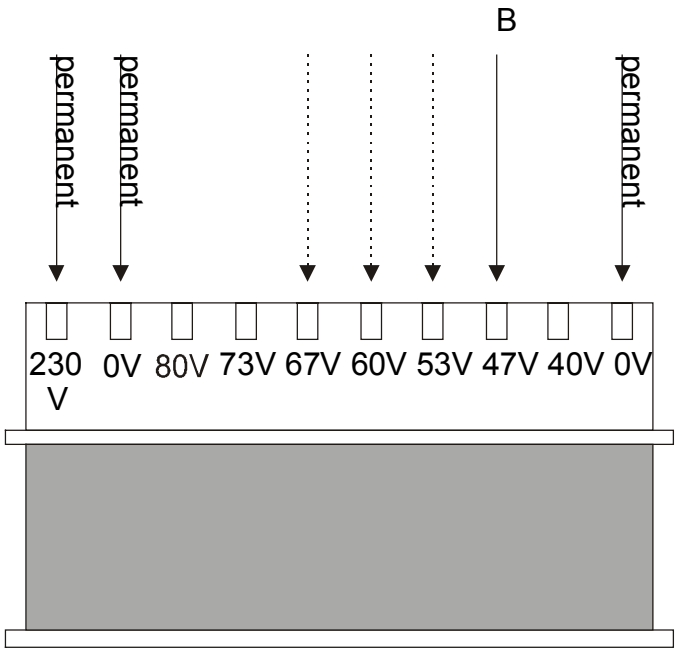

fig. S 6

WARNING: Switch ***OFF*** main power prior to working to prevent an electrical shock!

High Temperature Conversion

Elemental Analyzer (TC / EA)

INTRODUCTION

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INTRODUCTION (1/2)

High precision analysis of the stable isotopes of oxygen has been crucial for the development of stable isotope geochemistry. While procedures for the analysis of $^{18}O/^{16}O$ of carbonates, water and silicates have been worked out early and have until recently remained largely unchanged, this is not true for the analysis of most forms of organic and inorganic oxygen.

The isotopic analysis of organic oxygen largely bases upon carbon reduction (carbon reduction method of Unterzaucher and Schütze), in which oxygen is converted to CO. The reaction is generally carried out in quartz tubes at modest temperatures (i.e. 400 - 1500 °C) in the presence of graphite and nickel (as catalyst).

Since quartz contains oxygen, all current techniques are associated with a blank. Fluorine containing samples cannot be analyzed because of the reaction of hydrogen fluoride with quartz and the subsequent water formation. A lot of samples - e.g. sulfates - also cannot be measured either, because at higher reaction temperatures the in-creasing interaction of carbon and the quartz becomes unacceptable.

As a consequence, isotope ratio measurement of oxygen in organic matter has not kept pace with methodological advances that allowed rapid, easy and precise measurement of ^{13}C and ^{15}N by Dumas combustion, as embodied in the CE Elemental Analyzer analyzing via Continuous Flow (CF) inlet system.

To overcome these disadvantages, it was necessary to develop a new Elemental Analyzer, the Thermo Finnigan TC/EA, built especially for oxygen isotope analysis of a wide variety of organic and inorganic compounds (including water) at reaction temperatures up to 1500 °C.

INTRODUCTION (2/2)

The particularity of the TC/EA is a new two-tube technique:

The so called "High Temperature Conversion Reactor" consists of an outer ceramic mantle tube of aluminum oxide and an inner glassy carbon reactor. The space between internal and external tube is continuously flushed with helium to avoid any undesired oxidation.

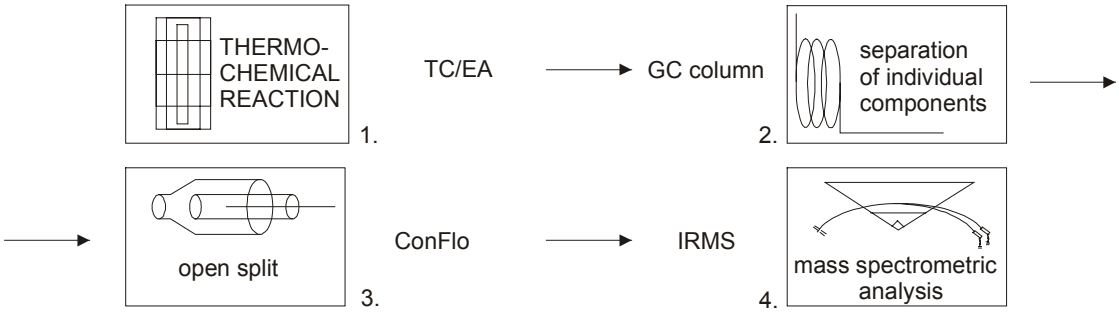

fig. 1

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High Temperature Conversion

Elemental Analyzer (TC / EA)

COMPONENTS OF TC / EA

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COMPONENTS OF TC / EA

Pos.	*Part No.*	*Notification*	*Quantity*	
1	112 10 20	reactor holder	1	piece
2	10 877 70	quartz wool	1	piece
3	111 73 32	graphite crucible	5	pieces
4	111 73 90	silver capsules 4 x 6 mm	1	box
5	111 74 30	silver wool	1	piece
6	112 11 20	O-ring, vitone	4	pieces
7	112 11 30	olive, ferrule	5	pieces
8	112 11 40	screw	5	pieces
9	111 74 00	glassy carbon granulate	50	gr
10	112 13 10	reactor, glassy carbon	1	piece
11	112 13 50	tube, graphite	1	piece
12	112 13 30	connector ox. Reactor	1	piece
13	112 13 20	ceramic tube	2	pieces
14	112 13 60	crosspiece	1	piece
15	069 11 30	hose	3	m
16	052 13 20	hose coupling	2	pieces
17	112 31 60	crucible holder	1	piece
18	060 54 70	stainless steel capillary 1/16´´ x 0.08 mm	2 x 3	m
19	112 10 40	fan (12V)	1	piece
20	106 90 90	main power supply cable	1	piece
21	201 18 40	fuse	1	set
22	112 33 30	benzoic acid	1	gr
23	109 13 00	gloves (small)	1	pair
24	109 12 90	gloves (medium)	1	pair
25	112 13 90	exhaust support	1	piece
26	114 13 80	graphite crucible remover	1	piece

NOTE: Before beginning the Setup, it is important to read the warning information in the chapters "Gas supply", "Working with the gas cylinders" and "Gas connections".

High Temperature Conversion

Elemental Analyzer (TC / EA)

HARDWARE LAYOUT

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HARDWARE LAYOUT (1/2)

TC / EA front panel

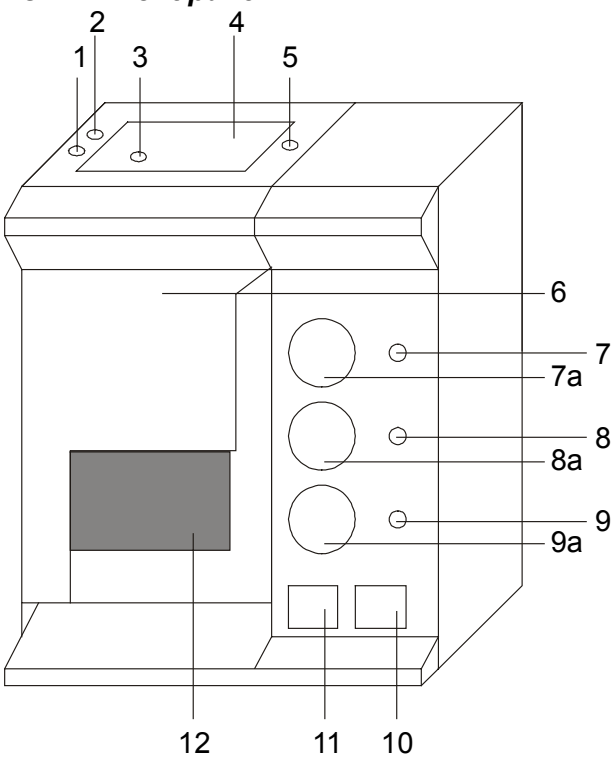

fig. 2

1	Compressed air Autosampler connection (permanent)
1a	Compressed air Autosampler connection (time controlled) Impulse from ConFlo II/III
2	Reactor inlet
3	Autosampler installation platform
4	Carrier gas (He) outlet to Autosampler
5	Purge gas (He) outlet to Autosampler
6	Front cover plate (removable by lifting)
7	Purge gas (He) pressure regulator
7a	Purge gas (He) gauge
8	Carrier gas (He) pressure regulator
8a	Carrier gas (He) gauge
9	1% H_2 in He pressure regulator
9a	1% H_2 in He gauge
10	Reactor microprocessor temperature controller
11	GC column microprocessor temperature controller
12	Furnace

HARDWARE LAYOUT (2/2)

Rear panel

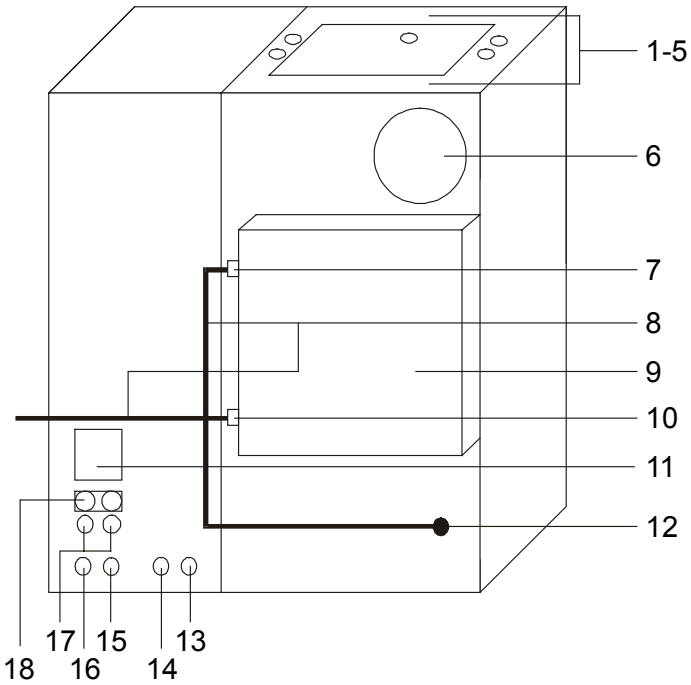

fig. 3

1 – 5	See ***fig. 2***
6	Fan
7	GC in
8	Stainless steel capillary 1/16´´
9	GC box
10	GC out (to ConFlo)
11	Main power (on/off switch)
12	TC/EA out (to GC)
13	Compressed air (permanently)
14	Compressed air (time controlled)
15	Carrier gas (He) in
16	1% H_2 in He
17	Fuses
18	Main power supply

High Temperature Conversion

Elemental Analyzer (TC / EA)

SETUP

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SETUP (1/2)

1 Fill the reactor as shown in fig. A.

2 Place the O-ring (vitone) at the top of the ceramic tube as shown in fig. B.

3 Remove the front cover of TC/EA as shown in fig. 2.

4 Place the properly filled ceramic tube inside the furnace through the reactor inlet (fig. 2).

5 Install the bottom outlet of the ceramic tube as shown in fig. C.

6 Stabilize the reactor by placing the holder beneath it (fig. D).
Put the fan close to the nut and connect the power supply wires.

7 Connect the Autosampler with the ceramic tube as shown in fig. E.

8 Connect time controlled compressed air from ConFlo II/III (manufactured at the end of 1997) to TC/EA (fig. G).

9 Connect permanently compressed air from IRMS to TC/EA.

Optional: If the ConFlo II/III has no compressed air outlets (manufactured before the end of 1997) ignore **9** and take both compressed air outlets (permanently and time controlled) from Elemental Analyzer (EA) to run the Autosampler.

10 Using the cross piece connect the main He supply to TC/EA as shown in fig. F
(see “gas supply”).

NOTE: “High Temperature Conversion” applications need He gas, which is free of water and oxygen. Although using He gas carrier of 99.999% purity, we recommend adding a gas purifier. The use of less pure gas may produce unstable results.

11 Set the main He supply to 4.0 bar (fig. H).

12 Adjust the pressure regulator of carrier gas (He) to 0.85 bar (fig. 2) ≅ 90 ml/min.

13 If operating with auxiliary gas (i.e. 1% H_2 in He), adjust this regulator to a slightly higher pressure (fig. 2). Otherwise, reduce pressure to a value below the carrier gas. The auxiliary gauge will automatically show the carrier gas pressure.

14 Measure He flow at the GC out (fig. 3). The He flow should be ≈ 90ml/min.

SETUP (2/2)

15 Perform a leak check!

NOTE: ***To perform a simple leak check, increase the He pressure using the pressure regulator. The corresponding pressure gauge should increase gradually, if there is no leak.***

16 Connect the power supply cable of TC/EA (fig. 3) to a 220V main power supply.

17 Switch main power “ON” (fig. 3) and make sure that the fan (fig. 3) is operating.

18 Ensure that the fan (fig. D) is operating.

19 Reinstall the front cover plate (fig. 2).

20 Set the GC column microprocessor temperature controller to 50°C.

(see: microprocessor temperature controller: (c) setting a new temperature value).

21 Set the reactor microprocessor temperature controller to 100°C (fig. 2).

22 When the temperature is stable, repeat the leak check.

23 Gradually increase GC column temperature to 300°C and reactor temperature to 600°C.

24 Leave the TC/EA unit for at least twelve hours (during the first installation only).

HOW TO GET STARTED WITH THE SYSTEM (1/2)

1 After achieving the temperatures mentioned above, repeat the leak check.

2 Set the He flow at 90 ml/min (GC column outlet).

3 Set the GC column temperature to 70°C and the reactor temperature to 900°C.

4 Connect the GC out (fig. 3) to the ConFlo II/III (fig. G) system and make sure that ConFlo II/III is connected via fused silica capillary and needle valve to your IRMS.

HOW TO GET STARTED WITH THE SYSTEM (2/2)

5 Implement all gas connections according to fig. G.

6 Switch the ion source of the IRMS ***"OFF"*** and slowly open the needle valve.

7 Make sure that the high vacuum in the ion source is at 3 - 1.5 x 10^{-6} mbar.

8 Switch the ion source "ON".

Expected background after one hour:

Mass	***measured in cup***			
2	2	< 200 mV		
3	3	< 20 mV	**NOTE:**	An electrostatic energy filter is required.
28	28	< 100 mV		
29	29	< 100 mV		
30	30	< 100 mV		
18	29	< 500 mV		
40	29	< 10 mV		
32	29	< 200 mV		

9 Repeat the leak check, if the background is 1.5 times higher than expected.

Set the reactor temperature at 1325°C.

Expected background after three days:

Mass	***measured in cup***			
2	2	< 200 mV		
3	3	< 20 mV	**NOTE:**	An electrostatic energy filter is required.
28	28	< 200 mV		
29	29	< 200 mV		
30	30	< 200 mV		
18	29	< 300 mV		
40	29	< 10 mV		
32	29	< 100 mV		

10 CO gas connection: see "Gas connections".

REACTOR FILLING (1/2)

1 filling for a sample wrapped in a silver capsule ***(diameter ≤ 3mm)***:

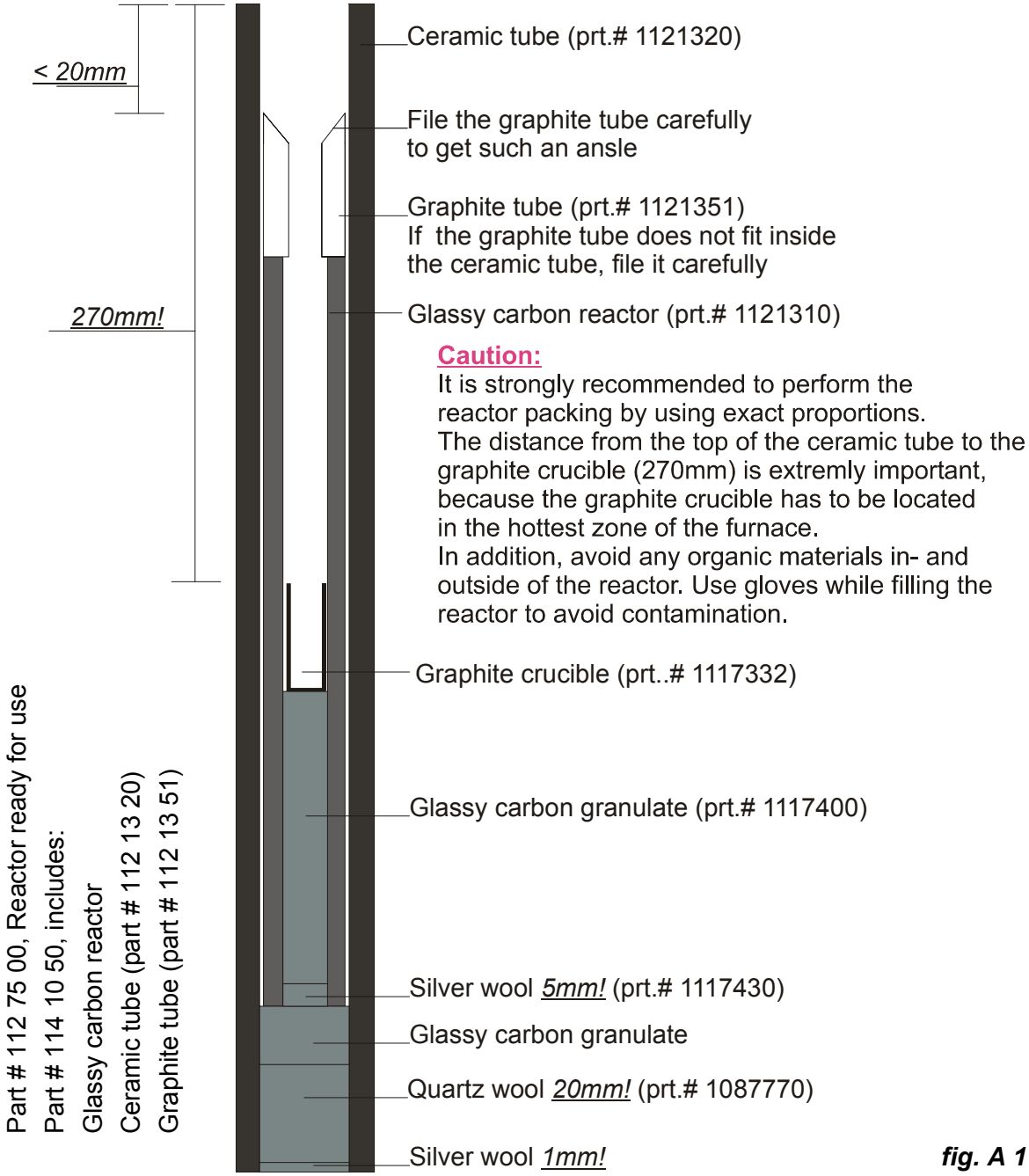
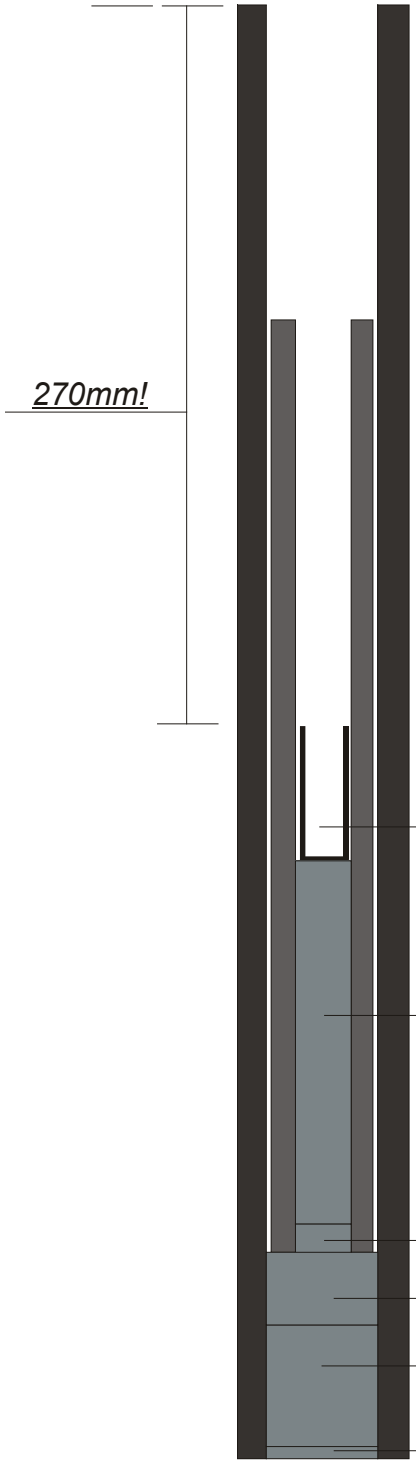


fig. A 1

REACTOR FILLING (2/2)

2 filling for a sample wrapped in a silver capsule ***(6 mm ≥ diameter ≥ 3mm)***:



Caution:
It is strongly recommended to follow the reactor packing by using exact proportions. The distance from the top of the ceramic tube to the graphite crucible (270mm) is extremly important, because the graphite crucible has to be located in the hottest zone of the furnace.
In addition avoid any organic materials from in- and outside of the reactor.

Graphite crucible (prt..# 1117332)

Glassy carbon granulate (prt.# 1117400)

Silver wool *5mm!* (prt.# 1117430)

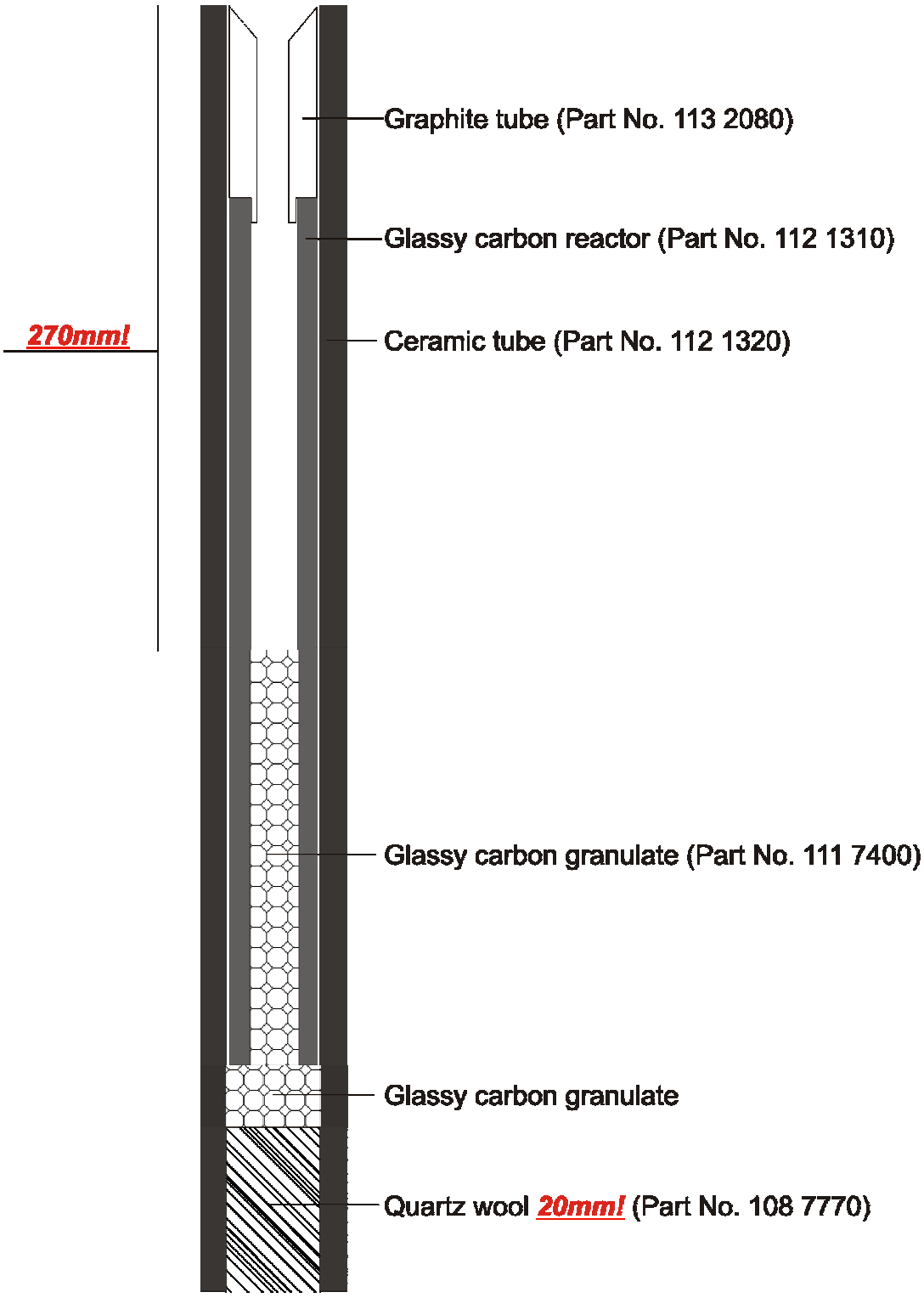
Glassy carbon granulate

Quartz wool *20mm!* (prt.# 1087770)

