# *DELTA*$^{plus}$

# OPERATING MANUAL

**Thermo** Finnigan

**Ident No.: 104 7400**

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## 1. Introduction

This manual describes the functions and the fundamental measuring procedures of your Thermo Finnigan MAT ***DELTA***$^{plus}$ mass spectrometer. In addition, further manuals are supplied, i.e.

the ISODAT Manual,

the Service Manual,

specific manuals for the purchased peripheral equipment.

To obtain a good understanding of the complete system, it is necessary to study the Operating and Software Manuals before starting up your instrument.

To reach a high level of performance with the Thermo Finnigan MAT ***DELTA***$^{plus}$, we recommend to make use of the Operator Courses provided by us at our facilities in Bremen, and/or on-site.

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### 1. 1 Basic Instrument

With the Thermo Finnigan MAT ***DELTA***$^{plus}$ you can perform gas isotope ratio measurements of

H/D, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$.

For classical applications, the basic instrument can be equipped with a dual inlet system. It is of modular design for the adaptation of different inlet modules, thus enabling a configuration of the instrument tailored to the requirements of the user. Options connecting to the sample side are:

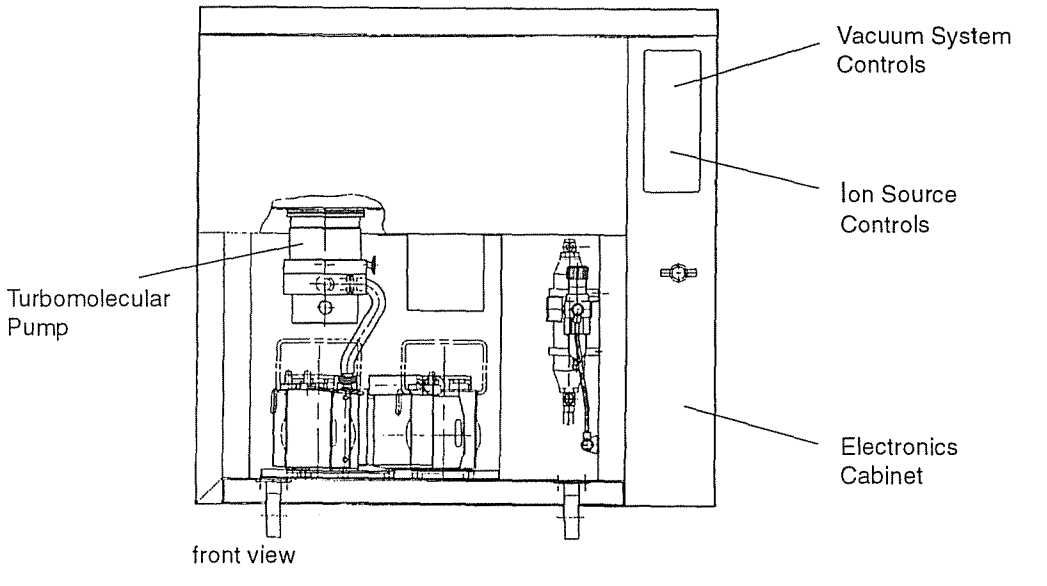
- a secondary inlet system for up to 20 samples, i.e. a multiport with or without automatic tube crackers.
- a microvolume for very small samples
- external multisample inlets for separating and purifying samples,
- installations for "on-line" coupling of gas chromatographs, elemental analyzers or other peripherals.

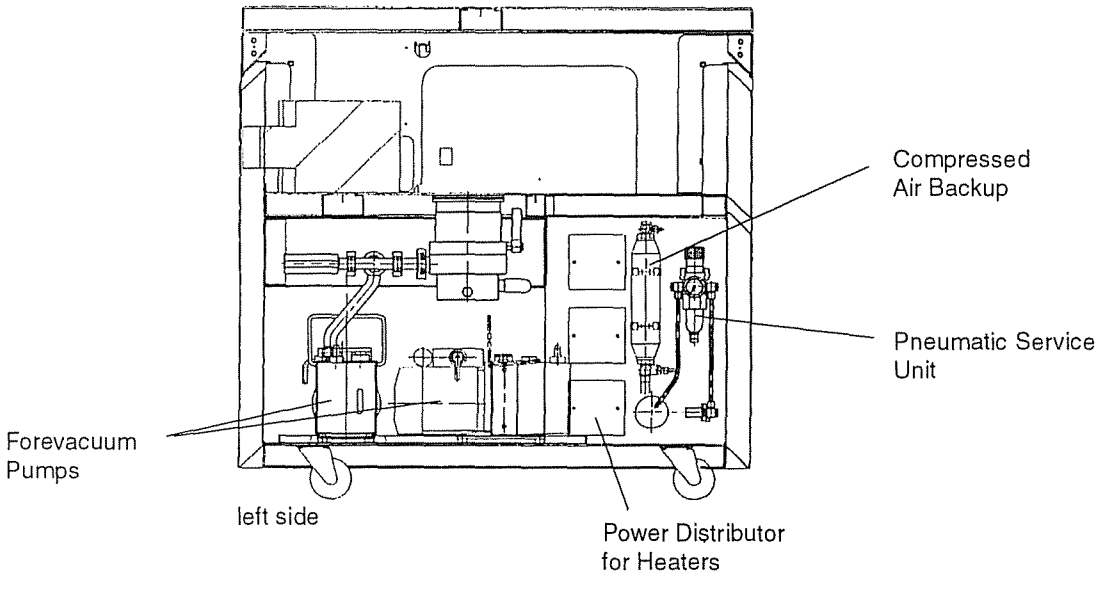
# 1 Introduction

The configuration of the inlet systems is described in this manual. Please refer to chapter 4, Inlet Systems.
Detailed information about other inlet sytems such as "on-line" coupling of gas chromatographs or elemental analyzers is provided in the manual describing the peripheral equipment.

Please make yourself familiar with the controls on the front and all the connections and installations on the rear of your instrument.

**Fig.: 1 - 1**
View of the ***DELTA***$^{plus}$ showing the location of the components



## 1. 2 ISODAT™ Software

The operation of the Thermo Finnigan MAT ***DELTA***$^{plus}$ is fully computerized and controlled by the Thermo Finnigan MAT software ISODAT operating in multitasking mode (realtime), i.e. different procedures such as

- instrument operation and control,
- sample preparation.
- data acquisition
- data processing for screen and printer output

are performed in parallel.

A separate manual describes the procedures of the ISODAT software and provide guidance on how to use the pop-up menus with a mouse or how to operate without a mouse using the function keys and to enter the appropriate commands.

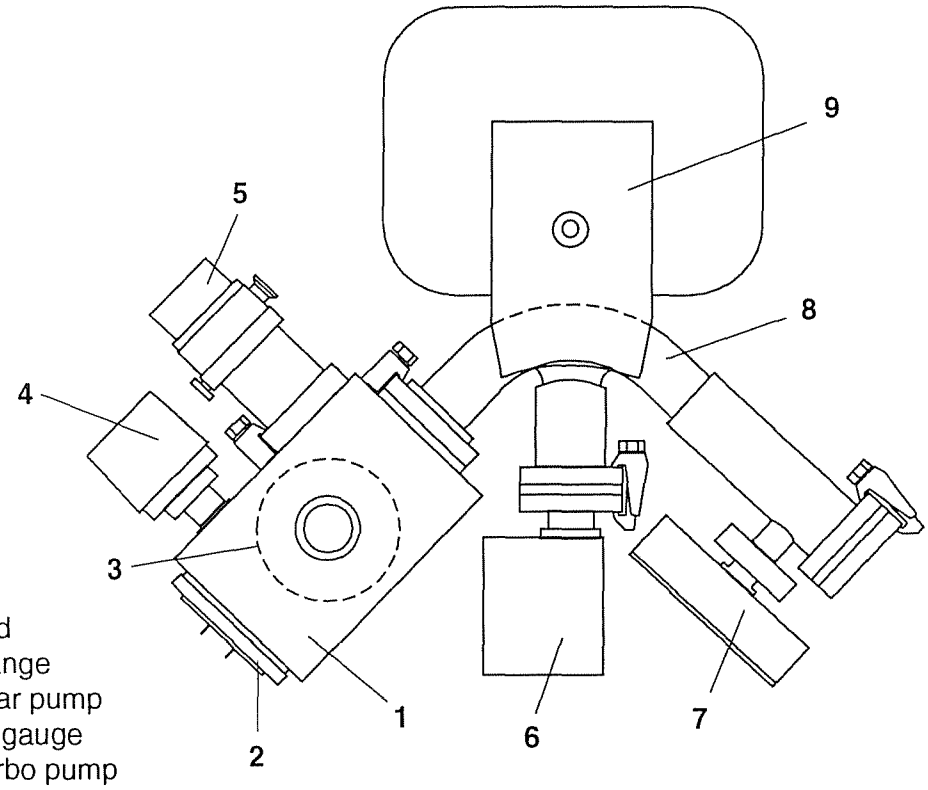
A basic knowledge of handling computers and of the ISODAT software is assumed for proper operation of the Thermo Finnigan MAT ***DELTA***$^{plus}$ mass spectrometer.

# Analyzer System 2

## 2. 1 General

A gaseous sample to be analyzed is fed into the ion source via the inlet system. In the ion source ions are generated in a high vacuum by the impact of electrons. The ions are then accelerated to an energy of up to 3 keV and focused by electrostatic lenses to form a beam (for details, see Fig. 2 - 3).

**Fig. 2 - 1**
Partial view of the instrument showing the arrangement of the analyzer



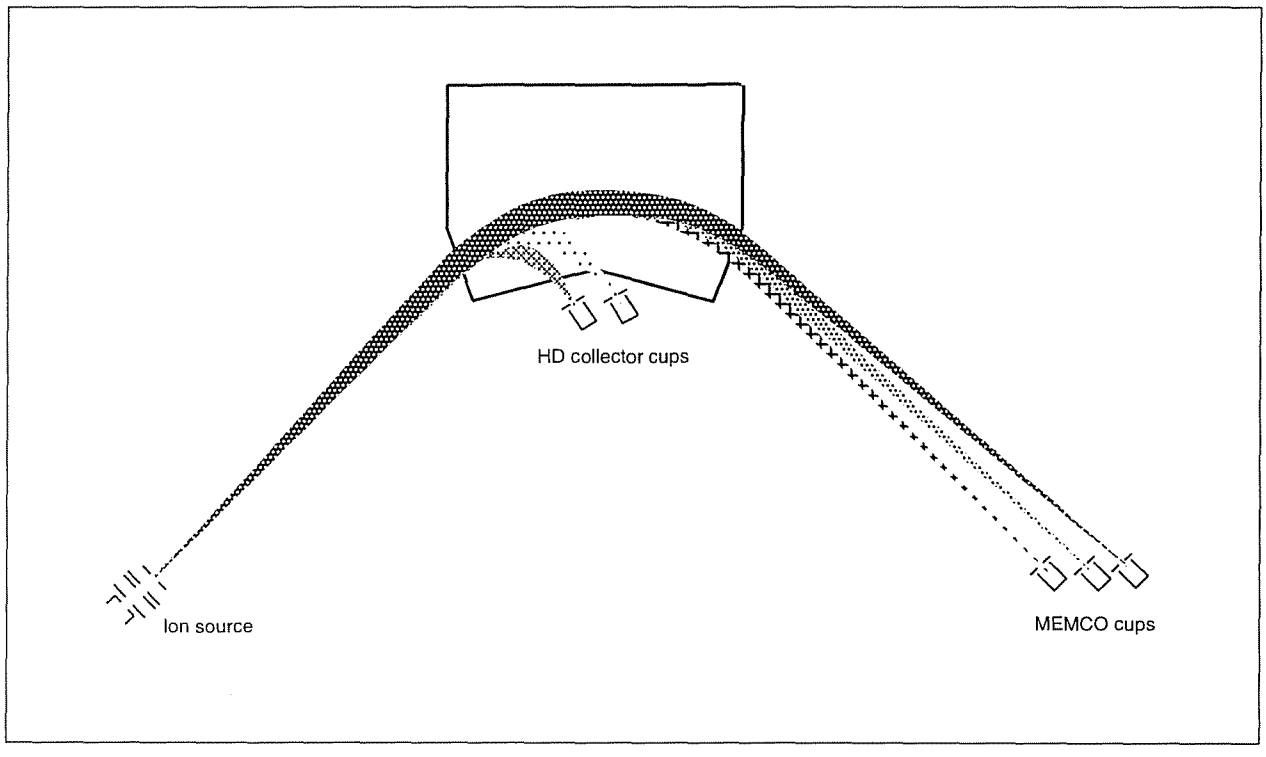

1 analyzer head
2 ion source flange
3 turbomolecular pump
4 high vacuum gauge
5 differential turbo pump
6 HD amplifier housing
7 MEMCO amplifier housing
8 flight tube
9 electromagnet

The ion beam exits the ion source into the magnetic field through a slit with a fixed width of 0.3 mm and enters the magnetic field boundary at an angle of 26.5°, traverses the 90° magnetic sector field, and a part of the ion beam exits at the same angle of 26.5° (see also Fig. 2 - 2).

This arrangement doubles the focal length of the system and, consequently, the mass dispersion is also double that of the conventional arrangement where the beam enters and exits the field normal to the boundaries. This results in the 9 cm radius system having the same mass dispersion as a conventional arrangement where the beam enters and exits the field normal to the boundaries with a sector radius of 18 cm.

# 2 Analyzer System

**Fig. 2 - 2**
Schematic of the ion path




The magnetic sector field is generated by an electro magnet with a maximum field strength of 0.75 Tesla, covering a mass range up to 70 amu at full accelerating voltage.

The mass setting is achieved by variation of the magnetic field strength and/or of the accelerating voltage.

The relation between the mass number $\frac{m}{z}$ of the ions reaching the ion collector and the magnetic field strength H is given by: $\frac{m}{z} = k_M \cdot H^2$ with

z = elementary charge;

$k_M = \frac{r^2}{2U}$ = const.;

r = nominal radius of ion path;

U = accelerating voltage.

The HD collectors are positioned in the middle of the flight tube because of the small radius of deflection for the light H and D ions. Their exit slit width is 2 mm and results in a resolution of

$$\frac{m}{\Delta m} = 10 \text{ (10\% valley)}$$

The collector slit width for the C, N, O and S-collectors (in short CNOS collectors) is 1.2 mm and results in a resolution of

$$\frac{m}{\Delta m} = 95 \text{ (10\% valley)}$$

Details on the CNOS and HD collectors are given in chapter 2. 5, Ion Detection - Collector Systems.

The electronic units which supply the analyzer system operating voltages and control the analysis are described in detail in chapter 2. 3, Ion Source Control Unit.

## 2. 2 Ion Source

The ion source of the Thermo Finnigan MAT ***DELTA***$^{plus}$ is designed for high sensitivity and linearity as well as low $H_3^+$ production at the same time. To ensure high sensitivity, the ion source is of gas tight design. The sample gas is fed into the ionization chamber via a ceramic tube and leaves it only via small apertures, which are required as a passage for the electron beam and the ions exiting into the analyzer.

The conductivity of these openings is much lower than the pumping speed of the vacuum pumps and thus the pressure within the ionization chamber is about 100 times higher than outside, resulting in high ion yields and high abundance sensitivity at the same time.

The ions are generated in the source by electron impact ionization. The ionizing electrons are emitted by a thermionic cathode. The emission is held constant by the emission regulator unit (see chapter 2. 3, Ion Source Control Unit).

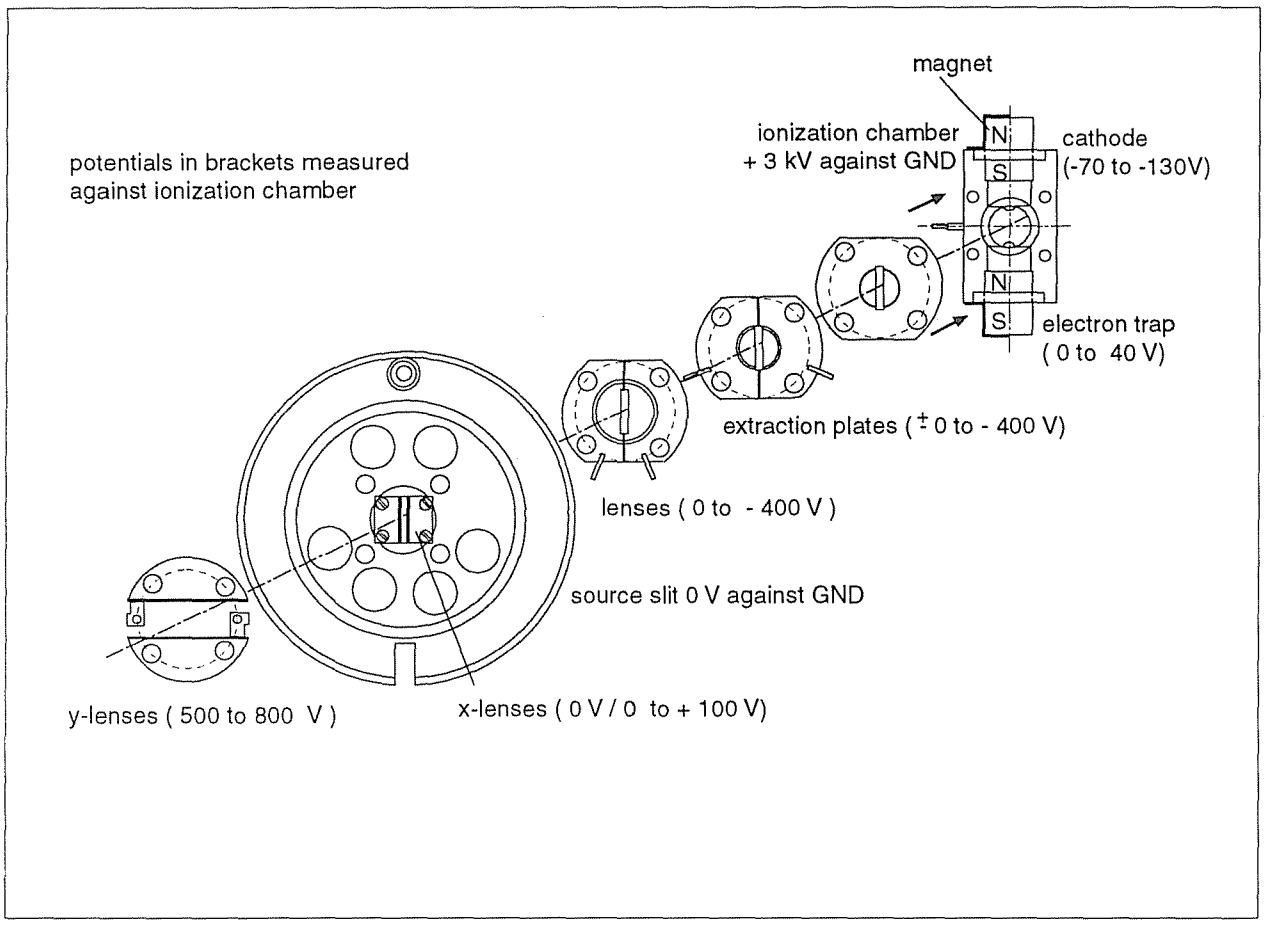
To confine the ionizing electron beam to a narrow cross-section, which provides high ion yield - while maintaining a small energy spread, two small permanent magnets are mounted to the ionization chamber (see Fig. 2 - 3), generating a magnetic field parallel to the electron beam.

The energy of the ionizing electrons, which is determined by the potential difference between cathode and ionization chamber, is about 80 eV.
The electron beam leaves the ionization chamber via a small opening opposite to the cathode and is collected in the electron trap, which is held on a positive potential relative to the ionization chamber.

Extraction plates accelerate ions out of the ionization chamber and the following lens system of different lenses focuses the ion beam onto the source slit.

Mechanical tolerances might cause a slight out-of-axis deflection of the ion beam. Some of the system´s lenses are half sections which are insulated from each other. This construction allows for compensation by applying different potentials to the halves of the lenses. Fig. 2 - 3 shows schematically the lens arrangement and the potentials applied to them with an ion accelerating voltage set to 3 kV.

**Fig. 2 - 3**
Potentials of the ion source in relation to ground at 3 kV ion acceleration voltage




When the ion accelerating voltage is set to lower values with the ISODAT software (selectable in three stages: 2.0,2.3,3.0 kV) the lens potentials are proportionally lower except for that of the extraction plate.

Setting the accelerating voltage to lower values results in an enhancement of the mass range beyond 70 u.

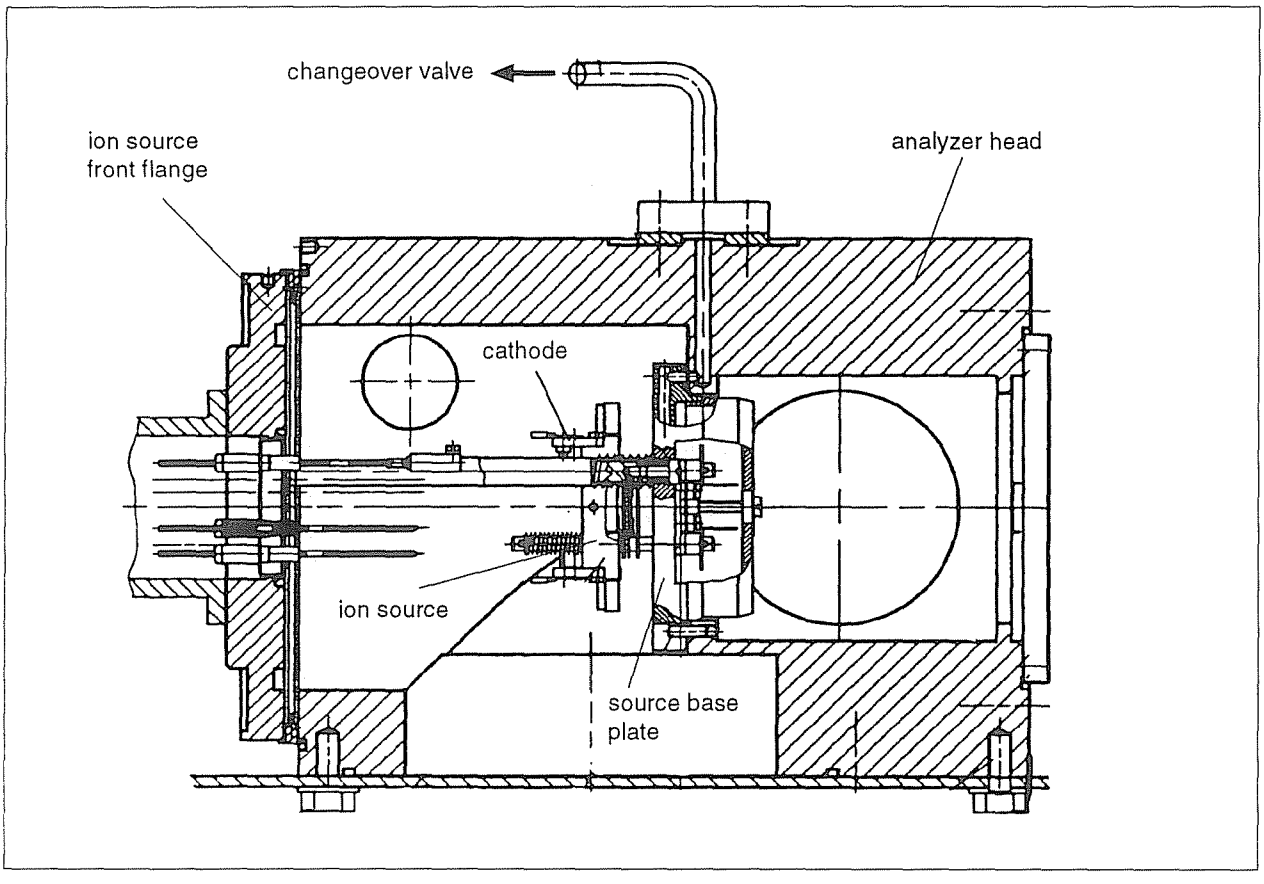
For example: a setting to

2.0 kV results in a mass range up to 105 u,
2.3 kV results in a mass range up to 90 u.

The ion source is mounted on the front flange for easy maintenance.

A correct alignment of the ion source relative to the analyzer tube is achieved by a mating surface with the analyzer head. Details of the ion source, e.g. the feedthroughs and correlation of lenses, are given in the respective chapter of the ***DELTA***$^{plus}$ Service Manual.

**Fig. 2 - 4**
Coupling of the inlet system to the ion source




## 2. 3 Ion Source Control Unit

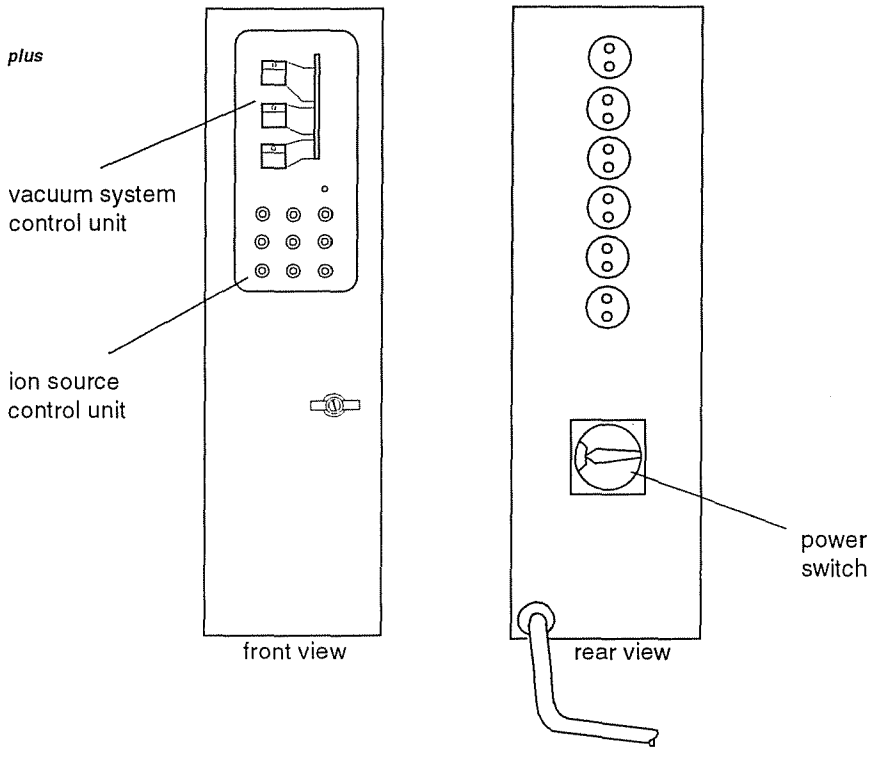
The ion source control unit is located in the electronics cabinet of the ***DELTA***$^{plus}$ (right side). It consists of three units mounted onto one electronic circuit board and provides the following:

| | |
|---|---|
| emission current | by the emission regulator unit, |
| ion accelerating voltage | by the high voltage supply unit, |
| ion source lens voltage | by the voltage divider unit. |

The potentiometers to adjust the potentials of the voltage divider unit are located on the front panel (see Fig. 2 - 5 on next page).

# 2 Analyzer System

**Fig. 2 - 5**
Controls of the ***DELTA*** *plus*




**Warning: Opening the electronics cabinet is only allowed for maintenance purposes by qualified personal.**

### 2. 3. 1 Emission Regulator

The emission regulator controls the current which heats the cathode of the ion source to such an extent that the ionizing electron current (emission current) is kept constant to the factory set level of approx. 1 mA.
The cathode heating current is about 3.5 A. The emission regulator is switched on by pressing the SOURCE push button on the front panel of the instrument. With the emission regulator activated, the LED "EMISSION", located on the front panel of the instrument, is lit.

### 2. 3. 2 High Voltage Supply

The high voltage unit provides the ion accelerating voltage. The voltage can be set via the key-board of the computer to 2, 2.3 or 3 kV.
A current overload circuit switches off the high voltage supply in case the load current exceeds 0.2 mA. A switch-off caused by an overload is indicated by the extinguished green LED "EMISSI-ON" located on the front panel (right to the SOURCE push button switch).

- Before you can switch on the high voltage again, you must reset the main power source by depressing the SOURCE push button switch on the front of the instrument.

- Wait for about 5 seconds before you activate the high voltage again by pressing the SOURCE push button switch.

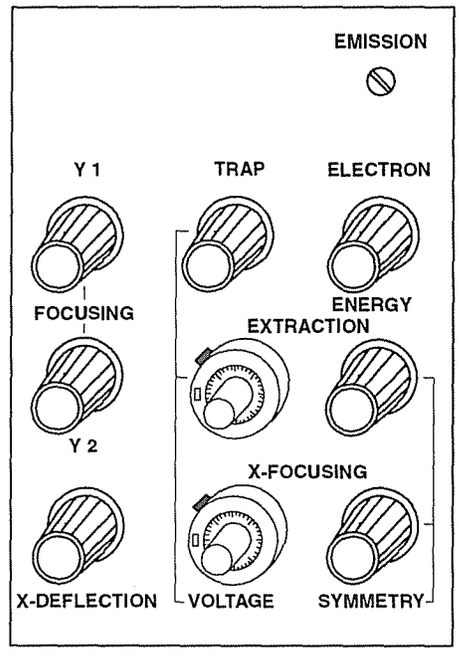
- If the reset was successful the green LED "EMISSION" and green LED "HIGH VOLTAGE" will be lit.

### 2. 3. 3 Voltage Divider

The voltage divider provides the potentials applied to the ion source for the emission of electrons and to the lenses focusing the ion beam. It consists of resistor chains to which the accelerating voltage is applied. From the resistor chains, the potentials for extraction plates, X-lenses and Y-lenses are tapped off.
The potentiometers of the control panel located on the

| | |
|---|---|
| left hand side | control the voltages of the deflection plates |
| middle hand side | control the voltages of the lenses |
| right hand side | control the symmetry, i.e. the potential difference between the two halves of the related lenses. |

**Fig. 2 - 6**
Panel of the ion source control unit




The deflection of the X-lenses is equal to zero with the potentiometer turned totally to the left. In this position the ion current should reach its maximum. The potentials of the extraction plate, X-lenses and Y-lenses should be centered, i.e. the potentiometer knobs dialed to the middle position.
In general, the variation range of the potentiometers is large enough to find the ion current maximum. It happens only in exceptional cases that one of the potentiometers stops at the right or left before the ion current maximum has been attained. In this case it may be necessary to open the ion source and to change the polarity of the X-lenses (see also Service Manual).

