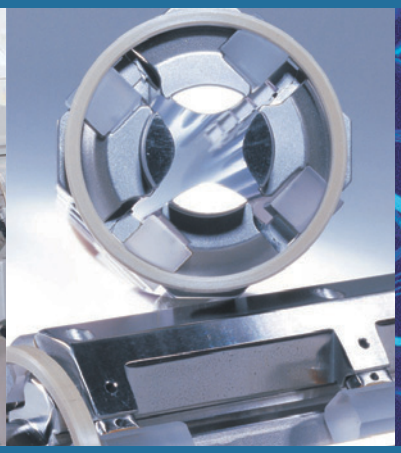
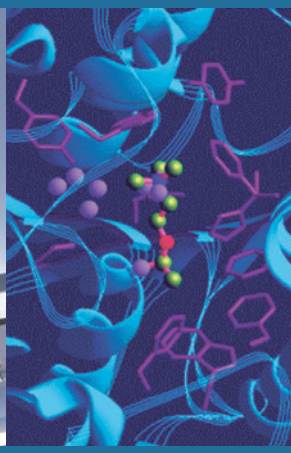
Thermo Fisher Scientific

FlashEA for IRMS
Operating Manual

Revision B - 1158550

Thermo SCIENTIFIC

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Read This First

Welcome to the Thermo Scientific, FlashEA for IRMS!

About This Guide

This FlashEA for IRMS Operating Manual describes how to setup and and use the FlashEA for IRMS.

Who Uses This Guide

This FlashEA for IRMS Operating Manual is intended for all personnel that need a thorough understanding of the instrument (to perform maintenance or troubleshooting, for example). This manual should be kept near the instrument to be available for quick reference.

Scope of This Guide

This manual includes the following chapters:

- Chapter 1: "Prior to Measurement" describes precaution measures and important steps to be performed in the beginning before a measurement is started.
- Chapter 2: "ConFlo III Interface and Elemental Analyzer" describes how to get started with ConFlo III plus Elemental Analyzer. Furthermore, it treats the general principles of editing methods and sequences.
- Chapter 3: "Elemental Analyzers" describes hardware layout, reactor filling, chemicals and gas supply. It treats the 1108, 1110 and 2500 Elemental Analyzers and the FlashEA as well.
- Chapter 4: "Nitrogen Measurement" describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for nitrogen. Furthermore, it provides a glance at nitrogen input by autosampler and oxygen dosage. Hardware preparation, method editing and sequence editing before a nitrogen measurement is started are extensively treated. Finally, results of this measurement are displayed.

Note This chapter treats the principles of blank measurement, reference measurement and amount percent determination. As they can be generalized for nitrogen, carbon and sulfur, the chapter already contains the remarks valid for any of the three elements. ▲

- Chapter 5: "Carbon Measurement" describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for carbon. Hardware preparation, method editing and sequence editing before a carbon measurement is started are extensively treated. Finally, results of this measurement are displayed.
- Chapter 6: "Dual Measurement" describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for dual measurement. Hardware preparation, method editing and sequence editing before a dual measurement is started are extensively treated. Finally, results of this measurement are displayed.
- Chapter 7: "Sulfur Measurement" describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for sulfur. Hardware preparation, method editing and sequence editing before a sulfur measurement is started are extensively treated. Finally, results of this measurement are displayed.

Contacting Us

There are several ways to contact Thermo Fisher Scientific.

Assistance

For technical support and ordering information, **visit us on the Web**:

www.thermoscientific.com/ms

Service contact details for customers in Europe are available under:

www.thermoscientific.com/euservicecontact

Customer Information Service

cis.thermo-bremen.com is the Customer Information Service site aimed at providing instant access to

- Latest software updates
- Manuals, application reports, and brochures

Thermo Fisher Scientific recommends that you register with the site as early as possible. To register, visit register.thermo-bremen.com/form/cis and fill in the registration form. Once your registration has been finalized, you will receive confirmation by e-mail.

Changes to the Manual

❖ **To suggest changes to this manual**

- Please send your comments (in German or English) to:

  Editors, Technical Documentation
  Thermo Fisher Scientific (Bremen) GmbH
  Hanna-Kunath-Str. 11

  28199 Bremen

  Germany

- Send an e-mail message to the Technical Editor at

  documentation.bremen@thermofisher.com

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

Typographical Conventions

This section describes typographical conventions that have been established for Thermo Fisher Scientific manuals.

Data Input

Throughout this manual, the following conventions indicate data input and output via the computer:

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

Topic Headings

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

Chapter 1 Chapter Name

Second Level Topics

Third Level Topics

Fourth Level Topics

Safety and EMC Information

In accordance with our commitment to customer service and safety, this instrument has satisfied the requirements for the European CE Mark including the Low Voltage Directive.

Designed, manufactured and tested in an ISO9001 registered facility, this instrument has been shipped to you from our manufacturing facility in a safe condition.

This instrument must be used as described in this manual. Any use of this instrument in a manner other than described here may result in instrument damage and/or operator injury.

Notice on Lifting and Handling of Thermo Scientific Instruments

For your safety, and in compliance with international regulations, the physical handling of this Thermo Scientific instrument *requires a team effort* for lifting and/or moving the instrument. This instrument is too heavy and/or bulky for one person alone to handle safely.

Notice on the Proper Use of Thermo Scientific Instruments

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

Notice on the Susceptibility to Electromagnetic Transmissions

Your instrument is designed to work in a controlled electromagnetic environment. Do not use radio frequency transmitters, such as mobile phones, in close proximity to the instrument.

Safety and Special Notices

Make sure you follow the precautionary statements presented in this guide. The safety and other special notices appear different from the main flow of text. Safety and special notices include the following:

Warning Warnings highlight hazards to human beings. Each Warning is accompanied by a Warning symbol. ▲

Caution Cautions highlight information necessary to protect your instrument from damage. ▲

Note Notes highlight information that can affect the quality of your data. In addition, notes often contain information that you might need if you are having trouble. ▲

Identifying Safety Information

This guide contains precautionary statements that can prevent personal injury, instrument damage, and loss of data if properly followed. Warning symbols alert the user to check for hazardous conditions. These appear throughout the manual, where applicable. The most common warning symbols are:

Warning General Hazard. This general symbol indicates that a hazard is present that could result in injuries if it is not avoided. The source of danger is described in the accompanying text. ▲

Warning Electric Shock Hazard. High Voltages capable of causing personal injury are used in the instrument. The instrument must be shut down and disconnected from line power before service is performed. Do not operate the instrument with the top cover off. Do not remove protective covers from PCBs. ▲

Warning Strong Magnetic Field. Strong magnetic fields are used in the instrument. Keep away from heart pacemakers, computers, credit cards, and any other magnetically sensitive device. Do not bring compressed gas cylinders within close proximity to the instrument. ▲

Warning Burn Hazard. Treat heated zones with respect. Parts of the instrument might be very hot and might cause severe burns if touched. Allow hot components to cool before servicing them. ▲

Warning Frostbite Hazard. Careless handling of cryogenic liquids might cause severe personal injury including frostbite. Wear protective clothing when operating this equipment including insulated gloves and face shield. ▲

Warning Corrosive Material. Wear gloves when handling toxic, carcinogenic, mutagenic, or corrosive/irritant chemicals. Use approved containers and procedures for disposal of waste solution. ▲

Warning Laser Radiation. Avoid eye or skin exposure to direct or scattered radiation! ▲

Warning Radio Frequency Radiation. Radio frequency radiation is generated to produce plasma. This radiation is present within the torch box area. Never attempt to override or defeat the interlock system. ▲

Warning Ultraviolet Radiation. Intense ultraviolet radiation is generated by the inductively coupled plasma. This radiation is present within the torch box area. Never attempt to override or defeat the interlock system. ▲

In addition to the above described, every instrument has specific hazards. So, be sure to read and comply with the precautions described in the subsequent chapters of this guide. They will help ensure the safe, long-term use of your system.

General Safety Precautions

Observe the following safety precautions when you operate or perform service on your instrument:

- The system should be operated by trained personnel only. Read the manuals before starting the system and make sure that you are familiar to the warnings and safety precautions!
- Accurate results can be obtained only, if the system is in good condition and properly calibrated.
- Service by the customer should be performed by trained qualified personnel only and should be restricted to servicing mechanical parts! Service on electronic parts should be performed by Thermo Fisher Scientific Service Engineers only!
- Before plugging in any of the instrument modules or turning on the power, always make sure that the voltage and fuses are set appropriately for your local line voltage.
- Only use fuses of the type and current rating specified. Do not use repaired fuses and do not short-circuit the fuse holder.
- The supplied power cord must be inserted into a power outlet with a protective earth contact (ground). When using an extension cord, make sure that the cord also has an earth contact.
- Do not change the external or internal grounding connections. Tampering with or disconnecting these connections could endanger you and/or damage the system.

- The instrument is properly grounded in accordance with regulations when shipped. You do not need to make any changes to the electrical connections or to the instrument's chassis to ensure safe operation.
- Never run the system without the housing on. Permanent damage can occur. When leaving the system, make sure that all protective covers and doors are properly connected and closed, and that heated areas are separated and marked to protect for unqualified personnel!
- Do not turn the instrument on if you suspect that it has incurred any kind of electrical damage. Instead, disconnect the power cord and contact a Thermo Fisher Scientific Service Engineer for a product evaluation. Do not attempt to use the instrument until it has been evaluated. (Electrical damage may have occurred if the system shows visible signs of damage, or has been transported under severe stress.)
- Damage can also result if the instrument is stored for prolonged periods under unfavorable conditions (e.g., subjected to heat, water, etc.).
- Always disconnect the power cord before attempting any type of maintenance.
- Capacitors inside the instrument may still be charged even if the instrument is turned off.
- Never try to repair or replace any component of the system that is not described in this manual without the assistance of your Thermo Fisher Scientific Service Engineer.
- Do not place any objects – especially not containers with liquids – upon the instrument. Leaking liquids might get into contact with electronic components and cause a short circuit.

Safety Advice for Possible Contamination

Hazardous Material Might Contaminate Certain Parts of Your System During Analysis.

In order to protect our employees, we ask you to adhere to special precautions when returning parts for exchange or repair.

If hazardous materials have contaminated mass spectrometer parts, Thermo Fisher Scientific can only accept these parts for repair if they have been properly decontaminated. Materials that due to their structure and the applied concentration might be toxic or that are reported in publications to be toxic are regarded as hazardous. Materials that will generate synergetic hazardous effects in combination with other present materials are also considered hazardous.

Your signature on the Health and Safety Form confirms that the returned parts have been decontaminated and are free of hazardous materials. Download the form from decon.thermo-bremen.com or order it from the Thermo Fisher Scientific field service engineer.

Parts contaminated by radioisotopes should not be returned to Thermo Fisher Scientific—neither under warranty nor within the exchange part program. If unsure about parts of the system possibly being contaminated by hazardous material, please make sure the Thermo Fisher Scientific field service engineer is informed before the engineer starts working on the system.

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Procedures

Chapter 1 Prior to Measurement

The Thermo Scientific Continuous Flow Interface (ConFlo III) provides an efficient and flexible way to couple an Elemental Analyzer (EA) to a stable isotope ratio mass spectrometer (IRMS) on-line. This combination has become standard for determining the isotope ratios of carbon (C), nitrogen (N), sulfur (S), hydrogen (H) and oxygen (O) of combustible organic materials in bulk samples. ConFlo III and Elemental Analyzer form an integrated and optimized sample preparation inlet system, which can be connected to any current Thermo Scientific IRMS equipped for on-line isotope ratio analysis. As a particularity of gas isotope mass spectrometers, any samples must be converted into simple gases prior to introducing them into the ion source. This is achieved by the Elemental Analyzer via oxidation and reduction furnaces (Elemental Analyzer) or by High Temperature Conversion (TC/EA). Passing through a gaschromatographic column the produced gases are separated and consecutively enter ConFlo III.

The ConFlo III can be connected to any current Thermo Scientific Elemental Analyzer and Thermo Scientific IRMS equipped for Continuous Flow application.

Precautions

Caution Place the system on a flat and solid surface that can carry at least 100 kg. Ensure that the ConFlo III is not exposed to direct sunlight! Keep the system away from heat, for example radiators, to avoid damage to the internal circuits and the external surface! ▲

Caution Do not clean the ConFlo III using paint thinner, alcohol or other organic solvents! Do not put any objects, especially liquids, upon the ConFlo III! ▲

Warning Avoid using aerosol sprays near the system as this could cause sudden ignition of the spray! ▲

About this Manual

This manual intends to be a user guide for working with the combined system of Elemental Analyzer (EA), ConFlo III and Isotope Ratio Mass Spectrometer (IRMS). As the system consists of three separate instruments with the Elemental Analyzer and IRMS having manuals of their own, this manual will mark on specific information about the ConFlo III system. It starts with an overview about Elemental Analyzers of different types followed by basic information about ConFlo III. Finally, isotope ratio determinations of C, N, S, H and O using ConFlo III are explained in turn. It is assumed that the user is not only familiar with clean operating procedures and sample preparation but also has already some working experience with IRMS and the Isodat software.

Chapter 2 ConFlo III Interface and Elemental Analyzer

This chapter describes how to get started with ConFlo III plus Elemental Analyzer. Furthermore, it treats the general principles of editing methods and sequences.

It treats the following topics:

Getting Started with ConFlo III and Elemental Analyzer

❖ **To get started with ConFlo III and Elemental Analyzer**

1. Connect the Elemental Analyzer to the ConFlo III for the transfer of the start signal.
2. In case you have Teflon tubing, replace it with stainless steel at your Elemental Analyzer, because atmospheric N_2 passes Teflon and interferes the quality of the determination.
3. Connect the reducing valves to the gas supplies (He, O_2, N_2, CO_2).
4. Connect the gas tank of O_2 and He to the Elemental Analyzer.
5. Connect He, N_2 (as Ref 2) and CO_2 (as Ref 1) to ConFlo III.
6. Open the main valves on the gas tanks and adjust the pressure. Refer to "Gas Supply" on page 3-5 and to "Working with Gas Tanks" on page 3-6.
7. Leak-check all connections and valves outside ConFlo III.
8. Make sure that the Elemental Analyzer is set up (for example oxidation and reduction reactors are packed and installed, water trap is installed, autosampler is fixed etc.).
9. Connect the Elemental Analyzer to the computer, if the Elemental Analyzer is run by separate software, that is Eager software.
10. Connect the Elemental Analyzer to the 220 V main power supply.
11. Connect compressed air to ConFlo III.
12. Connect compressed air to Elemental Analyzer if necessary (depending on the autosampler).
13. Connect ConFlo III to the IRMS (rear panel).
14. Ensure that the IRMS connection cable is connected to the driver board of the computer.
15. Make sure that the ConFlo III configuration has been installed during Isodat 2.0 setup.
16. By using the ConFlo III device window in Isodat 2.0, make sure that the respective pistons of ConFlo III are movable (click on them using your mouse) and watch them moving in the combi inlet of ConFlo III.
17. Connect the fused silica capillaries of ConFlo III to the needle valve of the IRMS.
18. Switch on the Elemental Analyzer.

19. Adjust the gas pressures of the Elemental Analyzer and ConFlo III. Take the settings of Table 2-1 as a guideline.

Table 2-1. Adjustment of gas pressures

He	Elemental Analyzer	100 kPa
O_2	Elemental Analyzer	120 kPa
Purge with	helium	110-200 mL/min depending on your autosampler: AS 200 and AS 128: 10 mL/min MAS 200: 200 mL/min
He	ConFlo III	0.8 bar
N_2	ConFlo III	1.3 bar
CO_2	ConFlo III	0.9 bar

Caution To prevent atmospheric air from entering the open split cell, never set the helium flow on the ConFlo III to less than 0.5 bar. ▲

20. Switch off the ion source.
21. Inject the He dilution capillary to ensure only helium entering the source.
22. Open the needle valve slowly.
23. Make sure the ion source high vacuum is between 3×10^{-6} mbar and 1.5×10^{-6} mbar.
24. Switch the ion source on. The expected background after approximately 30 min should be as summarized in Table 2-2.

Table 2-2. Expected background after approximately 30 min

mass	measured in cup for mass	resistor [Ω]	expected background
28	28	3×10^{8}	< 20 mV
29	29	3×10^{10}	< 20 mV
18	29	3×10^{10}	< 10 mV
40	29	3×10^{10}	< 10 mV

Note Background values may vary depending on sensitivity and focus settings. They are given here as a general guideline. ▲

25. Leak-check the needle valve.

Note Leak check can be performed using a triggling stream of argon while monitoring m/z 40 on the IRMS. ▲

26. Switch the needle valve heater on.
27. Switch the ion source heater on.
28. Leak-check all connections of the Elemental Analyzer.
29. Heat up the following parts of the Elemental Analyzer in three steps. See Table 2-3.

Note The Elemental Analyzer should not be connected to ConFlo III yet! ▲

Table 2-3. Heating up Elemental Analyzer parts in three steps

Part	Step 1	Step 2	Step 3
oxidation furnace	400 °C	750 °C	1020 °C
reduction furnace	400 °C	500 °C	650 °C
column	40 °C	75 °C	120 °C

30. Leak-check after each step and wait for two hours after reaching the final temperature.
31. Keep the system overnight in the last status to remove organic material and water and for column conditioning.
32. Also leave ConFlo III under the conditions mentioned above overnight to remove all organic material from the fused silica capillaries, connection lines, valves, manometers etc.
33. Cool down the GC column to 40 °C for measurements.
34. Before connecting the Elemental Analyzer to ConFlo III, measure the helium flow at the end of the stainless steel capillary. Adjust the pressure at the Elemental Analyzer to set the flow to 80 mL/min-100 mL/min depending on sample and application to be performed.
35. Connect the Elemental Analyzer to the ConFlo III.
36. Make sure that no standard gas is injected, He dilution is off and all other valves are closed.

The expected background is as shown in Table 2-4.

Table 2-4. Expected background

Mass	Measured in cup for mass	Resistor [Ω]	Expected background
28	28	3×10^{8}	< 20 mV
29	29	3×10^{10}	< 20 mV
18	29	3×10^{10}	< 2 mV
40	29	3×10^{10}	< 10 mV

Note Background values may vary depending on sensitivity and focus settings. They are given here as a general guideline. ▲

Note The above ion intensity depends on the sensitivity of the IRMS. If the ion intensity is higher than expected and no leak is present, the background must decrease after two or three days and stabilize. ▲

Defining a Method

The Acquisition mode of Isodat allows fully automated isotope ratio determination. All parameters relevant for data acquisition of a sample are stored in a method.

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

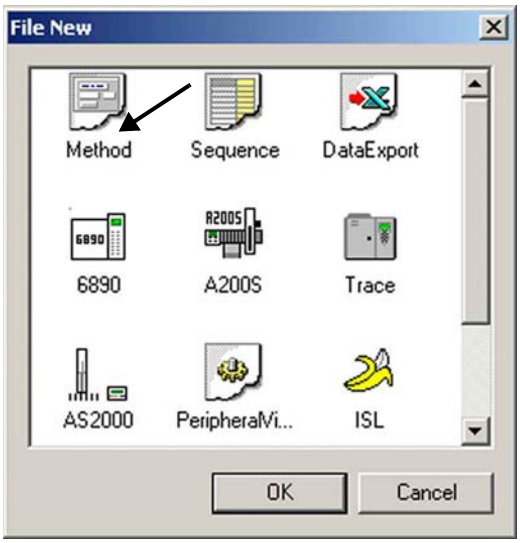
❖ **To define a method (here ^{13}C, that is CO_2 as an example)**

1. Open the **Acquisition** mode.

2. Select a configuration for ConFlo II/III applications, for example ***ConFlo III & AS***.

3. Select the gas configuration for ^{13}C determination, that is CO2.

4. Click on the **New** button.



5. Mark **Method** and confirm by **OK**.

The new method is structured in tab pages: Instrument, Time Events, Evaluation, Peak Detection, and Printout tab. In the following, the parameters of a CO_2 method will be explained.

Instrument Tab

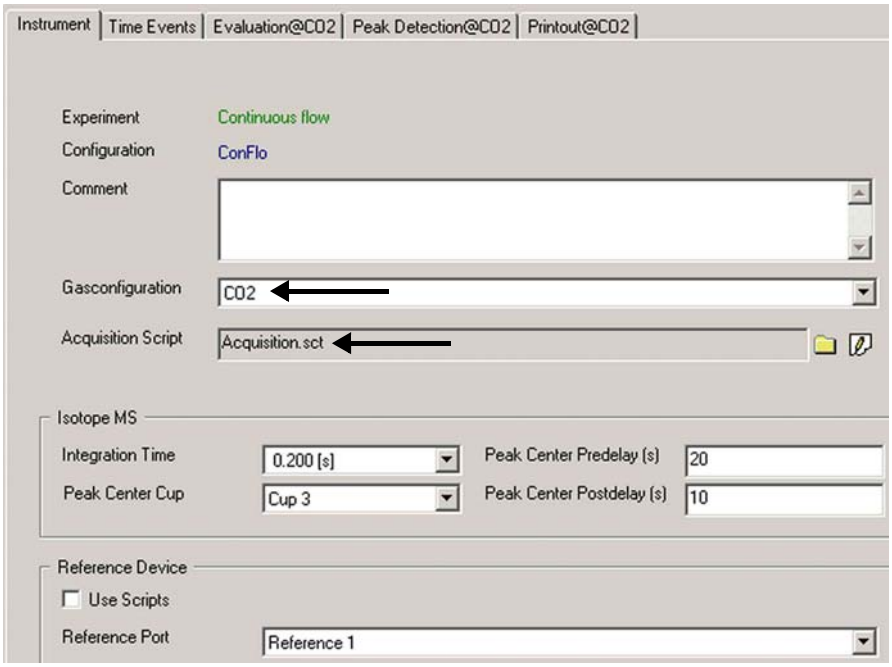


Figure 2-1. Instrument tab - gas configuration and acquisition script

Select the gas configuration for ^{13}C determination, that is CO2. The acquisition script controls the acquisition cycle. See Figure 2-1.

Note It should only be edited by users trained on script editing. ▲

Figure 2-2. Instrument tab - Isotope MS

Integration time: time integrated to form a data point triplet, for example 0.200 s. Select the Peak Center Cup, for example Cup 3 as narrow center cup for m/z 29 in a triple collector.

Peak Center Predelay is the time the system waits between activation of the reference gas and start of the peak center cycle, for example 20 s. See Figure 2-2.

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

Peak Center Postdelay is the time the system waits between the end of the peak center cycle and the start of data acquisition, for example 10 s.

Figure 2-3. Instrument tab - reference device

Select the appropriate Reference Port for peak center, for example Reference 1 for CO_2. Choose between Reference 1 and Reference 2. See Figure 2-3.

Time Events Tab

The time events list controls all operations during data acquisition. See Figure 2-4.

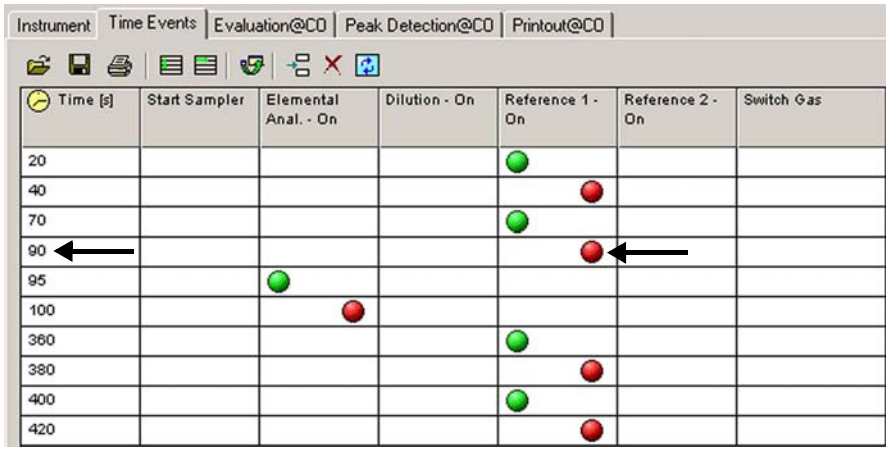


Figure 2-4. Time events tab - time events list

Insert lines using the right mouse button or click on  .

Edit the Time [s] at which the individual event will happen.

Double-click the field of a valve or use the space bar to set/toggle its status to active or inactive .

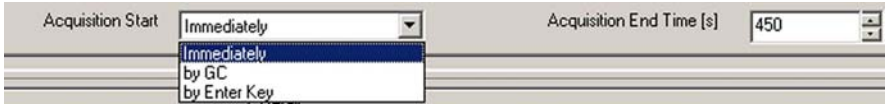


Figure 2-5. Time events tab - acquisition start and acquisition time

Select the Acquisition Start. The acquisition start defines the signal source to trigger the start of data acquisition. Choose between Immediately, by GC or by Enter Key. In the vast majority of cases, Immediately is used. By GC refers to a trigger signal from GC, while the user gives the trigger signal via keyboard by Enter Key.

Edit the Acquisition End Time. The Acquisition End Time is the end time of data acquisition. After the Acquisition End Time, no further actions will be executed from the Time Events list. Allow some time to finish the last event before ending the acquisition. See Figure 2-5.

Evaluation Tab

Figure 2-6. Evaluation tab - evaluation type

Select the Evaluation Type, that is the ion correction type (for example CO2_SSH).

Click on the >> button to add own scripts for ion corrections. See Figure 2-6.

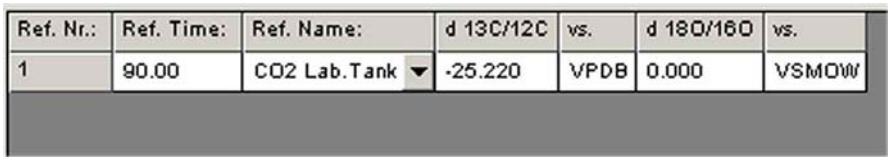


Figure 2-7. Evaluation Tab - defining a standard

Select a Ref. Name from your standard database (for example **CO2 Lab. Tank**) or edit the related δ values. In the latter case, User Defined will be shown at Ref. Name. More standards can be added using the right mouse button.

Enter the retention time in s (that is, Ref. Time, for example 90.00) of the standard peak(s) defined in the Time events list, which are used for calculating the corresponding δ value(s). See Figure 2-4.

If the assigned time for standard peak detection falls in between the Peak Start and Peak Stop marks of a peak, this peak will be used for δ value calculation. See Figure 2-7.

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

Figure 2-8. Evaluation tab - reference/blank/amount percent determination

Note The unit, for example mg, does not influence any calculation. It is used for reporting purposes. Keep it constant during method definition, for example do not switch between mg and µg. ▲

Blank: For a blank determination, a time window needs to be defined by significant peak start and stop in which the corresponding sample peaks will appear.

Reference: For Amount Percent determination, type in the appropriate element's weight percent of the reference compound used for calibration.

Peak Detection Tab

Figure 2-9. Peak Detection tab - peak detection and background detection

Mark the respective checkboxes, if you want to perform a peak detection or background detection, respectively. Type in the corresponding detection mass, for example 44 in case of CO_2. It is recommended to keep the default values. See Figure 2-9.

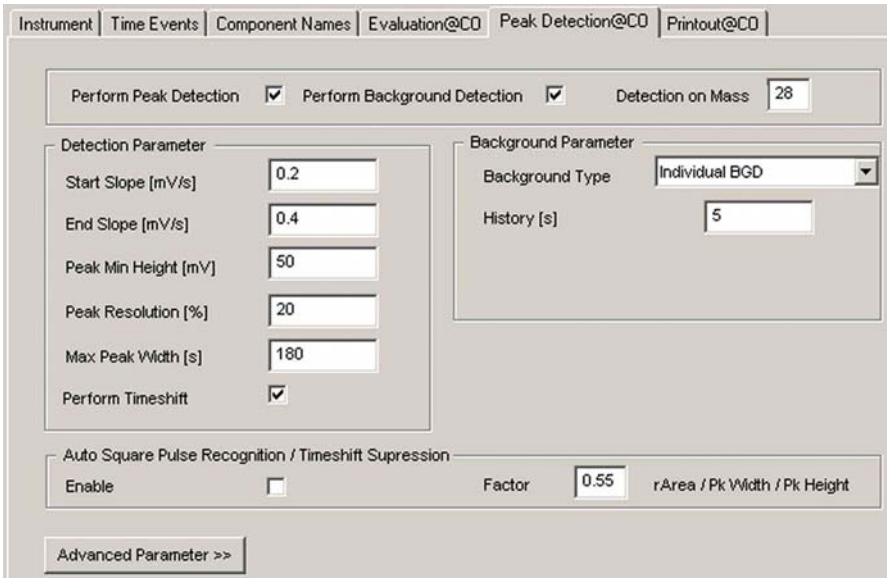


Figure 2-10. Peak Detection tab - detection parameters

Edit Start Slope, End Slope, and Peak Min Height or keep the default values: A five point average slope of 0.2 mV/s (Start Slope) and of 0.4 mV/s (End Slope) is recommended for safe recognition of the peak boundaries. The best slope values depend on the nature of the chromatogram.

Peak Min Height limits the number of reported peaks as it allows to exclude small ones from evaluation. Default is 50 mV. Individual BGD is the default Background Type. See Figure 2-10.

Figure 2-11. Peak Detection tab - Auto Square Pulse Recognition/Timeshift Suppression

As chromatographic peaks emanate from a GC column, an isotope effect is noticed during their detection: a slight delay of heavy isotopes' signal positions occurs compared to those of lighter ones. When integrating **chromatographic** peaks, this needs to be compensated by a timeshift (detection trace is fixed; the other traces are time-adjusted to the detection trace).

Reference pulses however, lead to **square** peaks. Here, no timeshift is necessary, because they simply are fed into the open split and do not emanate from a GC column. On square peaks, one does not want to perform a timeshift, whereas on chromatographic peaks, one wants to do.

The shape of a chromatographic peak or a square peak can be characterized by its height/width ratio, cf. the factor f in Figure 2-11. The factor f is dimensionless and defined as:

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

with:

A_{raw}raw area of the chromatographic or square peak (in Vs)

h peak height (in V)

w peak width (in s)

As square peaks and (gaussian) chromatographic peaks are considerably different with respect to f, this factor can be used for peak discrimination. It ranges between 0 and 1. A high f value alludes to square peaks, a low one to chromatographic peaks. Its default value 0.55 should be satisfactory for most chromatogram types.

In any chromatographic system however, chromatographic peaks may sometimes occur, which are of quite similar shape as are square peaks. Thus, although a peak is no square peak, it might wrongly be identified as such. In this case, it is recommended to change the default value of f. However, for most ConFlo III situations, f can be kept default.

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

As default, Enable is unmarked, because old chromatograms might have been calculated without automatic square peak detection. In case of recalculating them, Enable can be marked to include now automatic detection.

If Perform Timeshift is unmarked, no timeshift correction will be performed on any peak. Decide, whether you additionally want automatic square peak detection/suppression of timeshift correction to be performed or not.

As an example, you can perform a timeshift and additionally let the square peaks be automatically detected.

If you do not want to detect them automatically, you can define ranges instead where a timeshift will be performed or not (for example in case of many different peak shapes, one single factor f might not be sufficient).

Marking Enable is only useful, if you simultaneously mark Perform Timeshift as well.

Printout Tab

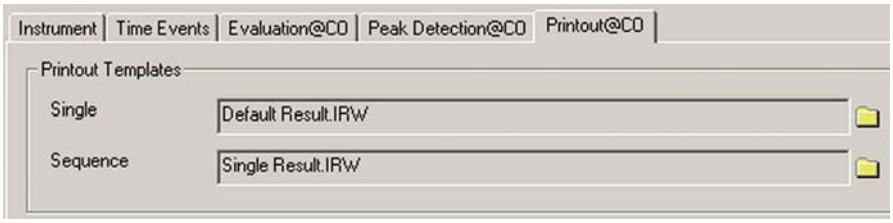


Figure 2-12. Printout tab

In Printout tab, the use of printout templates is controlled.

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

Sequence selects a print template from the Result Workshop for a reduced printout per sample within a sequence summary.

Saving a Method

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

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

❖ **To save a method**

Save command

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

Save As command

Click on the arrow and choose **Save as...** to optionally choose a new name and folder for the currently active single document (for example method or sequence).

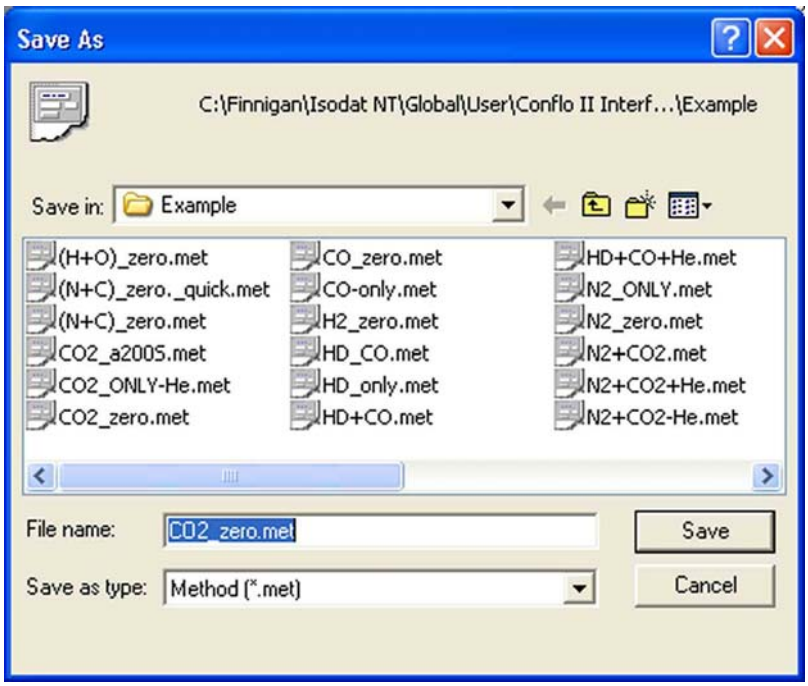
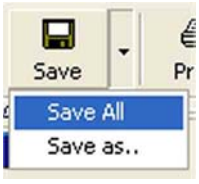


Figure 2-13. Naming a method

Notice that the particular folder is shown that contains the currently active method. Choose the folder above the Example folder, not the Example folder itself! This ensures not to mix or even overwrite the predefined example method with your own method.

Give the method a significant name, for example similar to the sequence it corresponds to. Keep the extension .met. Confirm by **Save**. See Figure 2-13.

Save All command



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

They will be stored without changing names and folders.

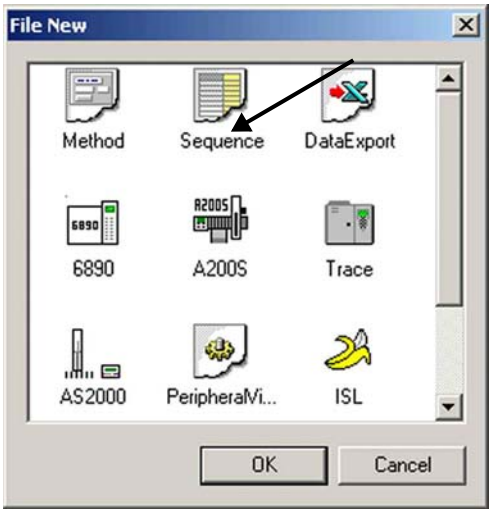
Defining a Sequence

After editing and saving a method (refer to "Defining a Method" on page 2-6), a sequence must now be edited.

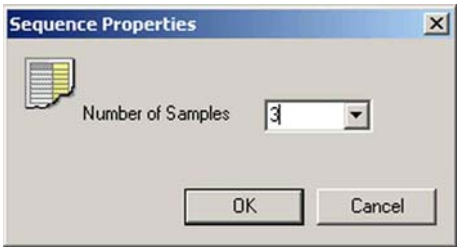
Caution As with methods, you must create and save a new sequence on your own! The predefined sequences delivered by Thermo Fisher Scientific (Bremen) in the Examples folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! Never overwrite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

❖ To define a new sequence

1. Click on the **New** button.



2. Mark **Sequence** and confirm by **OK**.



3. Define the number of samples, for example 3, and confirm by **OK**.

Line		Amount	Type	AS Sample	AS Method	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Sample		Disabled				N2_zero.met
2	✓	0.273	Sample		Disabled				N2_zero.met
3	✓	0.291	Sample		Disabled				N2_zero.met

Figure 2-14. Editing the sequence list

Edit the sequence list as follows:

Line: each line refers to an individual sample, that is it denotes the sample number.

Peak Center : marking it allows performing a peak center procedure prior to measuring the particular sample. This ensures the ion current to be centered on the cup selected in the method (always recommended). See Figure 2-2.

Amount: amount of sample (unit was selected in the method. See Figure 2-8).

Type: here Sample

AS Sample: a sample position will be loaded and communicated to the autosampler.

AS Method: an **autosampler** method will be loaded and communicated to the autosampler.

Note The columns AS Sample and AS Method only appear, if an autosampler for liquid injections (AS 200) has previously been selected in the configuration. ▲

Identifier: optionally, edit text to identifiy the sample.

Comment: optionally, type a comment.

Preparation: optionally, type information related to preparation.

Method: important; the **IRMS** method edited in "Defining a Method" on page 2-6 can be selected here from the pulldown list. By selecting it here, you determine the particular IRMS method to be used during measurement.

Note You get immediate access to the **IRMS** method by pressing the **Shift** key and the left mouse button simultaneously in the Method column. ▲

Note Without a selection from the pulldown list, no measurement will take place. Instead, the error message "No valid method found in sequence grid" will occur. ▲

Note After you typed data in only one cell of the sequence grid, easily fill each of its columns: therefore, right-click the column and choose the Fill Grid with Data command. ▲

Saving a Sequence

As done with a method (refer to "Saving a Method" on page 2-13), after defining the new sequence you must save it before it will start.

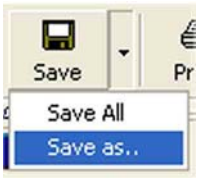
Caution The predefined sequences delivered by Thermo Fisher Scientific (Bremen) in the Examples folder are only example files. They only show guidance through helpful default values, but must never be used for measurements! Never overwrite a sequence example file with a sequence created on your own! Depending on your software version these examples may not work properly. ▲

❖ **To save a sequence**

Save command

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

Save As command



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

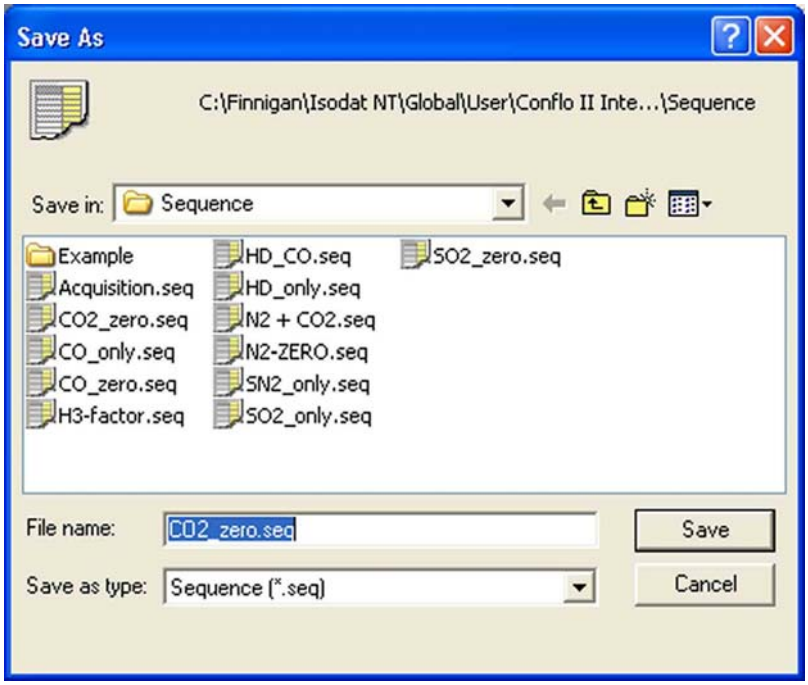
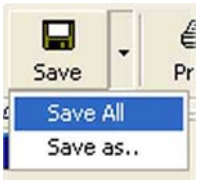


Figure 2-15. Naming a sequence

Notice that the particular folder is shown that contains the currently active sequence. Choose the folder above the Example folder, not the Example folder itself! This ensures not to mix or even overwrite the predefined example sequence with your own sequence.

Give the sequence a significant name, for example similar to the method it corresponds to. Keep the extension .seq. Confirm by **Save**. See Figure 2-15.

Save All command



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

They will be stored without changing names and folders.

Starting a Sequence

To start the sequence, click on the **Start** button. Figure 2-16 appears.

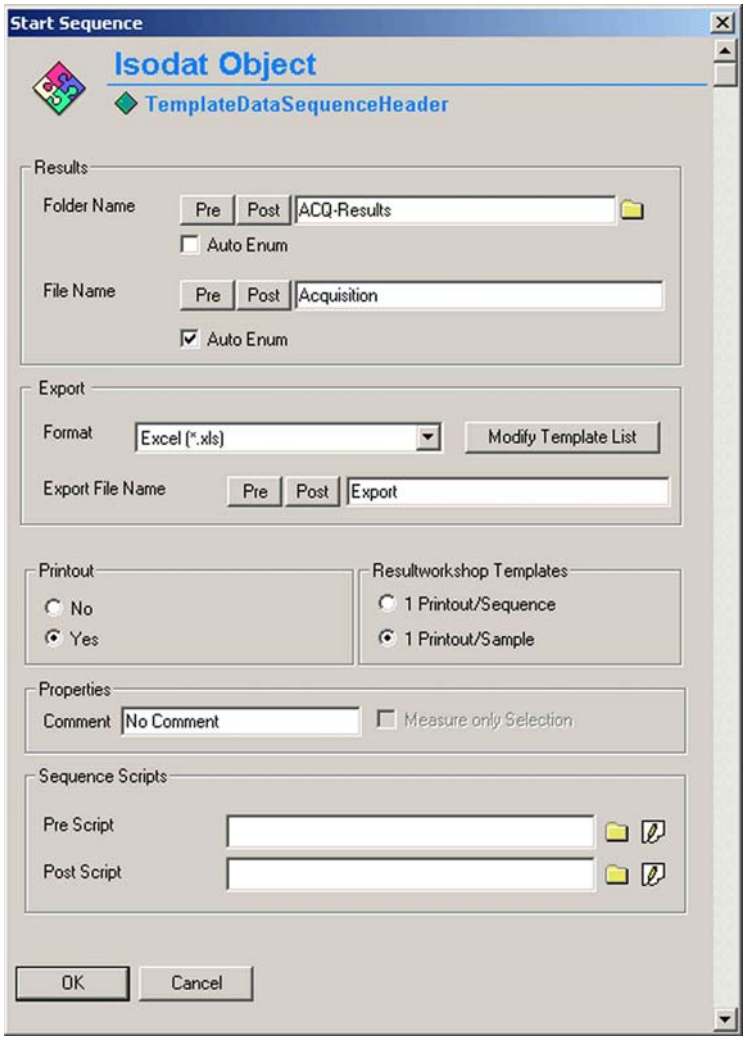


Figure 2-16. Defining results export and printout parameters

Results: define folder and file containing your measurement results.

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

Printout: decide, whether you want a printout. If so, choose between one printout per sample or per sequence. Finally, confirm by **OK**. See Figure 2-16.

If an error message indicates low memory, close other applications. The measurement will be started.

Chapter 3 Elemental Analyzers

This chapter gives an overview about working with the Elemental Analyzers EA 1108, EA 1110, EA 2500 and Flash EA 1112. For operating the TC/EA refer to the TC/EA operating manual (P/N 1127601).

The analytical method of the Elemental Analyzer is based on the so-called flash combustion. This reaction converts all organic and most inorganic substances into combustion products by instantaneous and complete oxidation of the sample. The resulting gaseous products (CO_2, N_2, NO_x, SO_2, H_2O etc.) pass through a reduction furnace and a water trap prior to entering the chromatographic column with helium acting as the carrier gas. As a result, isotopes of C, N and S are determined of CO_2, N_2 and SO_2.

After separation, the components are detected by the Isotope Ratio Mass Spectrometer (IRMS). The IRMS allows precise determination of the isotope ratios and the concentrations of the individual components of the mixture. See Figure 3-1.

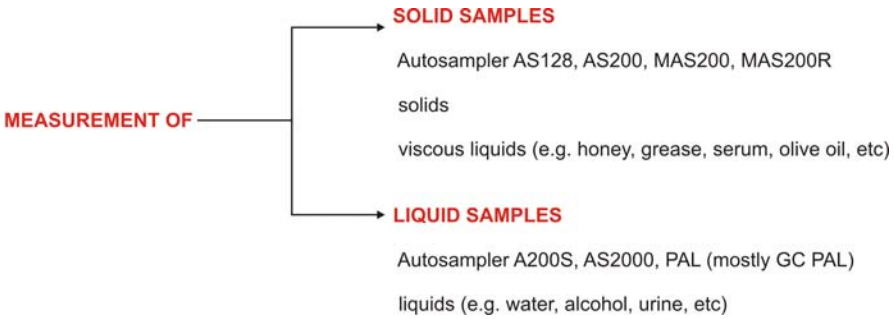


Figure 3-1. Schematic diagram of running solid and liquid samples

The chapter treats the following topics:

Procedure

The samples are packed into tin capsules (preferred) or silver capsules and placed into the autosampler, where they are purged with a continuous flow of helium or O_2. Upon a signal from the control software, they are dropped into a vertical quartz tube maintained at 900 °C- 1050 °C (combustion reactor).

When the samples are dropped into the reactor, the helium stream is temporarily enriched with pure O_2 and the sample and its container are oxidized by flash combustion reaction. Organic compounds are completely oxidized under these conditions.

Quantitative conversion is achieved by passing the mixture of gases over a catalyst layer of for example Cr_2O_3 or CuO. See Figure 3-2. Combustion gases then pass over copper at 650 °C to remove excess O_2 and to reduce nitrous oxide to N_2.

Note Flash combustion temperature depends on the filling material of the reactor: in case of CuO, a temperature of 900 °C is recommended. In case of Cr_2O_3, a temperature of 1020 °C is recommended. ▲

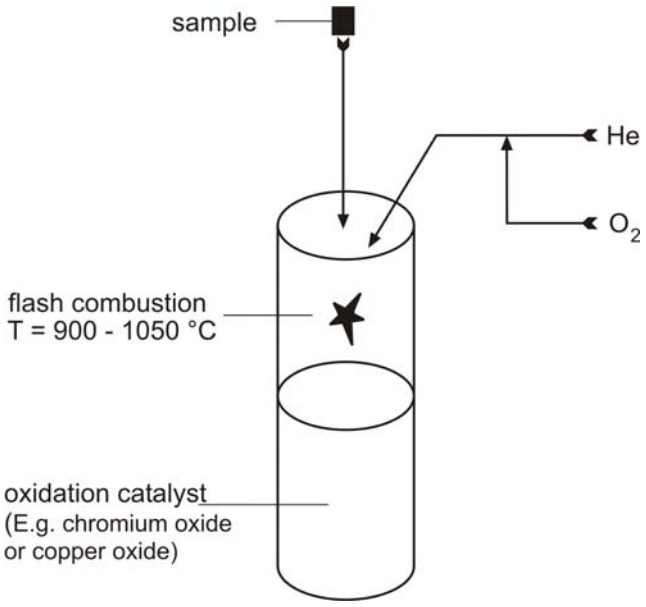


Figure 3-2. Flash combustion principle

Following the reduction furnace, the reaction gas mixture enters a water trap, filled with $Mg(ClO_4)_2$ or Anhydrone. See Figure 3-3. Then it passes a chromatographic column (Porapak QS). Here, the individual gaseous products are separated. They elute as a function of time: first N_2, then CO_2 and SO_2.