Silver wool *1mm!*

fig. A 2

Reactor Filling for Liquid Injection



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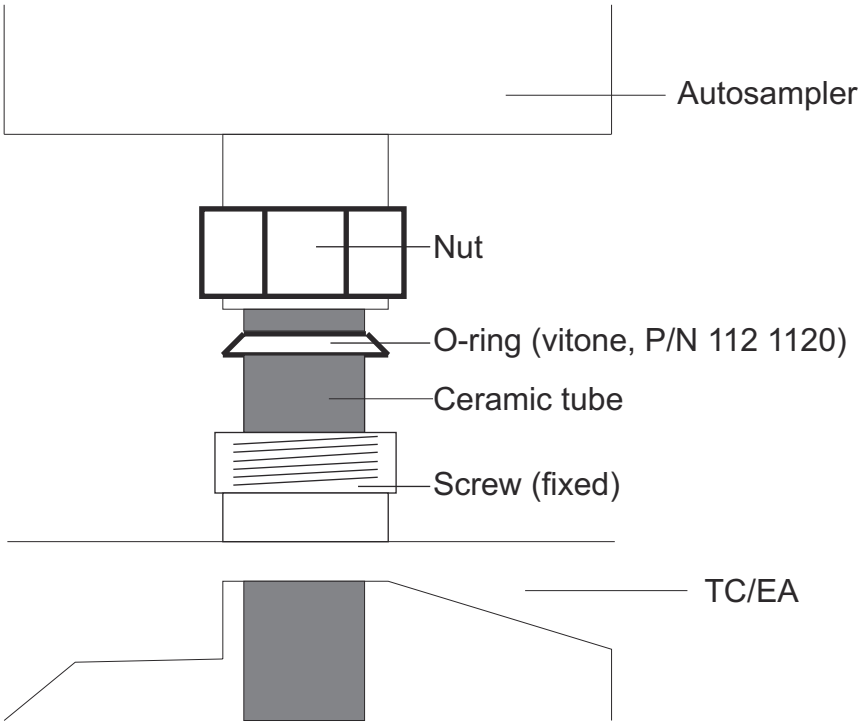
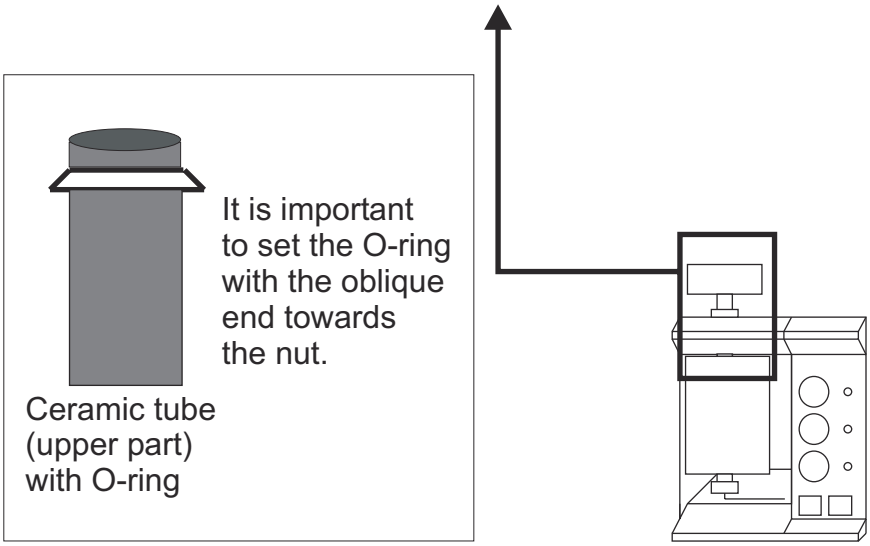
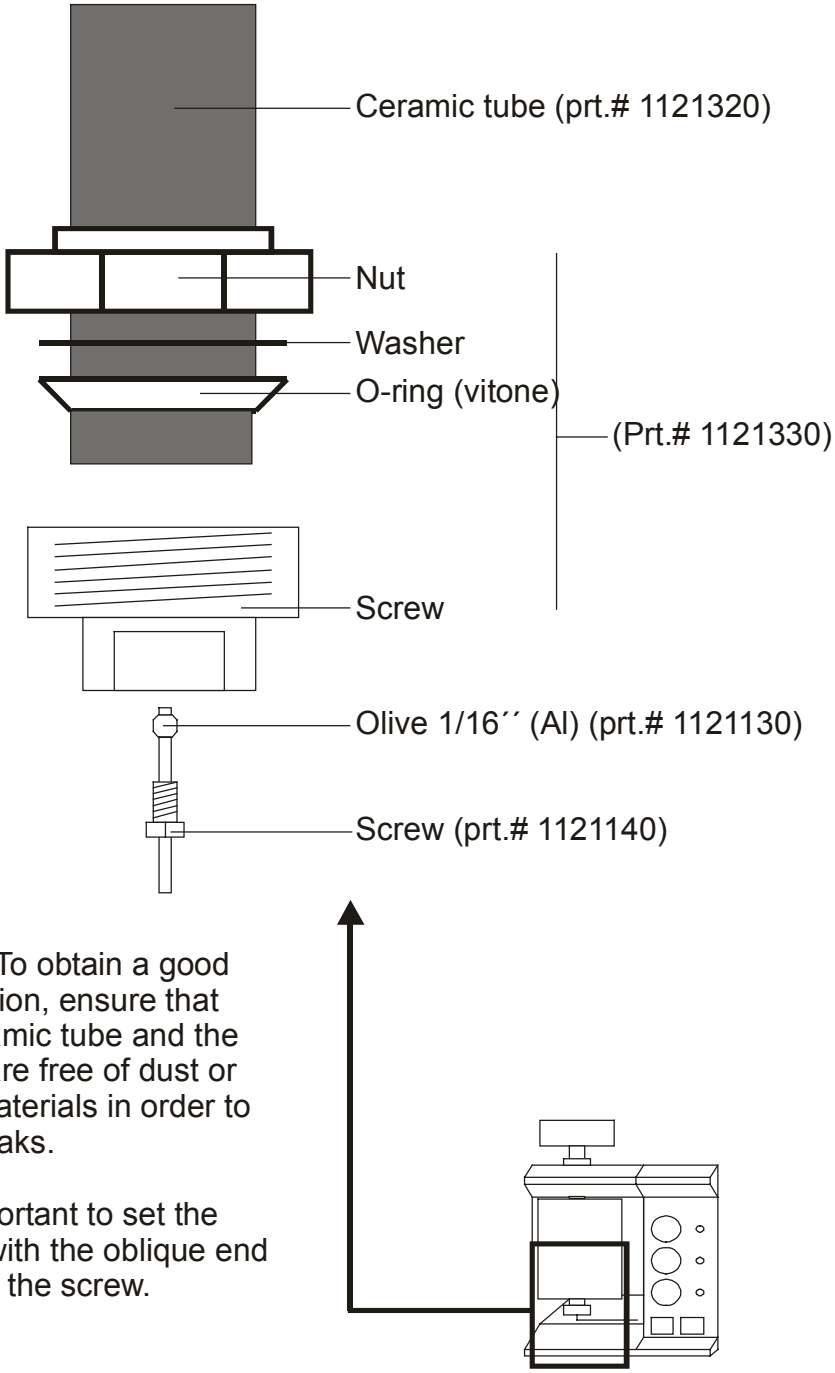
AUTOSAMPLER INSTALLATION



NOTE: To avoid any leaks make sure that the connection is properly established.



BOTTOM REACTOR CONNECTION

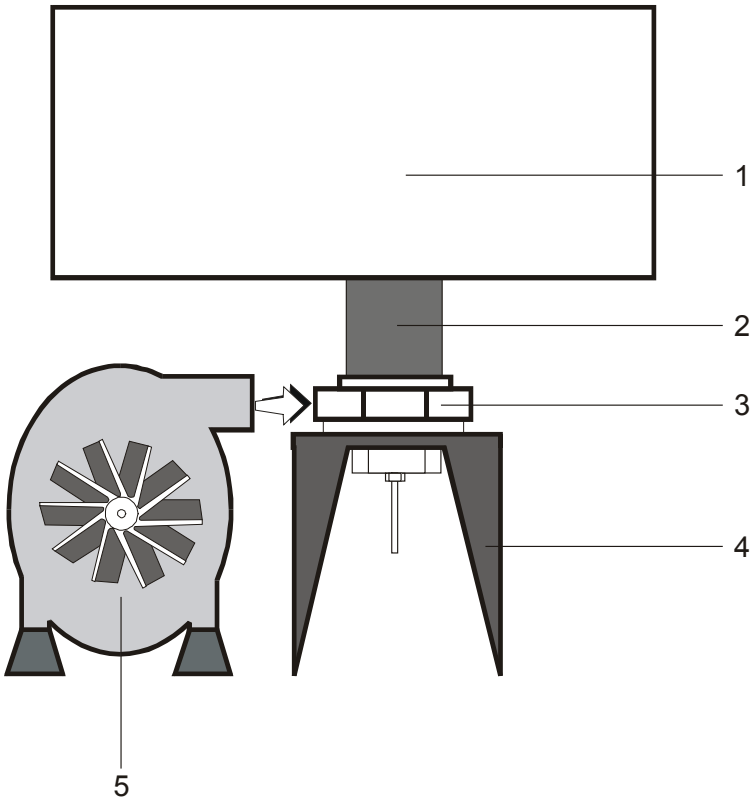


NOTE: To obtain a good connection, ensure that the ceramic tube and the O-ring are free of dust or other materials in order to avoid leaks.

It is important to set the O-ring with the oblique end towards the screw.

fig. C

REACTOR HOLDER AND FAN



1 Furnace
2 Ceramic tube
3 Nut
4 Reactor holder
5 Fan (12 V)
(# 112 10 40)

NOTE:

Connect the 12V fan to the power supply.

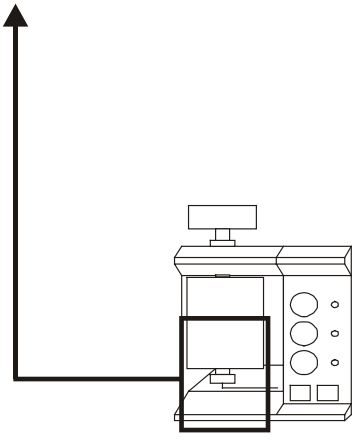


fig. D

MAIN HELIUM CONNECTION

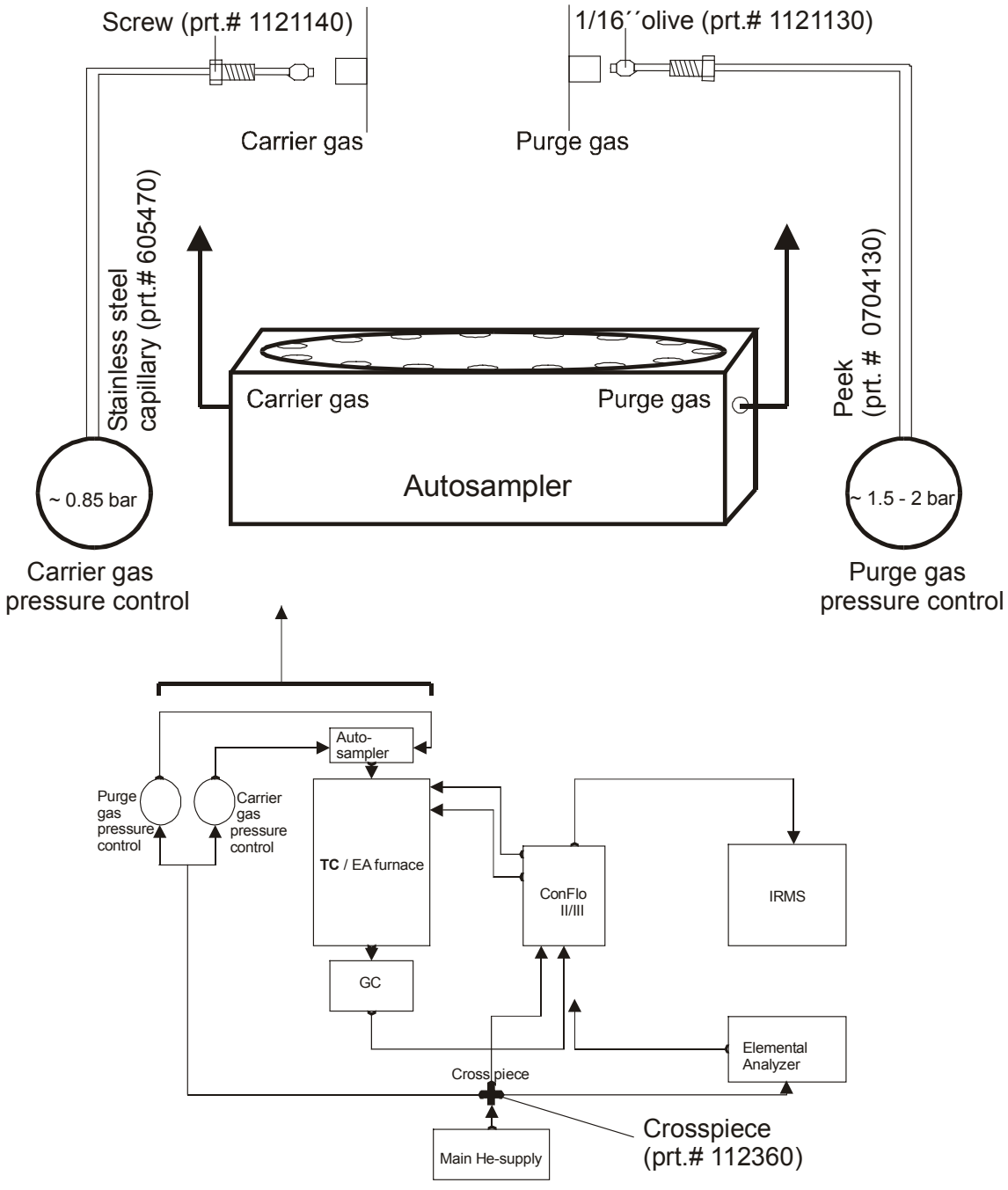


fig. F

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REACTOR CLEANING

After 200-300 samples have been measured (depending on application and size of samples) the reactor should be cleaned and the ash of the samples be removed.

Procedure

1 Reduce the reactor temperature to 50°C.
2 Reduce the column temperature to 50°C.
3 After reaching the temperatures turn ***"OFF"*** purge and carrier gas (He).
4 Switch ***"OFF"*** TC/EA (fig. 3).
5 Remove the Autosampler (fig. E).
6 Remove the front cover plate (fig. 2).
7 Put away the fan (fig. D).
8 Unscrew the bottom reactor connection (fig. C).
9 Pull out the reactor carefully.
10 Carefully pour the reactor filling on a clean and dust-free surface.
11 Separate the ash from the glassy carbon granulate (the granulate is still usable).
12 Exchange the graphite crucible.
13 Remove deposits from inside and outside of the reactor by using the graphite rod.
14 Renew the quartz wool. If necessary, renew the silver wool.

Replace Graphite Crucible

After approx. 70 - 100 samples have been measured (depending on sample amount and material) the graphite crucible should be cleaned.

Procedure

1 Set reactor temperature to 500° C.
2 After reaching a temperature of 500°C
(it takes approximately 45 min.) reduce He flow to < 0.2 bar
3 Switch "OFF" TC/EA (fig.3).
4 Insert He dilution if ConFlo III is installed
or close needle valve to IRMS.
5 Remove Autosampler (fig.E).
6 Remove graphite tube.
7 Insert special tool (crucible remover) inside graphite crucible (fig. F1).
8 Pull graphite crucible out of the reactor using gloves ***(crucible is hot!)***.
9 Drop new graphite crucible into the reactor or remove the deposits
outside of the graphite crucible and use it again.

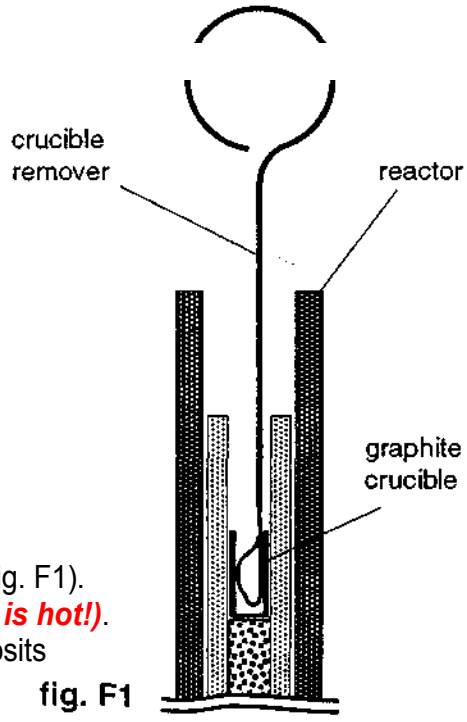

fig. F1

High Temperature Conversion

Elemental Analyzer (TC / EA)

GAS CONNECTIONS AND SUPPLY

Issue 11/2001

Thermo Finnigan

GAS CONNECTIONS

CO gas connection / H_2 gas connection

- Use the Ref 1 port of ConFlo II/III to connect standard gas (H_2, fig. G).
- Use the Ref 2 port of ConFlo II/III to connect standard gas (CO, fig. G).

Optional: If the IRMS has a dual inlet system, inject the standard gas (CO) via volume one or volume two.
Other external gas connections are also located at ConFlo II/III rear side (fig. G).

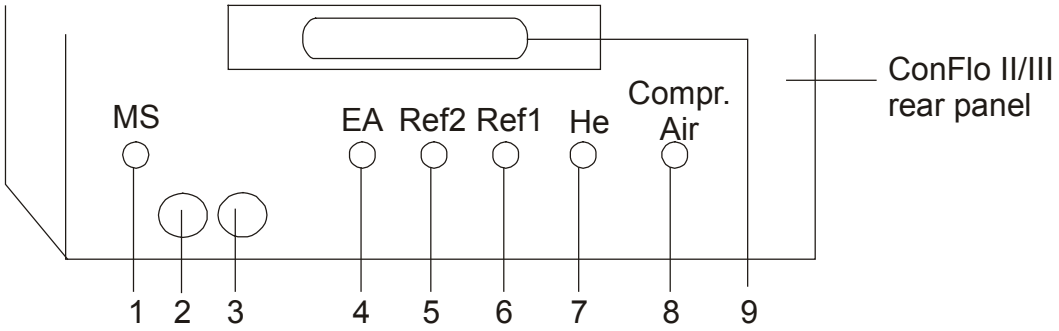

fig. G

1 Fused silica capillaries to IRMS
2 Remote EA start cable (not necessary, if position 3 is available)
3 Compressed air, time controlled (ConFlo II/III)
4 EA or TC/EA inlet
5 N_2 or H_2 for hydrogen determination
6 CO_2 or CO for oxygen determination
7 Carrier gas (He) in
8 Compressed air (permanently)
9 Cable connection

WARNING:

CO gas is toxic!
H_2 gas may form explosive mixtures with oxygen!

Inform yourself how to handle these gases by reading the directions for use and asking your local gas cylinder supplier.

Thermo Finnigan does not take any responsibility, if these gases (H_2, CO) are used incorrectly.

The ConFlo III system is provided with an exhaustor you should use.

Thermo Finnigan
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GAS SUPPLY

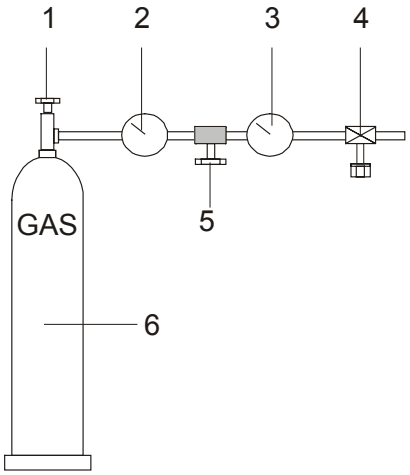
To operate the system of TC/EA, ConFlo II/III and IRMS, several gases are required.

The following purities are provided:

- purge gas (He), carrier gas (He): 99.996% pure helium
- standard gas (CO): 99.997% pure carbon monoxide
- standard gas (H_2): 99.996% pure hydrogen
- auxiliary gas (1% H_2 in He)

NOTE: The pressure of new gas cylinders is about 200 bar for helium and hydrogen and about 60 bar for carbon monoxide.

The pressure has to be adjusted to ca. ***4 bar*** via the reducing valves mounted at the gas cylinder (fig. H).



1 Main valve
2 Manometer 200 bar (He)
3 Manometer 4 bar (He)
4 On / off valve
5 Reducing valve
6 Cylindrical gas supply

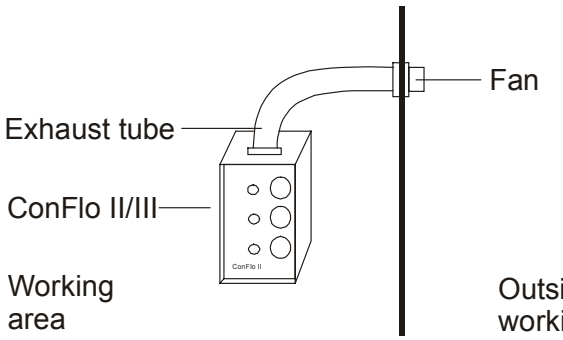
fig. H

WORKING WITH GAS SUPPLIES

WARNING: It is strongly recommended to fix the gas cylinders firmly to prevent them from toppling down!

WARNING: When working with carbon monoxide (CO) good ventilation is essential. Otherwise, the gas can be hazardous to your health!

1 Install an exhaust tube on top of your ConFlo II/III as shown in fig. K to remove the toxic carbon monoxide (CO) from inside the ConFlo II/III out of your working area.



NOTE: We strongly recommend a CO and H_2 detector with an alarm!

fig. K

WARNING: Fire or explosion may be caused by a leak in the hydrogen (H_2) supply!

2 Before starting the system, a leak check has to be performed.

- After mounting the reducing valve to the gas cylinder both valves (i.e. “on/off-valve” and “reducing-valve”) should be open as shown in fig. H.
- Open the main valve (fig. H) for two or three seconds to let the gas purge the whole valve system.
- Close “on/off-valve”. Then close “main-valve”.
- Mark manometer positions of “on/off-valve” and “main-valve” and wait for 10 - 15min.
- A leak may be present if the manometer positions have changed.
- To detect a leak, use soap solution on all valves and connections. Check for bubble formation.

High Temperature Conversion

Elemental Analyzer (TC / EA)

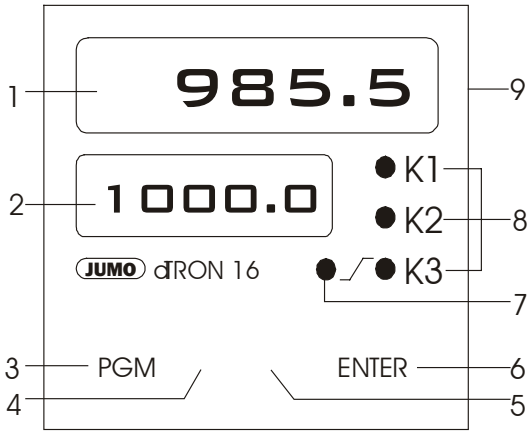
TEMPERATURE CONTROLLER

Issue 11/2001

Thermo Finnigan

MICROPROCESSOR TEMPERATURE CONTROLLER (1/2)

a) TC / EA reactor (microprocessor is factory programmed)



1 4-digit process display
2 4- digit setpoint display
3 PGM-key for parameter selection
4 Digt-key for selection of digit to be altered
5 Increment-key to alter the selected digit
6 Key for entering value
7 LED for ramp function (alight when configured)
8 Status indication output 1-3
9 Microprocessor temperature controller

fig. 4

Programming a new microprocessor temperature controller

- Press the ***ENTER*** key and hold it while simultaneously pressing the ***PGM*** key. Programming starts with the information: ***AI. 1000*** on the lower display.
- Select the following values to program the temperature controller:

AI.	1150	2	(GC box)
Pb.	1	15	(GC box)
d.t	2	15	(GC box)
r.t	12		
cy.	0.5		
Hys.	1		
y.	0		
rA.Sd	200	20	(GC box)

Selection is made using the ◄ and ▲ keys on the front panel of the temperature controller.

◄ moves the active position one to the left.
▲ increases the value by one.

Each selection has to be saved with ***ENTER***.
Press the ***PGM*** button to move to the next item.

MICROPROCESSOR TEMPERATURE CONTROLLER (2/2)

- After all selections are made restart programming and pass through the menu until ***y.*** is displayed again.
- Press the ***ENTER*** key and hold it while pressing the ***PGM*** key simultaneously to obtain the submenu.

C 111	4001	9001 (GC box)
C 112	10	
SP.L	0	
SP.H	1550	300 (GC box)
OFFS	0	

- End programming by pressing ***ENTER*** to save all values.
- After a while, the temperature set for the heater is displayed.
  The lower green numbers show the heater temperature set.
  The yellow LED indicates the heating action.
  The upper red numbers are the read-out of the actual heater temperature.
  The heating rate is fixed by the parameters given in the example above.
  Heat the system in steps of ~100 °C up to the final temperature.

b) GC-column reactor (microprocessor is factory programmed)

Programming of a new microprocessor temperature controller

- Follow the instructions used to set the TC/EA.
- Change ***"C 111"*** to ***9001*** and ***SP.H*** to ***300***!

c) Setting a new temperature value

- Press ***PGM*** only. ***"sp"*** will be displayed.
- Select a new temperature using the arrow keys.
- When finished press ***ENTER***. Then press ***PGM***.

Programming the microprocessor temperature controller of Jumo iTRON 16

- Press the ***"P"*** key and hold it for two seconds.
- Change the values using the up and down arrows.
- Select the following values to program the temperature controller:

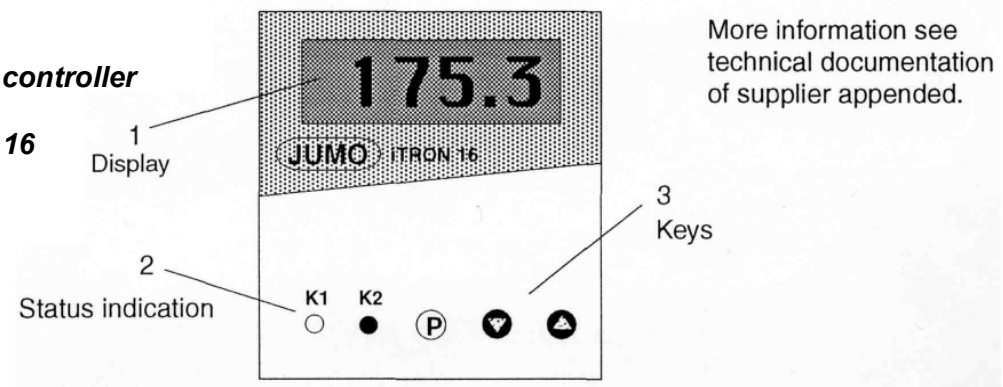
		reactor heater	***GC heater***
Pb.1	proportional band 1/factor	10	40
Pb.2	proportional band 2/factor	1	30
d.t.	derivative time in s	2	34
r.t.	reset time in s	12	125
CY.1	switch time output 1	2.0	2
CY.2	switch time output 2	2.0	2
Db		0	0
HyS.1		1	0
HyS.2		1	0
Y.0		0	0
Y.1		100	100
Y.2		0	0
d.F	filter	0.9	2
RA.Sd.		100	40

- After all selections are made restart programming. Pass through menu until ***"Y.O"***.
- Press ***"P"*** key and hold it for two seconds.

C 111	044	043
C 112	0	0
C 113	33	33
C 115	1	1
C 116	0	0
SP.L	0	0
SP.H	1550	300
OFFS	0	0

Temperature controller

Jumo iTRON 16



High Temperature Conversion

Elemental Analyzer (TC / EA)

OXYGEN MEASUREMENT

Issue 11/2001

Thermo Finnigan

PROCEDURE (1/2)

The TC/EA system promises to significantly simplify and improve current techniques for the analysis of ^{18}O / ^{16}O in a wide variety of organic and inorganic materials and compounds. The samples, wrapped in silver capsules and placed into the Autosampler, are continuously purged with helium to prevent contamination with traces of water, oxygen and nitrogen.

Dropping a sample into a graphite crucible, which is exactly positioned in the hottest zone of the glassy carbon reactor, starts the “High Temperature Conversion” (see fig. 5). The reaction temperature varies from 1100 °C for organic samples up to 1450 °C for inorganic samples.

Example 1: Reaction of benzoic acid at T= 1350 °C

$$C_6H_5COOH \rightarrow 3\,H_2 + 2\,CO + 5\,C$$

Example 2: Reaction of water at T= 1450 °C

$$H_2O + C \rightarrow H_2 + CO$$

The gaseous products (H_2, N_2, CO) of the High Temperature Conversion are separated by a 5 Å packed gaschromatographic molecular sieve column. Liquid organic samples and water can be injected using an Autosampler for liquids and an injection port on top of the reactor.

About 0.3% of the gases are transferred to the Isotope Ratio Mass Spectrometer via the Thermo Finnigan MAT open split Interface ConFlo II or III.