**WARNING! Before performing maintenance on the ion source make sure the high voltage supply is switched off by pressing the SOURCE push button switch.**

Before you start to adjust the potentials make sure that you have

- switched on the ion source,
- activated the ISODAT submenu M-SCALE CALIB (Mass scale calibration) of the ACON-MAIN MENU in the configuration D (Cnf-D, ACON-D, CONTROL),
- admitted gas into the inlet system and a sufficient amount of gas to the ion source. (See also chapter 5. 2, Dual Inlet System, $CO_2$ Measurement).

Focusing of the ion beam is performed as follows:

Start the adjustment with the potentiometers on the middle position, i.e. the VOLTAGE. Turn the indiviual potentiometer to the left or right until you find the maximum of the ion current. Watch the intensity of the signal on the monitor of the computer or the chart recorder while focusing (ISODAT Manual, chapter 3. 5).

Go on adjusting with the potentiometer arrangement, i.e.

EXTRACTION,

X - FOCUSING,

Y - FOCUSING,

X - DEFLECTION,

and repeat as described before.

Continue with the potentiometers for the SYMMETRY and repeat the adjustment procedure as outlined before.

It is advisable to note the position of the knob indicators for each potentiometer or to mark the indicator position with a felt pen on the cover plate.

## 2. 4 Ion Deflection

### 2. 4. 1 Electromagnet

The magnetic field providing the ion deflection is generated by an electromagnet with a maximum field strength of 0. 75 Tesla. Selection of the different masses is achieved by changing the magnetic field. In addition, the mass range covered can be selected in three steps by ion accelerating voltage switchover (2.0, 2.3, 3.0 kV).

The relation between the mass number $\frac{m}{z}$ of the ions reaching the ion collector and the magnetic field strength H is given by: $\frac{m}{z} = k_M \cdot H^2$ with

z = elementary charge;

k = $\frac{r^2}{2U}$ = const.;

r = nominal radius of ion path;

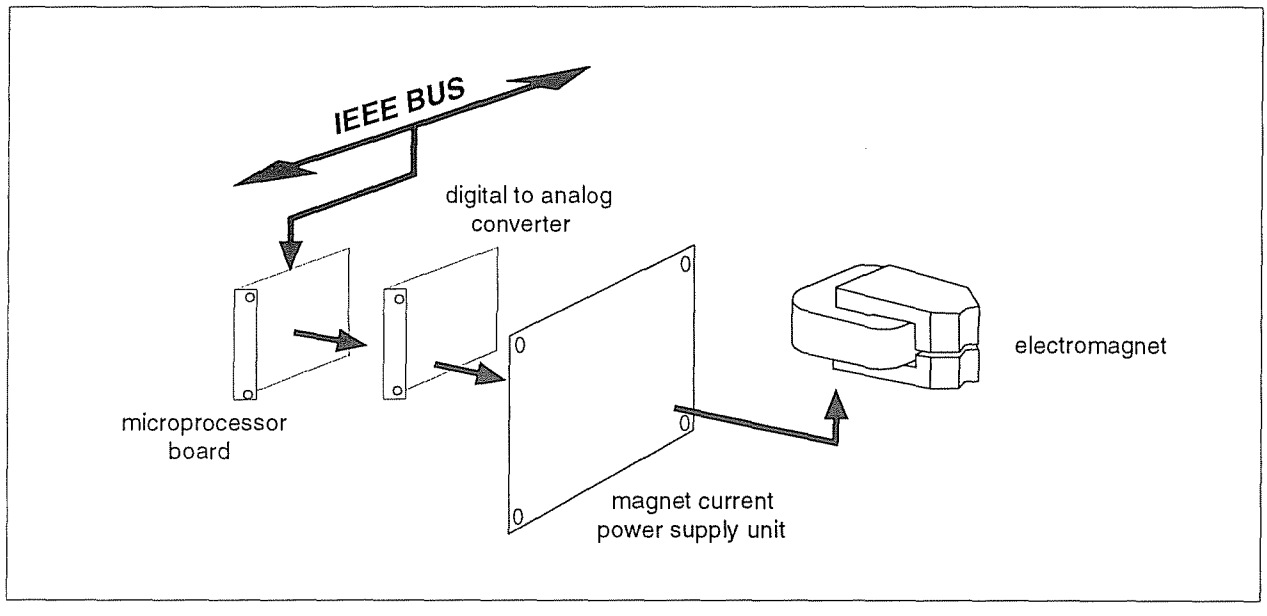
U = ion accelerating voltage.

### 2. 4. 2 Magnet Current Regulator

The magnet current regulator provides the current required to generate the electromagnetic field. The current is computer controlled via the DAC printed circuit board (digital-to-analog converter).

The computer feeds the information of the specified mass number via the IEEE bus to the microprocessor which controls the DAC printed circuit board. Here this information is converted into an output voltage which controls the power supply of the magnet current regulator. The magnet current ranges from 1.0 to 4.0 A.

**Fig. 2 - 7**
Schematics of the signal path regulating the magnet current




The relationship between magnet current and mass number is determined and stored by means of the mass calibration procedure.
For more details, see the ISODAT Manual chapter 3. 5, MASS-SCALE Calibration.
In case no analysis is performed the magnet can be switched off with a toggle switch located on the front panel of the magnet current regulator housing. A green control LED next to the switch will then extinguish. The magnet current regulator is located in the instrument´s electronic cabinet located at the right side. (To open, remove the right side panel, hold in place by magnet snappers. (See also Fig. 1 - 1)

## 2. 5 Ion Detection - Collector System

### 2. 5. 1 General

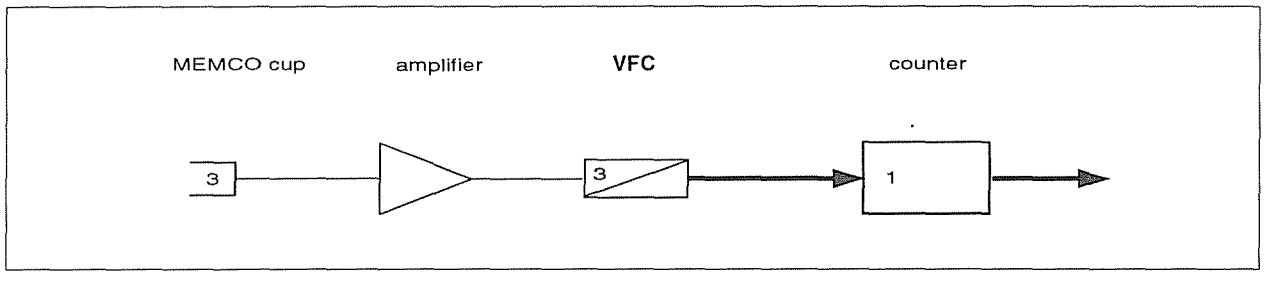
Different configurations of ion collector systems are available. For isotope analyses of the elements C, N, O, S, **M**ulti-**E**lement - **M**ulti**CO**llector (MEMCO) systems with 3 or 6 Faraday collector cups plus associated amplifiers are available. The MEMCO system is installed at the end of the flight tube.

For HD isotope analysis, an optional collector system with 2 Faraday collector cups and associated amplifiers is available. The HD collector system has a separate housing which is to be installed in the center of the analyzer region (flanged to the flight tube).

Each collector cup has its own amplifier and the feedback resistor of the amplifier can be matched to the abundance of the isotope to be collected in this cup (see Table 2 - 1).

Each collector cup and its amplifier is connected to a voltage-to-frequency converter (VFC). There are three or six VFCs for the MEMCO collector system and two VFCs for the HD collector system available and allotted via a multiplexer to one of the three counters forming a measuring channel as shown in the figure below.

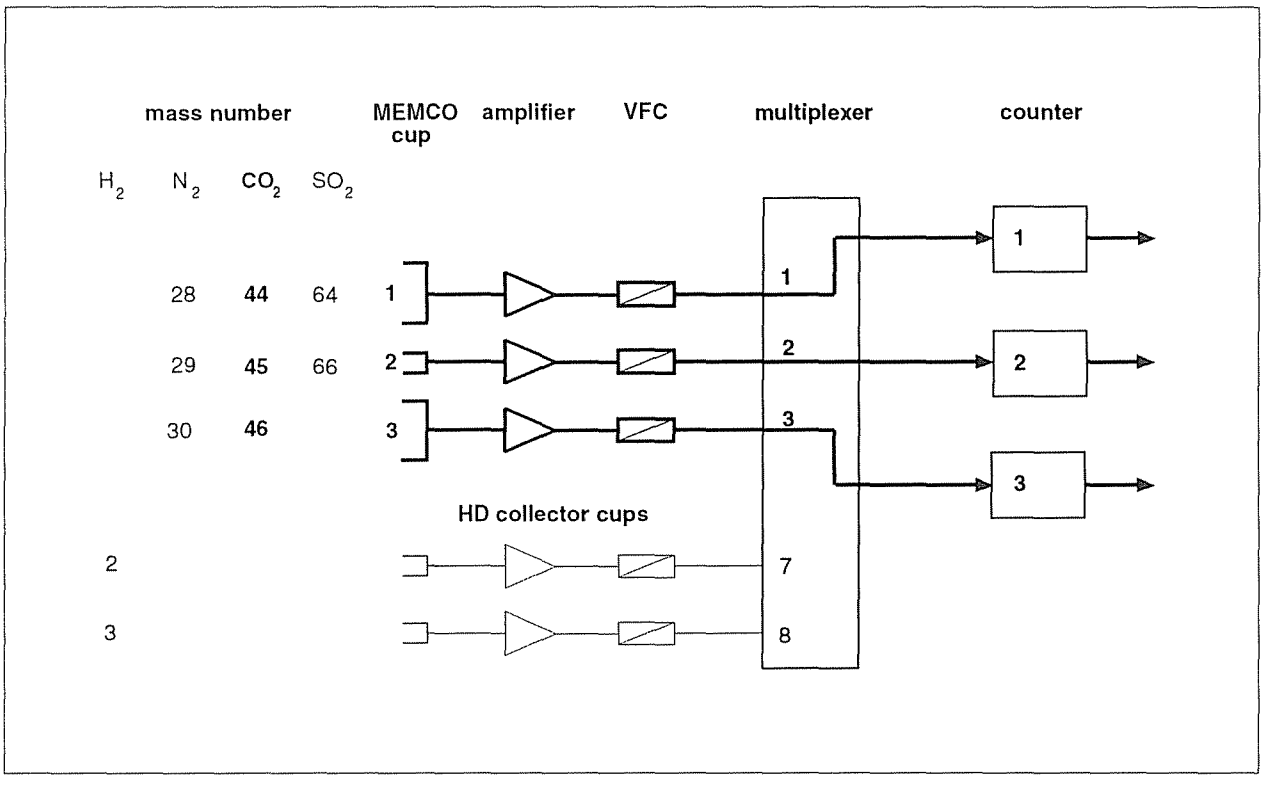
**Fig. 2 - 8**
Components that form a measuring channel




The converters transform the analog ion current signals into pulses. These pulses are fed to counters for a preselected integration time. At the end of each integration interval, the computer reads the number of counts and calculates the ion current ratios. See Fig. 2 - 10

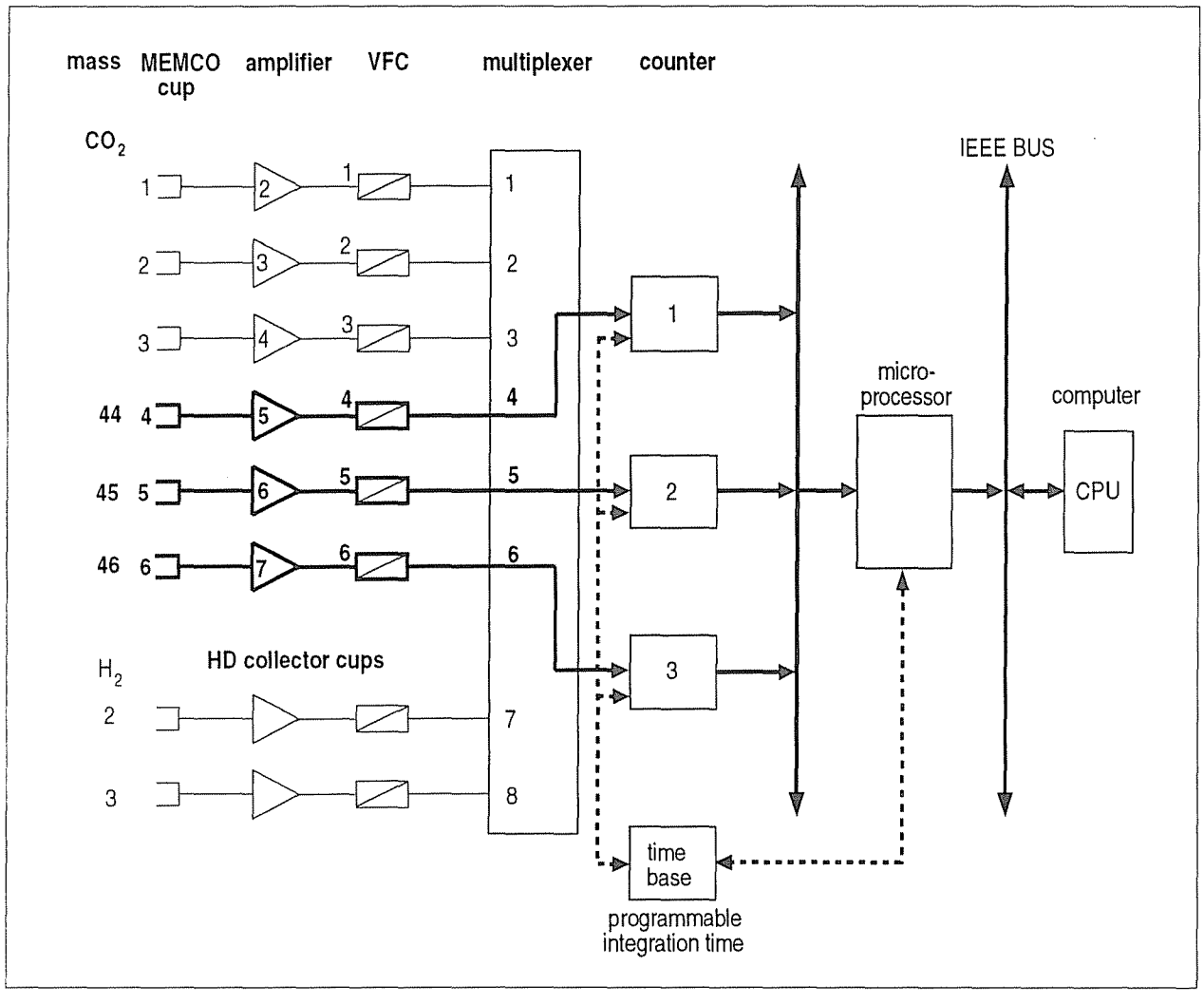
By multiplexing, any combination of three collector cups out of a 6-cup MEMCO system or the HD collector cups can be connected to the three measuring channels. One example of the assignment of mass numbers to collector cups for the 6-cup MEMCO system is shown in Fig. 2 - 9.

**Fig. 2 - 9** Example of a mass number assignment to the collector cups



With this combination there is no need to change the feedback resistors when changing from the analysis of $CO_2$ to that of $N_2$. The switching of the cup configuration is done automatically by the ISODAT software. Only in case of switching to $SO_2$ analysis, it is required to exchange the resistor for mass 66.
(See also chapter 6. 2. 1, Exchange of Feedback Resistors)

**Fig. 2 - 10**
Function Schematic of the Ion Detection System



### 2. 5. 2 Amplifier

A dedicated DC amplifier is assigned to each of the collector cups. All amplifiers of a **M**ulti-**E**lement **M**ulti**Co**llector system (MEMCO systems with 3 cups) are placed in a common housing which is flanged directly to the collector head. The two amplifiers of the HD collector system are installed in the separate HD housing.

The DC amplifiers have 100% inverse feedback. Their output voltage (10 V maximum) is the product of the input current and a feedback resistor.

The feedback resistor has to match the abundance of the isotope to be collected in the respective collector cup. Table 2 - 1 shows the resistance values to be used for the isotopes of the different gases.

**Table 2 - 1**
Values of the feedback resistors matching the natural abundance of the listed isotopes

| Gas | $\frac{m}{z}$ | Resistor | |
|---|---|---|---|
| $H_2$ | 2 | $1 \times 10^9$ | Ω |
| | 3 | $1 \times 10^{12}$ | Ω |
| $N_2$ | 28 | $3 \times 10^8$ | Ω |
| | 29 | $3 \times 10^{10}$ | Ω |
| | 30 | $1 \times 10^{11}$ | Ω |
| $O_2$ | 32 | $3 \times 10^8$ | Ω |
| | 33 | $1 \times 10^{12}$ | Ω |
| | 34 | $1 \times 10^{11}$ | Ω |
| $CO_2$ | 44 | $3 \times 10^8$ | Ω |
| | 45 | $3 \times 10^{10}$ | Ω |
| | 46 | $1 \times 10^{11}$ | Ω |
| $SO_2$ | 64 | $3 \times 10^8$ | Ω |
| | 66 | $1 \times 10^{10}$ | Ω |

**WARNING: Do not touch the surface of high ohmic resistors.**

Only a slight touch of your finger tip contaminates the resistor and will result in instability of the signal.

### 2. 5. 3 Collector Systems

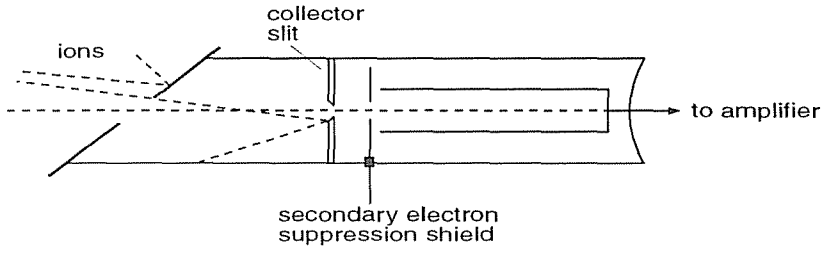
**MEMCO Collector System:**

The MEMCO collector systems (available in versions with 3 or 6 collector cups) cover the mass range from 10 to 70 $\frac{m}{z}$ at 3 kV accelerating voltage,

allowing a resolution of $\frac{m}{\Delta m}$ = 95 (10% valley).

Due to the high dispersion of the analyzer system, the distance between the collectors is extraordinary by large (e.g. approx. 4 mm between masses 44 and 45). Thus it was possible to design the Faraday collectors as deep, shielded buckets with integrated secondary electron suppression shields (Fig. 2 - 10), eliminating effects that might degrade the ion current measurement.

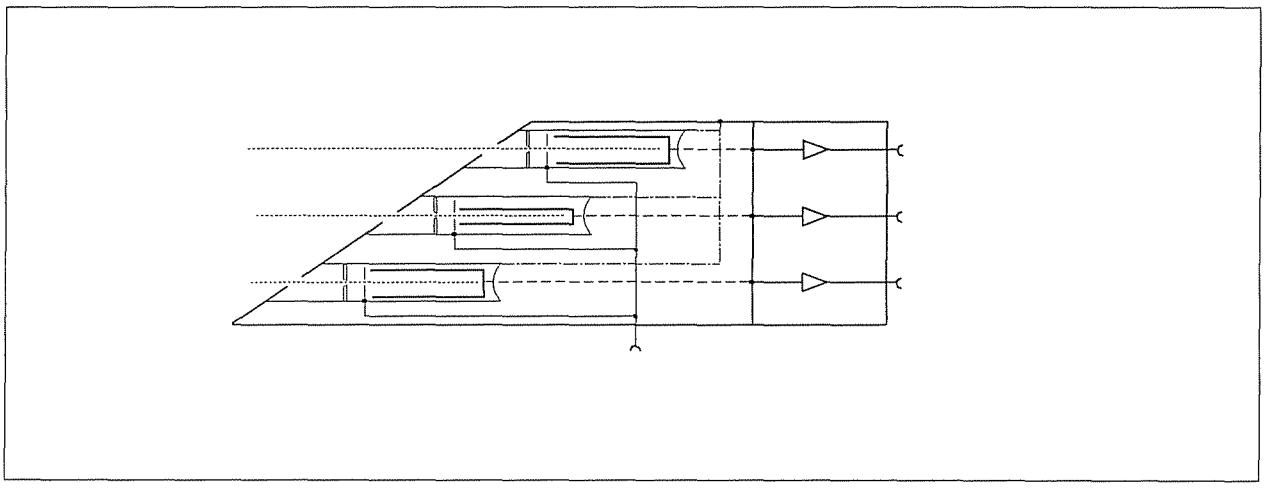
**Fig. 2 - 11**
Design of a Faraday collector cup




The 3-cup version allows simultaneous measurement of two isotope ratios from the same sample, e.g. $^{13}C/^{12}C$ and $^{18}O/^{16}O$ of $CO_2$.

The 6-cup version permits the cup configuration to be preset for the consecutive measurement of different gases, without having to break vacuum in order to alter the positions of the cups. As with the 3-cup version, simultaneous measurement of two isotope ratios of the same gas can be performed.
Fig. 2 - 9 shows the assignment of mass numbers to collector cups and channels as preset for the measurement of $N_2$, $CO_2$ and $SO_2$.

**Fig. 2 - 12**
Schematic of the 3-cup Universal MEMCO (**M**ulti-**E**lement **M**ulti**CO**llector)



**Note:** Different gases may jointly use one cup in order to reduce the total number of cup measuring channels.

**HD Collector System:**

The HD collector system is a dual Faraday collector assembly for hydrogen isotope measurement on a separate ion path, operating separately from the MEMCO systems.

The HD collector is located in the middle of the analyzer tube and covers the mass range from 1.5 u to 14 u (at 3 kV).

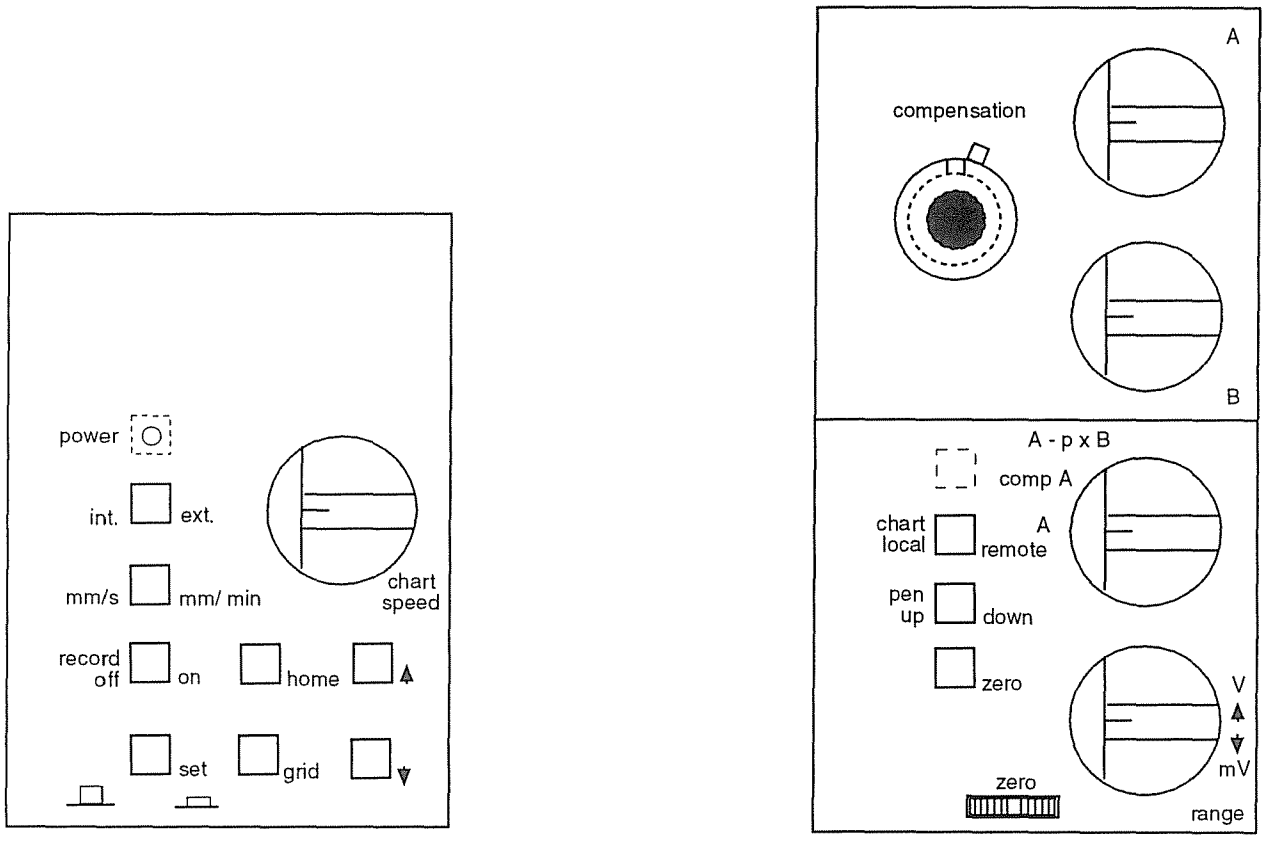
The HD collector is set to a resolution of $\frac{m}{\Delta m} = 20$ (10% valley)

The collector cups are designed like those of the MEMCO system.

### 2. 5. 4 Channel Selector

The strip chart recorder provides a selectable analog readout of the various ion currents for the different measuring channels.

**Fig. 2 - 13**
The channel selector facilities of the recorder.




The function of selector and push button switches is as follows:

**Selector Switches:**

A, B ... MODE: The combined settings of the selector switch A or the switches A and B and the MODE switch determine the mode of the output signal. Depending on the collector configuration of the instrument, e. g. for a MEMCO system, the numbers on the switch positions belong to the number of the corresponding Faraday cup. With a 6-cup MEMCO system only the switch positions 1 to 6 of the selector switches A and B are active.

The output signal of the different modes depends on the output voltage of the amplifier of a selected measuring channel.

The MODE switch allows the selection of the following modes:

DIRECT A MODE: This mode feeds the amplifier´s output voltage of a preselected measuring channel (selector switch A) directly to the strip chart recorder. The collector cups are counted from the inner one (lightest isotope) to the outer one (heaviest isotope).

COMP A MODE: This mode compensates for the difference between the output voltage of a preselected measuring channel (selected with switch A) and a defined voltage, which is then fed to the strip chart recorder. The reference voltage can be set between 0 V and 3 V with the 10-turn potentiometer of the recorder. This feature allows to track the small changes in signal intensity versus time.

A - p x B MODE: This mode compensates the output voltage of a measuring channel (selected with switch A) with a fraction p of the output voltage of a second measuring channel (selected with switch B).
The resulting output signal is fed to the strip chart recorder. The fraction p is also set with the 10-turn potentiometer of the strip chart recorder, which covers the range $0 < p < 1$.

Example:
selector switch A is set to position 2
and selector switch B to position 3,
the amplifier´s output of the measuring channel 2,
compensated by the fraction p
of the amplifier´s output of measuring channel 3
is fed to the strip chart recorder.

**Note:** The analog measurement with the strip chart recorder allows a rough but quick measurement of the isotope ratios. However, the results obtained do not have the precision and accuracy of the computer controlled digital measurement performance.

**Push Button Switches:**

(left side)
chart speed: With these push buttons the chart speed can be selected. The speed is set for a range from 20 to 0.1 mm per second (mm/s) or per minute (mm/min).

(right side)
zero: Press the push button "zero" at the recorder. Adjust the "zero" potentiometer with thumb wheel, used to position the pen on the paper. (For information, see the Instruction Manual of the manufacturer Kipp & Zonen).

# Vacuum System 3

## 3. 1 Pumping System

The Finnigan MAT ***DELTA$^{plus}$*** is supplied with differing pumping systems.

The standard version comes with a turbomolecular pump to evacuate the analyzer system at a rate of 240 l/s (type: TMH 260, manufacturer: Balzers). The required forevacuum is provided by a rotary pump rated at 1.5 m³/h (type: E2M1.5, manufacturer: Edwards).

The optionial differential pumping system with an additional turbomolecular pump improves the vacuum in the analyzer system of the instrument.

This improvement is required to eleminate the high portion of He carrier gas of peripherals such as an elemental analyzer or a GC and results in a better abundance sensitivity, better peak shape and improved signal to background ratio at high ion source pressures.

A vacuum lock or flow restriction separates the ion source section from the analyzer region. The additional turbomolecular pump evacuates the analyzer region at a rate of 60 l/s ( type: TMH 064, manufacturer: Balzers).

The required forevacuum for both pumps is provided by a rotary pump rated at 1.5 m³/h (type: E2M1.5, manufacturer: Edwards).

The inlet system is evacuated by a forevacuum pump rated at 1.5 m³/h (type: E2M1.5, manufacturer: Edwards).
For more information, see also paragraph 3.4 of this chapter: Turbomolecular Pump.