Figure 3-3. Water trap

Hardware Layout

The two reactors of the Elemental Analyzer are located in the single furnace section, with two independent heating elements. See Figure 3-4. The oxidation reactor is maintained at temperatures of 900 °C-1050 °C. Several packings for oxidation and reduction reactor are possible. In this manual, the most common reactor packing is explained for the different applications (N_2, CO_2 and SO_2).

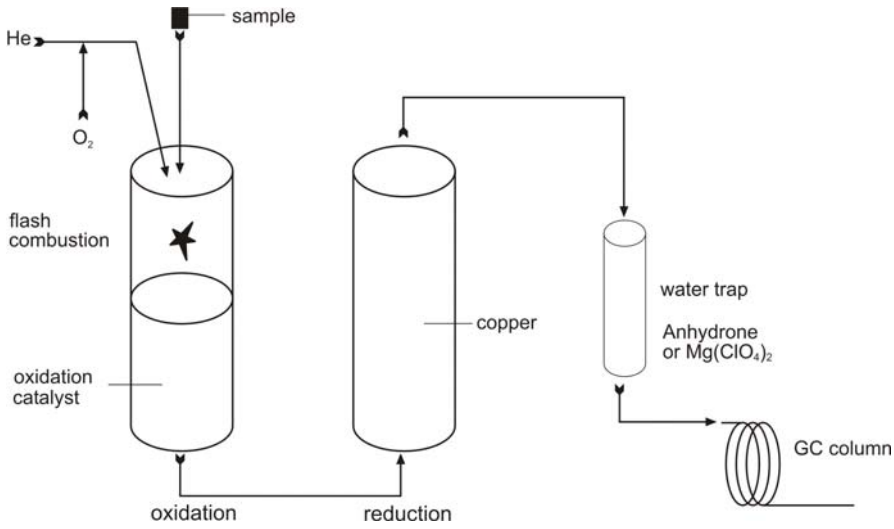


Figure 3-4. Elemental Analyzer reaction scheme

Chemicals

A basic kit of needed chemicals is supplied together with the Elemental Analyzer. The chemicals should always be kept under dry and cool conditions. They should be of extreme purity and by no means allowed to be contaminated by organic material.

Oxidation and Reduction Reactor Filling

Carbon and Nitrogen Measurement

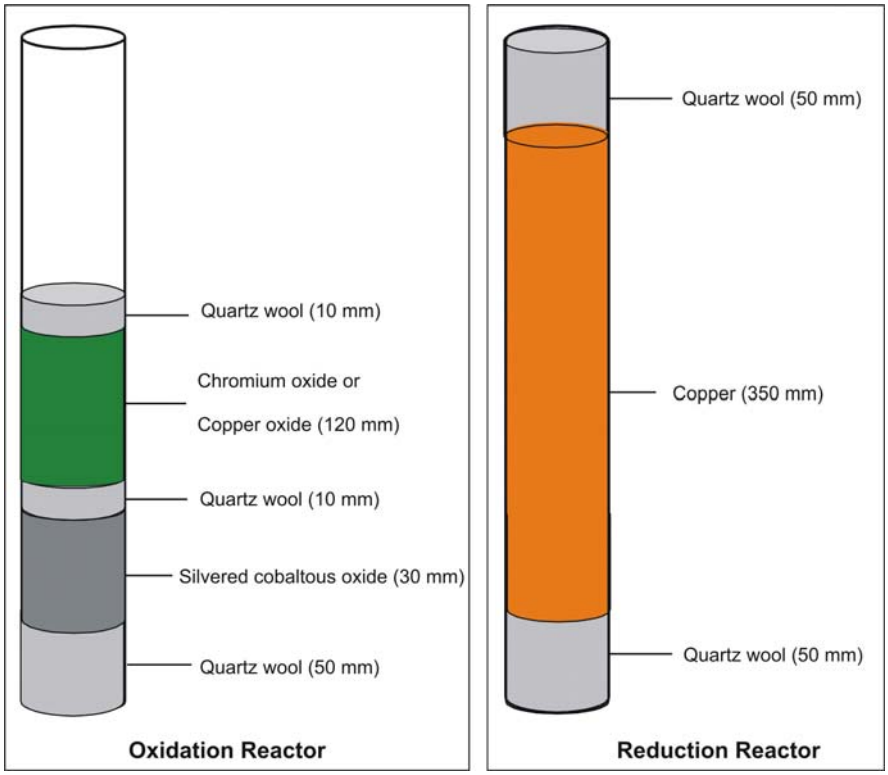


Figure 3-5. Oxidation reactor and reduction reactor filling

Note The number of samples that may be analyzed without changing the packing of the reactor tubes depends on many factors, for example sample type, weight, etc. Roughly 1000 measurements can be run without changing the packing of either the oxidation reactor or of the reduction reactor. Exhaustion of the copper reducing agent is indicated by the formation of a dark coloration of the copper due to the presence of CuO (black) or/and Cu_2O. Replace the copper at this point. It can not be seen from outside! ▲

When packing a new reactor tube or replacing exhausted material take care that:

- The packing is dense and homogeneous.
- Reactors must be packed tightly without leaving dead volume spaces by carefully knocking on the outside of the tube.
- Chemicals used are extremely clean. In no case they may be contaminated with any organic matter.
- The glass tube is extremely clean.

- You carefully clean the reactor tube outside using alcohol to remove any organic material (finger prints) after changing the reactor.

Gas Supply

To operate the combined system of Elemental Analyzer, ConFlo III and IRMS several gases are needed either from a gas tank or from the main gas supply provided in the laboratory (for example compressed air).

The purities summarized in are necessary. Refer to the ConFlo III chapter in the Delta^{plus} XP Pre-Installation Requirements; P/N 1991001.

Table 3-1. Gases and their required purities

Gas	Pressure	Purity
carrier gas (He), purge gas (He)	200 bar	99.999 % He
standard gas (N_2)	200 bar	99.999 % N_2
standard gas (SO_2)	4 bar	99.98 % SO_2
standard gas (CO_2)	60 bar	99.995 % CO_2
standard gas (CO)*	200 bar	99.997 % CO
standard gas (H_2)*	200 bar	99.999 % H_2 (-200 ‰ vs. SMOW)
oxidation gas (O_2)	200 bar	99.995 % O_2

* for TC/EA application only

Note The pressure of a new gas tank is about 200 bar (for example helium tank and hydrogen tank) or about 60 bar (for example CO_2 tank). The pressure needs to be adjusted to approximately 4 bar via the reducing valves mounted at the gas tank. See Figure 3-6. The pressure of the SO_2 tank must be adjusted to approximately 3 bar. ▲

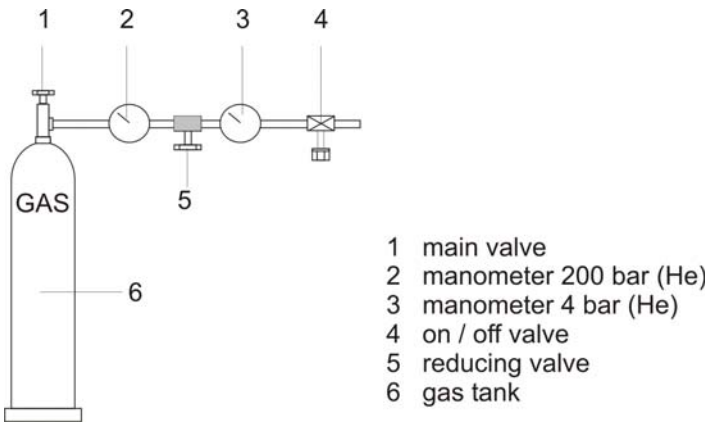


Figure 3-6. Gas supply

Working with Gas Tanks

Warning It is strongly recommended to install the gas tanks firmly. Anyway, tumbling has to be prevented! ▲

Warning Fire or an explosion may be caused by a leak in the hydrogen (H_2) and/or oxygen (O_2) supply! ▲

Warning To ensure operational safety, a CO_2, SO_2 and H_2 detector with an alarm must be installed! ▲

Warning When working with carbon monoxide (CO) or sulfur dioxide (SO_2), good ventilation is essential. Otherwise, these gases can be hazardous to your health! ▲

Install an exhaust tube on top of your ConFlo III as shown in Figure 3-7 to remove the toxic carbon monoxide (CO) and sulfur dioxide (SO_2) from inside of ConFlo III out of your working area.

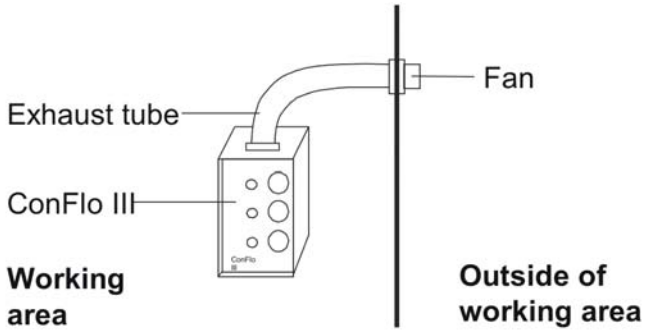


Figure 3-7. Exhaust tube

❖ **To perform a leak check before starting the system**

1. After mounting the reducing valve to the gas tank, both valves that is the on/off valve and the reducing valve, should be open. See Figure 3-6.
2. Open the main valve for two or three seconds to let the gas purge the whole valve system. See Figure 3-6.
3. Close the on/off valve.
4. Close the main valve.

5. Mark the manometer positions of on/off valve and main valve.
6. Wait for 10 min-15 min.
7. A leak may be present, if the manometer positions have changed.
8. To detect the leak, brush all valves and connections carefully with soapsuds.

1108 Elemental Analyzer

Figure 3-8 shows the front panel of the 1108 Elemental Analyzer.

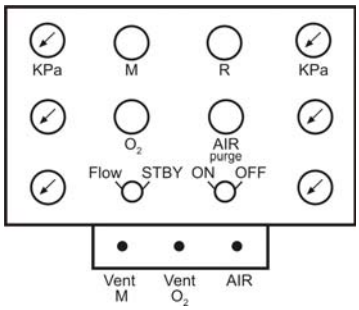


Figure 3-8. Elemental Analyzer 1108 - front panel

Regulating Carrier Gas Pressure

❖ **To regulate the carrier gas pressure**

1. At the helium gas tank adjust the carrier gas pressure to 4 bar.
2. Adjust the pressure regulator marked M at the front panel to 80 kPa (flow rate 80 mL/min-130 mL/min). See Figure 3-8.
3. Connect a flow meter to the outlet connector marked Vent-M on the lower front panel.
4. Adjust the pressure regulator to a flow rate of 80 mL/min-100 mL/min. See Figure 3-8.

Regulating Oxygen Pressure

❖ **To regulate oxygen pressure**

1. At the gas tank, adjust the oxygen pressure to 4 bar. See Figure 3-8.
2. Connect a flow meter to the outlet connector marked Vent-O_2 on the lower front panel.
3. Adjust the O_2 flow rate to 20 mL/min.

Note Be aware of leaks! ▲

Regulating Compressed Air

To regulate compressed air, adjust the compressed air pressure (servo air) via IRMS or the central supply to about 4 bar. Use the pressure regulator marked AIR. See Figure 3-8.

Elemental Analyzer Types 1110 and 2500

The Elemental Analyzer types 1110 and 2500 differ from version 1108 by the number of regulators at the front panel (right) and in the added touch panel. See Figure 3-9 and Figure 3-10.

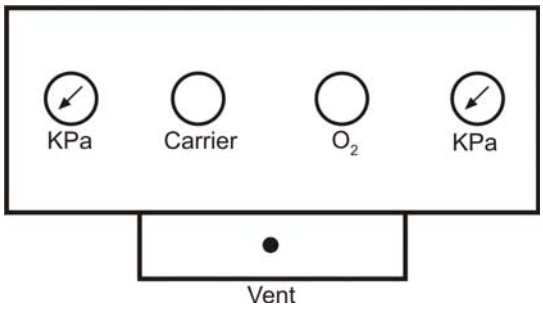


Figure 3-9. Number of regulators at front panel

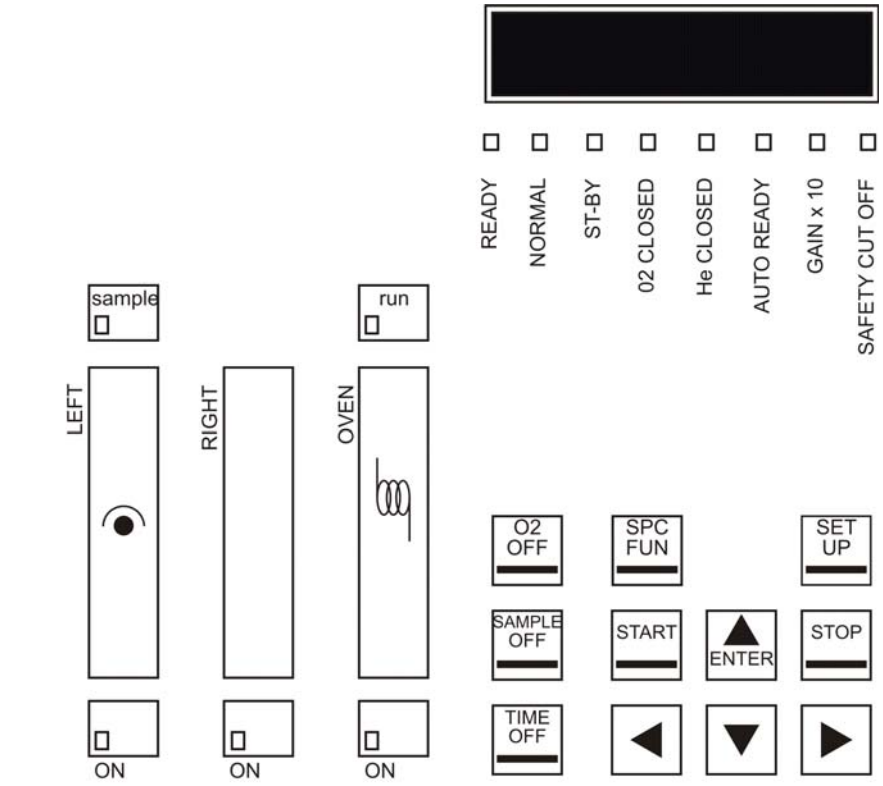


Figure 3-10. Touch panel

These versions feature an automatic flow regulation for the carrier gas pressure. It is managed via the touch panel at the front panel. It possesses an own processor and memory. Parameter input is made via the function keys on the touch panel as shown in Figure 3-10.

Working with the Touch Panel

Activation of the SET UP key results in the display of the parameter sets as given in Table 3-2:

Table 3-2. SET UP key and parameter sets

SET	SET	MAN	GAIN
TEMP	CYC	ZERO	×10

The parameter to be edited is flashing.

Change the parameter to be edited using the ▶ function key and additional parameters will be displayed:

for example:	SET	
	FLOW	etc.

The ▲ key (that is ENTER) has two functions:

a) to enlarge the number

b) to select the input

Regulating Gas Pressures

This section outlines how to regulate the carrier gas pressure, the compressed air and the oxyagen pressure.

Regulating Carrier Gas Pressure

Note It is recommended to operate in Manual mode when performing applications. ▲

❖ **To regulate the carrier gas pressure**

1. Adjust the pressure at the gas tank to 4 bar (400 kPa).
2. Press **SET UP**.

   The parameter set is displayed (with flashing parameters).
3. Select the parameter to be edited (**SET FLOW**) by pressing ▶ four times. SET FLOW is now flashing.
4. Press **ENTER**. The following will be displayed:

Flow	He
mL/min	nn

5. Select the He flow rate (approximately 80-90 mL/min) by using the ▼ and ▲ (that is, the **ENTER**) keys.
6. Press **SET UP** again to leave the input.

   The carrier gas supply is now adjusted automatically via the helium controller of the Elemental Analyzer.

Regulation of Compressed Air

Note It is not intended to regulate the compressed air flow via the Elemental Analyzer. ▲

❖ **To regulate the compressed air**

1. Connect the compressed air to the IRMS.
2. Adjust the pressure to 4 bar.

Regulating Oxygen Flow

Note The oxygen flow needs to be regulated manually because no automatic oxygen controller is available. ▲

❖ **To regulate oxygen flow**

1. Set the pressure of the gas tank to 4 bar (400 kPa).
2. Adjust the O_2 pressure regulators to 120 kPa.
3. Open the O_2 purge from the autosampler and connect a flow meter.
4. Adjust the flow rate to 40-50 mL/min. See Figure 3-11.

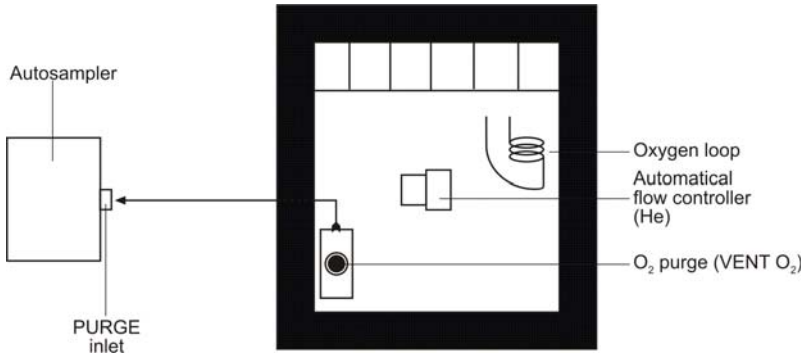


Figure 3-11. Elemental Analyzer 1110 and 2500 - top view

Additional Set Up Functions

Temperature

Three different temperatures may be set via the SET UP function of the touch panel:

- left: oxidation reactor
- right: reduction reactor
- oven: column

❖ **To set temperature**

1. Press **SET UP**. The parameter set described above will be displayed.
2. Select the parameter **SET TEMP** and press ▲ (that is, **ENTER**).
3. Select the left oven temperature using the ▲ and ▼ keys.

Note Temperatures below 400 °C and above 1100 °C are not valid. ▲

4. Switch to the right oven temperature using ▶. Set the temperature as discussed above.
5. Proceed the same way to set the column temperature.

Analysis Time

The parameter SET CYCL controls the Elemental Analyzer to be ready for the next acquisition.

Press **SET UP,** ▶, ▲ (that is, **ENTER**).

The parameter set is displayed:

END	CYCLE	OXY
sec	100	50

Move to CYCLE and select the time to end the cycle.

Note The total analysis time is set via Isodat. ▲

Injection of Oxygen

In case of most samples, additional oxygen is needed for the combustion process. Set the oxygen injection time via the SET CYCL parameter in the SET UP program.

❖ **To adjust oyxgen injection**

1. Press **SET UP**, ▶, ▲ (that is **ENTER**).
2. Move to **OXY** using ▶.
3. Select the time for oxygen injection, for example 50 s after acquisition started.

Note Excessive use of oxygen causes early exhaustion of the copper within the reduction reactor. ▲

❖ **To save oxygen overnight**

1. Activate **SPN FUN**.
2. Select **STBY** parameter and ▲ (that is **ENTER**).
3. Move to the parameter **O2 ON/OFF**.
4. Select **O2 OFF** to shut down the oxygen supply overnight.
5. Save by **SPN FUN**. The LED O2 CLOSED is now on.

Additional Applications of the SPC FUN Function

This section summarizes some additional applications of the SPC FUN function.

CNT (COUNTER)

Note The COUNTER function was invented to enable the system to count the number of measurements for each part of the system, for example the water trap. This is due to the fact that different parts of the system need to be replaced after different measurement cycles. After replacement of the respective system part the counter may be set to zero individually. ▲

❖ **To use the COUNTER function**

1. Move to the **CNT** parameter.
2. Press **SPC FUN**, ▲ (that is **ENTER**).

   The display will show:

A: nn	B: nn	C: nn
ZERO	ZERO	ZERO

3. Continue with ▶.

	D: nn	E: nn
ZERO	ZERO	ZERO

4. Set the counter to zero by ▲ (that is ENTER).

It is recommended to name the counter parameters as follows:

A	autosampler
B	oxidation reactor
C	reduction reactor
D	water trap
E	column

CLK (Set Clock)

Set clock	SET	ABSOLUTE	CLOCK
	Y = year	D = month/day	H = hour/min

Note It is recommended not to use the functions AUTRDY, MAIN ZERO and GAIN in conjunction with ConFlo III. ▲

❖ **To set the Elemental Analyzer to IRMS configuration**

1. Switch off the Elemental Analyzer.
2. Press ◀ and ▶ simultaneously.
3. Switch on the Elemental Analyzer while holding ◀ and ▶ pressed.
4. Select the relevant configuration:

   EA 1110NC MS ▶ or

   EA 2500NC MS by pressing the ▲ and ▼ keys.
5. Press **Start** to confirm.

For most applications, it is useful to operate with a manually set carrier flow.

❖ **To set the carrier flow to Manual mode**

1. Press **SET UP** ▶ ▶ ▶ ▶.

   SET FLOW and FIL ON are displayed. FLOW flashes.
2. Press **ENTER**.

   FLOW mL/min and He 60 are displayed.

3. Press ▼ several times until FLOW mL/min and He OFF are displayed.

4. Press **SET UP** to exit and save.

Sometimes, it may be useful to operate without an oven heater, for example dual measurement of N_2 and CO_2 in one run, if insufficient resolution is delivered by the GC column (the GC column is too short).

Note This procedure can be set only, if the Elemental Analyzer has already been set to IRMS configuration. ▲

❖ To set the TCD heater off

1. Select the parameter **SET TEMP** and press ▲ (that is ENTER).

2. Select **OVEN** and set the temperature to ***OFF*** using the ▲ and ▼ keys.

3. Press **SET UP** to confirm.

FlashEA

Note When operating Flash Elemental Analyzer, it is recommended to read the corresponding Operating Manual carefully. ▲

The Flash Elemental Analyzer is shown in two versions in Figure 3-12 and Figure 3-13.

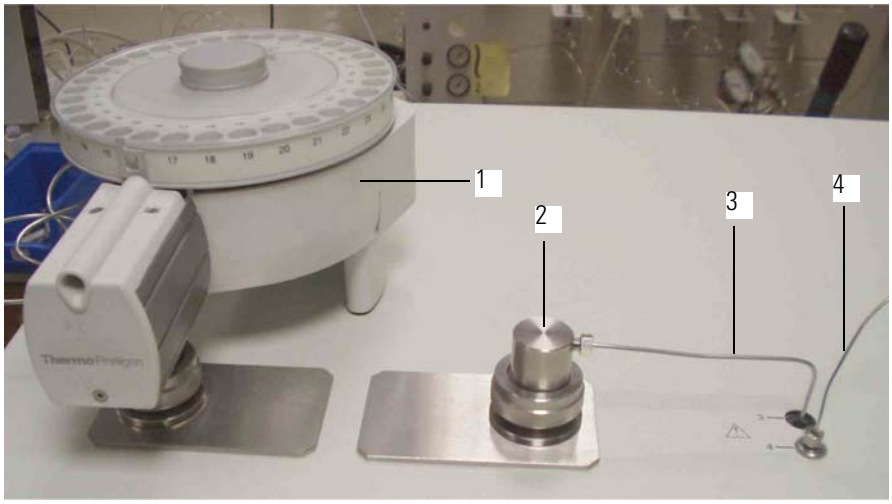
Figure 3-12. FlashEA (before summer 2003, with external carrier box outside) - front view (closed)

Labeled Components: 1=oxidation furnace, 2=reduction furnace, 3=half filled, 4=filled to top, 5=water trap, 6=pressure regulator for helium (and pressure display), 7=pressure regulator for oxygen (and pressure display)

Figure 3-13. FlashEA (since summer 2003, with external carrier box incorporated) - front view (open)

The GC column is located next to the water trap on the right. It is not shown in Figure 3-13.

Figure 3-14 shows the FlashEA in top view.



Labeled Components: 1=autosampler (here MAS200R)

Figure 3-14. FlashEA - top view

2 in Figure 3-14 must be screwed off when exchanging the reduction furnace. The capillary **3** comes from reduction reactor and leads to water trap. The capillary **4** comes from Elemental Analyzer and leads to ConFlo III.

Figure 3-15 depicts the principle of the FlashEA.

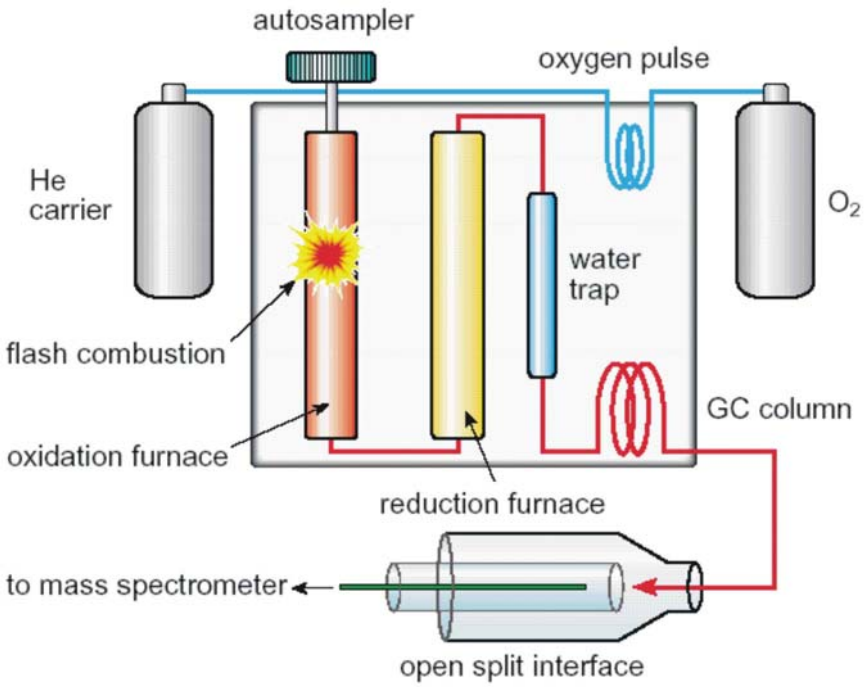


Figure 3-15. FlashEA - principle

The FlashEA can be run with autosamplers of different types. The most common autosamplers are:

- MAS200 (with an electronic control)
- AS200 (with a pneumatic control)
- AS128 (with a pneumatic control)

AS200 and AS128 need an external carrier box to operate with FlashEA, because they require compressed air supply.

Note The most recent version of Flash EA 1112 has built-in pressure regulators for helium and oxygen. The external carrier box is no longer necessary. With this Flash EA 1112 version, operating AS200 and AS128 is not possible anymore. ▲

Regulating Gas Pressure

The Flash EA is equipped with electronic flow controllers (EFC). To overcome these controllers, the carrier gas flow is set to 300 mL/min in the Eager software, and the actual flow is regulated manually via the pressure regulators.

Gas Connections and External Carrier Box

The gas connections and the external box are shown in Figure 3-16.

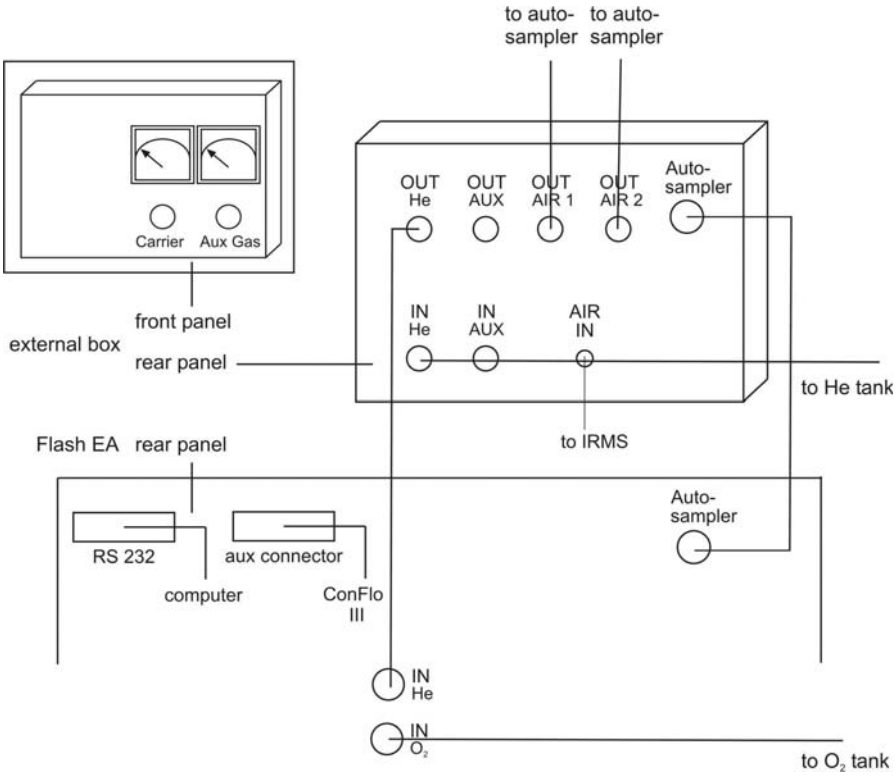


Figure 3-16. Gas connections and external box

Connecting Reactors

After the oxidation reactor has been packed, install it carefully.

❖ **To install the oxidation reactor**

1. Place the O-ring on top of the oxidation reactor as shown in Figure 3-19.
2. Carefully let the oxidation reactor down through the oven.
3. While twisting the reactor, gently push down the reactor in the lower tube connection with one hand on the upper side and the other hand on the lower side. See Figure 3-17.

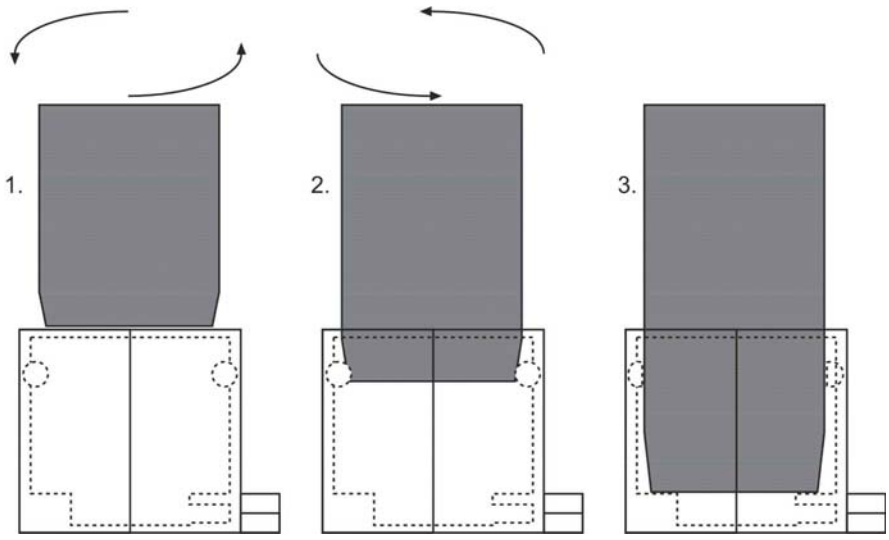


Figure 3-17. Pushing down reactor

Note Older versions of the Flash EA are equipped with bottom connectors. See Figure 3-17. Newer versions, however are treated according to Figure 3-19. ▲

After the lower connection is properly done, the autosampler can be installed on top of the reactor as shown in Figure 3-18.

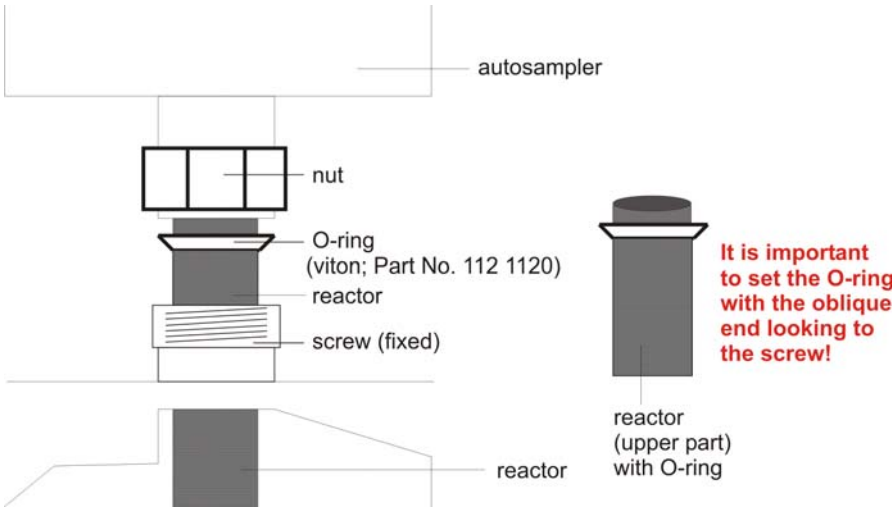


Figure 3-18. Installing autosampler on top of reactor

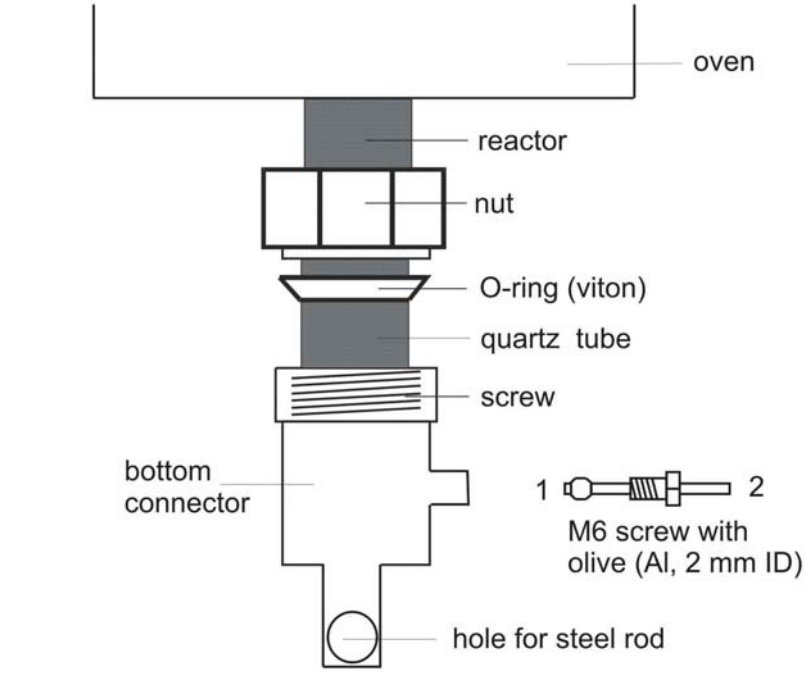


Figure 3-19. Preparing reactor - schematic

Figure 3-20. Preparing reactor - overview

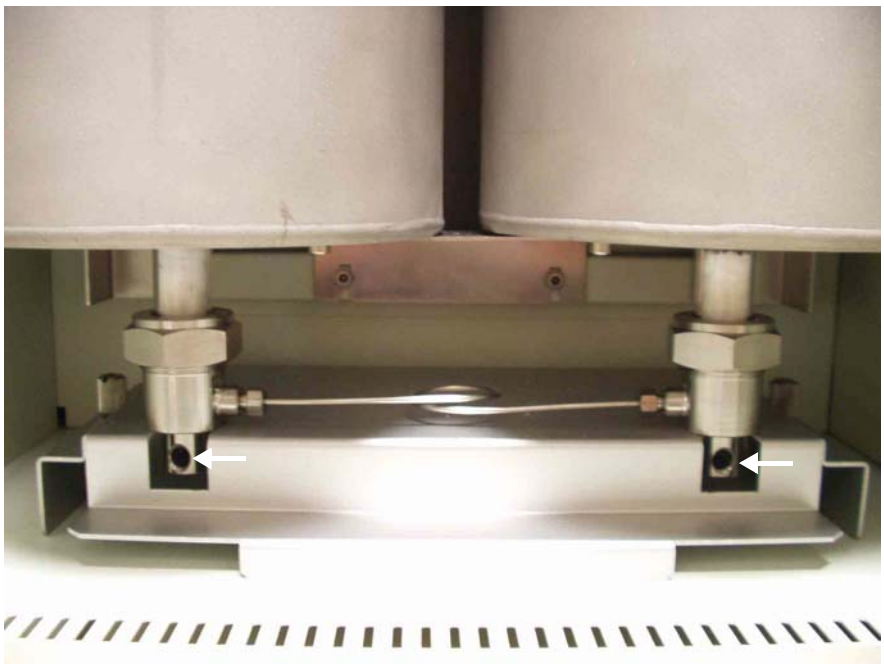


Figure 3-21. Preparing reactor - cut-out

1. Connect the M6 screw with 2 mm (ID, that is inner diameter) Al olive to the bottom connector (**1** in Figure 3-19).
2. Connect its other end (**2** in Figure 3-19) to the stainless steel capillary (2 mm) leading to the other reactor.
3. Insert the steel rod which is part of your equipment into the respective hole in order to apply counter-pressure when twisting the nut. See arrows in Figure 3-20 and Figure 3-21.

Note To obtain a good connection, ensure that the quartz tube and the O-ring are free of dust or other materials to avoid leaks. It is important to set the O-ring with the oblique end towards the screw! When using 1/16” capillaries, make sure that the Al olive also has 1/16” ID. ▲

Water Trap Filling

Figure 3-22 outlines the filling of the water trap. The tube has a length of 120 mm and an outer diameter of 15 mm. The thickness of the $Mg(ClO_4)_2$ zone varies depending on the length of the water trap.

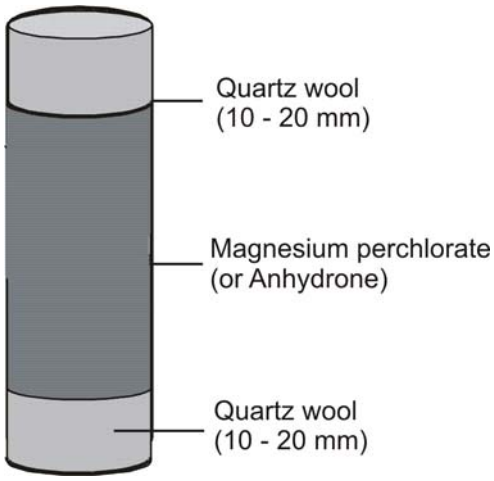
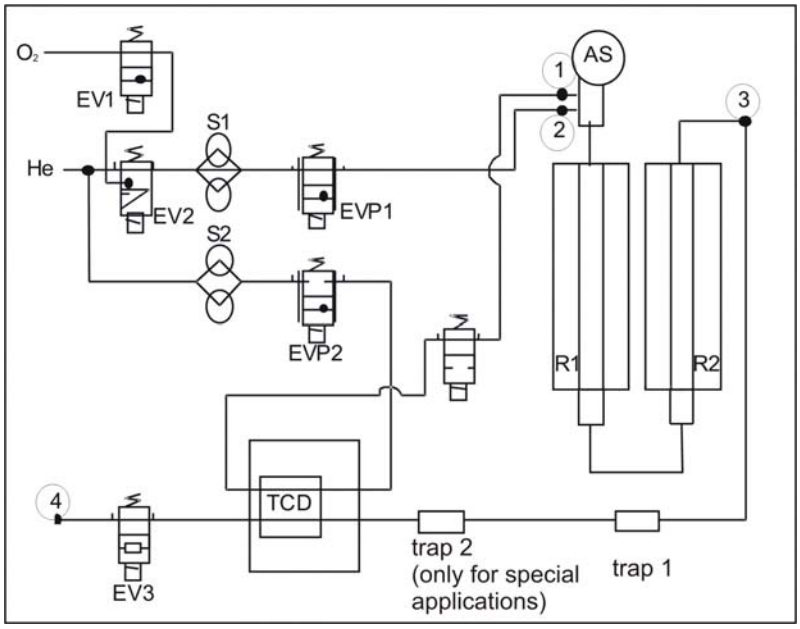


Figure 3-22. Water trap filling

Circuit Diagram for Using Both Reactors for CN Analysis

Figure 3-23 depicts the circuit diagram for using both reactors for CN analysis. For details, refer to the Elemental Analyzer manual of Thermo Fisher Scientific (Italy).



Labeled Components: 1=purge, 2=carrier gas, 3=reduction furnace exit to water trap, 4=vent to ConFlo III

Figure 3-23. Circuit diagram

Table 3-3. Components within circuit diagram

Component	Description
EV1	Two-way solenoid valve Controls O_2 inlet
EV2	Three-way solenoid valve Controls helium inlet and allows switching between helium and oxygen
EV3	Two-way solenoid valve Controls inlet of helium flowing back from the TCD detector analytical channel Normally open, but closed during leak test.
S1	Electronic flow sensor for helium as carrier gas and O_2 during sampling stage Cooperates with EVP1 electronic controller (proportional valve)
S2	Electronic flow sensor for helium as reference gas Cooperates with EVP2 electronic controller (proportional valve)
EVP1	Electronic flow controller for helium as carrier gas and O_2 Controls the flow rates of gases according to the set flow values
EVP2	Electronic flow controller for helium as reference gas Controls the flow rate of gases according to the required flow value

Flash Checklist

❖ **Before installing the Eager 300 software, work through the following checklist.**

1. Both reactors are filled and properly installed.
2. The water trap is filled and installed.
3. Helium and oxygen gas tanks are connected and pressure is adjusted. When running oxygen via pressure regulator, set the oxygen pressure to 3 bar (300 kPa).
4. All gas connections are established (purge, carrier, O_2 etc.).

5. When operating with the external carrier box: it is installed and connected to the autosampler plug of the Elemental Analyzer.
6. When operating the autosampler with an RS 232 cable (for example liquid autosampler): it is connected to a COM port of the computer.
7. The FlashEA is connected to the ConFlo III via two pin connector marked AUX connection and via RS 232 to a COM port of the computer.
8. When operating the autosampler using compressed air: the external box is connected to Mass Spectrometer compressed air, and the autosampler is connected to compressed air of the external box.
9. The FlashEA is connected to 220 V power supply, and the system is operating.

Installing Eager 300 Software

Note The Eager 300 software requires either Windows 95/98 or Windows NT or Windows XP operating systems. The free space on the hard disk of your computer must be at least 30 MB. ▲

❖ **To install the Eager 300 software**

1. When the CD is introduced into the CD drive of the computer, the installation menu is shown on the desktop. If the installation menu does not automatically appear, start the CD autorun program by the Windows **Start > Run** command.
2. Start the installation by clicking on the **INSTALL EAGER 300 FOR EA 1112** button.
3. Follow the instructions on the screen step by step.
4. At the end of the installation, in the **START PROGRAM EAGER 300** page, double-click on the **Eager 300 for Elemental Analyzer 1112** icon.

   Eager 300 proceeds with the registration and the activation of some drivers needed for the proper operatation of the software.
5. Click on **OK** to confirm the displayed answers step by step.
6. At the end of the operation, reboot your computer.
7. Start Eager 300 by selecting **Start > Programs > Eager 300 > Eager 300 for EA 1112**.
8. Double-click on the icon of the selected instrument.

The program is designed to work with four instruments. Each icon corresponds to one instrument. See Figure 3-24.

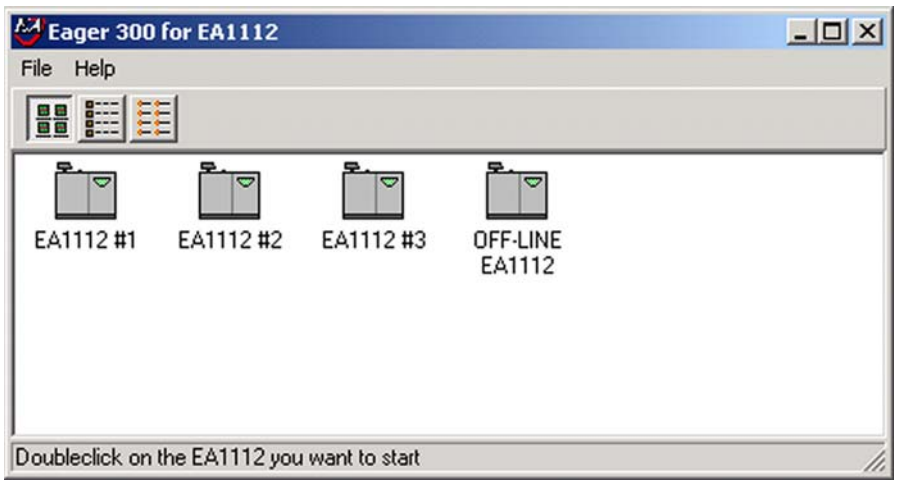
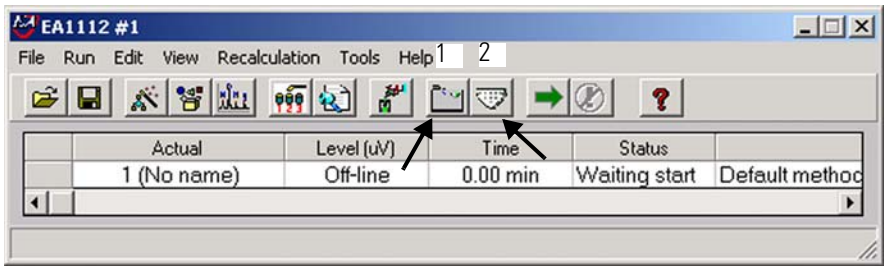


Figure 3-24. Starting Eager 300

9. Follow the displayed instructions. At the end of the software installation, the main menu shown in Figure 3-25 is displayed.



Labeled Components: 1=Edit Elemental Analyzer method command, 2=Elemental Analyzer status command

Figure 3-25. Eager 300 main menu

Getting Started with Eager 300 and FlashEA

Initial Setting

1. In the **Main Menu**, select **Edit Elemental Analyzer method** (that is **1** in Figure 3-25) or click on the corresponding button.

   Figure 3-26 appears. Set the parameters as shown there.

