
Variants Operating Instructions

vario MACRO cube

Analyzer

Version 31.07.2012



Elementar Analysensysteme GmbH

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Contents

CHAPTER 1 General	9
Revision history	10
About this document	11
Display conventions	12
Working with the operating instructions	12
General information on the operating instructions	12
Notes regarding modification	13
Warning notes during operation	13
CHAPTER 2 Sulfur determination with NDIR	15
Special features	16
Functional diagram	17
Modification to S operation	19
CHAPTER 3 Oxygen determination with TCD	25
Analytical characteristics and technical specifications	26
Substance digestion and functional diagram	26
Separation of the reaction gases	29
Detection	29
Tube fillings	30
Modification to O Mode	31
Conditioning the pyrolysis tube	36
Changing of the pyrolysis crucible	37
Establishing of the analysis readiness	38
Notes on performing calibration	39
Oxygen analyses in routine operation	40
Application notes for oxygen determination	43
Pyrolysis temperature	44
Difficult matrices	44
Lifetime of the pyrolysis tube	45
Additional error messages in O mode	46
CHAPTER 4 Oxygen determination with NDIR	47
Analytical characteristics and technical specifications	48
Substance digestion and functional diagram	48
Detection	52
Tube fillings	52
Modification to O Mode	54
Conditioning the pyrolysis tube	62
Changing of the pyrolysis crucible	64
Establishing of the analysis readiness	65
Notes on performing calibration	66
Oxygen analyses in routine operation	66
Application notes for oxygen determination	68
Pyrolysis temperature	69
Difficult matrices	69
Lifetime of the pyrolysis tube	70

Additional error messages in O mode	71
CHAPTER 5 Chlorine determination with EC cell	73
Analytical characteristics and technical specifications	74
Substance digestion and functional diagram	74
Detection	76
Tube fillings	76
Notes on performing calibration	78
Chlorine analyses in routine operation	79
Notes on sensitivity and measuring range	80
Cross-sensitivity of the EC cells	81
Quantitative conversion from Cl to HCl	82
Maintenance of the HCl EC cells	82
Leak test	83
Modification to Cl operation	84
CHAPTER 6 The TOC module	91
Special features	92
Functional diagram	93
Tube fillings	94
Performing an analysis	96
Modification to TOC operation	97
TOC maintenance work	101
CHAPTER 7 TIC solids module	103
General information	104
Scope of delivery	104
Safety instructions	104
Technical specifications	105
Analytical characteristics	106
Functional diagram TIC module	107
The components	109
Tube fillings	109
Installation and initial start up of the TIC module	111
Selecting the operating mode	114
General measuring principle TIC	114
Analysis run	116
Defining custom standard substances	118
Maintenance work	118
CHAPTER 8 CHNS determination with the liquid autosampler vario LS	121
CHNS determination with vario LS	122
Tube fillings	125
Selecting the operating mode	127
CHNS routine operation	127
Setting device parameters	128
Defining custom standard substances	130
Defining custom methods	131
Modification into CHNS liquid mode	131
Calibration	133
View of the analytical results	135
Check list, prior to the analysis run	136
Shut-down for measuring breaks	136
CHAPTER 9 CHN determination with the liquid autosampler vario LS	137
CHN determination with vario LS	138

Tube fillings	141
Selecting the operating mode.....	143
CHN routine operation.....	143
Setting device parameters.....	144
Defining custom standard substances.....	146
Defining custom methods.....	146
Modification into CHN liquid mode	147
Calibration	149
View of the analytical results	151
Check list, prior to the analysis run.....	151
Shut-down for measuring breaks.....	152
 Index	 153

C H A P T E R 1

General

Purpose

This chapter contains general topics of the document.

In this chapter

Revision history	10
About this document	11
Display conventions.....	12
Working with the operating instructions	12
General information on the operating instructions	12
Notes regarding modification	13
Warning notes during operation	13



Revision history

List of modifications in this document up to now

Date	Modification
15.11.2011	Creation.
22.11.2011	Description CI operation modified.
29.05.2012	Length of empty ash finger in the CI combustion tube modified.
30.07.2012	New tubing diagrams, since O ₂ MFC replaced by proportional valve.

About this document

Status of the operating instructions

The status of the operating instructions is: 31.07.2012.

Identification number

The operating instructions identification number is: 20.00-5007.

Validity

The operating instructions are valid for all instruments as from serial number: 20124041.

Display conventions

Before you start using this guide, it is important to understand the terms and typographical conventions used in the documentation. The following kinds of formatting in the text identify special information.

Formatting convention	Type of information
Triangular bullet (➤)	Step by step procedure. You can follow these instructions to complete a specific task.
Special bold	Items you must select, such as menu options (e. g. System > Sample position), command buttons (e. g. Cancel), or common accentuation.
<i>Italics</i>	Used to emphasize the importance of an item or for variable expressions such as parameters.
CAPITALS	Names of keys on the keyboard, for example, SHIFT, CTRL, or ALT.
KEY+KEY	Key combinations for which the user must press and hold down one key and then press another, for example, CTRL+P, or ALT+F4.
"Quotation marks"	Denote amongst others the names of dialogs in the software, e. g. the "Replace part" dialog.
{Symbolic name}	Denotes a symbolic name, e. g. {Element} stands for the corresponding name of an element.

Working with the operating instructions

Operating the analyzer

Read the operating instructions thoroughly before performing work with the analyzer.

Storing the operating instructions

Store the operating instructions carefully and make sure the instructions are accessible for all relevant personnel.

Passing on the operating instructions

If you pass on the analyzer, always pass on the operating instructions, too.

General information on the operating instructions

Pictures

The instruments of Elementar underlie a permanent development and adjustment regarding the optimum parameter settings. This may lead to deviations in terms of picture display of the manual and the current instrument status which are not relevant for the understanding of the instrument operation.

The valid numbers of the parameter settings and/or variables can be found in the current text part. Therefore, numbers in the pictures of software dialogs are mainly replaced by spaces or only reflect examples. They do not reflect the proper, recommended set values.

Reading aids

Subheadings are displayed in the left margin as reading aids. They sum up the content of the particular section and are useful for quick navigation.

Index

An index is given at the end of the operating instructions that helps you locate certain topics more easily. Index entries always refer to the first page of the section in which the index term is found. Therefore, don't be confused if the index term does not appear on the first page but rather on one of the following pages.

Notes regarding modification

Note

Due to the modular design of the analyzer, a large variety of modifications are possible. The individual modifications described in these instructions are limited to established scenarios in order to keep the comprehensiveness of the instructions within certain limits.

Warning notes during operation

Note

Always pay attention to careful handling when working with the instrument, especially for modifications, maintenance and repairing works. The following notes have to be strictly observed when performing the corresponding works.

Also observe the safety and warning notes in the operating instructions of the basic instrument.

Gas pressure

Please observe the following instruction:

Warning



Gas pressure and caustic substances in the instrument

Consumables may escape under pressure and cause chemical burns. Before performing the work:

Shut off the gas supply. To do so, execute the **Options > Maintenance > Replace parts** command.

Switching off the instrument

Please observe the following instruction:

Caution

Lack of ventilation of the analyzer!

A lack of ventilation leads to overheating of the analyzer. Before you switch off the instrument:

- Set the setpoint temperatures of the furnaces to 0 °C. To do so execute the command **Options > Settings > Parameter > Temperatures**
- Allow the furnaces to cool down until the temperature displayed is less than 55 °C.

Hot instrument parts

Please observe the following instruction:

Warning 	Hot components in the instrument When working inside the instrument there is a risk of burning as many parts of the instrument are hot. When working inside the instrument always wear protective glasses and the enclosed heat protection gloves.
---	---

Changing mode

Please observe the following instruction:

Caution	Overheating if tube fillings are not appropriate for the operating mode! Overheated tube fillings melt, run into the furnace area and destroy the furnace. Make sure that the tube fillings correspond to the selected operating mode.
----------------	---

Filling reaction tubes

Please observe the following instructions:

Warning 	Sharp pieces of broken glass! When cold quartz or glass components break there is a risk of cut injuries. Wear the enclosed protective leather gloves and protective glasses when handling cold quartz and glass parts.
Caution	Cutting sealing elements apart/out (o-rings, quad rings, half shells, ferrules). When cutting sealing elements apart/out with a knife you may damage sealing surfaces. Never remove sealing elements with a knife but rather with tweezers.

Installing and conditioning the reaction tubes

Please observe the following instructions:

Warning 	Hot components in the instrument When working inside the instrument there is a risk of burning as many parts of the instrument are hot. When working inside the instrument always wear protective glasses and the enclosed heat protection gloves.
Caution	Overheating if tube fillings are not appropriate for the operating mode! Overheated tube fillings melt, run into the furnace area and destroy the furnace. Make sure that the tube fillings correspond to the selected operating mode.

CHAPTER 2

Sulfur determination with NDIR

Target group

Personnel involved with the instrument.

Purpose

This section describes the special features of the sulfur determination with NDIR.

In this chapter

Special features	16
Functional diagram	17
Modification to S operation	19



Special features

General

Using a NDIR photometer for SO₂ measurement results in a significant improvement of the detection sensitivity.

The measurement of SO₂ by means of a NDIR photometer is performed in CNS mode.

All operation conditions and tube fillings are the same as for the operation with TCD.

Check "S/O with IR-detector" in the "Analysis mode" dialog under **System > Mode**.

Note:

If you do not work with IR detection, it is important to disconnect the connection between TCD and IR detector.

So, you can avoid possible damages which may occur to the IR detector.

However, you still have to maintain the drying tube regularly with a built-in IR detector.

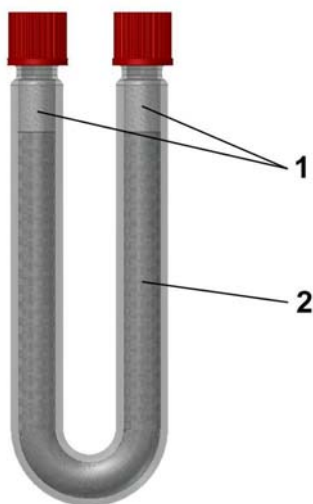
Attention should be paid to

In the analysis process the SO₂ measurement (S-peak) will be switched from TCD to NDIR photometer

Since the NDIR photometer is cross sensitive to water vapor, the measuring gas has to be dried before entering the NDIR photometer by means of a drying tube (small U tube, filled with Sicapent®, behind the left side door, below).