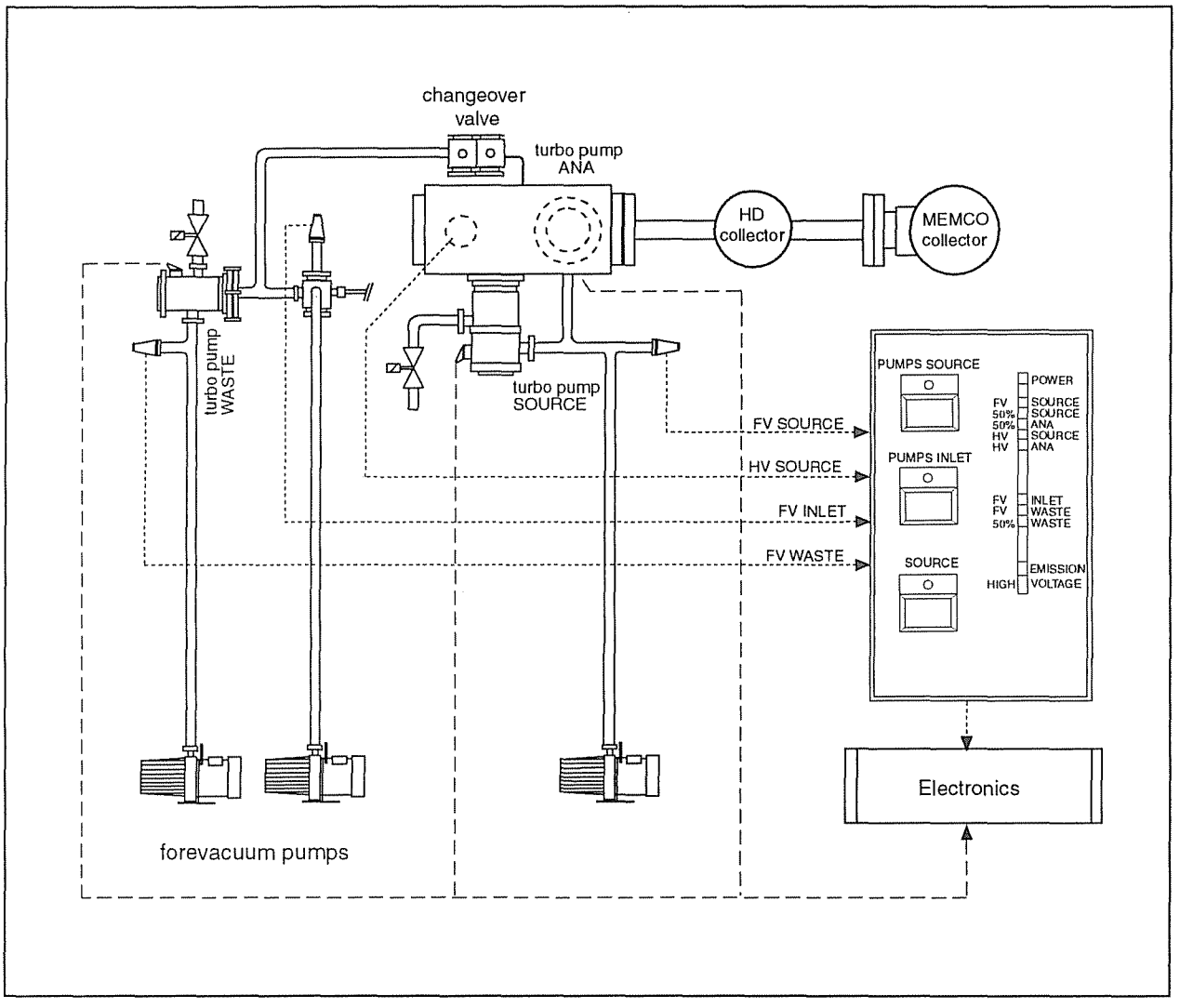
The wasteline turbomolecular pump (type: TMH 064) backed by a forevacuum pump (type: E2M1.5) is also used to provide high vacuum conditions in the inlet system.

# 3 Vacuum System

## 3. 2 Vacuum System Control Unit

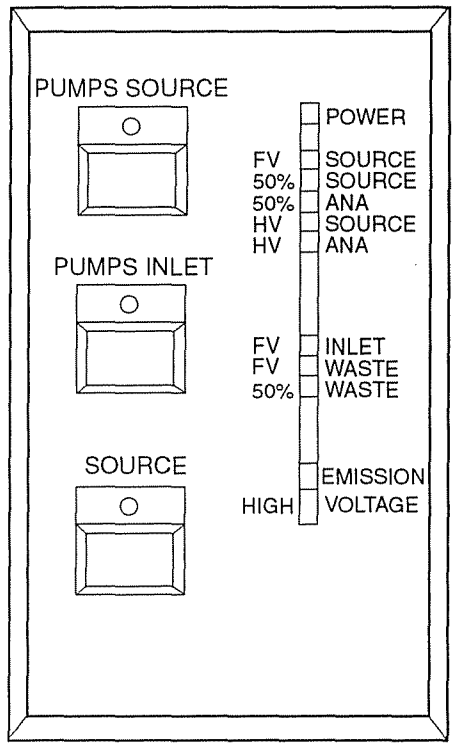
The high vacuum of the standard pumping system is monitored by a vacuum gauge (type: Penning), which is attached to the ion source.

**Fig. 3 - 1**
Schematic view of the differential pumping system




The forevacuum is controlled by three Pirani gauges located in the inlet and the wasteline system.

**Fig. 3 - 2**
Front View of the Vacuum System Control Unit




The switches activate the reading at different parts of the system for the high vacuum (HV) and the forevacuum (FV).

The row of LED´s is lit when the turbomolecular pumps reach 50% of their nominal rotational speed.

**Pushbuttons switches:**

| | |
|---|---|
| PUMPS SOURCE | starts pumping system (turbomolecular pumps and forevacuum pump for analyzer system). |
| PUMPS INLET | starts the wasteline turbomolecular pump as well as forevacuum pump and the forevacuum for the inlet system. |
| SOURCE | switches the high voltage and the heating of the cathode. If switched on, the LEDs EMISSION and HIGH VOLTAGE are illuminated. Activation is only possible when the vacuum conditions are correct and all other LEDs are lit. |

**NOTE:** In case of problems, e.g. a forevacuum pressure > $10^{-1}$ mbar or a high vacuum > $10^{-4}$ mbar, the source is cut off automatically.

# 3 Vacuum System

**LED´s:**

| | |
|---|---|
| POWER: | indicates the supply of main voltage. |
| EMISSION: | only lit when filament of the ion source operates. |
| HIGH VOLTAGE: | lit when high voltage is provided to ion source. |

**Guidance for Trouble Shooting**

If one of the vacuum control LED units is not lit, the instrument should be checked immediately.

| | |
|---|---|
| HV range:<br>one of the LEDs<br>is not illuminated<br>i.e.<br>SOURCE<br>ANALYZER<br>WASTELINE | There might be a leak in the system or a turbomolecular pump is not working properly.<br>Check the forevacuum pressure (FV range).<br>If the problem is caused by a leak, the forevacuum will indicate a high pressure (forevacuum > $10^{-1}$ mbar).<br>If the control LED of the FV range SOURCE is not lit, the turbomolecular pumps may not have reached their nominal speed. For further information on leak detection, see the Service Manual, chapter 5, Vacuum System. |
| **NOTE:** | Cathode, ion gauge, high voltage and turbomolecular pumps are tripped when the forevacuum of the ion source reaches its trip level ($10^{-1}$ mbar). The same applies to the wasteline side with its forevacuum control. If the forevacuum pressure on the wasteline pump exceeds $10^{-1}$ mbar, the wasteline turbomolecular pump and both forevacuum pumps (wasteline and inlet) are tripped. This may happen, if the valve between fore - vacuum pump and wasteline pump (valve 40) is opened before the inlet system is evacuated.<br>In this case the wasteline LED of the HV range (high vacuum) turns off. After a shutdown of the vacuum system immediately start it again by depressing and pressing the push button START UP INLET of the vacuum control unit. |
| FV range:<br>if LED SOURCE<br>is not illuminated: | The pressure of the forevacuum is most likely <$10^{-1}$ mbar. Check the pressure of the FV range with the multimeter. If high pressure is indicated a leak is causing the problem. |
| FV range:<br>if LED SOURCE<br>is not illuminated: | Either too much sample or standard gas entered the inlet system or valve 40 was opened before pumping commenced. In such a case the forevacuum pressure on the wasteline pump exceeds $10^{-1}$ mbar. The wasteline and both forevacuum pumps (wasteline and inlet) are tripped. Start the system again by depressing and pressing the push button START UP INLET of the vacuum control unit. |
| HIGH VOLTAGE<br>LED **on:**<br>EMISSION<br>LED **off:** | The cathode might be burned out. Checking and removal of the filament is decribed in detail in the appropriate chapter 5, Vacuum System, of the Service Manual. |

| | |
|---|---|
| HIGH VOLTAGE LED **off:** EMISSION LED **on:** | The high voltage is tripped when the current exceeds 0.2 mA. This may be caused either by sparking or by a short circuit in the source or connections to the source. |

### 3. 3 Turbomolecular Pump

The turbomolecular pump functions completely mechanically by the rotor disks imparting impulses to the gas molecules. Baffles or cryogenic traps are not necessary for retention of pump fluid vapors. This arrangement also obviates the need for a high vacuum pump valve, since the vacuum system can be roughed through the turbomolecular pumps and since the turbomolecular pumps can be started at atmospheric pressure. Thus the rated capacity of pump speed is available at the connecting flange of the source housing without restriction.

The molecular pump principle works in the molecular flow region only. Therefore, the turbomolecular pumps require a forevacuum pump. This pump is roughing the vacuum system through the turbomolecular pump down to the upper limit of the turbomolecular pump operating range.

The turbomolecular pumps installed in the instrument are air cooled. In case of mains failure there is a delayed venting provided by a venting valve, which is held closed through rotational speed of the turbo pump operating as a generator.

When starting the turbomolecular pump power supply unit (TCP 035) the venting valve is closed immediately. After stopping (by mains failure or switch-off) venting at 50% of the turbopump´s nominal speed is performed. The vent valve remains open until the next start cycle of the electronic unit. In absence of current the valve is open.

Operation of the turbomolecular pump is controlled by the pump drive unit described in the following paragraph.

For details regarding function and design of the turbomolecular pumps see the operating manual of the manufacturers.

# 3 Vacuum System

### 3. 4 Pump Drive Unit

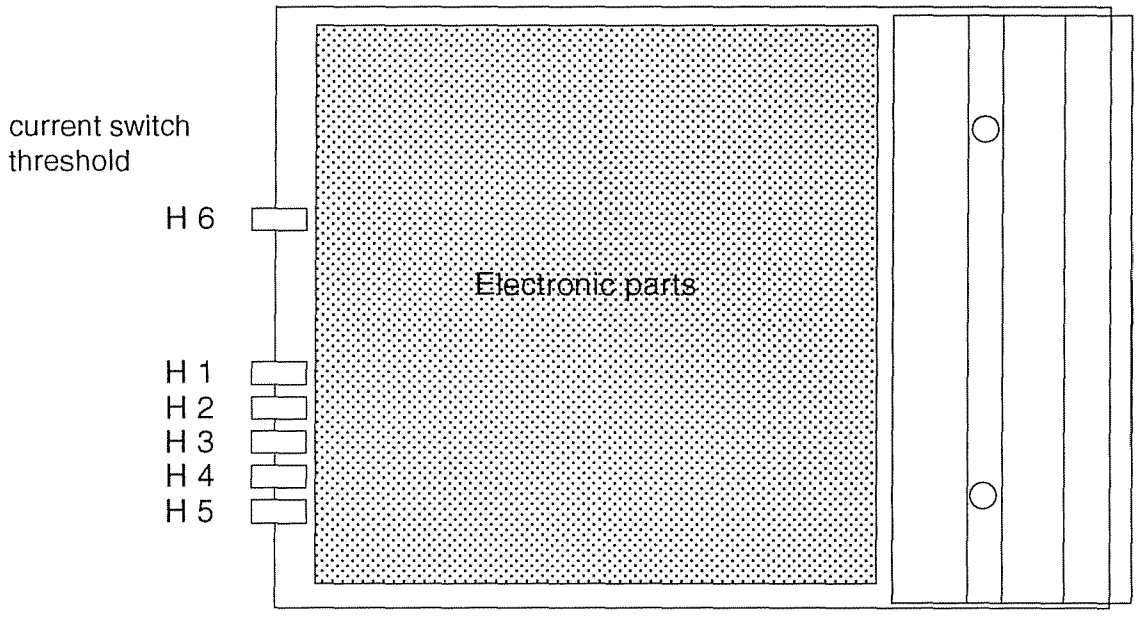
The pump drive unit combines the control electronics (type: TCP 035, manufacturer: Balzers - Pfeiffer) and a power supply for turbomolecular pumps.

The unit is in compliance with DIN VDE 0871 , limit curve value B.

Each turbomolecular pump has its own pump drive unit. They are located in the electronics cabinet.

For details regarding function and design of the pump drive unit, see the operating instructions of the manufacturers (Balzers-Pfeiffer).

**Fig. 3 - 3**
Electronic drive unit for the turbomolecular pump




Error and Operations Messages

To indicate errors, the TCP 035 is equipped with 5 light emitting diodes H 1 - H 5

Type of error see operating instructions of the manufacturers (Balzers-Pfeiffer) on page 33.

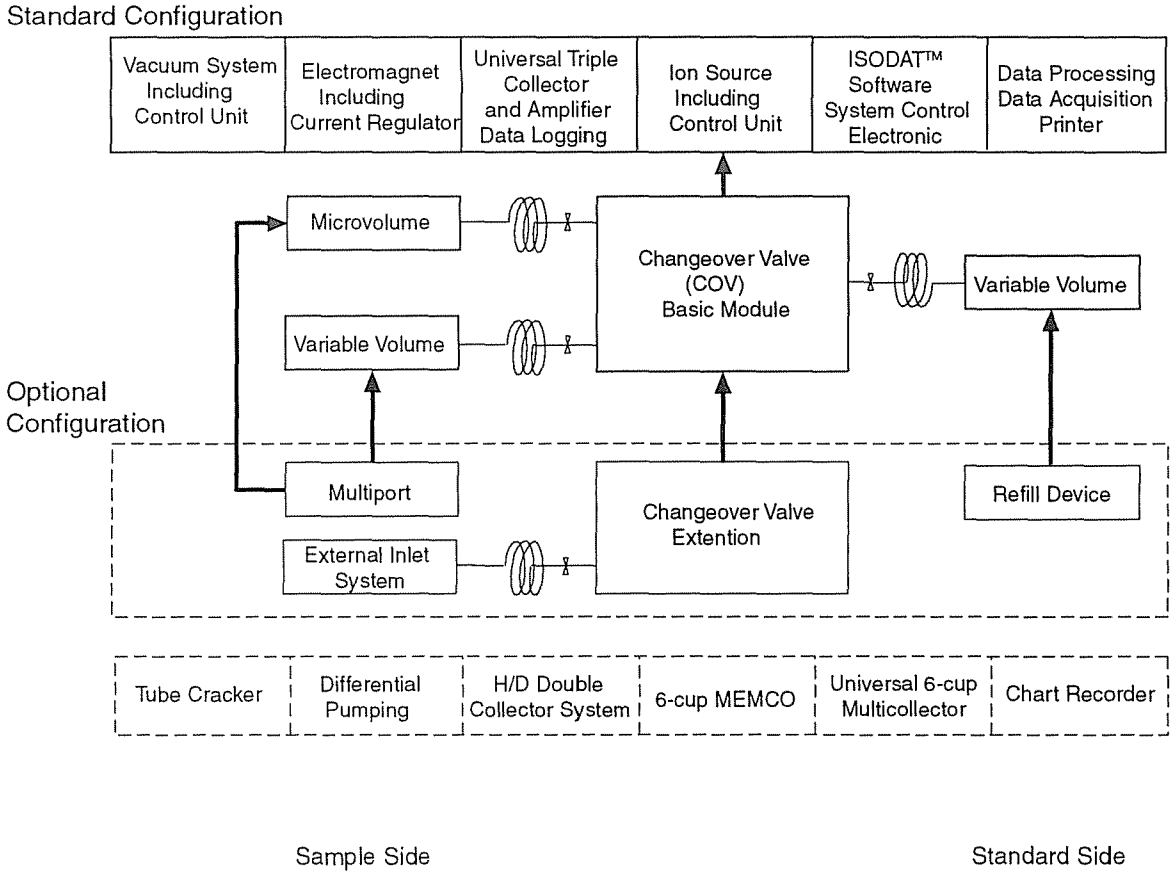
## Inlet System

### 4. 1 General Description

The inlet system of the ***DELTA***$^{plus}$ mass spectrometer is of symmetric design to allow alternating measurements of a sample and a standard gas.

The instrument is equipped with a dual inlet system **(optional)** with a configuration identical for the sample and standard side which enables a balanced flow. Each inlet side has two ports and a variable volume with the respective inlet capillary leading to the changeover valve. For very small samples, a microvolume with its own capillary may be installed.

**Fig. 4 - 1**
Overview of the Inlet System and optional modules for an individual configuration



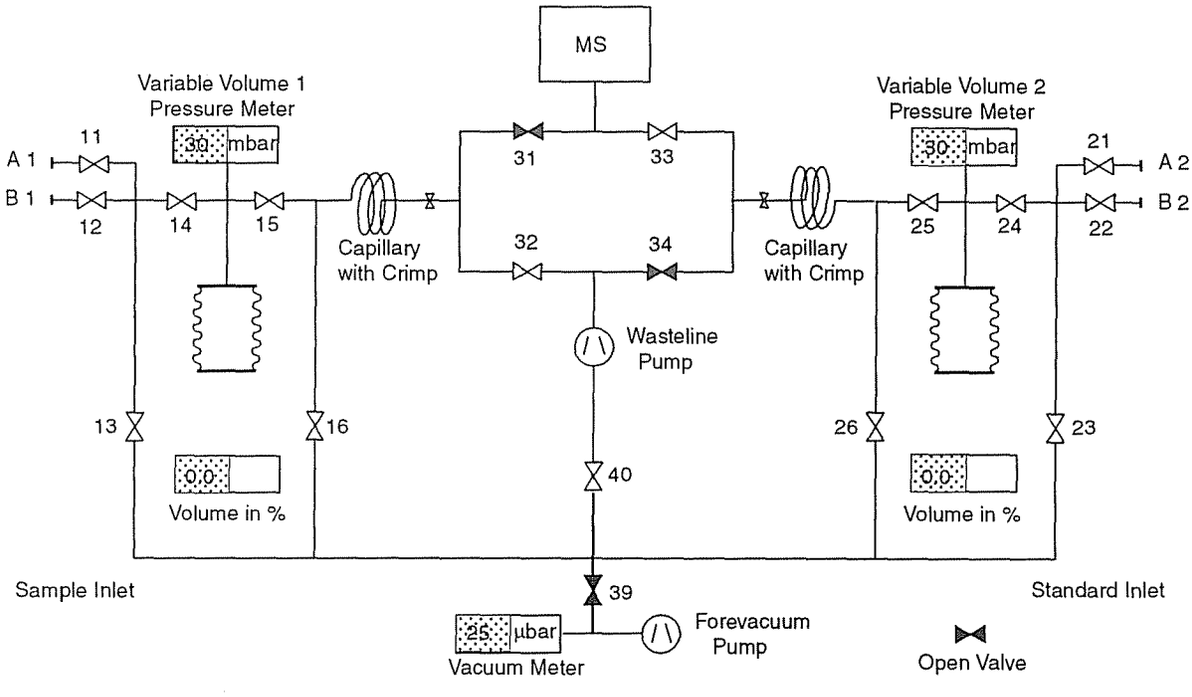
# 4 Inlet System

Before measurements can be performed and results compared, equal conditions of pressure and flow must to be provided for both sample and standard gas to obtain a balanced ion beam intensity.

Pressure adjustment for sample and standard gas is performed in reservoirs, which are adjustable in volume. These variable volumes are bellows which are operated by computer-controlled motors. An automated procedure balances the volumes to such an extent that the ion beam intensity of a selected mass attains a preset value. Balancing of the volumes can also be done manually.

The variable volumes are adjustable from about 3. 5 ml to 40 ml each.

**Fig. 4 - 2**
Schematic of the Dual Inlet System




To balance the ion beam intensity of the sample and standard, respectively, the flow conditions to the ion source have to be identical. The sample gas flows into the ion source an equal amount of a standard gas (or vice versa) is evacuated by the wasteline pump system. The flow conditions thus remain identical during measurement.

Flow conditions are also matched by adjusting the flow resistance through the capillaries to the ion source. The flow resistance is set to equal conditions by crimping the capillaries in front of the inlet port of the changeover valve.

The crimps of the capillaries are factory-set, but must be get new when a capillary is replaced. How to crimp a capillary to a specific flow resistance is described in chapter 6. 3, Technical Advice.

The variable volumes adjust the pressure for larger samples (> 50 barµl). Very small samples, as low as 5 barµl, can be analyzed using the optional microvolume inlet. For more details, please refer to chapter 4. 4, Microvolume.

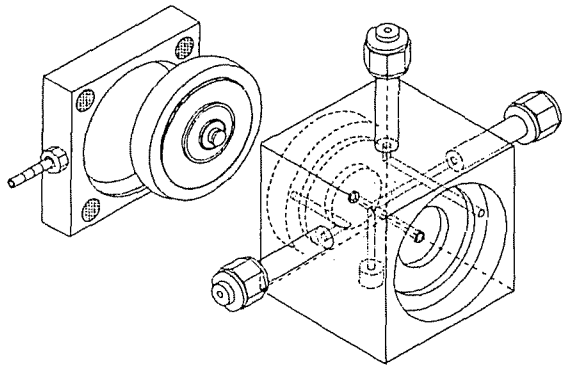
To avoid memory effects when measuring $SO_2$, the inlet system including the changeover valve and the ion source housing can be heated to a temperature of up to 80 °C.

### 4. 1. 1 Valve System

The inlet system is operated by pneumatic valves with a nominal closing pressure of 5 bar (70 psi). The compressed air is either supplied by an optional compressor attached to the mass spectrometer or by a user supplied pressure air line.

The valves are of all metal design. They are equipped with gold gaskets and gold seats acting on knife edges. Up to six valves are machined into one monoblock thus considerably reducing the volume in plumbing as well as possible leakage of the installation. This type of valve blocks is used throughout all inlet modules. For plumbing the valve blocks are fitted with 1/4" Swagelok connectors. Compressed air is fed to the pneumatically operated valves by solenoid valves. These are controlled by dedicated electronics linked to the computer via a data bus.

**Fig. 4 - 3**
Schematic view of a double valve block

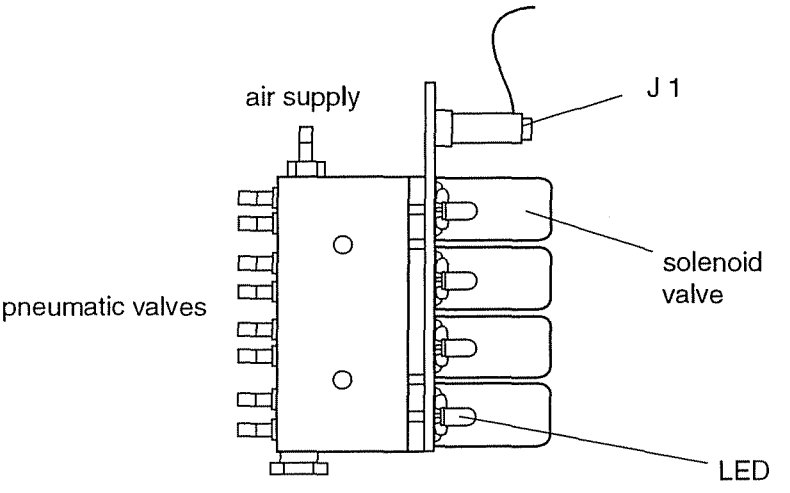


Four of the solenoid three-way valves are located on a "Manifold" block. The solenoid valves are operated with a voltage of 24 V. The voltage is supplied by the driver board via a distributor board. The driver board is located in the electronics cabinet whereas the distributor board is placed close to the inlet system on the right hand side of the cabinet.

# 4 Inlet System

The solenoid valves are normally open and the working condition is signaled by a red LED located on the printed board.

**Fig. 4 - 4**
A "Manifold" block with 4 solenoid valves.

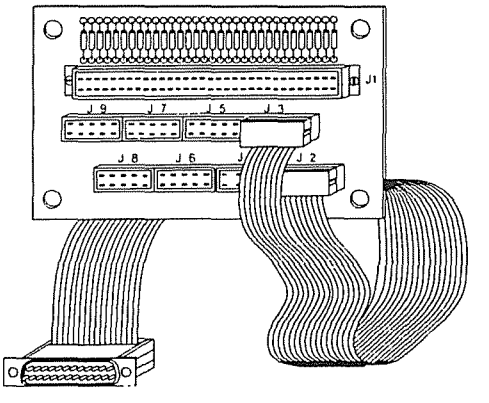



The cable connections are as follows:

The distributor board is linked to the driver board via a flat ribbon cable and a 64-pin connector.
On the distributor board the signals are distributed to eight 10-pin connectors.
In total 8 "Manifold" blocks or 32 valves, can be connected via one distributor board.
For the appropriate valve connections, please see the Service Manual.

In case of a power failure all solenoid valves open automatically. Thus the pneumatic valves close avoiding contamination of the inlet system.

**Fig. 4 - 5**
Distribution board linking the driver board and the "Manifold" board

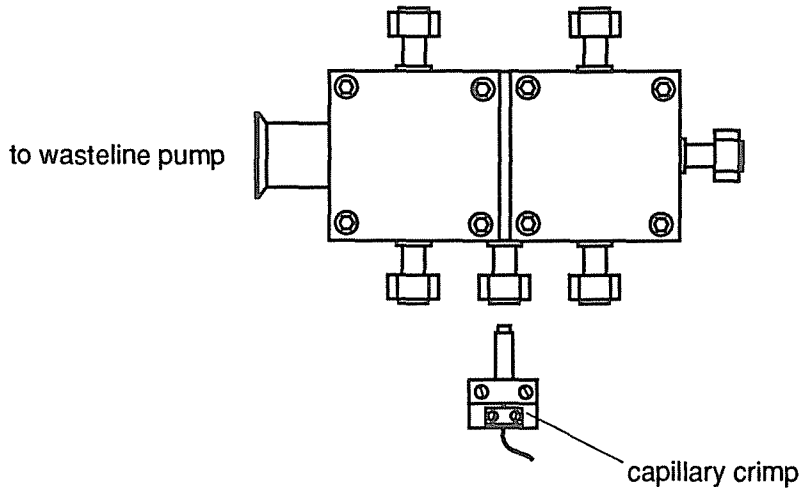


## 4. 2 Changeover Valve

### 4. 2. 1 Basic Module

The basic module of a changeover valve consists of a single block attached to the analyzer housing (see Fig. 3 -1) and accepts the coupling of capillaries for sample and standard gas. The changeover valve is operated automatically by the ISODAT software (in automatic mode) or manually via the monitor display of the inlet schematic .

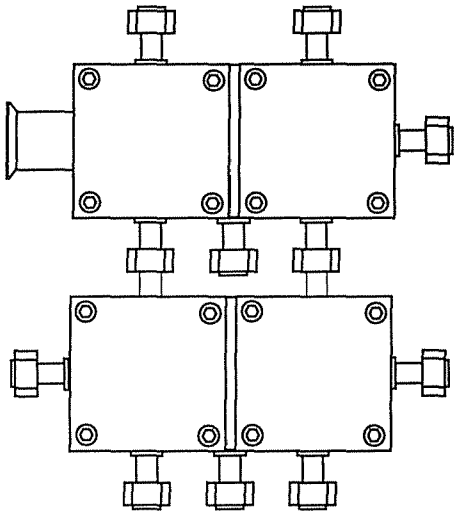
**Fig. 4 - 6**
Basic module of changeover valve block




### 4. 2. 2 Extension Module

An extension module may be added to the changeover valve as an option. The extension module is flanged to the changeover valve by 1/4" Swagelok connectors. It provides two additional inlet ports allowing the coupling of further inlet system options, e.g. a carbonate system. To monitor and to operate the extended changeover valve the respective ISODAT software routine must be activated .

**Fig. 4 - 7**
Extension module attached to the basic module of the changeover valve



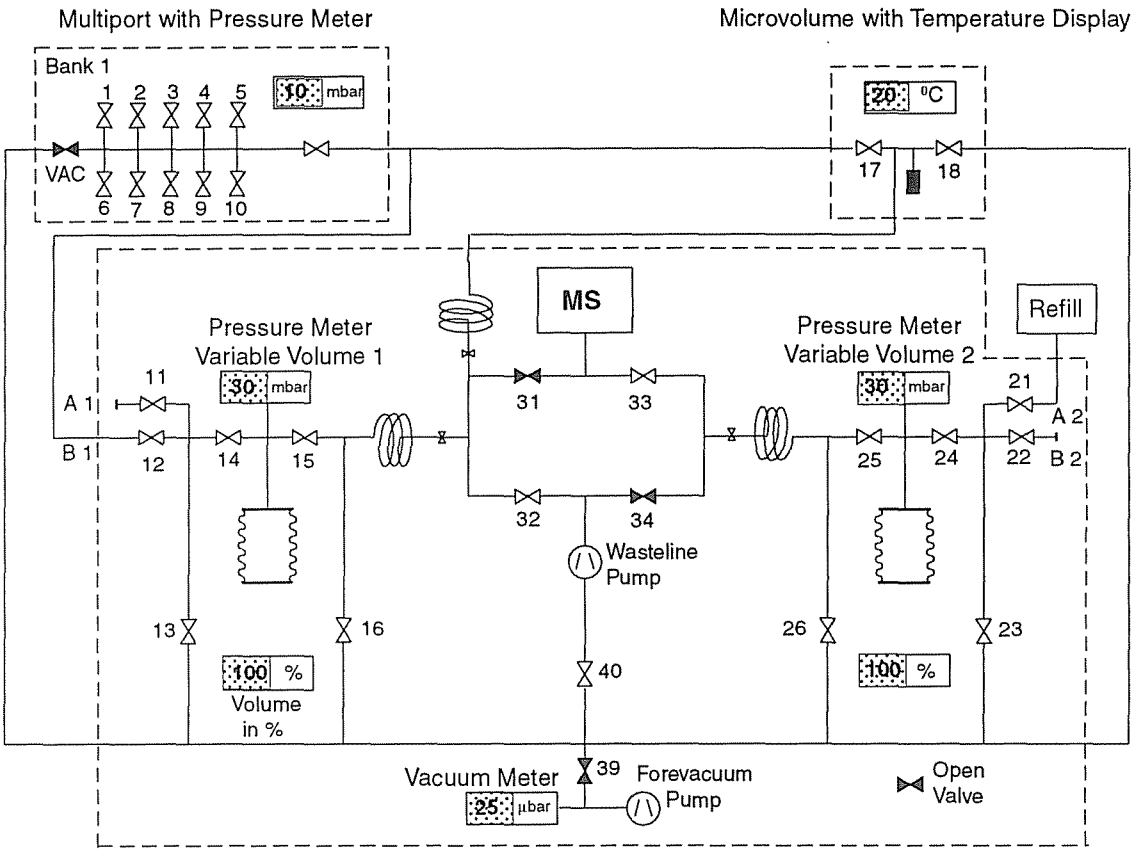
The extension module can be removed at any time. In this case a reinstallation of the ISODAT software for operating the basic changeover valve is necessary.