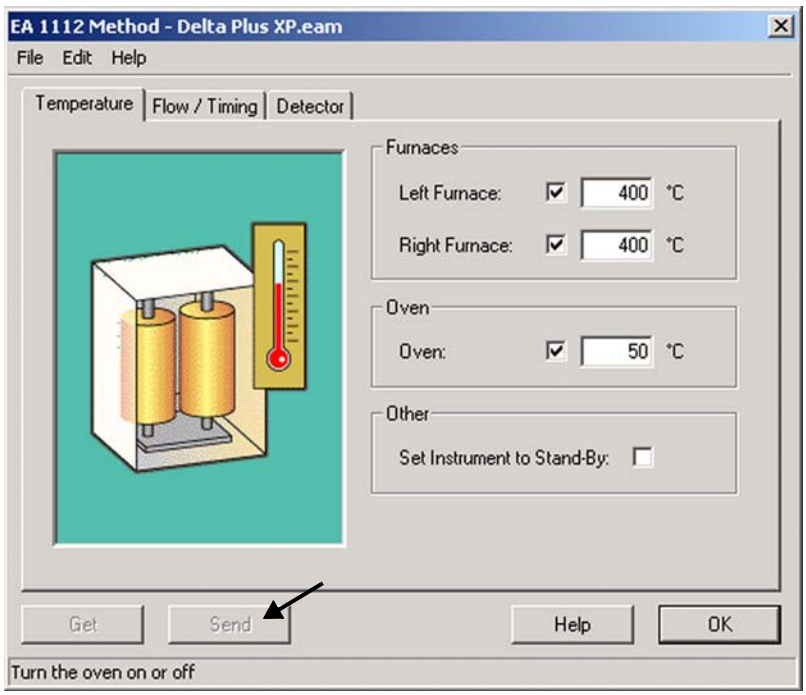


Figure 3-26. EA 1112 Method - Temperature tab

2. Click on the **Send** button. Select the **Flow/Timing** tab. See Figure 3-27. Set the parameters as shown there.

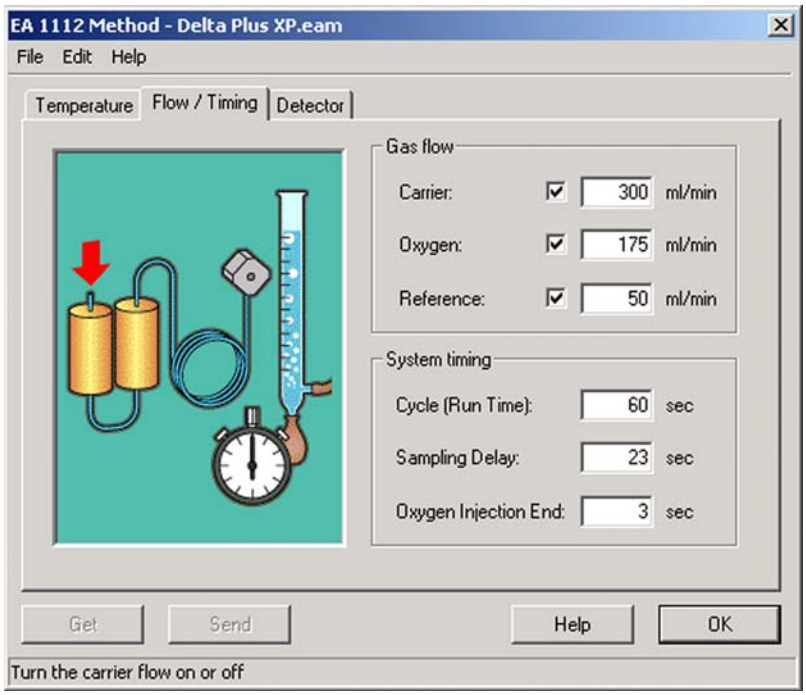


Figure 3-27. EA 1112 Method - Flow/Timing tab

3. To change the time of oxygen introduction, enter the desired value at **Oxygen Injection End**.

4. To change the oxygen flow rate, enter the flow value at **Oxygen**.
5. Click on the **Send** button.
6. Set the helium flow to approximately 1 bar (100 kPa, 90 mL/min) using the pressure regulator in the Elemental Analyzer or in the external box.

Note The helium flow can be checked at the vent of the FlashEA (**4** in Figure 3-23) using a flow meter or in the Elemental Analyzer status menu. The flow is set to 300 mL/min. The actual flow must be regulated via the pressure regulator. ▲

7. Click on the **OK** button.
8. The system reminds you to save the parameters. Click on the **OK** button and define it (for example **Setup**).

System Overview

In the Main Menu, select **Elemental Analyzer status** (that is **2** in Figure 3-25) or click on the corresponding button.

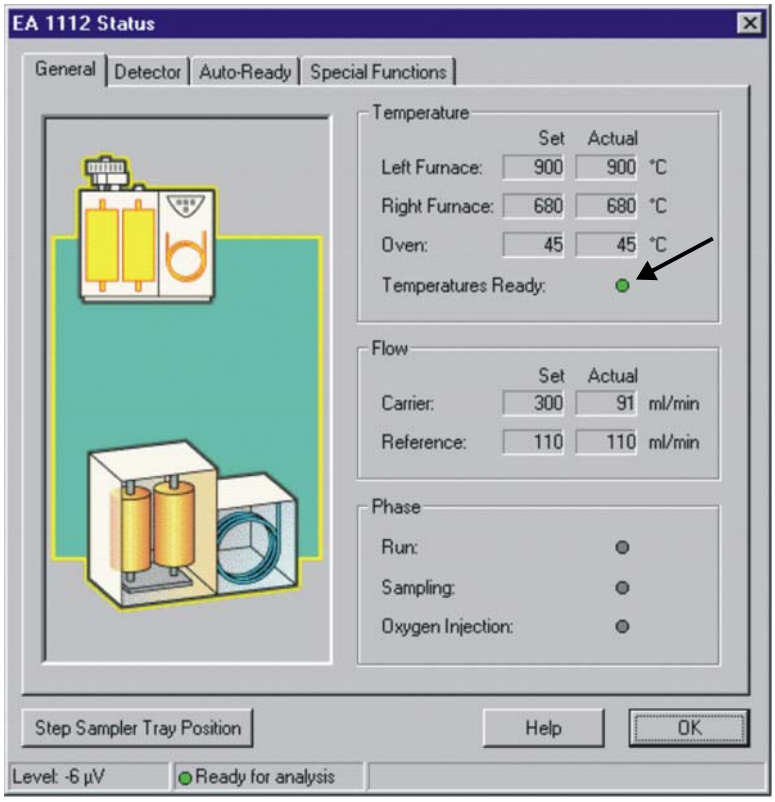


Figure 3-28. EA 1112 Status - General tab

Figure 3-28 shows the set parameters and the activity of the Elemental Analyzer. The Eager software offers an automatic leak test which can be performed when the Temperatures Ready LED is green.

Performing Leak Check

Note The leak check should be performed any time a component of the system is replaced. ▲

❖ **To perform a leak check**

1. Select the **Special Functions** tab. Figure 3-29 will be displayed.

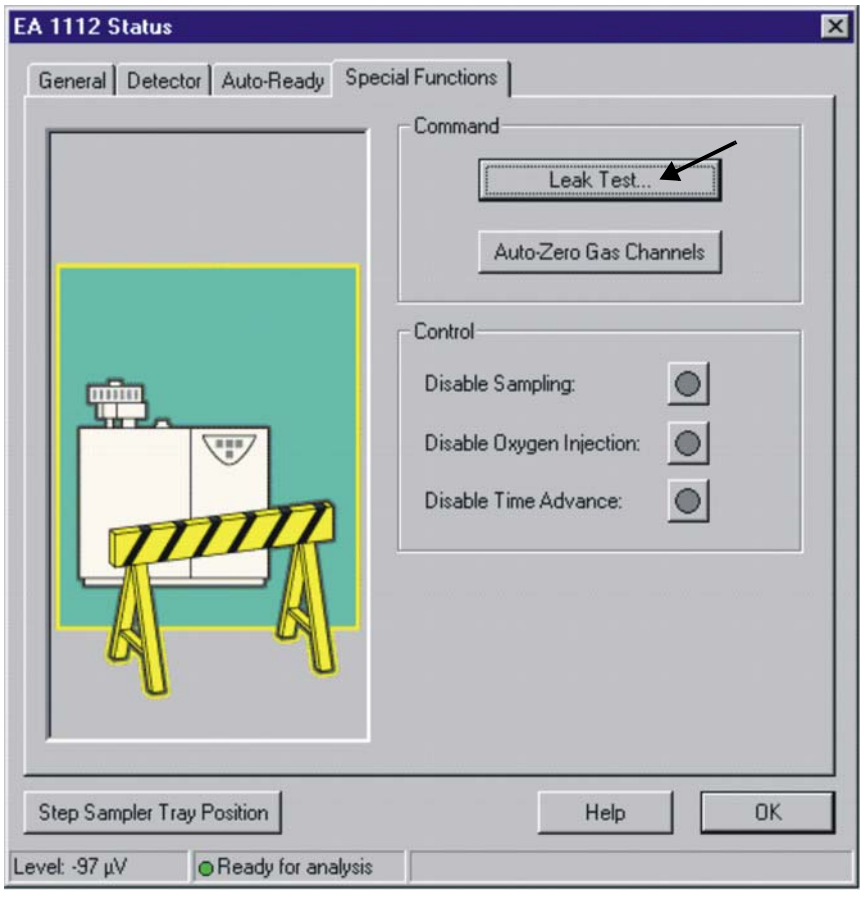


Figure 3-29. EA 1112 Status - Special Functions tab

2. Click on the **Leak Test** button.

Caution During the leak check period, ConFlo III is not purged with helium coming from the Elemental Analyzer. Therefore, it is recommended to put in the dilution capillary of ConFlo III to prevent a dry out of the IRMS. ▲

Figure 3-30 will be displayed.

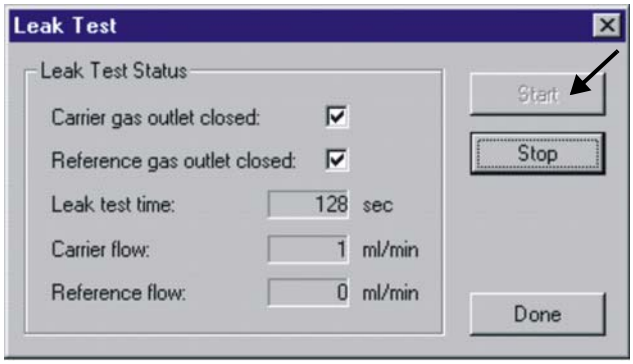


Figure 3-30. Leak Test window

3. Click on the **Start** button to begin the operation. A window will appear where you will be requested to perform the Autozero.

   After max 300-360 s (leak check time), the carrier flow and the reference flow must be within 0 and 3 mL/min. Higher flow values indicate that the system has a leak.

Note Leaks in the system are generally due to incorrect closure of the reactors and filter locking nuts. On rare occasions, leaks may be due to the autosampler. ▲

4. To terminate the leak check and restore the flow operating values, click on the buttons **Stop** and **Done**, respectively.

Note A passed leak check via Eager software does not necessarily indicate that maximum possible leak tightness was achieved. ▲

Take the automatic leak test as a rough and fast indicator for medium leaks.

Purging Oxygen

❖ **To purge oxygen**

1. Make sure all parameters are set as described above and the Temperatures ready LED in Figure 3-28 is green.
2. To start the Elemental Analyzer select **Run > Start single run acquisition** at the Main Menu. See Figure 3-25.
3. Repeat step 2 a few times to ensure that the oxygen line is purged properly.

Conditioning the System Overnight

Note The following procedure is necessary after the initial setting and from time to time after changing the reactors. ▲

❖ **To condition the system overnight**

1. In the Main Menu, select **Edit Elemental Analyzer method** or click on the corresponding button. See Figure 3-25.
2. Figure 3-26 appears. Set the parameters as summarized in Table 3-4.

Table 3-4. Parameter values in Temperature tab

Parameter	Value
Left furnace	1020 °C if using Cr_2O_3 900 °C if using CuO
Right furnace	650 °C
Oven	100 °C

3. Select the **Flow/Timing** tab. See Figure 3-27.
4. Set the parameters as summarized in Table 3-5.

Table 3-5. Parameter values at Flow/Timing tab

Parameter	Value
Carrier	300
Oxygen	off
Reference	off

Settings for Analysis

1. At the Main Menu, select **Elemental Analyzer method** or click on the corresponding button. See Figure 3-25.
2. Set the parameters as shown in Figure 3-31.

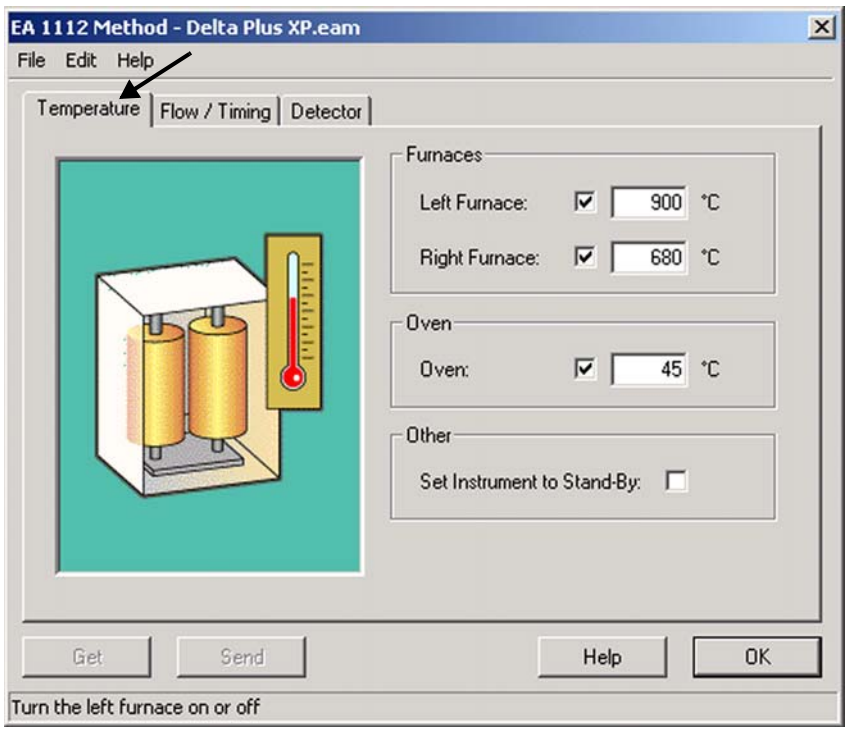


Figure 3-31. Settings for analysis - Temperature tab

The temperature of the left furnace depends on the reactor filling material: 1020 °C if using Cr_2O_3 or 900 °C if using CuO.

3. Select the **Flow/Timing** tab. Set the parameters as shown in Figure 3-32.

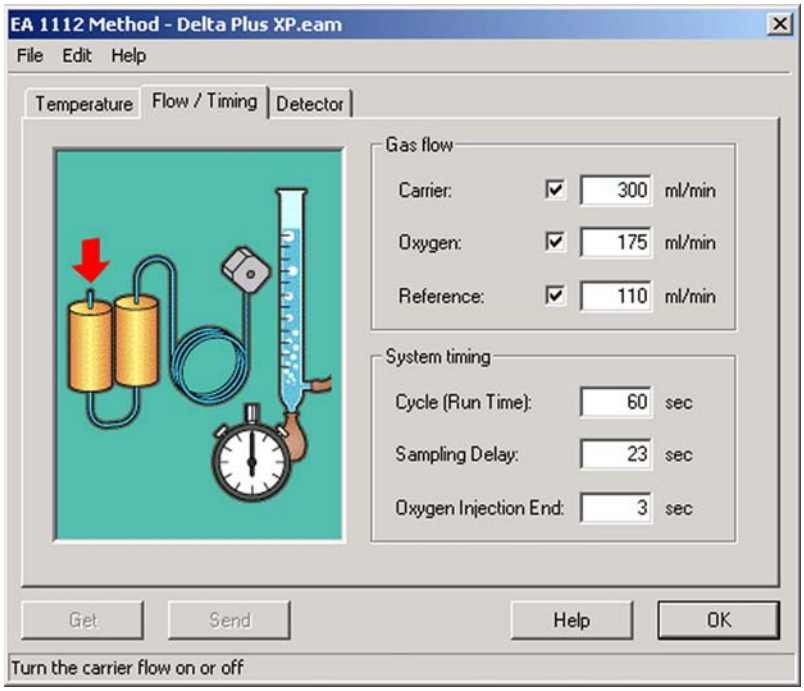


Figure 3-32. Settings for analysis - Flow/Timing Tab

4. To change the time of oxygen introduction, enter the desired value at **Sampling Delay**.

5. To change the oxygen dosage increase the flow rate of oxygen at **Oxygen** or increase **Oxygen Injection End**. It depends on the particular combustion. Here, just a recommendation is given.

6. To change the oxygen flow rate, enter the flow value at **Oxygen**.

7. Select **Main Menu** (Figure 3-25) and then **Elemental Analyzer status**.

   Figure 3-33 appears showing the set parameters and the activity of the Elemental Analyzer.

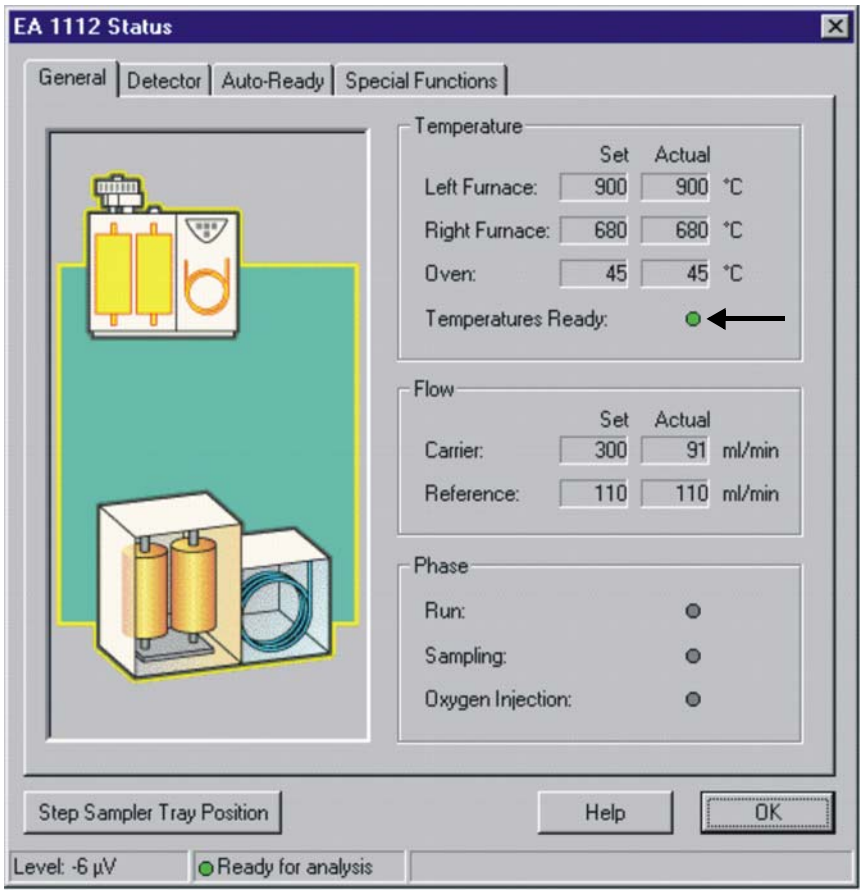


Figure 3-33. Settings for Analysis - General Tab

The system is ready to operate when the Temperatures Ready LED is green.

Chapter 4 Nitrogen Measurement

This chapter describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for nitrogen. Furthermore, it provides a glance at nitrogen input by autosampler and oxygen dosage. Hardware preparation, method editing and sequence editing before a nitrogen measurement is started are extensively treated. Finally, results of this measurement are displayed.

Note This chapter treats the principles of blank measurement, reference measurement and amount percent determination. As they can be generalized for nitrogen, carbon and sulfur, the chapter already contains the remarks valid for any of the three elements. ▲

The chapter treats the following topics:

Creating Gas Configuration for Nitrogen Measurement

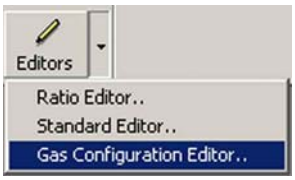
A gas configuration determines a combination of masses, which are collected in the cups, for evaluation of ratios and eventually δ values. The gas configuration is specific for the particular gas and is combined with a magnet field value taken from the mass calibration of your IRMS. The ratio groups determine the reported ratios of predefined masses.

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

For a ^{15}N measurement, a gas configuration must be available for m/z 28 (that is $^{14}N^{14}N$), m/z 29 (that is $^{15}N^{14}N$) and optionally m/z 30 (that is $^{15}N^{15}N$). Otherwise, it must be created as follows.

❖ **To create a gas configuration for nitrogen measurement**

1. Open Isodat **Acquisition**.



2. Open the **Gas Configuration Editor** (Figure 4-1).

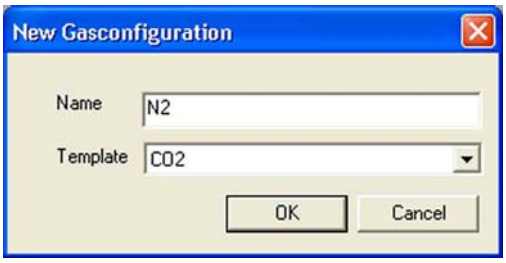
   It is only available, if no acquisition is running.

Figure 4-1. Gas Configuration Editor

Per default, the gas configuration CO2 is being created as the first one.

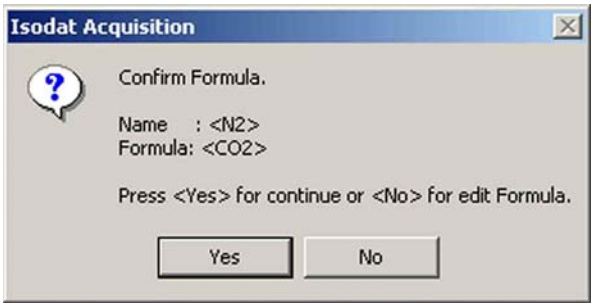
If the gas configuration N2 has already been created, it occurs in the list of Figure 4-1. However, if the gas configuration N2 has not been created yet, it does not occur in the list. In the latter case, proceed as follows.

3. Click on the **Add** button to add a new gas configuration.



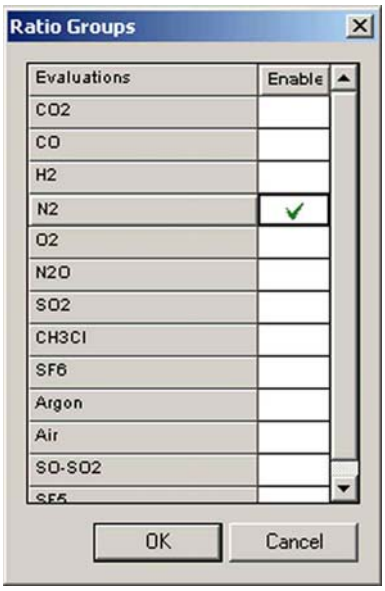
4. Type **N2** for the **Name**.
5. Select a Gas Configuration as **Template**, for example **CO2**.

   In the context menu, only the already existing gas configurations are displayed. When creating the first gas configuration, **CO2** is displayed.
6. Confirm by **OK**.



7. Type **No**.

   If you would type **Yes**, this would automatically mark the template (that is CO2) instead of N2 in the Ratio Groups window below.



8. Mark **N2**. If Ratio Groups other than N2 are marked, unmark them all.
9. Confirm by **OK**.

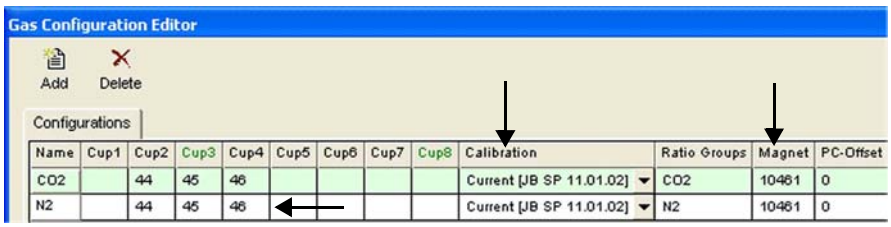


Figure 4-2. Creating new gas configuration

The new gas configuration N2 appears in the list as a row of its own. See Figure 4-2.

10. In the **Calibration** column of Figure 4-2 select your current calibration file.

Note Figure 4-2 shows a common cup configuration as used in most Delta mass spectrometers, that is universal triple collector. If you have a special cup configuration, the respective masses will be collected in other cups! ▲

11. In Figure 4-2 type in the correct masses (28, 29, 30 replace for example 44, 45 and 46) to the appropriate cups specific for your IRMS.

    When highlighting the specific gas configuration by a click on its row, the number of cups required for measurement is displayed together with the assigned masses (m/z 30 is only necessary for special applications). See Figure 4-3.

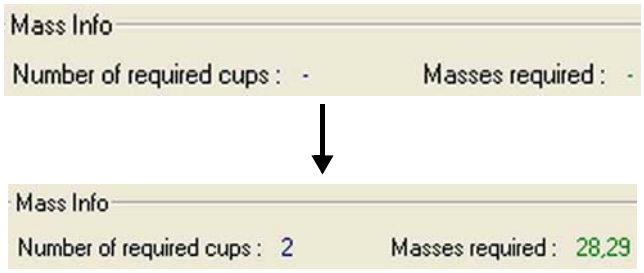


Figure 4-3. Required cups together with assigned masses

12. Select a calibration, which is valid for the selected cups.
13. Click on the **Save & Close** button 

.

Zero Enrichment of Nitrogen (Standard On/Off Test)

We assume that the user already has working experience with the ConFlo III interface and IRMS. It is recommended to perform a simple check in order to test the analytical condition of the ConFlo III and the IRMS before measuring any samples.The most important checks to test the analytical condition are zero enrichment and linearity test.

Note Use the method N2_zero.met from the Examples folder of the File Browser which will be described below only as a guideline! ▲

Instrument Tab

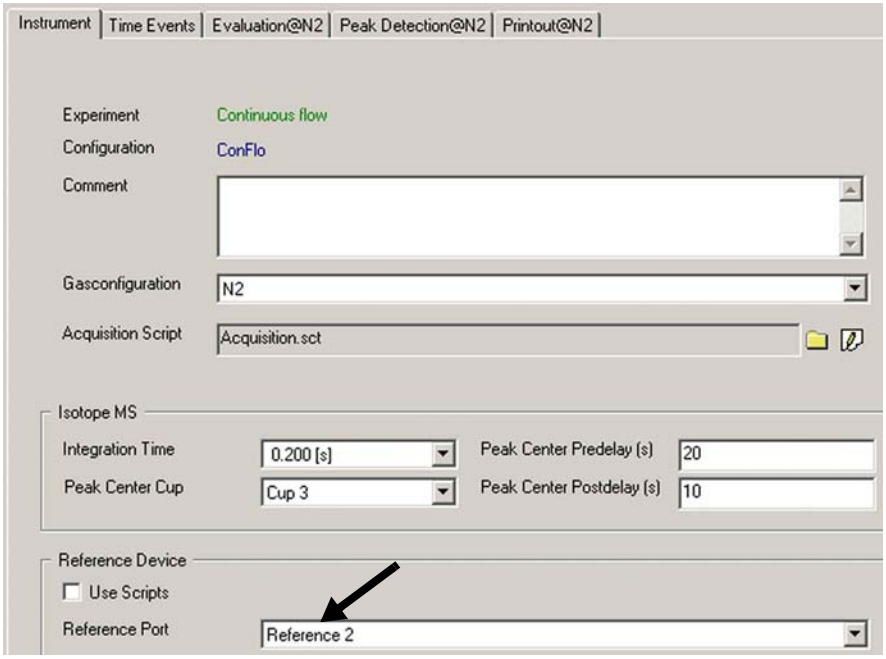


Figure 4-4. Zero Enrichment of nitrogen - Instrument tab

In Figure 4-4 select the **reference port** your reference gas is connected to at the ConFlo III interface (for example **Reference 2**).

Adapt the reference gas port to the respective column of the time events list: for example, if you choose **Reference 2**, the on-off entries must occur in the Reference 2-On column of the time events list. See Figure 4-5.

Time Events Tab

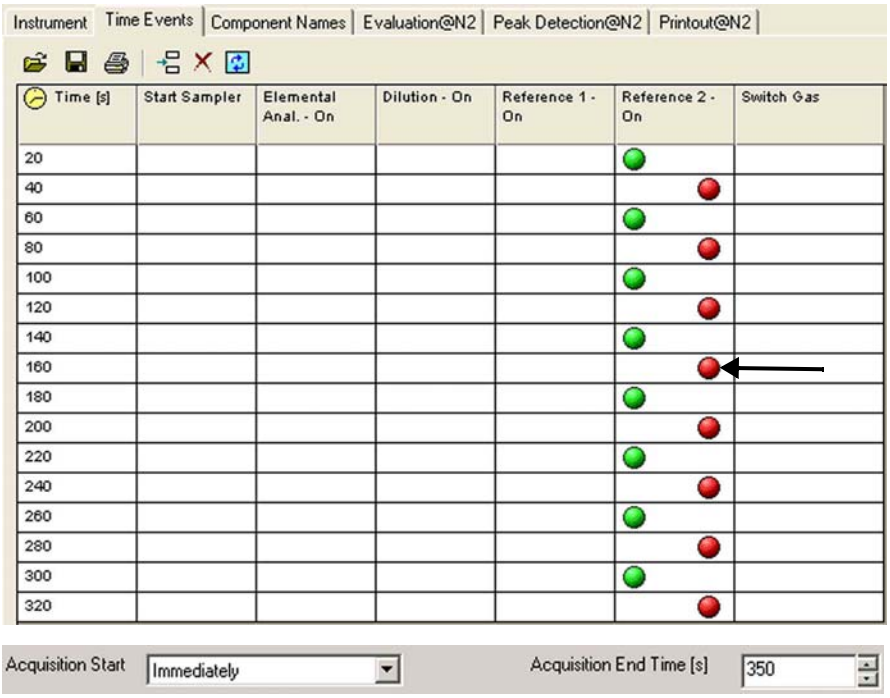


Figure 4-5. Zero Enrichment of nitrogen - Time Events tab

Recognize the eight on-off pulses shown in Figure 4-5 in the expected chromatogram, Figure 4-10. The off-time of the for example forth reference gas pulse is 160 s. See Figure 4-6.

Evaluation Tab

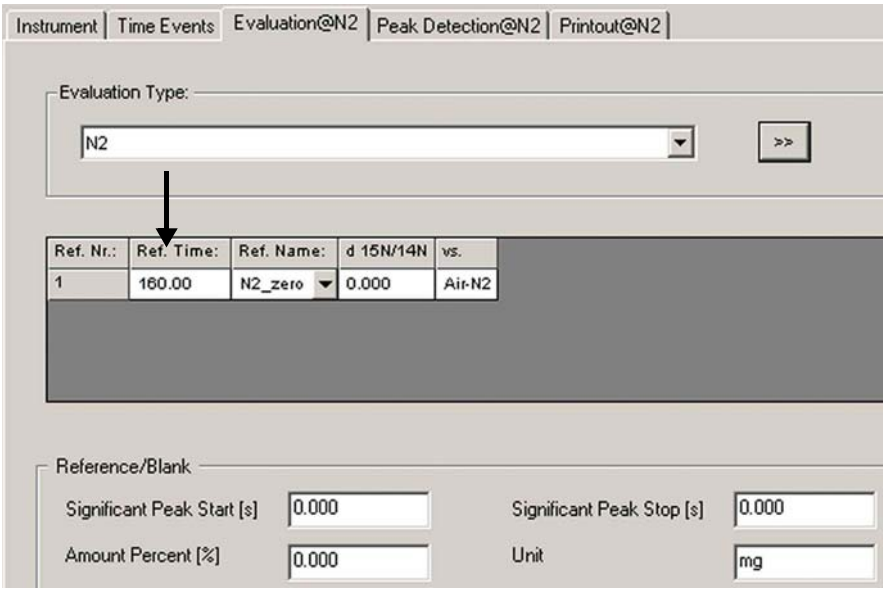


Figure 4-6. Zero Enrichment of nitrogen - Evaluation tab

Note At Ref. Time, the off-value of an arbitrary reference gas peak according to the Time Events list must be typed (for example 160 s as the off-value of the forth reference gas peak). See Figure 4-5. ▲

Peak Detection Tab

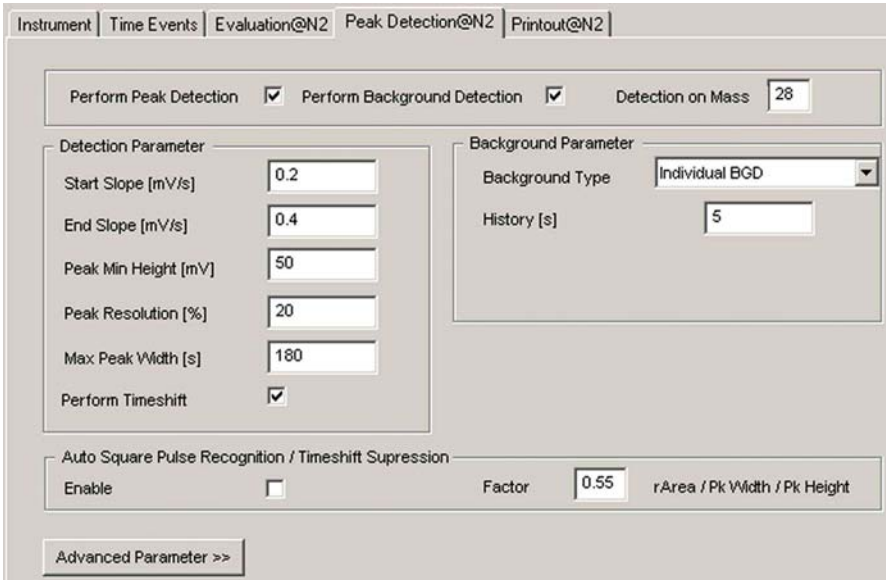


Figure 4-7. Zero Enrichment of nitrogen - Peak Detection tab

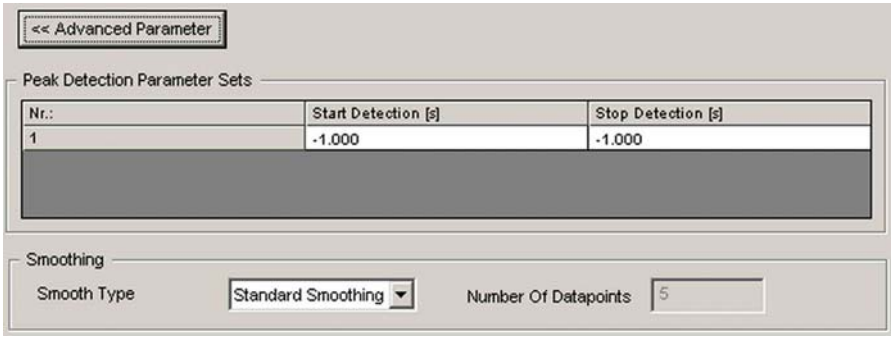


Figure 4-8. Zero Enrichment of nitrogen - Advanced Parameters in Peak Detection tab

Note A value of -1 denotes unlimited. ▲

Printout Tab

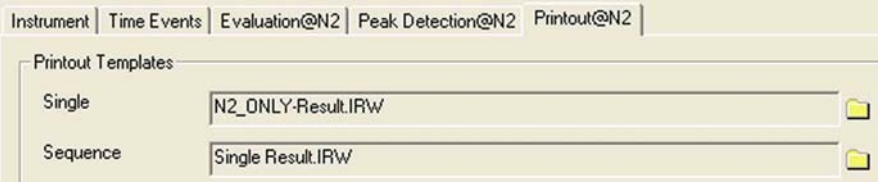


Figure 4-9. Zero Enrichment of nitrogen - Printout tab

14. At the corresponding pressure regulator of the ConFlo III, set the ion intensity of m/z 28 (that is $^{14}N^{14}N$) to 3-4 V.

15. Create a new sequence. Refer to "Defining a Sequence" on page 2-15.

16. Click on the **Start** button and confirm by **OK**.

The expected data after three or four measurements are given in Figure 4-10 (chromatogram) and Figure 4-11 (result grid).

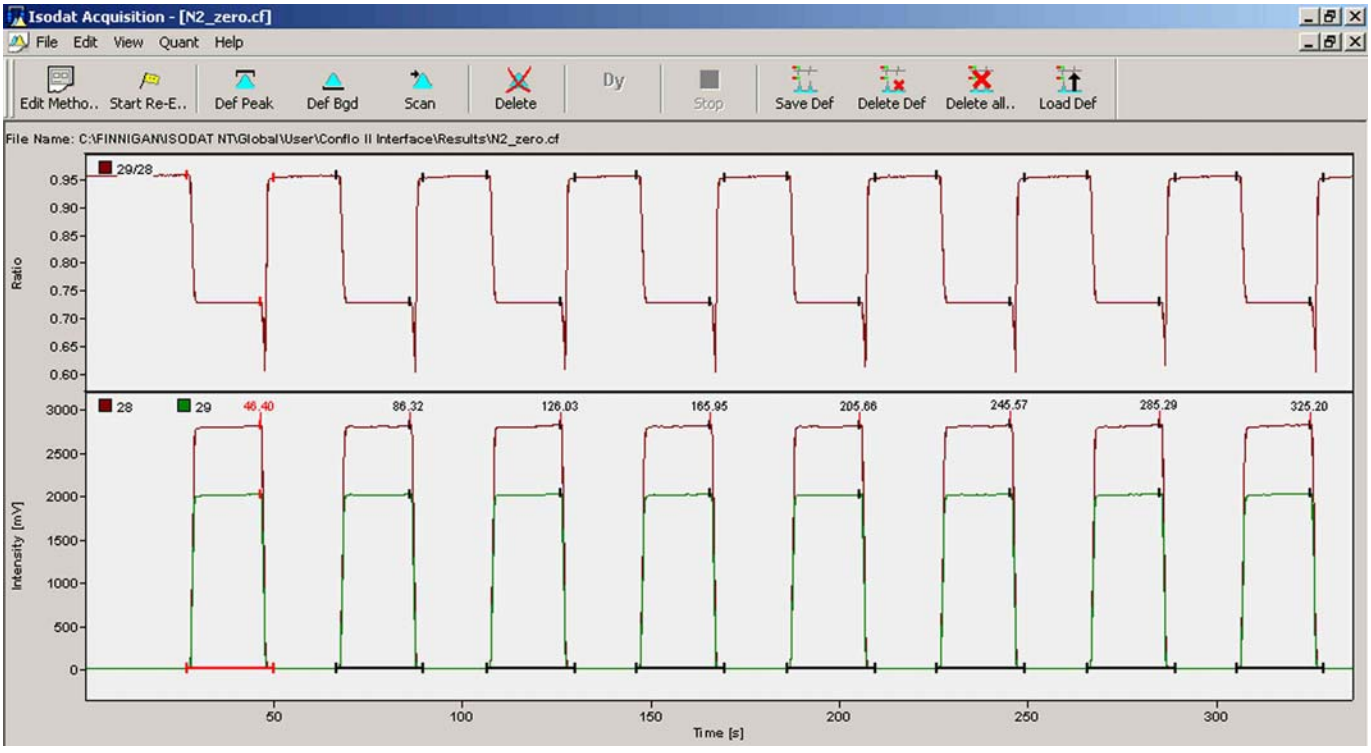


Figure 4-10. Zero Enrichment of nitrogen - chromatogram

Recognize the eight peaks shown in Figure 4-10 as the eight on-off pulses in the time events list, Figure 4-5.

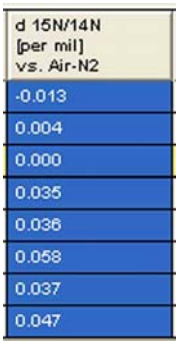
N2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 28 [mV]	Ampl. 29 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area All [Vs]	d 15N/14N [per mil] vs. Air-N2	AT% 15N/14N [%]
1	27.0	46.4	23.2	2805	2016	17.0	12.0	52.610	-0.013	0.366467
2	66.9	86.3	23.0	2805	2017	17.5	12.4	52.656	0.004	0.366473
3*	106.6	126.0	23.4	2812	2022	17.6	12.5	52.599	0.000	0.366472
4	146.5	165.9	23.2	2810	2020	17.6	12.5	52.725	0.035	0.366485
5	186.2	205.7	23.4	2805	2016	17.7	12.5	52.696	0.036	0.366485
6	226.1	245.6	23.2	2815	2024	17.8	12.5	52.822	0.058	0.366493
7	265.8	285.3	23.4	2813	2023	17.8	12.6	52.720	0.037	0.366485
8	305.8	325.2	23.0	2810	2020	17.8	12.6	52.829	0.047	0.366489

Figure 4-11. Zero Enrichment of nitrogen - result grid

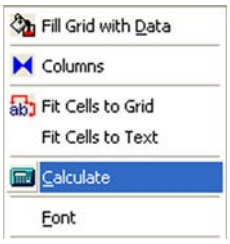
Note The standard deviation of δ15N (15N14N/14N14N) should be less than 0.05 ‰. See arrow in Figure 4-11. ▲

❖ **To obtain the standard deviation of all eight peaks**



1. Click on the column header of the **d 15N/14N [per mil] vs. Air-N2 column**.

   It will be highlighted.



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

The results will be calculated and summarized in Figure 4-12.

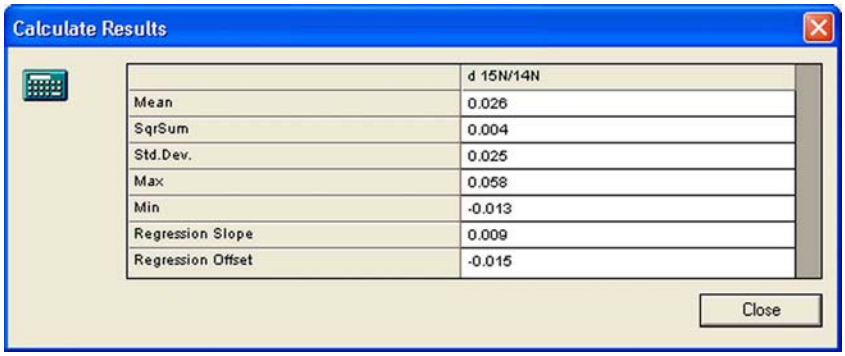


Figure 4-12. Calculation of results

Linearity Test of Nitrogen

Use the same method as defined for zero enrichment in "Zero Enrichment of Nitrogen (Standard On/Off Test)" on page 4-5. Start the acquisition as a single run. At each detection of a peak de- or increase the reference gas pressure at the ConFlo III.

The expected data after three or four measurements are shown in Figure 4-13 (chromatogram) and Figure 4-14 (result grid).

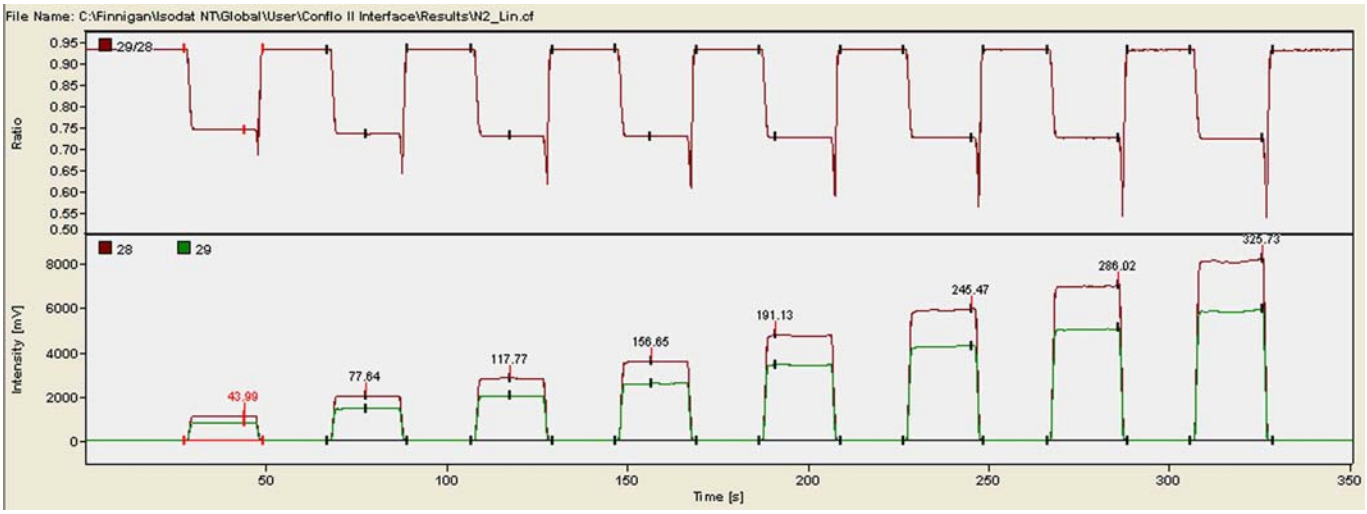


Figure 4-13. Linearity test of nitrogen - chromatogram

N2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 28 [mV]	Ampl. 29 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area All [Vs]	d 15N/14N [per mil] vs. Air-N2	AT% 15N/14N [%]
1	27.5	44.0	21.9	1109	800	36.8	27.8	20.617	0.050	0.366490
2	67.2	77.6	22.2	2008	1449	36.7	27.7	37.623	0.101	0.366509
3*	106.9	117.8	22.4	2809	2026	36.8	27.7	52.679	0.000	0.366472
4	146.8	156.6	22.4	3577	2581	36.9	27.8	67.121	0.016	0.366478
5	186.5	191.1	22.6	4758	3433	37.0	27.9	89.271	0.046	0.366489
6	226.5	245.5	22.4	5932	4281	37.1	28.0	111.019	0.097	0.366507
7	266.4	286.0	22.4	7029	5072	37.3	28.1	131.249	0.113	0.366513
8	306.1	325.7	22.8	8194	5913	37.5	28.2	152.882	0.170	0.366534

Figure 4-14. Linearity test of nitrogen - result grid

Note The linear regression of the δ15N/14N values vs. the working standard should be less than 0.06 ‰/V. ▲

Blank Measurement

This section outlines blank measurement of nitrogen and carbon, respectively. A blank measurement is an acquisition without a sample that can help to enhance precision. It is commonly used to determine the influence of a potential contaminant introduced with the sample, for example air or tin capsule. It is recommended to perform a blank measurement before a measurement of very small or highly enriched samples.

Nitrogen Input by Other Sources

Nitrogen is abundant in ambient air. Thus, for precise nitrogen measurement an absolutely leak tight system is necessary. If your system is sufficiently leak-tight, there are still two more possible sources of nitrogen input: autosampler and oxygen dosage.

Autosampler

❖ **To determine the nitrogen input of the autosampler**

1. Start a run as for blank measurement. Refer to "Blank Measurement" on page 4-12.

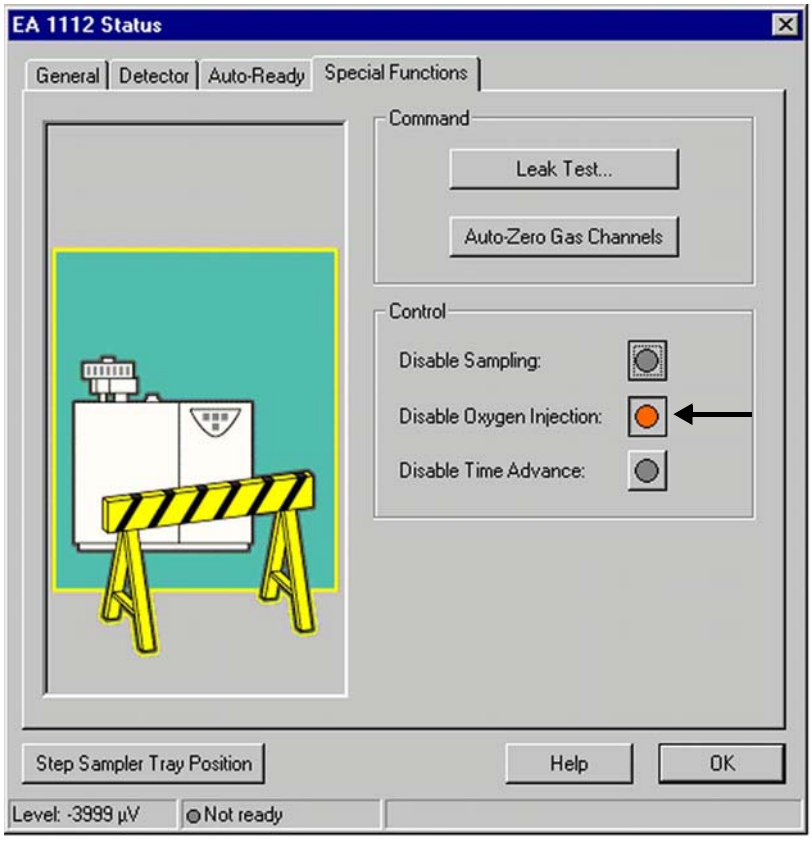


Figure 4-15. Disabling Oxygen Injection in Eager software

2. Before starting acquisition, switch to the Eager software and disable oxygen injection by clicking the **Disable Oxygen Injection** button. The button will turn into orange). See Figure 4-15.