Drying tube filling

The following picture shows the fillings of the drying tube:



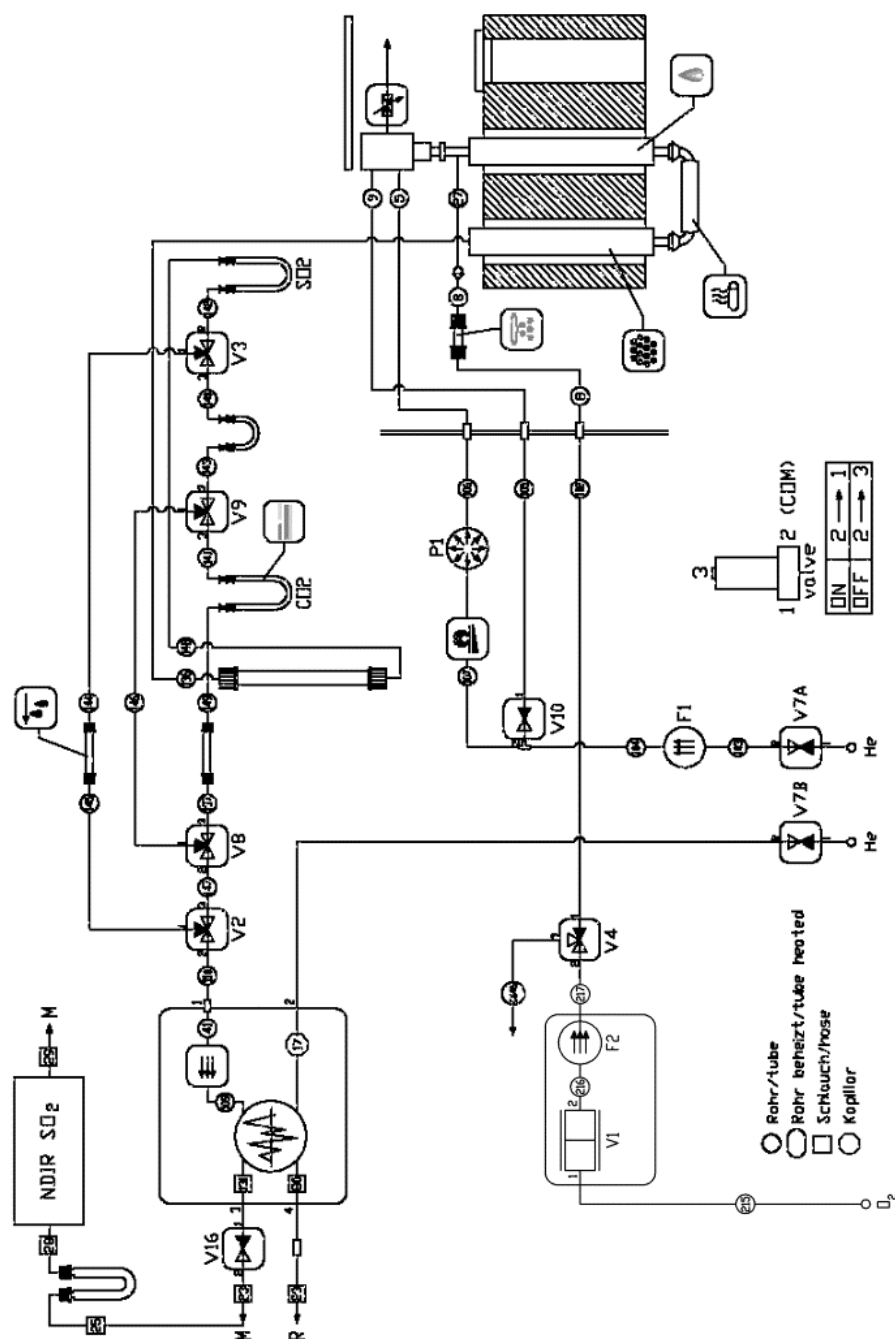
Legend:

- 1 Filter wool (approx. 10 mm)
- 2 Sicapent®

Functional diagram

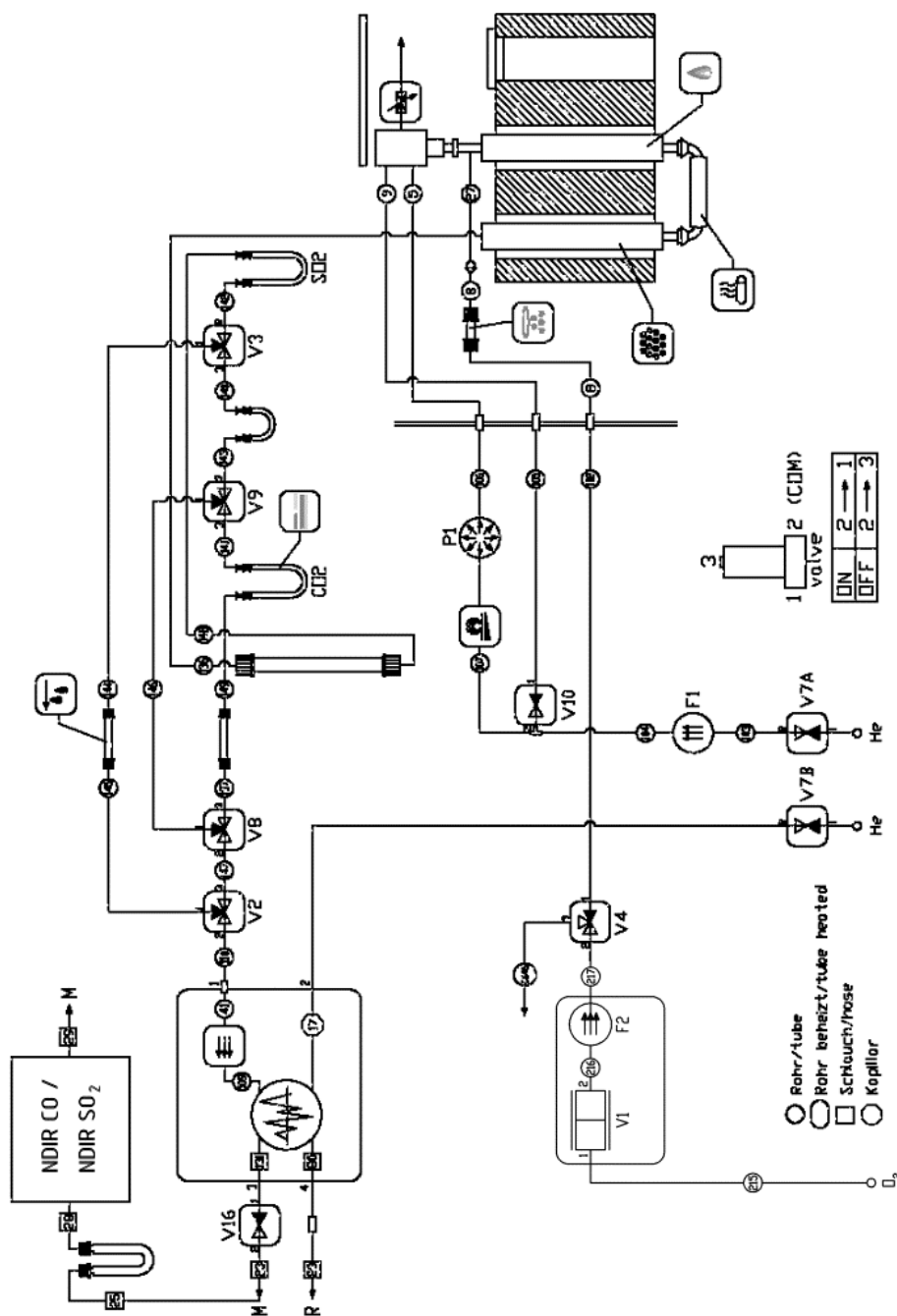
Flow diagram CNS mode with single NDIR detector SO_2

The following picture shows the functional diagram for the CNS mode with single NDIR detector:



Flow diagram CNS mode with dual NDIR detector CO/SO₂

The following picture shows the functional diagram for the CNS mode with dual NDIR detector:



Symbols

The following list names the functional and basic symbols:



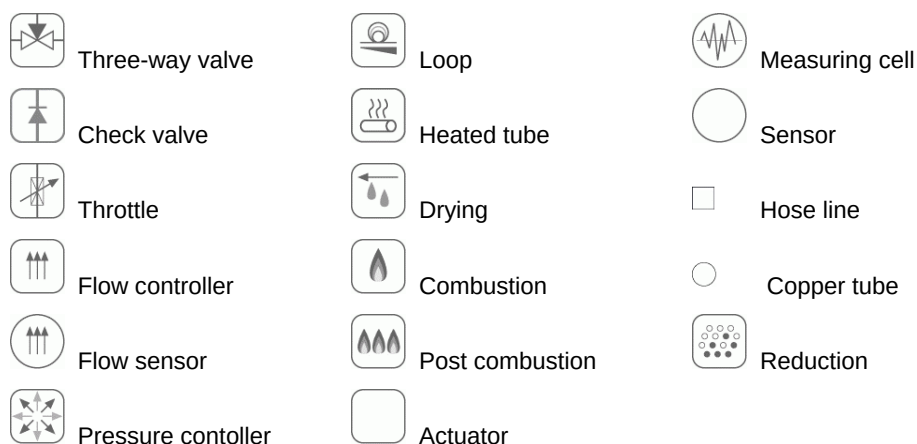
Two-way valve



Pressure sensor



Gas separation



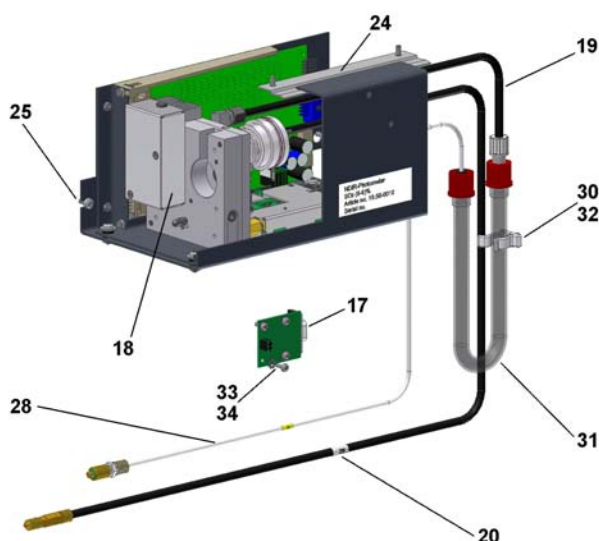
Modification to S operation

Scope of the upgrade kit for sulfur detection

All parts necessary for the tube modification are included in the S upgrade kit for detecting sulfur with NDIR and are labeled with numbers.