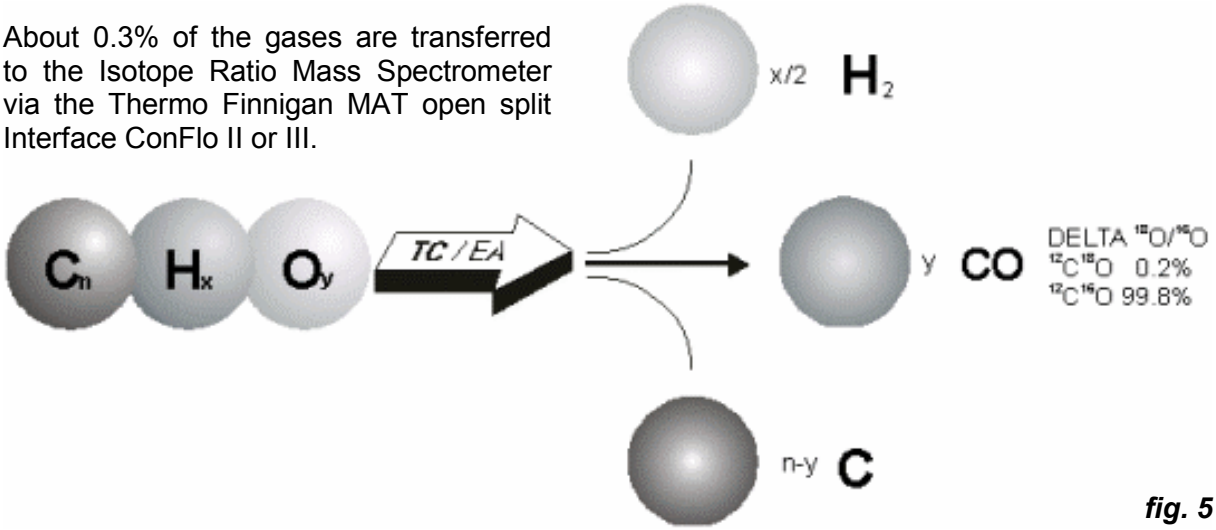


fig. 5

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PROCEDURE (2/2)

To prove total conversion to CO and H_2, the ion current intensity of the masses m/z = 44 (i.e. CO_2) and m/z = 18 (i.e. H_2O) can be monitored.

The highly precise and accurate $^{18}O/^{16}O$ measurements attainable with samples in the micro-gram range make the technique suitable for studying geochemical and biological processes at natural isotopic abundances as well as for point of origin and adulteration studies.

The very low blank and memory also make the technique suitable for the measure-ment of oxygen isotope tracers, e.g. doubly labeled water analysis.

WARNING: Wrong handling of the toxic CO gas and the explosive H_2 gas is perilous!

When working with carbon monoxide (CO) or hydrogen (H_2), good ventilation is essential. Ideally, the CO tank (H_2 tank) should be installed in a gas cabinet connected to an exhaust line.

Inform yourself about how to handle these gases by reading the directions for use and asking your local gas supplier. Thermo Finnigan does not take any responsibility if the standard gases (CO, H_2) are not used properly.

NOTE: "High Temperature Conversion" applications need He gas, which is free of water and oxygen. Although using He gas carrier of 99.999% purity, we recommend to add a gas purifier. The use of less pure gas may produce unstable results.

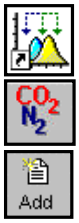
NOTE: Information about background ions from gas impurities is given on page 5 – 3.

DEFINITION OF A GAS CONFIGURATION FOR AN ^{18}O-MEASUREMENT

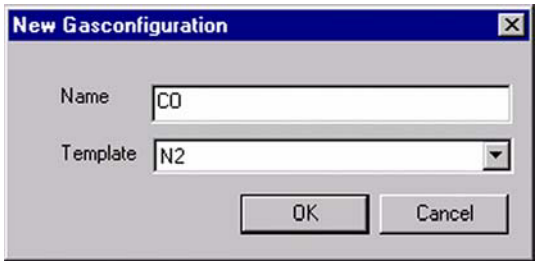
Prior to defining this gas configuration ensure the connected IRMS has the cups set for the simultaneous detection of masses 28, 29 and 30 and mass calibration for these cups has already been performed.

For an ^{18}O measurement, a new Gasconfiguration has to be created for the masses 28 ($^{12}C^{16}O$), 29 ($^{13}C^{16}O$) and 30 ($^{12}C^{18}O$).

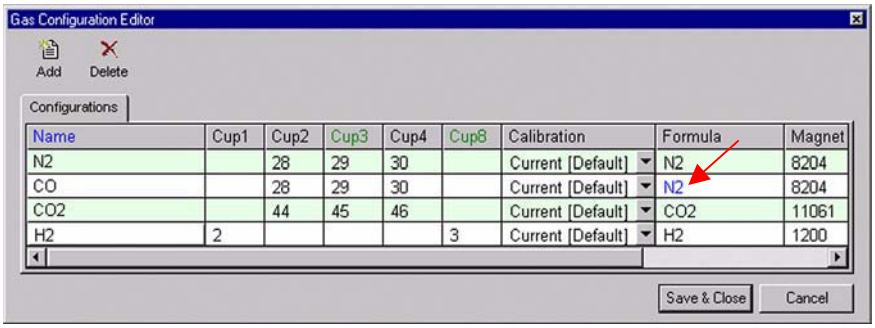
CREATE A GAS CONFIGURATION FOR AN ^{18}O-MEASUREMENT



- Open the ***Continuous Flow*** module.
- Open the ***Gas Configuration Editor***.
- ***Add*** a Gas Configuration.



- Select Gas Configuration ***N2*** as ***Template***.
- Type ***CO*** for the Name.
- Confirm with ***OK***.

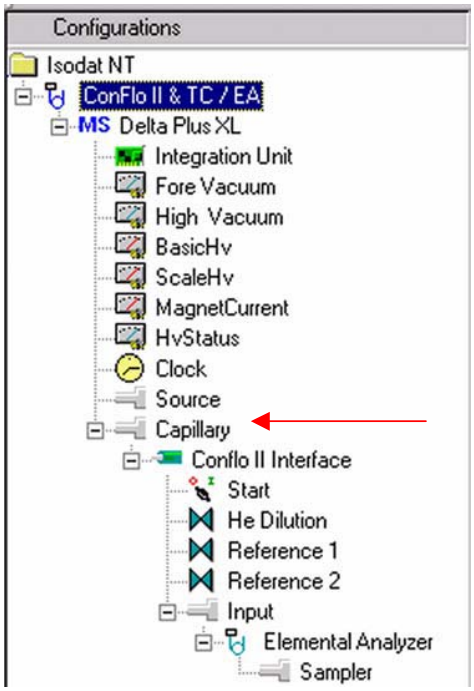


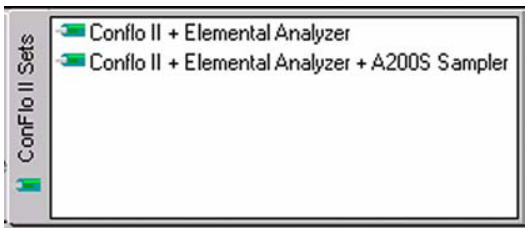
- Select a ***Calibration*** valid for the selected cups.
- Change the ***Formula*** from ***N2*** to ***CO***.
- Press ***Save & Close***.

TC / EA CONFIGURATION

Before operating the TC / EA, a Configuration containing the ConFlo II/III Interface and optionally an Autosampler needs to be created in the ***Configurator***.

- Add a new Configuration with the ***"Add Configuration"*** button.
- Give it a name, e.g. "ConFlo II & TC / EA".





- Select one of the "ConFlo II Sets" (also for ConFlo III) and drag it to the Source port or Capillary port in the new Configuration.
- Open the complete tree structure of the ConFlo II Interface to check for the attached hardware (TC / EA, Autosampler).
- In case of a ConFlo II and a liquid Autosampler with a RS232 interface to the computer the COM-Port settings can be checked in the "Advanced Mode".
- Activate the ***Advanced Mode*** in the ***Edit*** menu.
- Click with the right mouse button on the ***Communication Hardware*** object to open the ***Properties*** window.

NOTE: The COM-Port settings are essential for proper communication with the liquid Autosampler. Incorrect settings will lead to inactive liquid Autosampler control.

- Close the Configurator window. All settings will be saved automatically.

ConFlo II / III SOFTWARE (1/3)

The Continuous Flow application software allows fully automated isotope ratio determination of oxygen of bulk samples. All parameters relevant for data acquisition of a sample are stored in a ***Method***. The following steps are needed to ***Define a new Method***.

➢ Open the "Continuous Flow" module.

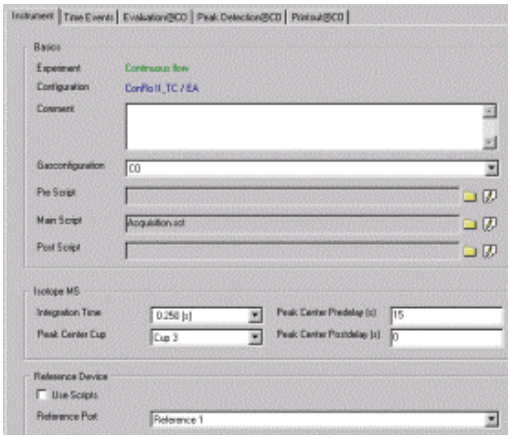
➢ Select the Configuration for ConFlo II/III applications (e.g. "ConFlo II & TC / EA").

➢ Select the Gasconfiguration for ^{18}O determination.

➢ Create a new Method.

The new Method is structured in Tab pages: Instrument, Time Events, Evaluation, Peak Detection, and Printout. The following Method explains the parameters of an ^{18}O Method.

Instrument



➢ Select ***Gas Configuration*** for ^{18}O determination (e.g. ***"CO"***).

➢ The ***Main Script*** controls the acquisition cycle.

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

➢ Select the ***Peak Center Cup***, e.g. **Cup 3** for a triple collector on a Delta^{Plus} XL (narrow center cup for m/z 29).

➢ ***Peak Center Predelay*** is the time the system waits between activation of the reference gas and start of the peak center cycle (e.g. > **15** s).

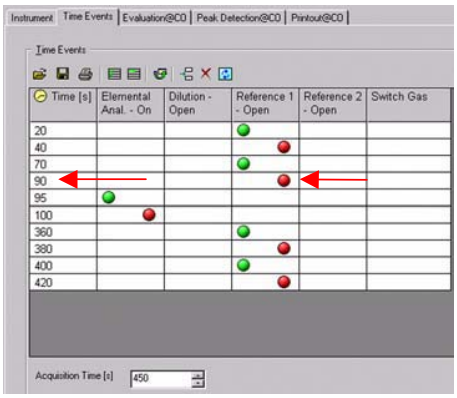
➢ ***Peak Center Postdelay*** is the time the system waits between the end of the peak center cycle and the start of the data acquisition (e.g. **0** s).

➢ ***Integration time*** is the time integrated to form a data point triplet (e.g. **0.25** s).

➢ Select the ***Reference Port*** to be used for peak center (e.g. Reference 1).

ConFlo II / III SOFTWARE (2/3)

Time Events

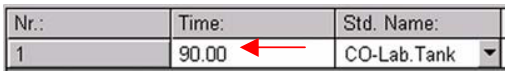


The “Time Events” list controls all valves of the selected Configuration during data acquisition.

- ***Insert lines*** using right mouse button or click on .
- Edit the ***Time*** at which the event will happen and ***double-click*** the field of a valve to set or toggle its status to active or inactive .
- Edit the ***Acquisition Time***. The acquisition time is the end time of data acquisition. After the acquisition time, no further actions will be executed from the time events list.

Evaluation

- Select an ***Ion Correction Type*** (e.g. ***“CO Santrock et al.”***).



- ***Add a standard*** using the right mouse button. Enter the retention time of the standard peak(s) defined in "Time Events" which are used for calculating the corresponding delta value(s).

The retention time must be set to the “Reference Out” value of the second CO Reference Gas pulse (in “Time Events”). This accommodates for the delay associated with the gas passage through the capillary to the IRMS.

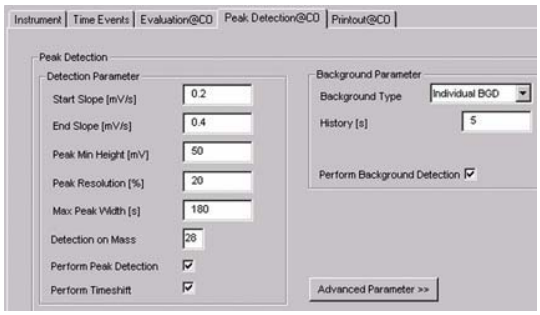
If the assigned time for Standard peak detection falls in between the Peak Start and Peak Stop marks of a peak, this peak will be used for delta value calculation.

- Select a ***Std. Name*** or edit the related delta values (user defined).

- ***Reference / Blank:*** For a blank determination, a time window needs to be defined by significant peak start and stop in which the corresponding CO peak will appear.
- For ***weight percent*** determination type in the appropriate oxygen weight percent of the reference compound used for Calibration.

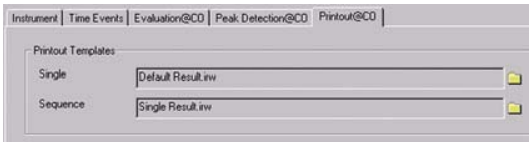
ConFlo II / III SOFTWARE (3/3)

Peak Detection



- Edit ***Start Slope***, ***End Slope***, and ***Peak Min. Height***. All other parameters can be kept default.
- A five point average slope of **0.2** mV/s (Start Slope) and of **0.4** mV/s (End Slope) is recommended for safe recognition of the peak boundaries. The best slope values depend on the nature of the chromatogram.
- ***Peak Min. Height*** limits the number of reported peaks. Default is **50** mV.
- ***Individual BGD*** is the default ***Background Type***.

Printout



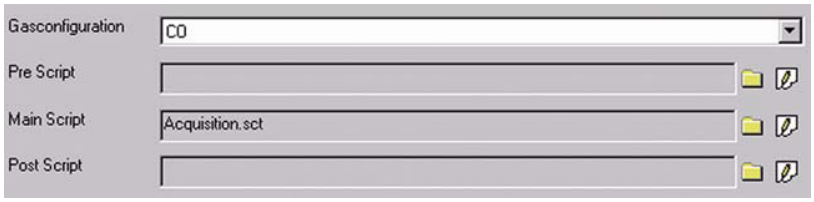
- ***Single Print*** selects a print template from the Result Workshop for an individual printout per sample.
- ***Sequence Print*** selects a print template from the Result Workshop for a reduced print per sample within a sequence summary.

ZERO ENRICHMENT (ST ON / OFF TEST, 1/4)

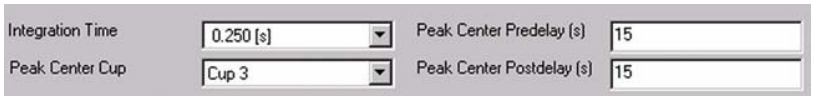
We assume that the user already has working experience with the ConFlo II / III Interface and IRMS. It is recommended to perform a simple check in order to test the analytical condition of the complete system (i.e. TC / EA, ConFlo II/III, IRMS) before measuring any samples.

1 Use the following default ***Method*** ("CO_zero.met") as a guideline.

Instrument



Isotope MS



Time Events

Time [s]	Start Sampler	Elemental Anal. - On	Dilution - Open	Reference 1 - Open	Reference 2 - Open	Switch Gas
30				●		
50						
80				●		
100						
130				●		
150						
180				●		
200						
230				●		
250						
280				●		
300						
330				●		
350						
380				●		
400						

Acq. End Time

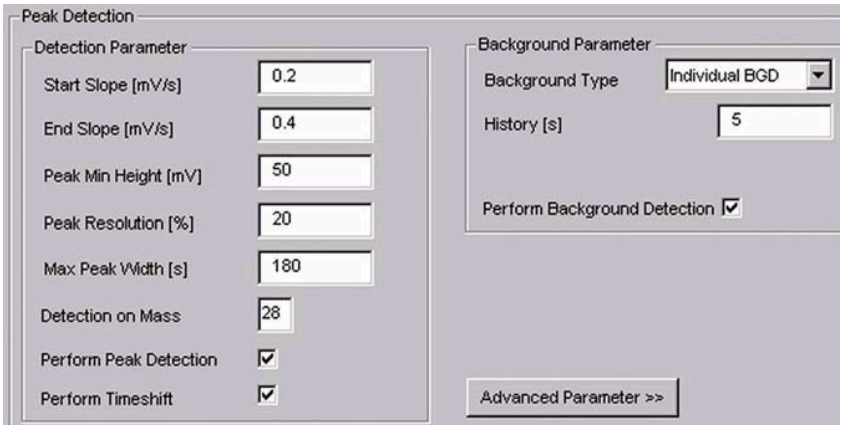
ZERO ENRICHMENT or ST ON / OFF TEST (2/4)

Method ***CO_zero.met*** continued

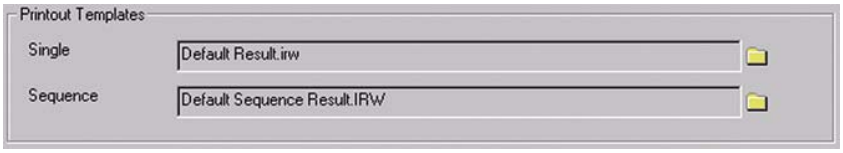
Evaluation

Nr.:	Time:	Std. Name:	δ 13C	δ 18O
1	150.00	CO_zero	0.000	0.000

Peak Detection



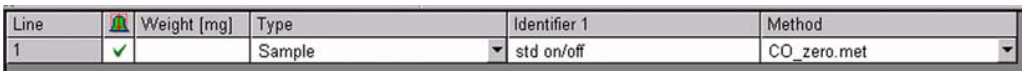
Printout



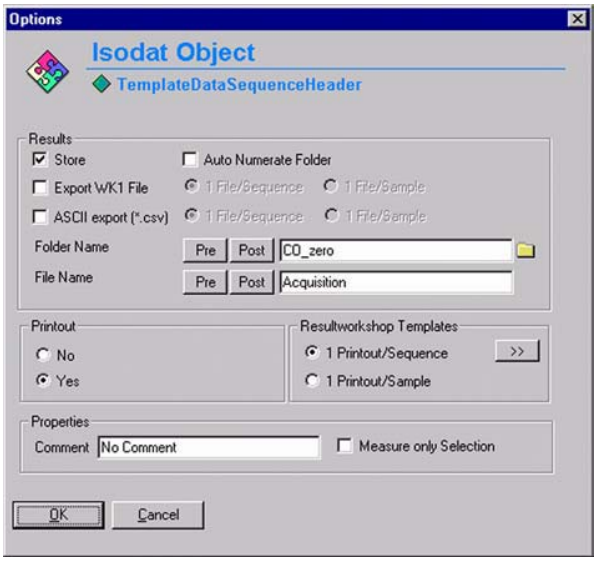
ZERO ENRICHMENT or ST ON / OFF TEST (3/4)

2 Set the ion intensity of mass 28 ($^{12}C^{16}O$) to approximately 3 - 4 V by opening Reference 1 and adjusting the pressure to the desired intensity.

3 Create a new ***Sequence*** or
select a predefined Sequence from the File Browser. Refer to page 8 – 15.



4 Press the Start button. 

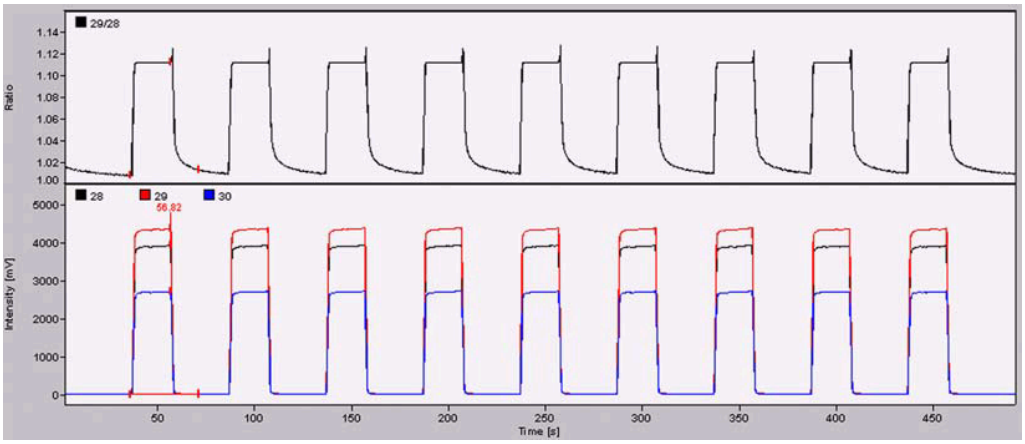


5 Select your destination folder.

Make your Printout decision (“Yes” / “No”).

Finally, confirm with “OK”.

ZERO ENRICHMENT or ST ON / OFF TEST (4/4)



CO | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 28 [mV]	BGD 28 [mV]	BGD 29 [mV]	BGD 30 [mV]	Area [Vs]	δ 13C [‰] vs. PDB	δ 18O [‰] vs. V-SMOW	AT% 18O [%]
1	56.8	35.7	3915	7.6	8.4	5.9	78.419	-0.016	-0.088	0.200101
2	106.6	34.9	3913	8.9	9.8	6.8	78.431	-0.039	-0.051	0.200109
3*	156.7	37.2	3915	9.1	10.0	6.9	78.711	0.000	0.000	0.200119
4	206.6	35.6	3919	9.2	10.2	7.1	78.638	-0.036	-0.062	0.200106
5	256.9	36.2	3921	9.3	10.3	7.1	78.571	-0.022	-0.033	0.200112
6	306.7	35.1	3917	9.4	10.4	7.1	78.435	-0.026	0.007	0.200120
7	356.7	35.6	3916	9.4	10.4	7.3	78.355	-0.026	-0.112	0.200096
8	406.8	35.1	3901	9.5	10.5	7.3	78.354	-0.050	0.034	0.200126
9	456.9	35.9	3907	9.5	10.6	7.4	78.407	-0.030	-0.098	0.200099

To calculate the standard deviation of ***delta 29 / 28*** ($^{13}C^{16}O$ / $^{12}C^{16}O$):

- Hold the Shift-key and mark the ***δ 13C vs. PDB*** column by a right-click.
- Then choose “Calculate” and finally look for the “Std. Dev.” value.

The standard deviation of *delta 29 / 28* ($^{13}C^{16}O$ / $^{12}C^{16}O$) should be < 0.08 ‰.

To calculate the standard deviation of ***delta 18 / 16*** ($^{12}C^{18}O$ / $^{12}C^{16}O$):

- Hold the Shift-key and mark the ***δ 18 O vs. V-SMOW*** column by a right-click.
- Then choose “Calculate” and finally look for the “Std. Dev.” value.

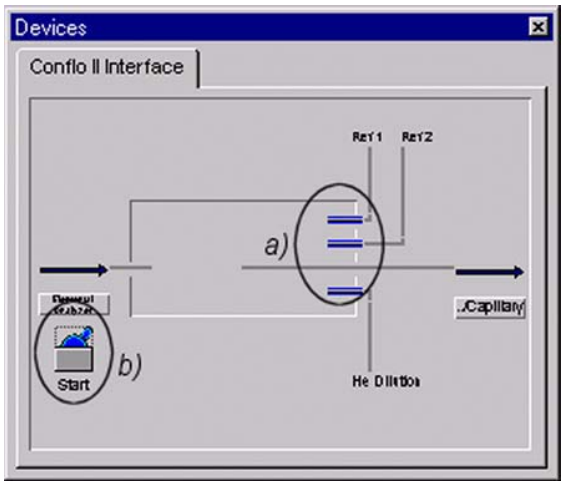
The standard deviation of *delta 18 / 16* ($^{12}C^{18}O$ / $^{12}C^{16}O$) should be < 0.1 ‰.

SOLID-AUTOSAMPLER LEAK TEST

While monitoring mass 28, start the solid-autosampler manually. The intensity of mass 28 should not increase more than 20 mV. If the measured value is 1.5 times higher than expected, increase the He purge and repeat the test.

NOTE: ***a)*** Neither Reference 1 nor Reference 2 nor He dilution should be open during the test.

b) To activate the solid-autosampler manually, switch the symbol to the position "Start" by a mouse click.



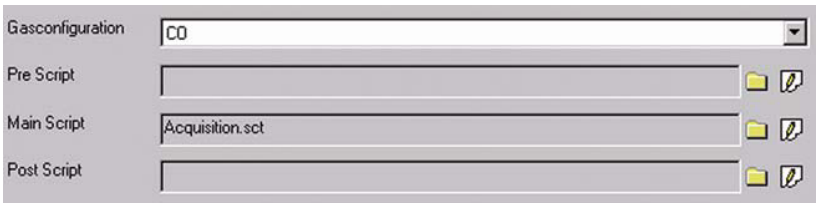
HOW TO START AN OXYGEN MEASUREMENT (1/5)

1 Hardware preparation

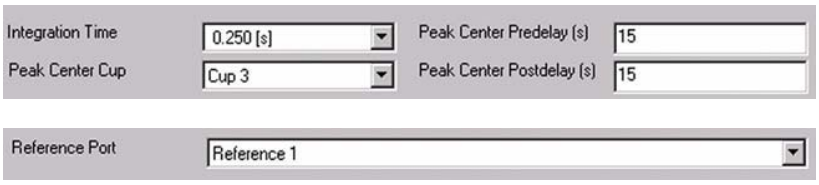
a) Reactor temperature: 1450 °C
b) GC column temperature: 90 °C
c) He flow: > 90 ml/min
d) Operating with 1% H_2 in He: set pressure regulator 0.1 bar higher than carrier gas (He).
e) Operating without aux. gas: turn down aux. pressure regulator so that auxiliary gas pressure decreases until shown pressure equals pressure of carrier gas.
f) Purge (He flow is sufficiently open)
g) Standard gas CO on ConFlo II/III (or inside variable volume) available
h) Needle valve (ConFlo II/III - IRMS connection) is open
i) Standard gas intensity (CO) is adjusted at about 3 - 4 V (as with zero enrichment)

2 Define a Method

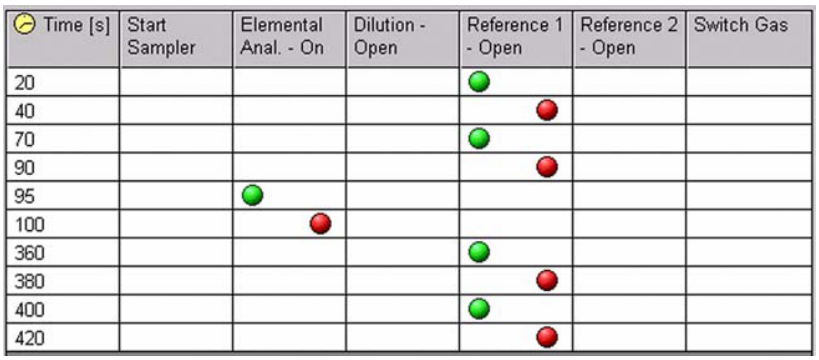
Instrument



Isotope MS



Time Events

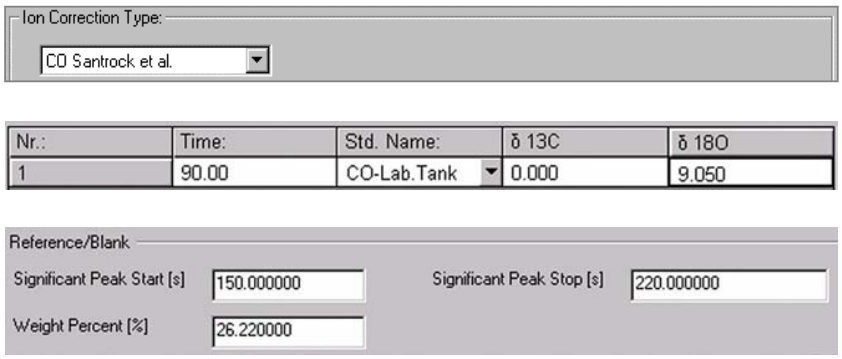


Acq. End Time

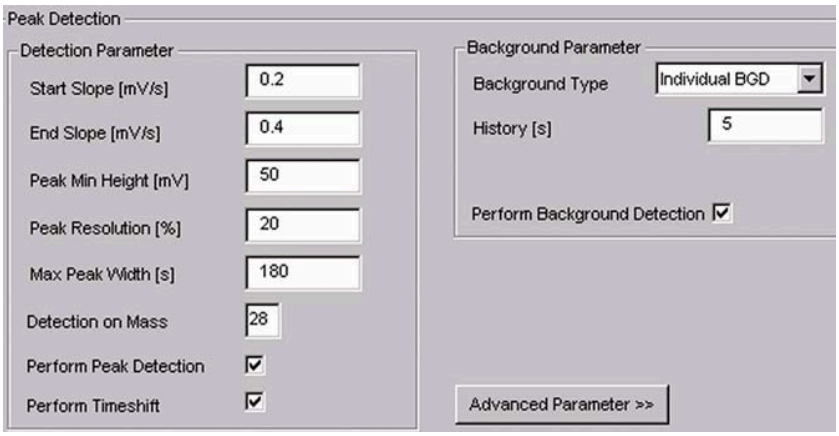
HOW TO START AN OXYGEN MEASUREMENT (2/5)

2 Define a Method (continued)

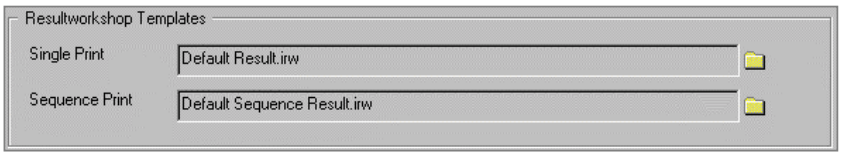
Evaluation



Peak Detection



Printout

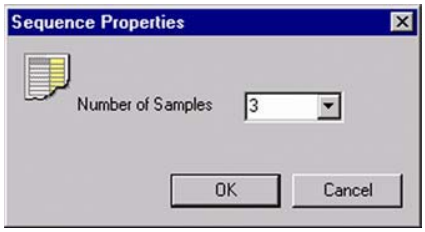


HOW TO START AN OXYGEN MEASUREMENT (3/5)

3 Place a sample (e.g. 0.285 mg of benzoic acid) in the solid-autosampler.

4 ***Create a new Sequence***.