   The intensity of m/z 28 should not increase more than 10 mV. If the measured value is 1.5 times higher than expected, increase the He purge and repeat the test.

Note Neither Reference 1 nor Reference 2 nor He dilution should be open during the test. See Figure 4-16. To activate the solid-autosampler manually click the button in Figure 4-16. ▲

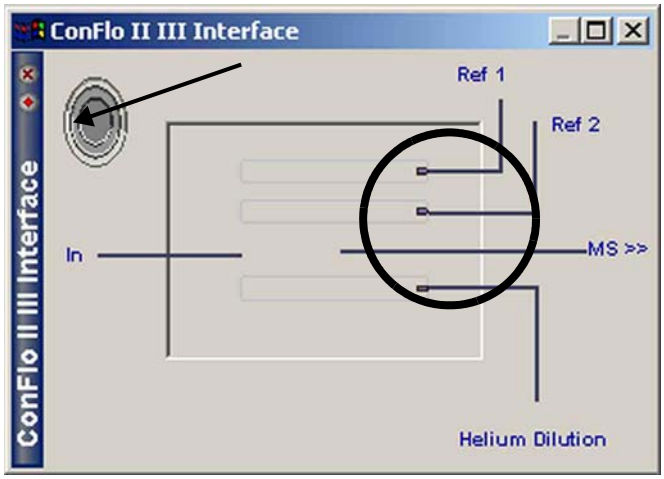


Figure 4-16. ConFlo II/III Interface window

Oxygen Dosage

❖ **To determine the nitrogen input of your oxygen**

1. Start a run as for a blank measurement. Refer to "Blank Measurement" on page 4-12.

2. Before starting the acquisition, switch to the Eager software and disable sampling by clicking on the **Disable Sampling** button. The button will turn into orange. See Figure 4-17.

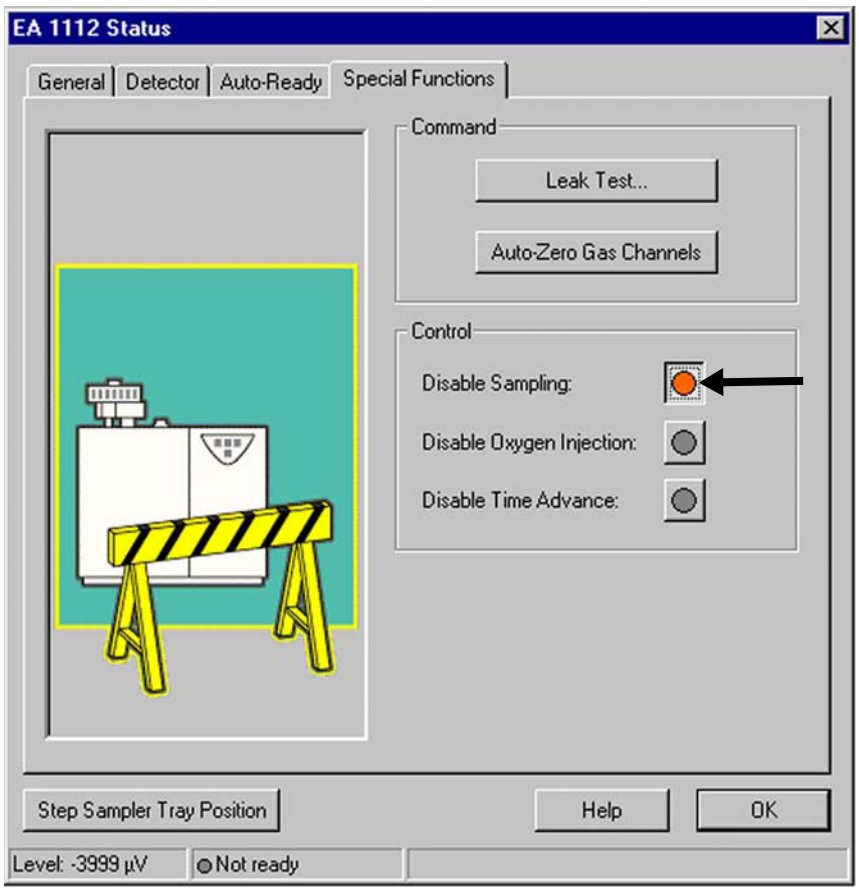


Figure 4-17. Disabling Sampling in Eager software

3. Proceed as described in "Autosampler" on page 4-12.

Principle of Blank Measurement

The resulting blank value is subtracted from the sample peak. Thus, the chronological order to proceed normally is:

1. Blank
2. Reference
3. Sample.

Blank values are stored in a separate database. In the result files, two δ values are given:

- the non-blank-corrected δ value and
- a blank-corrected δ value.

The blank value is stored in the database until a new blank value is determined.

❖ **To measure samples directly, that is without blank and reference before**

1. Load a chromatogram (that is a *.cf file) via the **Result** tab of the File Browser.

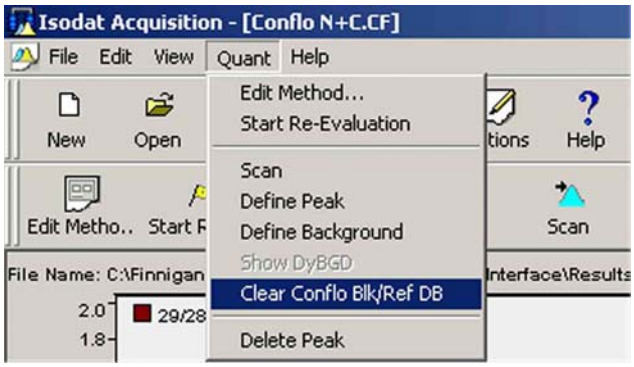


Figure 4-18. Deleting a database entry via Quant menu

2. Select **Quant > Clear ConFlo Blk/Ref DB**. See Figure 4-18.

Note Deleting the blank value will also delete reference values obtained during calibration for amount percent determination. Refer to "Amount Percent Determination" on page 4-28. ▲

In the following sections, the different commands for blank measurements will be explained.

Note In the Method column, select the IRMS method for the particular blank measurement type (for example N2_only.met for nitrogen, CO2_only-He.met for carbon). See Figure 4-19 and Figure 4-20. ▲

Blank Command

Figure 4-19. Blank measurement of nitrogen - Blank command

Figure 4-20. Blank measurement of carbon - Blank command

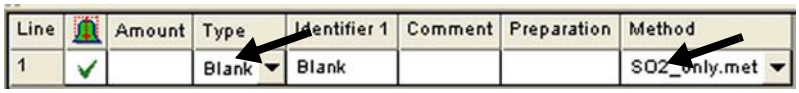


Figure 4-21. Blank measurement of sulfur - Blank command

From the **Type** Menu, select **Blank**. The previous blank value will be deleted. Instead, the result of this current blank measurement will be enlisted as new blank value.

At **Method**, choose the IRMS Method suitable for your blank measurement.

Start Blank Mean Command

Figure 4-22. Blank measurement - Start Blank Mean command

From the **Type** Menu, select **Start Blank Mean**. The previous blank value will be deleted. Instead, the result of this current blank measurement will be enlisted as new blank value. Further blanks can be added that are taken into account when determining the blank mean.

At **Method**, choose the IRMS Method suitable for your blank measurement.

Add Blank Mean Command

Figure 4-23. Blank measurement - Add Blank Mean command

At **Method**, choose the IRMS Method suitable for your blank measurement.

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

The old blank mean will be corrected using the new blank value to yield the new blank mean according to the equation:

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

with:

m_b' new blank mean

m_b old blank mean

n_b number of previously measured blank values (since blank start)

b new blank value

Procedure of Blank Measurement

❖ **To perform a Blank measurement**

1. Take an empty tin capsule and wrap it carefully.
2. Place the capsule in the autosampler.
3. For both carbon and nitrogen, adjust the system parameters as summarized in Table 4-1.

Table 4-1. Adjusting system parameters for Blank measurement

Parameter	Value
oxidation furnace	1020 °C for Cr_2O_3 filling (900 °C for Cu filling)
reduction furnace	650 °C
GC column	45 °C
He flow	80-100 mL/min
purge	110 mL/min (depending on autosampler and Elemental Analyzer)
reference gas	approximately 3.0 V
He flow at ConFlo III	0.8 bar

Nitrogen

Perform a normal run using a tin capsule without a sample in order to determine a blank value for the database.

Check the system performance with N_2 input from autosampler or N_2 input from O_2. See "Nitrogen Input by Other Sources" on page 4-12.

Carbon

Perform a normal run using a tin capsule without a sample in order to determine a blank value for the database.

Sulfur

A blank input of sulfur is not expected from air or capsules but may arise from impurities in the copper. Thus, the copper quality can be tested by starting a single measurement without sample material.

Defining a Method for Blank Measurement

Figure 4-24. Method for Blank measurement - blank information

Note In case of blank measurements, only Significant Peak Start and Significant Peak Stop are important and will be considered. The Amount Percent value, however, is unimportant. However, in case of reference measurements, all four parameters shown above are important and will be considered (including the Amount Percent value). See Figure 4-24. ▲

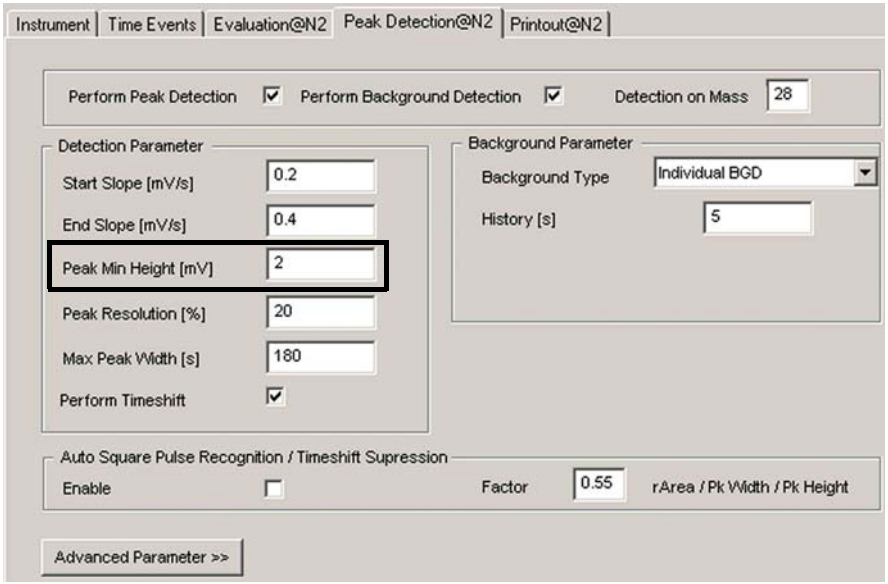


Figure 4-25. Method for Blank measurement - Peak Min Height

Note Set Peak Min Height (mV) to 2 as shown in Figure 4-25! If the blank is smaller, it will not be detected and no database entry will be created. ▲

Defining a Sequence for Blank Measurement

To define a sequence for Blank measurement see Figure 4-19, Figure 4-22 and Figure 4-23.

Note The ion intensity of blank for mass 28 should be less than 15 mV or the area less than 0.3 Vs. If the measured value is by the factor 1.5 higher than expected, increase or decrease the purge. ▲

Note The ion intensity of blank for m/z 44 should be less than 10 mV or the area less than 0.2 Vs. If the measured value is by the factor 1.5 higher than expected, your current batch of capsules may not be suitable to perform measurements. In this case, use a batch of capsules containing less carbon. ▲

Note The ion intensity of blank for m/z 64 should be less than 10 mV or the area less than 0.2 Vs. If the measured value is by the factor 1.5 higher than expected, your current reducing agent copper may not be suitable to perform measurements. In this case, use another batch of highly purified copper.. ▲

Results of Blank Measurement

The blank values for the following calculation are stored automatically.

Nitrogen

Figure 4-26 shows the sequence line for blank measurement of nitrogen.

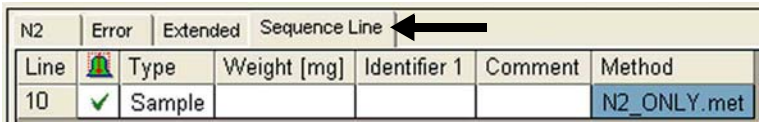


Figure 4-26. Blank measurement of nitrogen - sequence line

A typical chromatogram for blank measurement of nitrogen is depicted in Figure 4-27, whereas Figure 4-28 shows the related result grid.

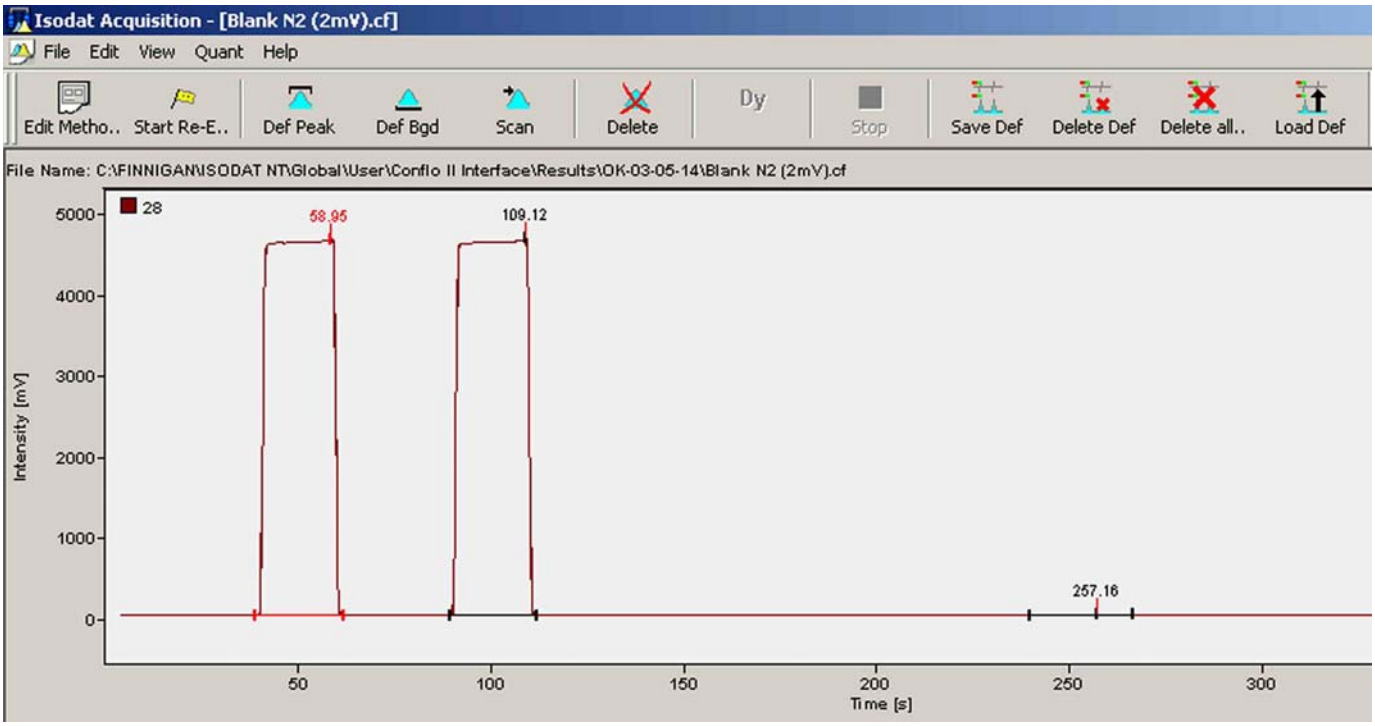


Figure 4-27. Blank measurement of nitrogen - chromatogram

N2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 28 [mV]	BGD 28 [mV]	d 29N2/28N2 [per mil] vs. N2 Lab.Tank	d 15N/14N [per mil] vs. Air-N2	AT% 15N/14N [%]
1	39.4	59.0	22.9	4629	47.3	-1.235	-1.235	0.366021
2*	89.6	109.1	22.7	4640	47.2	-1.250	-1.250	0.366016
3	239.9	257.2	26.7	2	47.1	-174.894	-174.894	0.302572

Figure 4-28. Blank measurement of nitrogen - result grid

Carbon

Figure 4-29 shows the sequence line for blank measurement of carbon.

CO2 | Error | Extended | Sequence Line

Line		Amount	Type	Identifier 1	Preparation	Method
1	✓		Start Blank Mean	Blank		CO2_only.met

Figure 4-29. Blank measurement of carbon - sequence line

A typical chromatogram for blank measurement of carbon is depicted in Figure 4-31, whereas Figure 4-31 shows the related result grid.

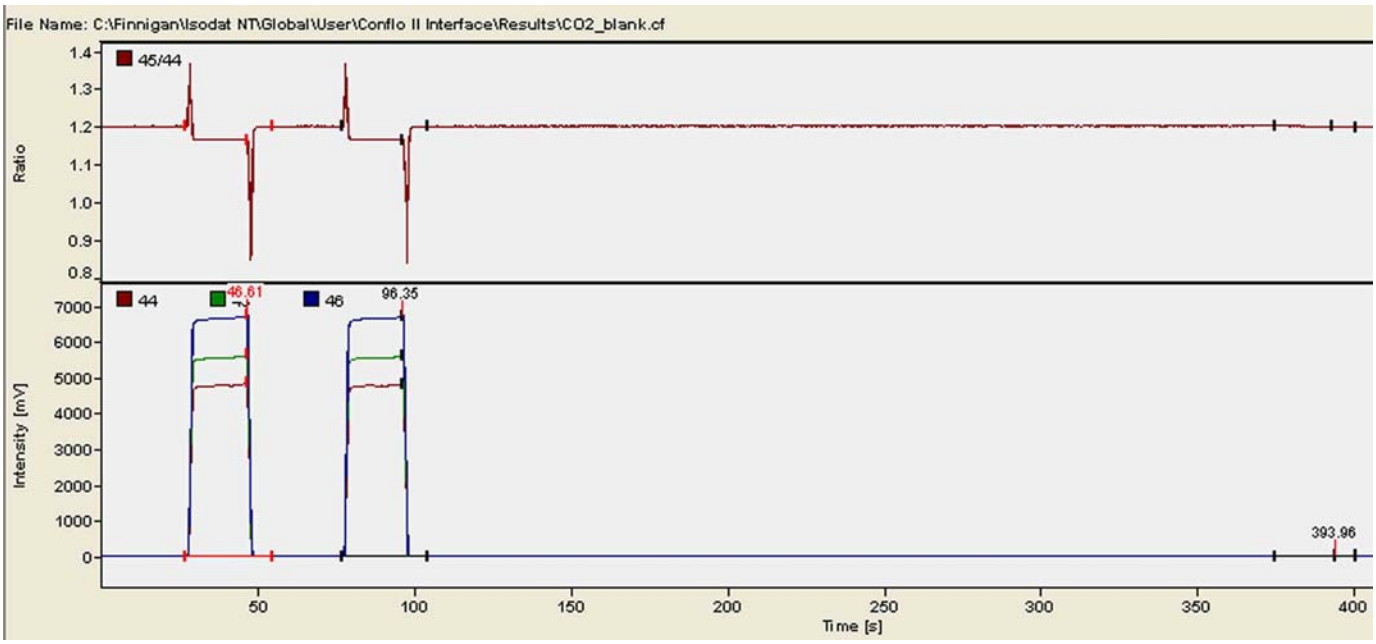


Figure 4-30. Blank measurement of carbon - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	BGD 44 [mV]	BGD 45 [mV]	BGD 46 [mV]	Area All [Vs]	Amt% [%]	d 13C/12C [per mil] vs. VPDB
1	27.2	46.6	27.6	4842.6	5636.7	1.9	2.4	3.0	90.837	-	-26.020
2*	76.9	96.3	27.6	4823.4	5613.8	2.1	2.6	3.2	90.821	-	-26.100
3	374.9	394.0	25.9	6.8	7.9	0.9	1.2	1.4	0.122	-	-23.694

Figure 4-31. Blank measurement of carbon - result grid

Sulfur

Figure 4-32 shows the sequence line for blank measurement of sulfur.

SO2 | Error | Extended | Sequence Line

Line		Amount	Type	Port	Identifier 1	Preparation	Method
21	✓		Sample		blank		SO2 short.met

Figure 4-32. Blank measurement of sulfur - sequence line

A typical chromatogram for blank measurement of sulfur is depicted in Figure 4-33, whereas Figure 4-34 shows the related result grid.

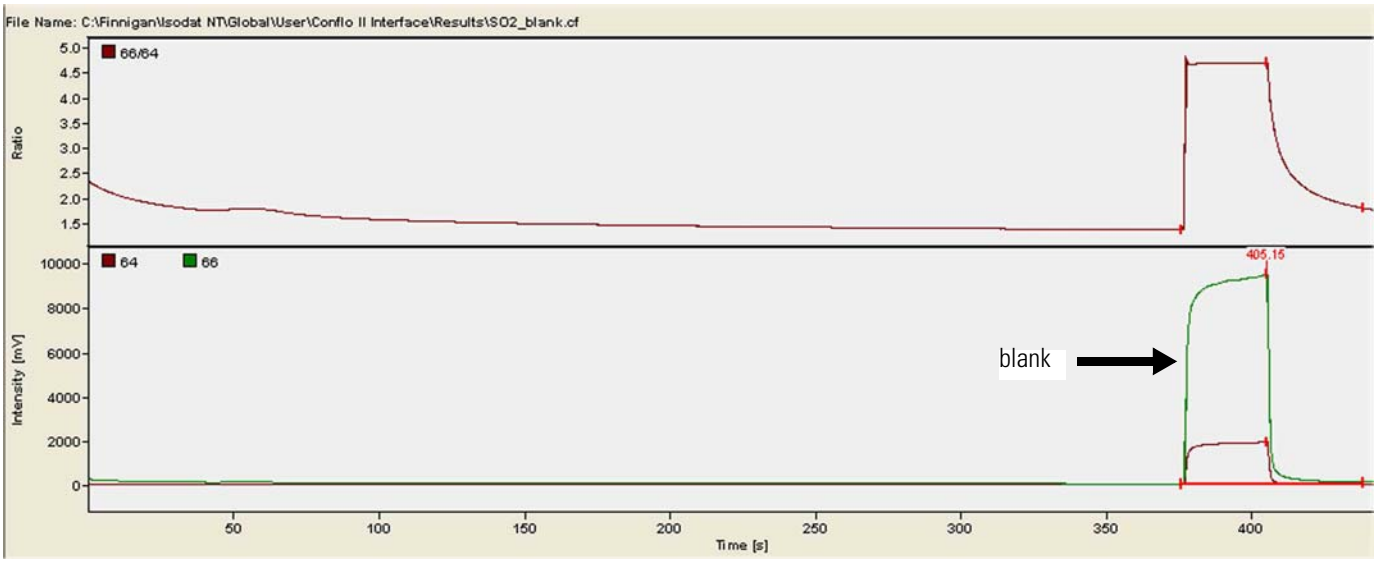


Figure 4-33. Blank measurement of sulfur - chromatogram

SO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 64 [mV]	BGD 64 [mV]	Area All [Vs]	δ 66 [‰]	δ 34S [‰] vs. VCDT	Amount% [%]
1*	376.1	405.1	62.5	1932	12.4	56.369	8.130	8.130	0.0000000

Figure 4-34. Blank measurement of sulfur - esult grid

Reference Measurement

Reference measurements are a means to determine the δ value of your reference gas and amount percentages (that is weight percentages, wt %) of unknown samples. Therefore, the system needs to be calibrated using a sample of known δ value and a sample of known amount percentage (not necessarily the same).

Reference Gas Calibration

The combination of Elemental Analyzer, ConFlo III as an interface and finally the mass spectrometer has become standard for isotope ratio determination of combustible bulk samples. Reference gas calibration can be generalized for both N_2, CO_2 and SO_2. As an example for reference gas calibration, the determination of isotope ratios requires a standard to calculate the δ value.

Nitrogen

To calibrate this reference gas versus atmospheric air, you must combust an internationally valid reference like the IAEA N1 (ammonium sulfate): IAEA N1 δ15N = 0.4 ‰ vs. atmospheric air.

Carbon

To calibrate this reference gas versus PDB, you must combust an internationally valid reference like the IAEA-C-6 (sucrose): δ13C = -10.43 ‰ vs. PDB.

Sulfur

The determination of $\delta\ ^{34}S/^{32}S$ ratios requires a standard to calculate the δ value. To calibrate this reference gas versus **VCDT** you must combust an internationally valid reference like NBS 123:

$$\text{NBS 123: } \delta^{34}S = 17.088\ ‰ \text{ vs. CDT}$$

The measurement is performed using the ratio of masses 66 and 64. Therefore, the following approximate formula must be applied:

$$\delta^{34}S/^{32}S = 1{,}09 \times \delta^{66}SO_2/^{64}SO_2$$

Combining both equations yields:

$$1{,}09 \times \delta^{66}SO_2/^{64}SO_2 = 17.088\ ‰ \text{ vs. CDT}$$

and finally:

$$\delta^{66}SO_2/^{64}SO_2 = 15.677 \text{ ‰ vs. CDT}$$

System Settings

Table 4-2 summarizes system settings for reference gas calibration.

Table 4-2. System settings for reference gas calibration

Parameter	Value
oxidation furnace	1020 °C for Cr_2O_3 filling 1020 °C for WO_3 filling (sulfur) (900 °C for Cu filling)
reduction furnace	650 °C
GC column	45 °C 100 °C (sulfur)
He flow (Elemental Analyzer)	80 - 100 mL/min
purge	110 mL/min (depending on autosampler and Elemental Analyzer)
reference gas is set to	approximately 3 V
He flow at ConFlo III	0.8 bar
oxygen	175 mL/min
cycle	60 s
sampling delay	23 s
oxygen injection	3 s

1. Define a method, for example N2_only.met for nitrogen, CO2_only.met for carbon or SO2_only.met for sulfur.
2. In its Evaluation tab, type the retention time of the sample peak into the **Ref. Time** column (for example 200 s, as example for nitrogen, see Figure 4-36 or 350 s as example for sulfur).
3. Type the δ value into the

- **d 15N/14N** column (for nitrogen, for example 0.4) or into the
- **d 13C/12C** column (for carbon) or into the
- **d 34S/32S** column (for sulfur, for example 15.68)

Note The entry in the Ref. Name column changes to User Defined. See Figure 4-35. ▲

Ref. Nr.:	Ref. Time:	Ref. Name:	d 15N/14N	vs.
1	200.00	User Defined	0.400	Air-N2

Figure 4-35. Method for reference measurement - Evaluation tab for nitrogen

Figure 4-36 shows the chromatogram of a reference measurement for nitrogen.

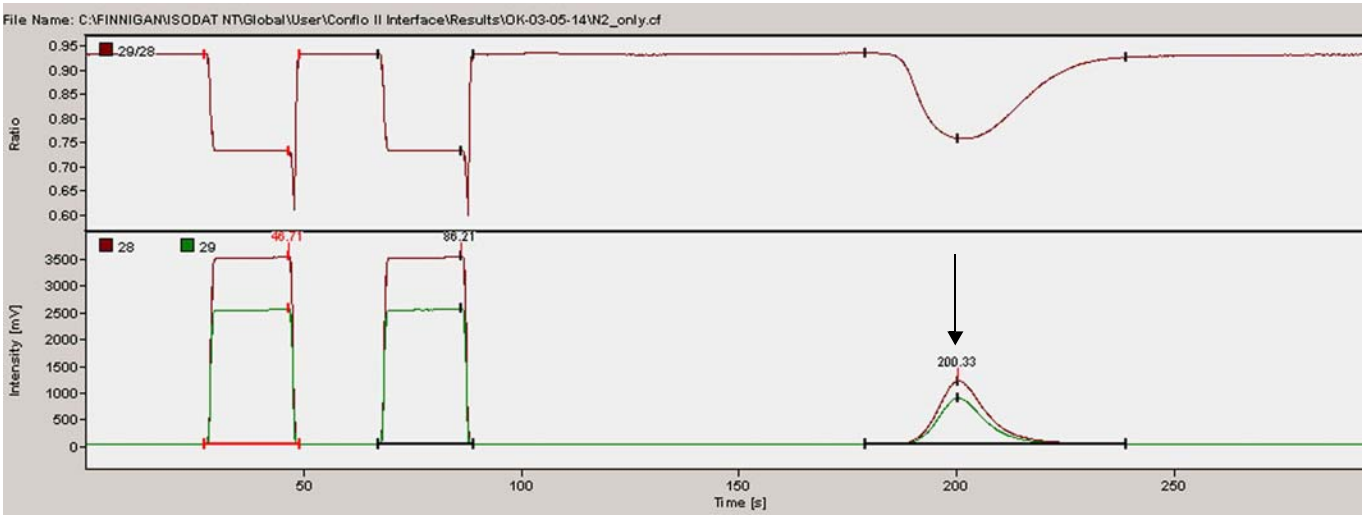


Figure 4-36. Reference measurement - chromatogram for nitrogen

4. Define a sequence. Refer to "Defining a Sequence" on page 2-15.
5. Put for example 346 µg ammonium nitrate IAEA N1 in a tin capsule, wrap it carefully and place it in the autosampler (for nitrogen).

   Put for example 120 µg IAEA-C-6 sucrose in a tin capsule, wrap it carefully and place it in the autosampler (for carbon).

   Put for example 200 µg NBS 123 in a tin capsule, wrap it carefully and place it in the autosampler (for sulfur).
6. Start the acquisition and repeat the measurement a few times.

   The δ values of the reference gases are now determined vs. the sample peak.
7. Calculate a mean value of all reference gas pulses and assign this value to your reference gas.

8. Open the Standard Editor.

   The standard gas database will be shown. See Figure 4-37.

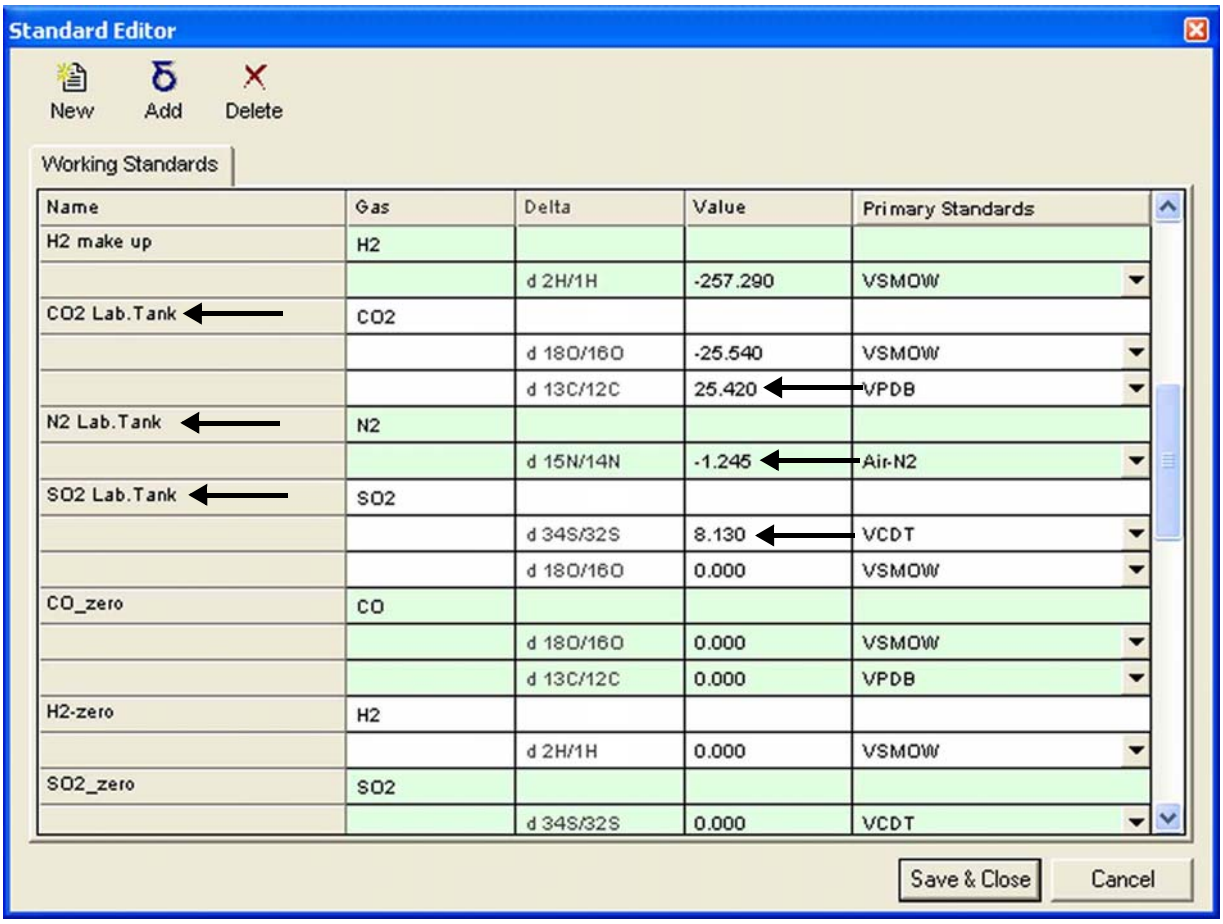


Figure 4-37. Storing mean value in standard gas database

9. Enter the value calculated in step 7 in the standard gas database:

- The calculated $\delta\ ^{15}N/^{14}N$ of standard gas is - 1.24 ‰ vs. air in the first measurement and - 1.25 ‰ vs. air in the second measurement. The mean value of - 1.245 ‰ vs. air is taken for later application and must therefore be stored in the standard gas database.
- The calculated $\delta\ ^{13}C/^{12}C$ of standard gas is - 25.44 ‰ vs. PDB in the first measurement and - 25.40 ‰ vs. PDB in the second measurement. The mean value of - 25.42 ‰ vs. PDB is taken for later application and must therefore be stored in the standard gas database.

- The calculated $\delta\ ^{34}S/^{32}S$ of standard gas is 8.22 ‰ vs. VCDT in the first measurement and 8.04 ‰ vs. VCDT in the second measurement. The mean value of 8.13 ‰ vs. VCDT is taken for later application and must therefore be stored in the standard gas database.

Note To obtain the correct δ values from the SO_2 measurements, take into account that sample and reference may vary in their oxygen isotope content. The oxygen used for the combustion in general will have another isotope ratio than oxygen of SO_2 reference gas. To eliminate this problem the SO_2 reference must be corrected daily. ▲

Amount Percent Determination

This section outlines amount percent determination.

Identifying Significant Peak's Position

In the Method's Evaluation tab, an amount percent determination can be chosen for the significant peak of references. It cannot be performed in case of blanks.

All calculations of amount percent determination refer to the so-called significant peak. To first and foremost determine its position, in the Evaluation tab of the method an interval must be defined by a Significant Peak Start value and a Significant Peak Stop value.

Since this interval will not automatically be identified, a sample chromatogram must be recorded which reveals the position of the significant peak. Consider that the position can vary slightly over time due to alteration processes. Choosing a sufficiently broad interval will prevent the significant peak from migrating outside it.

Calculating Amount Percent

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

First, a reference (that is a well-known substance; not necessarily identical to the compound of the later sample) is measured to obtain the k factor according to the formula:

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

The weight percent w_{ref} of the reference and its mass m_{ref} are given, whereas its peak area A_{ref} is obtained from the measurement. Possibly, A_{ref} can be used blank-corrected to enhance the precision of k factor calculation.

A linear relation between k factor and the mass m_{ref} of the reference is stored in the database. This linear relation is now used to determine the k factor of the unknown sample using the known sample weight m_{sample}.

The peak area A_{sample} from the chromatogram (possibly blank-corrected), sample weight m_{sample} and k factor are now well known, so that the parameter of interest, the sample's weight percentage w_{sample}, can be easily obtained rearranging the above equation:

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

Commands

Three procedures, that is commands, exist to perform reference measurements:

- Reference
- Start Reference Mean
- Start Reference Regression

Reference Command

From the Type menu select **Reference**. See Figure 4-38. The previous reference value will be deleted. Instead, the result of this current reference measurement will be enlisted as new reference value (one-point calibration).

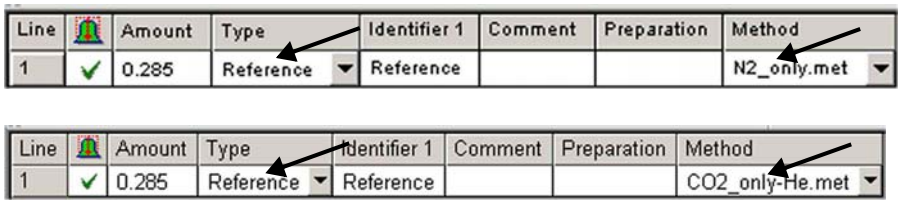


Figure 4-38. Reference measurement - Reference command

Start Reference Mean Command

From the Type menu, select **Start Reference Mean**. See Figure 4-39. The previous reference value will be deleted. Instead, the result of this current reference measurement will be enlisted as new reference value. Further references can be added that are taken into account when determining the Reference Mean.

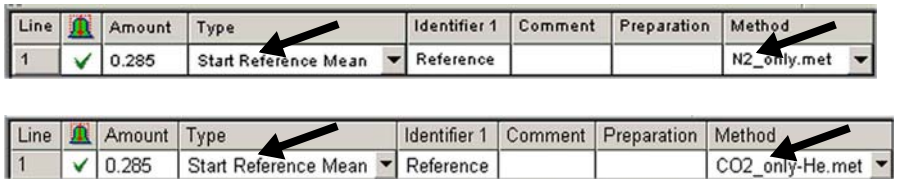


Figure 4-39. Reference measurement - Start Reference Mean command

Note A mean value is determined. This is only recommended, if the samples do not vary significantly in amount (for example liquids injection). ▲

Add Reference Mean Command

From the Type menu, select **Add Reference Mean**. See Figure 4-40.

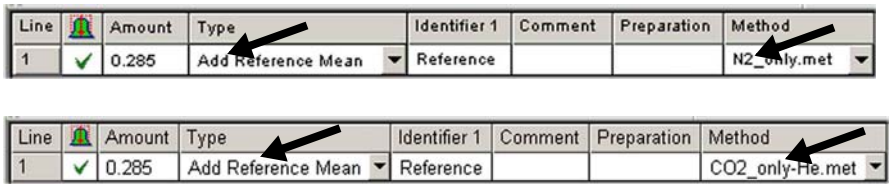


Figure 4-40. Reference measurement - Add Reference Mean command

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

$$m'_r = \frac{m_r \times n_r + r}{n_r + 1}$$

with:

m'_r new Reference Mean

m_r old Reference Mean

n_r number of previously measured reference values (since reference start)

r new reference value

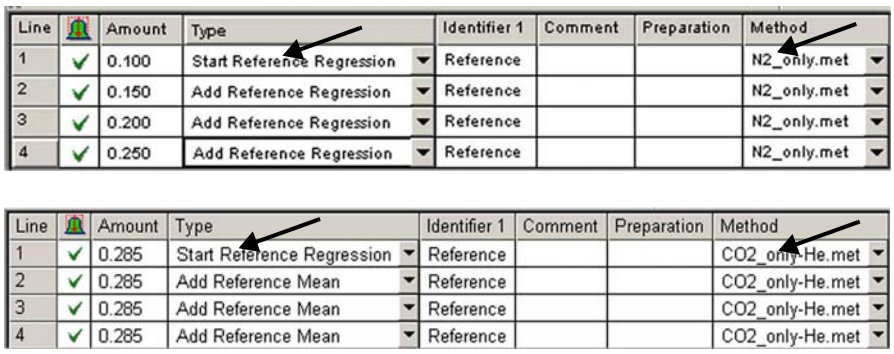
The Reference **Mean** is calculated in case of References of **very similar** weights. With References of **considerably differing** weights, it is advantageous to generate a reference calibration curve. Measuring a sample afterwards, a k factor can be acquired using the calibration curve.

Note It is recommended to weigh at least three samples of different weights, which approximately cover the range of unknown samples. ▲

Start Reference Regression Command

From the Type menu, select **Start Reference Regression**. This command corresponds to the Start Reference Mean command. See Figure 4-41 and refer to "Start Reference Mean Command" on page 4-29.

The previous reference value will be deleted. Instead, the result of this current reference measurement will be enlisted as new Reference value. Further references can be added to extend the Reference calibration curve.



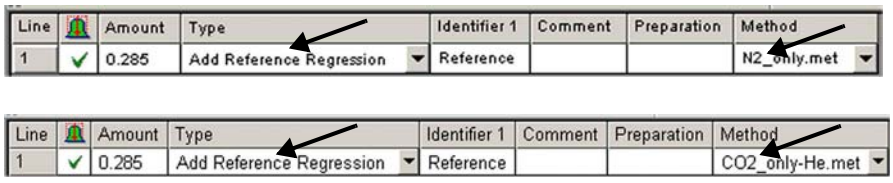
Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.100	Start Reference Regression	Reference			N2_only.met
2	✓	0.150	Add Reference Regression	Reference			N2_only.met
3	✓	0.200	Add Reference Regression	Reference			N2_only.met
4	✓	0.250	Add Reference Regression	Reference			N2_only.met

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Start Reference Regression	Reference			CO2_only-He.met
2	✓	0.285	Add Reference Mean	Reference			CO2_only-He.met
3	✓	0.285	Add Reference Mean	Reference			CO2_only-He.met
4	✓	0.285	Add Reference Mean	Reference			CO2_only-He.met

Figure 4-41. Reference measurement - Start Reference Regression command

Add Reference Regression Command

From the Type menu, select **Add Reference Regression**. This command corresponds to the Add Reference Mean command. See Figure 4-42 and refer to "Add Reference Mean Command" on page 4-30. A new point on the calibration curve is enlisted.



Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Add Reference Regression	Reference			N2_only.met

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Add Reference Regression	Reference			CO2_only-He.met

Figure 4-42. Reference measurement - Add Reference Regression command

Note After finishing each reference measurement Isodat stores the corrected calibration factor in a database. ▲

Note Once having calibrated the amount calculation, the analytical condition parameters should not be changed. As with all reference materials, it is recommended to choose material that is close to the sample in terms of matrix and "origin" (organic/inorganic). ▲

Calibration Procedure

The system, that is ConFlo III and IRMS, requires a calibration procedure in order to calculate the amount of nitrogen or carbon in the sample.

❖ **To perform the calibration procedure**

1. Weigh a reference compound, for example 0.285 mg of urea, in a tin capsule (in case of nitrogen) or a silver capsule (in case of carbon) and wrap it carefully.

Note The precision of weighing is directly related to the precision of amount percent determination. ▲

2. Place the capsule in the solid-autosampler.
3. Click on the Evaluation tab of the method.

   In case of nitrogen, the method N2_only.met is described in detail in "Starting Nitrogen Measurement" on page 4-34. The amount percent value of 46.646 % refers to urea. See upper part of Figure 4-43.

   In case of carbon, the method CO2_only.met is described in detail in "Starting Carbon Measurement" on page 5-11. The amount percent value of about 20.00 % refers to urea. See lower part of Figure 4-43.

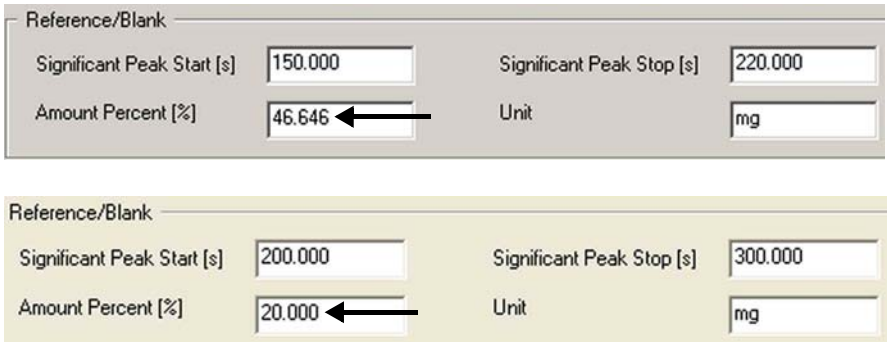
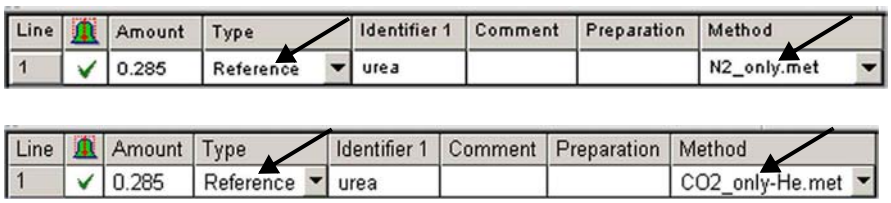


Figure 4-43. Reference/Blank information for amount percent determination

4. In the sequence grid, select **Reference** in the Type column. In the Method column, select the appropriate IRMS method. See Figure 4-44.



Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Reference	urea			N2_only.met

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Reference	urea			CO2_only-He.met

Figure 4-44. Sequence line for amount percent determination

5. Start the sequence.

Note Once having calibrated the amount percent calculation, the analytical conditions should not be changed. To obtain reasonable results, this calibration needs to be performed daily and after changing any parameters of the system, that is ConFlo II/III and IRMS. ▲

Starting Nitrogen Measurement

Before you start a nitrogen measurement, make sure that your system meets the hardware requirements summarized in Table 4-3.

Table 4-3. Hardware requirements for nitrogen measurement

Parameter	Value
oxidation furnace temperature	1020 °C for Cr_2O_3 filling; 900 °C for CuO filling
reduction furnace temperature	650 °C
GC column temperature	45 °C
helium flow	80-100 mL/min
purge	helium flow must be sufficiently open
standard gas (N_2) on ConFlo II/III	must be available
needle valve (ConFlo II/III-IRMS connection)	must be open
standard gas intensity (N_2)	is adjusted at about 3-4 V (as with zero enrichment)
Isodat	must be set to ConFlo configuration. See Figure 4-45.

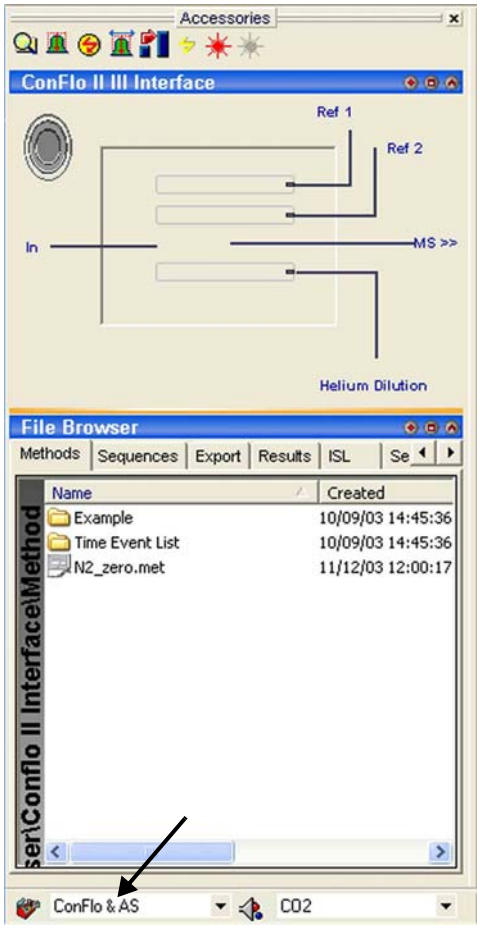


Figure 4-45. ConFlo configuration in Isodat

Defining a Method

From the Examples folder of the File Browser, take the method N2_only.met as a guideline.