Upgrade kit with single NDIR detector SO₂

The following picture shows the upgrade kit with single NDIR detector:

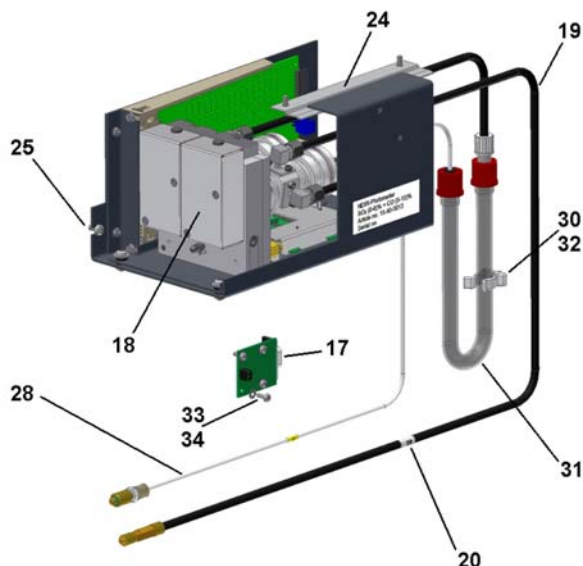


Legend:

- 17 RS 232 module
- 18 NDIR photometer SO₂
- 19 Tube no. 28
- 20 Tube no. 29
- 24 Guidance angle
- 25 Screws M4x8
- 28 Tube no. 25
- 30 Clamp
- 31 U tube
- 32 Screw M3x8
- 33 Serrated washer, 3.2
- 34 Screw M3x6

Upgrade kit with dual NDIR detector CO/SO₂

The following picture shows the upgrade kit with dual NDIR detector:



Legend:

- 17 RS 232 module
- 18 NDIR photometer SO₂
- 19 Tube no. 28
- 20 Tube no. 29
- 24 Guidance angle
- 25 Screws M4x8
- 28 Tube no. 25
- 30 Clamp
- 31 U tube
- 32 Screw M3x8
- 33 Serrated washer, 3.2
- 34 Screw M3x6

The following parts are also part of the kit but are not pictured.

- D-sub-adapter
- Software update CD.

Modification

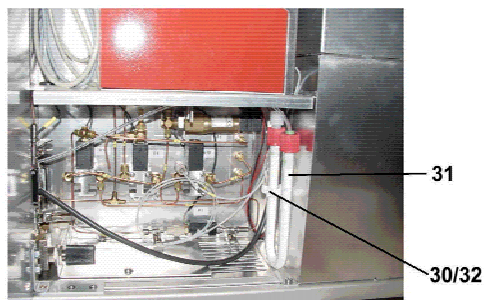
Proceed as follows:

- Turn off the instrument and pull the power supply plug.
- Open the left side wall.
- Fasten the guidance angle (2) with screws M4x8 (25).



Loosely insert two screws M4x8 (25) into the tap holes, so that the distance between screw heads and sheet is still 2 mm.

- Attach the clamp (30) in the gas insert by means of the screw (32). Fasten the filled U-tube (31) with the clamp (30).



- Mount the NDIR photometer (18) into the analyzer as displayed below: Push the two designated recesses over the loosely inserted screws (25) and then shift the photometer to the left up to the stop.



- Make sure the upper lug of the NDIR photometer will snap into the guidance angle.
- Now fasten the photometer by fixing both screws.
- Connect the photometer as follows:
 - (A) Cable #50 to RS232 module
 - (B) Cable #53 (internal IR)
 - (C) Cable #51 (power supply)

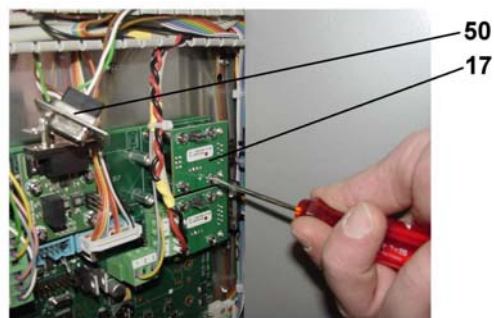
Connect the pre-installed cable no. 51 (C) with the double-pole plug on the IR board.

Connect the pre-installed data cable no. 50 (A) with the 9 pin D-SUB plug on the RS232 module of the IR photometer. In case the plug of the data cable does not fit to the RS232 module connector, use the enclosed "D-SUB adaptor" (part no. 05 001 961).



- Open the right side door.

- Attach the RS232 module (17) on the BCB board (JP5) by means of the four screws M3x6 and connect it (COM2).



- Connect the pre-installed data cable no. 50 to the RS232 module just installed.
- Remove the plugs from the rear wall.



- Remove the connecting piece of the measure gas outlet using a 7mm open jawed wrench.

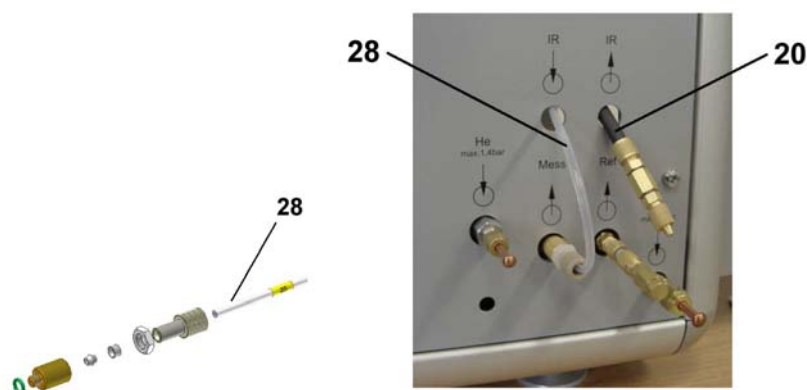


- Lead tube no. 25 (28) from inside to outside through the hole (IR inlet) and connect it to the measure gas outlet using a knurled reducing nipple.

Lead the outlet hose line of the NDIR photometer no. 29 (20) from inside to outside through the hole (IR outlet).

The double nipple connector at the end of the hose line no. 29 (20) is used to connect the on-site waste gas line.

CAUTION: Follow the notes about discharging the waste gases into the open or into a vent in the vario MACRO cube main operating instructions!



- Connect the opposite end of tube no. 25 (28) (red cap) as well as the inlet hose line no. 28 (19) of the NDIR photometer to the U tube (29).
- Close the left and right side door.

Installing the software

If necessary, you have to update the instrument software for operation with the IR photometer.

Proceed as follows:

- Insert the provided CD "IR option" to the CD drive of the PC and start the software update.
- The current software will be automatically installed on the PC.
- Follow the instructions on the screen.
- As the case may be, an update of the device firmware becomes necessary. During the re-start it will be recognized by the software and an update procedure will be performed automatically.

The installation of the NDIR photometer and the modification is completed.

Maintenance work to be performed by the customer

The IR detector requires the use of an absorption tube. This is located at the left sidewall. The absorption agent is Sicapent® and has to be exchanged regularly.

To ensure that this will not be forgotten, we recommend to set up a maintenance interval in the software.

Proceed as follows:

- Open the "Maintenance intervals" dialog in the operating software by selecting **Options > Maintenance > Intervals**.
- Enter the maintenance interval via the **New** button.
- Enter e.g. under "Event" the name *absorption tube* and under "Interval" the value *120* samples.
Note: depending on the sample matrix and sample size the interval may fluctuate.
- Press **Save** and close the menu.

CHAPTER 3

Oxygen determination with TCD

Target group

Personnel involved with the instrument.

Purpose

This section describes the special features of the oxygen determination with TCD.

In this chapter

Analytical characteristics and technical specifications.....	26
Substance digestion and functional diagram	26
Separation of the reaction gases	29
Detection	29
Tube fillings	30
Modification to O Mode.....	31
Conditioning the pyrolysis tube.....	36
Changing of the pyrolysis crucible	37
Establishing of the analysis readiness.....	38
Notes on performing calibration.....	39
Oxygen analyses in routine operation	40
Application notes for oxygen determination.....	43
Additional error messages in O mode	46

Analytical characteristics and technical specifications

Analytical characteristics

The following table explains the analytical characteristics:

Analytical characteristic	Comments
Analysis method	Oxygen determination by pyrolysis of samples, separation of foreign gases, separation of the desired measuring components, thermal conductivity detection.
Detector	Thermal conductivity detector (TCD)
Sample weight/sample volume	Approx. < 1 to 10 mg depending on the substance.
Working range (depending on kit and measuring mode)	O: 0.03 - 5 mg
Precision / standard deviation	<0,2 % with benzoic acid (approx. 2 mg)
Duration of analysis (depending on element content and sample weight)	O: 8 - 15 min
Calibration	Linear and non-linear curve adjustment; total work range.
Data storage and data output	Storage on hard disk or external storage media. LIMS transfer possible. Data output to screen and printer.

Technical specifications

The following table contains the technical specifications of the gas supply:

Reference value	Technical specifications
Supply gases	Helium, purity 99.995%
Consumption of supply gases	Per analysis approx. 1.4 to 2.6 liters helium

Substance digestion and functional diagram

Introduction

The following section explains:

- Which procedures in the pyrolysis tube of the furnace are processed.
- How the reaction gas mixture is prepared for adsorption and separation into its constituents.

Processes during substance digestion and preparation of the reaction gas mixture

The substance digestion will be improved with and additive of approx. 8 mg polyethylene (PE) (temporarily there is a H₂ concentration of > 10% in ambience of the sample).

The O recovery becomes more matrix independent. The PE can be inserted in the carousel in a second boat.