### 4. 3 Multiport

The multiport is a sample manifold inlet system consisting of one or two banks of 12 valves each. It may be optionally equipped with tube crackers (see Service Manual). When using the multiport as an inlet system, the multiport is connected directly to the sample side of the inlet system valve 12 (inlet port B 1). The multiport valve system is shown in the following figure indicated by the dash-lined box in the upper left corner. The valves of the multiport are operated the same way as the components of the dual inlet system, i.e. automatically by the computer or manually via the monitor display .

To monitor and to operate the multiport valve system on screen the respective ISODAT software routine has to be activated.

**Fig. 4 - 8**
Schematic of an inlet system with multiport and microvolume



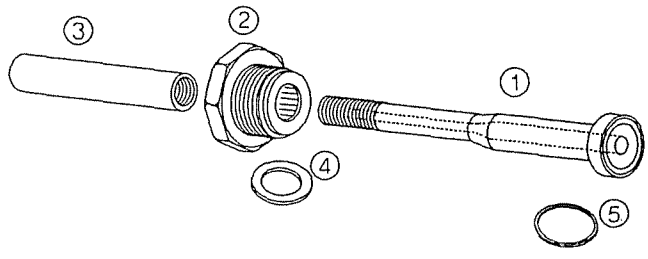

Measurement using a multiport as an inlet system is described in chapter 5, Measurement.

## 4. 4 Microvolume

The microvolume or "cold finger" is an optional inlet module for very small samples and may be installed in combination with a dual inlet system or a multiport. In both cases the microvolume is connected to port B 1 (valve 12) of the dual inlet system (see Fig. 4 - 2 dual inlet and 4 - 8 dual inlet with multiport/microvolume).

A microvolume consists of a "cold finger", a valve block, an autocool unit and a separate capillary. This capillary leads directly to the changeover valve of the system.

**Fig. 4 - 9**
Parts of a microvolume to be inserted into an autocool unit




1 "coldfinger"
2 fitting
3 copper rod
4 washer
5 gasket

The total volume in front of the capillary crimp, i.e. "cold finger" volume plus the connections including the capillary is ~250 µl. Due to the viscous flow conditions which require a pressure of at least 15 mbar in front of the capillary a sample of 5 to 50 barµl has to be concentrated into a small volume. The "cold finger" volume can be reduced (for even smaller samples) by inserting small steel spheres. The concentration in a microvolume is performed by freezing the small sample using liquid nitrogen and expanding it again by subsequent heating.

There are two different types of microvolumes to be used, depending on the gas to be measured. For $CO_2$ a smaller microvolume is required and for $N_2$ a larger one is used. The larger one contains a molecular sieve to freeze out $N_2$ at liquid nitrogen temperature.

The valves of the microvolume are operated the same way as the other components of the dual system, i.e. automatically by the computer or manually via monitor display . With the autocool unit the temperature can be set individually, if required, within arange of about -180 °C and +155 °C.

### 4. 4. 1 Autocool Unit

The temperature of the autocool unit which cools the "cold finger" can be set with the ISODAT software routine in the SUPPORT mode. If, for instance, the temperature level is set to -80 °C, the heater works against the temperature of the liquid nitrogen in order to keep the set temperature. Temperatures between -180 °C and +155 °C may be set in steps of 2 °C.

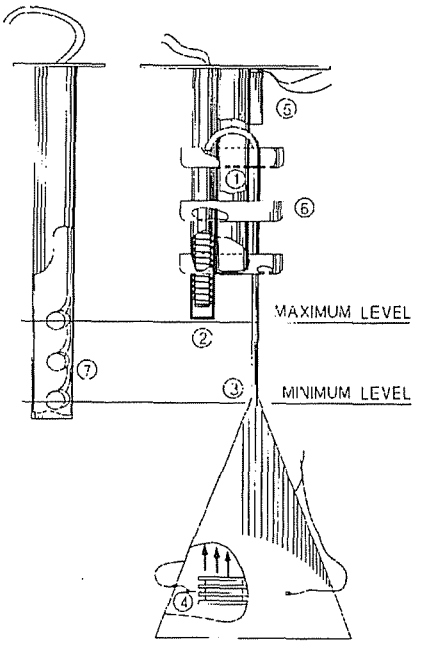
The time to get from: +50 °C down to -180 °C is less than 2 minutes,
-180 °C up to + 50 °C is about 1 minute.

The microvolume fits into a thermal contact pipe attached to the lid of a dewar.

The dewar contains liquid nitrogen up to a certain level. Fitted to the contact pipe are an electrical heater element, a temperature sensor and a cascade arrangement of 3 small bowls. See also Fig. 4 - 10.

All parts of the assembly are made of a high thermal conductivity material and are placed in close thermal contact to each other. This achieves a quick changeover from one temperature to another. To heat the microvolume to a defined temperature the heater element is activated.

**Fig. 4 - 10**
Schematic view of an autocool unit




1 thermal contact pipe
2 heater element
3 hood and standpipe
4 immersed heater element
5 temperature sensor
6 cascaded arrangement of bowls
7 level sensor with 3 thermistors

The heating phase is controlled by the temperature sensor.

To cool the microvolume, another electrical heater element immersed in liquid nitrogen is activated and causes evaporation as well as agitation.

Above the heater element a funnel-shaped hood of a standpipe is positioned which leads to the uppermost bowl of the cascaded arrangement of 3 bowls. This arrangement enables about one droplet of liquid nitrogen per second to be carried by the stream of evaporated nitrogen. Small holes in the bottom of the bowls enable a constant trickle of liquid nitrogen back into the dewar, and the continuous flow of liquid nitrogen rapidly cools down the microvolume. By suitable balancing of the liquid nitrogen flow and heating the microvolume any temperature within the temperature range can be attained.

The microvolume temperature rises very quickly when the immersion heater is switched off and the pipe heater is switched on, due to the very small quantity of liquid nitrogen held in the cascaded bowl arrangement.

A constant liquid nitrogen level in the dewar vessel is maintained by means of the liquid nitrogen refill device.

### 4. 4. 2 Autocool Refill Device

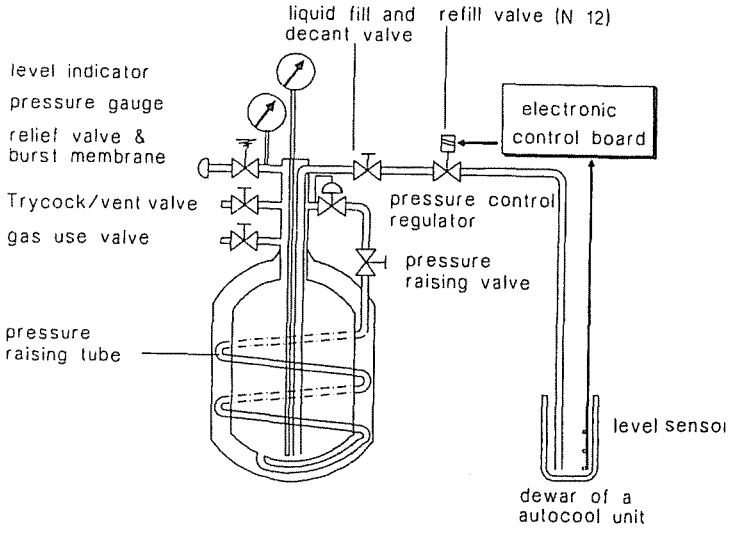
**General Description**

The refill device provides a constant level of liquid nitrogen in the dewar of the autocool unit. It consists of a storage dewar of 75 l or 25 l capacity and is equipped with the neccessary safety devices, valves and pressure gauges required for a safe handling of liquid nitrogen.

The transfer line to the dewar of the autocool unit is controlled by a solenoid-operated refill valve (N 12). The refill valve (N 12) is directly connected to the liquid fill and decant valve of the refill device.

The refill device is activated by a level sensor installed in the dewar of the autocool unit. The level sensor consists of three sensing thermistors, one each for the maximum, the intermediate and the minimum level.

**Fig. 4 - 11**
Schematic view of a refill device




The electronic control board of the refill device evaluates the signals of the sensors and activates the refill valve (N 12) to start or to end the Nitrogen transfer. The autocool unit control board is installed in the lower right cabinet of the instrument.

On the control board, three LEDs indicate which thermistor is sensing and the status of the liquid nitrogen level of the autocool unit can be controlled.

| | |
|---|---|
| green LED signals (upper position) | high liquid nitrogen level, indicates end of refill |
| green LED signals (middle position) | low liquid nitrogen level, indicates start of refill |
| red LED signals | alarm level, no refill was performed |

In case the signal of the thermistor positioned in the middle does not result in a refill and the lowest level is reached, i.e. the storage dewar of the refill device is also empty, the level sensor activates

- the red LED on the control board panel,
- a warning message of the system on the monitor,
- an interruption of the measurement.

# 4 Inlet System

**Safety Warning**

- Keep in mind: **Safety First !**
- Before operating the refill device, please read these notes as well as the manufacturer´s handling instructions carefully.
- The refill device contains extremely cold liquid gas and careless handling might cause severe personal injury including frostbite.
- Wear protective clothing when operating this equipment, including protective gloves and face shield. Do not overfill or tilt the refill device and prevent spills.
- Use the refill device only in well ventilated areas, poor ventilation might cause suffocation. Follow correct First Aid procedures; if gas was inhaled remove victim to fresh air, if necessary give artificial respiration and seek medical assistance immediately.
- Make sure that only authorized and fully trained operators use this equipment and they are fully conversant with these safety notes.
- Use only the cryogenic liquid specified on the label on the refill device.

### Working Principle

The transfer of liquid nitrogen is effected by a build-up of pressure in the self pressurizing dewar of the refill device. The pressure builds up by vaporization of liquid nitrogen in a coiled pressure raising tube located in the dewar´s vacuum interspace when the gas vent valve is closed and the pressure raising valve is opened.

A pressure gauge monitors the pressure. A pressure of 5 psi should be sufficient to transfer liquid nitrogen. A pressure of 10 psi will transfer liquid at about 10 l per minute. A higher pressure is not necessary and even wasteful.

As soon as a preset pressure is reached, the pressure regulator installed in the circulation cuts the flow through the coiled pressure raising tube. The working pressure can be set to an optimum level with the pressure regulator.

The blow-off valve is set to a limit of about 1. 5 bar. An additional burst membrane prevents a build-up of dangerous pressure. The gas vent valve allows to bleed excessive pressure, if necessary. The function schematic of the liquid nitrogen refill device is shown in Fig. 4 - 11.

The 75 l storage dewar is equipped with a level indicator monitoring the liquid nitrogen content.

### Maintenance

Hardly any routine maintenance is required. However, the components of the refill device should be regularly checked for damage or possible freeze-up. If it is necessary to dry and clean items, or to replace them, make sure that they are thoroughly degreased and dried, as moisture or lubricants will freeze at cryogenic temperatures. Do not use thread sealing compounds. Use P:T:F:E: tape, for example Teflon® , or other approved oxygen safe compounds instead.

Occasionally the pressure should be increased up to the **relief valve** setting to ensure satisfactory functioning of this safety device.

Setting the pressure control regulator is performed as follows:

**step 1:** Loosen hexagon locking nut below adjusting screw.

**step 2 :** Rotate adjusting screw counterclockwise to set to zero.

**step 3 :** Close vent valve and liquid valve and open pressure building valve

**step 4 :** Rotate adjusting screw clockwise to increase vessel pressure until gas escapes through the vent hole. Rotate adjusting screw counterclockwise again until gas stops escaping through the vent hole.

**step 5 :** The pressure is now set - tighten locking nut, to prevent further rotation or tampering of the adjusting screw.

### Checking the liquid nitrogen evaporation rate

If you suspect that the evaporation rate of the refill device is excessive, note down the decrease of the liquid nitrogen level over a certain period of time. To check the loss rate close the pressure raising valve and open the Trycock/vent valve. After the contents are fully vented down to atmopheric pressure, measure the boil off rate with a simple flow-meter. The normal boil-off rate for nitrogen is:

1 liter per minute for gas, i.e. about 2 liters of liquid per day.

The reason for a higher rate might be an abnormal cold or frost formation at the lower dished end of the outer casing which should be removed.

# 4 Inlet System

### Operating Instructions

For filling, dispensing and storage of liquid nitrogen the arrangement of valves is shown in the table below for quick reference:

| Operation | Liquid fill & decant valve | Gas use valve | Pressure raising valve | Trycock/ Vent valve |
|---|---|---|---|---|
| Filling Liquid | open | closed | closed | open |
| Dispensing Liquid | open | closed | open | closed |
| Gas Withdrawal | closed | open | open | closed |
| Storage: -Short Term- | closed | closed | open | closed |
| Storage: -Long Term- | closed | closed | closed | open |

Before using the microvolume check the contents of the refill device.
If filling is required proceed as follows:

1. Open the Trycock/vent valve
2. Close the pressure raising valve
3. Close the gas use valve
4. Fill via the opened liquid fill and decant valve

After having checked the refill device, first fill the dewar of the autocool unit with liquid nitrogen to about the required level. To enable the automated and computer controlled refill operation, follow the steps below:

1. Check the pipe connection leading to the dewar of the autocool unit.
2. Close the gas vent valve.
3. Open the liquid fill and decant valve.
4. Open the pressure raising valve

The refill device is now connected to the dewar of the microvolume via the opened liquid fill and decant valve and the flow is controlled via the refill valve N 12. The pressure building valve may be closed when the working pressure is reached, or it may remain open, provided the pressure regulator is set to a suitable working pressure.

### 4. 4. 3 Standard Refill (Reference gas refill)

When working with a multiport inlet system a reference gas refill may be necessary in order to avoid running out of reference gas during measurements.

There are two different methods of a reference gas supply to the inlet system, i.e.

Buffered Reference: With this method a buffer tank containing the standard gas is attached to the inlet port of the standard side for replenishment of the gas used during measurement performance.

The Reference Refill: This is a hardware option. It consists of a metal tank (contents approx. 5 l) with a manual valve connected via a capillary to one of the inlet ports on the standard side (see also Fig. 4 - 12). With the Reference Refill selected the standard side of the inlet system is completely pumped out before it is filled again for the next measurement sequence.

For the different methods of a standard refill, the appropriate parameter,

either **BR** for Buffered Reference

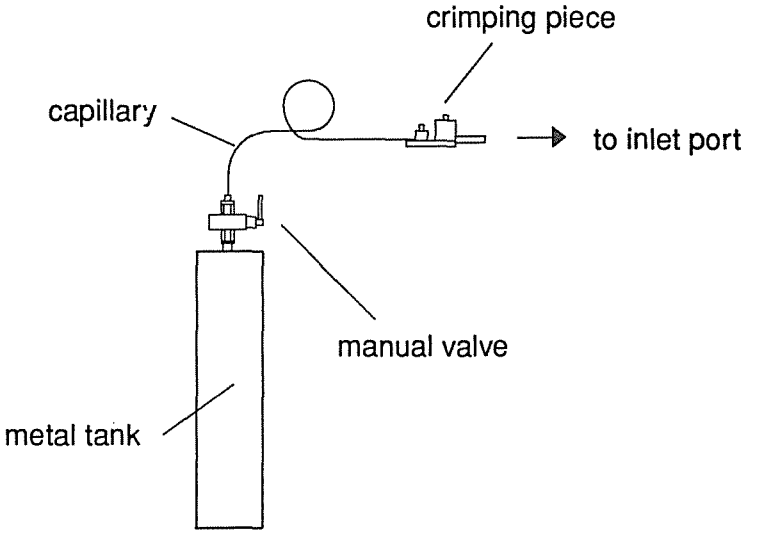
or **RR** for Reference Refill

must be entered in the sequence table for the action to be taken.
If no refill device is used the parameter to be entered is

**NO** for no action defind.

(see also ISODAT manual chapter 5. 3, Edit Sequence Editor)

**Fig. 4 - 12** Reference gas refill



## Measurements

### 5.1 How to Operate the Inlet System

The following paragraphs explain how to operate a single valve or a group of valves and the variable volumes of the instrument.

Beside the automated and computer controlled-performance of the inlet system as per created methods and sequences, a manual operation of components is possible depending on the configuration of the instrument and the version of the ISODAT software.

#### 5.1.1 Standard Equipment

If the instrument is of standard configuration, manual operation is controlled via the SUPPORT - MAIN MENU in configuration A (Cnf-A) (SUPP-A).

**step 1:** Switch on the monitor, the printer, chart recorder (if present) and then the computer. After booting, the computer system requests the operator to answer whether to "Load concurrent DOS Y/N?".

Enter <Y> and the ISODAT software is loaded into the system memory.
The ISODAT MAIN MENU will be displayed.

**step 2:** Choose the submenu INSTRUMENT CONTR and select from this submenu INLET CTRL or MULTIPORT CTRL.
This is done by.

- entering the number of the chosen access key box via the keyboard and pressing <ENTER>.
  or
- pointing the access key box, i.e. placing the mouse cursor onto the box and "clicking", i.e. pressing the left mouse button.

Keep in mind:

| | |
|---|---|
| a **filled valve symbol** means: | **valve open,** |
| an **open frame valve symbol** means: | **valve closed.** |

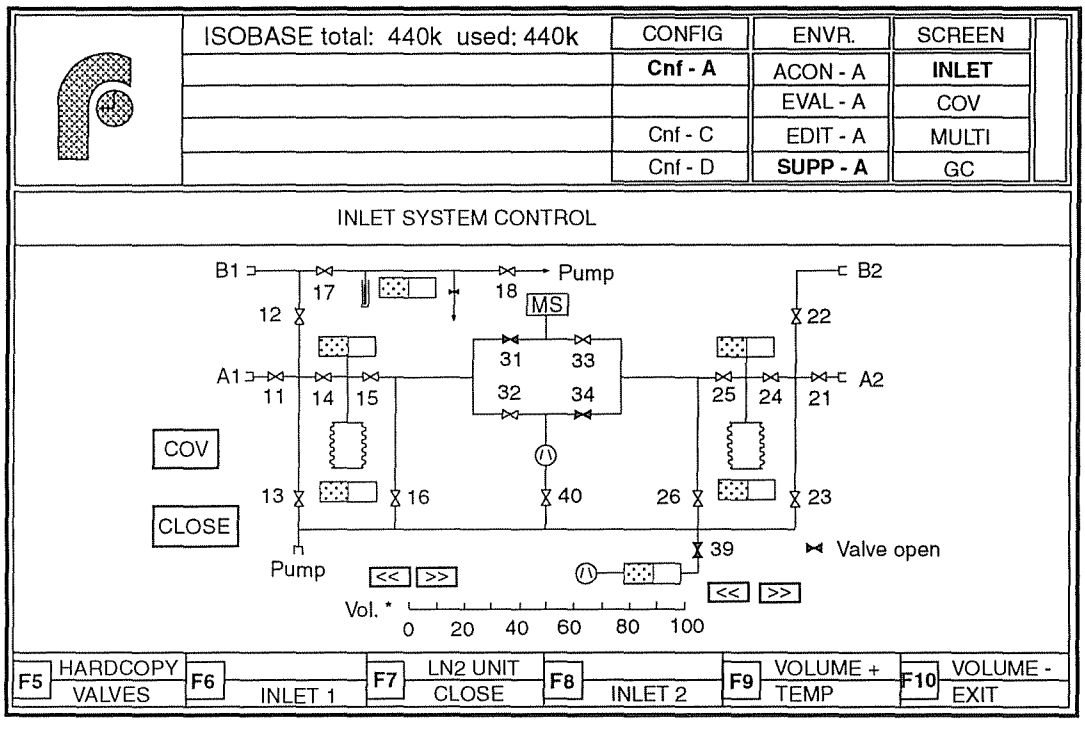
**To operate the valves:**
**with the mouse,**

- point the symbol, i.e. place the mouse cursor onto the symbol and click, i.e. press the left mouse button.
- "Grouped" valves may be operated with the mouse by pointing and "clicking" the following displayed symbols displayed:

| | |
|---|---|
| [COV] | switches the changeover valves to the sample side or vice versa, |
| [CLOSE] | closes the changeover valves to the ion source. |

# 5 Measurements

**Fig. 5 - 1**
Screen display of the inlet system for mouse operation




- **with the keyboard**

  - < F5 > activates the input line,

  - Enter a valve number followed by the command < o > to open or < c > to close and press < Enter >. Upper case characters are also acceptable.

  - By entering a parameter as mentioned below the following valve operations are performed:

    < c1 > switches the changeover valves to the sample side,

    < c2 > switches the changeover valves to the standard side,

    < cc > closes the changeover valves to the ion source.

  See also the key definition line at the bottom of the monitor display for further function key operations, i.e.:

| | |
|---|---|
| < F6 > (command: INLET 1) | switches the changeover valves to the sample side. |
| < F7 > (command: CLOSE) | closes the changeover valves to the ion source. |
| < F8 > (command: INLET 2) | switches the changeover valves to the standard side. |

**To operate the variable volumes:**

**with the mouse**

- Activate the variable volume to be adjusted by pointing and "clicking".
- To adjust a variable volume **continuously:**
  - * point the symbol [ << ] or [ >> ] below the variable volume and "click".

    Repeated "clicking" activates further automated steps of a volume adjustment. The volume in percent will be displayed below the symbol of the variable volume.

NOTE: Do not press the left mouse button permanently !

- To adjust a variable volume **to a certain percentage:**
  - * point the symbol of the variable volume and "click".

    Below the inlet scheme a percentage scale will become visible.
  - * Point to the percentage required and "click" for an automated volume adjustment .

**with the keyboard:**

by using the function keys as per key definition line.

- Activate the input line first:
  - * enter < F5 >.
- To activate a variable volume:
  - * enter the identification of a variable volume

    < V1 > or < V2 > and press < ENTER >.

# 5 Measurements

**NOTE:** The symbol of an activated variable volume displayed on the screen has a red frame.

- To adjust the variable volumes:

  * press simultaneously the keys

    < SHIFT > < F9 > the volume is expanded
    ( command: VOLUME +)

  * < SHIFT > < F10 > the volume is reduced
    ( command: VOLUME -)

**NOTE:** Repeated pressing of the function keys activates further automated steps of a volume adjustment.

## 5. 2 Dual Inlet System, $CO_2$ Measurement

Follow these instructions which also apply as well to the measurement of other gases.

**step 1:** Read the ISODAT Manual first and get familiar with the software and the operating instructions before you start your first analysis.

**step 2:** Switch on the monitor, the printer and then the computer.

**step 3:** This step describes how to admit gas to the inlet system.
If you have already entered your gases, proceed with step 7.

**NOTE: Make sure to have properly filled gas reservoirs attached to the inlet ports.**

1. Close all valves of the sample and standard sides, i.e. the valves numbered as follows:
   sample side: 11, 12, 13, 14, 15, 16
   standard side: 21, 22, 23, 24, 25, 26.

2. Open valve 39,
   watch the forevacuum pressure reading of the VM meter on the monitor (with submenu INLET CTRL or MULTIPORT CTRL activated)

3. Open valves
   sample side: 13, 11, 14
   standard side: 23, 21, 24

4. Open the variable volumes to maximum.

5. Open valves
   sample side: 15, 16
   standard side: 25, 26

Watch of the forevacuum status on the vacuum control unit .
The LED of the FV range INLET lights, when the pressure is reduced to $10^{-1}$mbar.

(See chapter 3. 2, Vacuum System Control Unit).

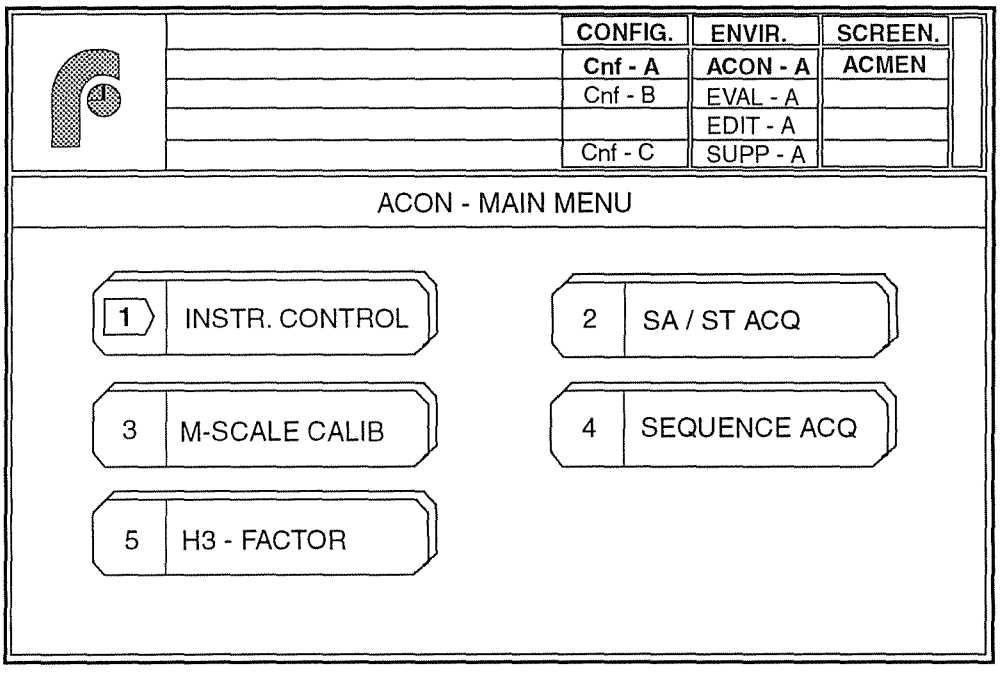
1. Open valve 40 when the pressure reaches $10^{-1}$ mbar.
   The pressure of the forevacuum pump may be read off the computer screen.

2. Close all valves.

**NOTE:** Valves 39 and 40 lock each other to prevent the high vacuum pump from "evacuating" the forevacuum pump. Both valves can be closed at the same time, but not opened.

**step 4:** After evacuation of the entire inlet system access the "Instrument Control Program" (INSTR. CONTROL of the ACON-MAIN MENU) by entering the number of the access key box or by pointing the cursor onto the number (use cursor keys or the mouse) and then press < ENTER > or a mouse button.

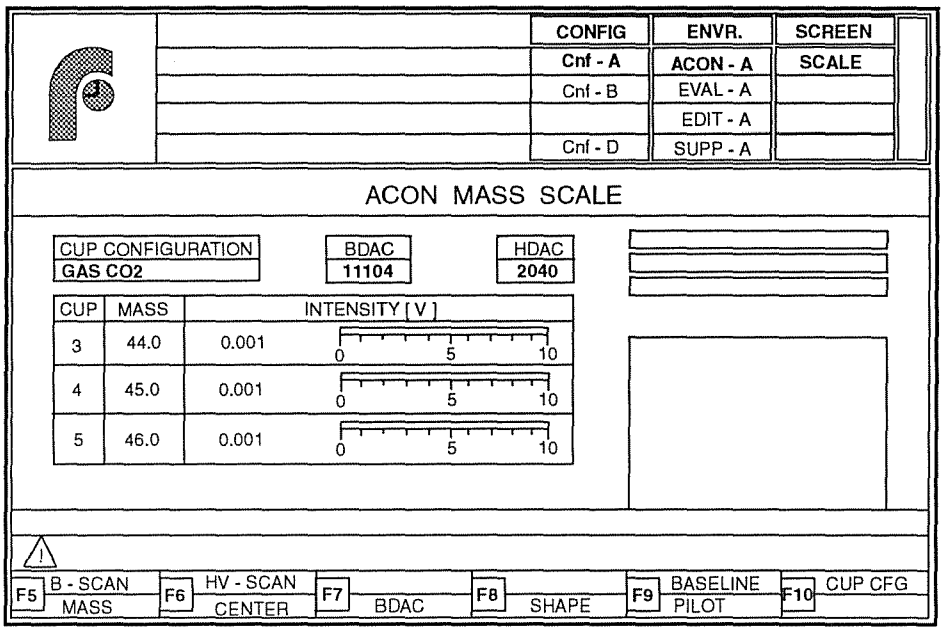
**Fig. 5 - 2**
Screen display of the ACON MAIN MENU




The next screen display then will show the signal intensities
( for more information, see ISODAT Manual).

# 5 Measurements

**Fig. 5 - 3**
By activating INSTR. CONTROL the ACON MASS SCALE is displayed




With the inlet system evacuated, the signal intensity on mass 44 should be close to zero. Check if this is true on both inlet sides by operating the changeover valve via the submenu SUPP-A, INLET CTRL or MULTIPORT CTRL.

**step 5:** Admit standard gas to the inlet system.

1. Open valve 25, keep all other valves closed.

2. Open valve 22 (if the standard gas reservoir is attached to port B 2) or valve 21 (if attached to port A 2), let in a proper amount of gas and allow the gas to equilibrate for a while (for about 50 to 60 sec, see also chapter 3. 2).

3. Close valve 22, or 21.

4. Open valve 24 and watch the pressure on the PM 2 pressure gauge on the monitor. The pressure should read 10 to 20 mbar corresponding to a signal of 1 to 4 V (variable volume completely opened). Adjust the volume to obtain a signal of about 5 V for measurement.