Instrument Tab

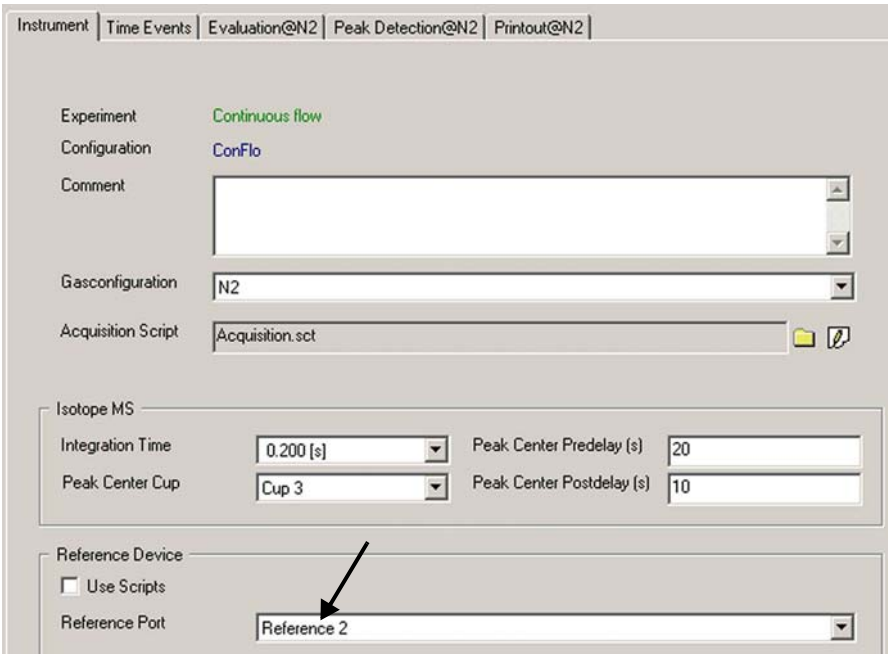


Figure 4-46. Starting nitrogen measurement - Instrument tab

Select the reference port your reference gas is connected to at the ConFlo III interface (for example Reference 2). See Figure 4-46.

Time Events Tab

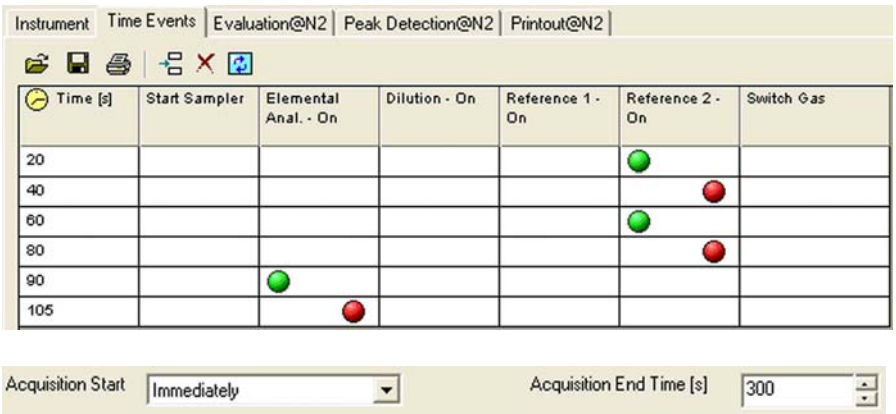


Figure 4-47. Starting nitrogen measurement - Time Events tab

Evaluation Tab

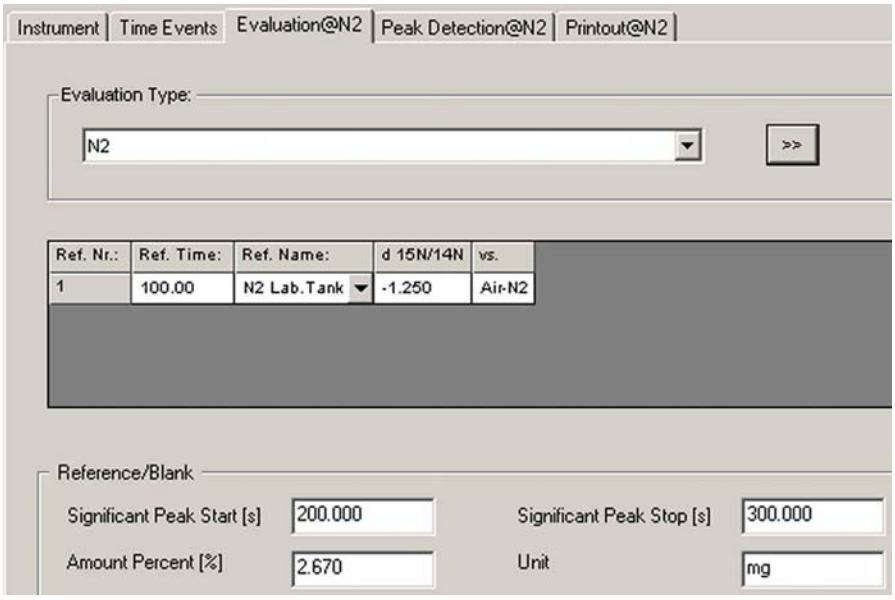


Figure 4-48. Starting nitrogen measurement - Evaluation tab

Peak Detection Tab

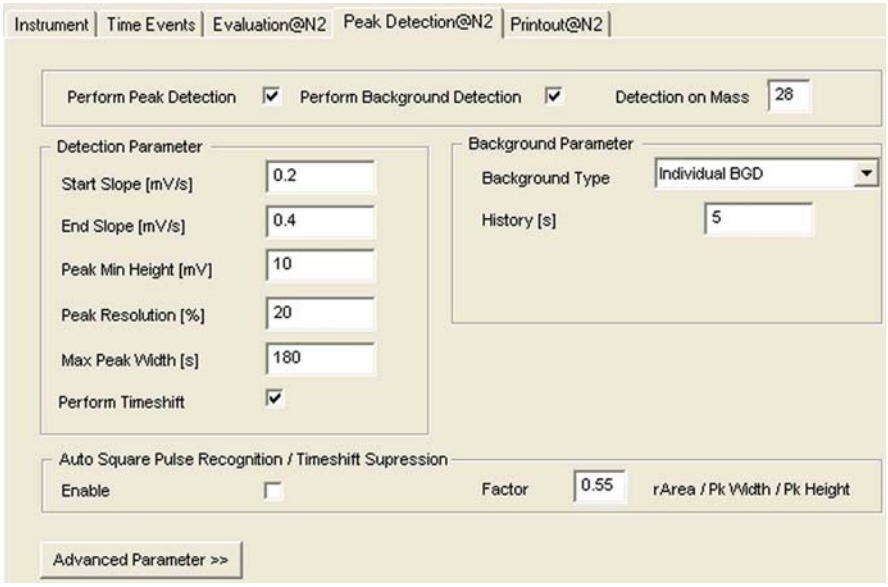


Figure 4-49. Starting nitrogen measurement - Peak Detection tab

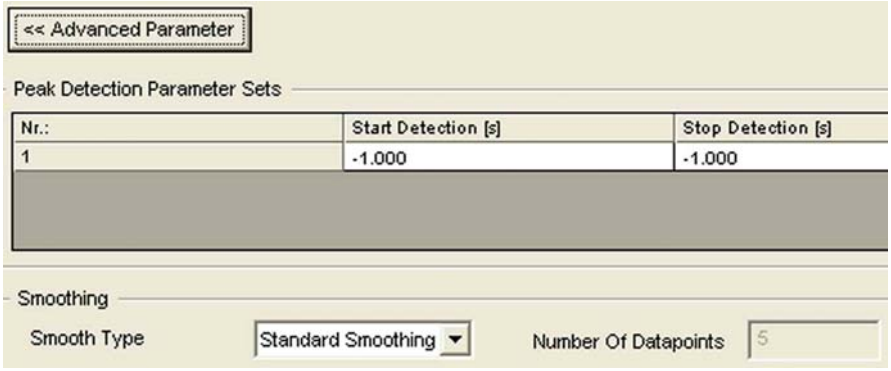


Figure 4-50. Peak Detection tab - Advanced Parameters

Note A value of -1 denotes unlimited. ▲

Printout Tab

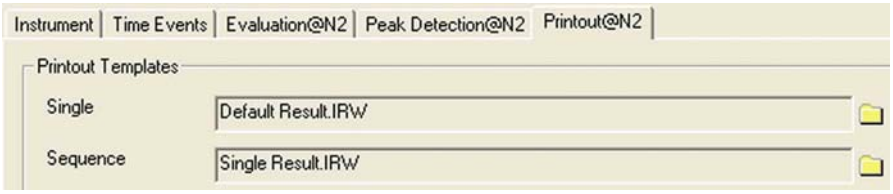


Figure 4-51. Starting nitrogen measurement - Printout tab

Defining a Sequence

❖ **To define a sequence for nitrogen measurement**

1. Place a sample in the solid-autosampler, for example 0.285 mg of urea.

2. To create a new sequence click on the **New** button.

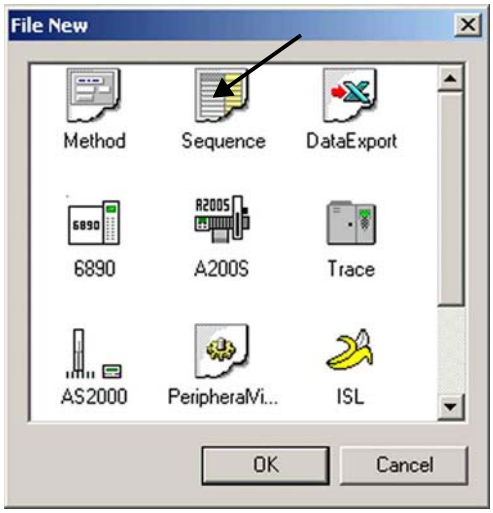
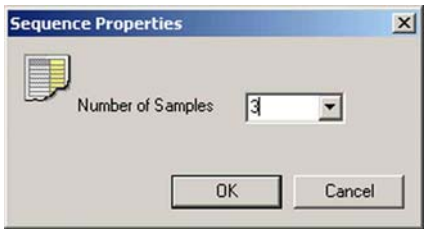


Figure 4-52. Creating new sequence

3. In Figure 4-52 mark the **Sequence** icon and confirm by **OK**.



4. Define the number of samples, for example 3. Confirm by **OK**.

5. Edit the sequence grid as shown in Figure 4-53 and Table 4-4.

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.285	Sample	urea			N2_only.met
2	✓	0.273	Sample	urea			N2_only.met
3	✓	0.291	Sample	urea			N2_only.met

Figure 4-53. Starting nitrogen measurement - editing sequence grid

Table 4-4. Sequence grid parameters for nitrogen measurement

Parameter	Comment
Peak Center	Enable ✓ to perform a peak center prior to measurement (always recommended).
Amount	amount of sample
Type	Select the kind of species, for example Sample
Identifier	Type in text to identifiy the sample (optionally)
Comment	Type in a comment (optionally).
Preparation	Type in information related to preparation (optionally).
Method	Select the IRMS method (here N2_only.met).

6. Click on the **Start** button.

7. Define a folder to save your result files as well as export and printout parameters. See Figure 4-54.

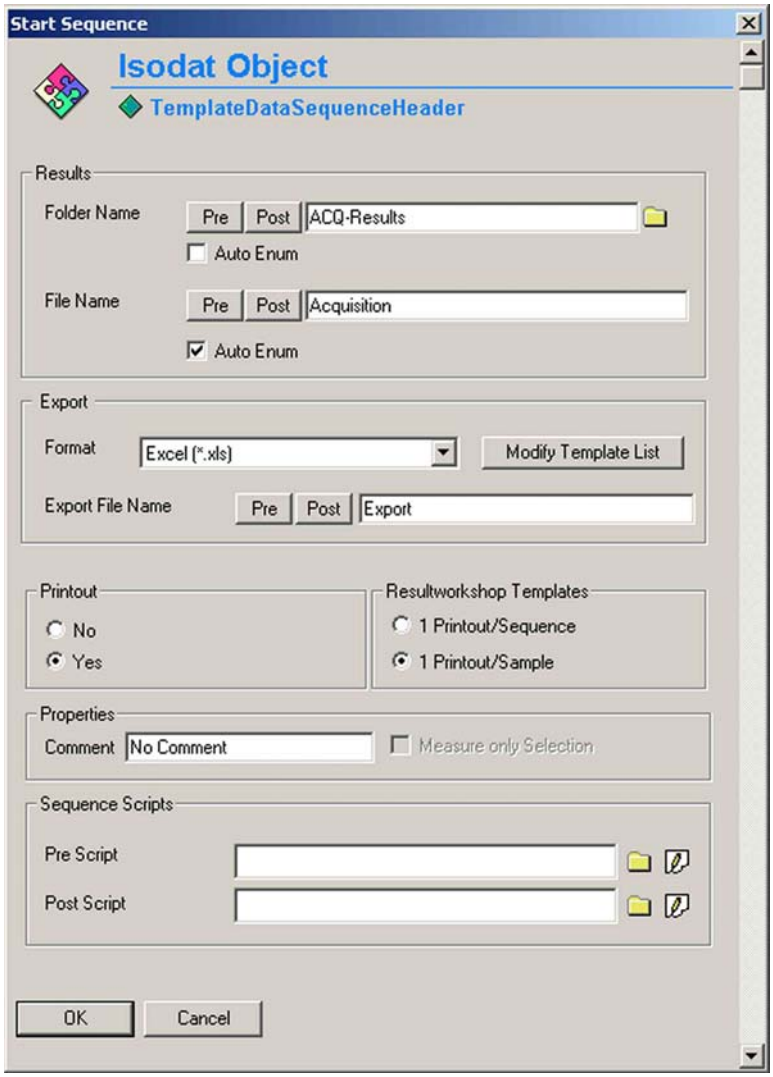


Figure 4-54. Starting nitrogen measurement - defining export and printout parameters

Events during Acquisition

This section summarizes the events that happen during data acquisition. See Figure 4-47, Figure 4-55 and Figure 4-56.

1. Peak center procedure

2. First N_2 reference gas pulse activated at 20 s (duration: 20 s).

3. Second N_2 reference gas pulse activated at 67 s (duration: 20 s). It is assigned as standard pulse for δ value calculation. See Time column in Figure 4-47 and Peak No. 2 in Figure 4-56.
4. Start signal to Elemental Analyzer and oxygen injection.
5. Autosampler activation with delay, that is sample input. The delay depends on the settings made in the Eager software. See Figure 3-27.
6. Depending mainly on the carrier flow, the sample peak appears approximately 200 s after acquisition start time (that is about 100 s after autosampler activation). See Figure 3-27.
7. Acquisition stops at 300 s.

Results

After finishing data acquisition a data output sheet will be created as defined by the selected Result Workshop template (*.irw). The results are also exported to a spreadsheet file, if the checkbox was marked in Figure 4-54. Figure 4-55 shows the chromatogram and Figure 4-56 the related result grid.

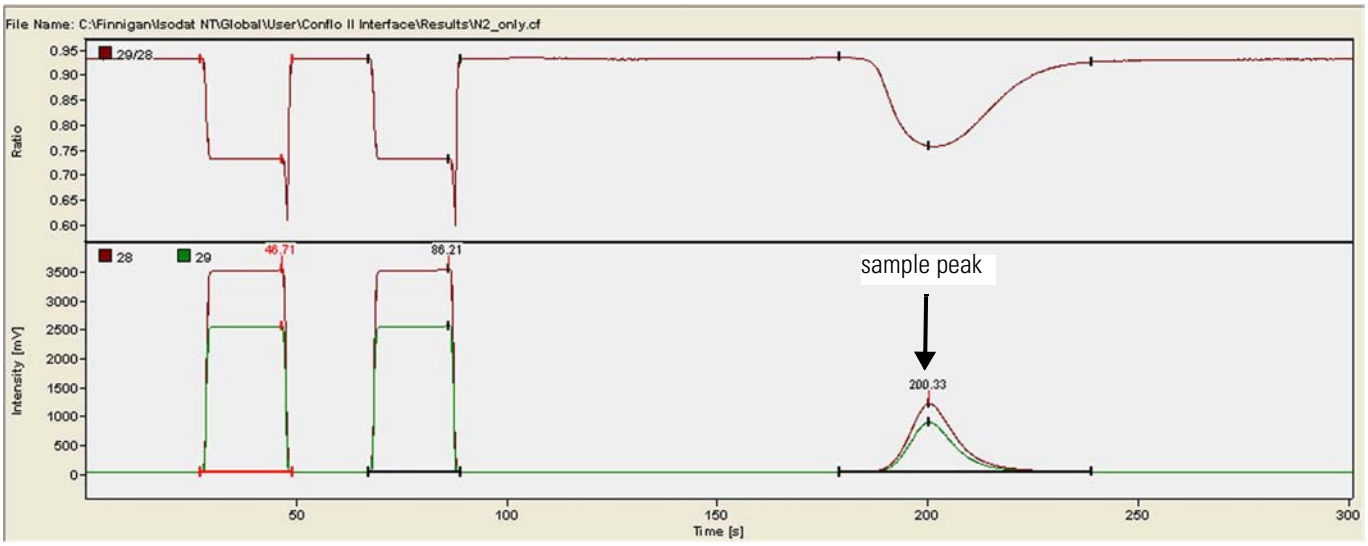


Figure 4-55. Nitrogen measurement - chromatogram

N2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 28 [mV]	Ampl. 29 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area All [Vs]	Amt% [%]	d 15N/14N [per mil] vs. Air-N2	AT% 15N/14N [%]
1	27.3	46.7	22.2	3500	2531	38.1	28.6	65.582	-	-12.892	0.361765
2*	67.2	86.2	22.2	3502	2532	38.1	28.7	65.613	-	-12.940	0.361747
3	179.2	200.3	60.0	1181	870	35.9	27.0	15.845	2.6700000	5.195	0.368369

Figure 4-56. Nitrogen measurement - result grid

Chapter 5 Carbon Measurement

This chapter describes creating a gas configuration, zero enrichment (standard on/off test) and linearity test for carbon. Hardware preparation, method editing and sequence editing before a carbon measurement is started are extensively treated. Finally, results of this measurement are displayed.

This chapter treats the following topics:

Creating Gas Configuration for Carbon Measurement

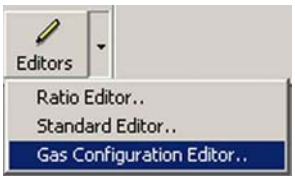
A gas configuration determines a combination of masses, which are collected in the cups, for evaluation of ratios and eventually δ values. The gas configuration is specific for the particular gas and is combined with a magnet field value taken from the mass calibration of your IRMS. The ratio groups determine the reported ratios of predefined masses.

Prior to defining this gas configuration ensure that the connected IRMS has the cups for the simultaneous detection of m/z 44, m/z 45 and m/z 46 and that mass calibration for these cups has already been performed.

For a carbon measurement, a gas configuration must be available for the m/z 44 (that is $^{12}C^{16}O^{16}O$), m/z 45 (for example $^{13}C^{16}O^{16}O$) and m/z 46. Otherwise, it must be created as follows.

❖ **To create a gas configuration for carbon measurement**

1. Open Isodat **Acquisition**.



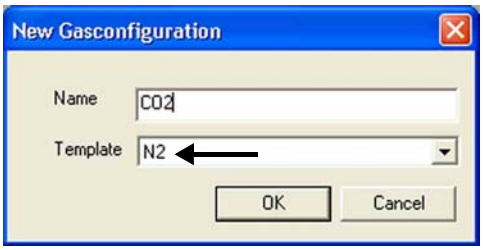
2. Open the **Gas Configuration Editor** (Figure 5-1).

   It is only available, if no acquisition is running.

Figure 5-1. Gas Configuration Editor

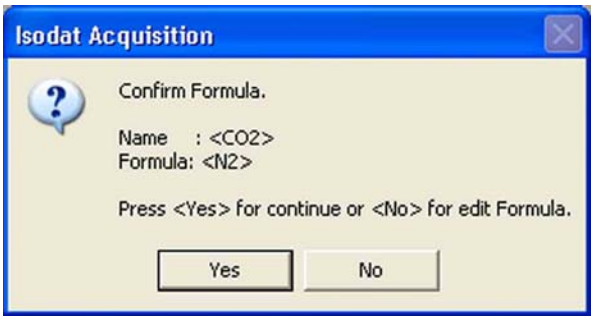
Per default, the gas configuration CO2 is being created as the first one. If you have deleted CO2 however, another gas configuration (for example N2) is shown in Figure 5-1.

3. Click on the **Add** button to add a new gas configuration.



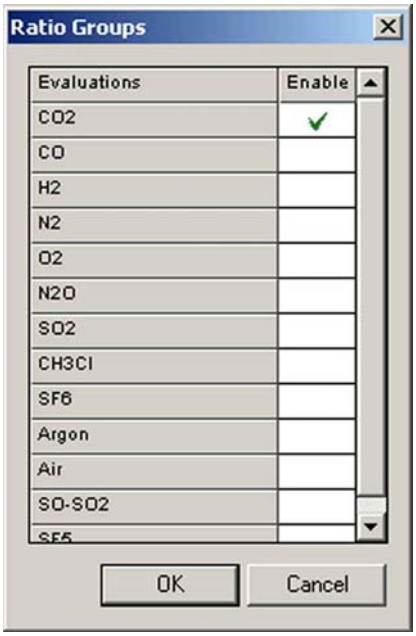
4. Type **CO2** for the **Name**.
5. Select a Gas Configuration as **Template**.

   In the context menu, only the already existing gas configurations are displayed (here for example N2). When creating the first gas configuration, **CO2** is displayed.
6. Confirm by **OK**.



7. Type **No**.

   If you would type **Yes**, this would automatically mark the template (that is N2) instead of CO2 in the Ratio Groups window below.



8. Mark **CO2**. If Ratio Groups other than CO2 are marked, unmark them all.
9. Confirm by **OK**.

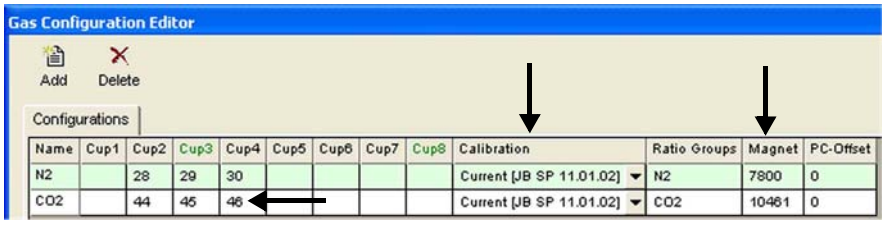


Figure 5-2. Creating new gas configuration

The new gas configuration CO2 appears in the list as a row of its own. See Figure 5-2.

10. In the **Calibration** column of Figure 5-2 select your current calibration file.

Note Figure 5-2 shows a common cup configuration as used in most Delta mass spectrometers, that is universal triple collector. If you have a special cup configuration, the respective masses will be collected in other cups! ▲

11. In Figure 5-2 type in the correct masses (44, 45 and 46) to the appropriate cups specific for your IRMS.

When highlighting the specific gas configuration by a click on its row, the number of cups required for measurement is displayed together with the assigned masses. See Figure 5-3.

Figure 5-3. Required cups together with assigned masses

12. Select a calibration, which is valid for the selected cups.
13. Click on the **Save & Close** button 

.

Zero Enrichment of Carbon (Standard On/Off Test)

We assume that the user already has working experience with the ConFlo III interface and IRMS. It is recommended to perform a simple check in order to test the analytical condition of the ConFlo III and the IRMS before measuring any samples.The most important checks to test the analytical condition are zero enrichment and linearity test.

Note Use the method CO2_zero.met from the Examples folder of the File Browser which will be described below only as a guideline! ▲

Instrument Tab

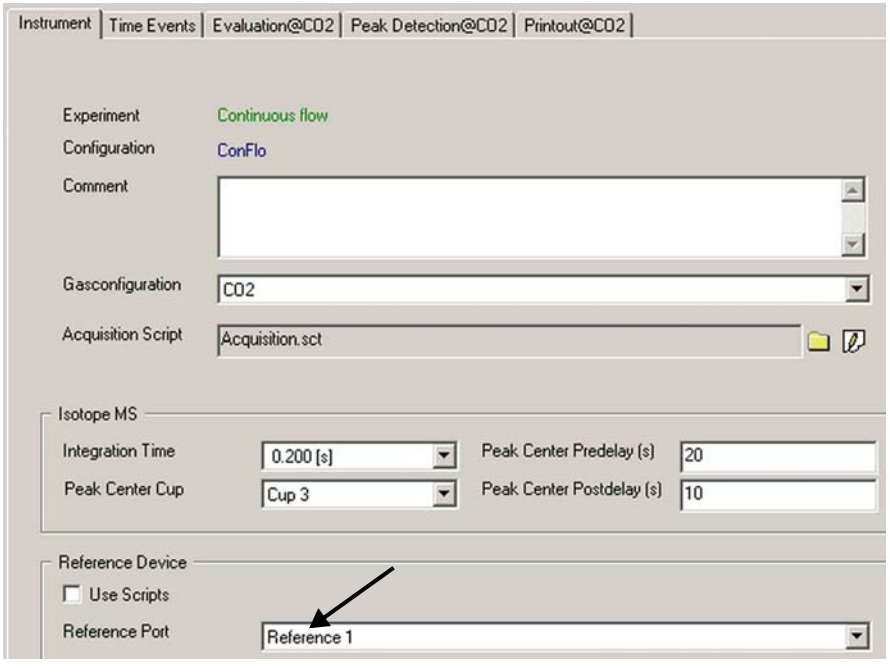


Figure 5-4. Zero Enrichment of carbon - Instrument tab

In Figure 5-4 select the **reference port** your reference gas is connected to at the ConFlo III interface (for example **Reference 1**).

Adapt the reference gas port to the respective column of the time events list: for example, if you choose **Reference 1**, the on-off entries must occur in the Reference 1-On column of the time events list. See Figure 5-5.

Time Events Tab

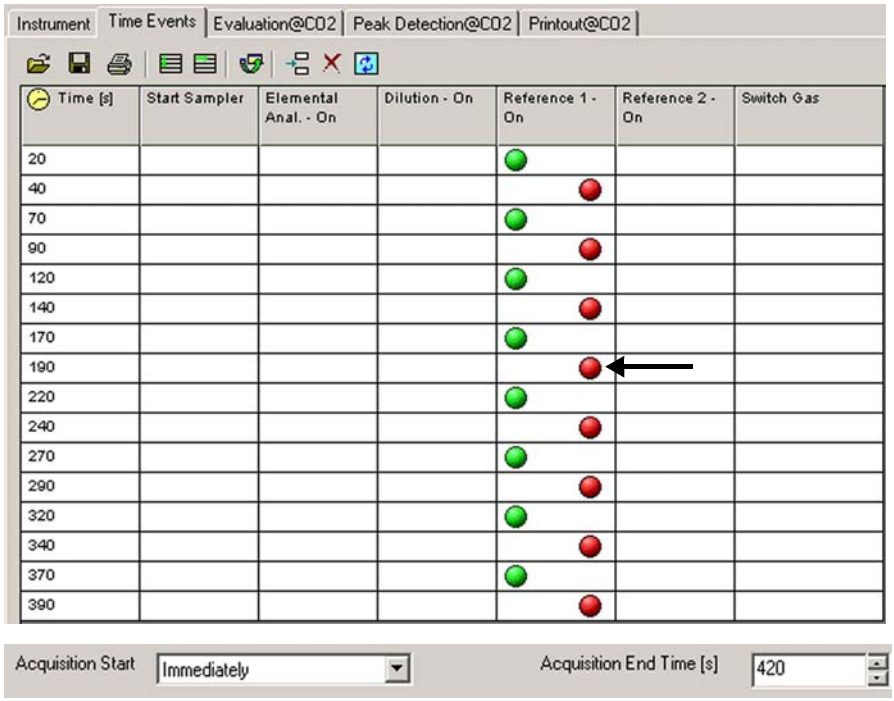


Figure 5-5. Zero Enrichment of carbon - Time Events tab

Recognize the eight on-off pulses shown in Figure 5-5 in the expected chromatogram, Figure 5-10. The off-time of the for example forth reference gas pulse is 190 s. See Figure 5-6.

Evaluation Tab

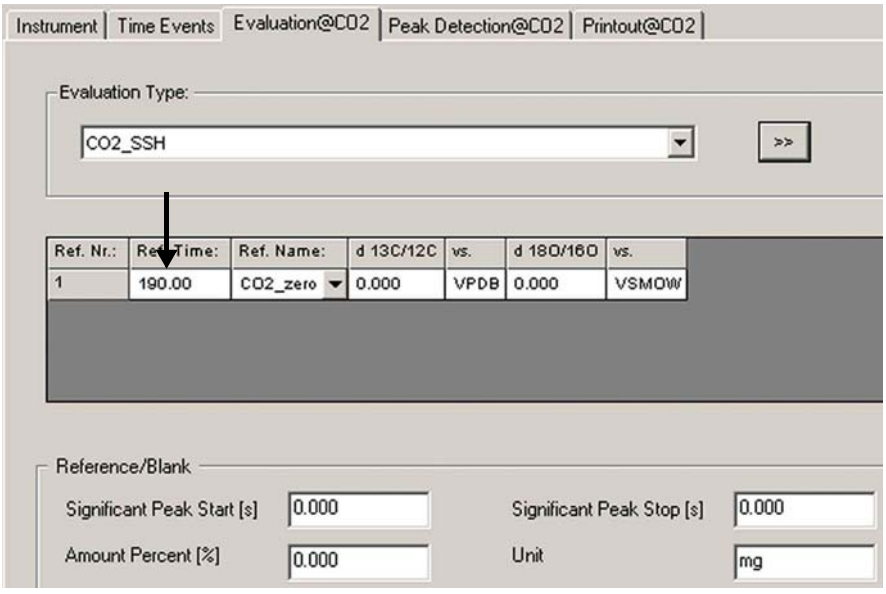


Figure 5-6. Zero Enrichment of carbon - Evaluation tab

Note At Ref. Time, the off-value of an arbitrary reference gas peak according to the Time Events list must be typed (for example 190 s as the off-value of the forth reference gas peak). See Figure 5-5. ▲

Peak Detection Tab

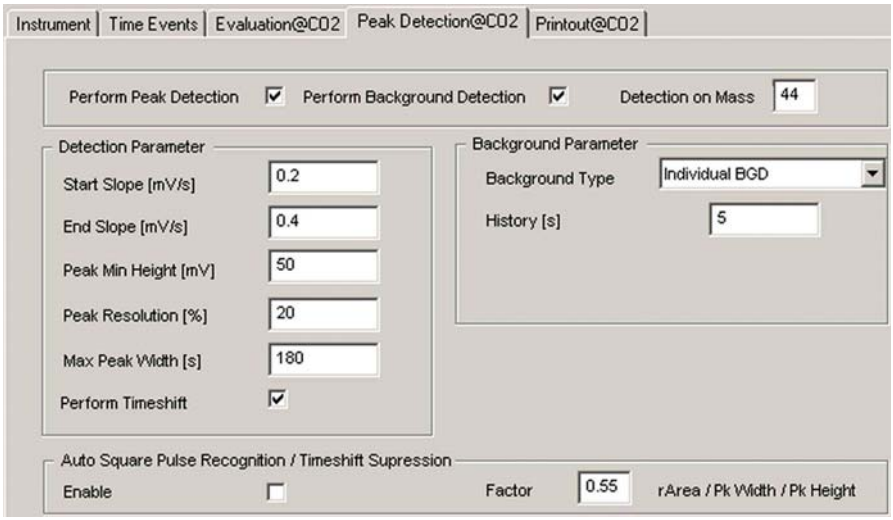


Figure 5-7. Zero Enrichment of carbon - Peak Detection tab

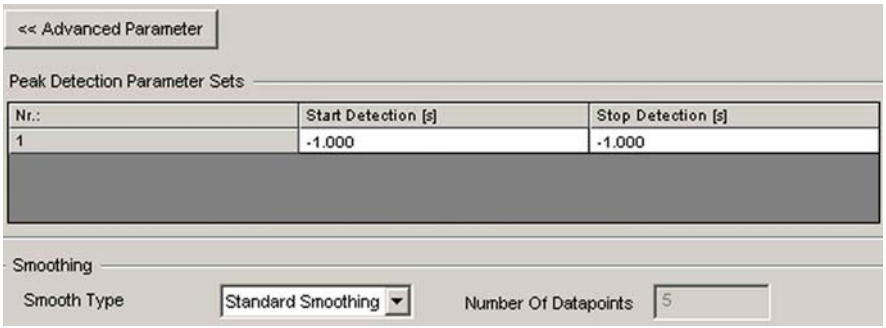


Figure 5-8. Zero Enrichment of carbon - Advanced Parameters in Peak Detection tab

Note A value of -1 denotes unlimited. ▲

Printout Tab

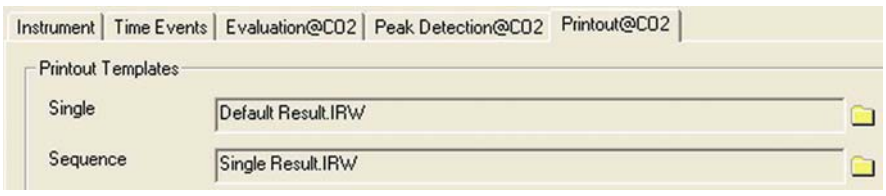


Figure 5-9. Zero Enrichment of carbon - Printout tab

1. At the corresponding pressure regulator of the ConFlo III, set the ion intensity of m/z 44 (that is $^{12}C^{16}O^{16}O$) to 3-4 V.
2. Create a new sequence. Refer to "Defining a Sequence" on page 2-15.
3. Click on the **Start** button and confirm by **OK**.

The expected data after three or four measurements are given in Figure 5-10 (chromatogram) and Figure 5-11 (result grid).

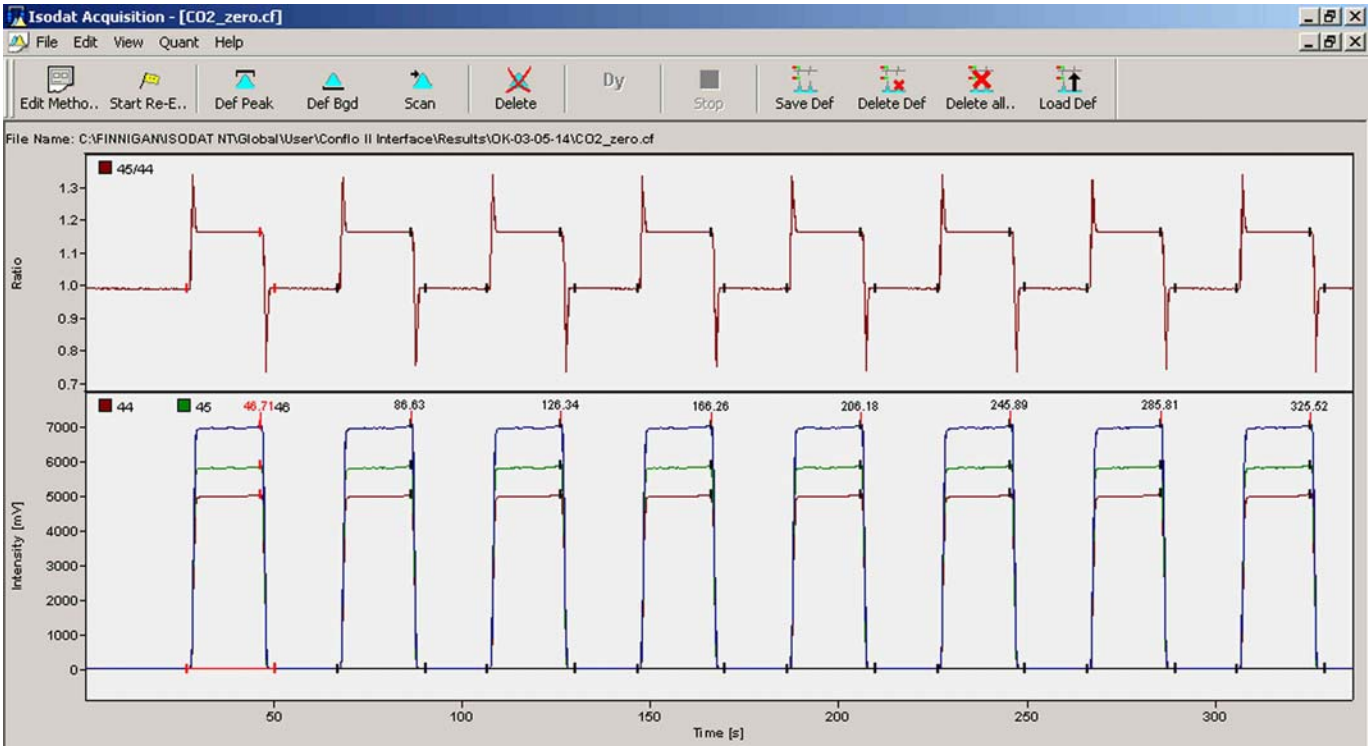


Figure 5-10. Zero Enrichment of carbon - chromatogram

Recognize the eight peaks shown in Figure 5-10 as the eight on-off pulses in the Time events list, Figure 5-5.

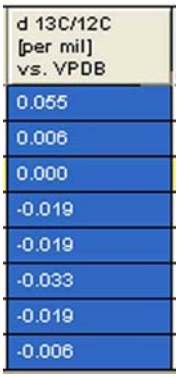
CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	BGD 44 [mV]	BGD 45 [mV]	Area All [Vs]	d 13C/12C [per mil] vs. VPDB	AT% 13C/12C [%]	d 18O/16O [per mil] vs. VSMOW
1	27.3	46.7	23.2	5040	5875	3.9	2.7	96.047	0.055	1.105719	0.084
2	67.0	86.6	23.4	5061	5897	4.0	2.8	96.074	0.006	1.105666	0.031
3*	106.9	126.3	23.4	5061	5898	4.0	2.9	96.170	0.000	1.105659	0.000
4	146.8	166.3	23.2	5053	5889	4.0	2.9	96.101	-0.019	1.105637	0.025
5	186.5	206.2	23.4	5055	5890	4.0	2.9	96.144	-0.019	1.105638	-0.012
6	226.5	245.9	23.2	5065	5904	4.0	2.9	96.209	-0.033	1.105622	-0.000
7	266.2	285.8	23.4	5066	5903	4.0	2.9	96.132	-0.019	1.105638	0.004
8	306.1	325.5	23.2	5056	5892	4.0	2.9	96.162	-0.006	1.105652	-0.001

Figure 5-11. Zero Enrichment of carbon - result grid

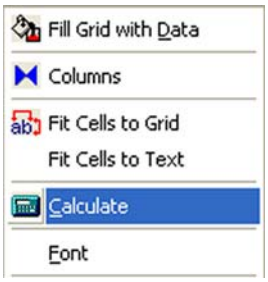
Note The standard deviation of δ13C/12C should be 0.05 ‰ or less. ▲

❖ **To obtain the standard deviation of all eight peaks**



1. Click on the column header of the **d 13C/12C [per mil] vs. Air-N2 column**.

   It will be highlighted.



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

The results will be calculated and summarized in Figure 5-12.

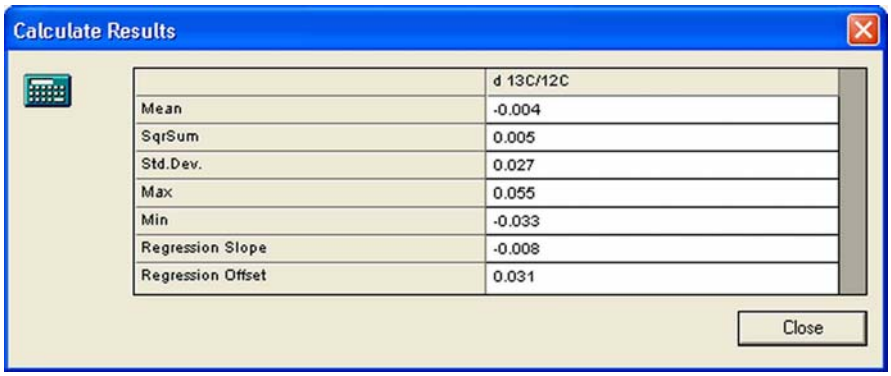


Figure 5-12. Calculation of results

Linearity Test of Carbon

Use the same method as defined for zero enrichment in "Zero Enrichment of Carbon (Standard On/Off Test)" on page 5-5, that is CO2_zero.met. Start the acquisition as a single run. At each detection of a peak de- or increase the reference gas pressure at the ConFlo III.

The expected data after three or four measurements are shown in Figure 5-13 (chromatogram) and Figure 5-14 (result grid).

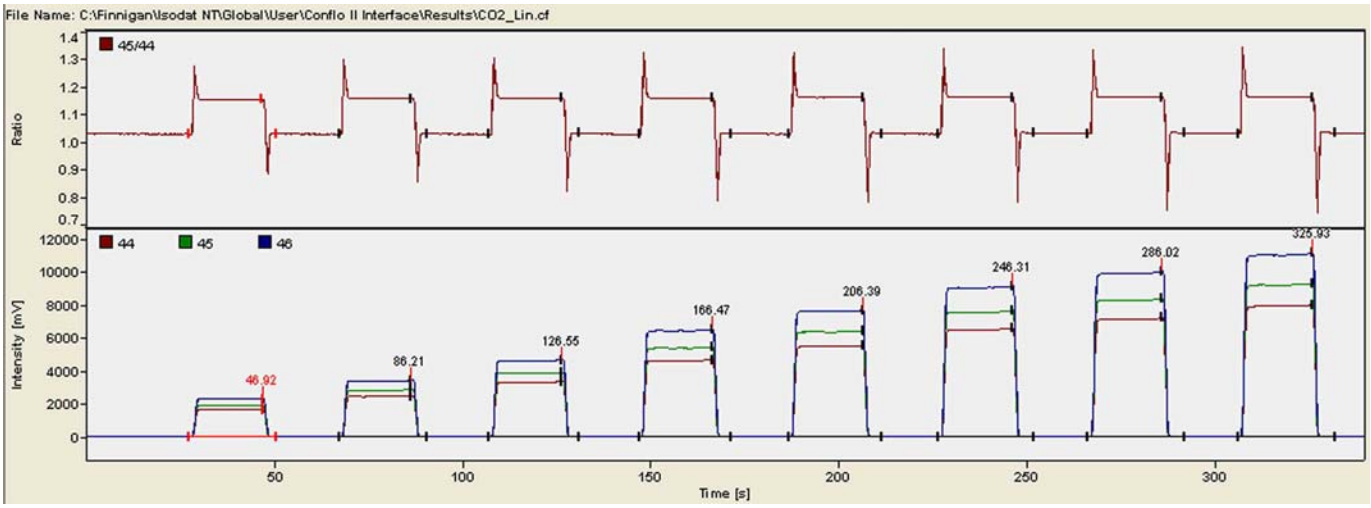


Figure 5-13. Linearity test of carbon - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	BGD 44 [mV]	BGD 45 [mV]	Area All [Vs]	d 13C/12C [per mil] vs. VPDB	AT% 13C/12C [%]	d 18O/16O [per mil] vs. VSMOW
1	27.5	46.9	23.0	1643	1910	12.3	15.4	31.347	-0.020	1.105637	0.126
2	67.4	86.2	23.4	2450	2847	12.2	15.3	46.763	-0.002	1.105656	0.132
3*	107.1	126.5	23.8	3343	3886	12.2	15.3	63.796	0.000	1.105659	0.000
4	147.0	166.5	24.5	4660	5417	12.3	15.3	88.951	-0.035	1.105621	-0.123
5	186.7	206.4	24.9	5514	6410	12.4	15.5	105.362	-0.083	1.105567	-0.213
6	226.7	246.3	25.3	6583	7650	12.5	15.6	125.489	-0.123	1.105525	-0.349
7	266.4	286.0	25.7	7203	8373	12.7	15.9	137.413	-0.181	1.105460	-0.422
8	306.3	325.9	25.7	8011	9310	12.9	16.0	153.033	-0.223	1.105415	-0.580

Figure 5-14. Linearity test of carbon - result grid

Note The linear regression of the δ13C/12C values vs. the working standard should be less than 0.06 ‰/V. ▲

Starting Carbon Measurement

- For blank measurement of carbon, see "Blank Measurement" on page 4-11.
- For reference measurement of carbon, see "Reference Measurement" on page 4-22.
- For amount percent determination of carbon, see "Amount Percent Determination" on page 4-27.

Before you start a carbon measurement, make sure that your system meets the hardware requirements summarized in Table 5-1.

Table 5-1. Hardware requirements for carbon measurement

Parameter	Value
oxidation furnace temperature	1020 °C for Cr_2O_3 filling 900 °C for CuO filling
reduction furnace temperature	650 °C
GC column temperature	45 °C
helium flow	80-100 mL/min
purge	helium flow must be sufficiently open
standard gas (N_2) on ConFlo II/III	must be available
needle valve (ConFlo II/III-IRMS connection)	must be open
standard gas intensity (N_2)	is adjusted at about 3-4 V (as with zero enrichment)
Isodat	must be set to ConFlo configuration. See Figure 5-15.

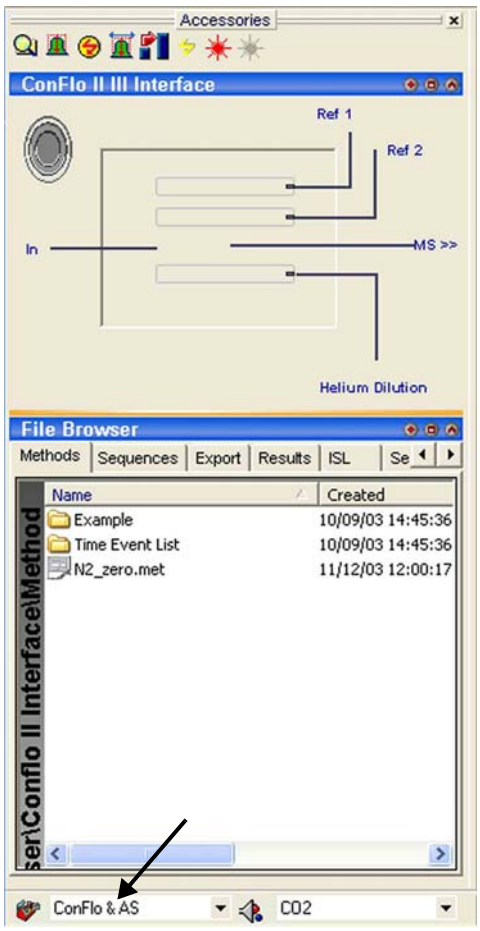


Figure 5-15. ConFlo configuration in Isodat

Defining a Method

From the Examples folder of the File Browser, take the method CO2_only-He.met as a guideline.