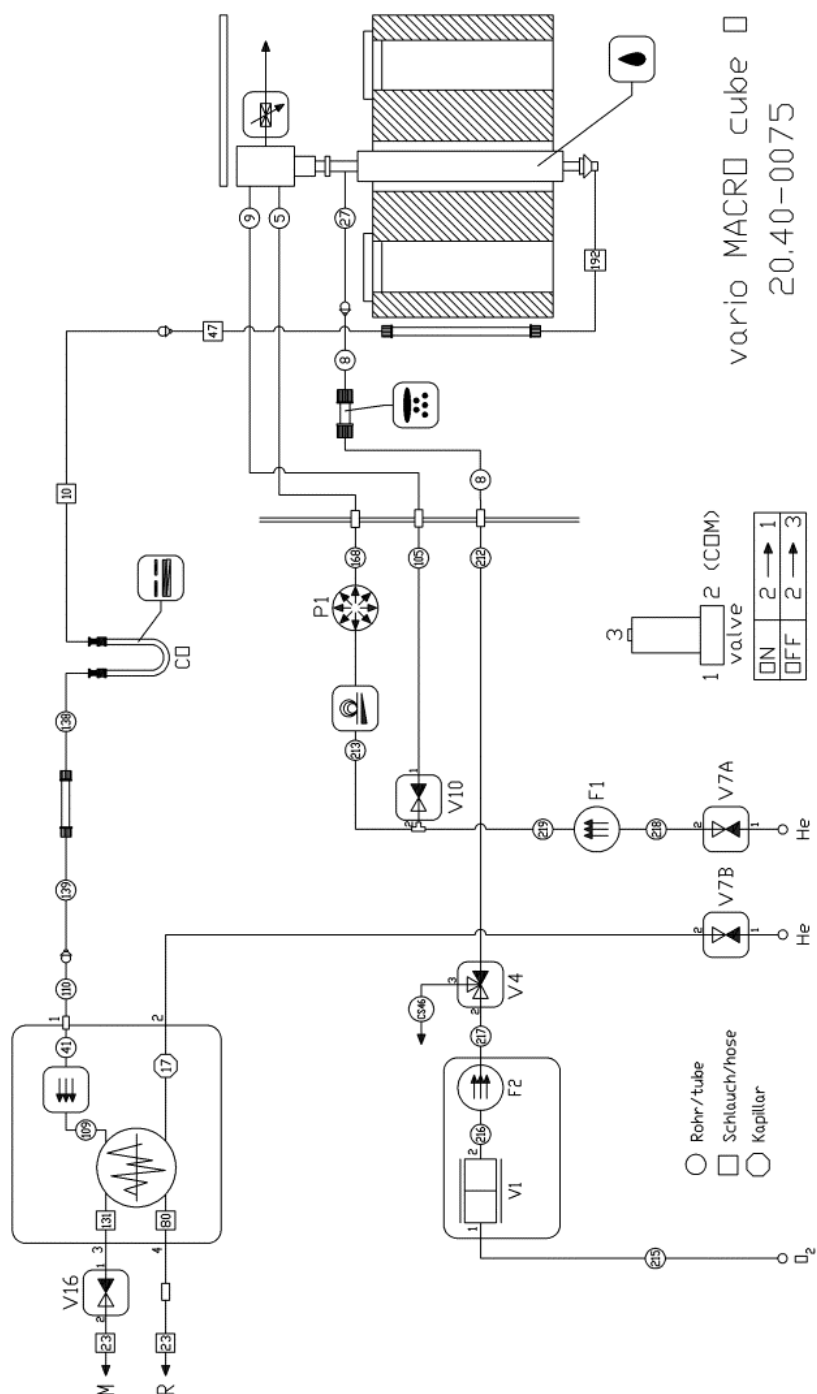
Substance digestion and preparation of the reaction gas mixture is divided into the following phases:

Phase	Process
1	The substance to be analyzed is digested in reductive atmosphere at a temperature of approx. 1,170 °C by means of pyrolysis (cracking).

- 2 For the digestion weigh in the sample into tin or silver boats (for liquid samples tin or silver capsules are available). The folded boat is thrown into the vertical quartz glass pyrolysis tube by means of an autosampler.
- 3 The oxygen containing radicals formed in the pyrolysis tube are converted quantitatively at a carbon contact (special carbon black) into carbon monoxide (Boudouard equilibrium).
- 4 Acidic pyrolysis products like e.g. H_2S , HCN , HCl etc. are absorbed at NaOH by means of an absorption tube which is downstream of the pyrolysis tube.
- 5 Usually, water is set free during the reaction of NaOH with an acidic medium. Therefore, the gas mixture is dried once again after the NaOH layer.
- 6 Neutral pyrolysis products like e.g. N_2 and CH_4 are led to a separation and measuring system together with the carbon monoxide to be detected.

Notes

For a better understanding see also the following illustration (tubing diagram, oxygen determination).



Symbols

The following list names the functional and basic symbols:



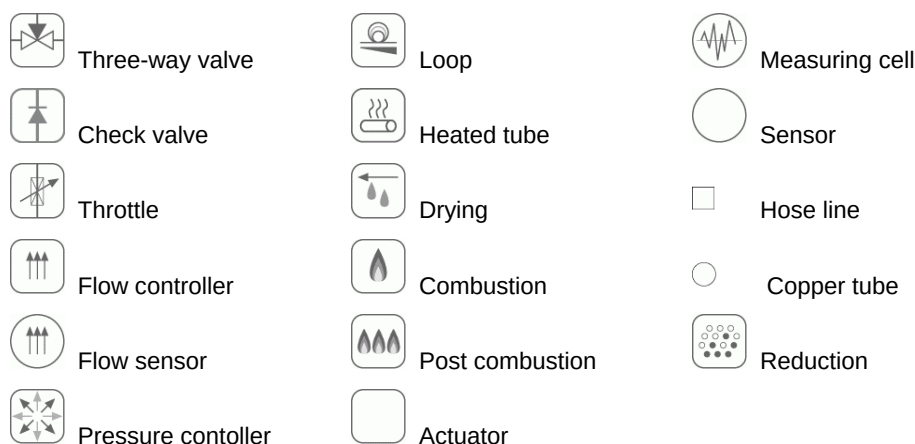
Two-way valve



Pressure sensor



Gas separation



Separation of the reaction gases

Introduction

The following section explains how the individual measuring components in the reaction gas mixture are separated from each other.

Procedures during separation

The separation of the measuring components is divided into the following phases:

Phase	Process
1	The gas mixture of CO and the by-products N ₂ , H ₂ and CH ₄ flow through the adsorption column at a temperature of 40 °C. Thus, the CO is removed quantitatively from the gas stream.
2	As the first component, the by-products unaffected by the adsorption column enter into the TCD together with the carrier gas helium.
3	The measurement of the N ₂ , H ₂ and CH ₄ fractions takes place. The result is ignored (dummy peak).
4	The adsorption column loaded with CO is heated up to 260°C whereby the CO is desorbed quickly and flushed by helium into the TCD.
5	A fan cools the adsorption column to cooling temperature of 40 °C and, thus making it ready for the next analysis sample.

Note

Samples containing fluorine and phosphorus may cause false O results. Fluorine may cause damages in the instrument, particularly at the quartz parts. Alkaline, earth alkaline and sulfurous samples have to be loaded with a 1:1 mixture of hexamethylenetetramine and ammonia chloride. When measuring heavy alkaline/earth alkaline samples the pyrolysis tube will corrode.

Detection

Introduction

The method of detection is described under *Detection of measuring components and evaluation of the measuring signal* in the vario MACRO cube operating instructions.

Variations relevant for the oxygen determination

O integration

- After the dummy peak integration has been finished, the following is possible:
 - Directly heat-out the CO collected on the adsorption column (approx. 260°C).
 - Heat-up the adsorption column to an "interim temperature" (approx. 60°C) in order to separate hydrocarbons from the CO if necessary.
- Prior to the start of the CO integration, another autozero alignment is carried out.
- The O integration has been finished if the process time "peak anticipation time for O" (factory set to 150 sec) has expired, and the detector signal is smaller than the cut-off threshold "O peak" (defined internally).

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.



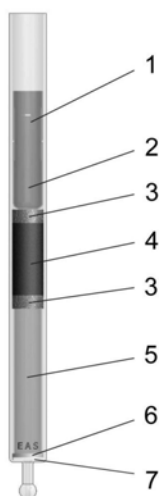
Safety instruction

Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Filling of the quartz pyrolysis tube (crack tube) for O determination

The arrangement of the filling must be carried out as shown in the following illustration.

The insert in the core of the tube contains the solid pyrolysis residue (particularly carbon) as well as the melted silver from the silver boats.



Legend:

- 1 Ash finger (used as protection tube)
- 2 Ash crucible
- 3 Graphite felt (10 mm)
- 4 Carbon black (55 mm)
- 5 Support rod (110 mm)
- 6 Quartz chips, coarse (2-4 mm)
- 7 Quartz wool (2 mm)

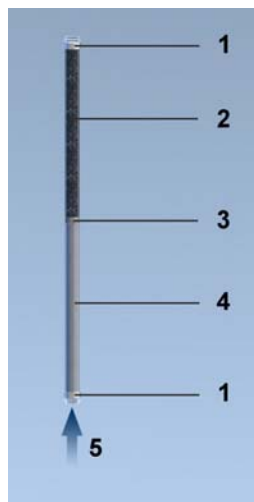
Removal of traces of moisture and other contaminations from the carrier gas

For gas drying insert commercial cleaning cartridges between gas delivery point and instrument, if necessary.

Humid carrier gas causes a CO base which will be collected as a blank on the adsorption column.

Filling the NaOH absorption tube

The following picture shows the fillings of the absorption tube:



Legend:

- 1 Cotton
- 2 Sicapent®
- 3 Quartz wool (10 mm)
- 4 NaOH
- 5 Gas inlet

Proceed as follows:

- Fill the tube with NaOH on carrier and with Sicapent® (identical fill heights).
- Close the tube ends with cotton.
- Insert the NaOH tube into the already mounted clamps at the left side of the combustion furnace.

Modification to O Mode

Scope of the modification kit for oxygen determination

All parts necessary for the tube modification are included in the O upgrade kit for detecting oxygen with TCD and are listed here.

- Pyrolysis tube
- Insulation plug
- Adsorption column
- Glass tube
- Quad ring, black
- Ball
- Ground-in clamp
- pan
- Hose tube no. 10, no. 47 and no. 192
- Combustion tube flange
- Tube no. 138 and no. 139
- 2 Clamps for fastening the glass tube at the furnace sheet metal
- Sheath tube
- Ash crucible

- D-sub-adapter
- Software update CD.