**step 6:** Admit sample gas to the sample side of the inlet system the same way as described for the standard. Proceed as described in the ISODAT Manual,"Getting Started", step 8.

**NOTE:** In case too much gas enters the inlet system the forvacuum trip level of the ion source may be reached and the filament, ion gauge, high voltage and turbomolecular pumps are switch off.
The gas volume may be reduced as follows:

1. Close valve 25, open valve 26,
   open valve 39 and subsequently valve 40
   To evacuate the inlet system up to this point
   close valves 26, 39, 40 and open valve 25 again,

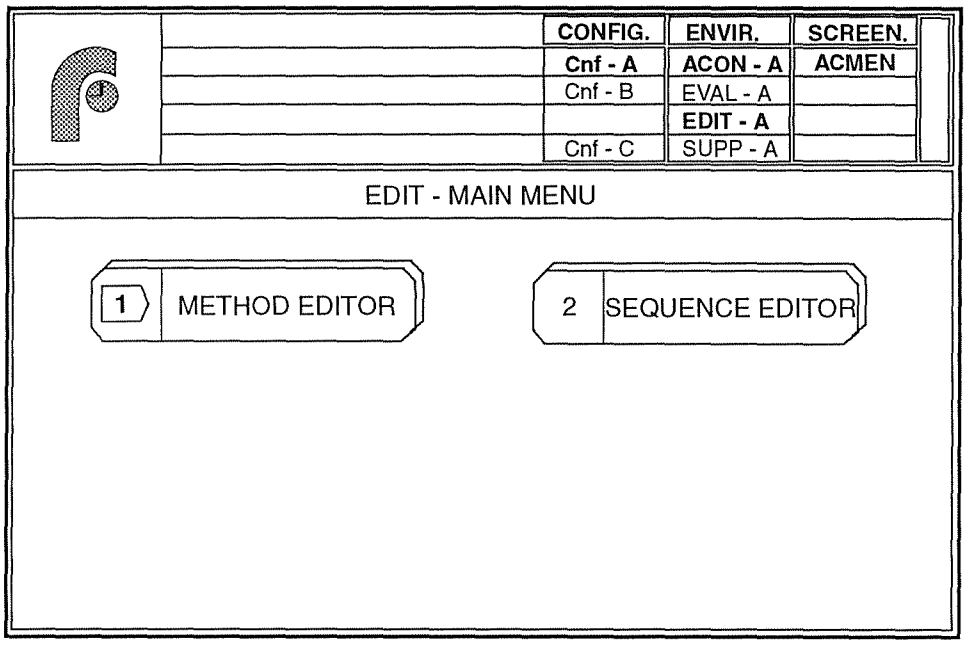
2. Close valve 24 and evacuate the inlet volumes.

3. Open valve 24 and reduce the variable volume, close valve 24 and evacuate.

4. Before you admitting standard gas to the inlet system, reduce the variable volume to 0 % and evacuate. Then reopen the volume to 100 %.

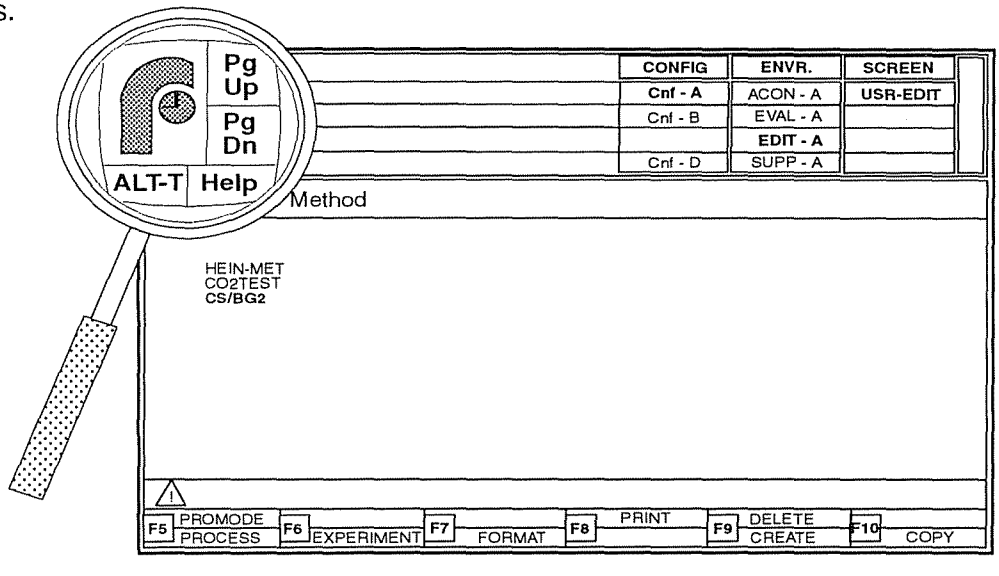
**step 7:** If no method has been created yet, you will have to edit a method for your measurement. How to create a method is described in detail in the ISODAT MANUAL (chapter: 5. 2, Edit Method Editor). The method editor is accessible from the EDIT MAIN MENU of the respective configuration.

**Fig. 5 - 4**
Screen display of the EDIT MAIN MENU




Activate the submenu METHOD EDITOR and the following display will appear with the list of existing methods.

**Fig. 5 - 5**
Screen display of the METHOD EDITOR



# 5 Measurements

After choosing and naming the method to be edited the individual parameters have to be entered for the processing mode of the

| | |
|---|---|
| sample handling, | i. e. the **"PROCESS"** |
| measurement, | i. e. the **"EXPERIMENT"** |
| data output, | i. e. the **"FORMAT"**. |

See also the following figures showing the individual screen display of the method editor. The tables 5.1 - 5. 3 show printouts of parameters entered as an example.

**NOTE:** The different processing modes mentioned on the key definition line of each screen page are accessible by either pressing the function keys < F5 >, < F6 > or < F7 > or by pointing the name of the command on the key definition line with the mouse cursor and "clicking".

When editing the EXPERIMENT mode the parameters are to be entered by using on five screen pages.The screen pages are accessible with the keys < Page Up > and < Page Down >.

When operating with the mouse point the mouse cursor onto the Finnigan logo in the upper left corner of the screen display and press the left mouse button.

The logo then changes its appearance into a window displaying command fields enabling you

to page up and down,
to activate the HELP screen,
and to quit the submenu < ALT-T >

just by "pointing and clicking" with the mouse (see also Fig. 5 - 5).

If no specific parameters are to be entered, the default parameters are automatically inserted by moving the highlighted cursor from line to line and pressing the function key < F8 > or pointing to the name of the command TAKE DEF on the key definition line with the mouse cursor and "clicking".
After having completed the editing, the method has to be checked by a software routine to ensure complete integrity of all parameters.

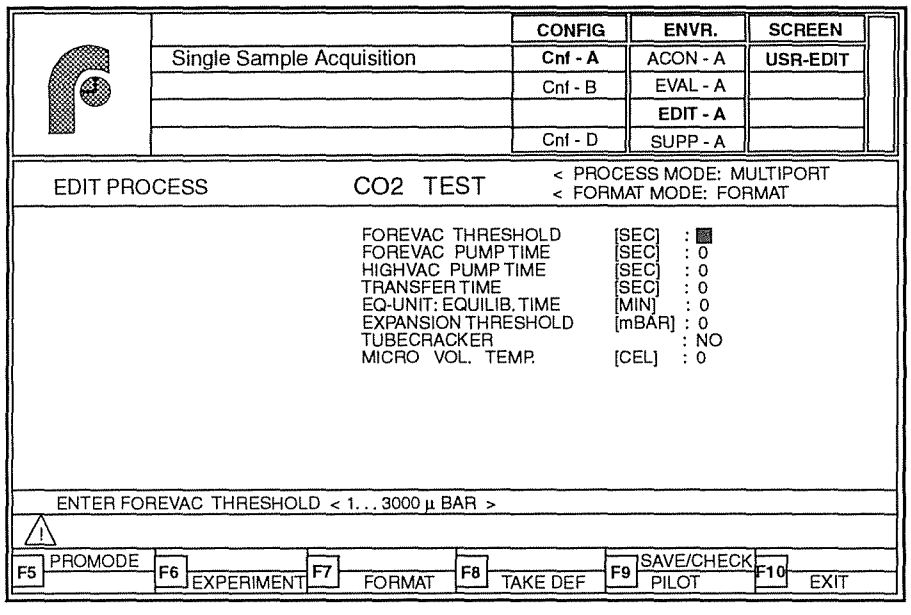
To activate this routine, press simultaneously the function keys < SHIFT > and < F9 > or point the command SAVE / CHECK with the mouse cursor and "click".

If all parameters are correctly edited the method name stated in the headline of the screen display will be tagged and the method saved.

**Editing parameters for the sample handling, i. e. the PROCESS:**

Depending on the gas isotope ratio to be measured, the configuration of the mass spectrometer and peripheral equipment installed, individual PROCESS parameters are to be edited.

**Fig. 5 - 6**
Screen display for editing the process parameters




FOREVAC THRESHOLD: [ µBAR] — Minimum pressure in µbar to be reached by the forevacuum pump before the next action of the instrument starts, e. g. HIGH VAC pumping.

FOREVAC PUMP TIME: [SEC] — Time allowed in seconds for pumping the system or part of it after the FOREVAC THRESHOLD was reached.

HIGHVAC PUMP TIME: [SEC] — Time allowed in seconds for high vacuum pumping the system or part of it before the next action of the instrument starts, e.g. sample transfer.

TRANSFER TIME: [SEC] — Time allowed for the sample transfer from the inlet port valve to the change-over valve. The transfer time depends on the type of gas to be measured.

EXPANSION THRESHOLD: — Maximum gas pressure to reach a signal between 1 and 7 V on the measuring channel for the mass to be measured. For pressures above this threshold part of the gas will be pumped off, e.g. a sample will be expanded for evacuation into the volume between valves 11, 12, 13, 14.

The parameters defining the utilization of the peripherals to be edited are as follows:

EQ-UNIT: EQUILIB. TIME: — With an equilibration unit connected, the time in minutes for equilibration of

$CO_2$ with $H_2O$ is to be entered. Otherwise enter **0** as a parameter.

TUBE-CRACKER: If a tubecracker is installed and to be uitilizied, the parameter is the BANK number to be activated. Otherwise the parameter is **NO.**

MICRO VOL. TEMP: If a microvolume operation is required, enter the freezing temperature for the gas to be measured. If no microvolume is used, the instrument´s ambient temperature should be entered (**30**° C).

**Table 5 - 1**
Printout of the **process** mode: $CO_2$ Test

METHOD: $CO_2$ TEST

>>>> PROCESS <<<< MODE: MULTIPORT

| | | | |
|---|---|---|---|
| FOREVAC THRESHOLD | [µBAR] | : | 50 |
| FOREVAC PUMP TIME | [SEC] | : | 60 |
| HIGH VAC PUMP TIME | [SEC] | : | 60 |
| TRANSFER TIME | [SEC] | : | 60 |
| EQ-UNIT.EQUILIB.TIME | [MIN] | : | 0 |
| EXPANSION THRESHOLD | [mBAR] | : | 50 |
| TUBECRACKER | | : | NO |
| MICRO VOL TEMP | [CEL] | : | 30 |

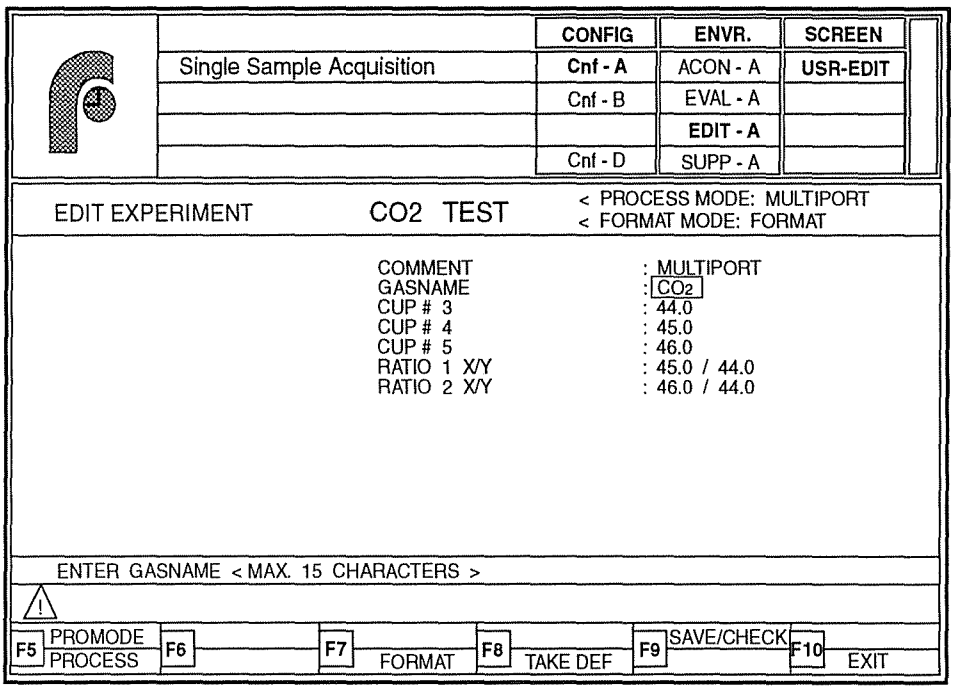
**Editing parameters for the measurement, i. e. the EXPERIMENT:**

The EXPERIMENT parameters are to be edited on 5 screen pages, i. e.

| | |
|---|---|
| page 1 | GAS |
| page 2 | CHANGEOVER |
| page 3 | MEASURE / BACKGROUND |
| page 4 | PEAKCENTER / PRESS ADJUST |
| page 5 | INTERFERING MASS. |

See also the printout of a created EXPERIMENT (Table 5 - 2).

**Fig. 5 - 7**
Screen display for editing the experiment parameters




**page 1:** GAS

GASNAME: The gas name must be the name for a valid cup configuration, e.g. $N_2$, $CO_2$,$SO_2$.
CUP#: The mass numbers (CUP #) for each cup and the ratios (RATIO n X/Y ) will then
RATIO: be entered automatically.
Whenever a cup configuration is altered, even when the name remains the same, it has to be entered into each method again by typing the name into its position.

**page 2:** CHANGEOVER

COV PORT#: The available changeover valve ports are automatically defined according to the configuration of the instrument. They can be altered only during a new installation or by editing the system table.

STANDARD PORT#: SAMPLE PORT#: The port numbers for the standard and sample inlet port are to be defined. The usual numbering is:

**SAMPLE PORT# = 1**
**STANDARD PORT# = 2**

**page 3:** MEASURE

ORDER: The actions of the instrument to take a measurements are determined by parameters to be entered in an order string. An order sequence is as follows:
C / B / P / H / M6 / I / S / V / Z . If a certain measurement performance is not required the parameter for the order is to be omitted in the order string.

The parameters listed below induce the following activities:

C: ( = center ) Activates a Peak Center.

B: ( = background ) Measures the Background.

P: ( = pressure adjust ) Performs a Pressure Adjust.

H: ( = $H_3$ factor ) Measures the $H_3$ factor for the HD determination.

I: ( = interfering mass ) Activates a measurement of interfering masses. Up to 10 masses may be measured. The measuring range of interfering masses is depends on the mass calibration and is controlled by the interfering masses table for the experiment to be edited.

Mn: (= measurement) Performs "n" measurement cycles of the standard and sample; n = the number of measuring cycles to be defined. A maximum of 32 standard / sample gas comparisons is allowed in any combination in the order string (e.g.: M32 or M8/M8/M8/M8).

S: (= standard side) Closes the standard inlet side, i.e. valve 25.

V: (= variable volume) Expands the variable volume VOL 2 to the maximum.

Z: (= zero) Closes the changeover valve, i.e. closes valves 31 and 33, opens valves 32 and 34.

**NOTE:** To obtain correct measurements it is vital to enter the order parameter for combined actions in a plausible order. The order H should only be used in HD measurements. Background should be measured before a press adjust, but after a peak center. A peak center after the measurement is meaningless. Interfering masses should be measured after the isotope ratio measurement, not before. The parameters S, V and Z are to be entered after the order for the defined number of measuring cycles. The sequence of the orders S / V / Z is not critical.

IDLE TIME: [SEC] Period of time in seconds between the opening of the changeover valve and start of the measurement (signal integration).

INTE-GRATION TIME: [SEC] Period of time for the data collection of the gas to be measured. Values to be entered for the integration are: 1,2,4,8 or 16 s, depending on the gas to be measured.

Typical value for

$CO_2$ = 8 s
$N_2$ = 4 s.

**page 4:**
PEAK CENTER

MASS: Ion beam signal of a mass to be used for the peak center routine to be performed.

DELAY TIME: [SEC] Period of time in seconds following a peakcenter routine allowing a stabilization of signals before the next instrument action.

PRESS ADJUST
MASS: Ion beam signal of a mass to be used for balancing sample pressures to attain comparable signals.

MASTER
LEVEL: The parameter to be entered is either a voltage at which the signals should be measured or a pilot signal.
The voltage range to which the signals of sample and standard can be balanced is 1.0 to 10.0 V.
If the signal of the standard is to be adjusted to the level of the measured sample signal, enter: **SA**

If the signal of the sample is to be adjusted to the level of the measured standard signal, enter: **ST**

If no signal balancing is to be performed, enter: **NO**

DELAY TIME: Period of time in seconds following after a signal balancing to allowing a stabilization of signals before the next instrument action.

**page 5:**
INTERFERING MASS The measurement of interfering masses allows to check the purity of the gas being measured as well as to detect a contamination of the instrument. The interfering mass measurement is an absolute measurement.

GAS NAME: The gas name to be entered must be a valid cup configuration, e.g. $N_2$, $CO_2$,
The cup # and mass number will then be entered automatically.

**page 6:**
INTERFERING MASS
IDLE TIME: Period of time in seconds between the last action of the instrument and the start of the next measurement (signal integration).

MASS n: (n= 1 to 10) A maximum of 10 interfering masses may be entered, i.e. if sample and standard gas are to be checked for the same inpurities, five interfering masses may be edited.
The range of interfering masses depends on the mass calibration of the instrument.

PORT: This parameter defines for which gas the interfering masses are to be measured. The parameters to be entered are for the:

sample side = **SA**
standard side = **ST**

CUP# The number of the cup to be entered as a parameter has to be one of the cups of the measuring channels calibrated for the gas measured. On which cup the interfering mass is to be measured depends on the mass and its signal intensity.

INT. TIME: [SEC] Period of time for the data collection of the interfering mass to be measured. Values to be entered for the integration are: 1, 2, 4, 8 or 16 s.

**Table 5 - 2**
Printout of the created **experiment** $CO_2$ TEST

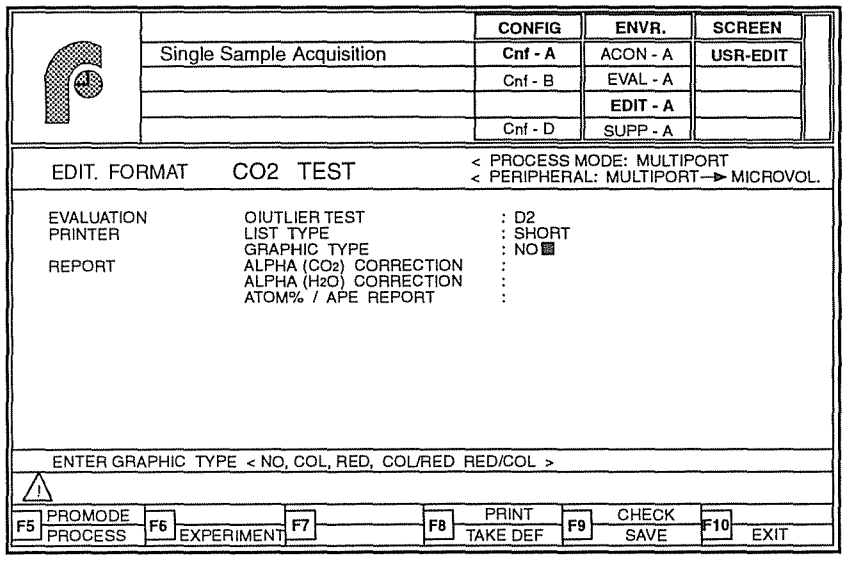
```
METHOD :      CO2 TEST
>>> EXPERIMENT <<<

              COMMENT                        :        MULTIPORT

GAS           NAME                           :        CO2
              CUP # 3                        :        44.0
              CUP # 4                        :        45.0
              CUP # 6                        :        46.0
              RATIO 1 X/Y                    :        45.0 / 44.0
              RATIO 2 x/Y                    :        46.0 / 44.0
CHANGEOVER
              COV PORT # 1                   :        VAR. VOLUME 1
              COV PORT # 2                   :        VAR. VOLUME 2
              COV PORT # 3                   :
              COV PORT # 4                   :
              STANDARD PORT #                :        2
              SAMPLE PORT #                  :        1
MEASURE ORDER
                                             :        C/B/P M8/I
              IDLE TIME          [SEC]       :        15
              INTEGRATION TIME   [SEC]       :        8
BACKGROUND
              IDLE TIME          [SEC]       :        30.0
              INTEGRATION TIME   [SEC]       :        4
              DELAY TIME         [SEC]       :        1.0
PEAKCENTER
              MASS                           :        44.0
              DELAY TIME         [SEC]       :        1.0
PRESS ADJUST
              MASS                           :        44.0
              MASTER LEVEL       [V]         :        4.0
              DELAY TIME         [SEC]       :        10.0
```

**Table 5 - 3**
continuation of the created **experiment** $CO_2$ TEST

```
INTERFERING MASS
                        GAS NAME      :        CO2
                        CUP # 1       :       44.0
                        CUP # 2       :       45.0
                        CUP # 3       :       46.0

INTERFERING MASS
                                                        IDLE TIME[SEC]    :30
MASS 1        : 18.0   PORT:ST       CUP#: 5           INT. TIME[SEC]    : 4
  "   2       :  0.0        :SA           : 5                             : 4
  "   3       :  0.0        :ST           : 5                             : 4
  "   4       :  0.0        :SA           : 5                             : 4
  "   5       :  0.0        :             : 0                             : 0
  "   6       :  0.0        :             : 0                             : 0
  "   7       :  0.0        :             : 0                             : 0
  "   8       :  0.0        :             : 0                             : 0
  "   9       :  0.0        :             : 0                             : 0
  "  10       :  0.0        :             : 0                             : 0
```

**Editing parameters for the data output, i.e. the Format:**

**Fig. 5 - 8**
Screen display to edit the parameters for the format




OUTLIER TEST Statistical outlier correction
Correction of mean values is either performed on SIGMA calculation or as per Dixon tables. The following parameters can be entered as correction factor:

Sigma 1 to 4
D(ixon) 1 to 7.

If no outlier test is to be performed, enter: **NO**

# 5 Measurements

LIST TYPE: The output to the printer is controlled via this entry. There are different types of listing available i.e. quick, long, short and a "specrun", see also tables 5.5 - 5.9. In addition, several user defined outputs are possible (see ISODAT Manual, chapter 5. 2, Edit Method Editor).
The "specrun" summary is a special format with a calculated δ-value for each sample (SA) and standard (ST) measurement. This table is included to allow the comparison of measurements performed with instruments from different manufacturers on the same basis. The 2 $\sigma_{10}$-values for this types of calculation are slightly better than using the same measurement but treating the Standard/ Sample comparisons as independent results thus obtaining one δ-value per comparison. The "specrun" summary will not convert the measured values to international standards!

GRAPHIC TYPE: A graph of the collection data (COL) and/or the data reduction datas (RED) are printed. If no graph printout is required, enter: **No**.
See also Fig. 5 - 8.

ALPHA CORRECTION: For carbonate and for $H_2O/CO_2$ equilibration a fractionation correction can be activated (see ISODAT Manual for details). If no correction is required, enter: **No**.

ATOM% / APE REPORT: Conversion of the measured delta values to ATOM% or APE (atom percent excess) is activated. The standard must be properly defined. (For details, see ISODAT Manual, ACON $H_3$ Factor)

**Table 5 - 4**
Printout of the format: $CO_2$ TEST

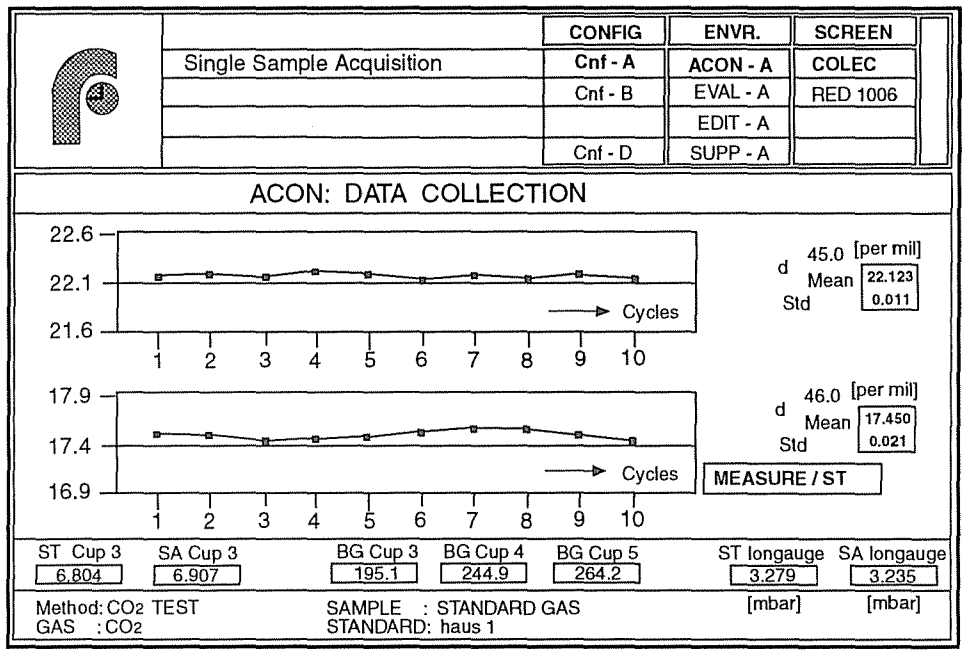
METHOD : $CO_2$ TEST

>>> FORMAT <<< MODE : FORMAT

| | | | |
|---|---|---|---|
| EVALUATION | | | |
| | OUTLIER TEST | : | D2 |
| PRINTER | | | |
| | LIST TYPE | : | SHORT |
| | GRAPHIC TYPE | : | NO |
| REPORT | | | |
| | ALPHA ($CO_2$) CORRECTION | : | NO |
| | ALPHA ($H_2O$) CORRECTION | : | NO |
| | ATOM% / APE REPORT | : | NO |

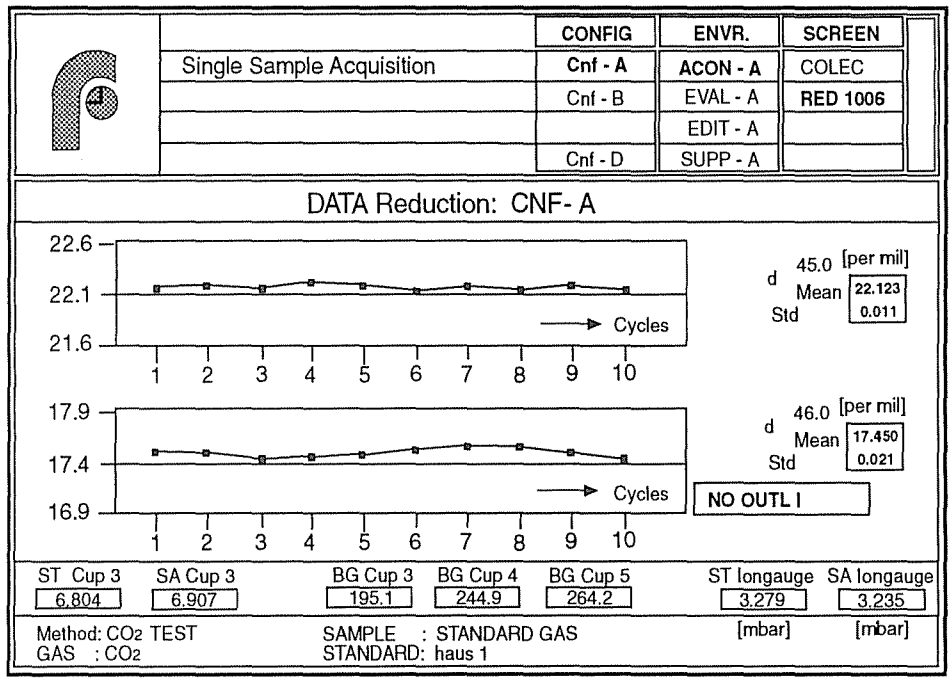
**step 7:** Go back to ACON MAIN MENU and start a single sample measurement by activating the submenu SA/ST ACQ (see also figure 5 - 2). Enter sample and standard ident and the method name.
Then start the measurement by pressing < F5 > or pointing and clicking the command MEASURE on the key definition line. The Data Collection page will show up.
The measurement is finished with a printout of listings and graphs as specified in the format part of the edited method.

**Fig. 5 - 9**
Screen display of the Data Collection procedure




Example listings are given in Tables 5 - 5 to 5 - 9.
Printout of a graph is shown in Fig. 5 - 11.