Note CO2_only-He.met is a method without dilution (-He). Some samples with high carbon content may require additional He (dilution) added in the sample section of ConFlo III to reduce signal intensity. This becomes more important when running samples of low nitrogen and high carbon content in a dual measurement. Refer to "Starting Dual Measurement" on page 6-9. ▲

Instrument Tab

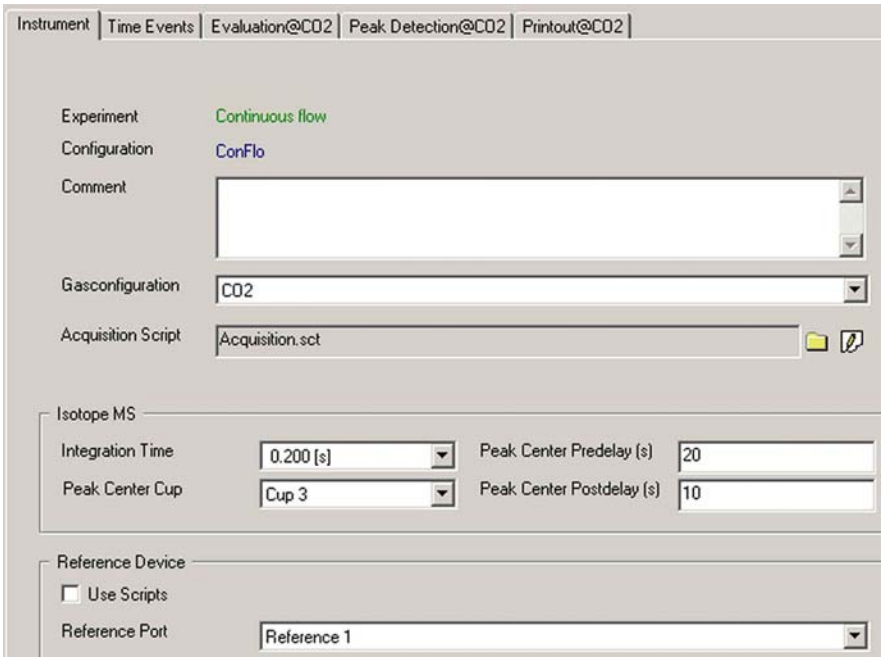


Figure 5-16. Starting a carbon measurement - Instrument tab

Select the reference port your reference gas is connected to at the ConFlo III interface (for example Reference 1). See Figure 5-16.

Adapt the reference gas port to the respective column of the time events list: for example, if you choose Reference 1, the on-off entries must occur in the Reference 1-On column of the time events list. See Figure 5-17.

Time Events Tab

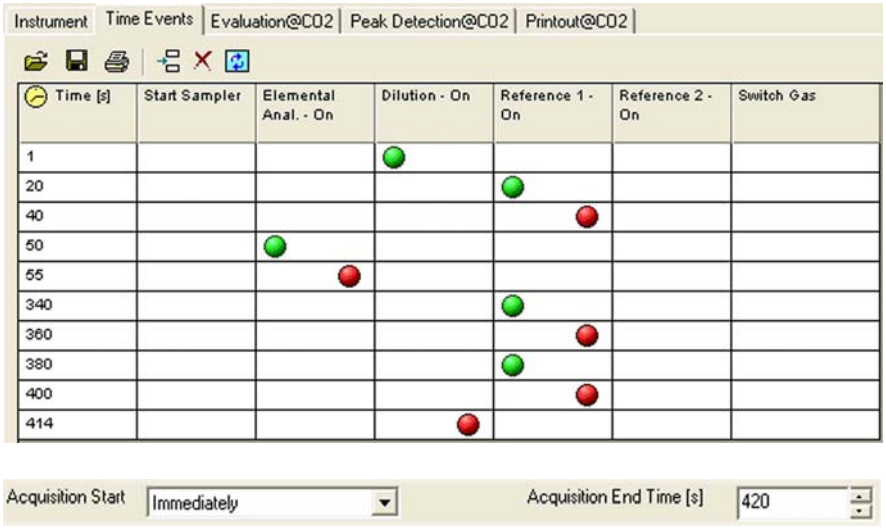


Figure 5-17. Starting a carbon measurement - Time Events tab

Evaluation Tab

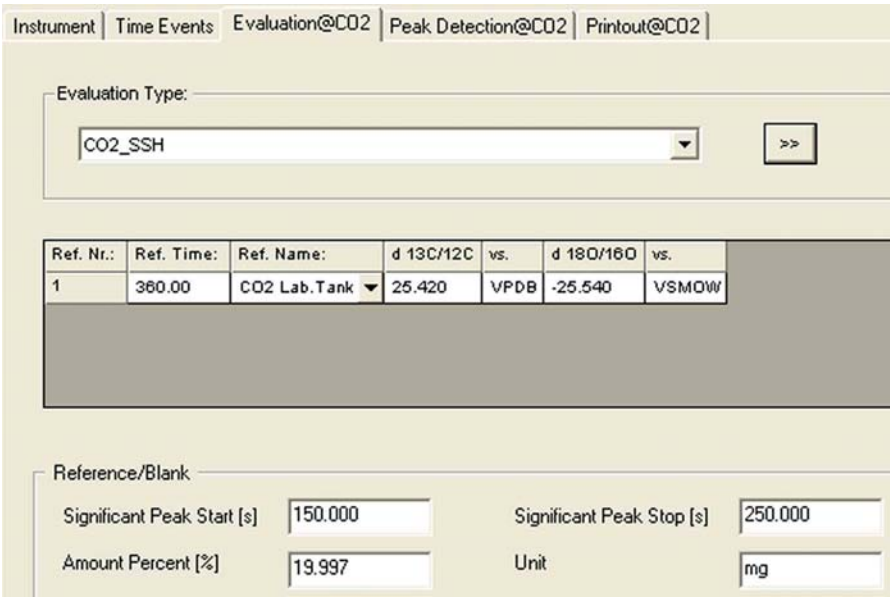


Figure 5-18. Starting a carbon measurement - Evaluation tab

Peak Detection Tab

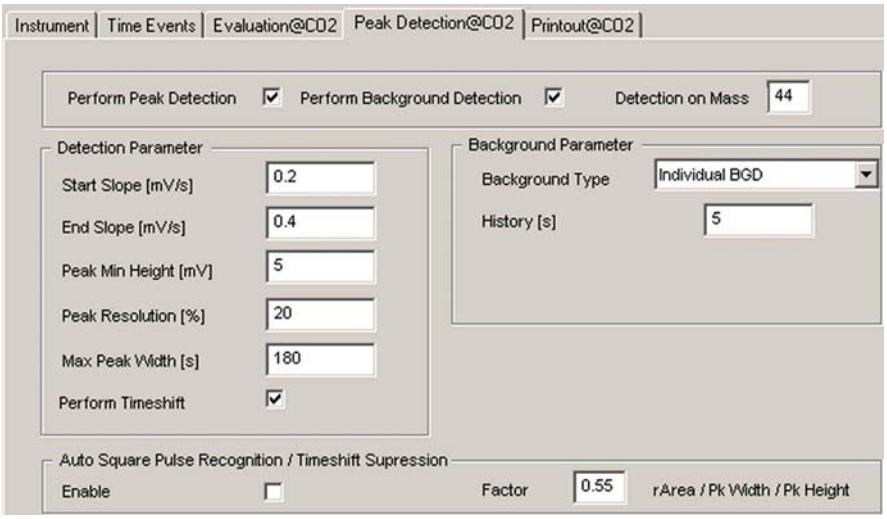


Figure 5-19. Starting a carbon measurement - Peak Detection tab

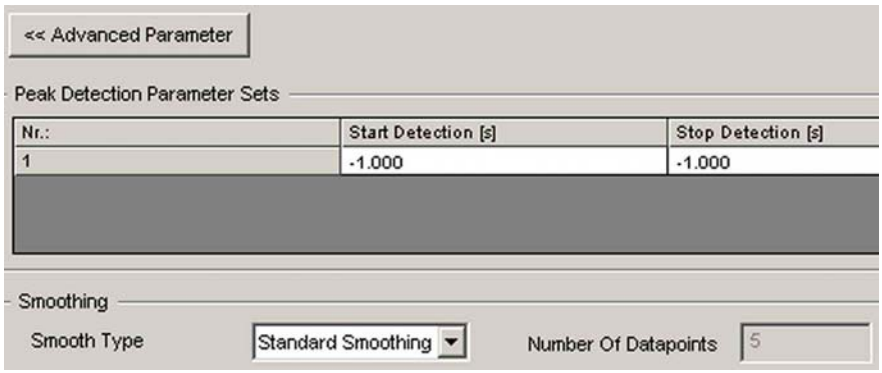


Figure 5-20. Starting a carbon measurement - Advanced Parameters

Note A value of -1 denotes unlimited. ▲

Printout Tab

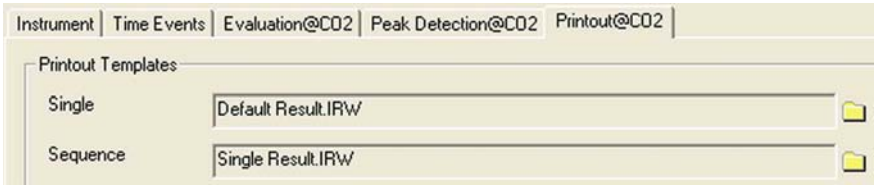


Figure 5-21. Starting a carbon measurement - Printout tab

Defining a Sequence

❖ **To define a sequence for carbon measurement**

1. Place a sample in the solid-autosampler, for example 0.285 mg of urea.

2. To create a new sequence click on the **New** button.

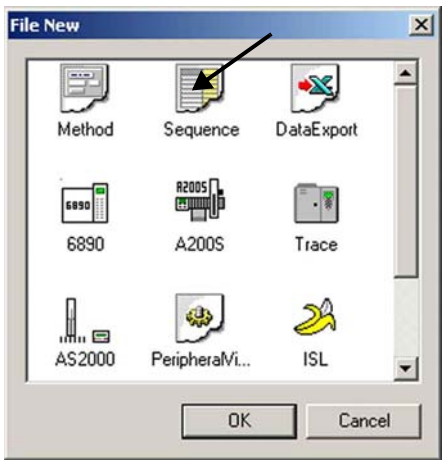
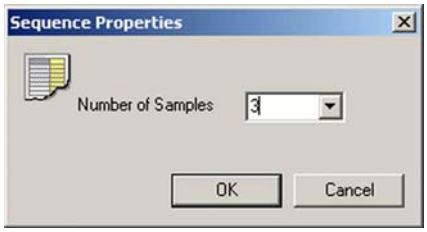


Figure 5-22. Creating new sequence

3. In Figure 5-22 mark the **Sequence** icon and confirm by **OK**.



4. Define the number of samples, for example 3. Confirm by **OK**.

5. Edit the sequence grid as shown in Figure 5-23 and Table 5-2.

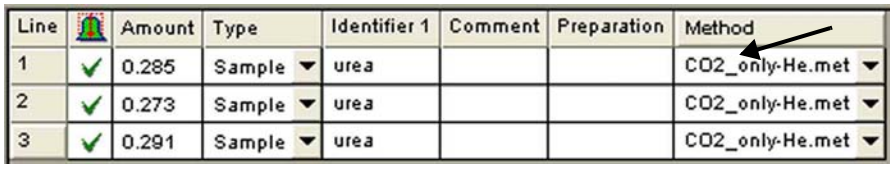


Figure 5-23. Starting carbon measurement - editing sequence grid

Table 5-2. Sequence grid parameters for carbon measurement

Parameter	Comment
Peak Center	Enable ✓ to perform a peak center prior to measurement (always recommended).
Amount	amount of sample
Type	here Sample
Identifier	Type in text to identifiy the sample (optionally)
Comment	Type in a comment (optionally).
Preparation	Type in information related to preparation (optionally).
Method	Select the IRMS method (here CO2_only.met).

6. Click on the **Start** button.

7. Define a folder to save your result files as well as export and printout parameters. See Figure 5-24.

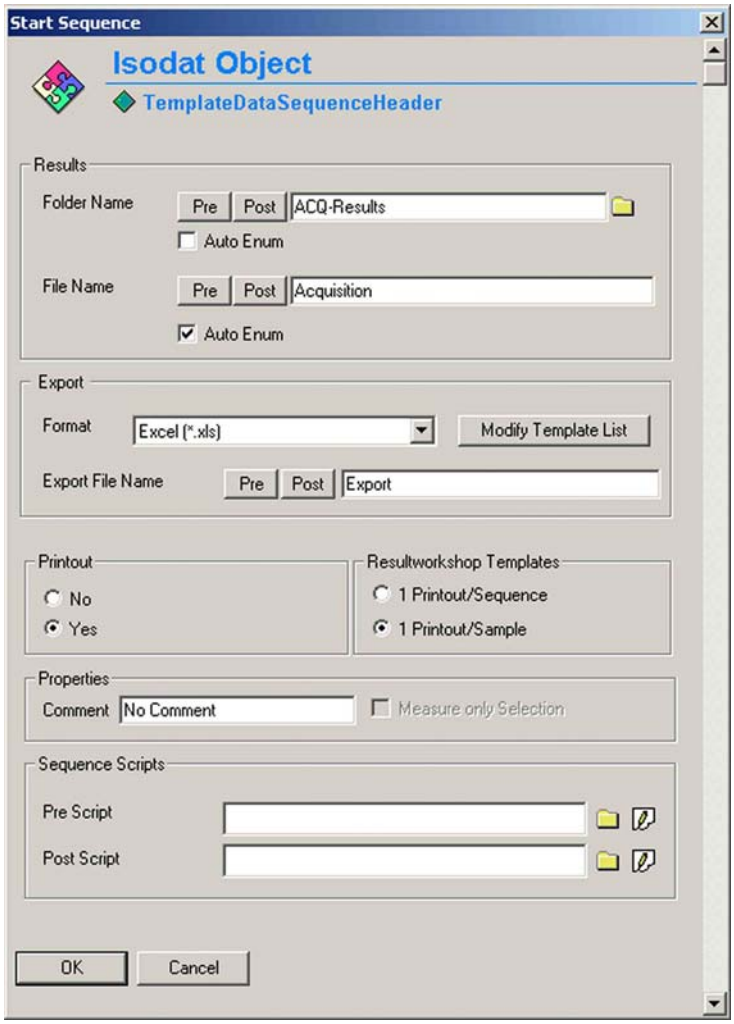


Figure 5-24. Starting carbon measurement - defining export and printout parameters

Events during Acquisition

This section summarizes the events that happen during data acquisition. See Figure 5-17, Figure 5-25 and Figure 5-26.

1. Peak center procedure
2. Dilution on at 1 s.
3. First CO_2 reference gas pulse activated at 20 s (duration: 20 s).
4. Start signal to Elemental Analyzer and oxygen injection at 50 s.

5. Autosampler activation with delay, that is sample input. The delay depends on the settings made in the Eager software. See Figure 3-27.
6. Depending mainly on the carrier flow, the sample peak appears approximately 260 s after acquisition start time (that is approximately 200 s after autosampler activation). See Figure 3-27.
7. Second CO_2 reference gas pulse activated at 340 s (duration: 20 s). It is assigned as Standard pulse for δ value calculation. See Figure 5-18. Refer to the Time column at topic "Starting a carbon measurement - Time Events tab" on page 5-13 and to Peak No. 3 in Figure 5-26.
8. Third CO_2 reference gas pulse activated at 380 s (duration: 20 s).
9. Dilution off at 414 s. Acquisition stops at 420 s.

Results

After finishing data acquisition a data output sheet will be created as defined by the selected Result Workshop template (*.irw). The results are also exported to a spreadsheet file, if the checkbox was marked in Figure 5-24. Figure 5-25 shows the chromatogram and Figure 5-26 the related result grid.

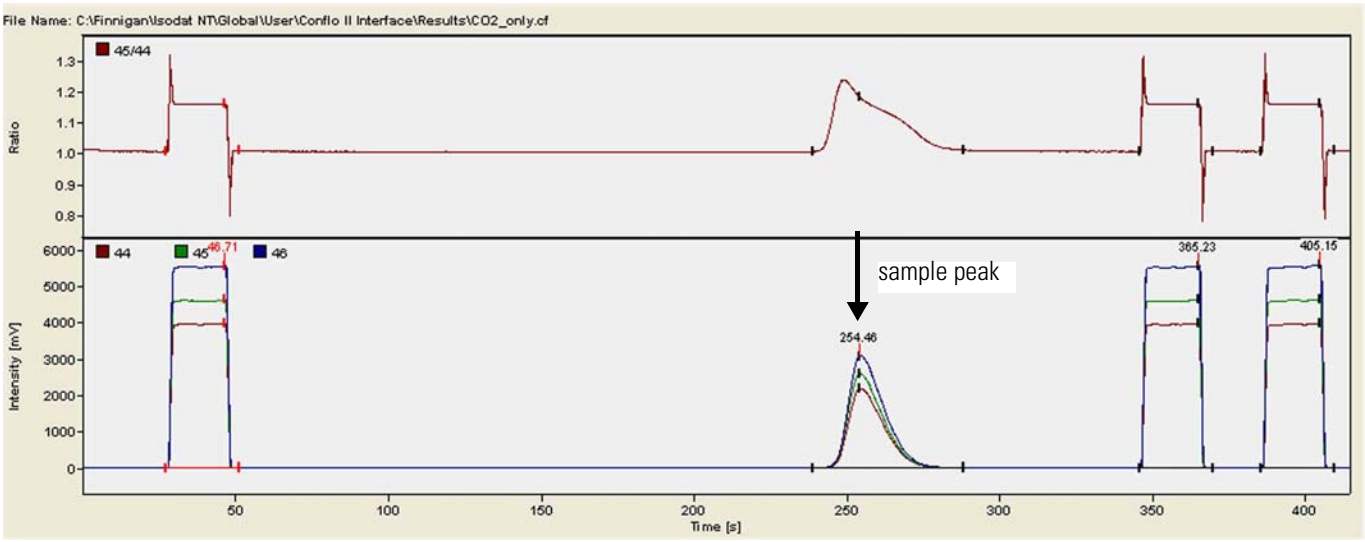


Figure 5-25. Carbon measurement - chromatogram

CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	BGD 44 [mV]	BGD 45 [mV]	Area All [Vs]	Amt% [%]	d 13C/12C [per mil] vs. VPDB	AT% 13C/12C [%]	d 18O/16O [per mil] vs. VSMOW
1	27.3	46.7	24.0	3974	4625	2.0	2.6	75.271	184.3658454	-25.092	1.078214	-0.175
2	239.2	254.5	49.3	2180	2593	1.4	1.9	29.633	73.0037261	-9.865	1.094871	12.575
3*	345.8	365.2	24.0	3977	4629	2.0	2.6	75.078	183.8982012	-24.860	1.078468	-0.000
4	385.7	405.1	23.8	3989	4642	2.1	2.7	75.215	184.2296958	-24.984	1.078332	-0.120

Figure 5-26. Carbon measurement - result grid

Chapter 6 Dual Measurement

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

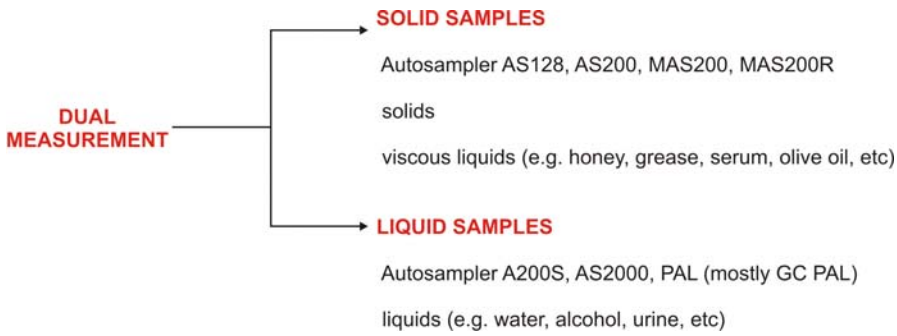


Figure 6-1. Schematic diagram of running solid and liquid samples

As shown in Figure 6-1, different autosamplers are used to measure different sample types. Concerning the installation of the autosamplers refer to the manuals of the corresponding manufacturers.

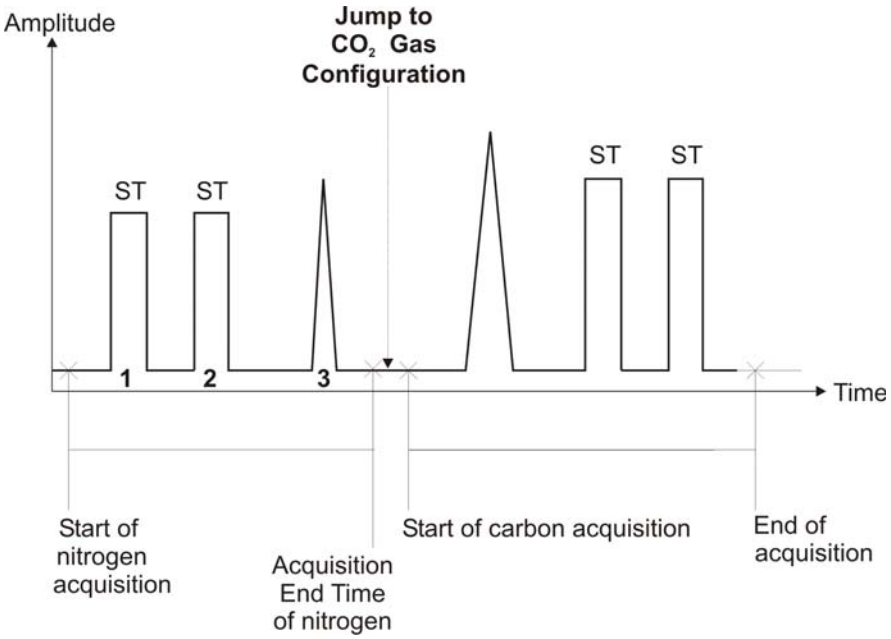
This chapter treats the following topics:

Procedure

For the analysis of two isotopic species (nitrogen and carbon) from a single sample, a method, which comprises both gas configurations must be defined. The acquisition can be completed after less than eight minutes.

Due to the separation of the gases on a GC column, nitrogen appears first. As soon as the nitrogen peak (**3** in Figure 6-1) has been identified, Isodat stops the nitrogen acquisition. The magnet "jumps" to the CO_2 configuration (see Switch Gas column in the time events list of Figure 6-10). A magnet jump means that the magnetic field is changed due to the entries from the mass calibration enabling the system to now collect m/z 44, m/z 45 and m/z 46 in the cups used for N_2 masses before.

If no nitrogen peak can be found, Isodat waits a certain time, which has been set in the method, before it automatically switches to the CO_2 configuration.



Labeled Components: 1, 2=reference gas peaks (N2), 3=sample peak (N2)

Figure 6-2. Dual measurement - schematic chromatogram

Performing Jump Calibration

To determine the isotope ratios of different elements during the same run, switching to another gas configuration is necessary.

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

For this reason, a Jump Calibration from the first gas configuration to the next gas configuration is necessary. It calibrates for a fast variation of the magnetic field.

After the Jump Calibration has been performed, the computer finds exactly the peak center even without performing any peak center procedure.

Temperature changes may influence the magnet performance on a daily basis. Therefore, a Jump Calibration should be performed daily.

Note Both gas configurations used (that is N2 and CO2) need to be configured prior to Jump Calibration. ▲

Note A ConFlo configuration needs to be set up. ▲

❖ **To perform a jump calibration**

1. Open **Instrument Control** of Isodat.

2. Switch to ConFlo configuration.

The ConFlo II III Interface window (Figure 6-3) must appear at the Accessories toolbar. If it does not appear, refer to "If ConFlo II III Interface window is not visible" on page 6-4.

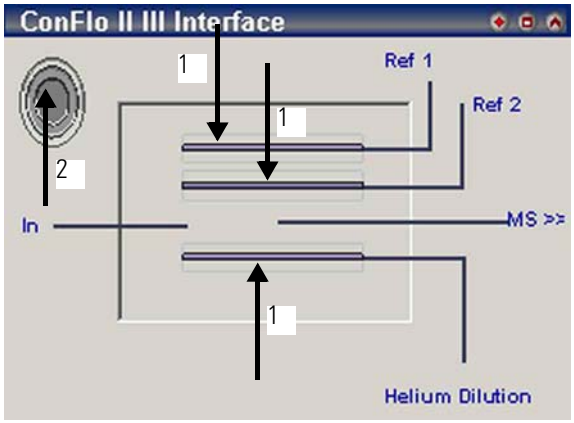


Figure 6-3. ConFlo II III Interface window

The ConFlo II III Interface window allows:

- reference gas inlet and/or dilution (**1** in Figure 6-3)
- autosampler/Elemental Analyzer start signal (**2** in Figure 6-3)
- Movement/activation of capillaries by mouse clicks.

  Open Reference 1 by a click on **Ref 1** capillary. If CO_2 is connected to Reference 2, click on **Ref 2** capillary. Thus, the blue capillary symbol elongates and CO_2 enters the system.

❖ **If ConFlo II III Interface window is not visible**

1. Right-click somewhere into the **Accessories toolbar**. Click on the **Administrative Panels...** button.

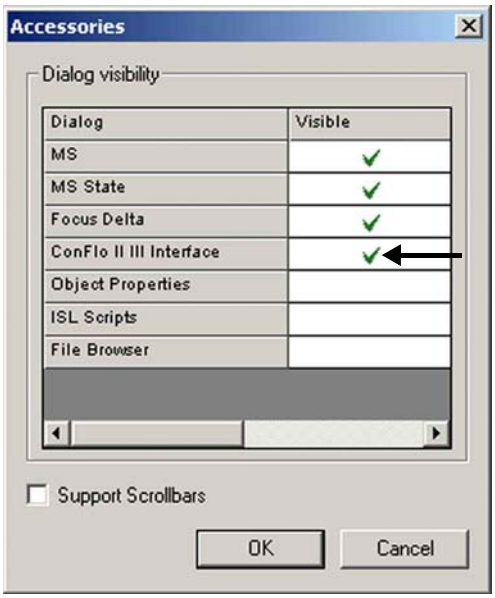


Figure 6-4. Windows visible windows at Accessories toolbar

Figure 6-4 allows to mark dialogs (that is windows) by ✔ . If you mark a dialog, the respective window will be shown at the Accessories toolbar.

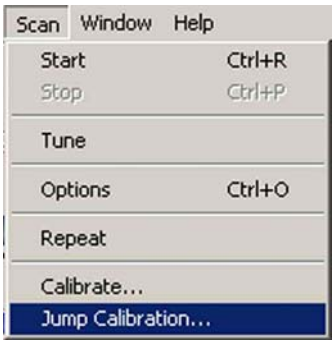
2. Mark **ConFlo II III Interface** and confirm by **OK**.

   The ConFlo II III Interface window will be shown at the Accessories toolbar.

Note If only the Title bar of the ConFlo II III Interface window is visible, click on the **Unshrink** button at the right corner of the Title bar. The ConFlo II III Interface window will appear. ▲

Before Starting Jump Calibration

❖ **Before starting a Jump Calibration**



1. Select **Scan > Jump Calibration...** or

   Alternatively, click on the **Jump** button on the toolbar next to the Instrument Control window.

The list of available Jump Calibrations appears. See Figure 6-5.

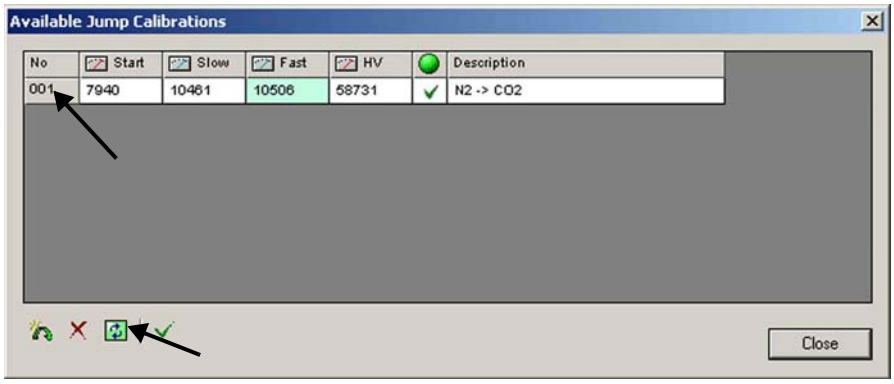


Figure 6-5. Available Jump Calibrations

2. In the list of available Jump Calibrations (Figure 6-5) mark the one for N_2 → CO_2 by clicking on its **No.**, for example **001**.

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

   Fast: magnet setting of Jump Calibration

   HV: high voltage setting of Jump Calibration

Note Before pressing the Recalibrate button, make sure that CO_2 reference gas is activated, that is that CO_2 enters the source. ▲

3. Click on the **Recalibrate** button.

If no Jump Calibration is available in the list (Figure 6-6), create a new one.

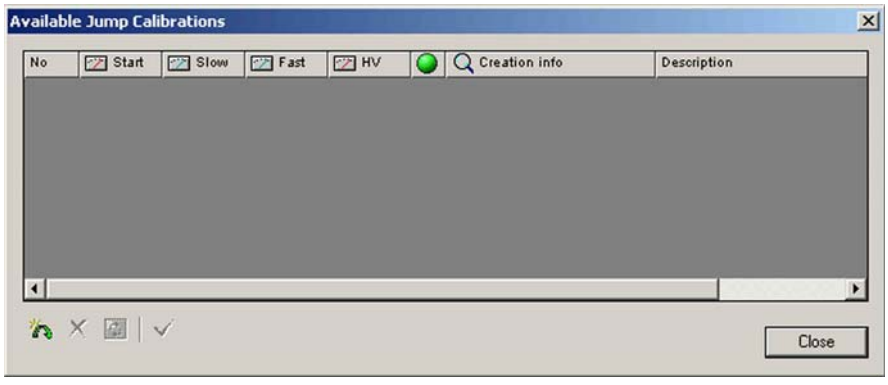


Figure 6-6. No Jump Calibration available

❖ To create a new Jump Calibration

1. Click on the **New** button.

2. Define the parameters of the new Jump Calibration as shown in Figure 6-7.

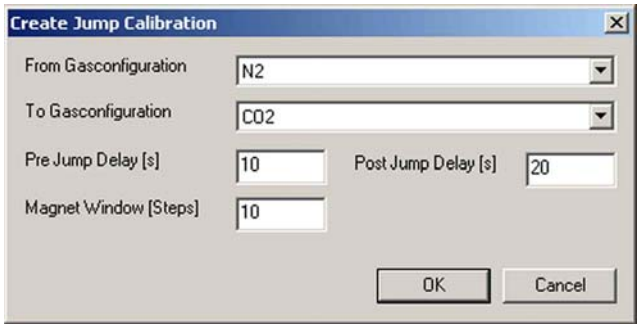


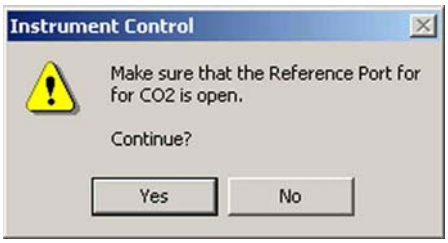
Figure 6-7. Defining parameters of new Jump Calibration

At **From Gas Configuration** select **N2**.

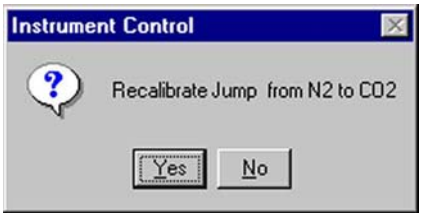
At **To Gas Configuration** select **CO2**.

At **Pre Jump Delay** [s], **Post Jump Delay** [s] and **Magnet Window** [Steps] accept the default values.

3. Confirm by **OK**.



4. If you have already opened the Reference Port for CO_2 as shown in Figure 6-3, confirm by **Yes**.



5. Confirm by **Yes** to start the Jump Calibration.

Performing Jump Calibration

❖ **To perform a Jump Calibration**

1. Jump to CO2 along the hysteresis curve.
2. Perform a peak center for CO2 to get the signal height.
3. Jump to N2 along the hysteresis curve (N_2 is origin).
4. Jump to CO2 (**not** along hysteresis curve).
5. Perform a peak center for CO2 to catch the peak. See Figure 6-8.

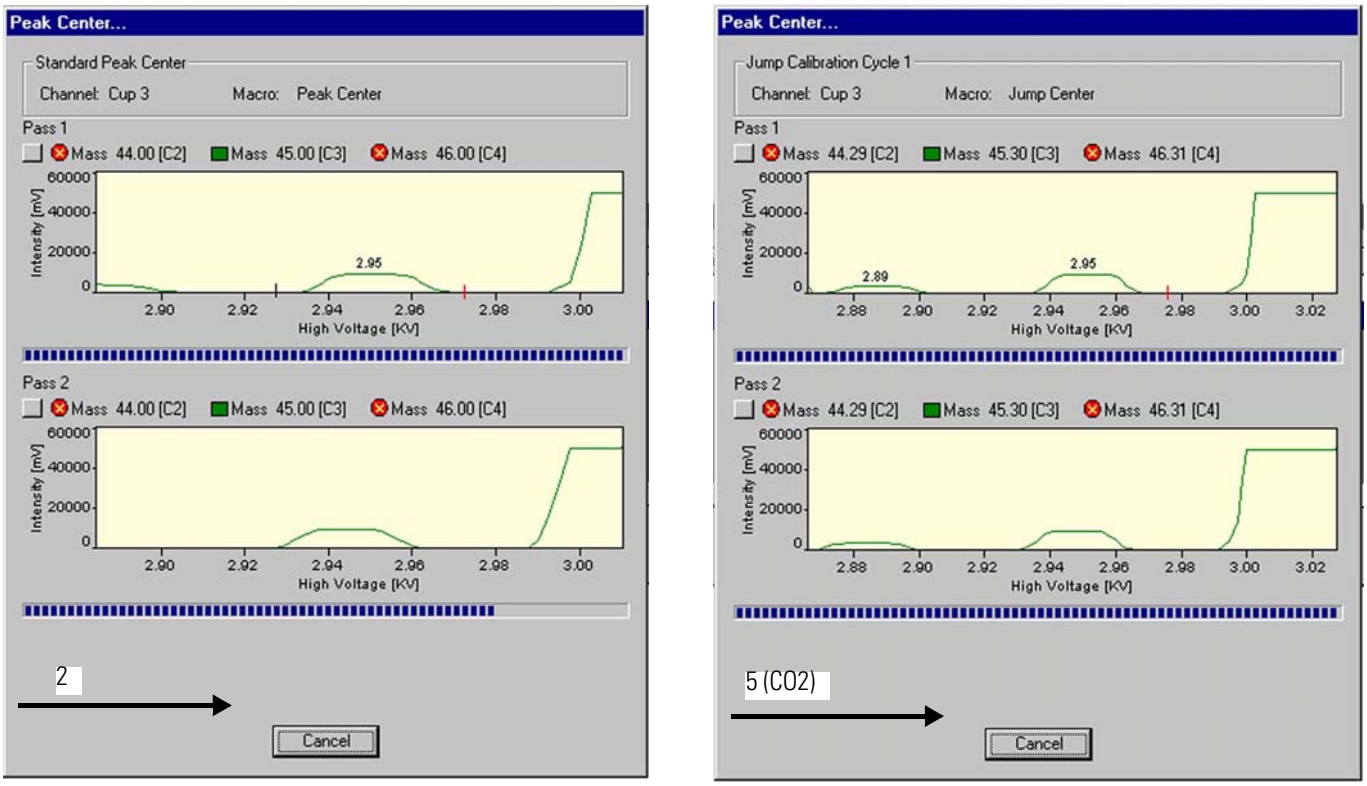


Figure 6-8. Performing peak center for CO2

Starting Dual Measurement

Before you start a dual measurement, make sure that your system meets the hardware requirements summarized in Table 6-1.

Table 6-1. Hardware requirements for dual measurement

Parameter	Value
oxidation furnace temperature	1020 °C for Cr_2O_3 filling 900 °C for CuO filling
reduction furnace temperature	650 °C
GC column temperature	45 °C
helium flow	90 mL/min
purge	helium flow must be sufficiently open depends on the autosampler
standard gas (N_2) on ConFlo II/III	must be available
needle valve (ConFlo II/III-IRMS connection)	must be open
Standard CO_2 intensity	is adjusted at about 3-5 V
Standard N_2 intensity	is adjusted at about 3-5 V

Defining a Method

Note Methods taken from the Examples folder may not work properly! Therefore, use them only as a guideline and create new methods on your own. ▲

From the Examples folder of the File Browser take the method N2+CO2.met only as a guideline.

Instrument Tab

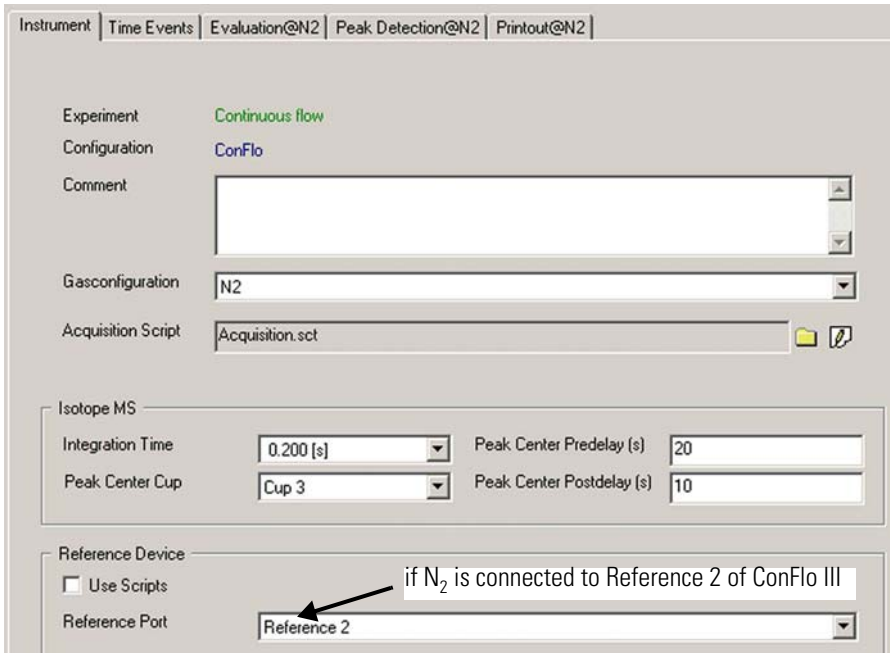


Figure 6-9. Dual measurement - Instrument tab

Time Events Tab

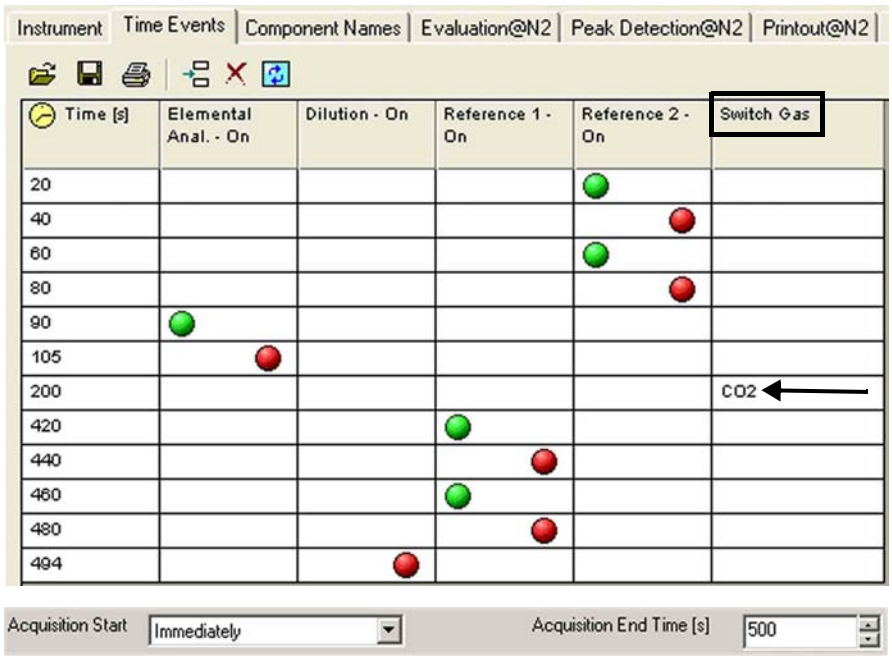


Figure 6-10. Dual measurement - Time Events tab

❖ **To define parameters for method switching**

1. Double-click on **CO2** in the Switch Gas column to edit. See arrow in Figure 6-10.

   The event time is active since for example 200 s. Figure 6-11 appears.

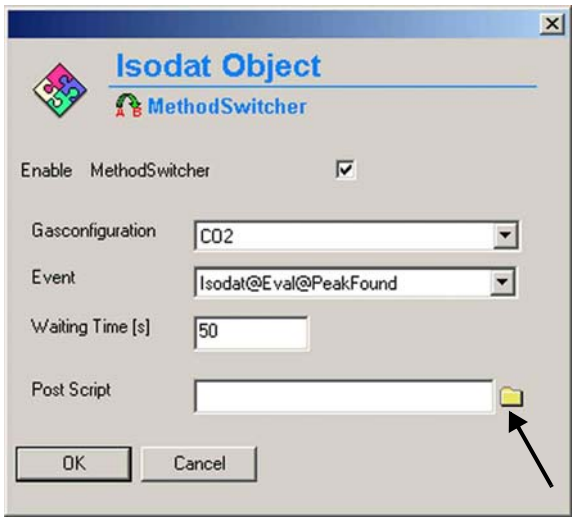


Figure 6-11. Parameters for method switching - without post script

2. At **Gas Configuration**, select the gas configuration to be switched to, for example **CO2**.
3. The switch will be performed when the peak has been found. This is defined at **Event** by selecting **Isodat@Eval@PeakFound**.
4. Type in the last jump time at **Waiting Time**.

   At for example 200 s, waiting for the peak begins. If a peak is found, the jump takes place. If no peak is found, the waiting time elapses before the jump takes place.

5. Click on  to browse to the ConFlo folder for a post script which will be executed during the jump. See arrow in Figure 6-11.

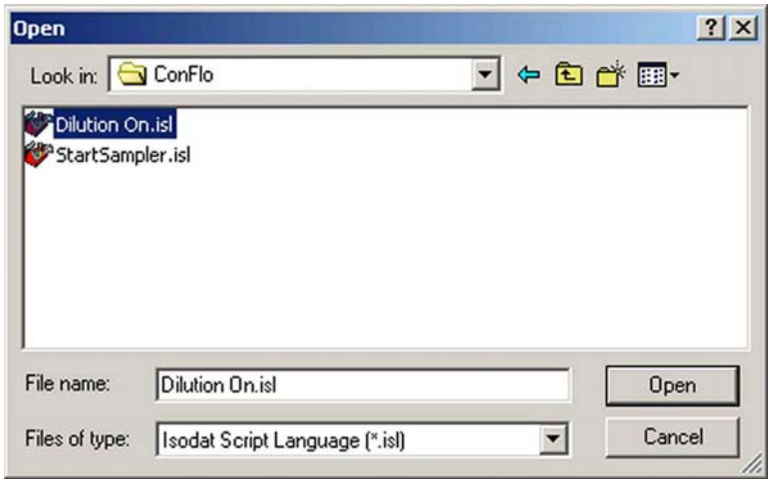


Figure 6-12. Browsing for post script

6. Select your post script, for example **Dilution On.isl**.

   This means that with a jump to CO_2, the dilution capillary in the ConFlo III is automatically activated. The selected post script is now displayed together with its path at Post Script. See arrow in Figure 6-13.

7. Confirm by **OK**.

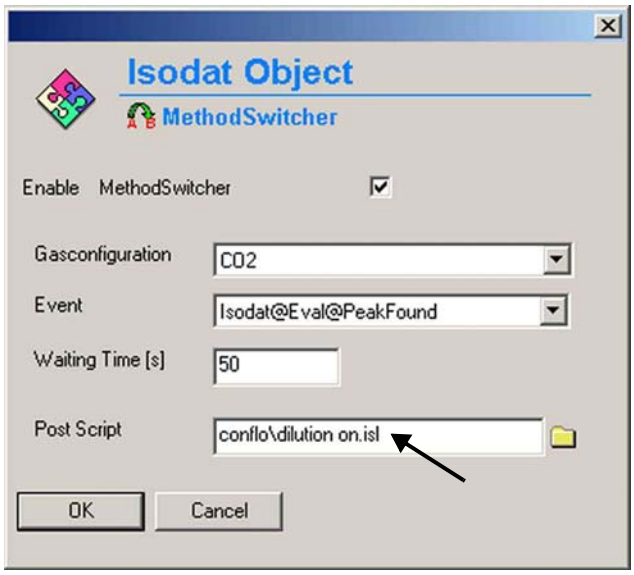


Figure 6-13. Parameters for method switching - with post script

Note For N_2 and CO_2, different Evaluation tabs, Peak Detection tabs and Printout tabs appear, for example Evaluation@N2 and Evaluation@CO2. ▲

Evaluation@N2 Tab

For the Ref. Time value in Figure 6-14 (40 s) see the time events list (40 s line of Figure 6-10).

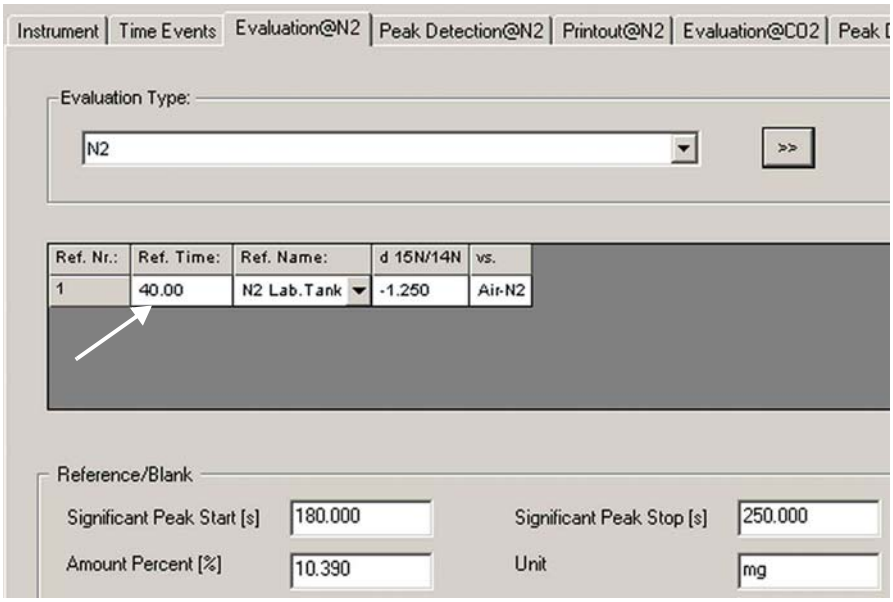


Figure 6-14. Dual measurement - Evaluation@N2 tab

Peak Detection@N2 Tab

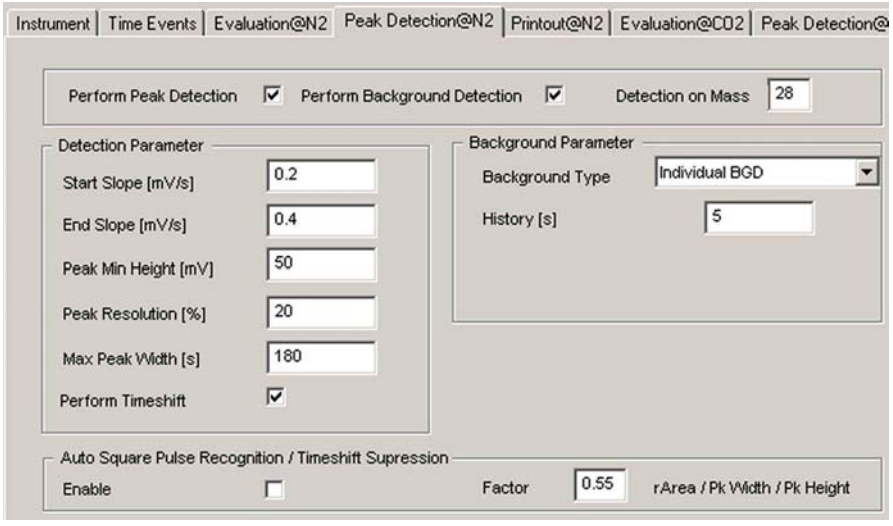


Figure 6-15. Dual measurement - Peak Detection@N2 tab

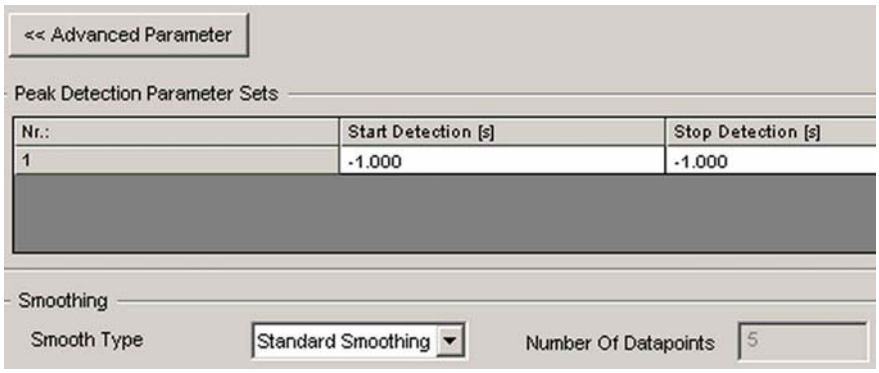


Figure 6-16. Dual measurement - Peak Detection@N2 tab - Advanced Parameters

Note A value of -1 denotes unlimited. ▲

Printout@N2 Tab

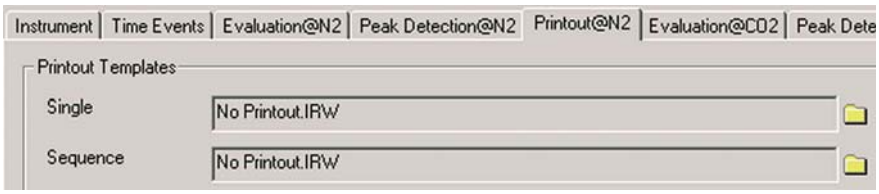


Figure 6-17. Dual measurement - Printout@N2 tab

Note Usually, the printout of results is performed not until the complete measurement has been finished. Therefore, it is recommended to choose No Printout.irw at Printout@N2 tab, because at this moment, data acquisition is still running. Instead, printout options are defined in the end at Printout@CO2 tab.