5 Define the number of samples.



6 Edit the Sequence list.

Line		Weight [mg]	Type	Identifier 1	Method
1	✓	0.285	Sample	benzoic acid	CO-only.met
2	✓	0.273	Sample	benzoic acid	CO-only.met
3	✓	0.291	Sample	benzoic acid	CO-only.met

Peak Center Enable ☑ to perform a Peak Center prior to measurement.

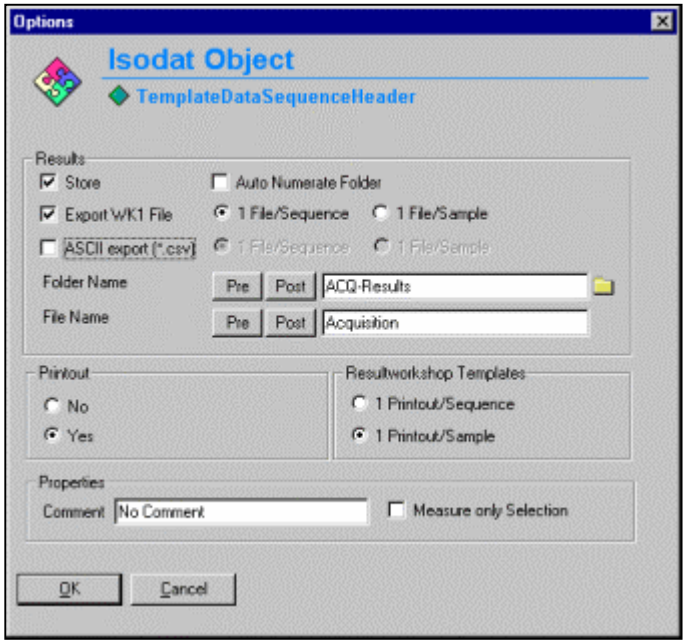
Identifier 1 Edit text to identify sample.

Method Select IRMS Method.

7 Press the “Start” button.

HOW TO START AN OXYGEN MEASUREMENT (4/5)

8 Define Results Export and Printout parameters.



9 Press “OK” to start Sequence Acquisition.

Events during Acquisition

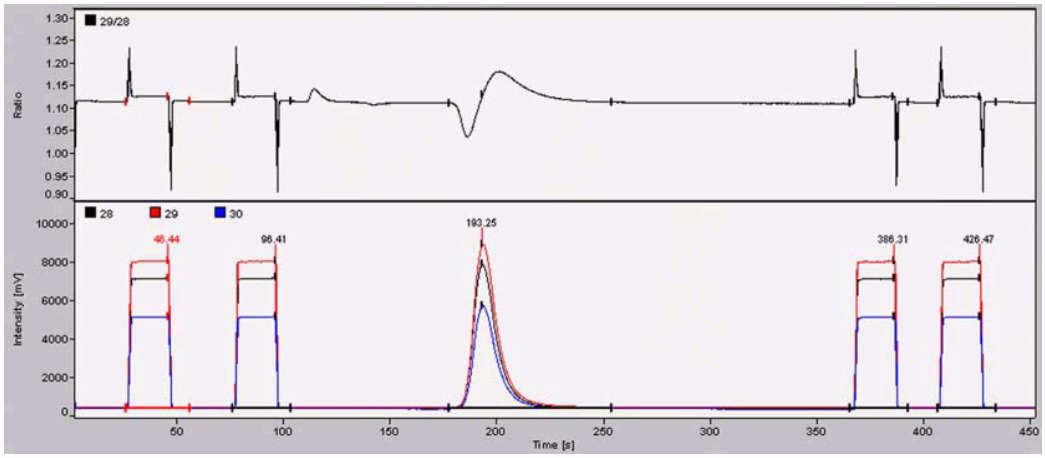
- Peak Center procedure
- First CO Reference Gas pulse activated at 20 s (duration: 20 s).
- Second CO Reference Gas pulse activated at 70 s (duration: 20 s).
  It is assigned as Standard pulse for delta value calculation.
  Refer to “Time” column in “Evaluation” tab on page 8 – 6.
- Sample is dropped into reactor.
- Sample peak appears approximately 100 s after start of reaction.
- Third CO Reference Gas pulse activated at 360 s (duration: 20 s).
- Forth CO Reference Gas pulse activated at 400 s (duration 20 s).
- Acquisition stops at 450 s.

HOW TO START AN OXYGEN MEASUREMENT (5/5)

After finishing data acquisition the printer creates a data output sheet as defined by the selected Results Workshop template (*.irw). The Results are also exported to a spreadsheet file.

C:\Finnigan\ISODAT NT\Global\User\Conflo II Interface\Results\Benzoic acid CO.CF

Line		Weight [mg]	Type	Identifier 1	Method
1	✓	0.285	Sample	benzoic acid	CO-only.met



CO | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 28 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area [Vs]	δ 13C [‰] vs. PDB	δ 18O [‰] vs. V-SMOW	AT% 18O [%]	Wt% [%]
1	46.4	29.8	6780	373.8	427.0	128.968	0.061	9.061	0.201928	-
2*	96.4	27.1	6784	373.0	426.0	128.724	0.000	9.050	0.201926	-
3	193.3	76.3	7490	369.5	421.3	98.534	10.316	25.803	0.205272	26.2200000
4	386.3	27.3	6760	368.2	419.1	128.499	0.017	9.147	0.201946	-
5	426.5	27.3	6750	371.1	423.2	128.486	-0.029	8.965	0.201909	-

WEIGHT PERCENT DETERMINATION - GENERAL

1 *Identification of the significant peak's position*

In the Method's Evaluation tab a weight percent determination can be chosen for the significant Peak of ***References***. It cannot be performed in case of Blanks.

All calculations of weight percent determination refer to the so called ***significant Peak***. To first and foremost determine its position, in the Method's Evaluation tab an interval must be defined by a Significant Peak *Start* value and a Significant Peak *Stop* value.

Since this interval will not automatically be identified, a sample chromatogram must be recorded which reveals the position of the significant Peak. Consider that the position can vary slightly over time due to alteration processes (e.g. of glassy carbon). Dimensioning the interval sufficiently broad will prevent the significant peak from falling or migrating outside it.

2 *Calculation of weight percent*

Weight percent determination bases upon the relationships between peak area of the significant peak and sample weight.

First, a Reference (i.e. a well-known substance; not necessarily identical to the compound of the later sample) is measured to obtain the k-Factor k according to the formula:

$$k = \frac{w_{ref} * m_{ref}}{A_{ref}}$$

The Reference's weight percent w_{ref} and mass m_{ref} are given whereas its peak area A_{ref} emerges from the measurement. Possibly, A_{ref} can be used blank-corrected to enhance the precision of k-Factor calculation.

Using the k-Factor just calculated, now the sample itself can be measured. Its peak area A_{sample} results (possibly blank-corrected), whereas sample weight m_{sample} and k-Factor k are well known, so that the parameter of interest, the sample's weight percentage w_{sample}, can be easily obtained rearranging the above equation:

$$w_{sample} = \frac{k * A_{sample}}{m_{sample}}$$

WEIGHT PERCENT DETERMINATION - PROCEDURE FOR OXYGEN

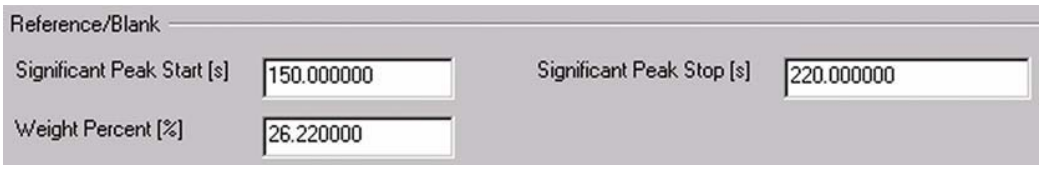
The system (i.e. TC/EA, ConFlo II/III, IRMS) requires a Calibration procedure in order to calculate the amount of oxygen in the sample.

1 Weigh a reference compound, e.g. 0.285 mg of benzoic acid, in a silver capsule and wrap it carefully.

NOTE: The precision of weighing is directly related to the precision of weight percent determination.

2 Place the capsule in the solid-autosampler.

3 Method (Evaluation tab)



4 Sequence

Line	Weight [mg]	Type	Identifier 1	Method
1	0.285	Reference	Benzoic acid	CO-only.met

The Method “CO-only.met” is described in detail on pages 8 – 8 and 8 – 9.

5 Start the Sequence. 

NOTE: In order to obtain reasonable results, this Calibration has to be performed daily and after changing any parameters of the system (TC/EA, ConFlo II/III, IRMS).

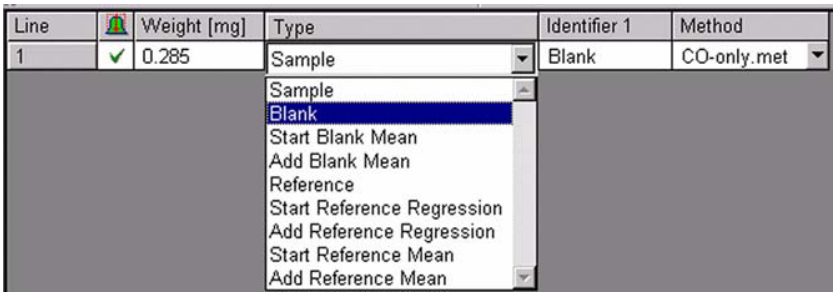
BLANK MEASUREMENT - GENERAL (1/2)

Blank value determination can help to enhance precision. The resulting blank value is then subtracted from both reference and sample peaks. Thus, the chronological order to proceed normally is: 1. Blank, 2. Reference, 3. Sample.

Blank and Reference values are stored in separate databases. A further criterion of separate storage is the gas name. To measure samples *directly*, i.e. without Blank and Reference before, delete these databases via ***Quant*** Menu.

In the following, the different commands for Blank measurement will be explained.

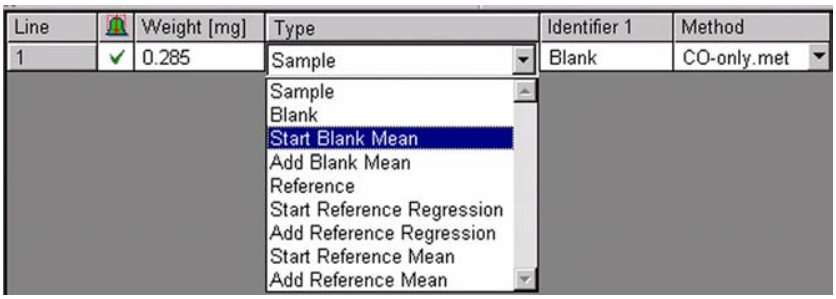
Blank command



➢ From the ***Type*** Menu select ***Blank***.

The previous Blank value will be deleted. Instead, the result of this current Blank measurement will be enlisted as new Blank value.

Start Blank Mean command

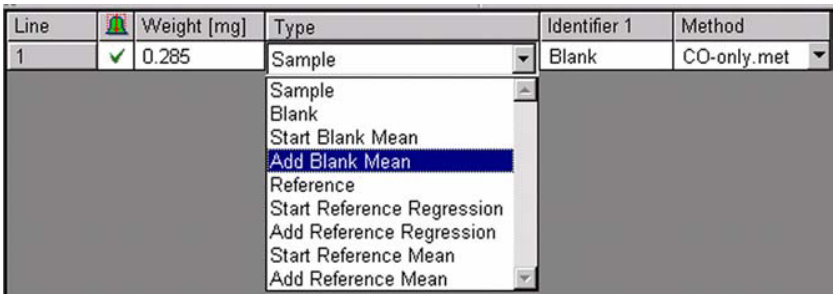


➢ From the ***Type*** Menu select ***Start Blank Mean***.

The previous Blank value will be deleted. Instead, the result of this current Blank measurement will be enlisted as new Blank value. Further Blanks can be added to be taken into account determining the Blank Mean.

BLANK MEASUREMENT - GENERAL (2/2)

Add Blank Mean command



➢ From the ***Type*** Menu select ***Add Blank Mean***.

The old Blank Mean will be corrected using the new Blank value to yield the new Blank Mean according to the formula:

$$m_b' = \frac{m_b * n_b + b}{n_b + 1}$$

where:

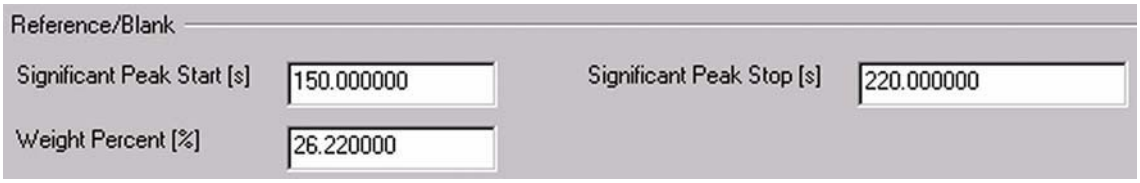
m_b'	new Blank Mean
m_b	old Blank Mean
n_b	number of previously measured Blank values (since Blank Start)
b	new Blank value

BLANK MEASUREMENT - PROCEDURE FOR OXYGEN

The tiny blank signal must be detected in the window.

1 Place an empty silver capsule into the solid-autosampler.

2 Method (Evaluation tab)



3 ***Sequence***

Line	Weight [mg]	Type	Identifier 1	Method
1	0.000	Blank	Blank	CO-only.met

The Method “CO-only.met” is described in detail on pages 8 – 8 and 8 – 9.

4 Start the Sequence. 

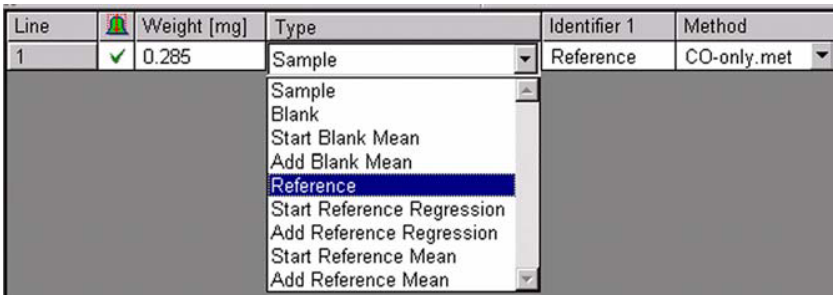
NOTE: In order to obtain reasonable results, this Calibration has to be performed daily and after changing any parameters of the system (TC/EA, ConFlo II/III, IRMS).

REFERENCE MEASUREMENT - GENERAL (1/2)

Three procedures (i.e. commands) exist to perform Reference measurements:

- Reference
- Start Reference Mean
- Start Reference Regression

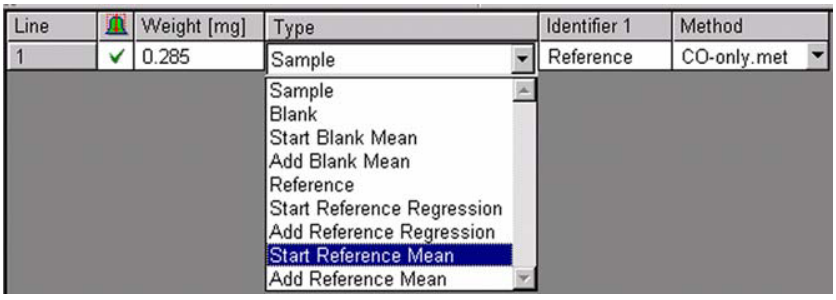
Reference command



- From the ***Type*** Menu select ***Reference***.

The previous Reference value will be deleted. Instead, the result of this current Reference measurement will be enlisted as new Reference value.

Start Reference Mean command

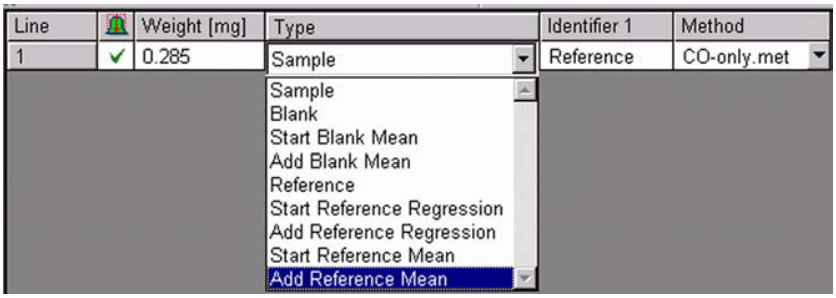


- From the ***Type*** Menu select ***Start Reference Mean***.

The previous Reference value will be deleted. Instead, the result of this current Reference measurement will be enlisted as new Reference value. Further References can be added to be taken into account determining the Reference Mean.

REFERENCE MEASUREMENT - GENERAL (2/2)

Add Reference Mean command



- From the ***Type*** Menu select ***Add Reference Mean***.

The old Reference Mean will be corrected using the new Reference value to yield the new Reference Mean according to the formula:

$$m_r' = \frac{m_r * n_r + r}{n_r + 1}$$

where:

m_r'	new Reference Mean
m_r	old Reference Mean
n_r	number of previously measured Reference values (since Reference Start)
r	new Reference value

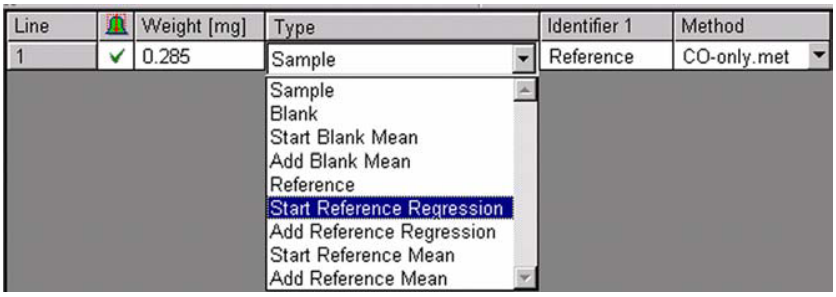
REFERENCE REGRESSION (1/2)

In addition to determining a Reference ***Mean*** (see above) a Reference ***calibration curve*** can be generated: the k-Factor is plotted vs. the sample weight.

The Reference *Mean* is calculated in case of References of *very similar* weights. With References of *considerably differing* weights, it is advantageous to generate a Reference *calibration curve*. Measuring a sample afterwards, the k-Factor can be acquired using the calibration curve.

REFERENCE REGRESSION (2/2)

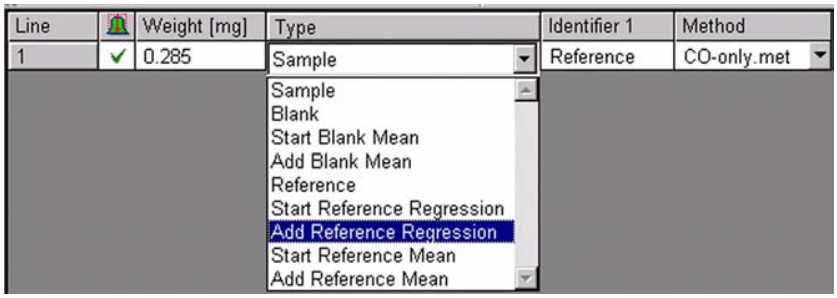
Start Reference Regression command



➢ From the ***Type*** Menu select ***Start Reference Regression***.

This command corresponds to the *Start Reference* ***Mean*** command (see above).
The previous Reference value will be deleted. Instead, the result of this current Reference measurement will be enlisted as new Reference value. Further References can be added to extend the Reference calibration curve.

Add Reference Regression command



➢ From the ***Type*** Menu select ***Add Reference Regression***.

This command corresponds to the *Add Reference* ***Mean*** command (see page 8 – 24).
A new point on the calibration curve is enlisted.

High Temperature Conversion

Elemental Analyzer (TC / EA)

HYDROGEN MEASUREMENT

Issue 11/2001

Thermo Finnigan

Hydrogen determination requires an isotope ratio mass spectrometer (IRMS) with Faraday collectors for the masses m/z = 2 and m/z = 3. The measurement of masses 2 and 3 of hydrogen in the presence of helium as carrier gas has posed experimental difficulties to be taken care of. A contribution of the large $^4He^+$ peak would corrupt the measurement of the small HD beam at mass 3. Collisions in the ion source of the IRMS and along the flight tube lead to an energy loss and therefore a tailing of $^4He^+$. A portion of this tail would be collected in the m/z = 3 cup. For a desired He flow of approximately 0.3 ml/min in the ion source, and with typical Faraday cup dimensions, the HD signal (~ 10^{-12} A) is superposed by $^4He^+$ ions of $2 * 10^{-10}$ A.

To overcome this effect, the Faraday cup of mass m/z = 3 has a special Electrostatic Energy Filter. It consists of a three-element deceleration ion arrangement, which is integrated within the ion collector between collector slit and Faraday cup (Delta^{Plus}XL, Delta^{Plus}XP, MAT 253).

PROCEDURE (1/2)

Among all elements, hydrogen has the largest naturally occurring variation in the ratio of its stable isotopes. H_2 gas can be produced quantitatively from micromole amounts of organic samples in continuously flowing gas systems.

Hydrogen and oxygen measurements are performed with the same reactor. Depending on the sample amount, either the reactor shown in fig. A1 (see page 5 – 4) or the reactor pointed at in fig. A2 (see page 5 – 5) is used.

The samples, wrapped in silver capsules and placed into the Autosampler, are continuously purged with helium to prevent contamination with traces of water, oxygen and nitrogen. Dropping one sample into a graphite crucible, which is exactly positioned in the hottest zone of the glassy carbon reactor starts the “High Temperature Conversion Reaction”. The measurements are generally carried out at a reaction temperature of 1450 °C. The HD ratios are determined by monitoring the masses 2 and 3 of hydrogen.

PROCEDURE (2/2)

The delta values (‰) are calculated versus H_2 reference gas pulses introduced via the interface.

Schematic:

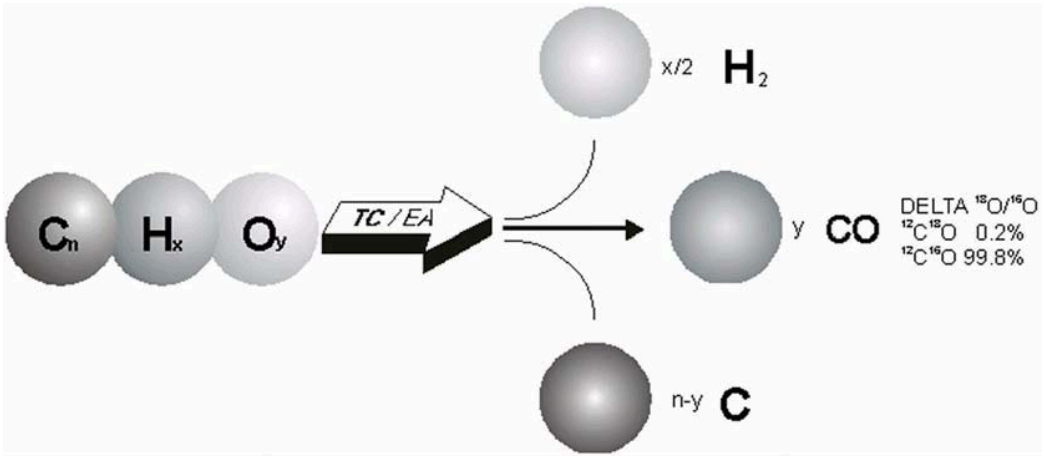
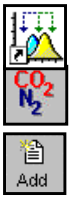


fig. 5

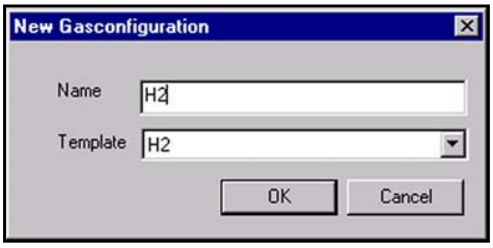
ConFlo II / III AND TC / EA CONFIGURATION

Hydrogen determination requires a mass spectrometer containing the cups for the masses m/z = 2 and m/z = 3 with an Electrostatic Energy Filter (Delta^{PLUS} XL, MAT 253). It is assumed that the mass calibration for these cups has already been performed. For a ^2H measurement, a new Gas Configuration has now to be created for the masses 2 and 3.

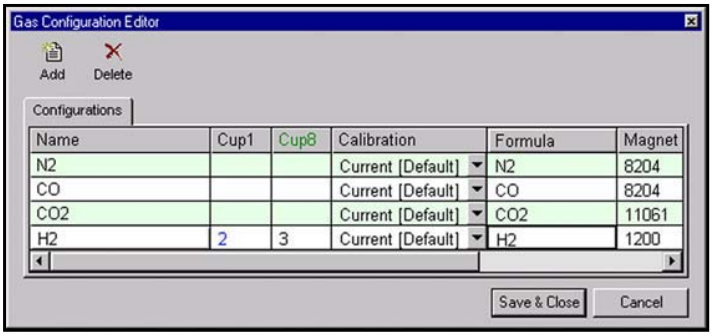
CREATE A GAS CONFIGURATION FOR A ^2H MEASUREMENT



- Open the ***Continuous Flow*** module.
- Open the ***Gas Configuration Editor***.
- ***Add*** a Gas Configuration, if a H_2 Gas Configuration is not yet available.