Safety instruction

Strictly observe the safety instruction "Gas pressure" under **Warning notes during operation** (on page 13).

Note

To remove/install the tubes proceed as described in chapter *Removing standard reaction tubes* of the vario MACRO cube main operating instructions.

Process

The section is divided into the following phases:

- Allow instrument to cool down and disconnect from the mains
- Modification
- Performing the necessary follow-up work



Safety instruction

Strictly observe the safety instruction "Modifying the instrument" under **Warning notes during operation** (on page 13).

Phase 1: Allow instrument to cool down and disconnect from the mains

Proceed as follows:

- Open the "Device parameters" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Set the setpoint temperature of the furnaces to 0 °C and confirm by clicking **OK**.
- Wait 2–3 hours until the instrument has cooled down to at least 55 °C.
- Quit the operating software. Execute the following command: **File > Exit**.
- Switch off the analyzer and its peripherals.
- Disconnect the analyzer from the mains. Disconnect the power supply plug.

Phase 2: Modification



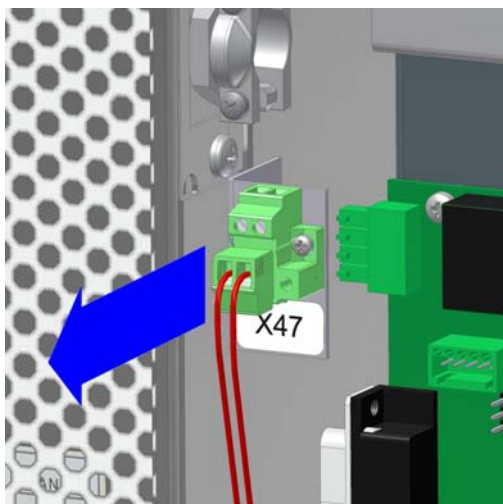
Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Open the right side door.

- Loosen the plug of the heating cartridge holder (X47) and close the right side door.



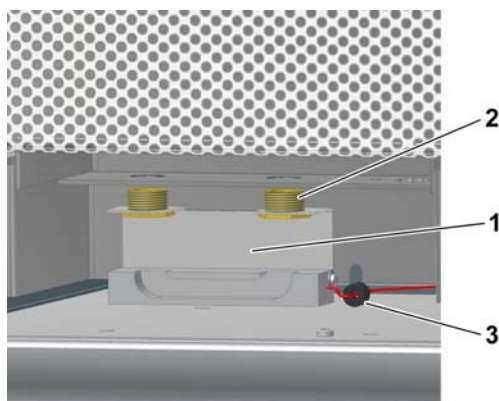
Note: For a modification to a mode with quartz glass bridge, the plug of the heating cartridge holder has to be plugged back into socket X47!

- Open the front door.
- Remove the heat protection below the furnace.



- If not already done, loosen all connections to the reaction tubes.
- Pull the furnace out of the instrument.
Remove the ground-in clamps, the quartz glass bridge and the combustion tubes.

- Remove the heating cartridge holder (1) by turning the adjusting bushings (2) out of the holder and press the grommet (3) located on the cable out of the recess toward the bottom.



Hinweis: If you want to operate the instrument without heating cartridge holder (depending on the mode), turn the adjusting bushings back into the holder located below the furnace.

- Insert the pyrolysis tube which is filled and mounted with the combustion tube flange into the middle tube of the furnace.

Note: The top o-ring used for sealing of the bayonet catch has to be checked frequently for mechanical damages and replaced if necessary.

- Cover the left and the right heating tube of the furnace with an insulation plug.
- Open the left side wall.
- Remove the valve area cover.
- Remove tube no. 108 from the instrument.
- Remove tube no. 132 from the instrument.
- Remove tube no. 133 from the instrument.
- Close all open column connections with a blind ball.
- Exchange the CO₂ adsorptions column against the CO adsorption column.

Bend tube no. 141 slightly aside.

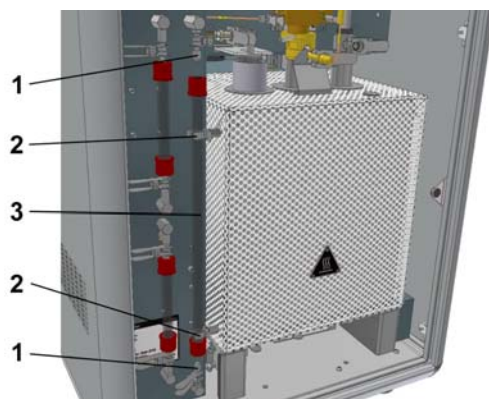
Proceed as described under *Removing/installing and conditioning the adsorption column* of the vario MACRO cube main operating instructions.

- Loosen the ground-in clamp from tube no. 137 and bend the tube slightly aside.
- Remove the large drying tube from the instrument. Close the inlets with the blind plugs (1) at the instrument.

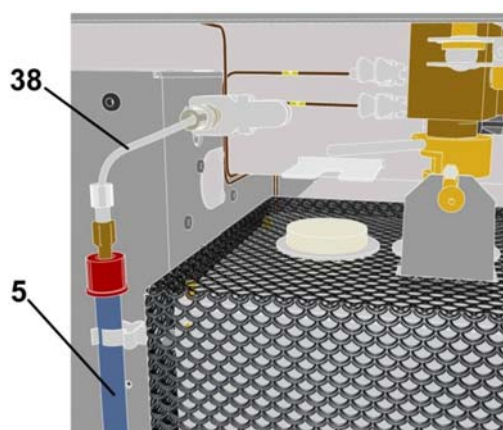
Fasten the holding clamps (2) at the furnace sheet metal at the left side.

Replace the screws by the holding clamps.

Push carefully the filled absorption tube (3) into the clamps (2) located at the left side of the furnace. Observe that the NaOH layer is on the bottom (gas inlet).



- Connect the pyrolysis tube outlet with the NaOH tube inlet by means of the tube No. 192.
- Push the furnace back into the instrument.
- Connect the outlet of the NaOH absorption tube (5) (top) with tube no. 47 (38). Connect the other end of the tube by means of the ground-in clamp to the ball of hose line no. 10 located at the instrument.



- Fasten the pyrolysis tube to the ball valve by means of the bayonet catch. The centering bolt has to be within the notch of the centering angle (lock against rotation).
- Instead of tube no. 27 (O₂ supply) close the open tubes with a pan and a ball. (Combustion tube flange, tube no. 8)
- Connect tube no. 10 with the CO column (rear connector) by means of the ground-in clamp. In doing so, lead the tube from the furnace area to the valve rack through the borehole.
- Connect the CO column (front connector) with the upper small absorption tube (bottom connector). Use tube no. 138.
- Connect the upper small absorption tube (top connector) with tube no. 110 (TCD). Use tube no. 139.
- Close the outlet (pan) at the valve with a ball.

Phase 3: Performing the necessary follow-up work

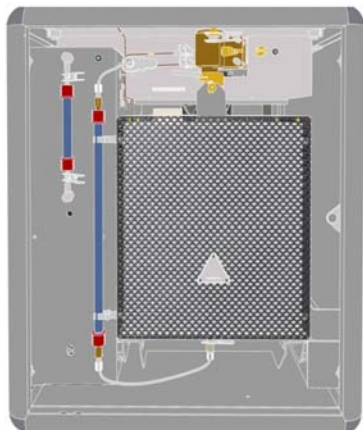
Proceed as follows:

- Perform a leak test. If a leak test was passed, the instrument is ready for operation.
- Test the proper operation of the instrument with conditioning samples, blanks and standard samples.

The modification has now been completed and the instrument is ready for the O determination in routine operation.

View after the modification has been completed

The following picture shows the oxygen mode after the modification has been completed.



Conditioning the pyrolysis tube

Introduction

The following section describes in detail how to condition the pyrolysis tube.

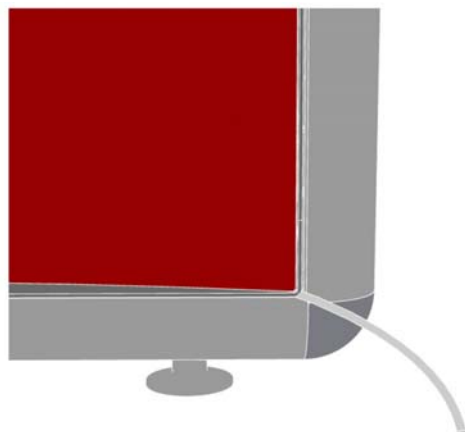
Prior to routine analysis the pyrolysis tube has to be conditioned. For this purpose flush the carbon black filling for approx. 12 hours at 1,170°C under helium in the instrument; subsequently, analyze 5 samples polyethylene (weight 8 mg).

Conditioning the pyrolysis tube

Proceed as follows:

- Turn on PC and printer. Wait until the boot process has been finished.
- Switch on the instrument.
- The instrument performs now a reference run of the ball valve and autosampler.
- Switch on the operating gas. Set the intake pressure at the delivery point to 0.5 bar.
- Open the gas connection to the NaOH tube.

- Connect tube no. 48 with the outlet of the pyrolysis tube. Lead the end of the hose line through the crack in the door into the open. The front door has to be closed.



- Connect the end of tube no. 48 with the furnished black hose (Article No. 03 651 010, 25 m) and lead the gases resulting from conditioning (e.g. H_2S , water vapor) into an exhaust hood or into the open.
- Start the instrument software and select in the menu **System > Mode** the operation mode "O", option "TCD" checked.
- Leave the mode menu by clicking **OK**; if necessary a new initialization of the instrument occurs.
- To heat up the furnace call the menu **Options > Settings > Parameters**. Set the temperature of oven 1 to 1170°C .

Note: The modification of the instrument parameters is only possible with the appropriate access rights.

- After reaching the setpoint temperature (after approx. 1.5 hours) heat-out the pyrolysis tube for another 12 hours (over night).
- Remove tube no. 48.
- Connect the 25 m long exhaust hose with the outlet at the instrument rear.
- Close the gas connection at the NaOH tube and adjust the intake pressure at the delivery point until the PC displays a pressure of approx. 1.2 bar.
- Analyze 5 samples polyethylene each 8 mg (conditioning) and 10 samples benzoic acid each approx. 1.5 mg (stability test) after the flush process.
- Now the instrument is ready for the O determination in routine operation.