Evaluation@CO2 Tab

For the Ref. Time value in Figure 6-18 (440 s) see the time events list (440 s line of Figure 6-10).

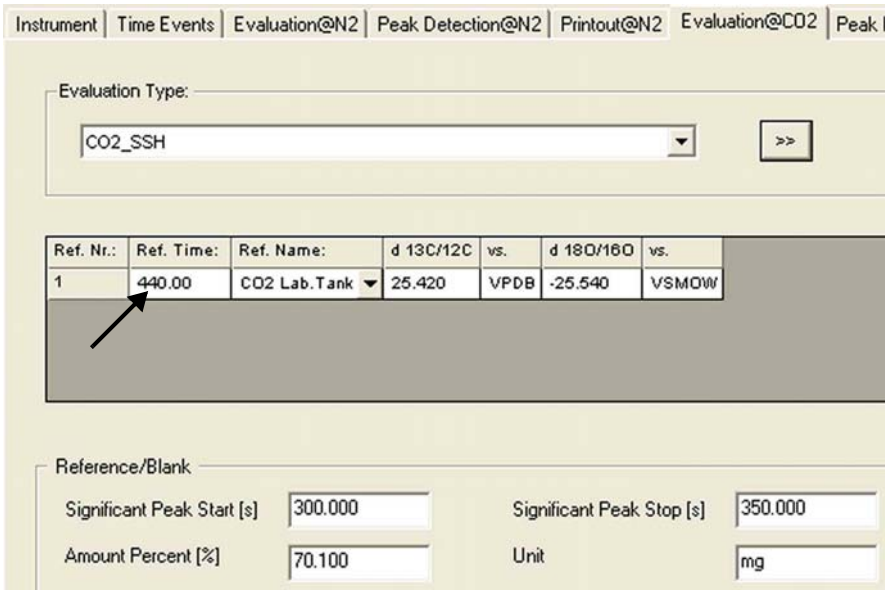


Figure 6-18. Dual measurement - Evaluation@CO2 tab

Peak Detection@CO2 Tab

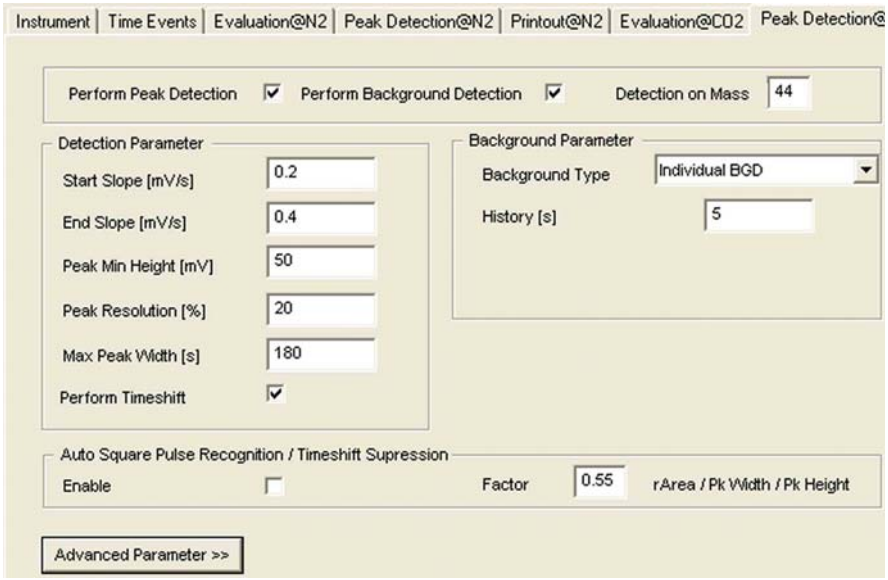


Figure 6-19. Dual measurement - Peak Detection@CO2 tab

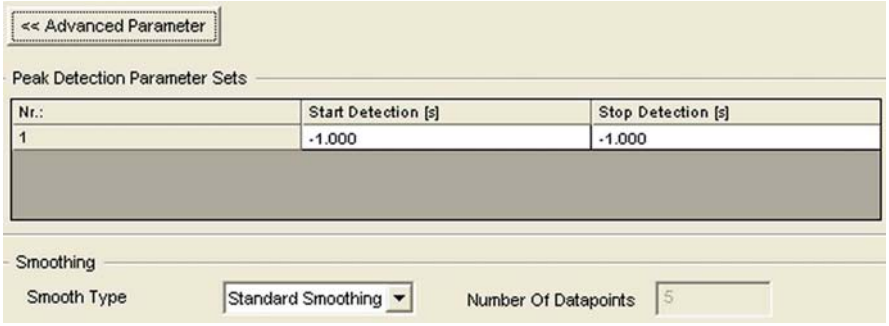


Figure 6-20. Dual measurement - Peak Detection@CO2 tab - Advanced Parameters

Note A value of -1 denotes unlimited. ▲

Printout@CO2 Tab

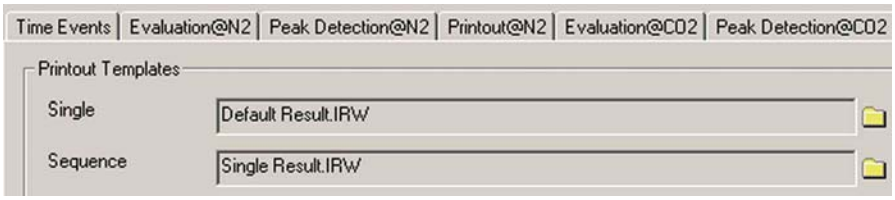


Figure 6-21. Dual measurement - Printout@CO2 tab

Defining New Sequence

❖ **To define a new sequence**

1. Place a sample, for example 0.281 mg of urea, in the solid-autosampler as shown in Figure 6-23.

2. To create a new sequence click on the **New** button.

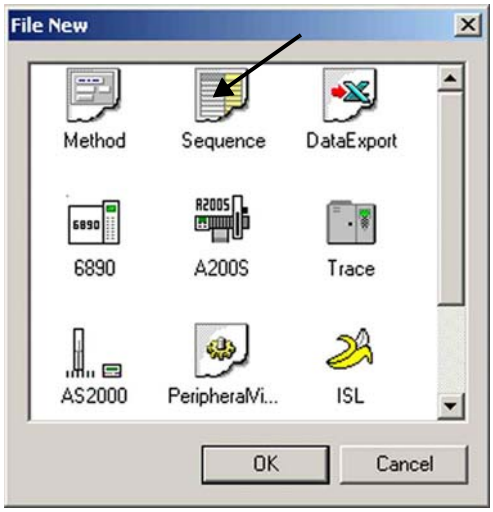
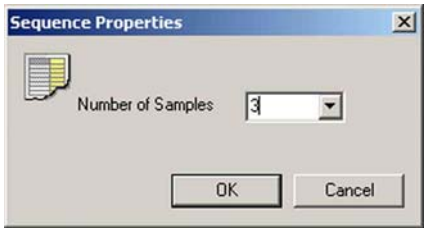


Figure 6-22. Creating new sequence

3. In Figure 6-22 mark the **Sequence** icon and confirm by **OK**.



4. Define the number of samples, for example 3. Confirm by **OK**.

5. Edit the sequence grid as shown in Figure 6-23 and Table 6-2.

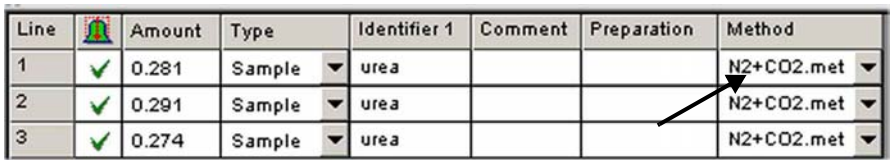


Figure 6-23. Dual measurement - editing sequence grid

Table 6-2. Sequence grid parameters for dual measurement

Parameter	Comment
Peak Center	Enable ✓ to perform a peak center prior to measurement (always recommended).
Amount	amount of sample
Type	Select the kind of species, for example Sample
Identifier	Type in text to identifiy the sample (optionally)
Comment	Type in a comment (optionally).
Preparation	Type in information related to preparation (optionally).
Method	Select the IRMS method (here: N2+CO2.met)

6. Click on the **Start** button.

7. Define a folder to save your result files as well as export and printout parameters. See Figure 6-24.

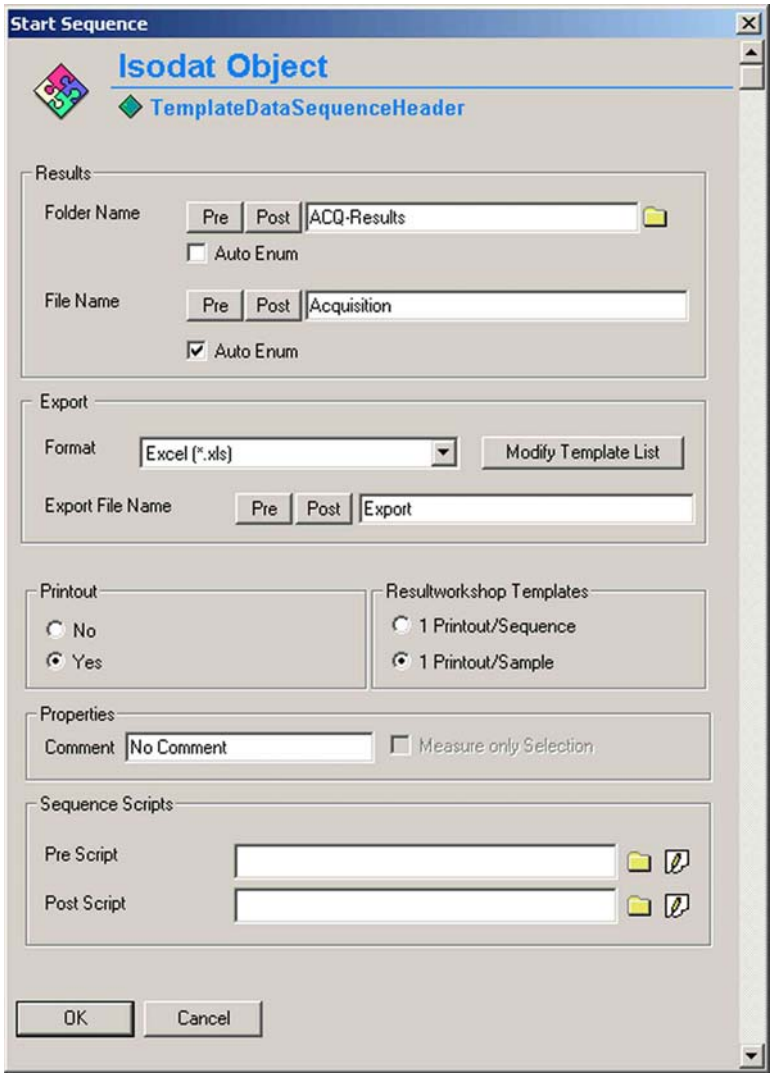


Figure 6-24. Starting dual measurement - defining export and printout parameters

Events during Acquisition

This section summarizes the events that happen during data acquisition. See the time events list (Figure 6-10) and the result chromatogram (Figure 6-26).

1. Peak center procedure

2. First reference gas pulse (N_2) activated at 20 s (duration: 20 s). See Figure 6-10 and Figure 6-26.

3. Second reference gas pulse (N_2) activated at 60 s (duration: 20 s). See Figure 6-10 and Figure 6-26.
4. The Elemental Analyzer gets a start signal from Isodat at 90 s See Figure 6-10.

Note After receiving a start signal from Isodat, the Elemental Analyzer follows its own protocol (that is oxygen injection, sample delay). ▲

5. Sample peak (N_2) appears approximately 80 s after combustion. See Figure 6-26.
6. Jump at 212 s. See Figure 6-26.
7. Sample peak (CO_2) appears approximately 200 s after combustion See Figure 6-26.
8. CO_2 reference gas pulse activated at 420 s (duration: 20 s), See Figure 6-10.
9. CO_2 reference gas pulse activated at 460 s (duration: 20 s). See Figure 6-10.
10. Dilution off at 494 s.
11. Acquisition stops at 500 s. See Figure 6-10.

Results

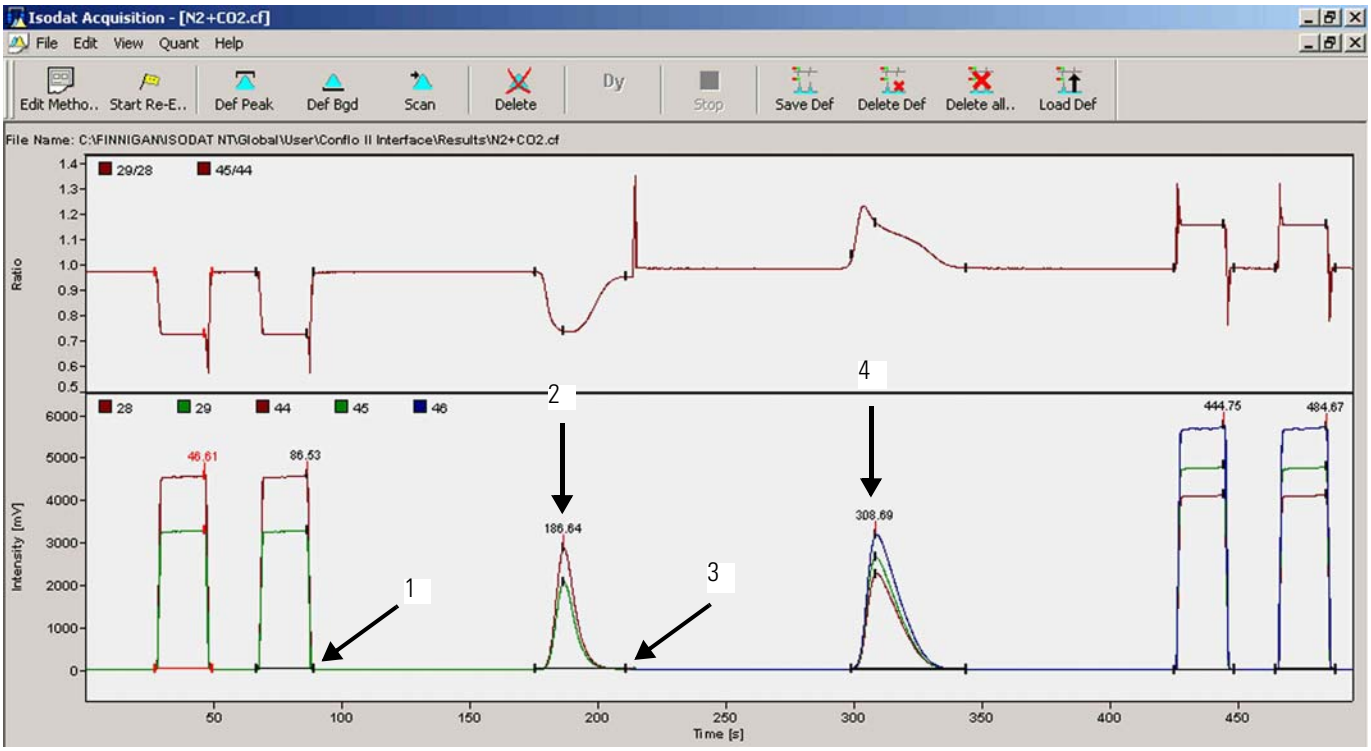
After finishing data acquisition the printer creates a data output sheet as defined by the selected Result Workshop template (*.irw). The results are also exported to a spreadsheet file, if the checkbox has been marked previously in Figure 6-22.

Figure 6-25 shows the first sequence line for a dual measurement.

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.281	Sample	urea			N2+CO2.met

Figure 6-25. Sequence line for dual measurement

Figure 6-26 shows the chromatogram and Figure 6-27 the related result grid.



Labeled Components: 1=Elemental Analyzer activation, 2=N_2 sample peak, 3=jump, 4=CO_2 sample peak

Figure 6-26. Dual measurement - chromatogram

N2 | CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	End [s]	Width [s]	Ampl. 28 [mV]	Ampl. 29 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area All [Vs]	Amt% [%]	d 15N/14N [per mil] vs. Air-N2	AT% 15N/14N [%]
1	27.2	46.6	49.5	22.4	4565	3274	14.7	11.1	85.595	-	-12.930	0.361751
2*	67.1	86.5	89.2	22.2	4584	3288	14.7	11.1	85.647	-	-12.940	0.361747
3	175.8	186.6	211.5	35.7	2850	2068	14.3	10.7	25.117	10.4000000	-0.760	0.366194

Figure 6-27. Dual measurement - nitrogen-related peaks

The N2 tab of Figure 6-27 reveals information about the nitrogen-related peaks.

N2 | CO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	End [s]	Width [s]	Ampl. 44 [mV]	Ampl. 45 [mV]	BGD 44 [mV]	BGD 45 [mV]	Area All [Vs]	Amt% [%]	d 13C/12C [per mil] vs. VPDB	AT% 13C/12C [%]	d 18O/16O [per mil] vs. VSMOW
4	299.5	308.7	344.2	44.7	2261	2649	3.3	1.5	33.246	71.1000000	-29.781	1.073084	14.238
5*	425.3	444.8	448.7	23.4	4149	4813	3.3	1.5	77.788	-	-26.100	1.077112	-0.000
6	465.0	484.7	488.4	23.4	4141	4802	3.5	1.7	77.876	-	-26.204	1.076998	-0.128

Figure 6-28. Dual measurement - carbon-related peaks

The CO2 tab of Figure 6-28 reveals information about the carbon-related peaks.

Chapter 7 Sulfur Measurement

In comparison to isotope ratio measurements of nitrogen ($^{15}N/^{14}N$) and carbon ($^{13}C/^{12}C$) in organic and inorganic matter, the analysis of sulfur ($^{34}S/^{32}S$) has always been difficult. Analyzing biological sulfur makes experimental difficulties caused by the low abundance of sulfur in organisms (for example 0.2 wt % [mg/mg] in plants), as well as by the fact that sulfur is present as a mixture of organic and inorganic compounds. Difficulties in using the Elemental Analyzer arise due to a large amount of carbon in the same samples, which quickly exceeds the capacity of combustion reactors. This causes incomplete combustion.

Thermo Fisher Scientific (Bremen) has developed a technique for precise, accurate and fast sulfur measurement which puts it on a par with carbon and nitrogen in terms of ease of use and sample size.

Due to the high natural abundance of the heavier isotope ^{34}S, less amplification is required and may become necessary for all Delta IRMS before Delta^{plus} XP (since 2002). It is recommended to use a smaller resistor (1×10^{10} Ω) on the cup for m/z 66 (usually 3×10^{10} Ω).

This chapter treats the following topics:

Procedure

Sulfur measurements are performed using a specially equipped Elemental Analyzer. Combustion and reduction are carried out in a single reactor filled with tungsten oxide (WO_3) and copper (Cu) as reducing agent. Alternatively, CuO can be used instead of WO_3.

The technique used for sulfur determination is based on the quantitative "Dynamic Flash Combustion" method. The samples - sometimes together with V_2O_5 - are wrapped in tin capsules and placed into the autosampler. Then they are continuously purged with helium (or oxygen using NA 2500 or EA 1110) to remove any traces of water and nitrogen. When a sample is dropped into the reactor, the helium stream is temporarily enriched with pure oxygen. The sample and its container melt as the tin promotes a violent reaction (flash combustion). Under these favorable conditions, even thermally resistant substances are completely oxidized.

In the reactor, for example $BaSO_4$ is thermally decomposed within a tin capsule. The following reactions can then take place:

$$BaSO_4 \rightarrow BaO + SO_2 + \frac{1}{2}O_2$$

$$BaSO_4 \rightarrow BaO + SO_3$$

$$SO_3 \rightarrow SO_2 + \frac{1}{2}O_2$$

Note Refer to Bailey, S.A. and Smith, J.W. (1972): An improved method for the preparation of sulfur dioxide from barium sulfate for isotope ratio studies. Anal. Chem. **44**, 1542-1543. ▲

Although the process does not require oxygen, better combustion has been experienced when oxygen is injected and vanadium pentoxide (V_2O_5) is added to the sample. If either the oxygen pressure is low or a bad catalyst is selected or the reactor contains too much ash, combustion will proceed slowly. A slow stream of SO_2 through the system causes adsorption at the tubing wall.

Note It is important that enough reduced copper is present in the combustion tube. If this is not assured, SO_3 will only be reduced partially and isotope fractionation will occur. "Light" isotopes ($^{32}SO_3$) are reduced more easily than "heavy" isotopes ($^{34}SO_3$). Therefore, SO_2 gas is depleted in ^{34}S compared to the original sample, and the δ value becomes more negative. ▲

Sulfur Measurement Kits

To perform a sulfur measurement you can get two sulfur measurement kits provided by Thermo Fisher Scientific(Bremen):

- sulfur measurement kit for ConFlo III and
- sulfur measurement kit for FlashEA

Sulfur Measurement Kit for ConFlo III

The sulfur measurement kit for ConFlo III has the P/N 1157100 and consists of the parts summarized in Table 7-1.

Table 7-1. Parts of sulfur measurement kit for ConFlo III

Designation	P/N	Qty.
attachment for exhaust tube	1121390	1
self-adhesive heating foil for ConFlo III	1141180	1
power supply for self-adhesive heating foil for ConFlo III	2048580	1

Sulfur Measurement Kit for FlashEA

The sulfur measurement kit for FlashEA has the P/N 1157110 and consists of the parts summarized in Table 7-2.

Table 7-2. Parts of sulfur measurement kit for FlashEA

Designation	P/N	Qty.
sulfanilamide	1069140	1
Teflon® GC column	1141170	1
Al olive (2 mm)	1141210	5
nut	1121370	5
Teflon tube	1141220*	3.5 m
combustion reactor (packed, “ready for use”)	1118121	2
union	1141230	3
capillary tube (1/16”×0.8 mm)	0605470	0.05 m

* For additional part numbers (for example of nuts) refer to “Installing Teflon® Tubing” on page 7-5 and especially to Figure 7-2.

Warning When working with sulfur dioxide (SO_2), good ventilation is essential. Otherwise, the gas can be hazardous to your health. ▲

Warning To ensure operational safety, a CO, SO2 and H2 detector with an alarm must be installed! ▲

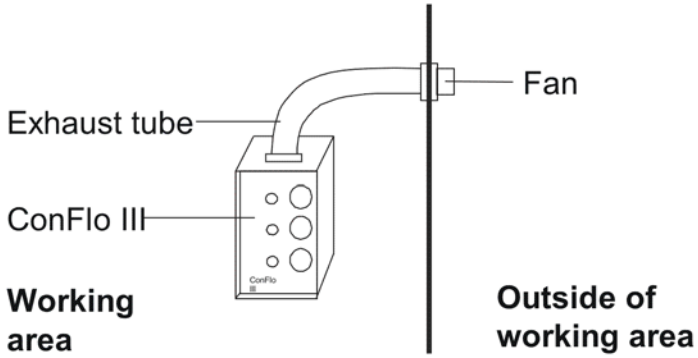


Figure 7-1. ConFlo III Interface with exhaust tube and fan

The exhaust tube should be installed on top of the ConFlo III Interface as shown in Figure 7-1 to remove the toxic sulfur dioxide (SO_2) from inside of ConFlo III out of your working area.

Preparing System for Sulfur Measurement

❖ **To prepare the system for a sulfur measurement**

1. Install the exhaust tube on ConFlo III. See Figure 7-1.
2. Install the self-adhesive heating foil as outlined in "Installing Self-Adhesive Heating Foil" on page 7-6 and especially in Figure 7-3.
3. Install the properly packed reactor within the Elemental Analyzer. Refer to "Filling Reactor" on page 7-7 and especially to Figure 3-5.
4. Replace all stainless steel tubing with Teflon tubing. See Figure 7-2.
5. Install the SO_2 GC column. Refer to "Stainless Steel GC Column" on page 7-10 and to "Teflon GC Column" on page 7-10.

Installing Teflon® Tubing

To perform a sulfur measurement, a part of the stainless steel tubing needs to be replaced by Teflon tubing. Figure 7-2 provides an overview.

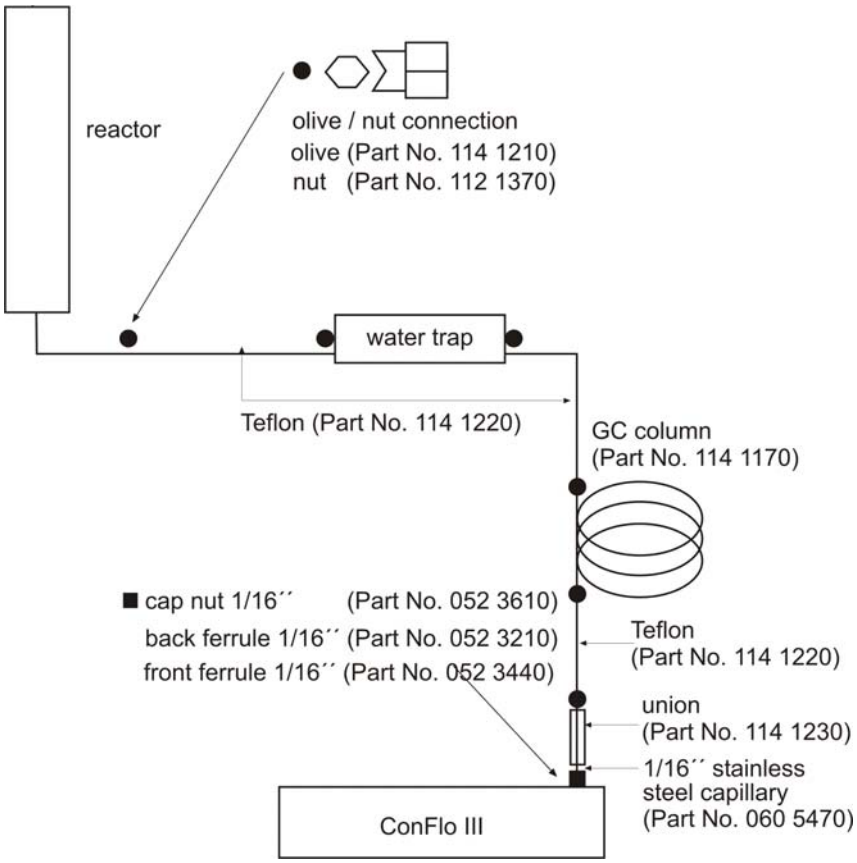


Figure 7-2. Installing Teflon tubing

Installing Self-Adhesive Heating Foil

Note SO_2 is liquid at higher pressures. Therefore, the manometer should be heated to avoid condensation of SO_2. The temperature must be between 60 °C and 70 °C. It may vary with ventilation. ▲

❖ **To install the self-adhesive heating foil**

1. Remove the backing paper from the self-adhesive heating foil.
2. Paste the heating foil in the middle of the rear side of the manometer (of Ref 2) as shown in Figure 7-3.

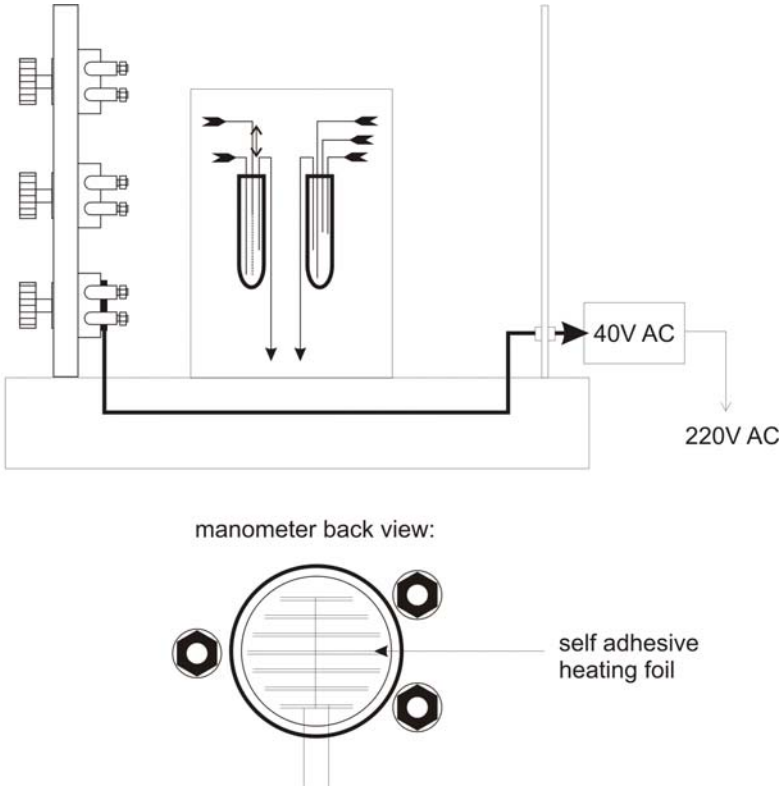


Figure 7-3. Installing self-adhesive heating foil

Note Take care that the wires of the heating foil point downwards when pasting it on the rear side of the manometer. ▲

3. Simply insert the wires into the plug socket where they fix themselves.

Filling Reactor

We recommend using a Thermo Fisher Scientific “ready for use” reactor (P/N 1118121). The reactor is 470 mm long. If it must be packed by the user, the packing should be as shown in Figure 7-4.

About 150 to 200 analyses can be performed using the reactor type described above. With the exception of tungsten oxide, no parts of the reactor can be used a second time.

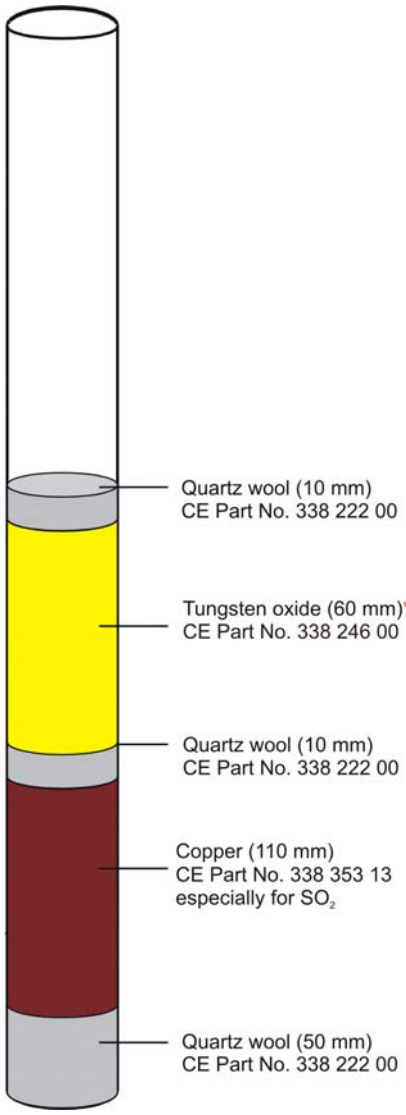


Figure 7-4. Packing of reactor

Note Instead of tungsten oxide also 60 mm of copper oxide (CE P/N 33821710) can be used as an option for packing the reactor. ▲

Before Starting Sulfur Measurement

We assume that the user already has working experience with the isotope ratio mass spectrometer.

❖ **Before starting a sulfur measurement make sure that**

1. The Elemental Analyzer is set up, that is the SO_2 reactor is packed and installed, and the water trap is installed.
2. The special SO_2 stainless steel (or Teflon) GC column is installed.
3. The connection between reactor, water trap, GC column and ConFlo III is made up of Teflon tubing.
4. The gases needed (He, O_2) are available and have been connected to the corresponding positions.
5. Leak-check all connections outside the ConFlo III by brushing all fittings carefully with soapsuds.
6. The exhaust tube is connected to the ConFlo III and ventilation is working.
7. SO_2 is connected to Ref 2 of the ConFlo III.
8. The self-adhesive heating foil is installed/switched on.
9. Compressed air is connected to the ConFlo III and to the Elemental Analyzer.
10. A ConFlo III configuration is installed and has already been in use for for example nitrogen or carbon analysis.
11. The IRMS has been calibrated for SO_2 measurements.
12. Switch the eElemental Analyzer on.
13. Adjust the gas pressure of the Elemental Analyzer and the ConFlo III.

Take the following settings as a guideline.

Settings for EA 1108, EA 1110 and NA 2500

Table 7-3 summarizes the settings for EA 1108, EA 1110 and NA 2500.

Table 7-3. Settings for EA 1108, EA 1110 and NA 2500

Parameter	Value
He (Elemental Analyzer)	100 kPa
O_2 (Elemental Analyzer)	150 kPa
Purge with O_2	40 mL/min
Purge with He	110 mL/min (depending on the autosampler)
He (ConFlo III)	1 bar
Ref. 2 (ConFlo III)	1 bar

Settings for FlashEA

Table 7-4 summarizes the settings for the FlashEA.

Table 7-4. Settings for FlashEA in Eager software

Parameter	Value
Carrier	300 mL/min
Oxygen	175 mL/min
Reference	110 mL/min (depending on autosampler)
Cycle run time	60 s
Sampling delay	23 s
Oxygen Injection End	3 s

14. Switch off the ion source and inject the He dilution capillary.
15. Slowly open the needle valve. Make sure that the needle valve is heated.
16. Make sure that the ion source heater and the change over valve heater are operating, if available.
17. Switch on the ion source.
18. After approximately 30 min, the expected background at the respective reactor and column temperature should be as summarized below.

Stainless Steel GC Column

Table 7-5 lists the backgrounds to be expected when a stainless steel GC column is used.

Table 7-5. Expected backgrounds using stainless steel GC column

reactor temperature	column temperature	mass	28	29	Ar	H_2O	64	66
		cup	28	29	29	29	64	66*
		range	mV	mV	mV	V	mV	mV
30 °C	30 °C		50	60	180	1.5		
400 °C	100 °C		110	140	350	1.8		
1020 °C	100 °C		70	65	220	1.2	< 5	< 10

* Ri = 10^{10} Ω

Note Background values may vary depending on sensitivity and focus settings. They are given here as a general guideline. ▲

Teflon GC Column

Table 7-6 lists the backgrounds to be expected when a Teflon GC column is used.

Table 7-6. Expected backgrounds using Teflon GC column

reactor temperature	column temperature	mass	28	29	Ar	H_2O	64	66
		cup	28	29	29	29	64	66*
		range	mV	mV	V	V	mV	mV
30 °C	30 °C		295	223	0.93	3.9		
400 °C	100 °C		422	337	1.30	5.6		
1020 °C	100 °C		330	243	0.99	2.1	< 5	< 10

* Ri = 10^{10} Ω

Note Background values may vary depending on sensitivity and focus settings. They are given here as a general guideline. ▲

Note Teflon tubes are not absolutely tight against atmosphere. Therefore, the backgrounds of argon and nitrogen are higher than those of carbon and nitrogen measurements. Nevertheless, take care of leaks. ▲

Note When using normal amplification (that is, resistor of 3×10^{10} Ω on cup for m/z 66), the background values will be three times higher. ▲

Creating Gas Configuration for Sulfur Measurement

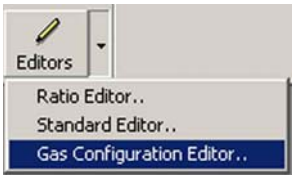
A gas configuration determines a combination of masses, which are collected in the cups, for evaluation of ratios and eventually δ values. The gas configuration is specific for the particular gas and is combined with a magnet field value taken from the mass calibration of your IRMS. The ratio groups determine the reported ratios of predefined masses.

Prior to defining this gas configuration ensure that the connected IRMS has the cups for the simultaneous detection of m/z 64 and m/z 66 and mass calibration for these cups has already been performed.

For a $^{34}S/^{32}S$ measurement, a gas configuration must be available for m/z 64 (that is $^{34}S^{16}O^{16}O$) and m/z 66 (that is $^{32}S^{16}O^{16}O$). Otherwise, it must be created.

❖ **To create a gas configuration for sulfur measurement**

1. Open Isodat **Acquisition**.



2. Open the **Gas Configuration Editor** (Figure 7-5).

   It is only available, if no acquisition is running.

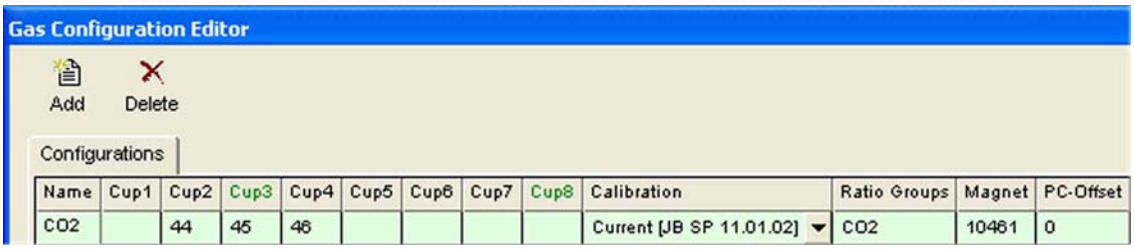
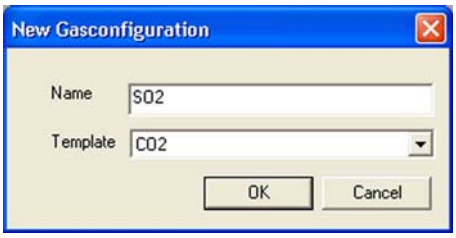


Figure 7-5. Gas Configuration Editor

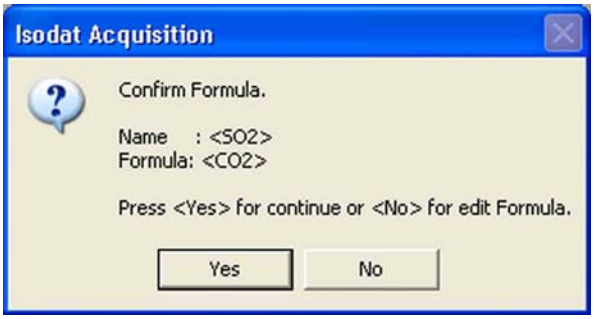
Per default, the gas configuration CO2 is being created as the first one. If the gas configuration SO2 has already been created, it occurs in the list of Figure 7-5. However, if the gas configuration SO2 has not been created yet, it does not occur in the list. In the latter case, proceed as follows.

3. Click on the **Add** button to add a new gas configuration.



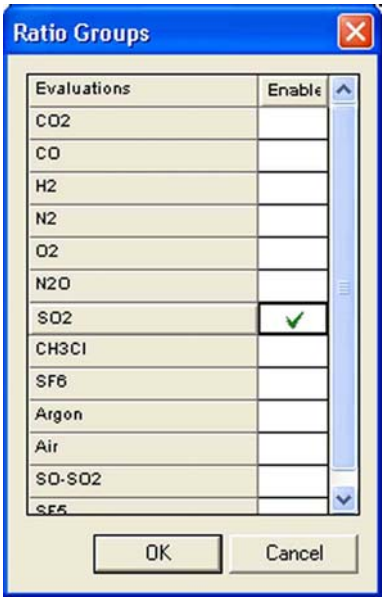
4. Type **SO2** for the **Name**.
5. Select a gas configuration as **Template**, for example **CO2**.

   In the context menu, only the already existing gas configurations are displayed. When creating the first gas configuration, **CO2** is displayed.
6. Confirm by **OK**.



7. Type **No**.

   If you would type **Yes**, this would automatically mark the template (that is CO2) instead of SO2 in the Ratio Groups window below.



8. Mark **SO2**. If Ratio Groups other than SO2 are marked, unmark them all.
9. Confirm by **OK**.

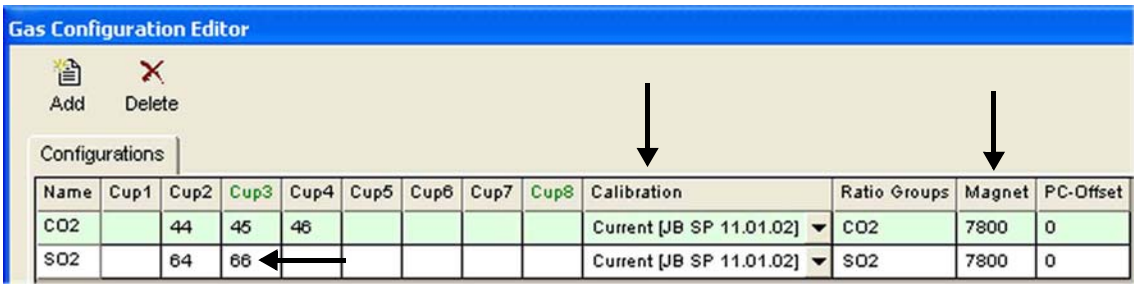


Figure 7-6. Creating new gas configuration

The new gas configuration SO2 appears in the list as a row of its own. See Figure 7-6.

10. In the **Calibration** column of Figure 7-6 select your current calibration file.

Note Figure 7-6 shows a common cup configuration as used in most Delta mass spectrometers, that is universal triple collector. If you have a special cup configuration, the respective masses will be collected in other cups! ▲

11. In Figure 7-6 type in the correct masses (64 and 66 replace for example 44, 45 and 46) to the appropriate cups specific for your IRMS.

    When highlighting the specific gas configuration by a click on its row, the number of cups required for measurement is displayed together with the assigned masses. See Figure 7-7.

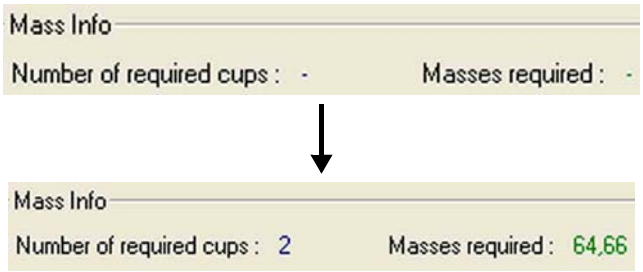


Figure 7-7. Required cups together with assigned masses

12. Select a calibration, which is valid for the selected cups.
13. Click on the **Save & Close** button Save & Close.

Zero Enrichment of Sulfur (Standard On/Off Test)

We assume that the user already has working experience with the ConFlo III Interface and IRMS. It is recommended to perform a simple check in order to test the analytical condition of ConFlo III and IRMS before measuring any samples.The most important checks to test the analytical condition are zero enrichment and linearity test.

1. Use the following method SO2_zero.met from the Examples folder of the File Browser only as a guideline.

Instrument Tab

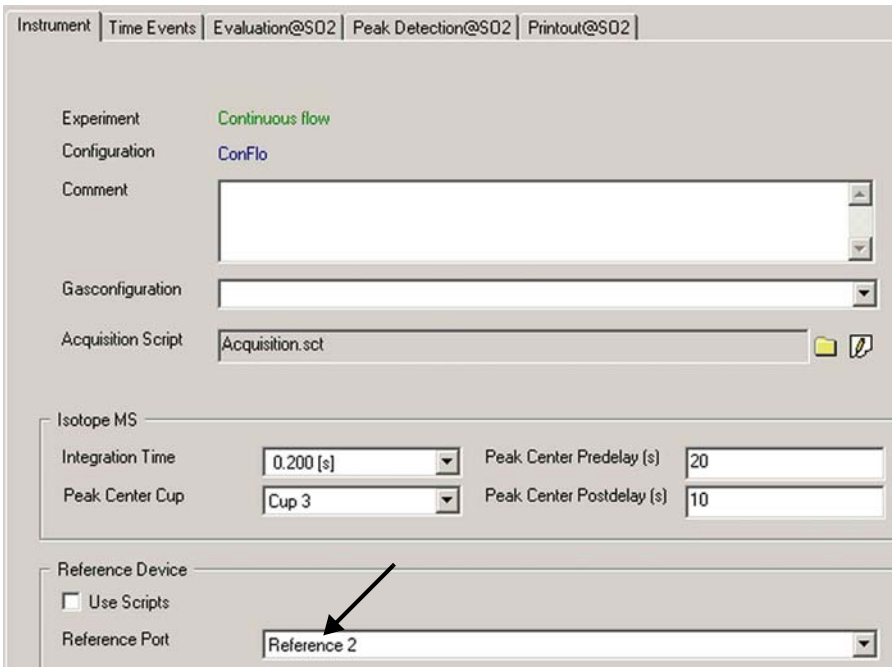


Figure 7-8. Zero Enrichment of sulfur - Instrument tab

In Figure 7-8 select the **reference port** your reference gas is connected to at the ConFlo III interface (for example **Reference 2**).

Adapt the reference gas port to the respective column of the time events list: for example, if you choose **Reference 2**, the on-off entries must occur in the Reference 2-On column of the time events list. See Figure 7-9.