**Fig. 5 - 10**
Screen display of the Data Reduction procedure



# 5 Measurements

**Fig. 5 - 11**
Printout of a $CO_2$ measurement graph

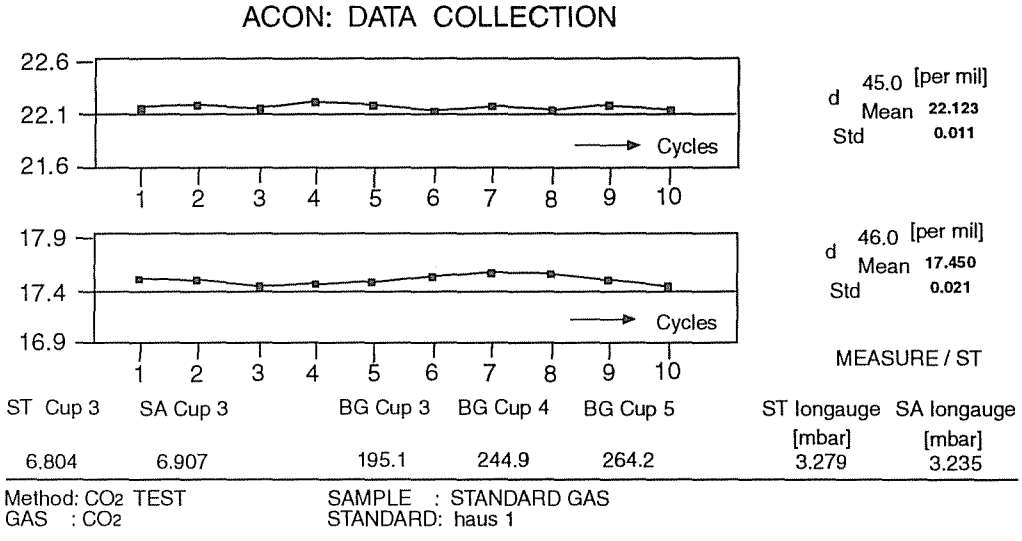



**Table 5 - 5**
Quick list of a RUN SUMMARY

```
Date/Time ..............: Tue- Feb-26-1996 / 14:12:45
Spec.- No ..............: 3
Sample Ident ...........: CJ / GB

--------------------------- standardized data ------------------------
                                    13/12-C                  18/16-0
Sample [17-0 corr]                   -0.131                   -0.255
Sample vs. PDB                      -28.297                  -19.030
Sample vs. VSMOW                                              11.291
```

**Table 5 - 6**
Short list of a RUN SUMMARY

RUN SUMMARY

Date / Time .....: Wed-Mar-21-1990 / 09:55:22
Spec.- No.....: 1
Sample Ident ....: Standard W2/
Port number .....:
Method Name.....: $CO_2$ TEST
Standard Name ...: Haus 1
Cup Config .....: $CO_2$
Comment.....: MAGNETPOSITION 51.2 MM
ACTION.....:

Process information:

| Mass | | 44 | 45 | 46 |
|---|---|---|---|---|
| BGND-1 | | 220.032 | 224.500 | 226.864 |
| | ION-GAUGE | | | |
| ST[V] | 3.279 | 6.851 | 8.656 | 9.573 |
| SA[V] | 3.235 | 6.770 | 8.553 | 9.465 |
| ST-MEAN | 1.263442 | +/- 0.000017 | 1.397357 +/- | 0.000027 |
| SA-MEAN | 1.263411 | +/- 0.000013 | 1.398164 +/- | 0.000016 |
| N | | 8 | | 8 |
| DELTA-MEAN | | -0.023 | | 0.576 |
| Std.Deviation | | 0.013 | | 0.011 |
| Std. Error | | 0.005 | | 0.004 |
| corrected for outliers | | | | |
| probability of error | | 20% => | 2 of 8 | |
| N | | 7 | | 8 |
| S1 Outliers | | 1 | | 0 |
| Delta-Mean | | -0.020 | | 0.276 |
| Std.Deviation | | 0.010 | | 0.011 |
| Std.Error | | 0.004 | | 0.004 |
| Student-factor t (95%) | | 1.943 | | 1.895 |
| Std.Error * t | | 0.007 | | 0.007 |
| standardized data | | | | |
| | | 13/12-C | | 18/16-0 |
| Sample [17-O corr] | | -0.020 | | 0.576 |
| Sample vs. PDB | | -31.237 | | 19.379 |
| Sample vs. VSMOW | | | | 12.337 |
| Atom % Excess | | 0.031 | | 0.002 |

**Table 5 - 7**
Long list of a RUN SUMMARY

RUN SUMMARY

Date/Time .....: Wed-Mar-21-1990 / 09:45:04
Spec.-No.....:
Sample Ident ....: Standard W1
Port Number .....:
Method Name .....: $CO_2$ TEST
Standard Name ...: HAUS1
Cup Config .....: $CO_2$
Comment .....: MAGNETPOSITION 51.2 MM
Action .....:

Process information:

| Mass | | 44 | 45 | 46 |
|---|---|---|---|---|
| BGND- | 1 | 193.823 | 243.934 | 261.252 |
| | Ion Gauge | | | |
| ST | 3.0E-1[mbar] | 6.988[V] | 8.817[V] | 9.764[V] |
| SA | 3.0E-1[mbar] | 6.984[V] | 9.008[V] | 9.930[V] |

| Cycle | 45/44---DELTA [%o] | | 46/44---DELTA [%o] | |
|---|---|---|---|---|
| ST 1 | 1.261654 | | 1.397284 | |
| SA 1 | 1.289808 | 22.340080 | 1.421841 | 17.579112 |
| ST 1 | 1.261594 | | 1.397273 | |
| SA 2 | 1.289804 | 22.376108 | 1.421821 | 17.582185 |
| ST 2 | 1.261556 | | 1.397236 | |
| SA 3 | 1.289753 | 22.357560 | 1.421757 | 17.564651 |
| ST 3 | 1.261538 | | 1.397196 | |
| SA 4 | 1.289729 | 22.353777 | 1.421693 | 17.547768 |
| ST 4 | 1.261492 | | 1.397125 | |
| SA 5 | 1.292334 | 22.395677 | 1.425959 | 17.468512 |
| ST 5 | 1.264125 | | 1.391419 | |
| SA 6 | 1.289692 | 22.372898 | 1.421704 | 17.612262 |
| ST 6 | 1.264147 | | 1.397070 | |
| SA 7 | 1.289694 | 22.392748 | 1.421677 | 17.619228 |
| ST 7 | 1.261447 | | 1.397054 | |
| SA 8 | 1.289648 | 22.348390 | 1.421625 | 17.579795 |
| ST 8 | 1.261466 | | 1.397075 | |
| ST-Mean | 1.261503 | +/- 0.000078 | 1.397140 | +/- 0.000094 |
| SA-Mean | 1.289713 | +/- 0.000060 | 1.421706 | +/- 0.000077 |
| N | | 10 | | 10 |
| Delta-Mean | | 22.364 | | 17.584 |
| Std.Deviation | | 0.017 | | 0.026 |
| Std.Error | | 0.005 | | 0.008 |

**Table 5 - 8** SPECRUN SUMMARY

Date/Time .....: Wed-Mar-21-1990 / 10:52:12
Spec.- No.....:
Sample Ident ....: Standard W3
Port Number .....:
Method Name .....: $CO_2$ TEST
Standard Name ...: HAUS1
Cup Config. .....: $CO_2$
Comment .....:
Action .....:
Process information:

| Mass | | 44 | 45 | 46 |
|---|---|---|---|---|
| BGND- | 1 | 193.823 | 243.934 | 261.252 |
| | Ion Gauge | | | |
| ST | 8.1E-1[mbar] | 6.036[V] | 7.632[V] | 8.459[V] |
| SA | 8.1E-1[mbar] | 6.018[V] | 7.778[V] | 9.582[V] |
| Cycle | | 45/44--- DELTA [%o] | | 46/44--- DELTA [%o] |
| ST 1 | 1.264462 | | 1.401588 | |
| SA 1 | 1.292544 | 22.253197 | 1.426052 | 17.456974 |
| ST 1 | 1.264352 | 22.256256 | 1.401581 | 17.447634 |
| SA 2 | 1.242439 | 22.237390 | 1.426019 | 17.452353 |
| ST 2 | 1.264295 | 22.244301 | 1.401536 | 17.455515 |
| SA 3 | 1.292399 | 22.258976 | 1.425981 | 17.452056 |
| ST 3 | 1.264220 | 22.270813 | 1.401508 | 17.435801 |
| SA 4 | 1.292352 | 22.270858 | 1.425908 | 17.399992 |
| ST 4 | 1.264174 | 22.282642 | 1.401535 | 17.408369 |
| SA 5 | 1.292334 | 22.295677 | 1.425959 | 17.468512 |
| ST 5 | 1.264125 | 22.310999 | 1.401419 | 17.466579 |
| SA 6 | 1.292323 | 22.312489 | 1.425835 | 17.421983 |
| ST 6 | 1.264110 | 22.305473 | 1.401421 | 17.421622 |
| SA 7 | 1.292290 | 22.278514 | 1.425836 | 17.423647 |
| ST 7 | 1.264144 | 22.271637 | 1.401416 | 17.421048 |
| SA 8 | 1.292307 | 22.291238 | 1.425824 | 17.421059 |
| ST 8 | 1.264113 | | 1.401403 | |
| ST-Mean | 1.264222 | +/- 0.000124 | 1.401490 | +/- 0.000075 |
| SA-Mean | 1.292373 | +/- 0.000084 | 1.425927 | +/- 0.000089 |
| N | | 15 | | 15 |
| Delta-Mean | | 22.276 | | 17.437 |
| Std.Deviation | | 0.024 | | 0.022 |
| Std.Error | | 0.006 | | 0.006 |
| corrected for outliers | | | | |
| probability of error | | 20.0% => 3 of 15 | | |
| N | | 15 | | 15 |
| S1 Outliers | | 0 | | 0 |
| Delta-Mean | | 22.276 | | 17.437 |
| Std. Deviation | | 0.024 | | 0.022 |
| Std. Error | | 0.006 | | 0.006 |
| Student-factor t (95%) | | 1.761 | | 1.761 |
| Std. Error * t | | 0.011 | | 0.010 |

**Table 5 - 9**
Continuation of the long list RUN SUMMARY

| | | |
|---|---|---|
| ---------- corrected for outliers ---------- | | |
| probability of error | 0.5 % => | 0 of 8 |
| N | 8 | 8 |
| D2 Outliers | 0 | 0 |
| Delta-Mean | 22.364 | 17.584 |
| Std. Deviation | 0.017 | 0.025 |
| Std. Error | 0.005 | 0.008 |
| Student-factor t (95%) | 1.833 | 1.833 |
| Std. Error * t | 0.010 | 0,015 |

| | | |
|---|---|---|
| ---------- standardized data ---------- | | |
| | 13/12-C | 18/16-0 |
| Sample [17-o corr.] | 23.295 | 17.549 |
| Sample vs.PDB | -5.532 | -1.560 |
| Sample vs.VSMOW | | 29.252 |
| Atom% Excess | | |

| | | | | | |
|---|---|---|---|---|---|
| ----------interfering masses ---------- | | | | | |
| Mass BGZ: 8.0 | Port: | ST | 183.4 | 228.4 | 247.6 |
| Mass 1 : 18.0 | Port: | SA | Cup: 3 | | 0.044[V] |
| Mass 2 : 18.0 | Port: | ST | Cup: 3 | | 0.044[V] |
| Mass 3 : 40.0 | Port: | SA | Cup: 4 | | 0.246[V] |
| Mass 4 : 40.0 | Port: | ST | Cup: 4 | | 0.159[V] |
| Mass 5 : 32.0 | Port: | SA | Cup: 3 | | 0.019[V] |
| Mass 6 : 32.0 | Port: | ST | Cup: 3 | | 0.014[V] |

### 5.3 Microvolume Inlet System

An optional microvolume may be installed in combination with a dual inlet system or a multiport inlet system. A microvolume is connected via a separate capillary directly to port number 1 of the changeover valve (sample port). In addition to the multiport mode there are two modes to operate the microvolume:

- Freeze mode
- Direct Freeze mode

#### 5.3.1 Freeze Mode

In the Freeze mode the **computer decides** whether a sample has to be frozen or not in order to provide a sufficiently large pressure in front of the capillary. For an efficient utilization of this mode the instrument should be equipped with a multiport. Table 5 - 10 shows the process parameters for the Freeze mode.

**Table 5 - 10**
Printout of the process: Freeze

```
Method : CS/GB

>>> PROCESS <<<                          MODE: FREEZE

                    PUMP TEMPERATURE     [CEL] :  30
                    FOREVAC THRESHOLD   [µBAR] :  30
                    FOREVAC PUMP TIME    [SEC] :  10
                    HIGHVAC PUMP TIME    [SEC] :  60
                    FREEZE TEMPERATURE   [CEL] :-180
                    HEAT TEMPERATURE     [CEL] :  30
                    HEAT TIME            [SEC] :  20
                    EQUILIBRATION TIME 1[SEC] :  90
                    EQUILIBRATION TIME 2[SEC] : 180
                    EQUILIBRATION TIME 3[SEC] :  90
                    PMx THRESHOLD 1     [mBAR] : 0.5
                    PMx THRESHOLD 2     [mBAR] : 2.0
```

PUMP TEMPERATURE [CEL] — The temperature to which the microvolume is to be heated before evacuation starts.

FOREVAC THRESHOLD [µBAR] system — The pressure in µbar to which the forevacuum pressure has to be reduced before high vacuum pumping starts evacuation of the inlet or any section of it.

| | |
|---|---|
| FOREVACUUM PUMP TIME [SEC] | The period of time for forevacuum pumping after the pressure has reached the set parameter FOREVAC THRESHOLD. |
| HIGHVAC PUMP TIME [SEC] | The period of time for high vacuum pumping after the pressure as per parameter FOREVAC THRESHOLD is attained. |
| FREEZE TEMPERATURE [CEL] | The temperature to be applied to freeze the sample gas in the microvolume. |
| HEAT TEMPERATURE [CEL] | The temperature to which the microvolume is to be heated to release the frozen sample. |
| HEAT TIME [SEC] | The period of time to be applied for releasing the sample from the microvolume before measurement sequence begins. |
| EQUILIBRATION TIME 1, 2, 3 [SEC] | The period of time allowed for equilibration of a sample gas in the inlet system after the PMx parameters have been reached and before a pressure reduction or expansion starts. |

Three parameters for the thresholds for the pressure meter (in short PM) determine the details of different actions for the sample handling:

PMx THRESHOLD 1: If the pressure in the microvolume of the sample side is smaller than threshold 1 the whole sample will be frozen and after evaporation subsequently measured from the microvolume.

PMx THRESHOLD 2: With a pressure below this value, but above the pressure defined with a value for threshold 1, part of the sample is frozen into the microvolume and measured from there.

PMx THRESHOLD 3: If the pressure in the variable volume of the inlet system exceeds this value, no further action is performed. The sample will be measured directly via the inlet system capillary.

**NOTE:** The values stated are example values which were used for a multiport with a pressure meter in each bank. The values should always be verified by experiment.

### 5.3.2 Direct Freeze

In this mode the **operator decides** whether **to freeze** a sample or not. If you are working with very small sample amounts you should choose the direct freeze mode. Each sample will then be frozen. For accurate measurement of the $^{18}O/^{16}O$ ratio, it is necessary to minimize the residence time of the gas. Any trace of water absorbed on the surface might exchange its oxygen with $CO_2$ and thereby alter the isotopic information of the sample gas. The process parameters for this mode are given in Table 5 - 11.

No pressure threshold is provided, because it is assumed that the sample is so small that it has to be concentrated in the microvolume in any case. The transfer time in Table 5 - 11 is the time for freezing the sample into the microvolume.

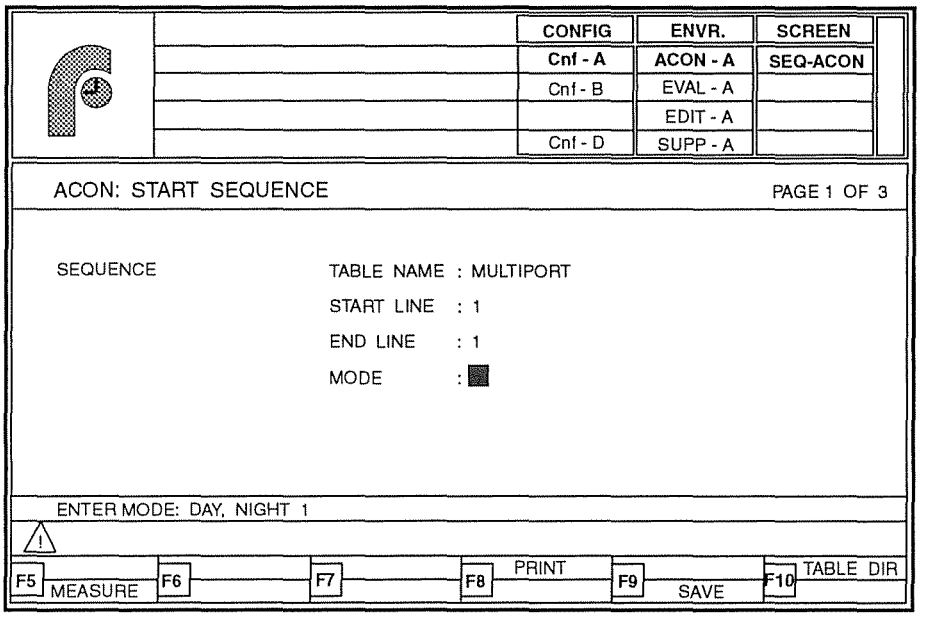
**Table 5 - 11**
Printout of the **process**: Direct Freeze

```
Method : CS/GB

>>> PROCESS <<<                          MODE : DIRECT FREEZE

                    PUMP TEMPERATURE     [CEL] :  30
                    FOREVAC THRESHOLD   [µBAR] :  30
                    FOREVAC PUMP TIME    [SEC] :  10
                    HIGHVAC PUMP TIME    [SEC] :  60
                    FREEZE TEMPERATURE   [CEL] :-180
                    TRANSFER TIME        [SEC] :  60
                    HEAT TEMPERATURE     [CEL] :  30
                    HEAT TIME            [SEC] :  20
```

The measurement is started from the ACON: MAIN MENU in the form of a sequence acquisition by activating submenu SEQUENCE ACQ. For editing the sequence table, please refer to the ISODAT Manual, chapter 3. 6, ACON Sequence Acquisition.

Three screen pages are available during acquisition. The first screen page gives information about the Process or sample handling (see Fig. 5 - 12). The second and third screen page are the Collection and Reduction screen also used in the single sample acquisition mode.

**Fig. 5 - 12**
Screen display of the sequence acquisition (page 1 of 3)

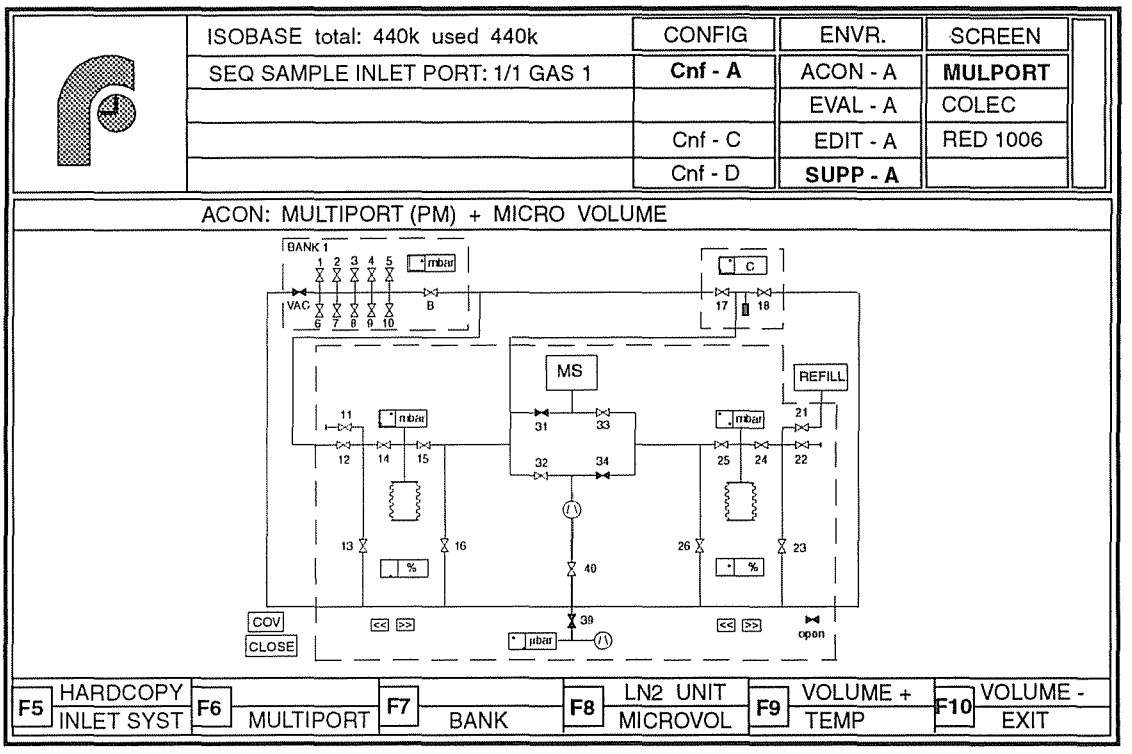


# 5 Measurements

## 5. 4 Multiport Inlet System

If the instrument is equipped with an optional multiport inlet system, the corresponding software is installed as well. The multiport system is connected to valve 10 (inlet port B1) of the instrument´s dual inlet system.

**Fig. 5 - 13**
Screen display of the Multiport control with pressure meter und microvolume (command MICROVOL activated)




### Measurement procedure

**step 1:** After loading the samples to the multiport, create the method(s) you want to use for the measurements using the method editor in the enviroment in which the multiport software is stored.

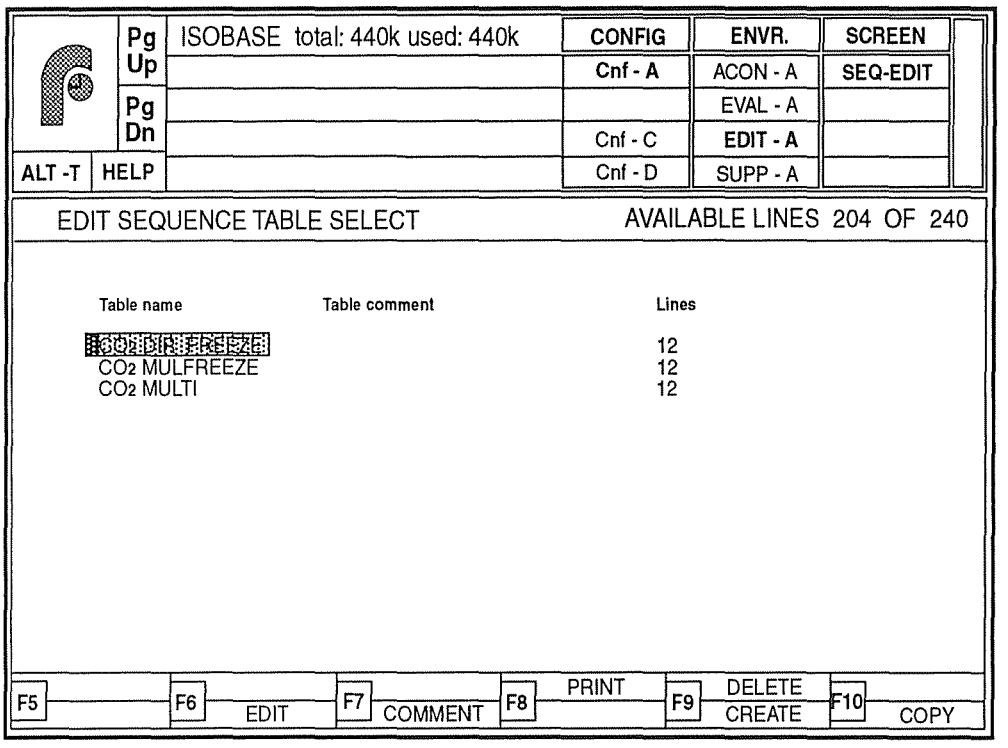
See also page 5 - 11 and following pages of this chapter.

When editing the **process** parameters for measurements with the multiport with tube crackers enter as parameter **YES**, only if you are sure a tube cracker is installed!

Otherwise your sample may be lost before the measurement is started, because the corresponding inlet port is automatically evacuated in preparation of the tube cracker operation.

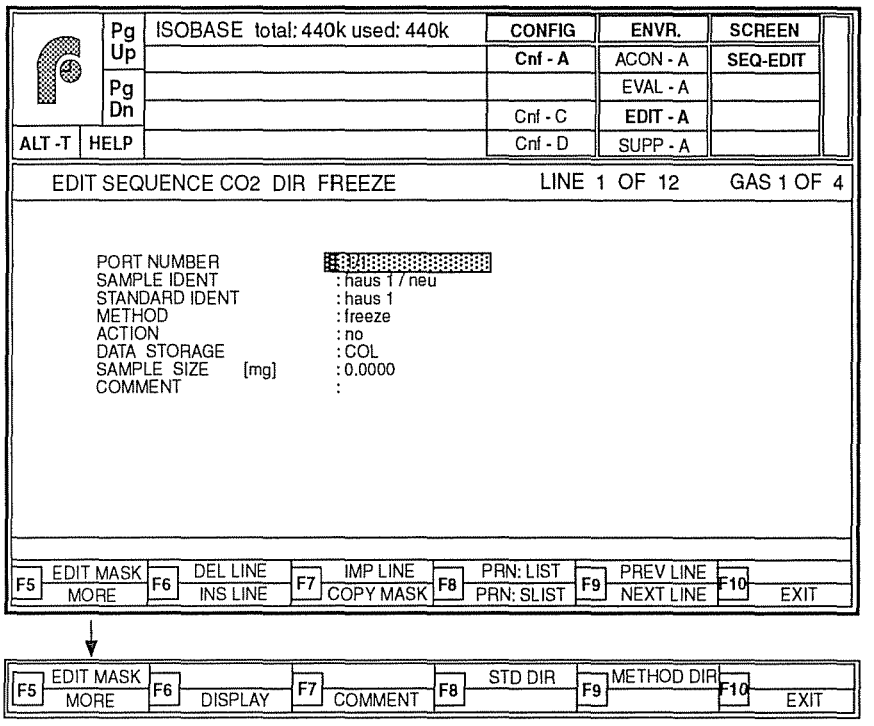
**step 2:** Next define a new sequence table or edit, an existing one for your analysis.

**Fig. 5 - 14**
Screen display of the Sequence Editor




Each sequence table may contain several sequence lines describing different methods of measurements. One single measurement method for a sample and/or standard gas is considered one sequence line. A total of 240 different lines may be used in the ISODAT system as a standard.

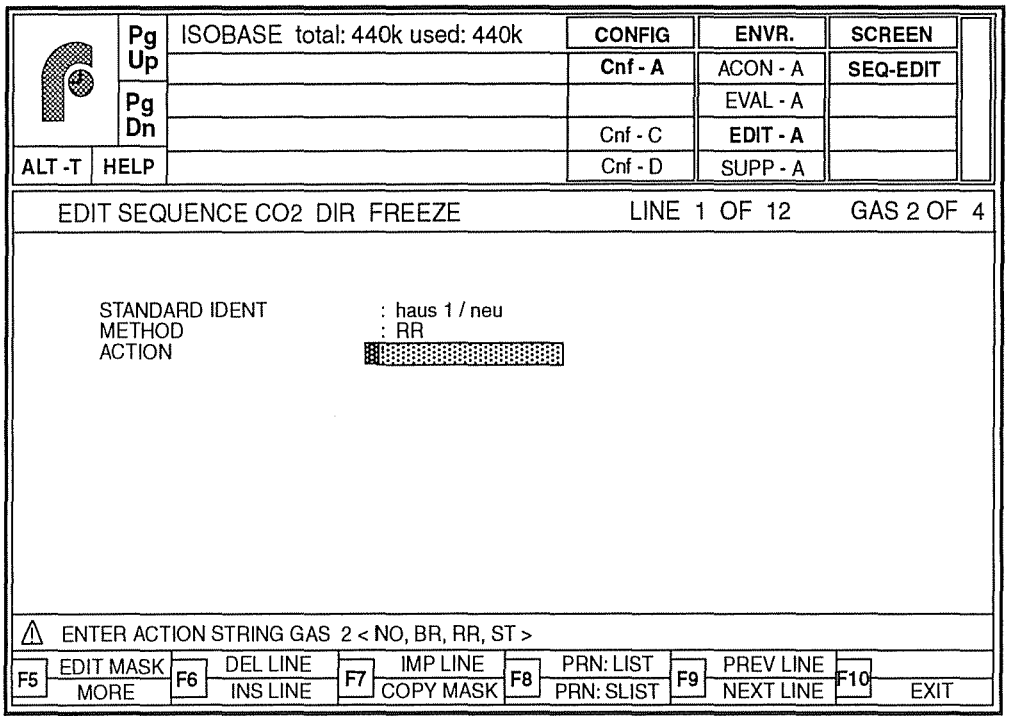
**Fig. 5 - 15**
Next editor page on screen is activated with command EDIT. The extended command line is called up with < F5 >.




With one sequence line ion beam triplets gases can be measured from one sample.

# 5 Measurements

**Fig. 5 - 16**
Screen display of the 2nd page




For each gas

the standard identity,
the method of measurement,
the action to be taken during measurement

is to be entered on separate pages of a sequence line.

The additional pages are accessible by using the <Page Down> and <Page Up> keys of the keyboard
or
by pointing with the mouse cursor and "clicking" the command fields **Pg Dn** and **Pg Up** in the upper left corner of the screen display.
For writing a sequence table, see ISODAT Manual, chapter 5.3, Edit Sequence Editor.
If the instrument is equipped with one of the standard refill options described in chapter 4.4 the respective parameter to be entered in the action line for refilling standard gas is, for instance,

**BR** = for Buffered Reference
**RR** = for Reference Refill.

For measurements with an instrument equipped with an equilibration unit the first sample can be declared as a standard. In such a case the action parameter to be entered for the first sequence line is

**ST** = for standard

If no standard refill equipment is used, the parameter to be entered is

**NO** = for no action

**step 3:** After creating a sequence table go back to ACON: MAIN MENU and start submenu SEQUENCE ACQ. Enter the correct start and stop line from your sequence. If you use the same line for start and stop, only one sample will be measured.