Note

Samples containing fluorine and phosphorus may cause false O results. Fluorine may cause damages in the instrument, particularly at the quartz parts. Alkaline, earth alkaline and sulfurous samples have to be loaded with a 1:1 mixture of hexamethylenetetramine and ammonia chloride. When measuring heavy alkaline/earth alkaline samples the pyrolysis tube will corrode.

Changing of the pyrolysis crucible

Changing of the pyrolysis crucible

In addition to the common maintenance work, the replacement of the pyrolysis crucible for oxygen determination will be described here. The crucible has to be emptied after approx. 80 samples, if you work with the polyethylene additive.



Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Cool the furnace down to approx. 600°C.
- Open the front door.
- Initiate a pressure drop by clicking the menu command **Options > Maintenance > Replace parts**.
- After completion of the pressure drop procedure detach the ground-in clamp at the NaOH tube outlet.
- Open the bayonet catch at the ball valve.
- Pull the furnace out of the instrument.
- Pull the combustion tube flange out of the pyrolysis tube.
- Pull the sheath tube and the crucible with the tongs out of the pyrolysis tube.
- Empty the crucible.
- Install...
 - ... either the emptied crucible once again, or
 - ... a new crucible immediately after the filled crucible has been removed. This has to be conditioned by running 5 samples polyethylene (weight 8 mg). See **Conditioning the pyrolysis tube TCD** (on page 36).
- Push the furnace into the instrument. Observe that the ball valve adaptor is centered in the bayonet catch.
- Close both the bayonet catch at the ball valve and the ground-in ball-and-socket joint at the NaOH tube.
- Leave the "Replace part" dialog by clicking **Finish**.
- Flush the apparatus for approx. 1 hour and set the furnace temperature back to 1,170 °C.
- Wait until the PC display of the baseline of the detector is stable.

The flushing time depends on the amount of atmospheric nitrogen penetrated into the apparatus during the replacement of the tube insert.

In unpropitious cases, the flushing procedure can last up to 45 minutes.

Establishing of the analysis readiness

Establishing of the analysis readiness

Proceed as follows:

- Turn on PC and printer and wait until the boot process has been completed.
- Switch on the instrument.

The instrument performs now a reference run of the ball valve and carousel.
- Switch on the operating gases.
- Launch the operating software.
- Open the "Analysis mode" dialog in the operating software by selecting **System > Mode**. Select the desired operation mode ("O" for oxygen).

- Set the detector mode to "TCD".
- Leave the mode dialog by clicking **OK**; a re-initialization of the system takes place.

Defining test/standard substances

By means of the menu **Options > Settings > Standards** you can see whether the test substances to be used are stored there.

A description how to define a new and/or modify an existing standard is given under *Edit standard samples* in the vario MACRO cube operating instructions.

If no modifications have been carried out in the standard samples dialog, leave it by clicking **Close**, otherwise by clicking **Save** followed by **Close**.

Note:

If the value "0" stands for the element content percentage of a test substance, this test substance will be ignored for the respective element during calibration and/or during the calculation of the daily factor.

Routine operation

For a description of the particular software terms refer to *Menu and dialog descriptions* in the vario MACRO cube operating instructions.

Setting the furnace temperature

Proceed as follows:

- Open the "Device parameter" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Check and/or enter the following oven temperature (oven 2 is not needed here):
For operating mode O: Pyrolysis tube (oven 1): 1170 °C
- Leave the dialog by clicking **OK** (or by clicking **Cancel**). The modules are now re-initialized if necessary.

In the sataus view you can observe how the temperature of oven 1 increases.

The heat-up time takes approx. 60 minutes.

For an optimum lifetime of the instrument, the tubes and the consumables, we recommend to leave the instrument turned on.

Once the setpoint temperature has been reached the instrument is ready to measure.

Notes on performing calibration

Background

The calibration serves for creating a correlation between the measured peak area of the individual element and the concentration of the element in the sample.

This correlation is established via the so called calibration coefficients which are calculated from the calibration run.

Checking the calibration

Prior to the beginning of each series of measurements, it has to be checked if the instrument is calibrated.

Proceed as follows:

- Open the "Calibration coefficients" dialog in the operating software by selecting **Math. > Coefficients**.
- The coefficients dialog allows manual input of the calibration coefficients as well as of the limit values of the corresponding calibration range.

Sample weights

In practice, the following sample sequence has proven for a measuring range of 0.03 mg to 2.0 mg O:

- 10 conditioning samples of benzoic acid, approx. 2 -3 mg each for O conditioning
- 3 conditioning samples, 0.1-0.15 mg each
- 27 samples with sample weights as follows:
0.1 - 0.1 - 0.15 - 0.2 - 0.25 - 0.3 - 0.4 - 0.5 - 0.6 - 0.7 - 0.8 - 0.9 - 1.0 - 1.5 - 2.0 - 2.5 - 3.0 - 4.0 - 4.5 - 5.0 - 5.5 - 6.0 - 6.5 - 7.0 - 7.5 - 8.0 mg.

If the measuring range is to be extended, the following sample weights can be added:

- Benzoic acid 9 - 10 - 12 - 14 - 16 - 18- 19 mg.

Thus, a measuring range up to 5 mg absolute oxygen will be covered.

Polyethylene additive

The polyethylene additive improves the absolute accuracy and/or recovery. In practise an addition of approx. 8.0 mg per sample has proven to be of value.

Attention should be paid to:

Conditional of manufacturing, polyethylene contains minor concentrations of oxygen (approx. 0.2 ... 0.4%).

Prior to a measuring series start, especially during the calibration, the blank value of the used polyethylene has to be determined. Enter the blank value area in the column "O-blank", e.g. the mean value from 4 or 5 measurements.

Example:

Sample weight polyethylene	Blank value area
8,014	504
8,03	508
8,04	505
8,006	502

The mean value of the blank value area is 505 and has to be entered for the analysis samples / calibration samples in the column "O-blanks".

To ensure a correct calculation of the calibration select the manual calculation under **Options > Settings > Calculation > Blank Value Determination > Manual Input**.

Subsequently, start the calculation of the calibration under **Math. > Calibrate**, where the mathematical treatment of the blank values is done automatically.

Oxygen analyses in routine operation

Sample sequence

In routine operation, the following sample sequence (if necessary with PE additive of each 8 mg per sample) is recommended:

- 3 x conditioning sample (approx. 2.0 mg benzoic acid)

- 4 x benzoic acid (approx. 2.0 mg) for the determination of the daily factor
- 20 real samples
- 3 x benzoic acid (approx. 2.0 mg) for the monitoring of the daily factor
- 20 real samples
- 3 x benzoic acid (approx. 2.0 mg) etc.

The sample weight values can be entered either directly from a connected balance or manually via the keyboard.

Parameter menu settings

The instrument has factory set analysis parameters for test substances defined in the standards menu (e.g. acetanilide, benzoic acid).

Note: The modification of the instrument parameters is only possible with the appropriate access rights.

Temperature parameters

The following table shows the pre-set temperatures and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Oven 1 (pyrolysis tube) in O mode	Pyrolysis tube	1,170 °C
Ads. col. standby	Adsorption temperature of the CO column	40 °C
Adsorp. column, Cooling temp.	At the end of analysis, the program waits until column temperature drops below this value.	60 °C

Note: All other furnaces are not necessary in the O mode.

Time parameters

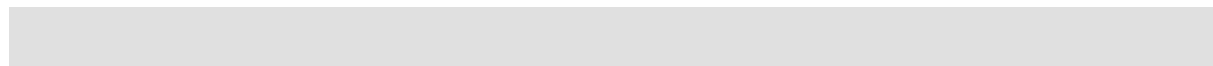
The following table shows the pre-set times and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Flushing time	Time in which the blind hole of the ball valve is flushed, so the atmospheric oxygen will be removed.	15 s
Integrator reset delay dummy	This time comes into effect for the first peak of the respective operation mode after the sample is fed and prevents the ensuing detector instabilities from being jointly integrated.	1 sec, operating mode O
Integrator reset delay peak O	See above.	1 s
Desorpt. mid.		1 s

Further process times and parameters are set via the "Method" dialog:

Parameter	Meaning	Factory setting
Autozero delay dummy	On starting up, the autozero alignment is carried out after the autozero delay.	2 sec, operating mode O
Autozero delay O	See above.	2 s
Peak Anticipation dummy	The anticipation time comes into effect after the integrator reset. During this time the integrator waits for a measuring peak. If the measuring peak does not appear within this time, the integration is concluded and the next analysis is started.	250 s
Peak Anticipation O	See above.	150 s

Desorpt. O	Corresponds to the desorption temperature of the column in O/TCD mode.	260 °C
Desorpt. midtemp.		40 °C



Application notes for oxygen determination

Target group

Personnel with basic knowledge of chemistry and experience with laboratory work, e.g. chemistry laboratory workers.

Purpose

This section gives additional notes about the application for oxygen determination.

In this section

Pyrolysis temperature.....	44
Difficult matrices	44
Lifetime of the pyrolysis tube	45

Pyrolysis temperature

Pyrolysis temperature

The method provides correct results only, if the carbon black filling in the pyrolysis tube is operated at a temperature of at least 1120°C.

In order to set the correct pyrolysis temperature, some samples of benzoic acid (approx. 2,0 mg) are analyzed with different pyrolysis temperatures.

The optimum temperature value has been reached if the analysis results with the increase of temperature do no longer vary significantly (< 0.2 % absolute).

Difficult matrices

Organic substances

Samples hard to digest (crackable) may be digested by hydrogen containing, carbon containing and/or chlorine containing additives like graphite, polyethylene, hexamethylenetetramine or NH_4Cl .

The additives must be dry and must not contain any oxygen.

Substances containing fluorine

Substances containing fluorine react with the quartz glass forming silicon tetrafluoride and discharge oxygen which will be measured as CO .

Additives, containing blank values

Partially, the recommended additives are hygroscopic and therefore they will deliver a oxygen blank value.

This blank value has to be determined in order to be able to correct the analysis results.

Procedure example:

- 6 x analysis of 15 - 16 mg additive.
- If the results are stable, compute the mean value from samples 4, 5 and 6 and then subtract this value from all samples which have been weighed in with an additive. (Input in column "Blank")

Measuring alkaline/earth alkaline samples

When measuring alkaline/earth alkaline samples the pyrolysis tube will corrode and its lifetime will be shortened.