- Select any Gas Configuration as ***Template*** or ***H2***, if already available.
- Type ***H2*** for the Name.
- Confirm with ***OK***.



- Select a ***Calibration*** valid for the selected cups.
- Press ***Save & Close***.

NOTE: Ensure that a Configuration for Con Flo II/III with TC/EA is available.
To set up a new Configuration also refer to page 8 – 3.

NOTE: For detailed information refer to the ***ISODAT NT Help System (Configurator)***, which is delivered on your ISODAT NT CD.

H_3-FACTOR DETERMINATION (1/3)

- It is assumed that ion source setting for hydrogen determination and mass calibration for hydrogen have already been performed.
- Standard gases (i.e. CO and H_2) are installed as shown in fig. G on page 6 – 1.
- The reactor is properly filled and installed.
- Setup is completed (refer to page 5 – 1).
- Background for the masses 28, 29, 30, 18, 40 and 32 are within the range (refer to page 5 – 3).

The background for the masses 2 and 3 should be:

mass:	intensity:
2	between 180 - 200 mV*
3	< 20 mV

***set electron energy in order to get this range.**

NOTE: During the first setup, the H_3-Factor determination must be performed before any other procedure. Later on, at least once a day, a H_3-Factor determination is recommended.

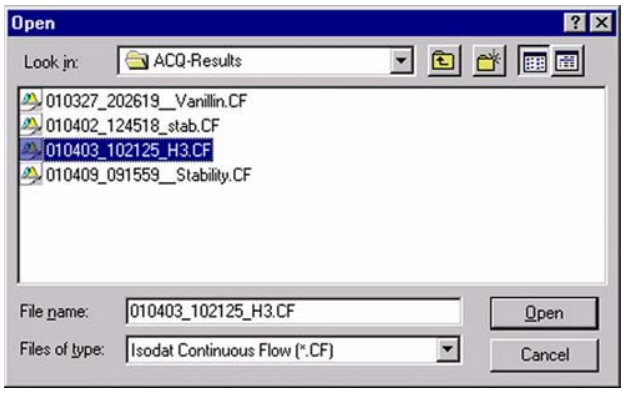
H_3-FACTOR DETERMINATION (2/3)

Protonation reactions in the ion source result in H_3^+ ion production. The H_3^+ portion of the m/z ion beam is determined as H_3-Factor. The H_3-Factor is used to correct the H_3^+ contribution to the m/z 3 signal. A low and stable H_3-Factor is needed for a good DH/ H_2 determination.

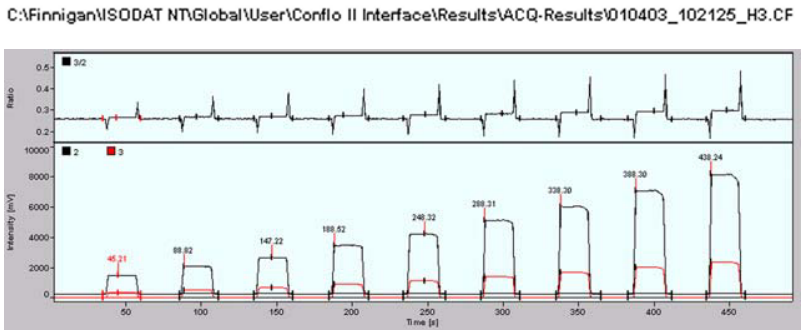
➢ Open the ***Continuous Flow*** module.

The H3-Factor determination is based on the peak area information of a standard gas on/off chromatogram (*.cf) with standard gas pulses of different amplitudes. Chromatograms are stored in result folders, e.g.:
C:\Finnigan\ISODAT NT\Global\User\ConFlo II Interface\Results\ACQ-Results.

➢ To load it, press the ***Open*** button.



➢ Localize your *.cf file and press ***Open***.

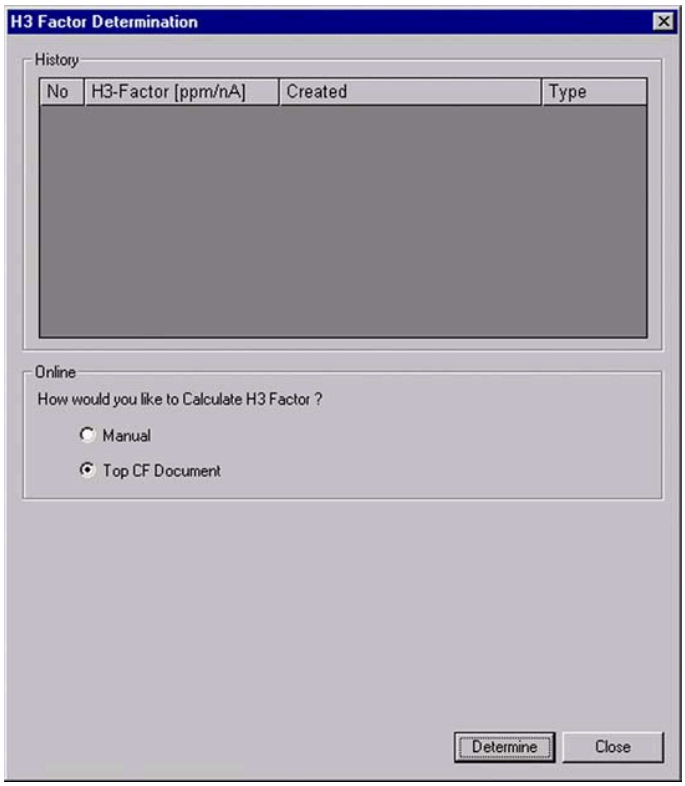


➢ The chromatogram will be loaded.

To see how such a chromatogram is obtained (i.e. via stepwise increases of the reference gas pressure using the Method “H2_zero.met”), refer to pages 9 – 7 to 9 – 11.

H_3-FACTOR DETERMINATION (3/3)

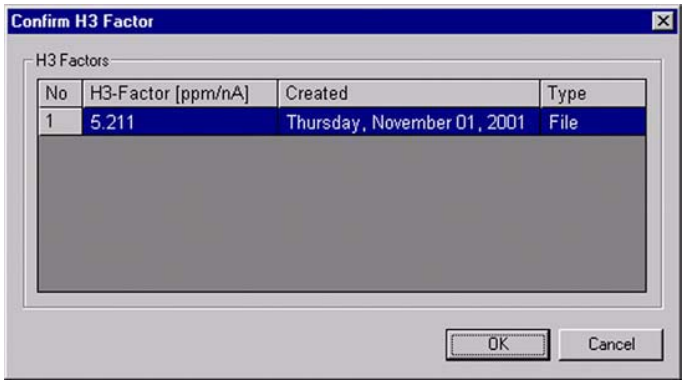
➢ Click the ***H3-Factor*** button (on Smart Isotope MS bar or on Isotope MS bar).



➢ The H3-Factor is calculated on the basis of a chromatogram (*.cf).

➢ Select ***Top CF Document***.

➢ Press ***Determine***.



➢ Confirm the calculated H3-Factor by ***OK***.

➢ Upon ***Cancel***, a new H3-Factor can be determined.

The calculated H3-Factor is also displayed in the ***H3-Factor*** tab page beneath the chromatogram and will be used for further data acquisitions (see page 9 – 16).

ZERO ENRICHMENT (ST ON / OFF TEST, 1/5)

We assume that the user already has some working experience with ConFlo II/III Interface, TC/EA and IRMS, and that H_3-Factor determination has already been performed (refer to pages 9 – 4 to 9 – 6). It is recommended to perform a simple check in order to test the analytical condition of the IRMS before measuring any samples.

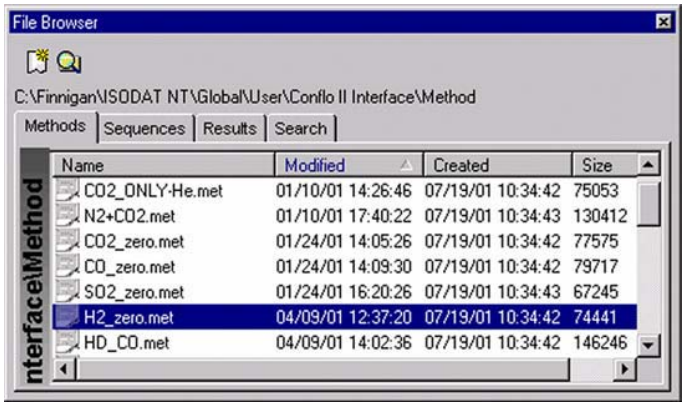
The following steps need to be performed to ***Define a Method***

- Open the ***Continuous Flow*** module.

- Select the ***Configuration*** for ConFlo II/III applications.

- Select the ***Gas Configuration*** for ^{18}O determination.

- Create a new Method **or**



Select a Method from the File Browser.

- On the File Browser, click the ***Methods*** tab.
- Double-click the Method ***H2_zero.met***.

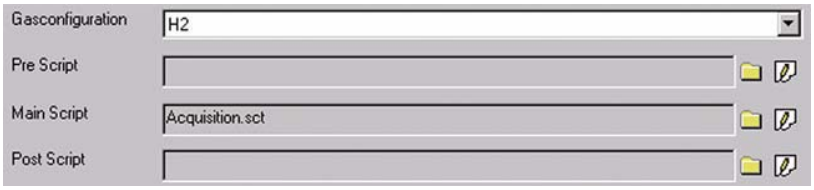
The Method is structured in Tab-pages: Instrument, Time Events, Evaluation, Peak Detection, and Printout.

For a detailed explanation of the Method's structure and editing refer to ***Define a new Method*** on pages 8 – 5 to 8 – 7.

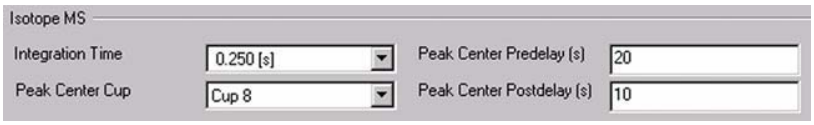
ZERO ENRICHMENT or ST ON / OFF TEST (2/5)

As a guideline, use the following Method (***"H2_zero.met"***).

Instrument



Isotope MS



Time Events

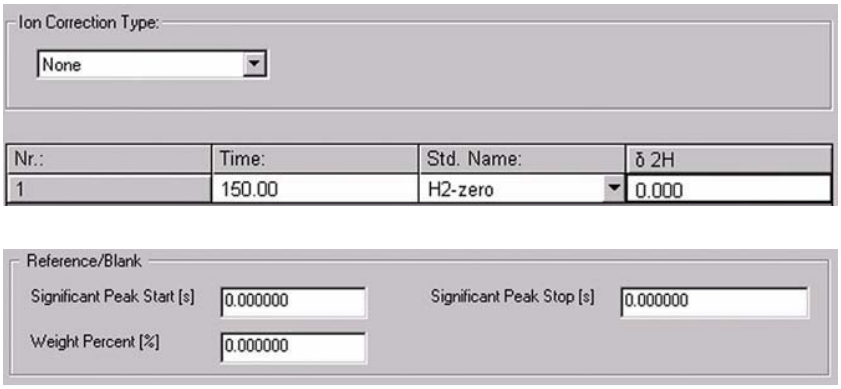
Time [s]	Start Sampler	Elemental Anal. - On	Dilution - Open	Reference 1 - Open	Reference 2 - Open	Switch Gas
30				●		
50					●	
80				●		
100					●	
130				●		
150					●	
180				●		
200					●	
230				●		
250					●	
280				●		
300					●	
330				●		
350					●	
380				●		
400					●	

Acq. End Time

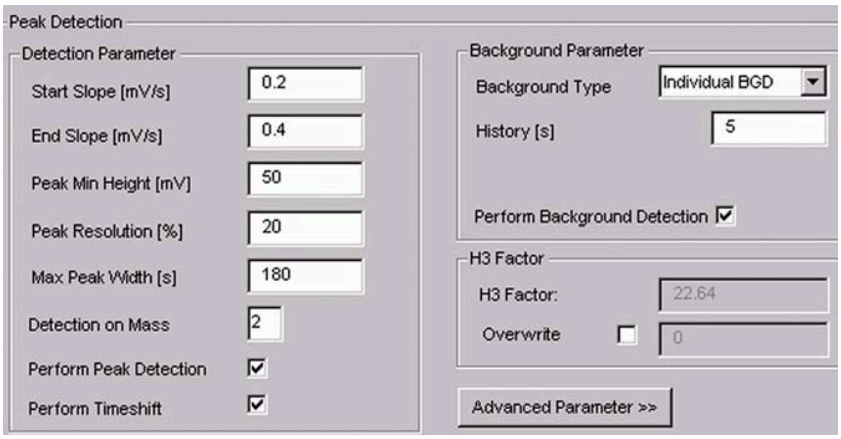
ZERO ENRICHMENT or ST ON / OFF TEST (3/5)

Method ***H2_zero.met*** continued

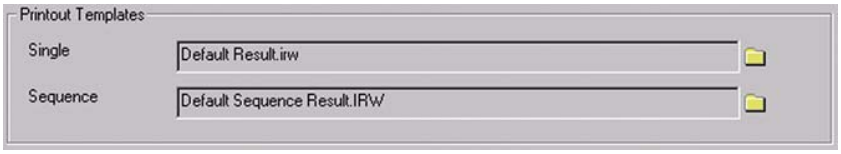
Evaluation



Peak Detection



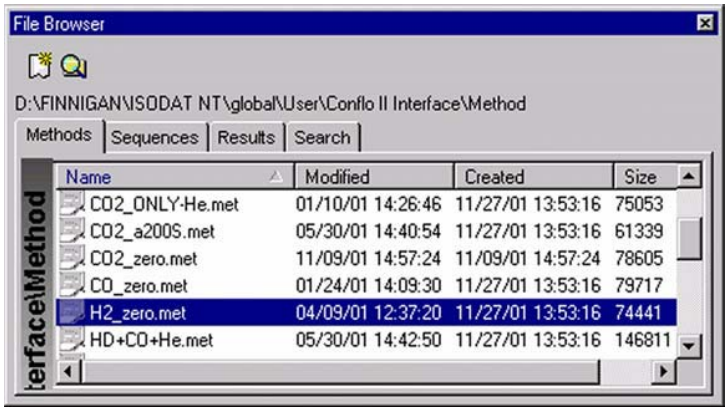
Printout



ZERO ENRICHMENT or ST ON / OFF TEST (4/5)

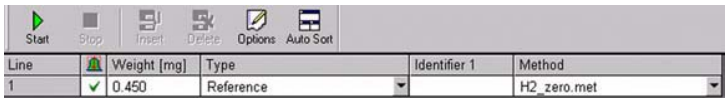
2 Set the ion intensity of mass 2 (H_2) to approximately ***4 V***.

3 Create a new Sequence or select a predefined Sequence from File Browser.

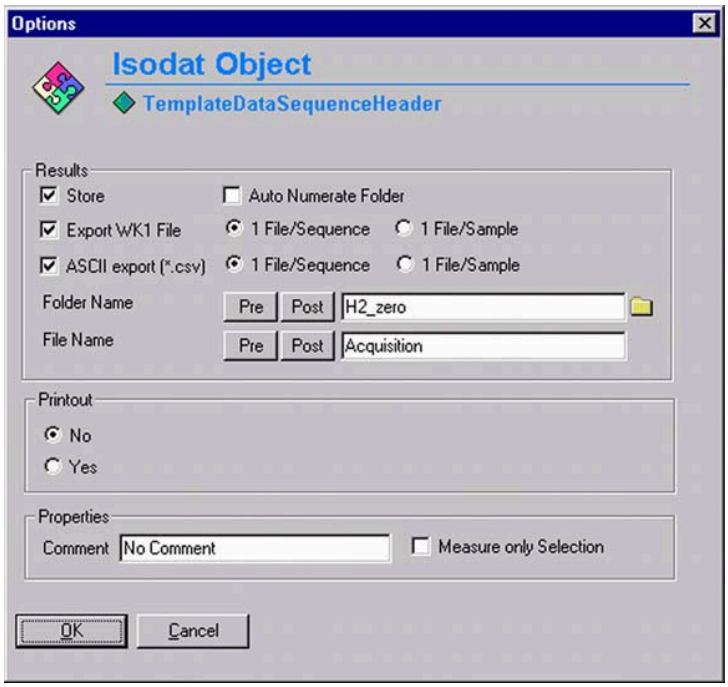


➢ Click the ***Sequences*** tab.

➢ Doubleclick the Sequence file ***H2_zero.seq***.



➢ Click the ***Start*** button.



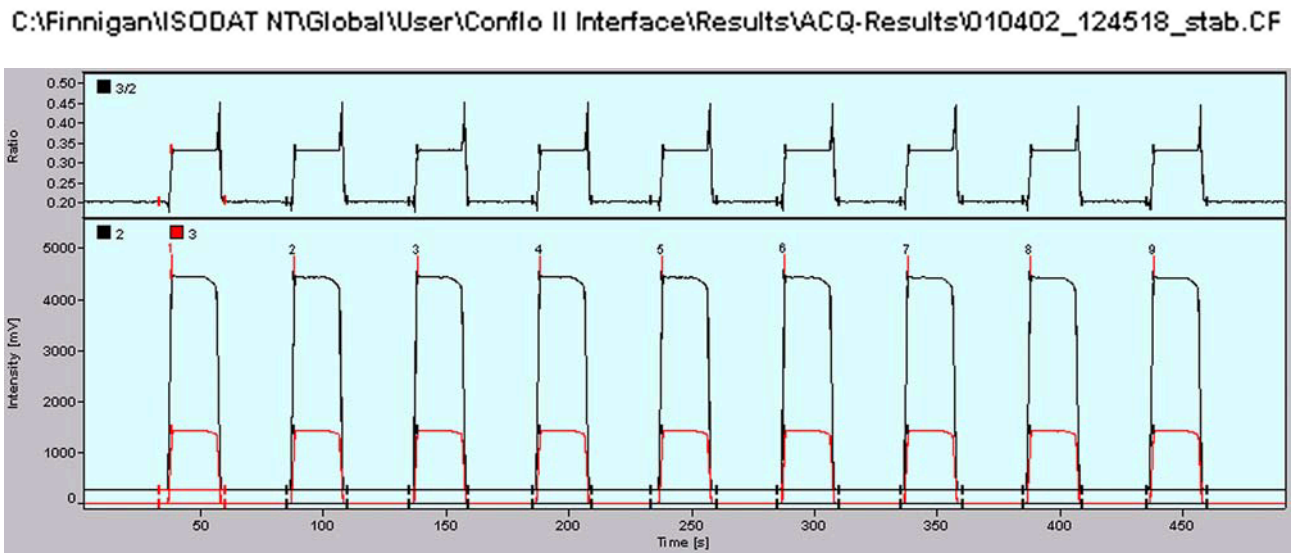
➢ Edit how to export results.

➢ Name folder and file for data storage.

➢ Activate or deactivate ***Printout***.

➢ Confirm your decision with ***OK***.

ZERO ENRICHMENT or ST ON / OFF TEST (5/5)



H2 | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 2 [mV]	Ampl. 3 [mV]	BGD 2 [mV]	BGD 3 [mV]	Area [Vs]	δ 2H [‰] vs. V-SMOW	AT% 2H [%]
1	38.2	26.9	4212	1448	255.5	-18.4	81.858	-0.406	0.015566
2	88.4	24.6	4198	1444	255.1	-18.0	81.536	-0.439	0.015566
3*	138.4	24.4	4201	1444	255.1	-18.6	81.535	0.000	0.015573
4	188.2	24.1	4206	1443	254.5	-18.4	81.503	-0.292	0.015568
5	238.2	26.7	4205	1443	254.8	-18.2	81.589	-0.426	0.015566
6	288.2	24.9	4209	1444	254.5	-18.5	81.528	-0.340	0.015567
7	338.3	24.9	4197	1442	253.9	-18.3	81.526	-0.792	0.015560
8	388.3	23.9	4198	1442	253.7	-18.1	81.249	-0.908	0.015558
9	438.3	24.4	4196	1440	253.3	-18.5	81.328	-0.764	0.015561

A chromatogram with equal peak heights results. Beneath the chromatogram, the corresponding parameter values are listed.

NOTE: The mean value of standard deviation of delta 3/2 should be < 1‰.

HOW TO START A HYDROGEN MEASUREMENT (1/5)

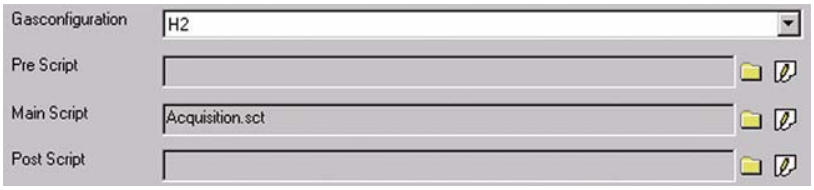
1 *Hardware preparation*

a) Reactor temperature 1450 °C
b) GC column temperature 85 °C
c) He flow > 110 ml/min
d) Operating with 1% H_2 in He:
set the pressure regulator 0.1 bar higher than carrier gas (He).
e) Operating without auxiliary gas:
turn down auxiliary pressure regulator so that auxiliary gas pressure decreases until shown pressure equals pressure of carrier gas.
f) Purge (He flow is sufficiently open).
g) Standard gas H_2 on ConFlo II/III (or inside variable volume) available.
h) Needle valve (ConFlo II/III - IRMS connection) is open.
i) Standard gas (H_2) intensity is adjusted at about: 5.5 V.

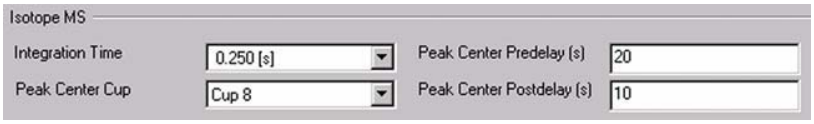
2 ***Define a Method*** (as shown on pages 8 – 5 to 8 - 7).

As a guideline, use the following Method ***(HD_only.met)***:

Instrument



Isotope MS



Time Events

Time [s]	Start Sampler	Elemental Anal. - On	Dilution - Open	Reference 1 - Open	Reference 2 - Open	Switch Gas
20					●	
40						●
60					●	
80						●
90		●				
95			●			

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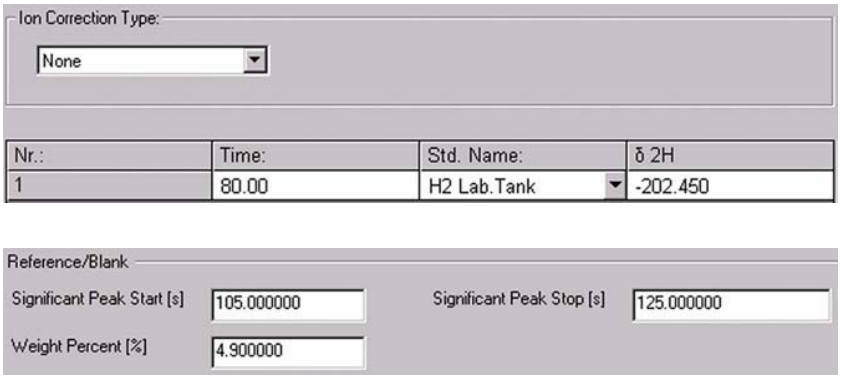
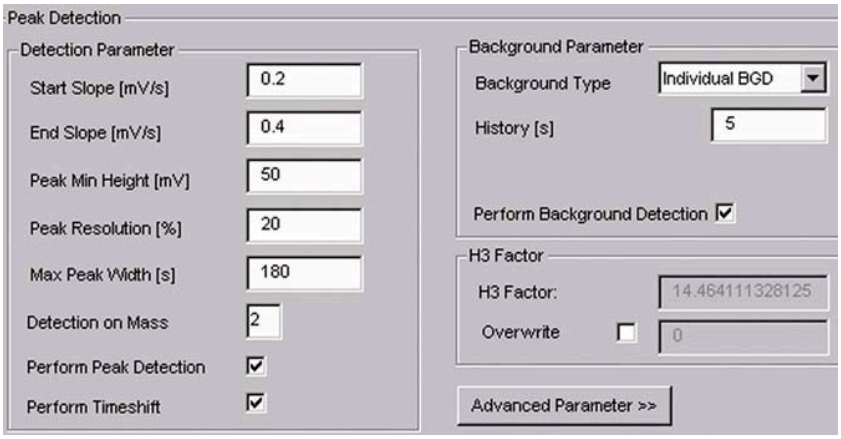
HOW TO START A HYDROGEN MEASUREMENT (2/5)

Acq. End Time

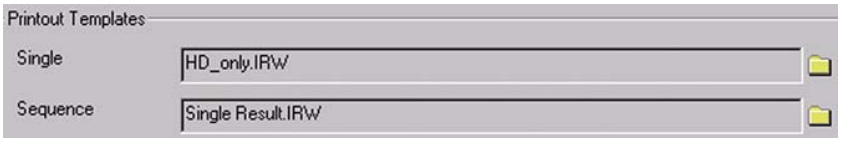
Evaluation



Peak Detection



Printout

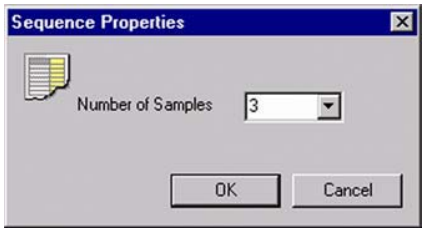


HOW TO START A HYDROGEN MEASUREMENT (3/5)

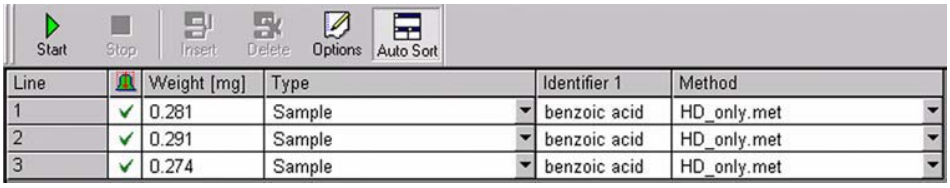
3 Place a sample (e.g. 0.281 mg of benzoic acid) in the solid-autosampler.

4 ***Create a new Sequence***.

5 Define number of samples.



6 Edit the Sequence list.



Line		Weight [mg]	Type	Identifier 1	Method
1	✓	0.281	Sample	benzoic acid	HD_only.met
2	✓	0.291	Sample	benzoic acid	HD_only.met
3	✓	0.274	Sample	benzoic acid	HD_only.met

Peak Center Enable ☑ in order to perform a Peak Center prior to measurement.