Start the measurement by pressing < F5 > or pointing and "clicking" with the mouse the command MEASURE. The ACON: MULTIPORT/S + MICRO VOLUME screen display will show up.

The acquisition is done automatically. Valves are opened and closed, pumping as well as gas admittance are performed automatically under computer control. In addition the valves may be opened and closed manually by using the keyboard or the mouse with the activated multiport screen display from the support enviromental.

## 5. 5 Measurement of $N_2$, $SO_2$ and HD:

### 5.5.1 $N_2$ Measurement

The measurement of $N_2$ is similar to that of $CO_2$ described in detail in chapter 5.1.1. For small samples, a dedicated microvolume or "cold finger" filled with an adsorbent is used to freeze nitrogen at liquid nitrogen temperature.

### 5.5.2 $SO_2$ Measurement

To measure $SO_2$ (masses 64 and 66) it is mandatory that the ion source head and the changeover valve are heated (70° C). Longer idle times (16 - 32 s) help to minimize cross contamination in the changeover valve and/or ion source. $SO_2$ may be analyzed in a sequence from a multiport inlet system. In this case, multiport and sample inlet system as well as a microvolume if available, must also be heated. Allow long periods of evacuation time to minimize memory effects in the inlet system.

### 5.5.3 HD Measurement

Measurements of HD may be performed with a dual inlet or a multiport system. In both cases prepare your HD measurement as follows:

**step 1:** Activate the ISODAT program INSTR. CONTROL via the ACON MAIN-MENU. When the ACON MASS SCALE is displayed on screen enter < Shift > < F10 > or point and "click" the command CUP CFG in the key definition line. Then select HD as the name of the gas. The software switches the cup configuration to the required collector cups and presents a specific key definition line.

**step 2:** For HD measurement focus the ion source such, that the $H_3^+$-factor is as small as possible. $H_3^+$ is produced in the ion source in an ion-molecule reaction and the amount of $H_3^+$ depends on pressure and temperature, $H_3^+$ interferes with the HD measurements and therefore has to be reduced to minimum. The production of $H_3^+$ is lowest at high lens potentials. The focusing of the ion source is done as described in chapter 2.3.4. After focusing, a calibration should be performed manually.

**step 3:** Enter < SHIFT F7 > or point and "click" the command CALIB HD in the key definition line to find the center of the peak. Using the direction keys scan along until the rising edge of the peak is found. Note the BDAC setting.
Continue scanning over the peak until the falling edge is found.
Note also this BDAC setting.
For example:

| BDAC | BDAC MEAN |
|---|---|
| 5123 | 5058 |
| 4993 | |

The mean value is stored as the BDAC reference value or center of the peak.
Fig. 5 - 17 shows the shape of an HD peak.
Thereafter exit the subroutine by entering < F10 > or pointing and "clicking" with the mouse the command < ALT > < T >.

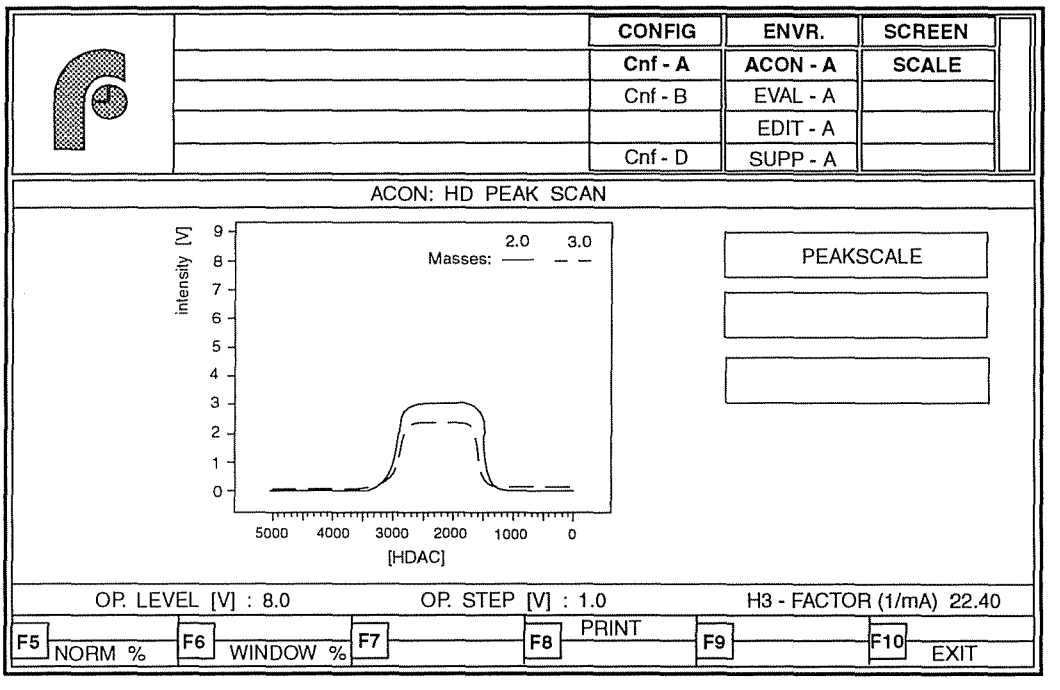


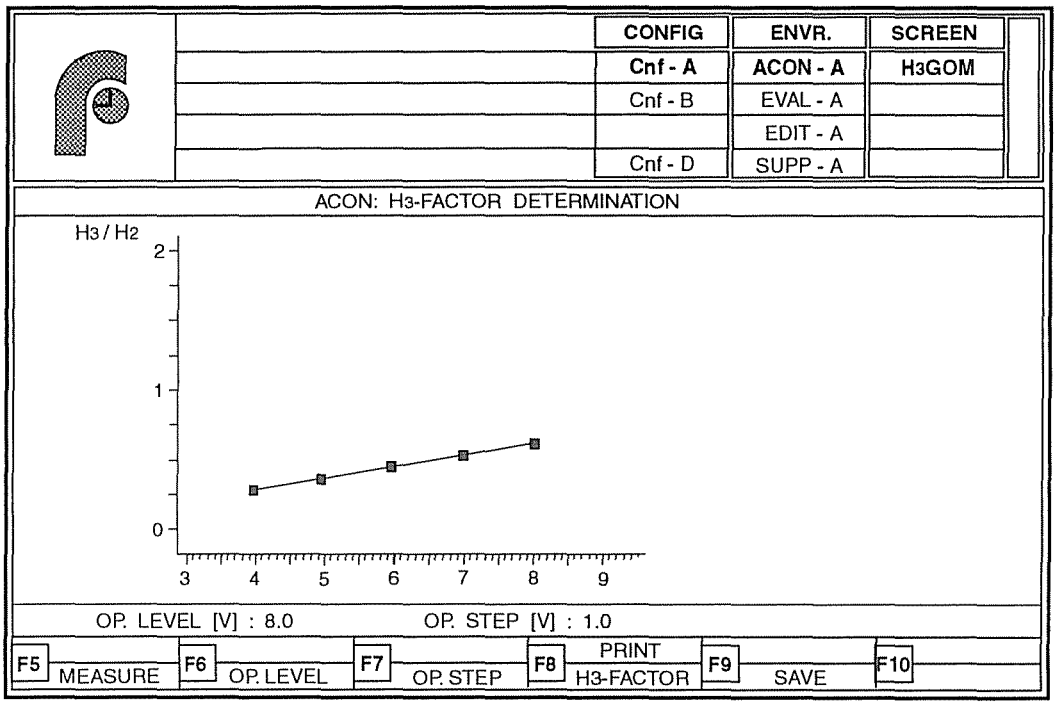

**Fig. 5 - 17**
Screen display of an HD peak shape

For more details, see the ISODAT manual, ACON INST. CONTROL, chapter 3.2, $H_2$ Instrument Control.

**step 4:** Before starting the HD measurement the factor of $H_3^+$ has to be determined, because the HD measurements have to be corrected for. The $H_3^+$-procedure is described in detail in the ISODAT Manual, chapter 3. 7, ACON: $H_3$-FACTOR.

**NOTE :** The $H_3^+$ function is not linear for low voltages (5 V and below).
Therefore start the measurement at a voltage of about 9 V.
The hydrogen sample is automatically set to five lower signal levels and the m3/m2 ($HD/H_2$) ratio is measured. (See Fig. 5 -18). The factor of $H_3^+$ is calculated for the range of signals measured and stored for future data reductions.
A typical value should be below 30. You may include the $H_3^+$ factor determination into the method of your measurement via the order string when editing a method. A determination of $H_3^+$ is then made with each acquisition.

**Fig. 5 - 18**
Screen display of an $H_3$ - Factor determination




If you are using a multiport you will have to create a sequence table (see ISODAT Manual, chapter 5.3, Edit Sequence Editor).

After the preparations are done, start your measurement from the ACON: MAIN MENU by activating the submenu SEQUENCE ACQUISITION.

Enter the correct parameters i.e.

the gas name: HD

the standard name: $H_2$

the cup configuration: HD

# Technical Advice

## 6. 1 Checking Performance Data

Finnigan MAT has developed several instrument test routines for checking the performance data of the ***DELTA$^{plus}$*** mass spetrometer.
For the user´s convenience, a test program containing these routines is included in the supplied version of the ISODAT software. It is to be noted that the operation of some of these test routines may require some technical knowledge of the instrument´s internals. Also, the successful execution of some of these tests is contingent upon instrument preconditions.

When running the test routines a highly sensitive focusing of your instrument will result in the best specifications results. (See chapter 2.3.4, How to Focus the Ion Source).

The program **INSTR. CHECK** contains the following routines to test:

1. **Amplifiers and VFCs**
2. **Resolution**
3. **Pressure Ratio**
4. **System Stability**
5. **Signal Stability**
6. **Relative Sensitivity**
7. **Peak Flatness**
8. **Abundance Sensitivity**
9. **Absolute Sensitivity**
10. **Ratio Linearity**

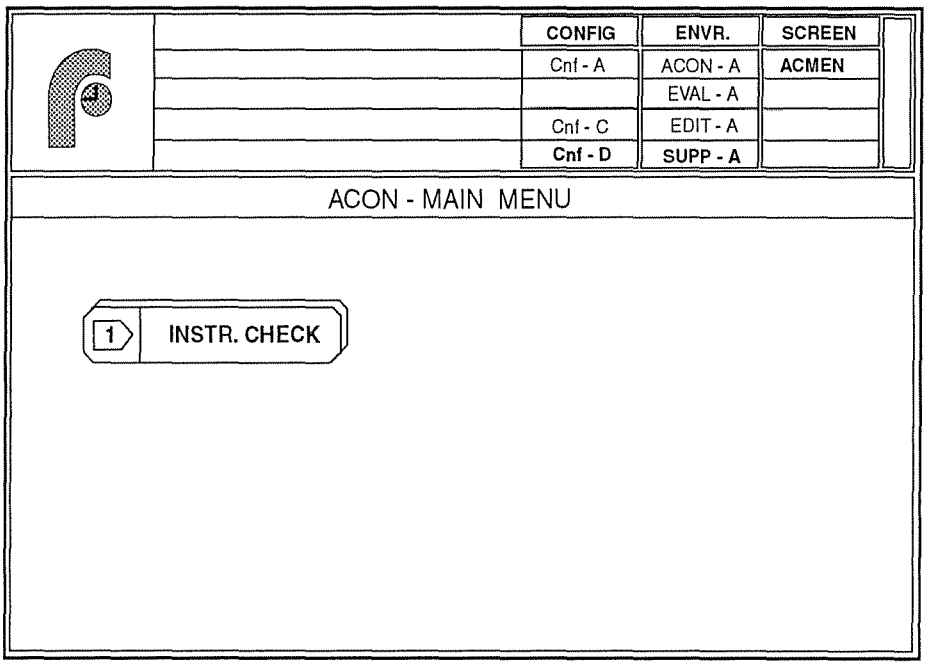
**Note: The reference gas for all performance data is $CO_2$**

Make sure before starting the test program to have properly filled $CO_2$ reservoirs attached to the inlet system.

The test program is normally installed in the ACON environment of the configuration D (**Cnf. - D**, **SUPP - D**).

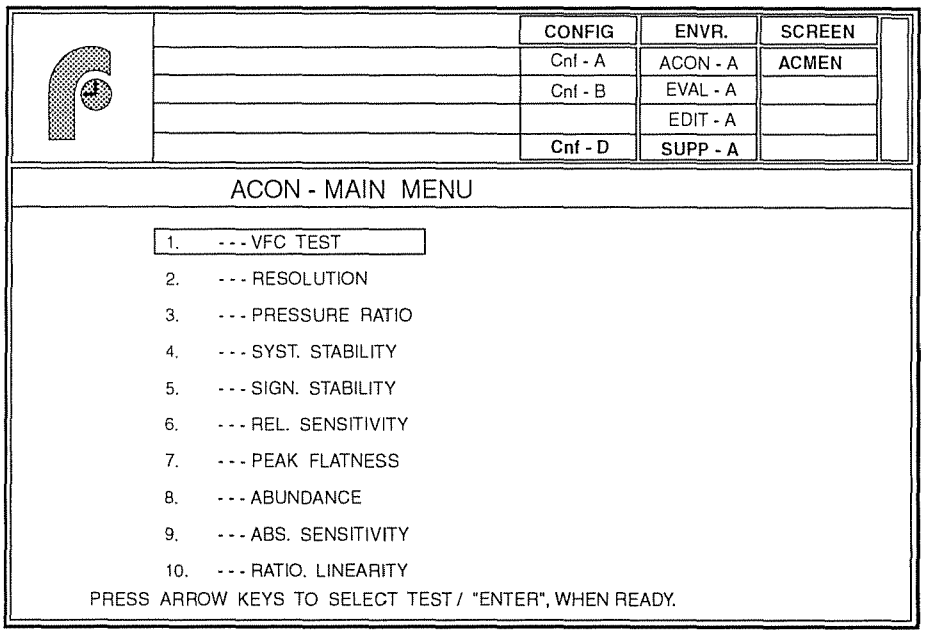
# 6 Technical Advice

**Fig. 6 - 1**
To start the test program activate the ACON Main Menu first.




To start the program **INSTR. CHECK**, activate the ACON - Main Menu and enter either the number of the access key box or place the mouse cursor onto the program name and press the left mouse button. The menu of the program will be displayed and the test routine to be used then has to be selected with the cursor direction keys and activated by pressing <ENTER>.

**Fig. 6 - 2**
Menu of the test program instrument check



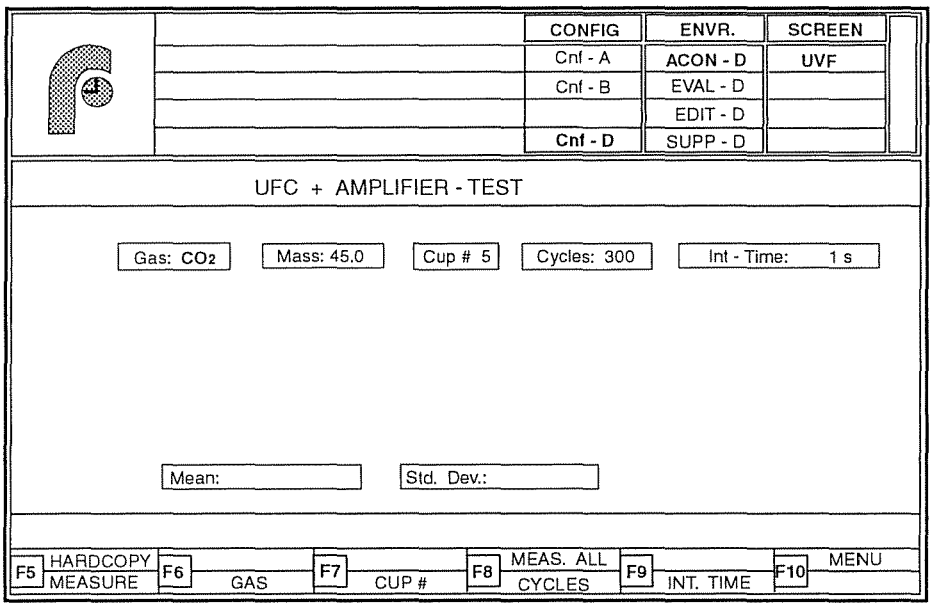
**Note:** The screen display of all test routines shows a key definition line for different subroutines at the bottom. These subroutines are activated by pressing the related function key or by pointing the command with the mouse cursor and "clicking", i.e. pressing the left mouse button.

### 6.1.1 Amplifier and VFC Test

This test routine checks the instrument´s ion detection performance with no ions present. Therefore **switch off the ion source before** starting a test measurement.

**Fig. 6 - 3**

Screen display of the Amplifier and VFC Test.




The amplifier´s baseline must be determined without an interfering signal. The counts per measuring channel are measured for a defined number of cycles and each channel can be tested individually.

The counts for each channel should be at least 200 (absolute value is not important).

**Note:** 200 counts correspond to a signal of 0.1 V.

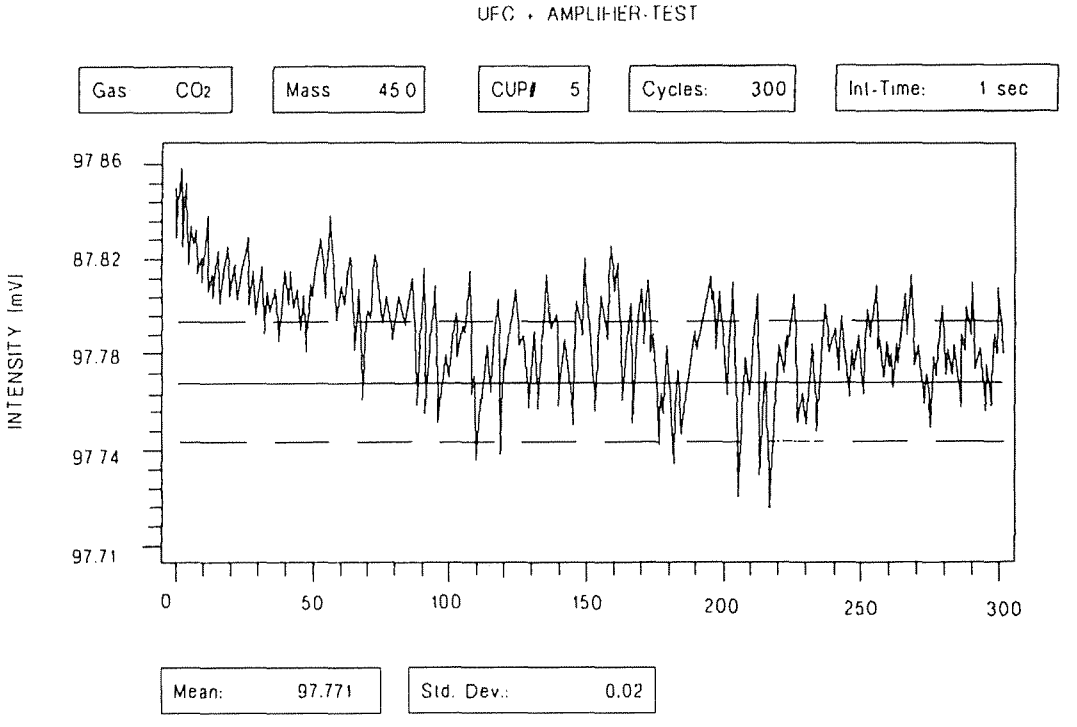
Mean value and standard deviation are calculated from the count of cycles and displayed on screen. For your information, see Fig. 6 - 4 on the following page showing a copy of an example printout.

# 6 Technical Advice

SPECIFIC COMMANDS:

| | |
|---|---|
| OLD BOUND: | brings back the screen display of measurements |
| ZOOM: | enlarges or reduces the scale of graphs |
| MEAS ALL: | all cups are measured for the reference gas. The mean values as well as standard deviations are calculated and automatically printed (provided the printer connected was switched on). |

**Fig. 6 - 4**
Sample printout of a performed Amplifier and VFC Test



### 6.1.2 Resolution

The resolution is determined according to the 10% valley definition. You may enter the start mass and end mass for the magnetic field scan. When $CO_2$ is used for the test, the mass ranges from about 43 to 45.5. The BDAC values referring to masses 44 and 45 are determined and the resolution is calculated via the relation:

$$\frac{\text{Peak Distance}}{\text{Peak Width} \cdot 44} = \text{Resolution}$$

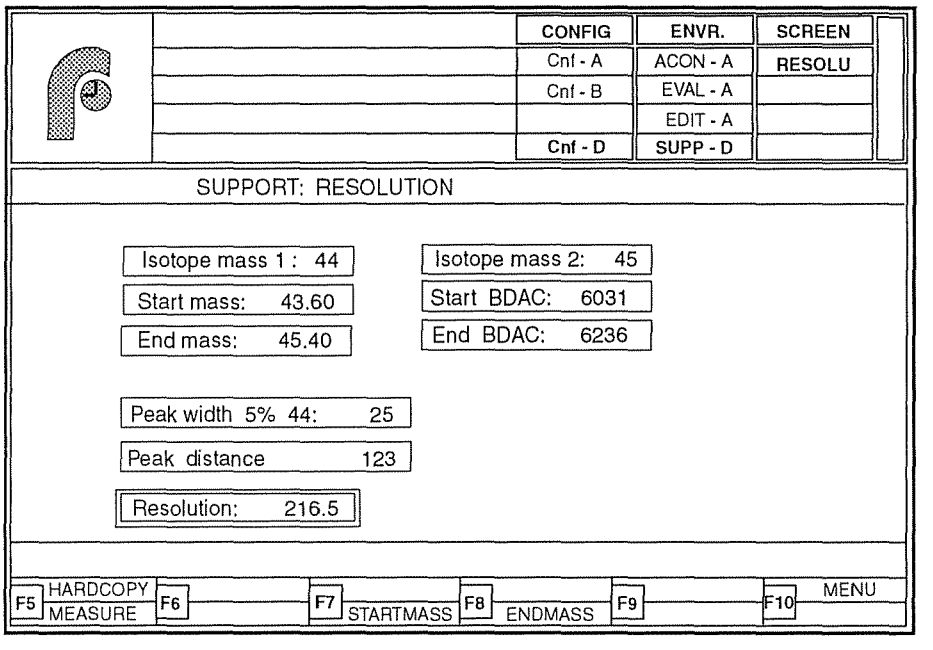
Peak Distance: the distance between two neighboring peaks

Peak Width: width of mass 44 peak, measured at 5% of its height. The resolution should be about

$$\frac{M}{\Delta M} = 95 \text{ (10\% valley)}$$

**Fig. 6 - 5**

Screen display of the Resolution Test

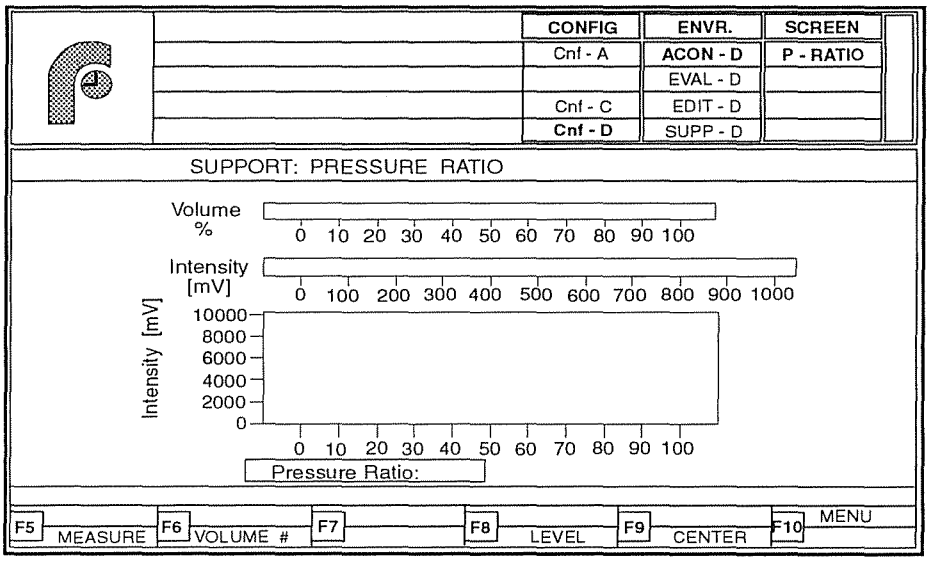


### 6.1.3 Pressure Ratio

This test routine determines the dynamic range of the variable volumes VOl 1 and VOl 2. The peak intensity for mass 44 is measured starting with the maximum volume (100%) down to the minimum (0%). A level (i.e. 200 mV) sets the starting point for the measurement. The signal for the variable volume expanded to the maximum should be at this level. If this is not true, the inlet system is expanded and pumped automatically until the reference level is reached.
See also chapter 5.1 Measurement, step 5)

**Fig. 6 - 6**

Screen display of the Pressure Ratio Test




From the measurement the pressure ratio is calculated and displayed on the monitor.

For your information, see also Fig. 6 - 7 on the next page showing a copy of an example printout.

The pressure ratios should be about the same for both variable volumes and should read at least 1 : 10 or higher.

SPECIFIC COMMANDS

V - SCALE: shows the graph of intensity versus volume.

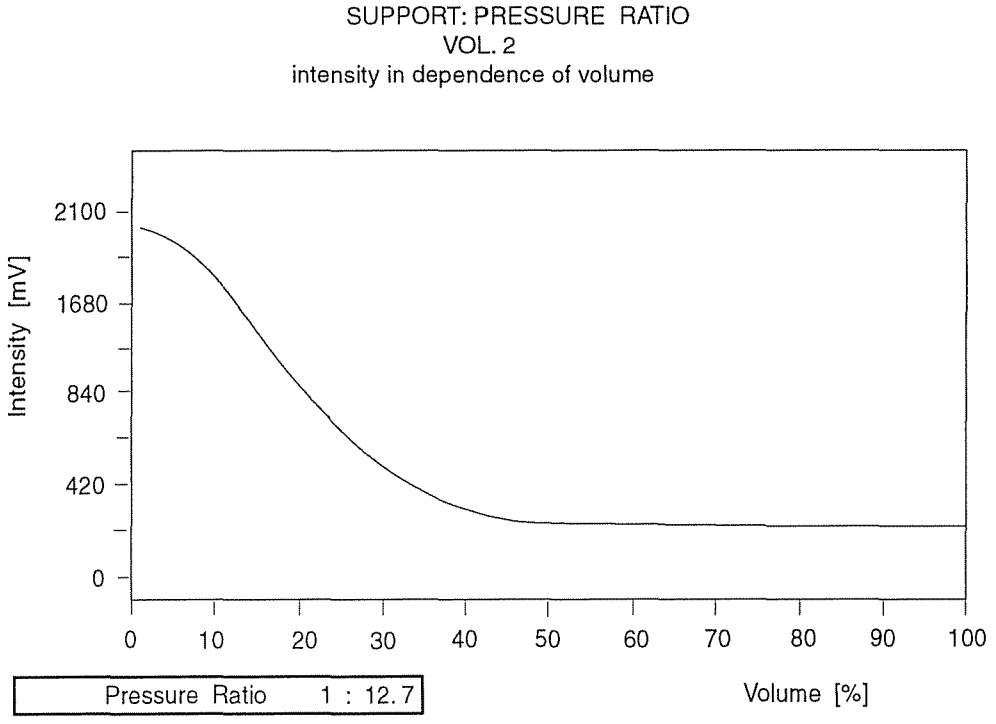
P - SCALE: shows the graph of intensity versus pressure.

BOUNDARY: with this command you may change the scales of the measured values.

LOWER BOUNDARY: sets the starting point of the new scale

UPPER BOUNDARY: sets the end of the new scale

**Fig. 6 - 7** Sample printout of a performed Pressure Ratio Test.

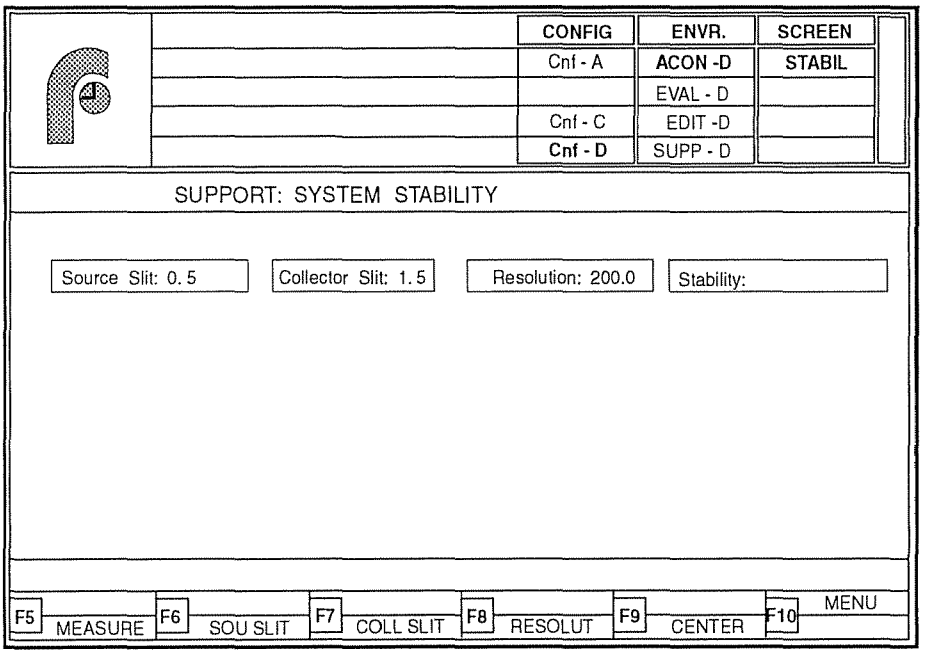



### 6.1.4 System Stability

In this test routine a peak centering for mass 44 is performed and the peaks flanks are determined. High voltage fluctuation of the peak flank is measured for a period of 15 minutes and thereafter a second peak centering routine is performed. The fluctuation is measured at the peak flank, because changes in high voltage or the magnetic field strength have a much higher impact on the peak intensity at the flank than on the top. A good system stability is 5 x $10^{-4}$ measured for a period of 15 minutes.