The system pressure will bloat the tube until it eventually bursts.

This may lead to destruction of the furnace.

It is recommended to check the tube regularly for bloatings and to replace it in time with original spare parts.

Notes on matrix dependency

Due to the nature of pyrolysis, differences in recovery may occur, depending on the molecular structure and bond type of the oxygen. This fact has to be considered when very precise measurements are required.

To guarantee the absolute accuracy of the measuring results, it is recommended to use standard substances for calibration and daily factor determination which have the same bond type like oxygen. For general measurements of unknown substances use the average daily factor of 2 measured standards.

The following table shows some examples for determining the daily factor and/or the calibration:

Analysis of ...	Calibration and/or daily factor substance
amino acids	Glutamic acid
nitrates	KNO ₃ , AgNO ₃
Coal	commercially available coal standard
general applications, unknown substance classes	calibration with benzoic acid; daily factor averaged from benzoic acid and acet anilide

Lifetime of the pyrolysis tube

Lifetime of the pyrolysis tube (and/or the carbon black filling)

Permanent flushing the tube with carrier gas has proven to be the most efficient procedure. The tube can be stored for example in an exsiccator during longer breaks, and then used again.

Note that under the existing measuring conditions the quality of the quartz glass is very important. Under the prevailing circumstances use only original spare parts from Elementar to avoid the destruction of the furnace.

If the pyrolysis tube is used again, a conditioning of the tube prior to the actual measurements shall be done.

- Flush for approx. 2 hours with carrier gas at 1170 °C
- Measurement of 5 samples polyethylene and 10 samples benzoic acid each approx. 2 mg.

Only if the carbon black filling in the pyrolysis tube has decreased significantly, the installation of a newly filled pyrolysis tube with subsequent flushing and conditioning is recommended.

Additional error messages in O mode

The following table lists possible error messages, explaining the causes of the errors and giving tips for troubleshooting:

Error	Possible causes	Corrective action
Wide peaks with test substances	- Contaminated carbon black filling in the pyrolysis tube. - Used up carbon black filling in the pyrolysis tube. - Pyrolysis crucible contaminated.	Replace pyrolysis tube. Replace pyrolysis tube. Replace and/or empty crucible by more than 80 samples.
Wide peaks with samples	Indicates to uncompleted pyrolysis.	Add additives as described under Difficult matrices (on page 44).
Wide peaks	Contamination of the CO adsorption column.	Bake out CO adsorption column.
Measuring values vary	- Contaminated carbon black filling in the pyrolysis tube. - Used up carbon black filling in the pyrolysis tube. - Pyrolysis crucible contaminated. - Leakages - Varying boat blank values.	Replace pyrolysis tube. Replace pyrolysis tube. Replace and/or empty crucible by more than 80 samples. Carry out leak test, eliminate leak if necessary. Run at least 20 blank samples with empty silver boats.
Peak end error	- Sample weight too high. - Element content of sample too high.	Reduce sample weight. Increase peak end threshold of dummy peak.

CHAPTER 4

Oxygen determination with NDIR

Target group

Personnel involved with the instrument.

Purpose

This section describes the special features of the oxygen determination with NDIR.

In this chapter

Analytical characteristics and technical specifications.....	48
Substance digestion and functional diagram	48
Detection	52
Tube fillings	52
Modification to O Mode.....	54
Conditioning the pyrolysis tube.....	62
Changing of the pyrolysis crucible	64
Establishing of the analysis readiness.....	65
Notes on performing calibration.....	66
Oxygen analyses in routine operation	66
Application notes for oxygen determination.....	68
Additional error messages in O mode	71

Analytical characteristics and technical specifications

Analytical characteristics

The following table explains the analytical characteristics:

Analytical characteristic	Comments
Analysis method	Oxygen determination by pyrolysis of the samples, specific detection of the measuring component CO with NDIR.
Detector	NDIR detector
Sample weight/sample volume	Approx. < 1 to 10 mg depending on the substance.
Working range (depending on kit and measuring mode)	O: 0.005 - 2 mg
Precision / standard deviation	<0,2 % with benzoic acid (approx. 2 mg)
Duration of analysis (depending on element content and sample weight)	O: 8 - 15 min
Calibration	Linear and non-linear curve adjustment; total work range.
Data storage and data output	Storage on hard disk or external storage media. LIMS transfer possible. Data output to screen and printer.

Technical specifications

The following table contains the technical specifications of the gas supply:

Reference value	Technical specifications
Supply gases	Forming gas N ₂ /H ₂ 95/5 (95 % N ₂ , 5 % H ₂), water free, CO ₂ free, O ₂ free
Consumption of supply gases	Per analysis approx. 1.4 to 2.6 liters.

Substance digestion and functional diagram

Introduction

The following section explains:

- Which procedures in the pyrolysis tube of the furnace are processed.
- How the reaction mixture is prepared for the detection.

Processes during substance digestion and preparation of the reaction gas mixture

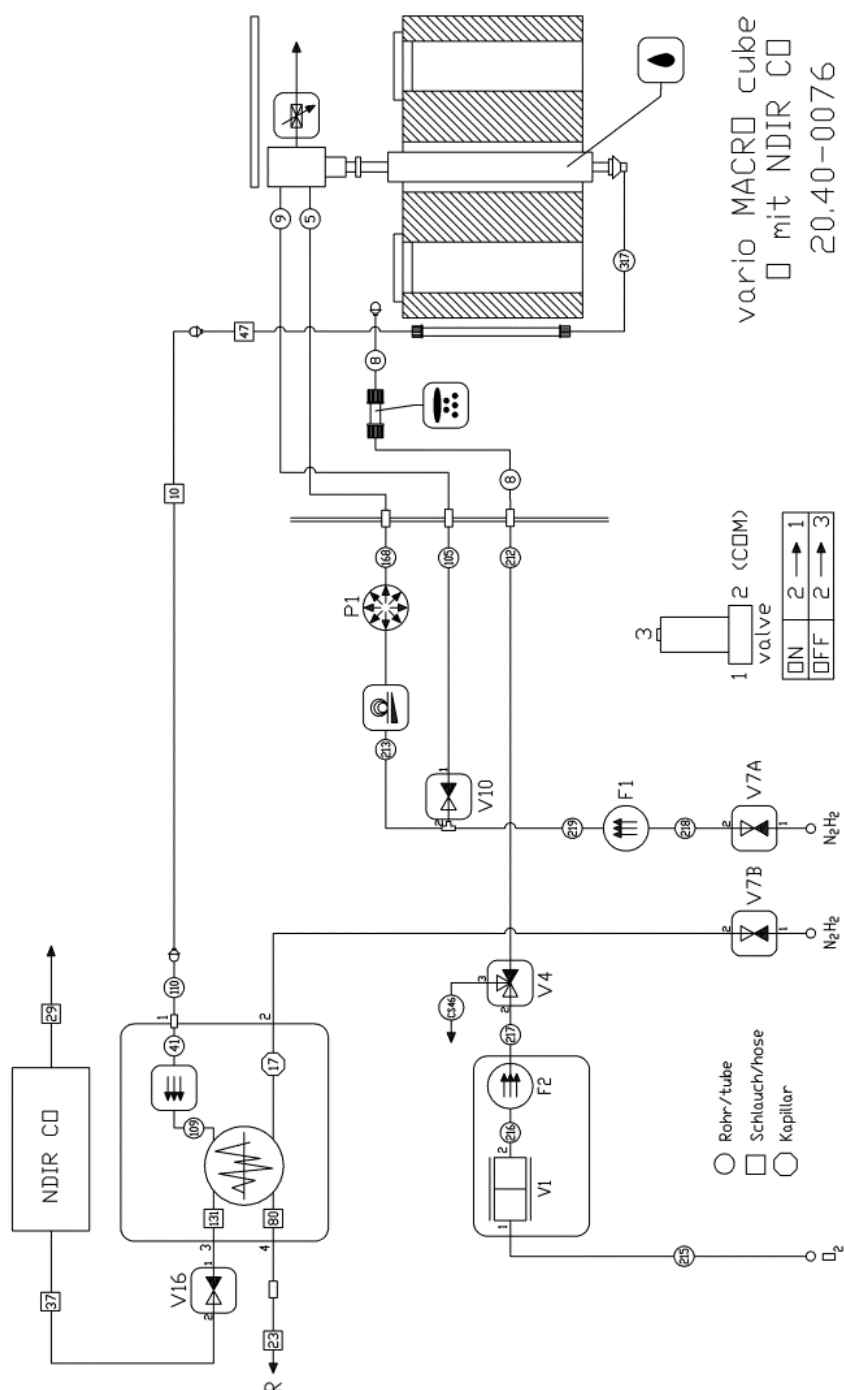
Substance digestion and preparation of the reaction gas mixture is divided into the following phases:

Phase	Process
1	The substance to be analyzed is digested in reductive atmosphere at a temperature of approx. 1,150 °C (1,170 °C) by means of pyrolysis (cracking).
2	For the digestion weigh in the sample into tin or silver boats (for liquid samples tin or silver capsules are available). The folded boat is thrown into the vertical quartz glass pyrolysis tube by means of an autosampler.
3	The oxygen containing radicals formed in the pyrolysis tube are converted quantitatively at a carbon contact (special carbon black) into carbon monoxide (Boudouard equilibrium).

- 4 | Acidic pyrolysis products like e.g. H_2S , HCN , HCl etc. are absorbed at NaOH by means of an absorption tube which is downstream of the pyrolysis tube.
- 5 | Usually, water is set free during the reaction of NaOH with an acidic medium. Therefore, the gas mixture is dried once again after the NaOH layer.
- 6 | Neutral pyrolysis products like e.g. N_2 and CH_4 are led to a measuring system together with the carbon monoxide to be detected.
Since the NDIR detector does only respond to CO , foreign gases, like e.g. N_2 and CH_4 does not have to be separated.