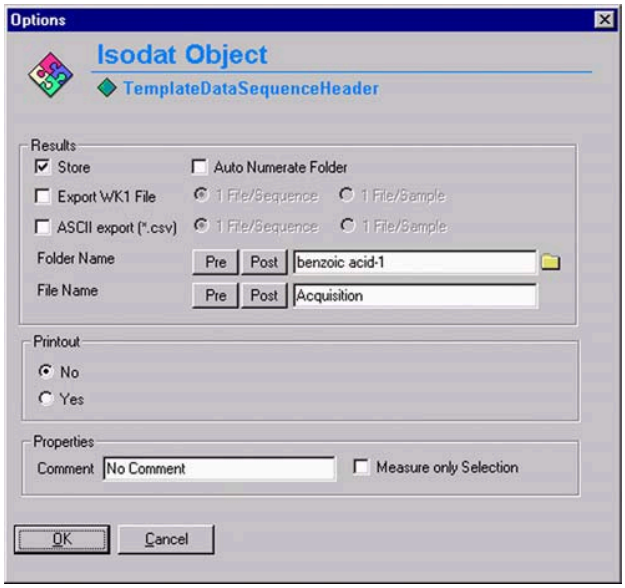
Identifier 1 Edit text to identify sample.

Method Select IRMS Method.

7 Press the “Start” button.

HOW TO START A HYDROGEN MEASUREMENT (4/5)

8 Define Results Storage, Export, and Printout parameters.



9 Press “OK” to start Sequence Acquisition.

Events during Acquisition

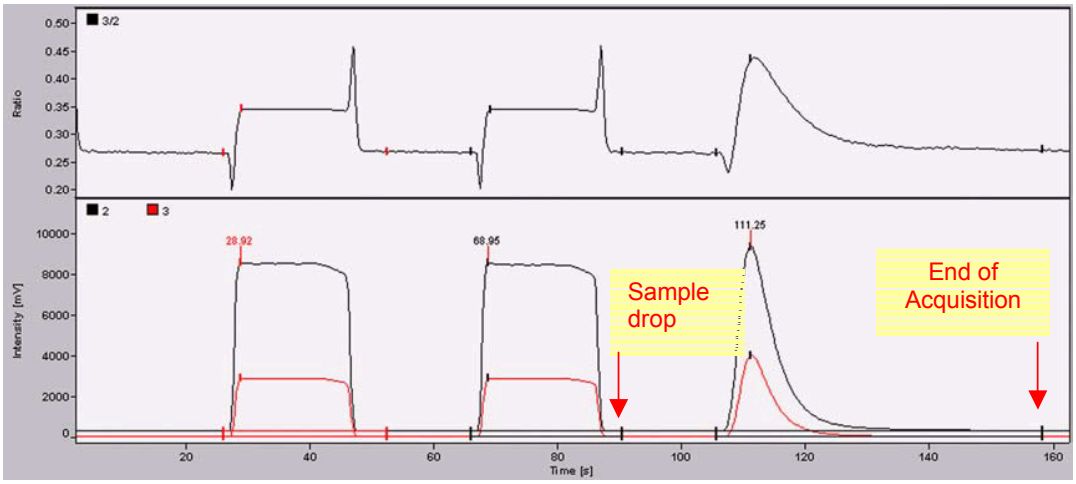
- Peak Center procedure
- First H_2 Reference Gas pulse activated at 20 s (duration: 20 s).
- Second H_2 Reference Gas pulse activated at 60 s (duration: 20 s).
- Sample is dropped into reactor at 90 s.
- H_2 sample peak appears approximately 15 s after start of reaction.
- Acquisition stops at 160 s.

HOW TO START A HYDROGEN MEASUREMENT (5/5)

After finishing data acquisition the printer creates a data output sheet as defined by the selected Results Workshop template (*.irw).
The Results will also be exported to a spreadsheet file, if activated.

C:\FINNIGAN\ISODAT NT\Global\User\Conflo II Interface\Results\Benzoic acid HD.CF

Line		Weight [mg]	Type	Identifier 1	Method
1	✓	0.281	Sample	benzoic acid	HD_only.met



H2 | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 2 [mV]	Ampl. 3 [mV]	BGD 2 [mV]	BGD 3 [mV]	R 3/2	Area [Vs]	δ 2H [‰] vs. V-SMOW	AT% 2H [%]	Wt% [%]
1	28.9	26.5	8288	2883	272.9	-0.7	0.0002259	152.806	-274.768	0.011294	10.9420167
2*	68.9	24.4	8266	2872	272.4	-0.6	0.0002259	151.501	-274.779	0.011294	10.8485299
3	111.3	52.6	9074	4005	273.3	-0.8	0.0002850	65.185	-85.232	0.014245	4.9321373

High Temperature Conversion

Elemental Analyzer (TC / EA)

10

DUAL MEASUREMENT

Issue 11/2001

Thermo Finnigan

INTRODUCTION

It is possible to perform dual measurements of hydrogen and oxygen from a single sample with the system (TC/EA, ConFlo II/III and IRMS) in less than 7 minutes offering fast sample throughput and high productivity. The technique is suitable for both solid and liquid samples.

Schematic diagram:

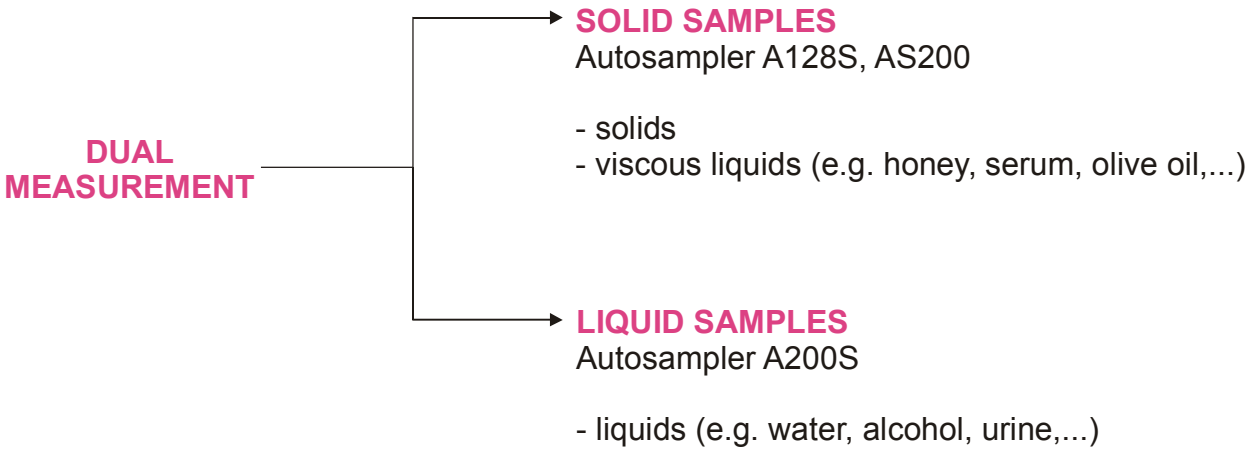


fig. 12

As shown in fig. 12, different Autosamplers are used to measure different sample types.

Concerning the installation of the A128S Autosampler (solid samples) refer to page 5 – 6.
For the corresponding reactor packing refer to pages 5 – 4 and 5 – 5.

PROCEDURE

For the analysis of two isotopic species (hydrogen and oxygen) from a single sample, a Method, which comprises both of them has to be defined. The acquisition can be completed after less than 7 min (400 s).

As soon as the hydrogen peak (3) has been identified, ISODAT NT stops the HD acquisition. The magnet jumps to the CO Configuration (see: “Switch Gas” column in the Time Events list on page 10 – 8).
If no hydrogen peak can be found, ISODAT NT waits a certain time (e.g. 25 s).
After each injection, immediately data acquisition follows.

Schematic chromatogram:

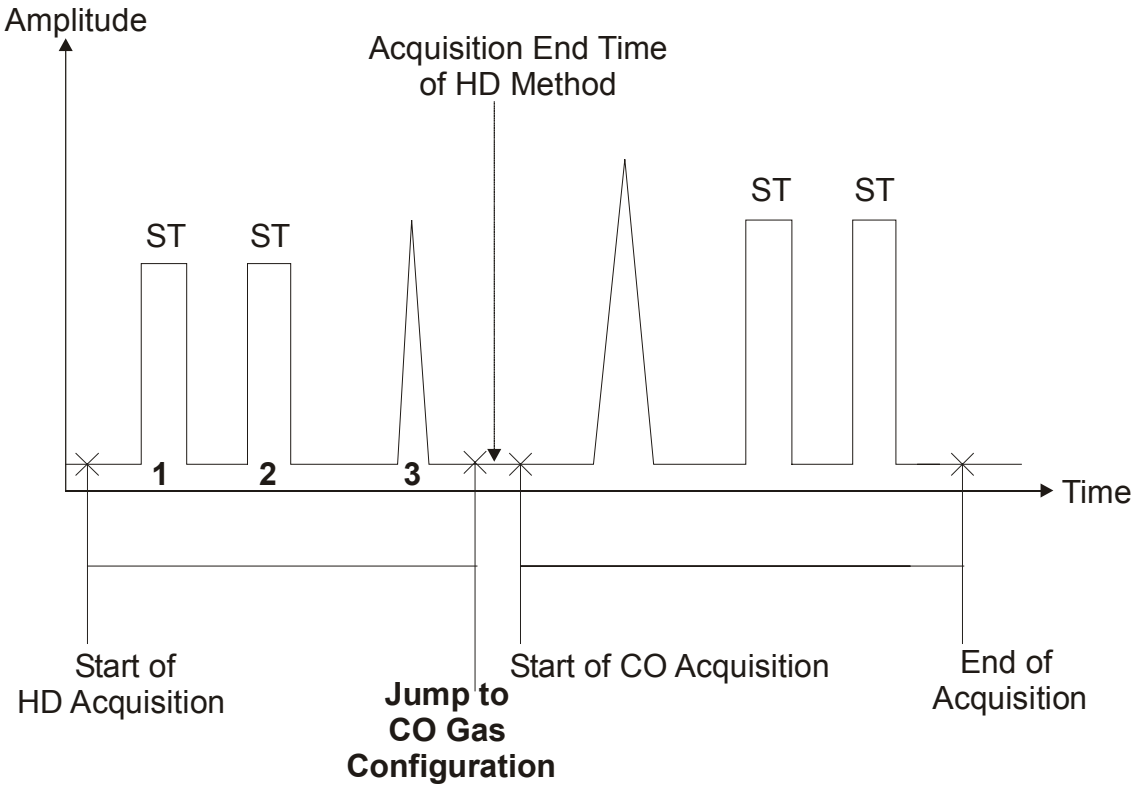


fig. 13

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HOW TO PERFORM A JUMP CALIBRATION (1/4)

After determining the H3-Factor (refer to page 9 – 4), a so-called ***Jump Calibration*** must be performed. A Jump Calibration calibrates for a fast variation of the magnetic field.

In order to determine the isotope ratios of different elements during the same run, switching to another Gas Configuration is necessary.

In contrast to a ***single*** element measurement, in which the magnetic field runs the gamut from high to low and after that to the pre-calculated magnetic field, there is not sufficient time in ***dual*** measurement to perform this procedure for the next gas configuration.

For this reason, a Jump Calibration from the first gas configuration to the next gas configuration is necessary.
After the Jump Calibration has been performed, the computer finds exactly the peak center even without performing any peak center procedure.

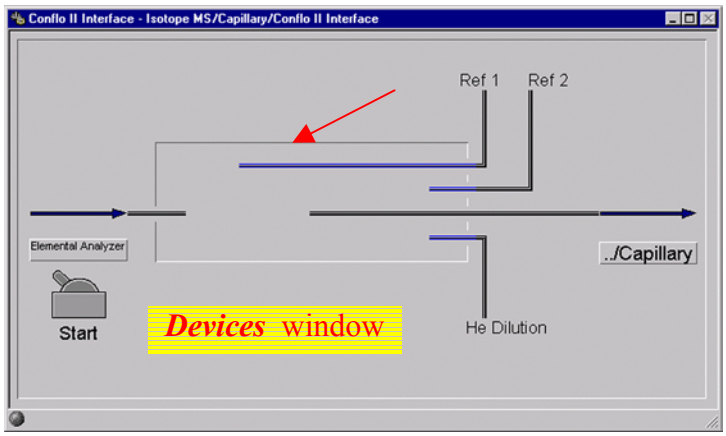
A Jump Calibration should be performed daily to stabilize the performance of the magnet.

NOTE: Both Gas Configurations used (i.e. “H2” and “CO”) need to be calibrated prior to Jump Calibration.

Open Instrument Control.

Choose your ***Configuration*** containing ConFlo II and TC/EA (also in case of ConFlo III interface).

Turn to the ***Devices*** window by pressing this Icon.



Open Reference 1 by a click on ***Ref 1*** capillary.

Thus, the blue capillary symbol elongates and CO enters the system.

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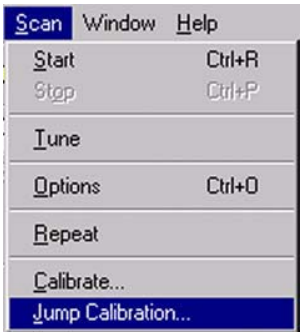
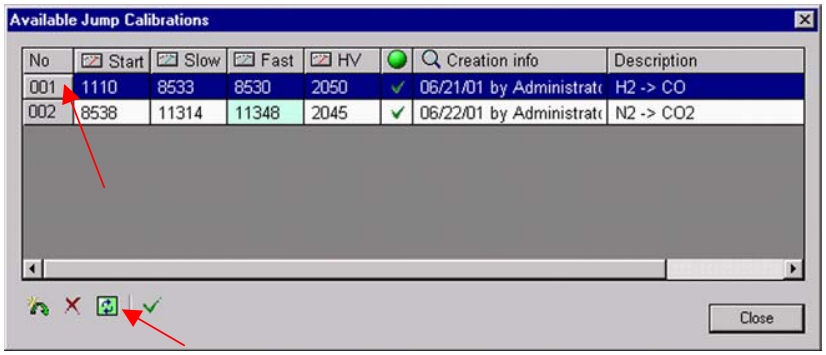
HOW TO PERFORM A JUMP CALIBRATION (2/4)

Return to the Instrument Control window by this Icon.



Select ***Scan*** > ***Jump Calibration*** or alternatively:

on the toolbar next to the Instrument Control window press the ***Jump*** button.



a In the list of available Jump Calibrations mark the one for H_2 → CO by clicking its No. (e.g. 001).

b Press “Recalibrate” Icon.

Slow: compensate hysteresis by Max/Min settings of the magnet.

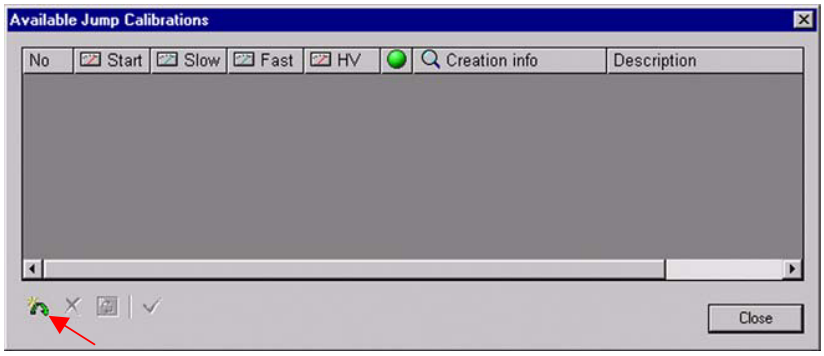
Fast: magnet setting of Jump Calibration

HV: high voltage setting of Jump Calibration

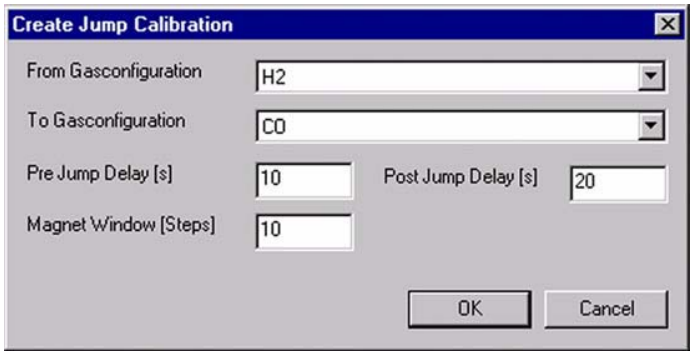
NOTE: If no Jump Calibration is available in the list, create a new one as shown below.

HOW TO PERFORM A JUMP CALIBRATION (3/4)

Comment: How to create a **new** Jump Calibration



Press the ***New*** button.



From Gasconfiguration select ***H2***.

To Gasconfiguration choose ***CO***.

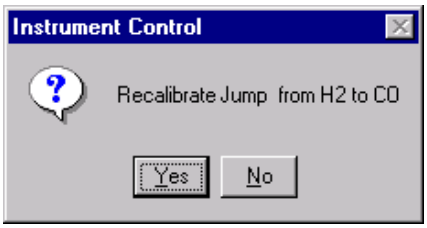
Accept the default values.

Press ***OK***.

NOTE: Magnet jumps are always from a low mass to a high mass (e.g. 2 to 28 at $H_2 \rightarrow CO$ or 28 to 44 at $N_2 \rightarrow CO_2$).

Confirm with ***Yes***, because you have already opened the Reference Port.

HOW TO PERFORM A JUMP CALIBRATION (4/4)



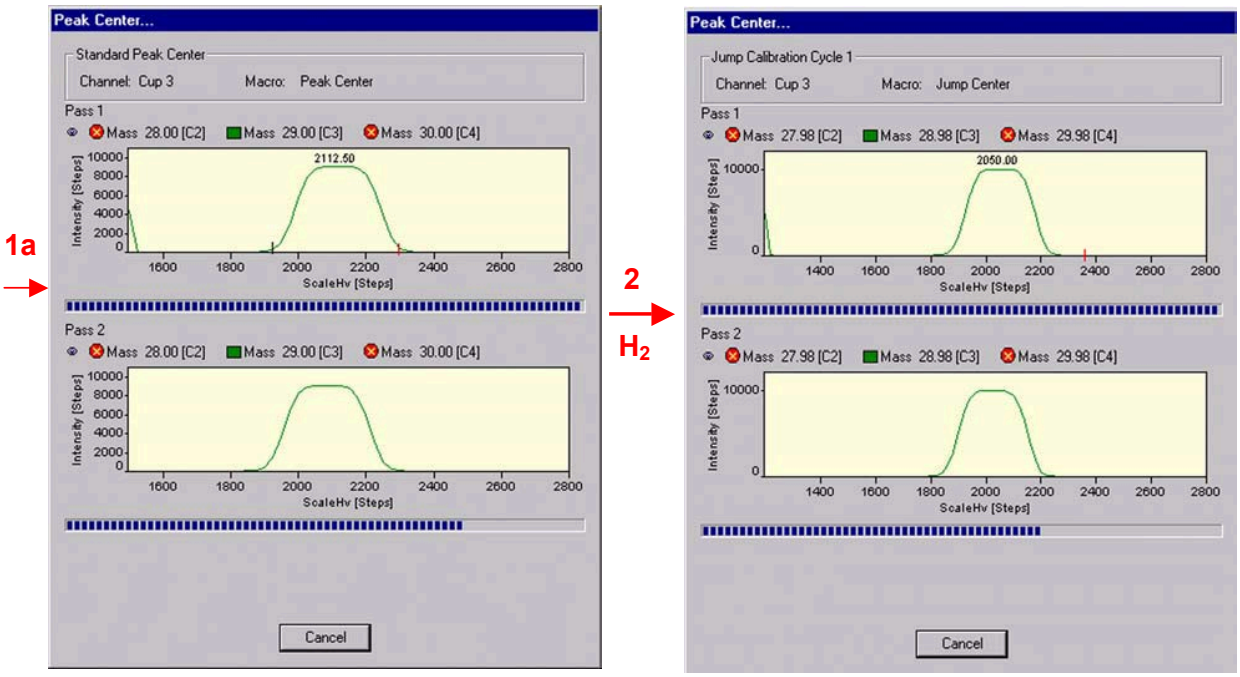
➢ Press ***Yes*** to start Jump Calibration.

Jump Calibration Procedure

1a Jump to CO (along hysteresis curve).
1b Perform a peak center for CO in order to get the signal height.

2 Jump to H_2 (along hysteresis curve; H_2 is origin).

3a Jump to CO (***not*** along hysteresis curve).
3b Perform a peak center for CO in order to catch the peak.



Repeat until magnet field setting is within the “magnet window” defined.

Thermo Finnigan

HOW TO START A DUAL MEASUREMENT (1/7)

1 *Hardware preparation*

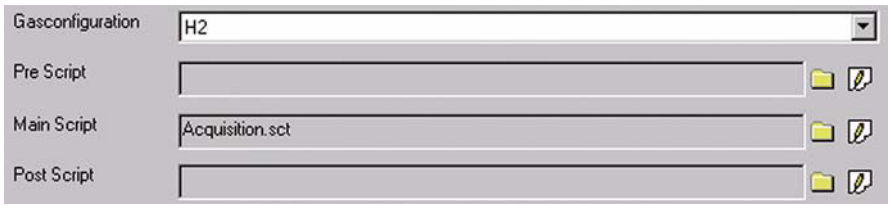
a) Reactor temperature 1450 °C
b) GC column temperature 90 °C
c) He flow > 80 ml/min (≈ 1 bar)
d) *Operating with 1% H_2 in He:*
set the pressure regulator 0.1 bar higher than carrier gas (He).
e) *Operating without auxiliary gas:*
turn down auxiliary pressure regulator so that auxiliary gas pressure decreases until shown pressure equals pressure of carrier gas.
f) Purge (He flow is sufficiently open).
g) Standard gas H_2 on ConFlo II/III - or inside variable volume - available
h) Standard gas CO on ConFlo II/III - or inside variable volume - available
i) Needle valve (ConFlo II/III - IRMS connection) is open.
j) Standard intensity (H_2) is adjusted at about 5.5 V.
k) Standard intensity (CO) is adjusted at about 3 - 4 V.

2 Determine ***H3-Factor*** as described on pages 9 – 4 to 9 – 6.

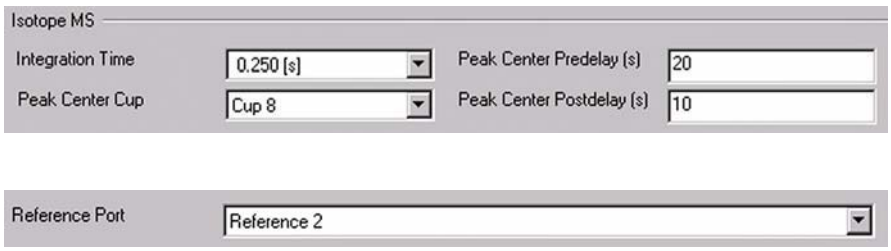
3 ***Define a Method*** (as shown on pages 9 – 12 to 9 – 13).

As a guideline, use the following Method ***("HD_CO.met")***:

Instrument



Isotope MS



Thermo Finnigan

HOW TO START A DUAL MEASUREMENT (2/7)

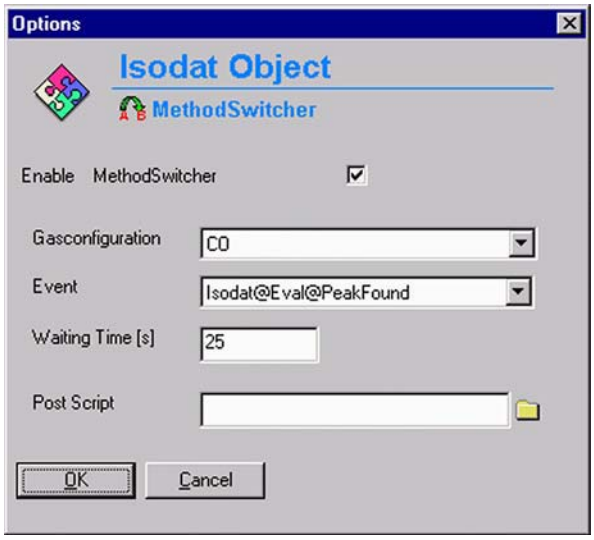
Time Events

Time [s]	Start Sampler	Elemental Anal. - On	Dilution - Open	Reference 1 - Open	Reference 2 - Open	Switch Gas
20						
40						
60						
80						
90						
95						
130						CO
340						
360						
400						
420						

Double-click on ***CO*** in the ***Switch Gas*** column to edit.

(The Event Time is active since e.g. 130 s).

Acq. End Time



- The Gas Configuration to be switched to is selected in the ***Gasconfiguration*** menu (e.g. “CO”).
- The switch will be performed when the peak has been found. This is defined in the ***Event*** menu (e.g. “Isodat@Eval@PeakFound”).
- Type in the last jump time at ***Waiting Time***. At e.g. 130 s, waiting for the peak begins. If a peak is found, the jump takes place. If no peak is found, the waiting time elapses before the jump takes place.
- Select a ***Post Script***, which will be executed during the jump.

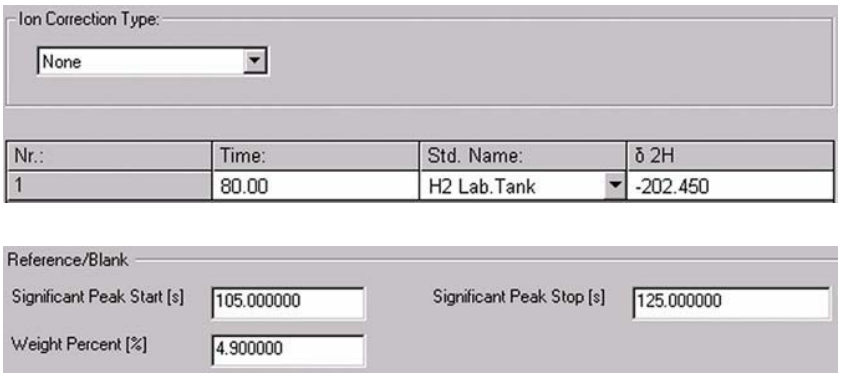
NOTE: For samples with a high O to H ratio, the activation of the dilution can be directly linked to the magnet jump to CO. In this case, use the ***He dilution Script***.

HOW TO START A DUAL MEASUREMENT (3/7)

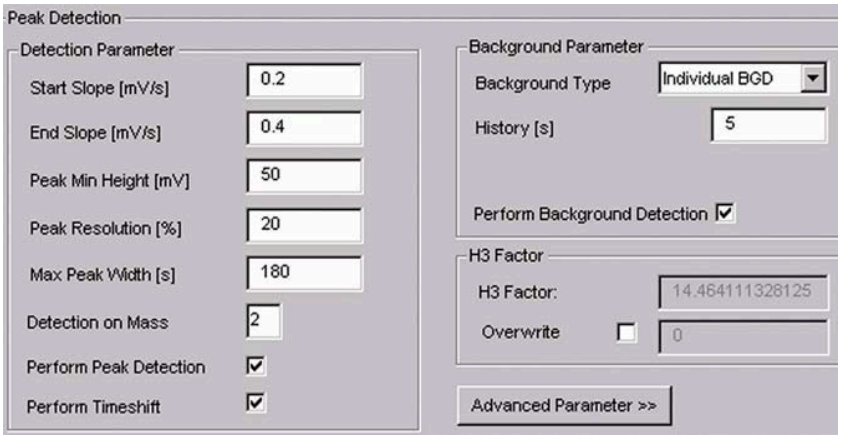
2 Define a Method (continued)

NOTE: For H_2 and CO ***different*** Evaluation tabs, Peak Detection tabs and Printout tabs appear (e.g. “Evaluation@H2”, “Evaluation@CO2”).