**Fig. 6 - 8**

Screen display of the System Stability Test

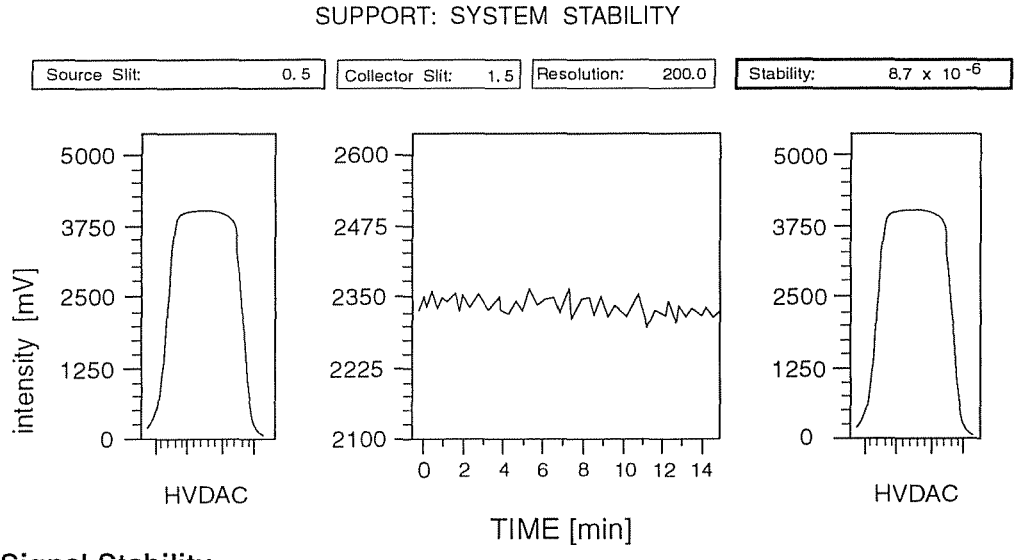


# 6 Technical Advice

For special collector system, source and collector slit width may be entered into the testing program.
For your information, see also Fig. 6 - 7 on the next page showing a copy of an example printout.

SPECIFIC COMMAND:
CHANGE: This command changes the active windows of the screen display. Red framed graphics are active, black framed are inactive, e.g. you may use the ZOOM function for the red framed graphic.

**Fig. 6 - 9**
Sample printout of a performed System Stability Test.




### 6.1.5 Signal Stability

This routine tests the signal stability. It is similar to that of testing the system stability. The difference is that the stability of the signal is measured at the peak center for a period of 5 minutes. (see Fig. 6 - 11)
The value for signal stability should be about 2 x $10^{-4}$ for 5 minutes. Instabilities of the emission may cause an instable signal although a stable high voltage and magnet field are given. Another source of error may be pressure fluctuactions (check the oil of the forevacuum pumps!) or temperature fluctuactions in particular at the crimps.

**Fig. 6 - 10**

Screen display of the Signal Stability Test.

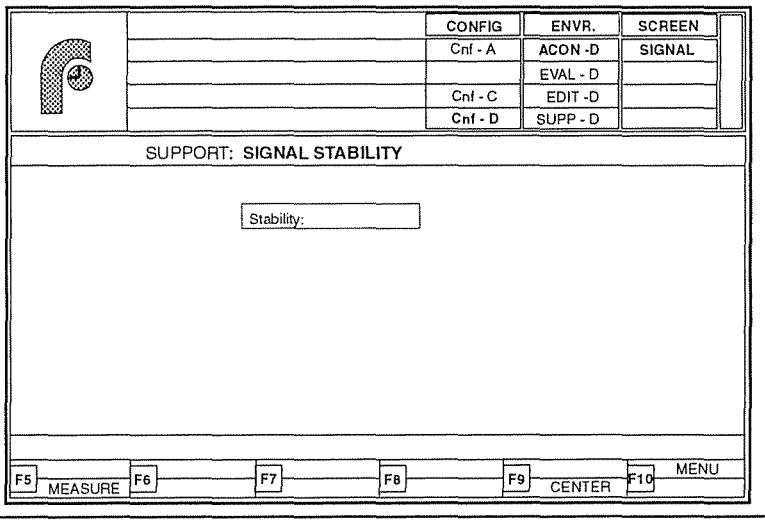
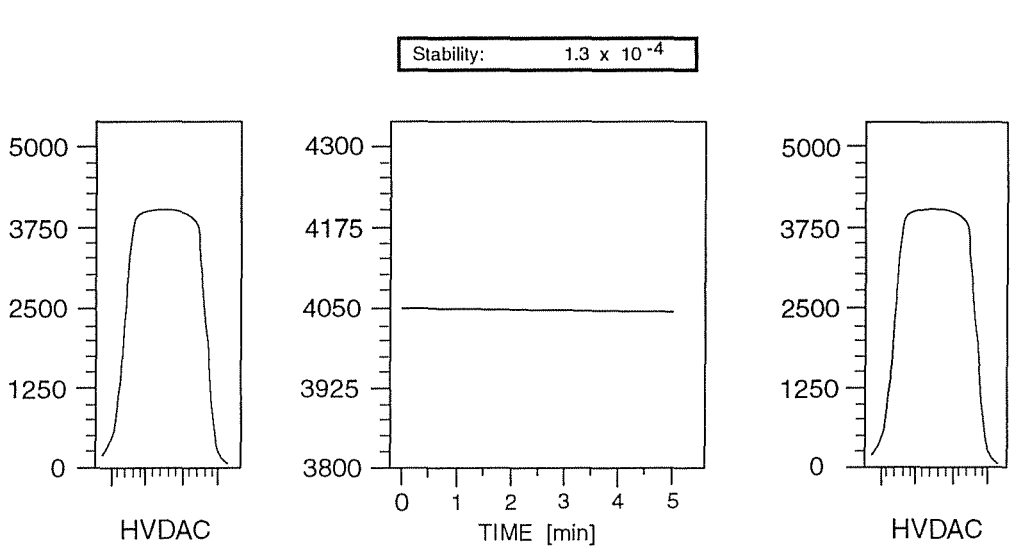


**Fig. 6 - 11** Sample printout of a performed Signal Stability Test.




### 6.1.6 Relative Sensitivity

**NOTE:** While measuring the pressure difference there is no screen activity, you will only hear the opening and closing of the valves. Be patient. After a while the first calculated value will show up.

The relative sensitivity $\frac{A}{mbar}$ is obtained via the relation

$$\frac{U}{R \cdot p \cdot 0.69} = \frac{A}{mbar}$$

U = Voltage measured at the amplifier of the collector cup mnumber 3 (mass 44)

R = Resistor value ($3.0 \cdot 10^8\ \Omega$)

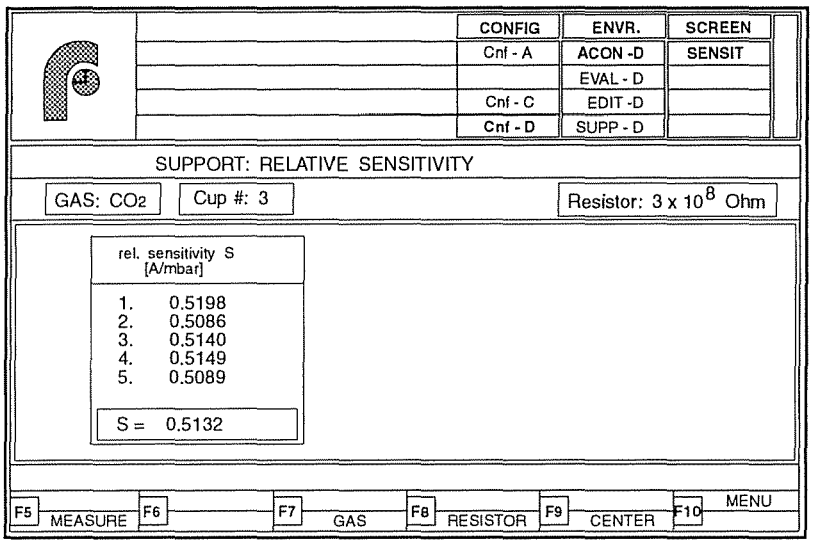
This value is the same with $CO_2$ and $N_2$ as a reference gas, it needs to be changed in special cases, only.

p = Difference between the measured pressure with and without gas. The pressures can be read off the multimeter of the vacuum gauge control unit.

0.69 Correction factor for $CO_2$. This factor is due to the ionizing probability of $CO_2$ versus $N_2$. The ion gauges are calibrated for $N_2$.

**Fig. 6 - 12**

Screen display showing data of the Relative Sensitivity Test



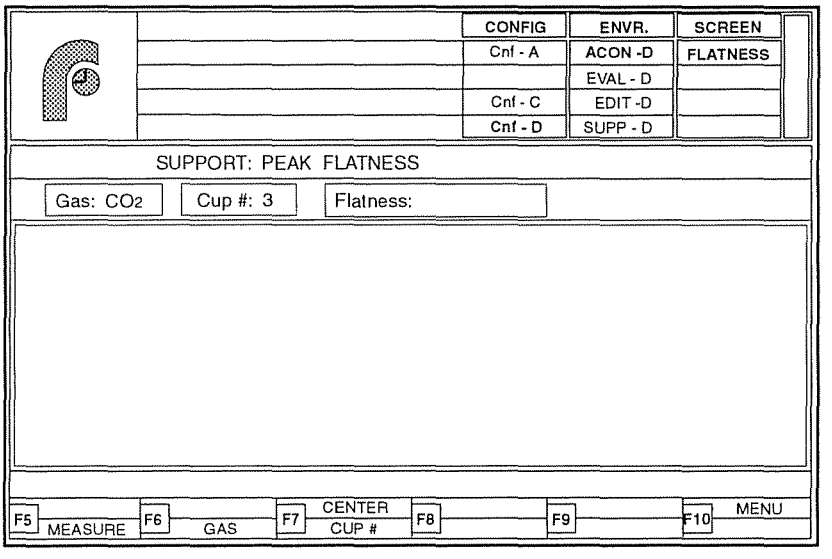

After a cycle of five measurements and calculation of the relative sensitivity a mean value is displayed on the screen. This value should be about 0.2 A / mbar for a standard system and 0.5 A / mbar for a differentially pumped system. The values depend on the pumping capacity of the turbomolecular pumps.

**NOTE:** The relative sensitivity gives only a comparable figure, when pumping speed, conductance, location of the ion gauge, etc. Are identical. To compare different types of instruments it is therefore useless. Please keep in mind that for a ***DELTA***$^{plus}$ there are also two different values for relative sensitivity depending on whether the instrument is equipped with or without a differential pumping system. The difference is due to different pressure readinds at the same flow. But the **absolute** sensitivity (molecules / ion) is the same.

### 6.1.7 Peak Flatness

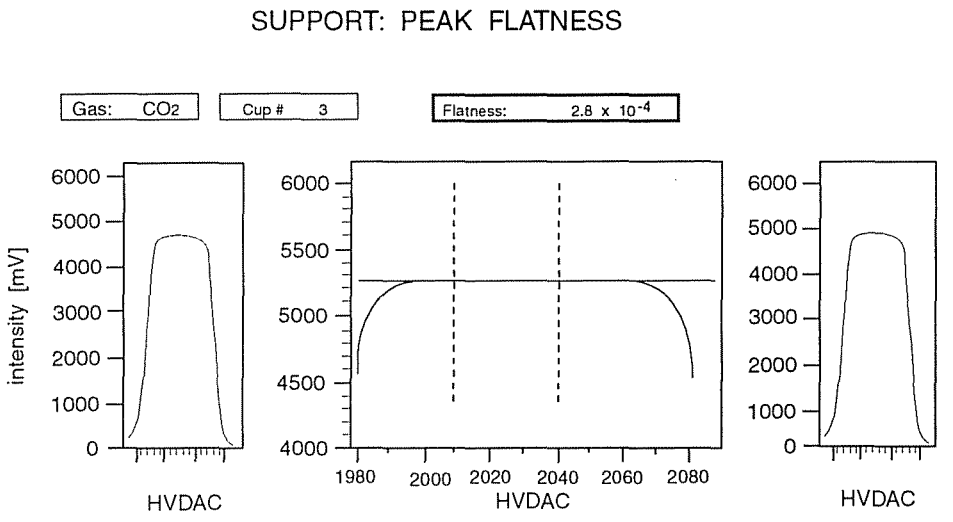
The program determines the peak top flatness for different gases and collector cups. An energy correction is necessary in order to eliminate the effects of a descending peak plateau with increasing voltage.

**Fig. 6 - 13**
Screen display of the Peak Flatness Test.



Three peak routines are provided in order to obtain the signal correction. The loss of high voltage sensitivity and sample loss is determined. Peak top flatness should be in the range of about $1 \cdot 10^{-3}$ for a 5 V signal on mass 44 (ion current $1.5 \cdot 10^{-8}$ A). For less intensive ion currents the peak top flatness will be worse.

**Fig. 6 - 14** Sample printout of a performed Peak Flatness Test.

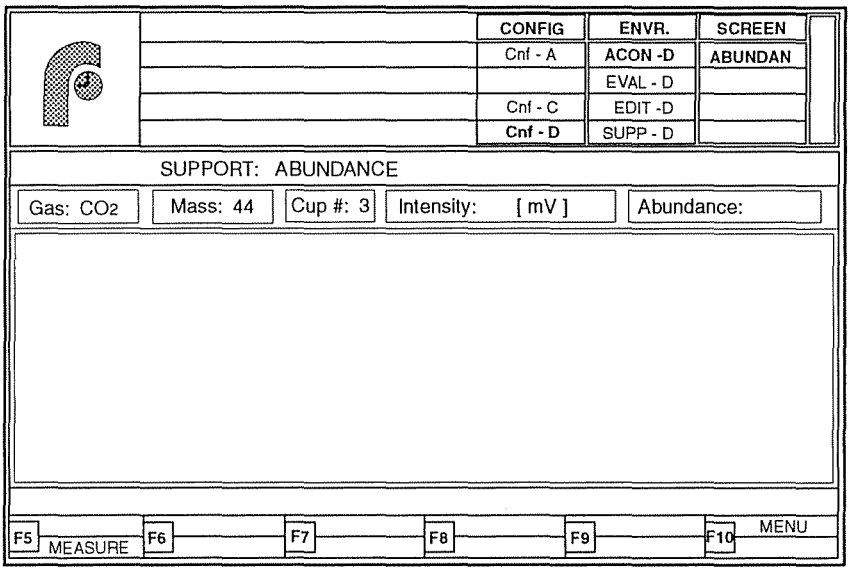



### 6.1.8 Abundance Sensitivity

The abundance sensitivity gives quantitative information on the relative amount of the contribution of one mass intensity (e.g. 44) to the intensity of the neiboring peak (e.g. 45). This contribution should be less than $2 \times 10^{-6}$ (see also fig. 6 - 16).

**Fig. 6 - 15**

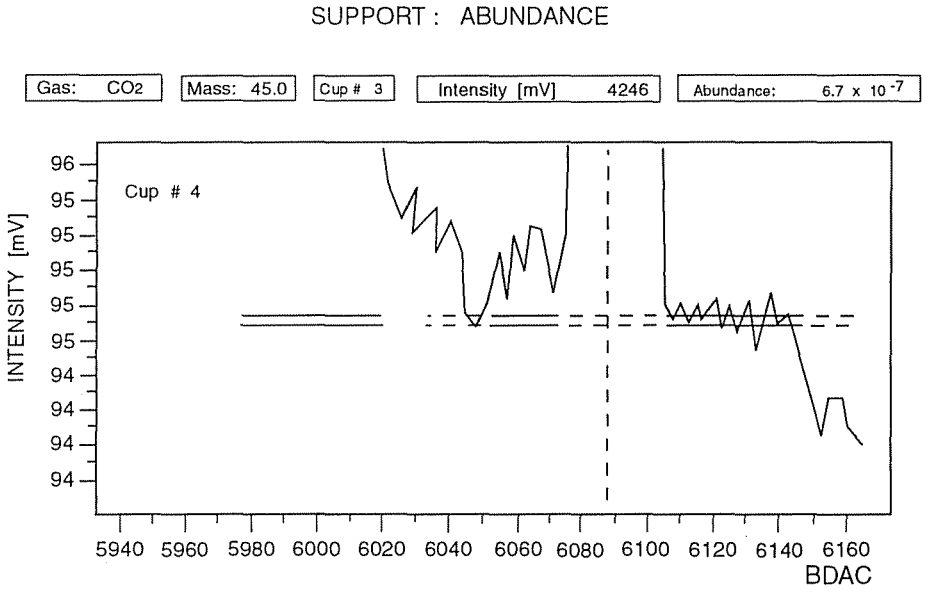
Screen display of the Abundance Sensitivity Test.



The determination is performed as follows:
First the signal intensity (mass 44) is determined (in mV) in the appropriate collector cup (cup number 3).
Then the magnetic field is scanned from mass 44 to 45 and the intensities are measured in, the next collector cup (cup number 4) with its bigger resistor value. This is required in order to keep the signal in the detection range.

The Abundance Sensitivity is calculated via the relation: $\frac{\delta}{\text{intensity of peak 44}} = \text{mV}.$

**Fig. 6 - 16** Sample printout of a performed Abundance Sensitivity Test.

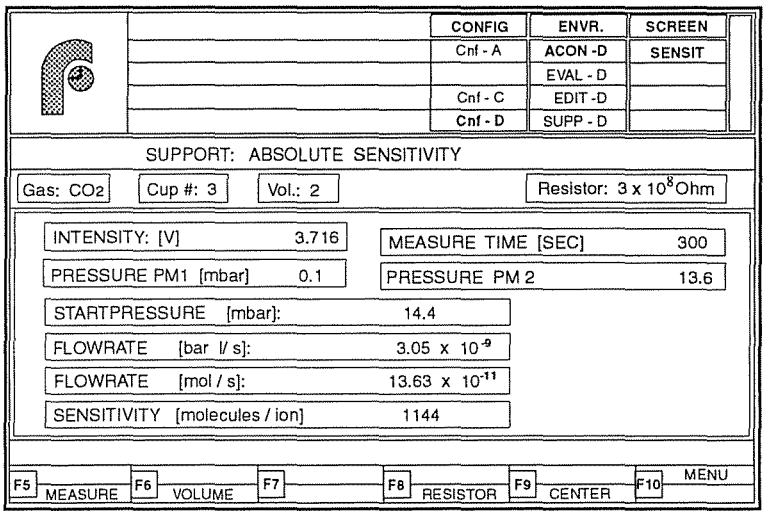



### 6.1.9 Absolute Sensitivity

A defined volume is used to determine the ion current as a function of the loss of sample and, as a result, the number of molecules needed to collect one ion of mass 44 in the collector cup.

**Fig. 6 - 17**

Screen display of the Absolute Sensitivity Test



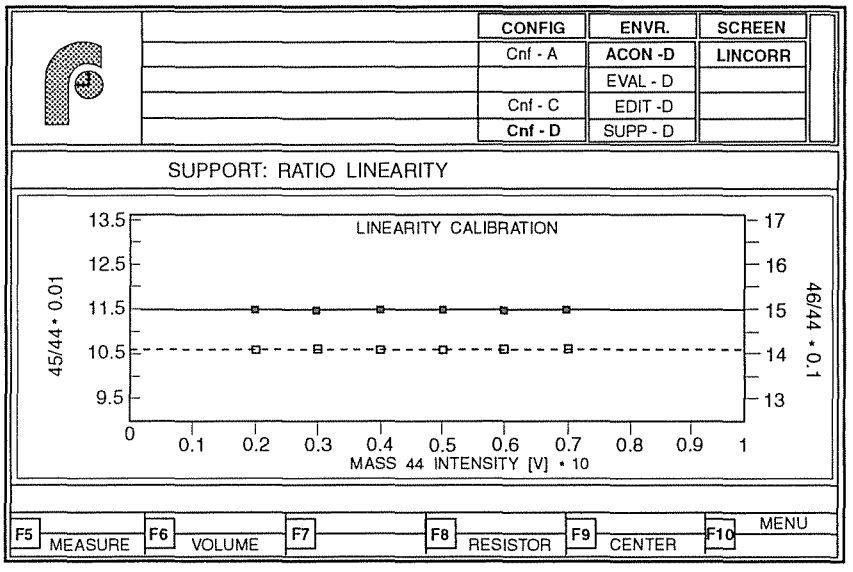
The defined volume is a volume of 250µl between valve 25 of the inlet system and the inlet capillary. The measurement starts with a pressure and intensity determination, then the volume is reduced to the defined volume by closing valve 25 of the inlet system. The system is in a waiting position until the start pressure and intensity are reached (system message: "waiting for start level"). Then the ion current is measured for the preset time. The absolute sensitivity should be about 5000 molecules $CO_2$ per mass 44 at the collector cup.

### 6.1.10 Linearity Ratio (Linearity Calibration)

With this test routine over a range of varying signals the signal linearity can be checked versus the beam intensity. The signal intensity is measured and the isotope ratios (i.e. mass 46/44) versus the beam intensity are either displayed as a graph or listed.
To start a test, enter <F5> or point with the mouse cursor the command MEASURE in the key definition line and "click". Then set the first signal as per requirement by adjusting the variable volume. Repeat procedure for further signals to be set.

**Fig. 6 - 18**

Screen display of the Linearity Calibration Test




SPECIFIC COMMANDS:

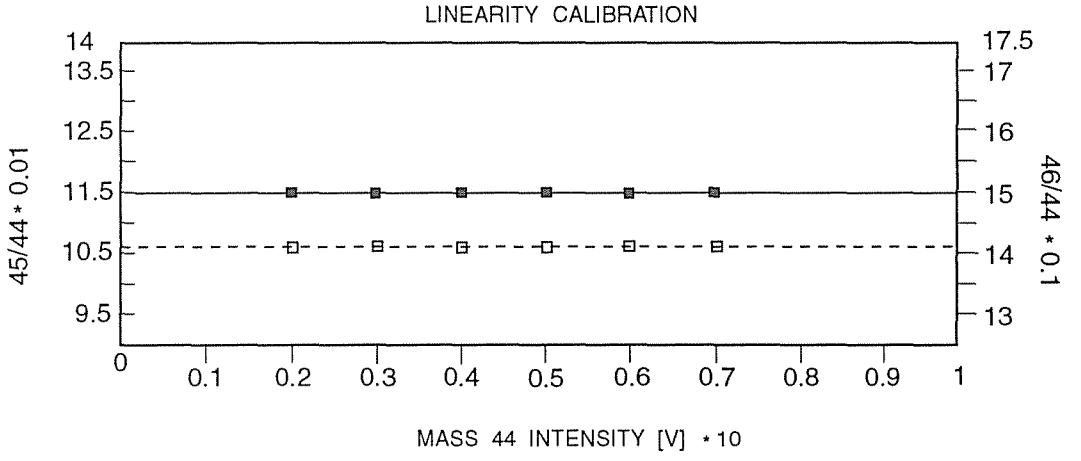
| | |
|---|---|
| SET PAR | allows the adjustment of the parameters limiting the measurement range of the signal intensities. |
| CALC | shows the graph of the ratios. |
| EDIT | enables you to edit the measured values either for the ratio or the δ - display |
| BASELINE | takes a baseline measurement. The measurement is to be performed with the changeover valves closed. |

**Table 6 - 1**
Listing of signals taken during the linearity calibration and the evaluation.

| | 44 [V] | 45/44 | 46/44 | 45 [%O] | 46 [%O] |
|---|---|---|---|---|---|
| 1: | 1.90620 | 1.14919 | 1.40855 | 0.00000 | 0.00000 |
| 2: | 2.98267 | 1.14921 | 1.40871 | 0.01843 | 0.10979 |
| 3: | 4.05237 | 1.14920 | 1.40869 | 0.00924 | 0.09799 |
| 4: | 4.96302 | 1.14918 | 1.40880 | - 0.00928 | 0.17717 |
| 5: | 6.01696 | 1.14906 | 1.40868 | - 0.11492 | 0.08879 |
| 6: | 6.98864 | 1.14907 | 1.40864 | - 0.10378 | 0.05783 |
| SLOPE : | | -0.00003 | 0.00001 | -0.02631 | 0.00882 |
| INTERC : | | 1.14929 | 1.40862 | 0.08463 | 0.04904 |
| SYSTEM BASELINE 44 : | | | 0.09863 | | |
| SYSTEM BASELINE 45 : | | | 0.09838 | | |
| SYSTEM BASELINE 46 : | | | 0.09898 | | |

**Fig. 6 - 19**

Printout of the Linearity Calibration graph



## 6.2 Conversion to Other Gases

Depending on the number of collector cups installed it may be necessary to exchange the feedback resistor of an amplifier, when intending to analyze different gases. An example of a collector assignment with six cups is given below:

**Table 6 - 2**
Example of an assignment of a collector with 6 cups.

| measuring channel | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| VF - converter | 1 | 2 | 3 | 4 | 5 | 6 |
| element / mass: | | | | | | |
| $N_2$ | 28 | 29 | 30 | | | |
| $CO_2$ | | | | 44 | 45 | 46 |
| $SO_2$ | | | 64 | 66 | | |

With this combination there is no need to change the feedback resistors when changing from $CO_2$ analysis to $N_2$ analysis. The switching is done automatically by the ISODAT software by changing the cup configuration. Only in case of switching to $SO_2$ analysis it is necessary to exchange the resistors for mass 64 and 66.

### 6. 3 Heating Inlet Capillaries

In case a contamination of the instrument is detected, also the inlet capillaries should be heated. With the instrument a transformer (90VA / 220V/ 7, 7 V/ 12 A) is supplied for heating purpose. To heat all capillaries simultaneously it is advisable to acquire additional heating transformers.

**step 1:** Before heating the capillary the surrounding of the capillary has to be heated first to approximately 80° C for about 30 to 60 minutes, i.e.

the valves of the inlet system,
(incl, the valves of a multiport, if in use)
the changeover valve
and the ion source and analyzer housing.

During the heating periode all valves have to be open.
Swagelok connectors should be heated separately for a short while with a flame.

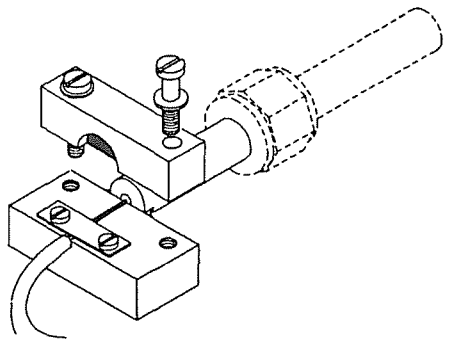
**step 2:** Plug 2 cables parallel to one socket of the transformer and clip on the ends with the alligator clips to each end of the capillary to be heated or to the related Swagelok connector.
Plug the third cable to the second socket and connect the clip to the middle of the capillary.
If the capillary is rubber silicon protected cut off the insulation with a sharp knife to the width of an alligator clip. Wrap the capillary with a strip of thin copper plate or similar material to improve the electrical contact between the clip and the capillary.
Capillaries recently supplied by Finnigan MAT have a metal sleeve attached in the middle for a better electrical contact.

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

**step 3:** Now connect the transformer to the mains and switch it on. The heating phase should be controlled by monitoring the signal intensity of the mass $^{18}O$ (measured on the channel for mass 45) by activating INSTR. CONTROL / ACON MASS SCALE and/or by using the chart recorder. Switch the chart recorder to the lowest speed of paper transport when utilising it.
It is recommended to heat also the crimped part of the capillary with a flame separately for a few minutes.

**NOTE:** Before removing the upper crimp block mark the parts of the crimping device to avoid a mismatch when reassembling.

**Fig. 6 - 20** Crimping device at the end piece of a capillary



**step 4:** When fitting again the crimp block, make sure that the capillary is exactly placed in the grove of the base and the die of the upper block in the crimp of the capillary. After heating the capillary, the flow resistance of the crimp has to be checked and reset if required to 1 Volt per 10 mbar (see also next page, Replacing an Inlet Capillary). During the start phase of the heating the signal intensity is increasing but will later decrease and stabilize. The best results of decontaminating capillaries are achieved by heating for approx. 6 to 8 hours. With a stabilized signal intensity lower than the first signal a successful decontamination can be assumed.
With a zero-measurement, i.e. measuring the same gas on sample and standard side, the result can be checked.

### 6. 4 Replacing an Inlet Capillary

Replacement of an inlet capillary may become necessary in case of contamination or mechanical damage. After replacement the flowrate of the new capillary has to be set by crimping. The crimping device consists of two metal blocks. The base is attached to the end piece of the new capillary which is to be fitted to the changeover valve. The second block, to be boltet on top of the base block, holds a metal pin in a spacing which will squeeze the capillary when bolting the two blocks together.

To replace a capillary proceed as follows:

**NOTE:** Make sure that all valves are closed before venting the surrounding area of the capillary which is to be exchanged.

**step 1:** Vent the parts of the inlet system and changeover valve which are connected by the capillary.

**step 2:** Loosen the Swagelok fittings holding both end pieces of the capillary to be exchanged. New capillaries are delivered with close ends. Use a diamond file to cut a capillary end at opposite sides before breaking off the tip, then smoothen the capillary´s end.

**step 3:** Fasten the end pieces of the new capillary with the Swagelok connectors. The end piece with the crimp block is to be connected to the changeover valve. Fasten the upper crimp block loosely onto the base with the capillary.

**step 4:** Pump out the inlet system.

**step 5:** Admit a proper amount of $CO_2$ into the inlet system, so that the storage reservoir pressure is about 20 mbar on both sides of the capillary.

**step 6:** Activate the ISODAT routine INSTR. CONTROL.(Cnf-A, ACON-A) MASS SCALE select the mass 44.

**step 7:** Now tighten the screws of the crimp block carefully and squeeze the capillary until the output signal reaches 1 Volt per 10 mbar pressure with $CO_2$ used for measurement.

**step 8:** After crimping the capillary has to be heated (see also chapter 6.3)

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