Time Events Tab

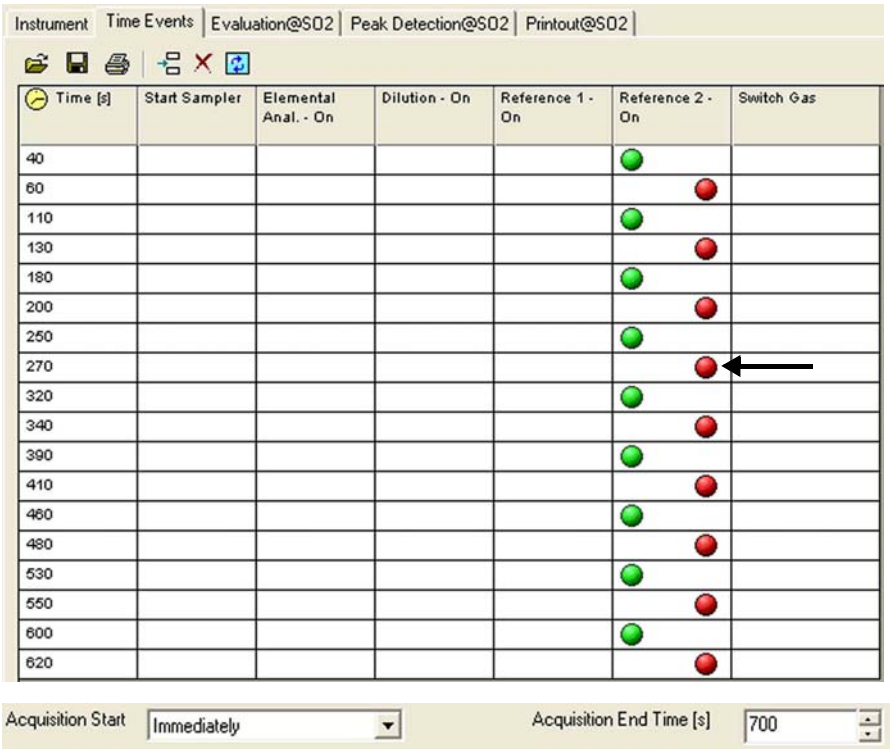


Figure 7-9. Zero Enrichment of sulfur - Time Events tab

Recognize the nine on-off pulses shown in Figure 7-9 in the expected chromatogram, Figure 7-13. The off-time of the for example forth reference gas pulse is 270 s. See Figure 7-10.

Evaluation Tab

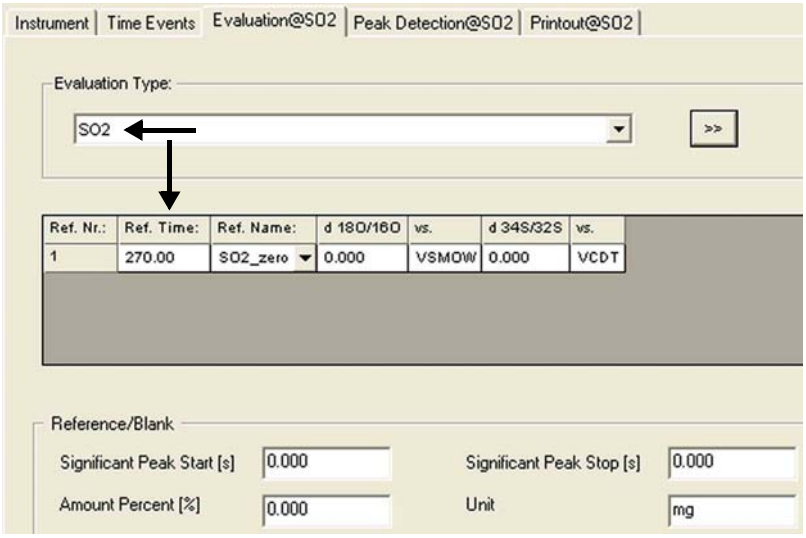


Figure 7-10. Zero Enrichment of sulfur - Evaluation tab

Note At Ref. Time, the off-value of an arbitrary reference gas peak according to the time events list must be typed (for example 270 s as the off-value of the forth reference gas peak). See Figure 7-9. ▲

Peak Detection Tab

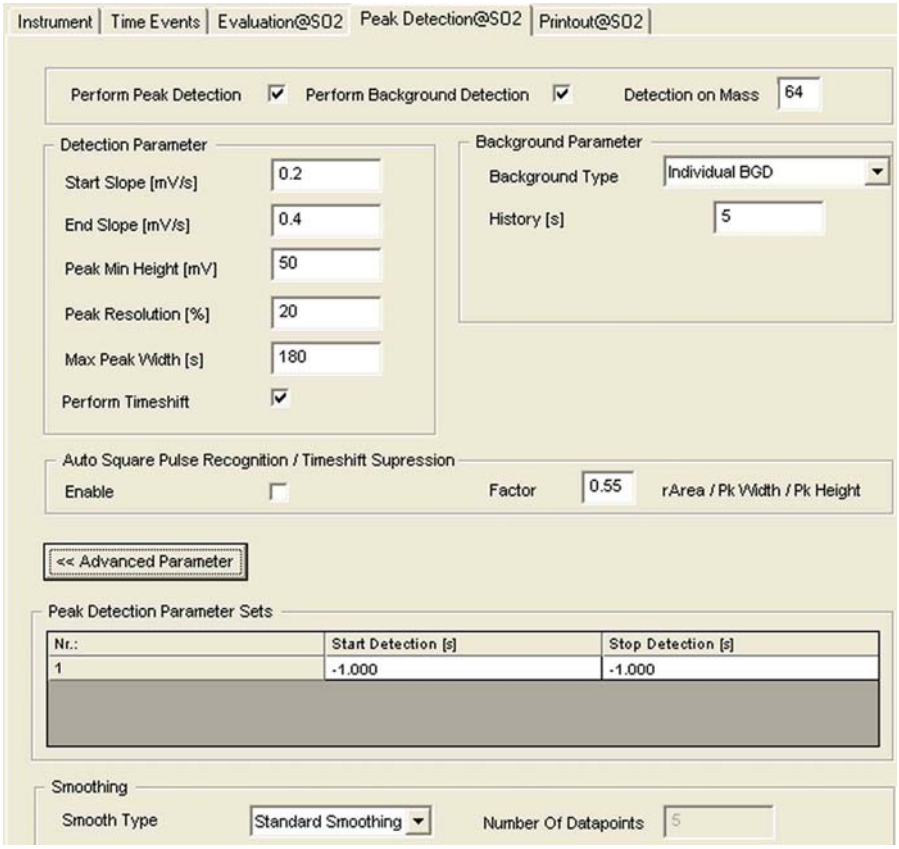


Figure 7-11. Zero Enrichment of sulfur - Peak Detection tab

Note A value of -1 denotes unlimited. ▲

Printout Tab

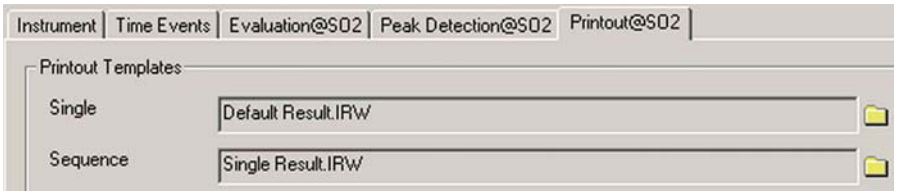


Figure 7-12. Zero Enrichment of sulfur - Printout tab

1. At the corresponding pressure regulator of ConFlo III, set the ion intensity of m/z 64 (that is $^{32}S^{16}O^{16}O$) to approximately 3 V.
2. Create a new sequence. Refer to "Defining a Sequence" on page 2-15.
3. Click on the **Start** button and confirm by **OK**.

The expected data after three or four measurements are given in Figure 7-13 (chromatogram) and Figure 7-14 (result grid).

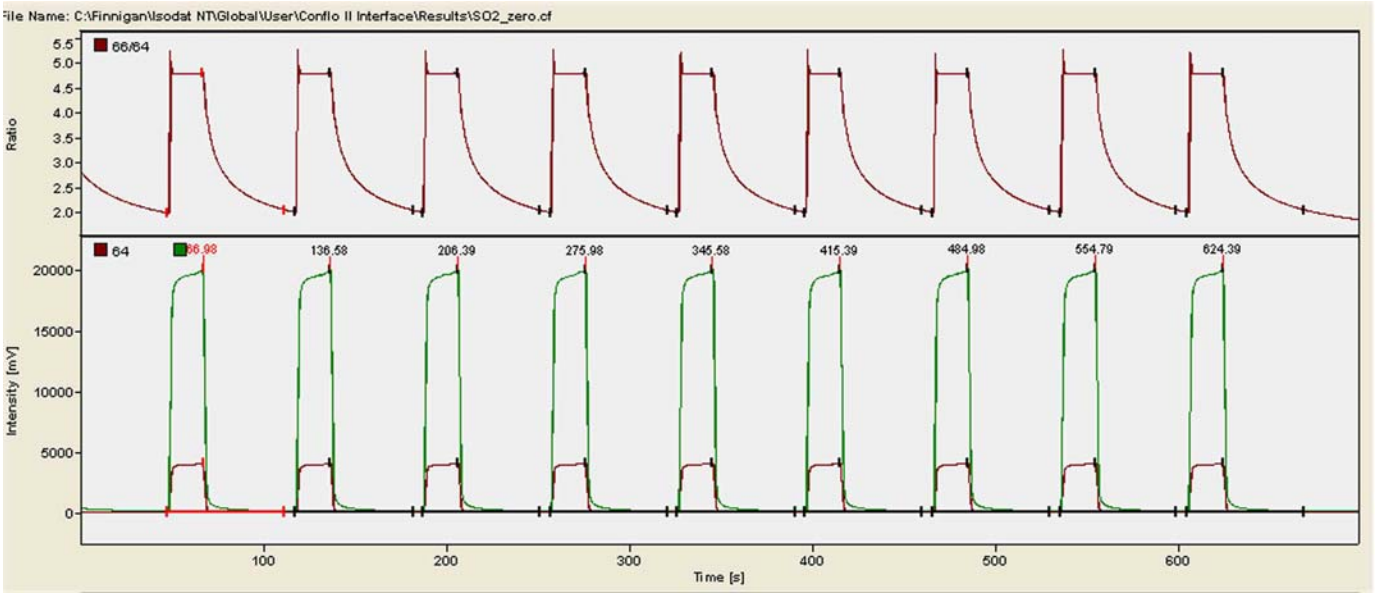


Figure 7-13. Zero Enrichment of sulfur - chromatogram

Recognize the nine peaks shown in Figure 7-13 as the nine on-off pulses in the time events list, Figure 7-9.

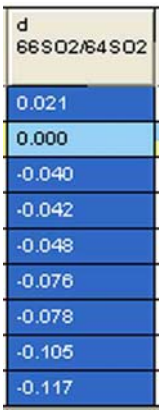
SO2 | Error | Extended | Sequence Line

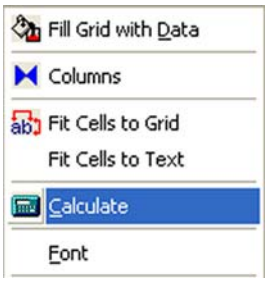
Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 64 [mV]	Ampl. 66 [mV]	BGD 64 [mV]	BGD 66 [mV]	Area All [Vs]	Amt% [%]	d 66SO2/64SO2 [per mil] vs. SO2_zero	d 34S/32S [per mil] vs. VCDT
1	47.8	67.0	63.7	4085	19953	33.5	163.9	79.345	-	0.021	0.022
2*	117.4	136.6	64.4	4061	19838	34.1	166.8	79.141	-	0.000	0.000
3	187.2	206.4	64.0	4070	19878	34.0	166.3	79.308	-	-0.040	-0.044
4	256.8	276.0	64.4	4072	19887	33.9	165.8	79.329	-	-0.042	-0.046
5	326.4	345.6	64.2	4075	19904	33.9	165.9	79.465	-	-0.048	-0.052
6	396.2	415.4	63.7	4068	19869	33.8	165.8	79.164	-	-0.076	-0.083
7	465.8	485.0	63.7	4094	19995	33.8	165.8	79.399	-	-0.078	-0.085
8	535.6	554.8	63.7	4091	19981	33.8	165.9	79.386	-	-0.105	-0.114
9	605.2	624.4	64.0	4083	19944	33.9	166.2	79.401	-	-0.117	-0.128

Figure 7-14. Zero Enrichment of sulfur - result grid

Note The standard deviation of $\delta\ ^{66}SO_2/^{64}SO_2$ should be 0.05 ‰ or less. ▲

❖ **To obtain the standard deviation of all nine peaks**





1. Click on the column header of the **d 66SO2/64SO2 [per mil] vs. SO2_zero column**.

   It will be highlighted.

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

The results will be calculated and summarized in Figure 7-15.

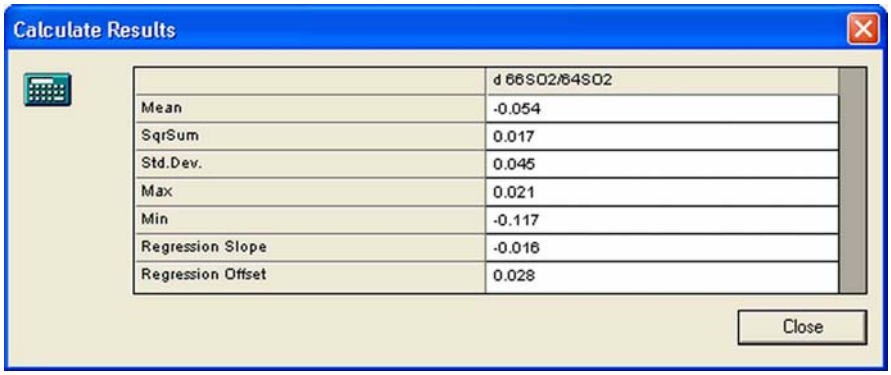


Figure 7-15. Calculation of results

Linearity Test of Sulfur

Use the same method as defined for zero enrichment in "Zero Enrichment of Sulfur (Standard On/Off Test)" on page 7-15, for example SO2_zero.met. Start the acquisition as a single run. At each detection of a peak de- or increase the reference gas pressure at the ConFlo III. The expected data after three or four measurements are shown in Figure 7-16 (chromatogram) and Figure 7-17 (result grid).

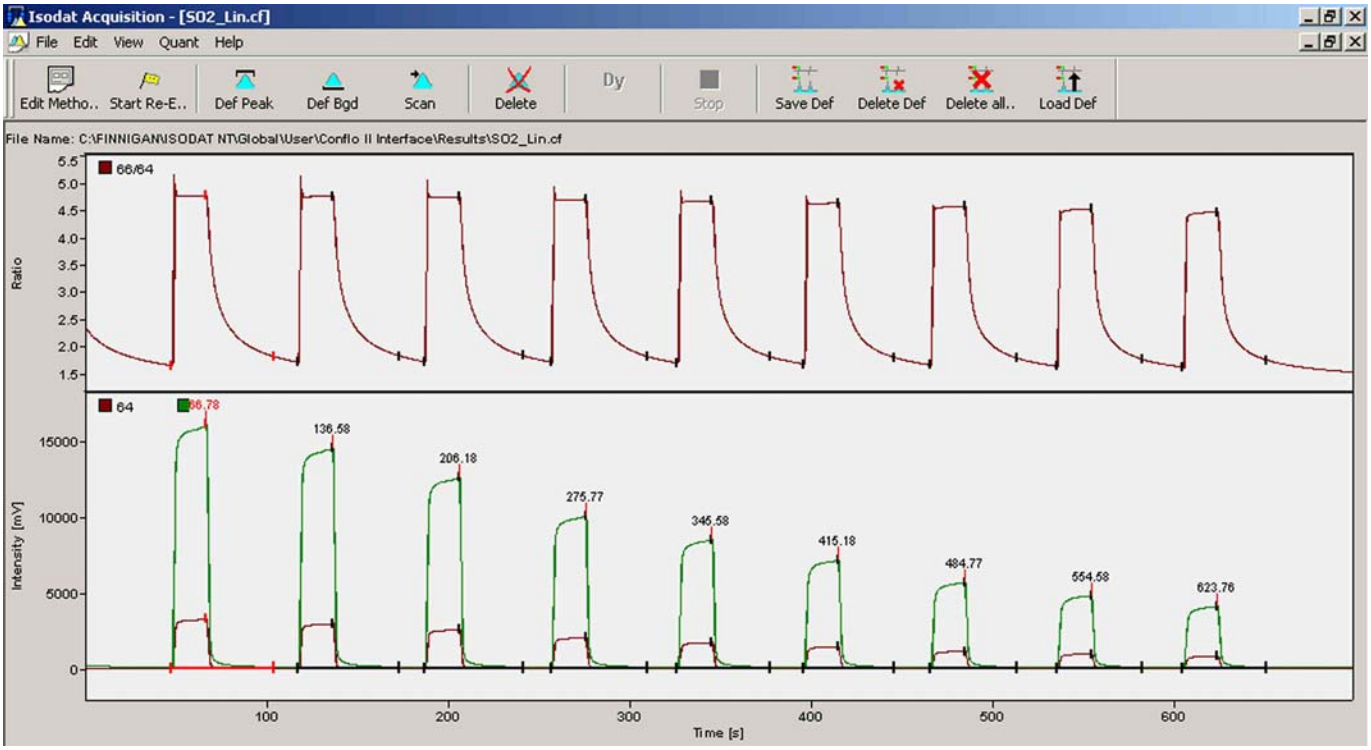


Figure 7-16. Linearity test of sulfur - chromatogram

SO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 64 [mV]	Ampl. 66 [mV]	BGD 64 [mV]	BGD 66 [mV]	Area All [Vs]	Amt% [%]	d 66SO2/64SO2 [per mil] vs. SO2_zero	d 34S/32S [per mil] vs. VCDT
1	47.5	66.8	56.6	3289	16053	22.7	102.8	63.885	-	-0.008	-0.009
2	117.4	136.6	56.0	2964	14464	24.8	113.7	57.796	-	-0.031	-0.034
3*	186.9	206.2	54.5	2579	12586	25.2	115.4	50.025	-	0.000	0.000
4	256.8	275.8	53.1	2046	9986	24.9	114.2	39.707	-	0.038	0.042
5	326.4	345.6	51.2	1728	8433	24.2	110.8	33.495	-	0.099	0.108
6	396.2	415.2	49.5	1448	7066	23.6	107.6	28.036	-	0.131	0.142
7	465.8	484.8	48.1	1145	5590	22.9	104.1	22.150	-	0.260	0.283
8	535.6	554.6	47.2	972	4744	22.1	100.0	18.758	-	0.288	0.314
9	605.2	623.8	45.8	827	4034	21.5	96.8	15.917	-	0.359	0.392

Figure 7-17. Linearity test of sulfur - result grid

Note The linear regression of the $\delta\ ^{66}SO_2/^{64}SO_2$ values vs. the working standard should be less than 0.06 ‰/V. ▲

Starting Sulfur Measurement

Before you start a sulfur measurement, make sure that your system meets the hardware requirements summarized in Table 7-7.

Table 7-7. Hardware requirements for sulfur measurement

Parameter	Value
oxidation furnace temperature/reduction furnace temperature	1020 °C for WO_3 filling
GC column temperature	100 °C
helium flow	80-100 mL/min
purge	helium flow must be sufficiently open
standard gas (SO_2) on ConFlo II/III	must be available
needle valve (ConFlo II/III-IRMS connection)	must be open
standard gas intensity (SO_2)	is adjusted at about 3-5 V (as with zero enrichment)
Isodat	must be set to ConFlo configuration. See Figure 7-18.

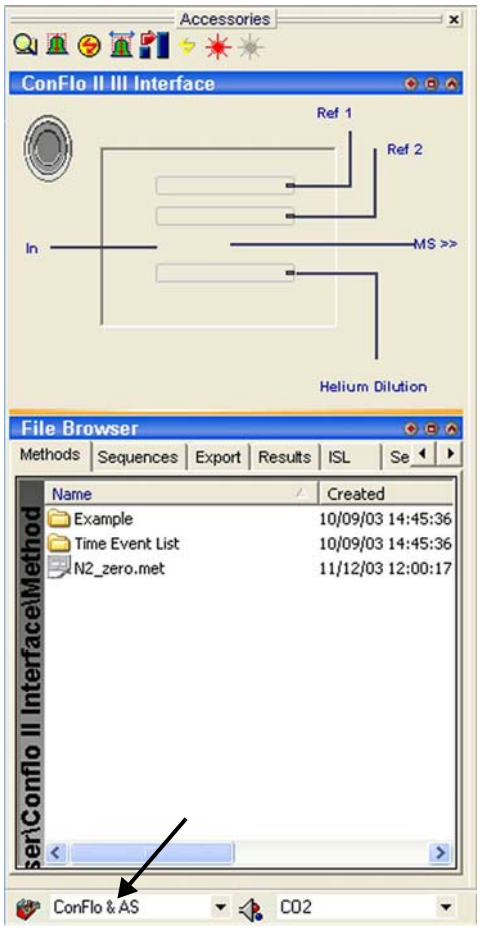


Figure 7-18. ConFlo configuration in Isodat

Defining a Method

From the Examples folder of the File Browser take the method SO2_only.met only as a guideline.

Instrument Tab

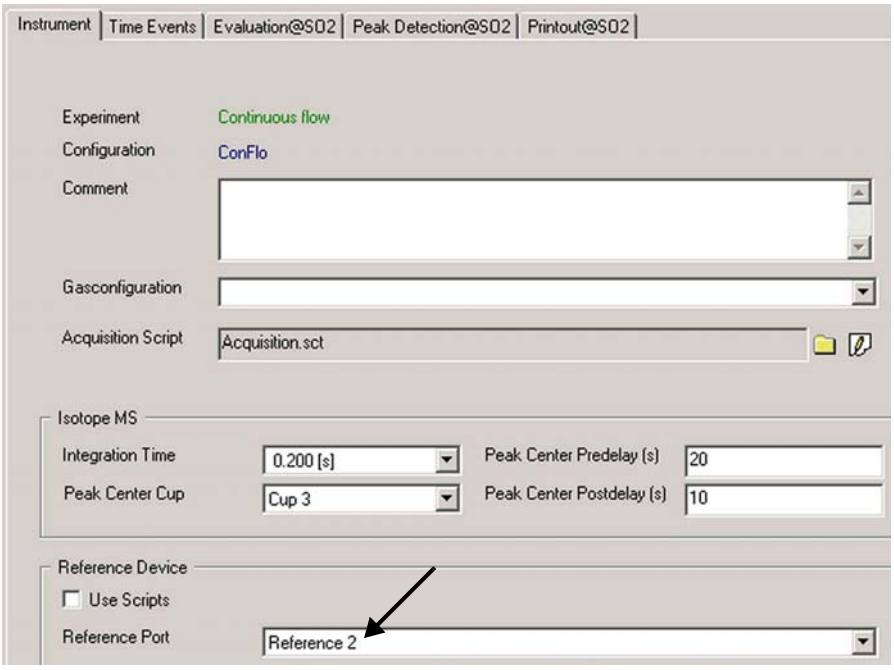


Figure 7-19. Starting sulfur measurement - Instrument tab

Select the reference port your reference gas is connected to at the ConFlo III interface (for example Reference 2). See Figure 7-19.

Time Events Tab

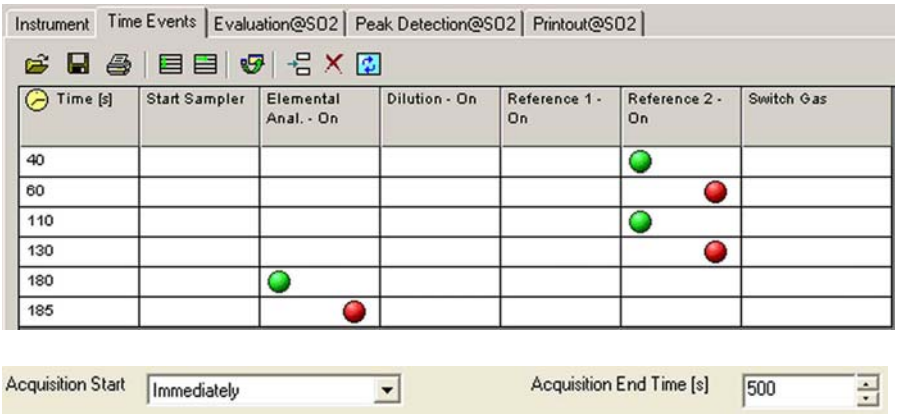


Figure 7-20. Starting sulfur measurement - Time Events tab

Evaluation Tab

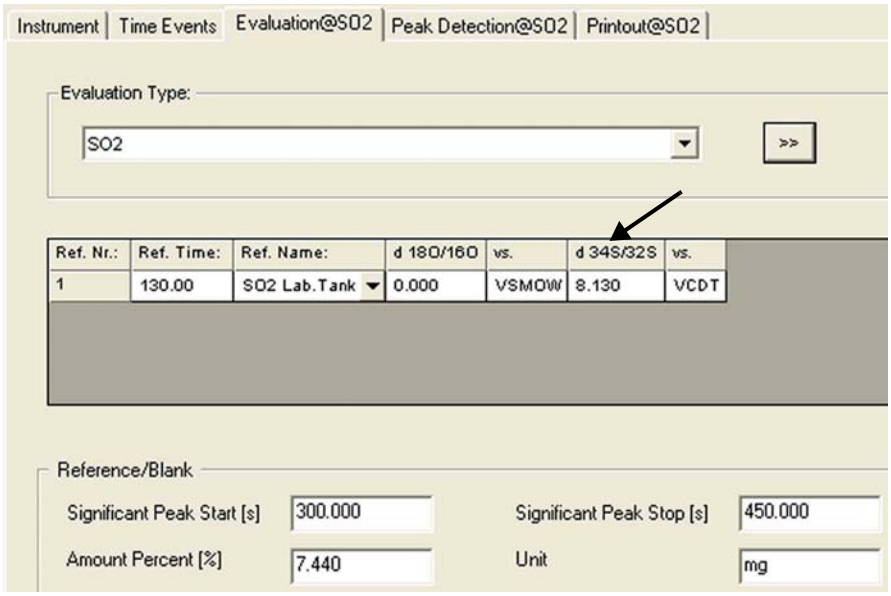


Figure 7-21. Starting sulfur measurement - Evaluation tab

Peak Detection Tab

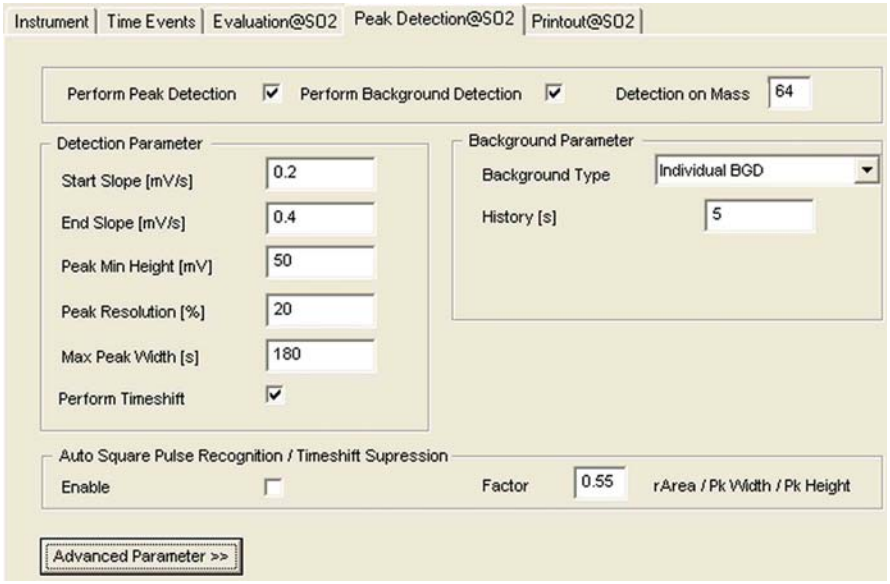


Figure 7-22. Starting sulfur measurement - Peak Detection tab

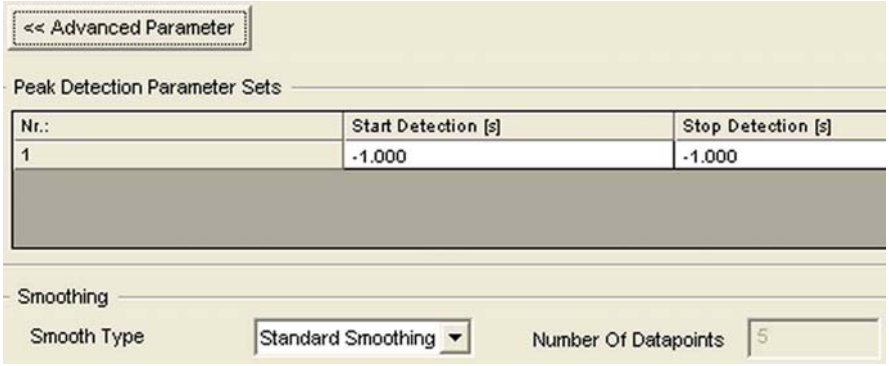


Figure 7-23. Starting sulfur measurement - Peak Detection tab - Advanced Parameters

Note A value of -1 denotes unlimited. ▲

Printout Tab

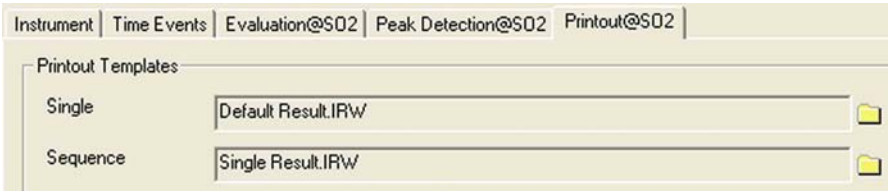


Figure 7-24. Starting sulfur measurement - Printout tab

Defining a Sequence

❖ **To define a sequence for sulfur measurement**

1. Place a sample in the solid-autosampler, for example 0.355 mg of $BaSO_4$.

2. To create a new sequence click on the **New** button.

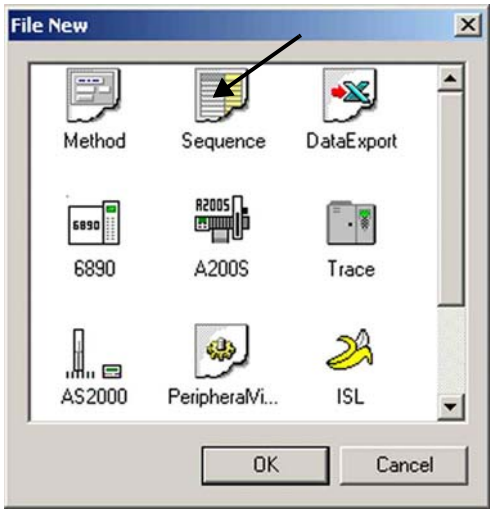
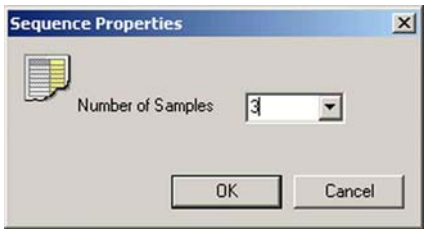


Figure 7-25. Creating new sequence

3. In Figure 7-25 mark the **Sequence** icon and confirm by **OK**.



4. Define the number of samples, for example 3. Confirm by **OK**.

Edit the sequence grid as shown in Figure 7-26 and Table 7-8.

Line		Amount	Type	Identifier 1	Comment	Preparation	Method
1	✓	0.355	Sample	BaSO4			SO2_only.met
2	✓	0.352	Sample	BaSO4			SO2_only.met
3	✓	0.358	Sample	BaSO4			SO2_only.met

Figure 7-26. Starting sulfur measurement - editing sequence grid

Table 7-8. Sequence grid parameters for nitrogen measurement

Parameter	Comment
Peak Center	Enable ✓ to perform a peak center prior to measurement (always recommended).
Amount	amount of sample
Type	Select the kind of species, for example Sample
Identifier	Type in text to identifiy the sample (optionally)
Comment	Type in a comment (optionally).
Preparation	Type in information related to preparation (optionally).
Method	Select the IRMS method (here N2_only.met).

5. Click on the **Start** button.

6. Define a folder to save your result files as well as export and printout parameters. See Figure 7-27.

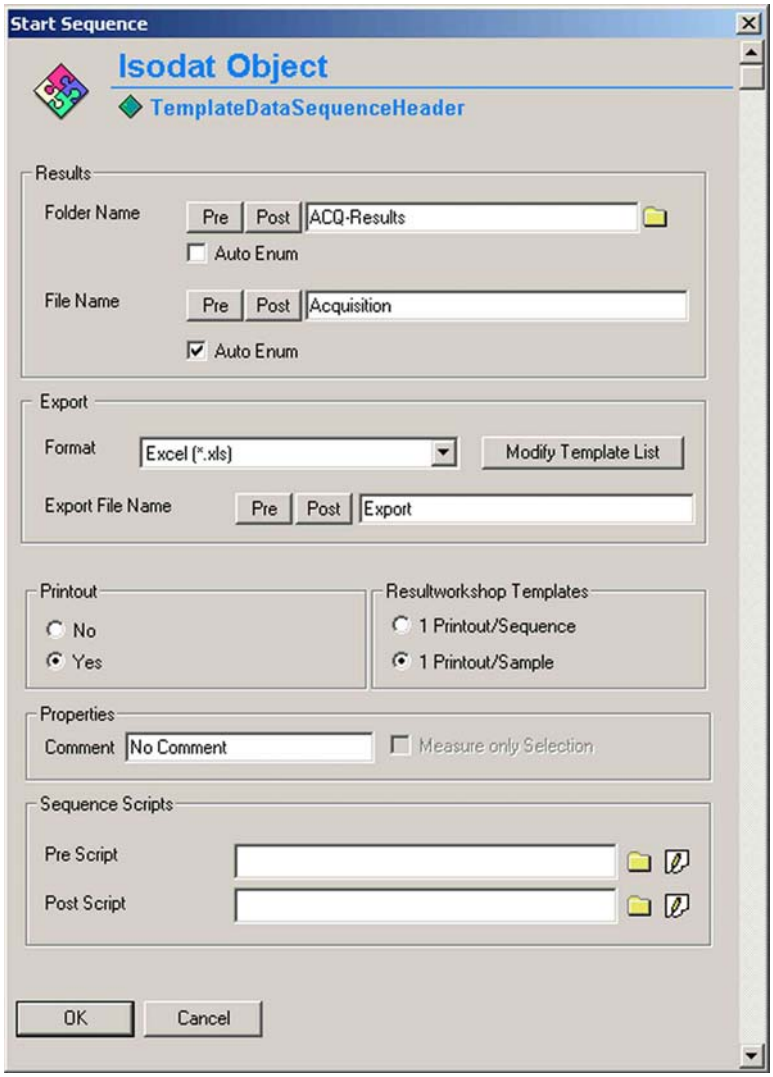


Figure 7-27. Starting sulfur measurement - defining export and printout parameters

Events during Acquisition

This section summarizes the events that happen during data acquisition. See Figure 7-20, Figure 7-29 and Figure 7-30.

1. Peak center procedure

2. First SO_2 reference gas pulse activated at 40 s (duration: 20 s).

3. Second SO_2 reference gas pulse activated at 110 s (duration: 20 s). It is assigned as standard pulse for δ value calculation. See Time column in Figure 7-20 and to Peak No. 2 in Figure 7-30.
4. Sample input (solid-autosampler)
5. Autosampler activated by compressed air from ConFlo III at 180 s.
6. Sample peak appears approximately 350 s after acquisition start time (that is 170 s after autosampler activation).
7. Acquisition stops at 500 s.

Results

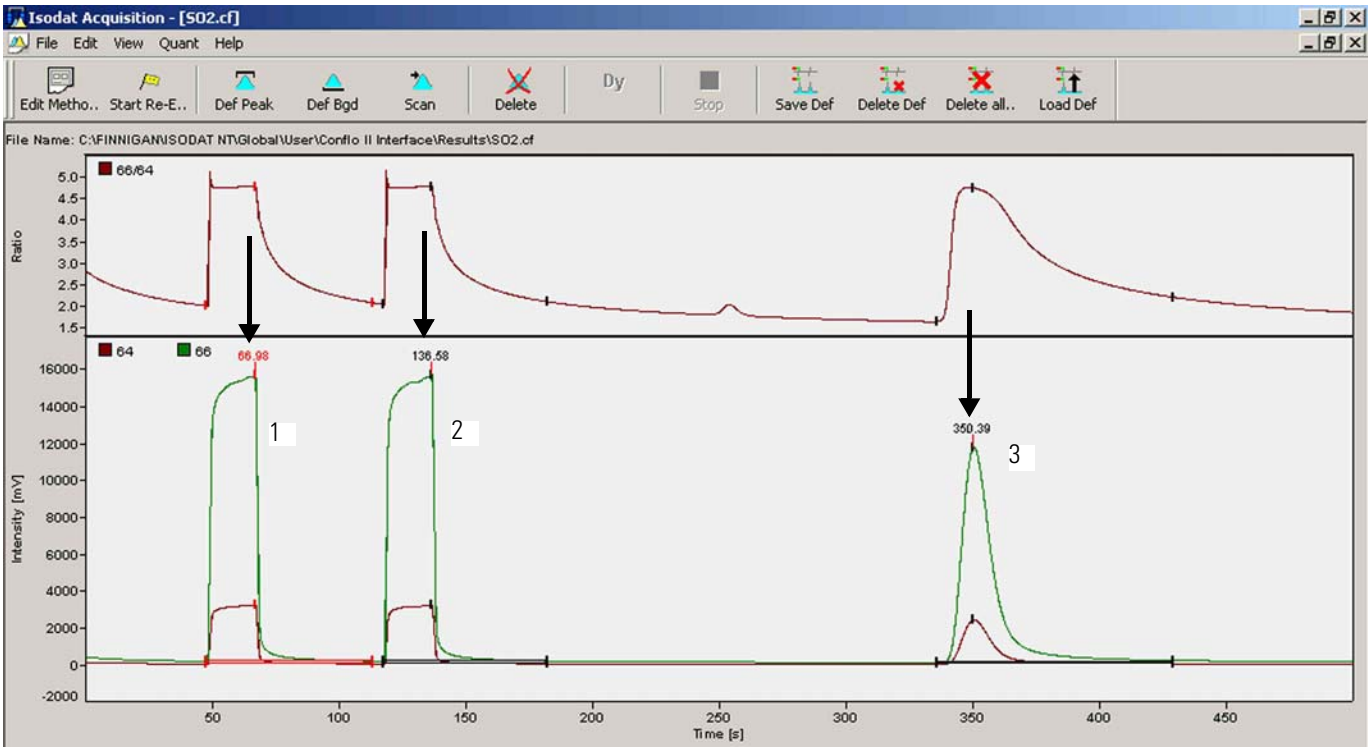
After finishing data acquisition the printer creates a data output sheet as defined by the selected Result Workshop template (*.irw). The results are also exported to a spreadsheet file, if the checkbox was marked in Figure 7-27.

SO2 | Error | Extended | Sequence Line

Line		Amount	Type	Port	Identifier 1	Comment	Preparation	Method
13	✓	0.355	Reference		BaSO4			SO2.met

Figure 7-28. Sequence line of sulfur measurement

Figure 7-29 shows the chromatogram and Figure 7-30 the related result grid.



Labeled Components: 1=first SO_2 reference gas pulse, 2=second SO_2 reference gas pulse (assigned as standard pulse for δ value calculation), 3=sample peak

Figure 7-29. Sulfur measurement - chromatogram

SO2 | Error | Extended | Sequence Line

Peak Nr.	Start [s]	Rt [s]	Width [s]	Ampl. 64 [mV]	Ampl. 66 [mV]	BGD 64 [mV]	BGD 66 [mV]	Area All [Vs]	Amt% [%]	d 66SO2/64SO2 [per mil] vs. SO2 Lab.Tank	d 34S/32S [per mil] vs. VCDT
1	47.8	67.0	65.4	3182	15505	31.4	162.7	61.789	-	8.129	8.129
2*	117.6	136.6	64.8	3186	15523	32.7	170.3	61.678	-	8.130	8.130
3	335.8	350.4	93.4	2394	11688	17.6	91.9	36.499	-	12.873	13.300

Figure 7-30. Sulfur measurement - result grid

Glossary

This section lists and defines terms used in this manual. It also includes acronyms, metric prefixes, symbols, and abbreviations.

A

A ampere

ac alternating current

ADC analog-to-digital converter

AP acquisition processor

API atmospheric pressure ionization

ASCII American Standard Code for Information Interchange

B

b bit

B byte (8 b)

baud rate data transmission speed in events per second

BEST Brightly Enhanced Sample Transfer

BF backflush

C

°C degrees Celsius

CE European conformity. Mandatory European marking for certain product groups to indicate conformity with essential health and safety requirements set out in European Directives.

cfm cubic feet per minute

CI chemical ionization

CID collision-induced dissociation

cm centimeter

cm^3 cubic centimeter

Continuous-Flow (CF) Automated preparation device and mass spectrometer in which sample analysis is conducted in a continuous stream of helium carrier gas.

CPU central processing unit (of a computer)

CRC cyclic redundancy check

CRM consecutive reaction monitoring

CSIA Compound Specific Isotope Analysis

<Ctrl> control key on the terminal keyboard

D

d depth

Da dalton

DAC digital-to-analog converter

dc direct current

driver A device-specific control program that enables a computer to work with a particular device.

DS data system

DSP digital signal processor

DSQ™ Dual Stage Quadrupole

See also ITQ™.

Dual Inlet (DI) Inlet method in which a pure gas sample is admitted into an isotope ratio mass spectrometer (IRMS) by a variable volume bellows. A reference gas is admitted into the IRMS via a second variable volume bellows. The bellows are balanced to provide sample and reference signal responses of equal intensity.

E

ECD Electron Capture Detector

EI electron ionization

Elemental Analyzer (EA) Automated sample preparation instrument in which samples are automatically converted into pure gases for isotope ratio analysis. An elemental analyzer contains the following elements: (i) furnace for combustion, reduction or pyrolysis of sample material; (ii) chemical traps for analyte gas purification; (iii) gas chromatography for time separation of these analyte gases.

EMBL European Molecular Biology Laboratory

<Enter> Enter key on the terminal keyboard

ESD electrostatic discharge

ESI electrospray ionization

eV electron volt

F

f femto ($10^{-15)}$

°F degrees Fahrenheit

FID Flame Ionization Detector

FM flow meter

forepump The pump that evacuates the foreline. A rotary-vane pump is a type of forepump.

ft foot

FTP file transfer protocol

FWHM Full Width at Half Maximum

G

g gram

G Gauss; giga (10^9)

GC gas chromatograph; gas chromatography

GC/MS gas chromatograph/mass spectrometer

GISP Greenland Ice Sheet Precipitation. International reference standard for hydrogen and oxygen isotopes.

See also SLAP and VSMOW.

GLT Glass Lined Tubing

GUI graphical user interface

H

h hour

h height

HF high flow

HOT OC High Oven Temperature Cold On-Column

HPLC High Performance Liquid Chromatography. Standalone liquid chromatography system (or inlet for mass spectrometry detector).

HTC High Temperature Conversion

HV high voltage

Hz hertz (cycles per second)

I

IAEA International Atomic Energy Agency

ICIS™ Interactive Chemical Information System

ICL™ Instrument Control Language™

ICP inductively coupled plasma

ICP-OES inductively coupled plasma optical emission spectroscopy

ID inside diameter

IEC International Electrotechnical Commission

IEEE Institute of Electrical and Electronics Engineers

in. inch

I/O input/output

ion optics Focuses and transmits ions from the ion source to the mass analyzer.

ion source A device that converts samples to gas-phase ions.

irm isotope ratio monitoring

IRMS isotope ratio mass spectrometer

ITQ™ Ion Trap Quadrupole

See also DSQ™.

K

k kilo (10^3, 1000)

K kilo (2^{10}, 1024)

KEGG Kyoto Encyclopedia of Genes and Genomes

kg kilogram

L

l length

L liter

LAN local area network

lb pound

LC Liquid chromatography. A process that separates a chemical mixture carried by liquid into components as a result of differential distribution of the solutes as they flow around or over a stationary or solid phase.

LC/MS liquid chromatograph / mass spectrometer

LED light-emitting diode

LF low flow

log file A text file, with a .log file extension, that is used to store lists of information.

LVSL Large Volume Splitless Injector

µ micro (10^{-6})

M

m meter

m milli (10^{-3})

M mega (10^6)

M^+ molecular ion

MB Megabyte (1 048 576 bytes)

MH^+ protonated molecular ion

min minute

mL milliliter

mm millimeter

MP measuring point

MS mass spectrometer; mass spectrometry

MS MS^n power: where n = 1

MS/MS MS^n power: where n = 2

MS^n MS^n power: where n = 1 through 10

MTBE methyl tert-butyl ether

MVFC multifunctional valve cluster

m/z Mass-to-charge ratio. An abbreviation used to denote the quantity formed by dividing the mass of an ion (in u) by the number of charges carried by the ion. For example, for the ion $C_7H_7^{2+}$, m/z=45.5.

N

n nano (10^{-9})

Natural Abundance The concentration of isotopes as found in nature.

NCBI National Center for Biotechnology Information (USA)

NIST National Institute of Standards and Technology (USA)

noise Any random disturbance that obscures the clarity of a signal

NPD nitrogen/phosphorous detector

O

OC On-Column

OD outside diameter

OS open split

Ω ohm

outlier A calibration data point that does not appear to correlate to other calibration data points within experimental error.

P

p pico (10^{-12})

Pa pascal

PCB printed circuit board

PDD Pulsed Discharge Detector

PE protective earth

PEEK polyether ether ketone

PID proportional/integral/differential

P/N part number

P/P peak-to-peak voltage

ppm parts per million

psig pounds per square inch, gauge

PTV Programmable Temperature Vaporizing

R

RAM random access memory

relative standard deviation A measure of the dispersion of a group of measurements relative to the mean of the group. Relative standard deviation is expressed as a percentage of the average value. The percent relative standard deviation is calculated as:

$$\%\,\mathrm{RSD} = 100 \cdot \frac{\mathrm{SD}}{\bar{x}}$$

where SD is the standard deviation and $\bar{X}$ is the sample mean.

RF radio frequency

RMS root mean square

ROM read-only memory

rotary-vane pump A mechanical vacuum pump that establishes the vacuum necessary for the proper operation of the turbomolecular pump. (Also called a roughing pump or forepump.)

RS-232 An accepted industry standard for serial communication connections. This Recommended Standard (RS) defines the specific lines and signal characteristics used by serial communications controllers to standardize the transmission of serial data between devices.

S

s second

serial port An input/output location (channel) for serial data transmission.

SIM selected ion monitoring

SLAP Standard Light Antarctic Precipitation; international reference standard for hydrogen and oxygen isotopes.

See also VSMOW.

SPME Solid Phase Micro Extraction

SRM selected reaction monitoring

standard deviation In statistics, the standard deviation SD is a measure of the dispersion of a group of measurements. For example, masses, times, or intensities. Standard deviation is calculated as follows:

$$\sigma = \mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

See also relative standard deviation.

T

TCD Thermal Conductivity Detector

TCP/IP transmission control protocol / Internet protocol

TIC total ion current

Torr A unit of pressure, equal to 1 mm of mercury and 133.32 Pa.

turbomolecular pump A vacuum pump that provides a high vacuum for the mass spectrometer and detector system.

U

u atomic mass unit

UHV ultra high vacuum

V

V volt

V AC volts alternating current

V DC volts direct current

VFC voltage-frequency converter

vol volume

VCDT Vienna Canyon Diablo Troilite; international reference standard for sulfur isotopes.

VPDB Vienna Pee Dee Belemnite; international reference standard for carbon and oxygen isotopes.

VSMOW Vienna Standard Mean Ocean Water; international reference standard for hydrogen and oxygen isotopes.

See also SLAP.

W

w width

W watt

WEEE European Union Waste Electrical and Electronic Equipment Directive. Provides guidelines for disposal of electronic waste.

Index

Symbols

Numerics

A

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T

U

V

W

Z

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