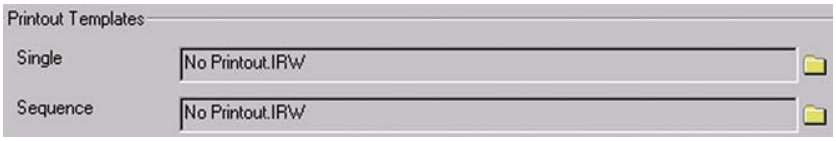
Evaluation@H2



Peak Detection@H2



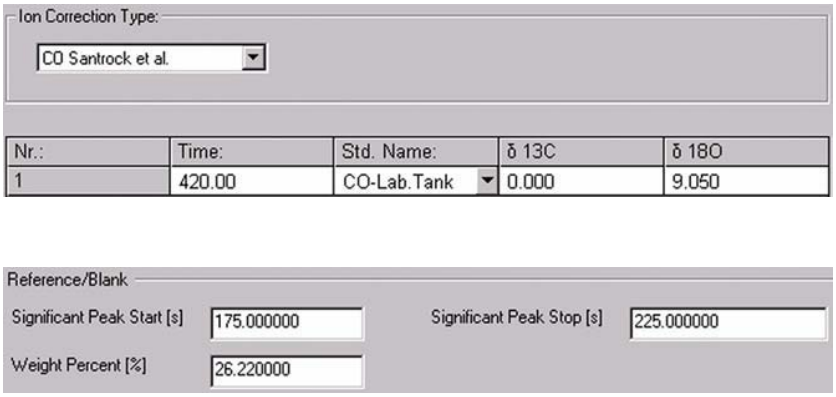
Printout@H2



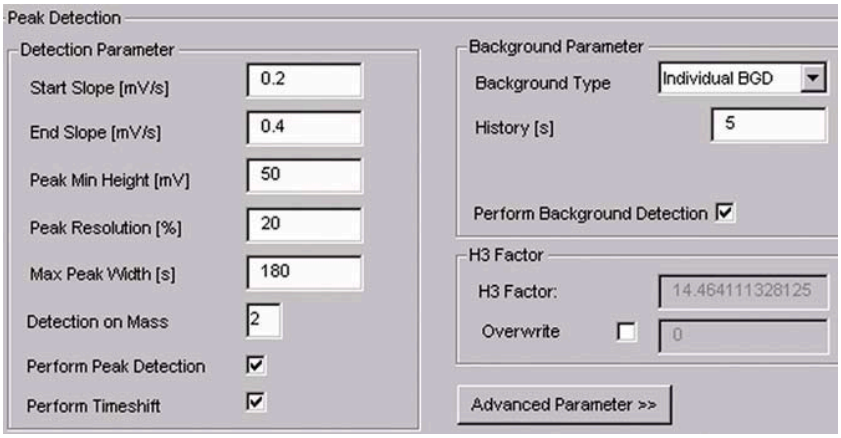
HOW TO START A DUAL MEASUREMENT (4/7)

NOTE: Usually, the printout of results is performed not until the complete measurement has been finished. Therefore, it is recommended to choose “No Printout.irw” at “Printout@H2” tab, because at this moment, data acquisition is still running. Instead, printout options are defined at the end at “Printout@CO” tab.

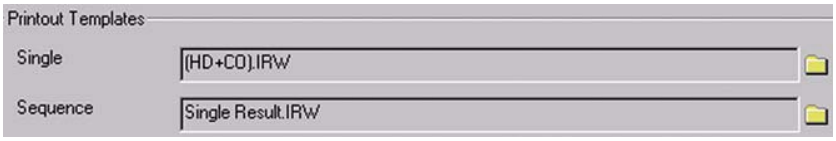
Evaluation@CO



Peak Detection@CO



Printout @CO

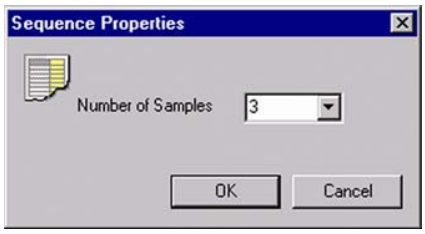


HOW TO START A DUAL MEASUREMENT (5/7)

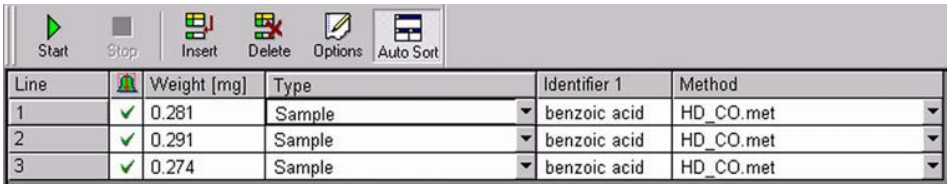
3 Place a sample (e.g. 0.281 mg of benzoic acid) in the solid-autosampler.

4 **Create a new Sequence**

5 Define number of samples.



6 Edit the Sequence list.



Peak Center Enable ☑ to perform a Peak Center prior to measurement.

Weight Type in sample mass [mg].

Type Select kind of species (e.g. “Sample”).

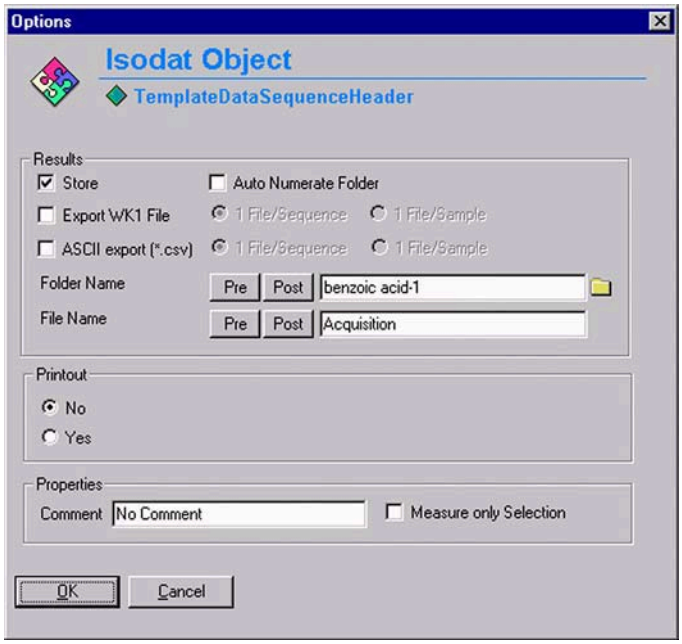
Identifier 1 Edit text to identify sample.

Method Select IRMS Method (e.g. “HD_CO.met”).

7 Press the ***Start*** button.

HOW TO START A DUAL MEASUREMENT (6/7)

8 Define Results Storage, Export and Printout parameters.



9 Press ***OK*** to start Sequence Acquisition.

Events during Acquisition

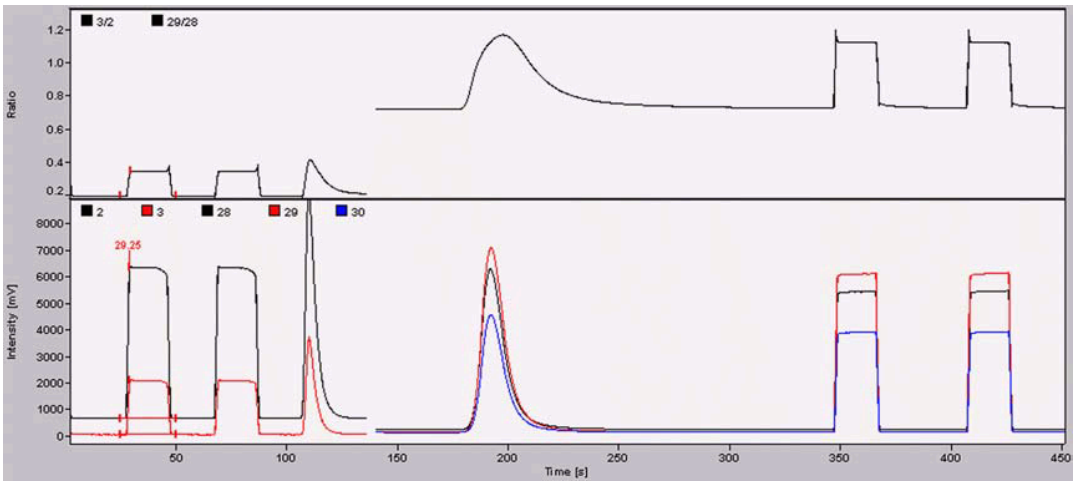
- Peak Center procedure
- H_2 Reference Gas pulse activated at 20 s (duration: 20 s).
- H_2 Reference Gas pulse activated at 60 s (duration: 20 s).
- Sample is dropped into reactor.
- Sample peak (H_2) appears approximately 15 s after reaction start.
- Sample peak (CO) appears approximately 100 s after reaction start (see page 8 – 16).
- CO Reference Gas pulse activated at 340 s (duration: 20 s).
- CO Reference Gas pulse activated at 400 s (duration: 20 s).
- Acquisition stops at 450 s.

HOW TO START A DUAL MEASUREMENT (7/7)

After finishing data acquisition the printer creates a data output sheet as defined by the selected Result Workshop template (*.irw). The Results will also be exported to a spreadsheet file, if activated.

C:\FINNIGAN\ISODAT NT\Global\User\Conflo II Interface\Results\Benzoic acid HD-CO.CF

Line		Weight [mg]	Type	Identifier 1	Method
1	✓	0.281	Sample	benzoic acid	HD_CO.met



H2 | CO | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 2 [mV]	Ampl. 3 [mV]	BGD 2 [mV]	BGD 3 [mV]	R 3/2	Area [Vs]	δ 2H [‰] vs. V-SMOW	AT% 2H [%]	Wt% [%]
1	29.3	25.4	5725	2053	637.6	38.5	0.00025	104.756	-169.779	0.012929	-
2*	69.1	27.3	5723	2051	637.0	38.4	0.00025	104.970	-169.895	0.012927	-
3	110.0	29.2	8695	3675	638.0	38.5	0.00028	45.597	-75.440	0.014398	4.9000000

The “H2” tab reveals information about the hydrogen related peaks.

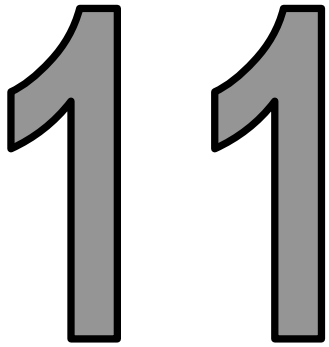
H2 | CO | Sequence | Error | Extended

Nr.	Rt [s]	Width [s]	Ampl. 28 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area [Vs]	δ 13C [‰] vs. PDB	δ 18O [‰] vs. V-SMOW	AT% 18O [%]	Wt% [%]
4	192.2	96.6	6055	218.8	128.1	80.238	12.284	29.314	0.205973	26.2200000
5	366.0	33.5	5232	225.0	135.1	99.372	0.571	9.649	0.202046	-
6*	426.1	36.2	5252	225.8	135.9	99.709	0.000	9.050	0.201926	-

The “CO” tab reveals information about the oxygen related peaks.

High Temperature Conversion

Elemental Analyzer (TC / EA)



TECHNICAL INFORMATION

Issue 11/2001

Thermo Finnigan

INTRODUCTION

NOTE: This chapter is intended for trained personnel only.
Thermo Finnigan denies liability for this Manual.
Thermo Finnigan denies responsibility for failures in this Manual.

WARNING: Close standard gas (CO or H_2) to prevent health problems or an explosion!

WARNING: The reactor and GC column may be hot!
Cool down prior to working on the system!

WARNING: Switch **OFF** main power prior to working in order to prevent an electrical shock!

This section contains general remarks concerning the mechanical and electronical parts of the Service Manual. The TC / EA contains elaborate and expensive components. Therefore, only qualified and skilled personnel should perform servicing.

Important hints prior to performing servicing the TC/EA

- Cool down reactor and GC to ambient temperature.
- Switch main power supply “OFF” and remove cable from mains.
- Turn carrier gas (He) and auxiliary gas to a minimum.
- Be very careful when removing Autosampler installation platform/cover plates!
- When replacing fuses only use the correct type.
- It is recommended to use Thermo Finnigan spare parts only.

STRUCTURE OF THIS CHAPTER

Chapter 11 is area-structured (front panel, side panels, top, rear panel). The part numbers of the specific component parts are mainly written beside them. In addition, a spare part list provides an overview about the part numbers and the quantity of all components. The list is also area-structured so that the specific information easily can be found.

NOTE: Continuous improvement of the performance of our products may result in technical modifications without a notification to the user.

SIDE PANEL (LEFT) OPEN

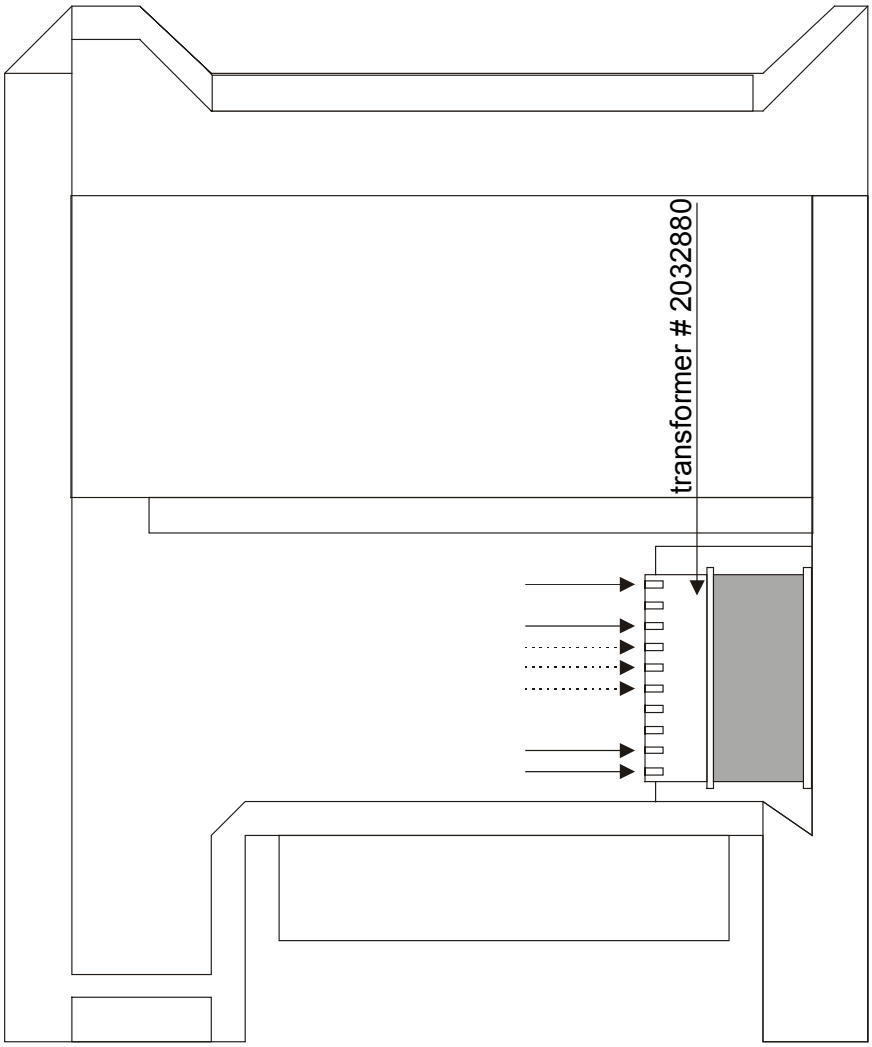


fig. S1

WARNING: Switch **OFF** main power while working in order to prevent an electrical shock!

SIDE PANEL (RIGHT) OPEN

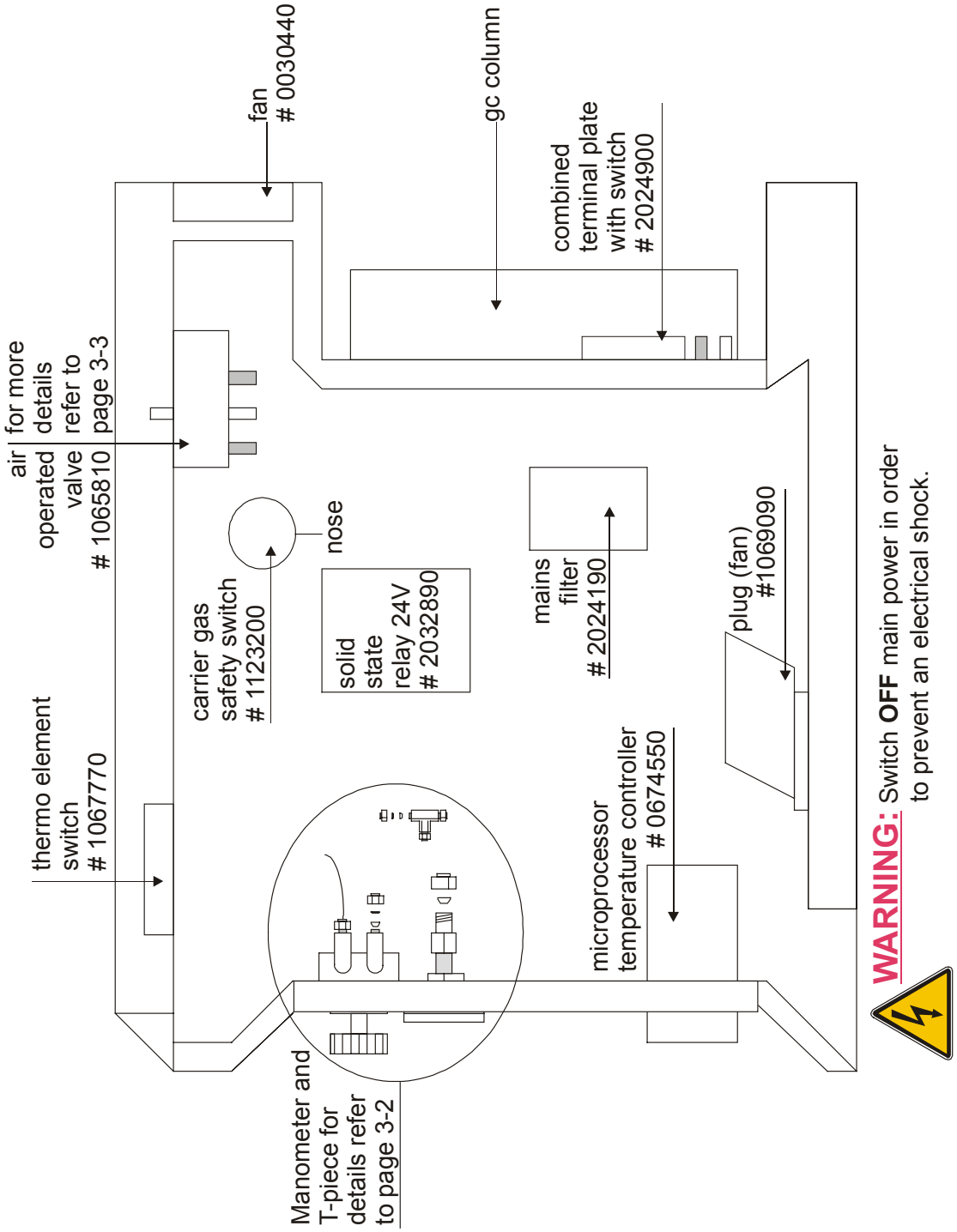


fig. S 2

Thermo Finnigan

TC / EA MANOMETER

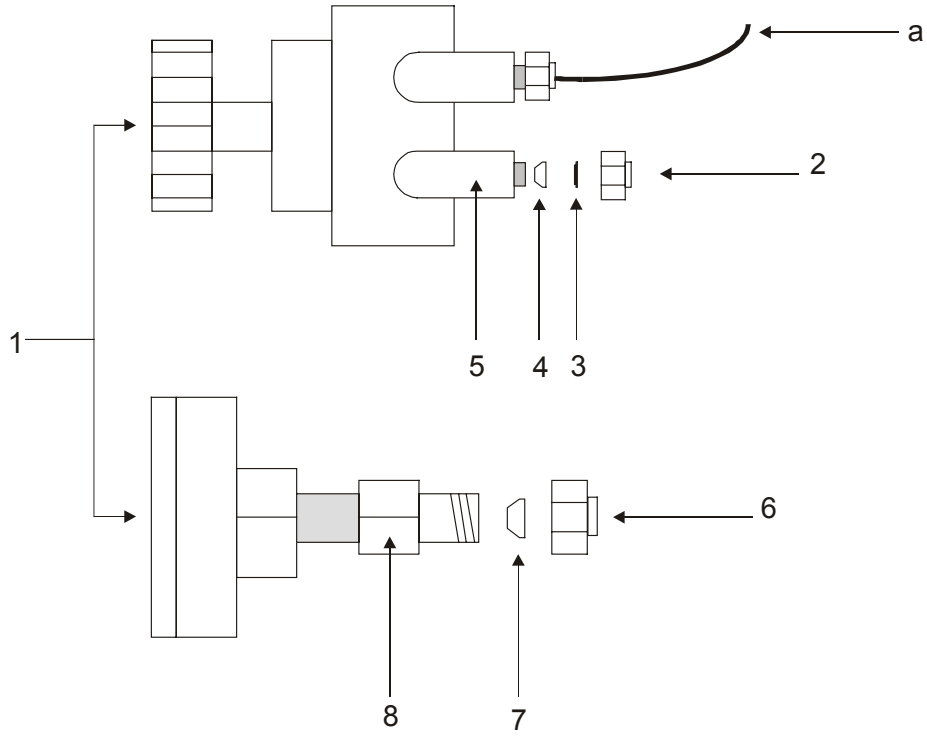
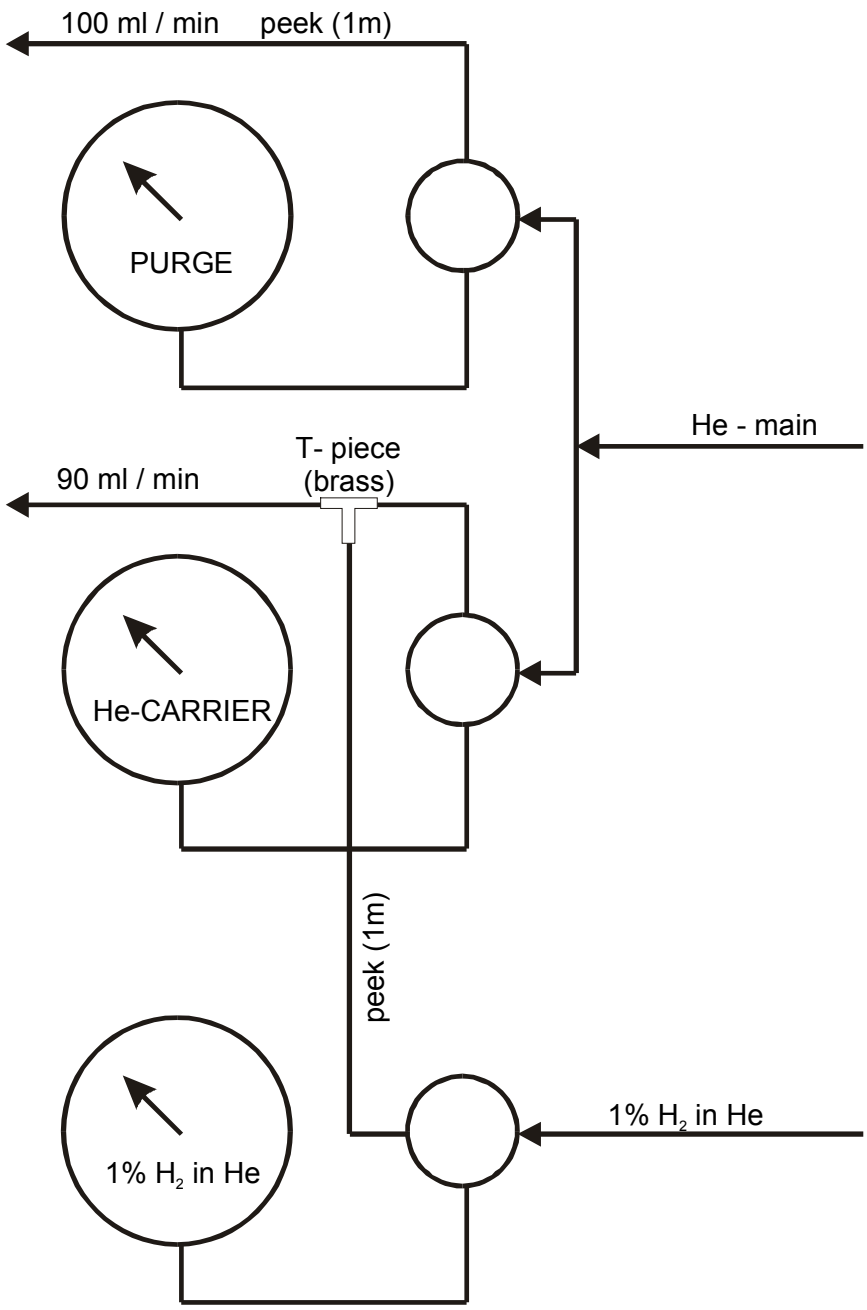


fig. S 3

Pos.	*Notation*	*Part Number*
a	Peek tubing	# 0 70 41 30
1	Manometer 0 - 2,5 bar	# 0 52 43 91
2	Cap nut 1/16´´	# 0 52 36 10
3	Back ferrule 1/16´´	# 0 52 32 10
4	Front ferrule 1/16´´	# 0 52 34 40
5	Elbow	# 0 49 31 90
6	Cap nut 1/8´´	# 0 52 15 00
7	Ferrule; teflon 1/8´´	# 0 67 47 90
8	Coupling 1/8´´	# 0 74 33 60

GASFLOW DIAGRAM



TC / EA T-PIECE AND AIR OPERATED VALVE

T- piece
0 52 34 60

Air operated
valve
1 06 85 10

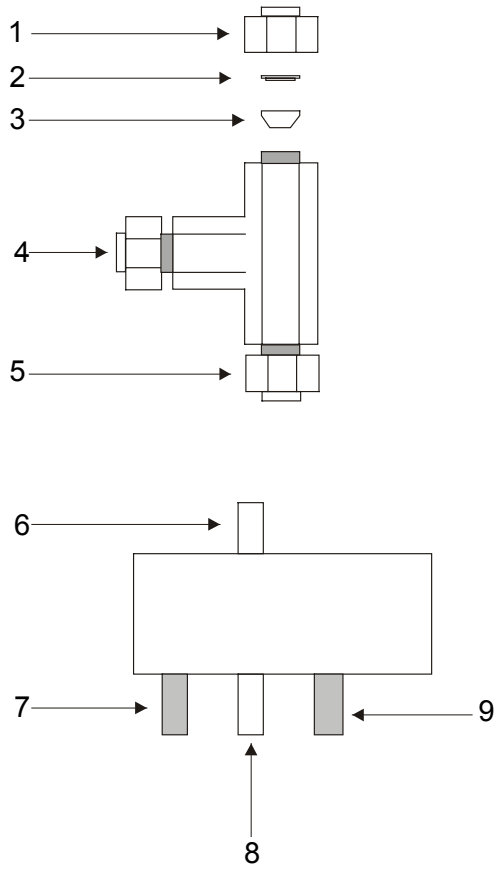


fig. S 4

Pos.	*Notification*	*Part Number*
1	Cap nut 1/16´´	# 0 52 36 10
2	Back ferrule 1/16´´	# 0 52 32 10
3	Front ferrule 1/16´´	# 0 52 34 40
4	Cap nut 1/16´´	# 0 52 36 10
5	Cap nut 1/16´´	# 0 52 36 10
6	Helium: permanent in	
7	Helium: time controlled in	
8	Helium: permanent out	
9	Helium: time controlled out	

REAR PANEL OPEN

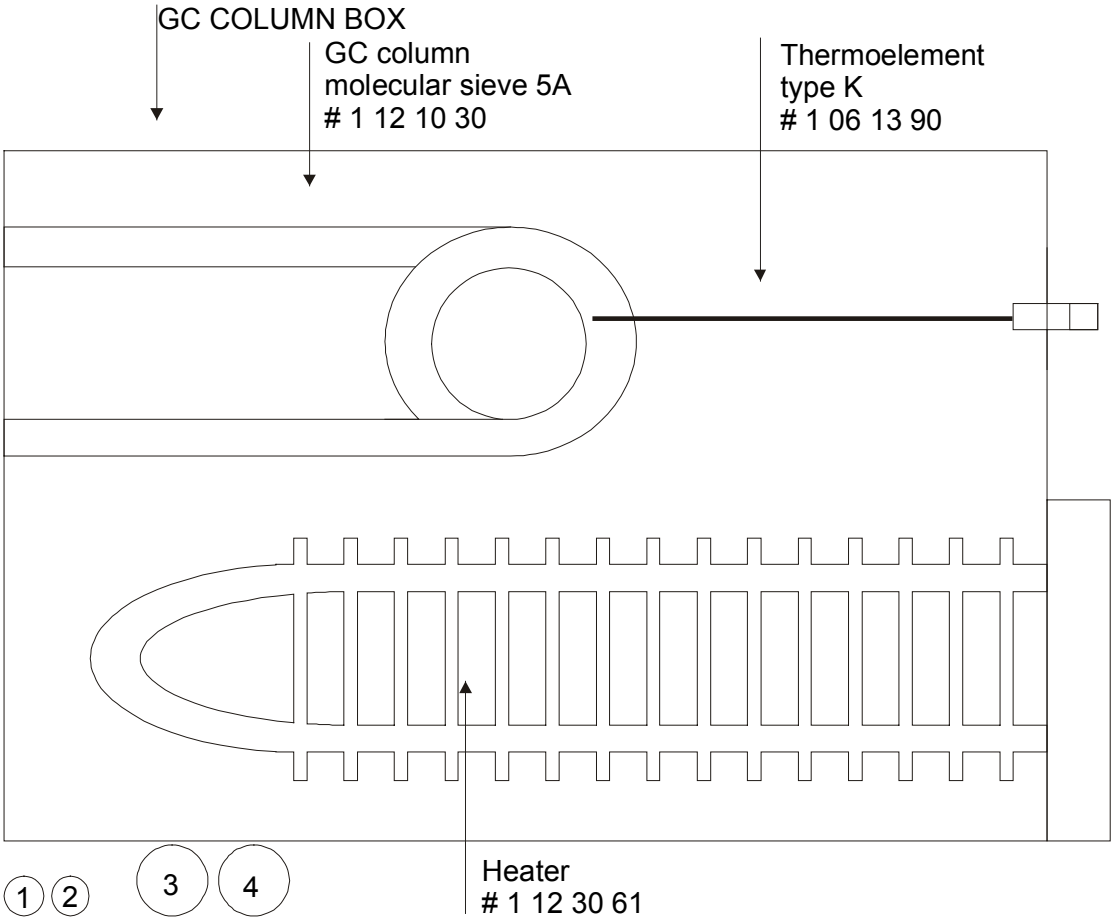


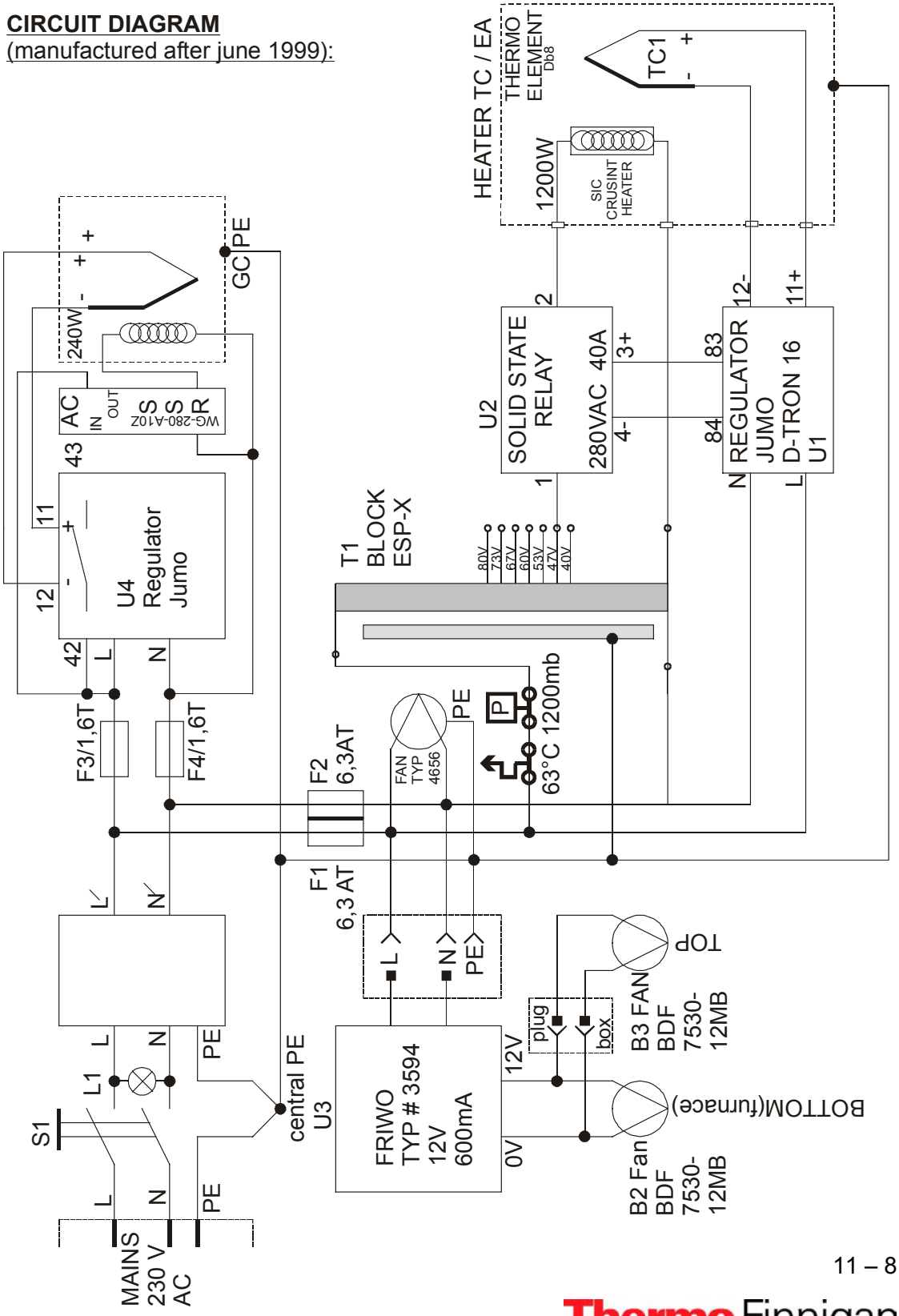
fig. S 5

1 Auxiliary gas (1% H_2 in He)
2 Standard gas (He)
3 Compressed air permanent (# 0674651)
4 Compressed air time controlled (# 0674651)

WARNING: Make sure the temperature has cooled down prior to working near the GC-column

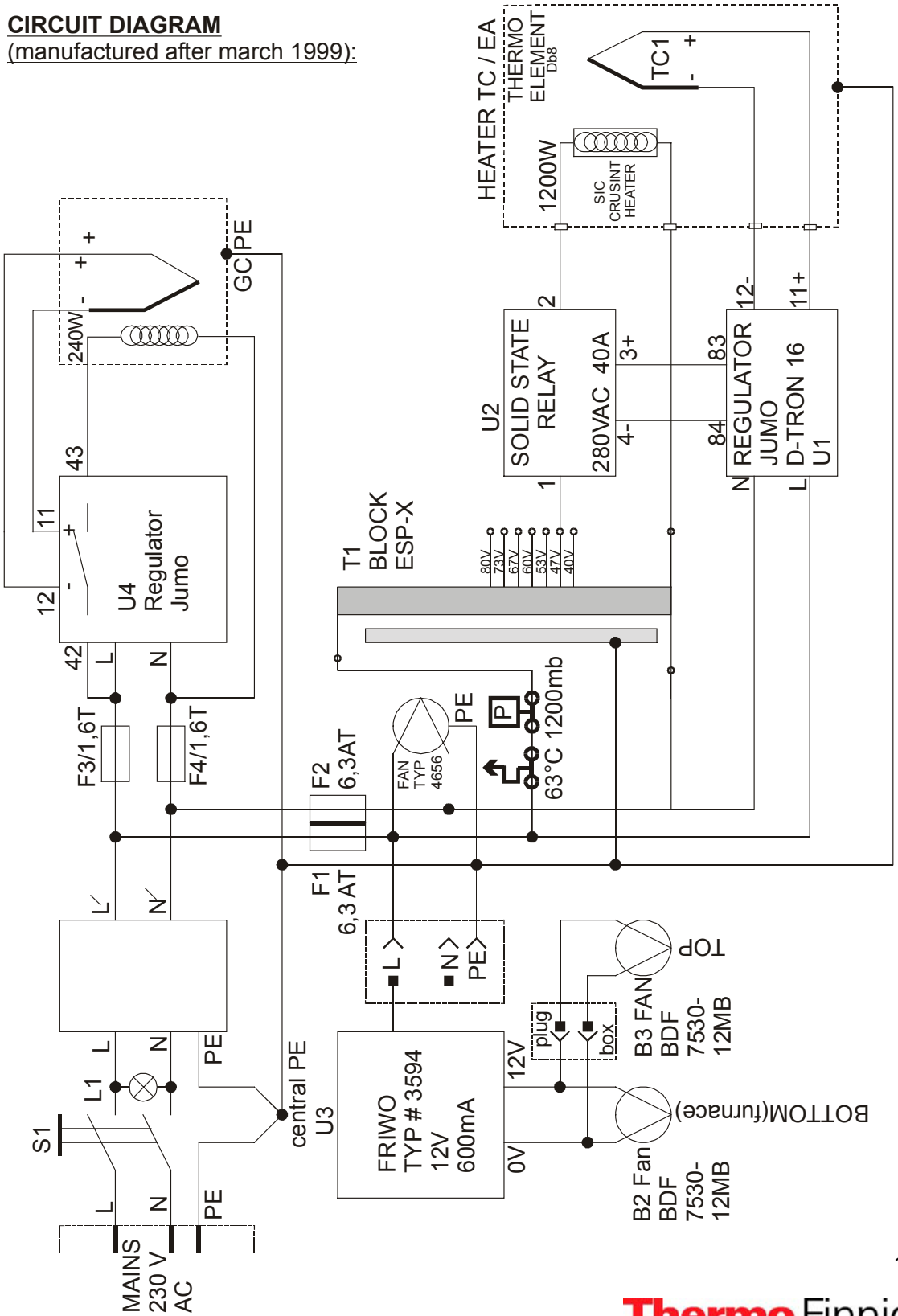
WARNING: Switch **OFF** main power while working in order to prevent an electrical shock!

CIRCUIT DIAGRAM
(manufactured after june 1999):



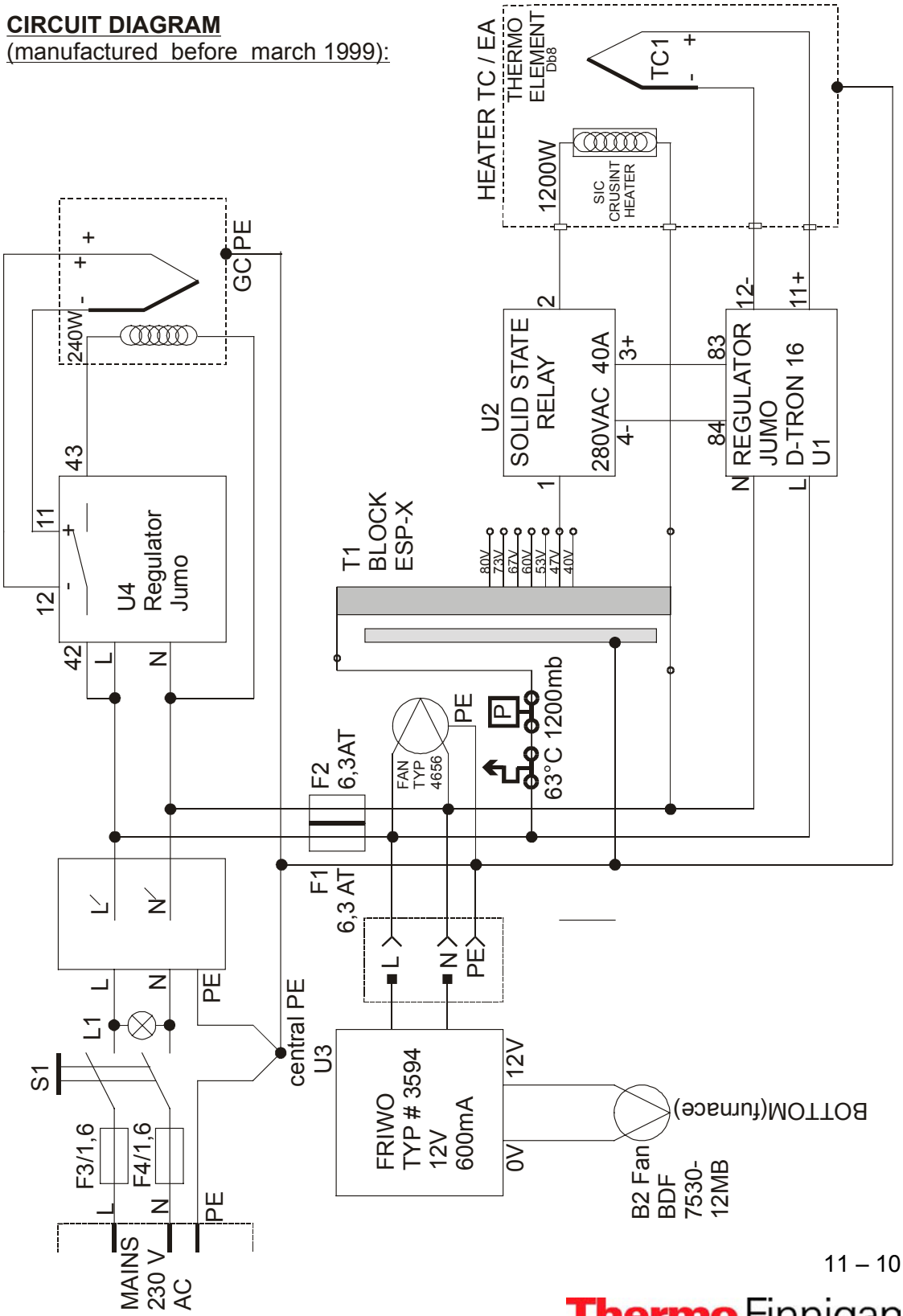
Thermo Finnigan

CIRCUIT DIAGRAM
(manufactured after march 1999):



Thermo Finnigan

CIRCUIT DIAGRAM
(manufactured before march 1999):



Thermo Finnigan

SPARE PART LIST (1/2)

	Notation	Part Number	Quantity
1	***Front panel***		
	Fan (12V)	# 1 12 10 40	1 piece
	Bottom reactor connection (nut, washer, o-ring (viton), screw	# 1 12 13 30	1 set
	Ceramic tube	# 1 12 13 20	1 piece
	Glassy carbon granulate	# 1 11 74 00	50 gram
	Glassy carbon reactor	# 1 12 13 10	1 piece
	Graphite crucible	# 1 11 73 30	10 pieces
	Graphite tube (big)	# 1 12 13 51	1 piece
	Graphite tube (thin)	# 1 12 13 50	1 piece
	Olive 1/16´´ (Al)	# 1 12 11 30	5 pieces
	O-ring (viton)	# 1 12 11 20	4 pieces
	Quartz wool	# 1 08 77 70	1 piece
	Reactor holder	# 1 12 10 20	1 piece
	Screw	# 1 12 11 40	5 pieces
	Silver wool	# 1 11 74 30	1 piece
2	***Side panel (right)***		
	Air operated valve	# 1 06 85 10	1 piece
	Carrier gas safety switch	# 1 12 32 00	1 piece
	Combined terminal plate with switch	# 2 02 49 00	1 piece
	Fan	# 0 03 04 40	1 piece
	Fuse 1,6	# 2 01 17 80	2 pieces
	Fuse 6,3	# 2 01 18 40	2 pieces
	Mains filter (1X6 A; 230V)	# 2 02 41 90	1 piece
	Manometer	# 0 52 43 91	2 pieces
	-Back ferrule 1/16´´	# 0 52 32 10	
	-Cap nut 1/16´´	#	
	-Cap nut 1/8´´	# 0 52 15 00	2 pieces
	-Coupling 1/8´´	# 0 74 33 60	3 pieces
	-Elbow	# 0 49 31 90	6 pieces
	-Ferrule (teflon) 1/8´´	# 0 67 47 90	3 pieces
	-Front ferrule 1/16´´	# 0 52 34 40	
	Microprocessor temperature controller	# 0 67 45 50	2 pieces
	Peek tubing	# 0 70 41 30	1.1 m
	Plug (fan)	# 1 06 90 90	1 piece
	Safety switch	# 0 07 12 60	2 pieces
	Thermo element switch	# 1 06 77 70	1 piece
	T-piece	# 0 52 34 60	2 pieces

SPARE PART LIST (2/2)

	Notification	Part Number	Quantity
3	***Side panel (left)***		
	Transformer	# 2 03 28 80	1 piece
4	***Rear panel***		
	Compressed air	# 0 67 46 51	2 piece
	GC column "Molecular sieve 5A"	# 1 12 10 30	1 piece
	Heater	# 1 12 30 61	1 piece
	Thermoelement	# 1 06 13 90	1 piece
	Aperture (fan)	# 1 12 34 10	1 piece
5	***Top***		
	O-ring (viton)	# 1 12 11 20	4 pieces
6	***Additional***		
	Gloves (small)	# 1 09 13 00	1 pair
	Gloves (medium)	# 1 09 12 90	1 pair

TROUBLESHOOTING

Symptom	*Cause / Remedy*
( ) power does not turn on	- mains cable not connected or fuse is defective
( ) power is on but heater does not operate	- safety device is operating - leak present / insufficient He-flow
( ) Reactor heater switches at higher temperatures	- safety devices are operating - autosampler installation platform too hot rear fan is defective or no sufficient He-flow - thermo element switch is defective
( ) increasing the pressure regulator the He-flow does not increase gradually	- leak present
( ) CO, N2 peak width is too large / large peak tail / resolution between CO, N2 is too bad	- GC-column is contaminated heat it at 300°C / He-flow 90 ml/min for 12 hours - graphite crucible is located too tight to glassy carbon reactor (file it carefully) - graphite crucible has run over
( ) Background peak of N2, H2O, O, Ar is too high	- leak present - GC-column is contaminated (heat it as above)
( ) reactor heating limits at lower temperature than selected	- refer to section “Transformer”
( ) reactor heater does not work	- reactor heater is broken (refer to “Furnace”) - no He-flow - fuse is defective
( ) heating action of reactor heater does not limit	- thermo element is defective - solid state relays is defective - microprocessor temperature contr. is defective
( ) heating action of GC column does not limit	- thermo element is defective - microprocessor temperature contr. is defective

TRANSFORMER

The reactor heating stops at a lower temperature than selected, because the resistor value increases over time. Therefore, a higher voltage setting becomes necessary.

NOTE: A new reactor heater has a resistor of approximately 3.0 Ω.
After six months of operation, the resistor is about 8 - 9 Ω.

For a new setting proceed as follows:

- Switch “OFF” main power supply.
- Remove the left side panel.
- Move wire (B) to the next higher value (see fig. S 6).

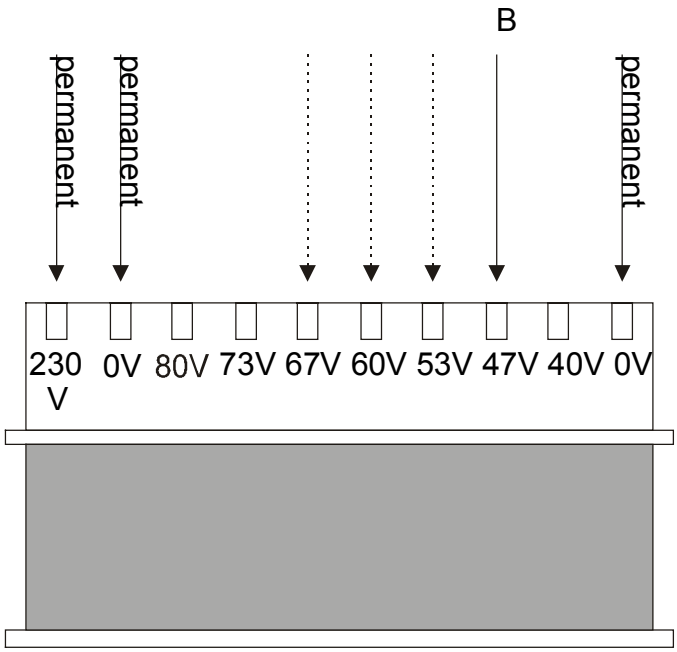


fig. S 6

WARNING: Switch ***OFF*** main power prior to working to prevent an electrical shock!

FURNACE (1/2)

a) The heating action of the reactor does not limit because of a defective thermo element. Proceed as written below.

b) The heater does not work because it is broken. Proceed as written below.

1 Cool down the system to ambient temperatures.
2 Switch “OFF” main power and unplug TC/EA from main power supply.
3 Close He gas and auxiliary gas supplies.
4 Remove the Autosampler.
5 Disconnect top and bottom connection and pull out the reactor carefully.
6 Unscrew the Autosampler installation platform (fig. 7).
a7) Unscrew the wires from the terminal block for light fixtures of thermo element.
a8) Pull out the thermo element carefully.

NOTE: Remember to contact the red marked wire with the plus pole when connecting the new thermo element (# 1 12 14 70).

NOTE: If the heater is broken, it is recommended to replace the whole furnace.

b7) Unscrew the wires A - D.
b8) Unscrew and remove the upper screws E.
b9) Unscrew the lower screws E ***but do not remove them!***
Otherwise, the furnace will fall down.
b10) Take the furnace out (by lifting).

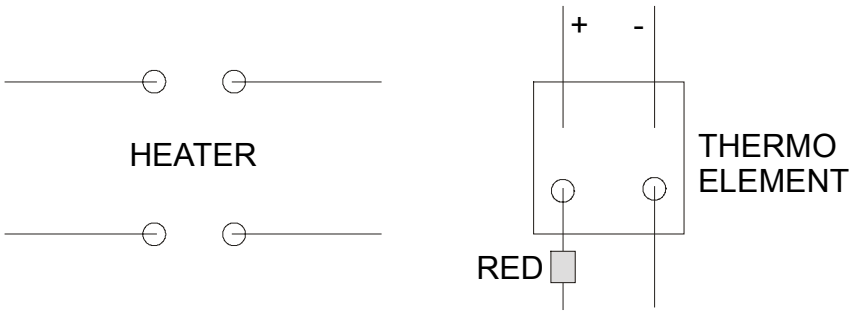


fig. S 7

Connections

new: varying, but mostly < 5 Ω (The value increases with time, depending on temperature).
old: approximately 9 Ω.

FURNACE (2/2)

Top view

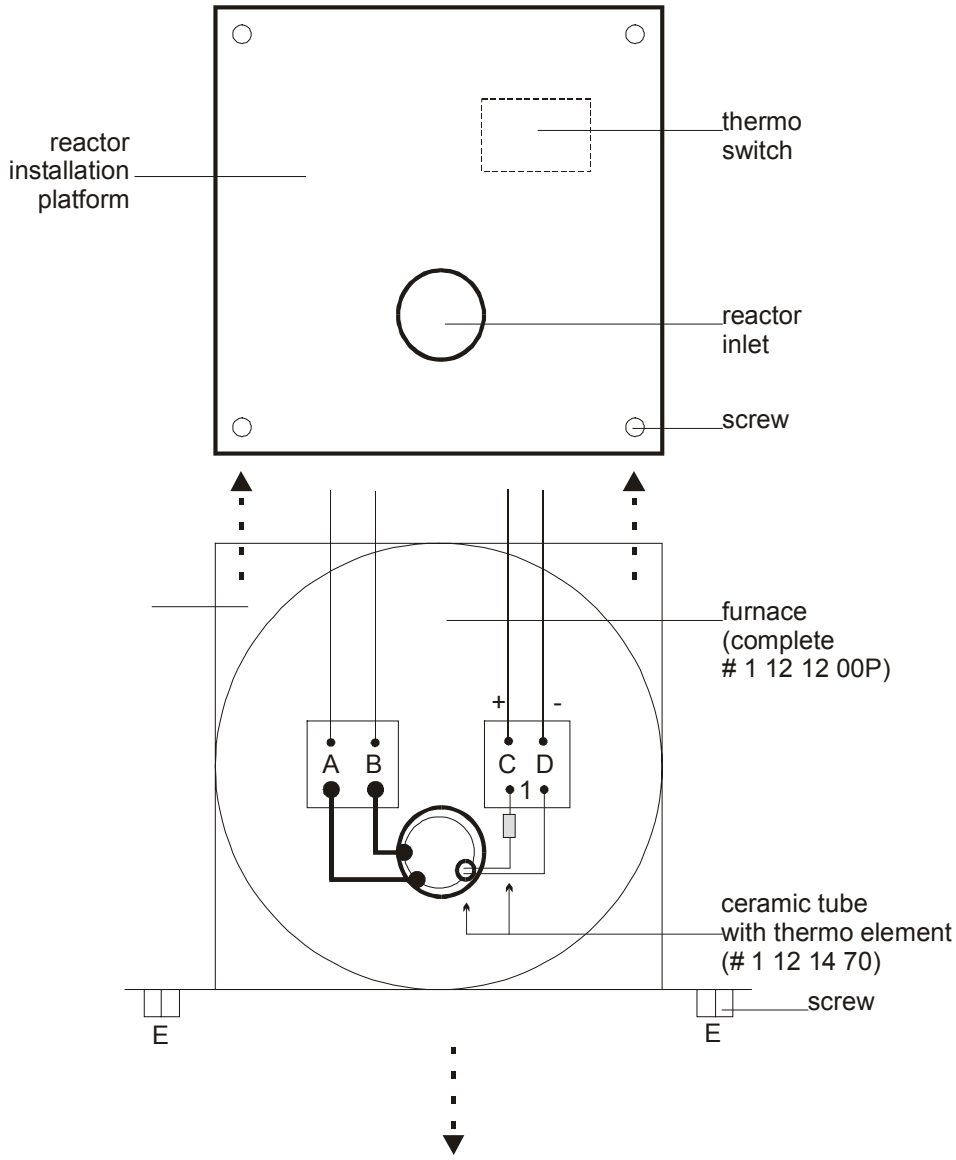


fig. S 8

WARNING: **If the furnace or parts of it are damaged, always protect it using the transportation lock to avoid more damage during transport!**

The transportation lock will also be necessary for protecting the furnace during return transport.

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MANUAL HISTORY

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