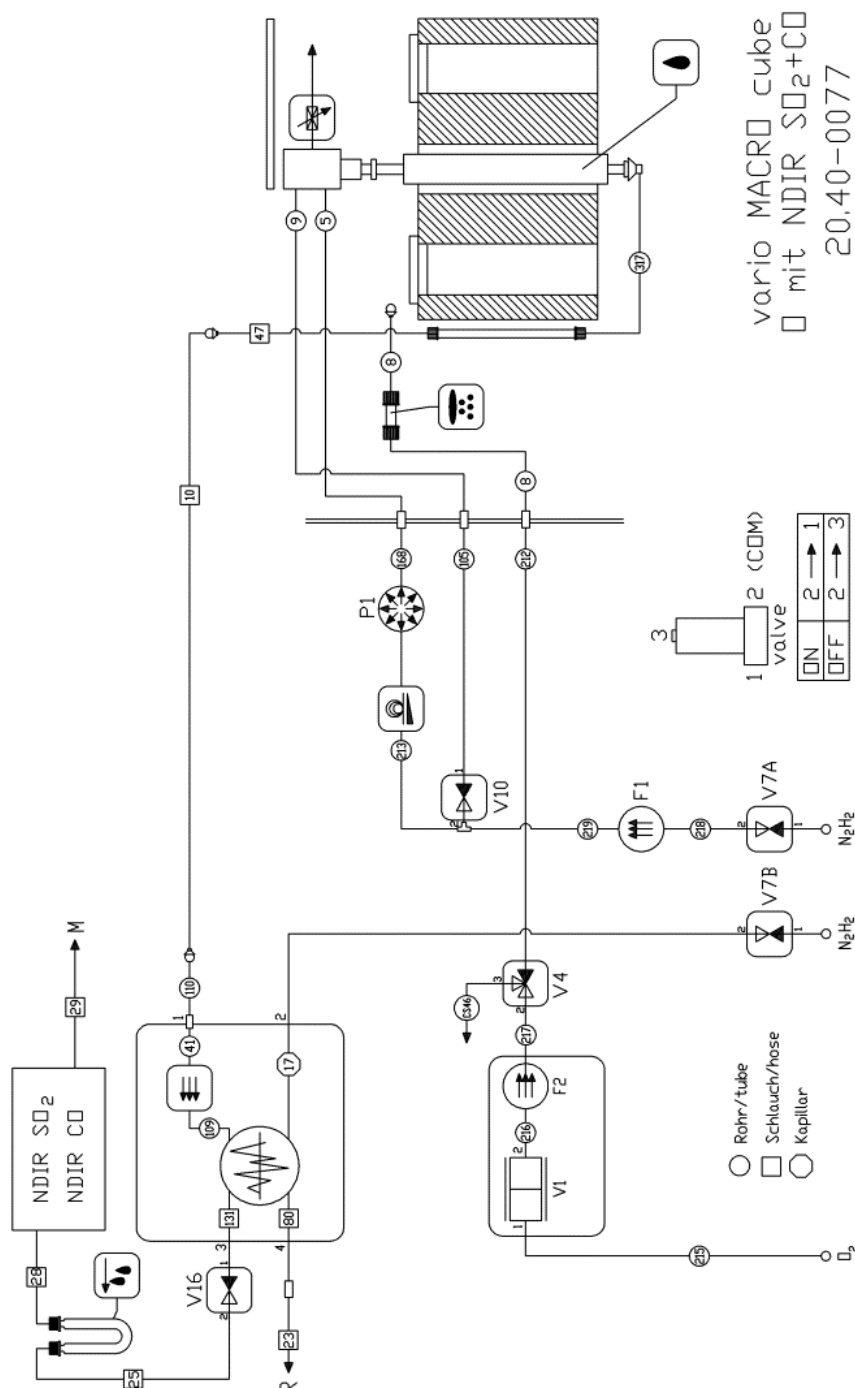
Oxygen determination with single NDIR detector CO

For a better understanding see also the following illustration (tubing diagram, oxygen determination).



Oxygen determination with dual NDIR detector CO/SO₂

For a better understanding see also the following illustration (tubing diagram, oxygen determination).



Symbols

The following list names the functional and basic symbols:



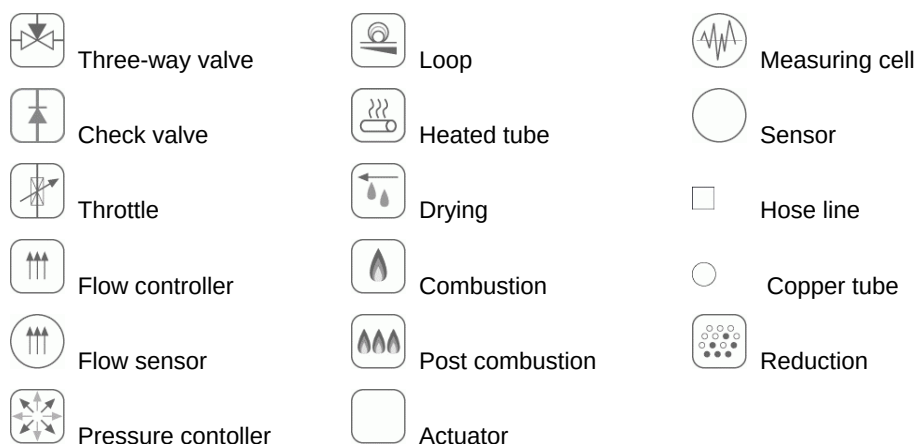
Two-way valve



Pressure sensor



Gas separation



Detection

Introduction

The detection of the measuring component CO is carried out with a CO specific NDIR detector. Depending on the individual application, either the single NDIR detector CO or the dual NDIR detector CO/SO₂ is used. The resulting differences are described in this chapter at the relevant positions.

O integration

After the analysis start, first the auto zero adjust of the NDIR takes place.

Subsequently, insertion of the sample takes place.

Shortly after the sample feeding the CO peak starts and the peak integration with it.

The O integration has been finished if the process time "peak anticipation time for O" (factory set to 150 sec) has expired, and the detector signal is smaller than the cut-off threshold "O peak" (defined internally).

To secure an optimum accuracy of the measuring results, the cut-off threshold is set very low.

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.



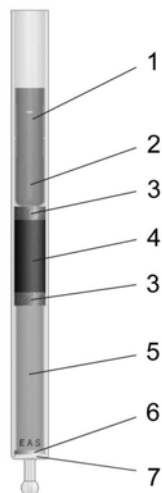
Safety instruction

Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Filling of the quartz pyrolysis tube (crack tube) for O determination

The arrangement of the filling must be carried out as shown in the following illustration.

The insert in the core of the tube contains the solid pyrolysis residue (particularly carbon) as well as the melted silver from the silver boats.



Legend:

- 1 Ash finger (used as protection tube)
- 2 Ash crucible
- 3 Graphite felt (10 mm)
- 4 Carbon black (55 mm)
- 5 Support rod (110 mm)
- 6 Quartz chips, coarse (2-4 mm)
- 7 Quartz wool (2 mm)

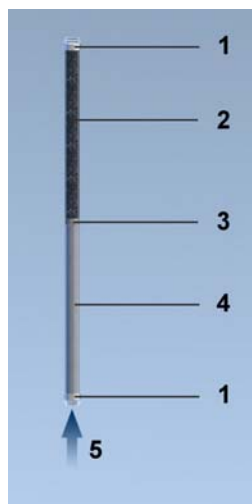
Removal of traces of moisture and other contaminations from the carrier gas

For gas drying insert commercial cleaning cartridges between gas delivery point and instrument, if necessary.

Humid carrier gas causes a CO base which will be collected as a blank on the adsorption column.

Filling the NaOH absorption tube

The following picture shows the fillings of the absorption tube:



Legend:

- 1 Cotton
- 2 Sicapent®
- 3 Quartz wool (10 mm)
- 4 NaOH
- 5 Gas inlet

Proceed as follows:

- Fill the tube with NaOH on carrier and with Sicapent® (identical fill heights).
- Close the tube ends with cotton.
- Insert the NaOH tube into the already mounted clamps at the left side of the combustion furnace.

Modification to O Mode

Scope of the modification kit for oxygen determination

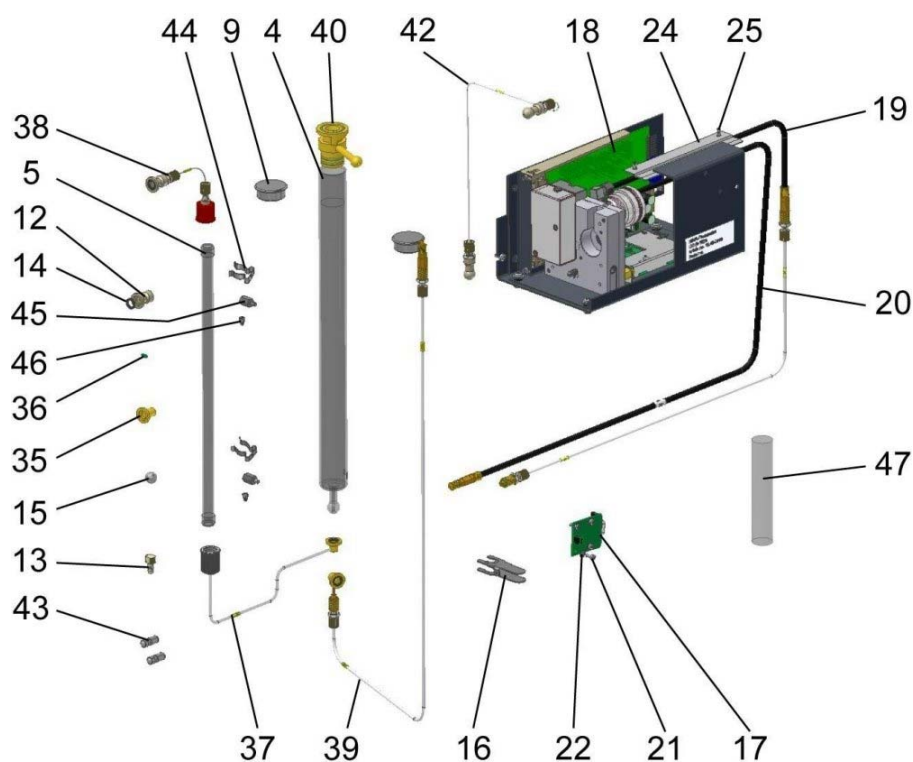
All parts necessary for the tube modification are included in the O upgrade kit for detecting oxygen with NDIR and are labeled with numbers.

With the new delivery of a complete system the RS 232 module and the NDIR detector are already installed in the instrument (NDIR: left instrument side, behind the left side door, RS 232 module: right instrument side, electronics).

Upgrade kits

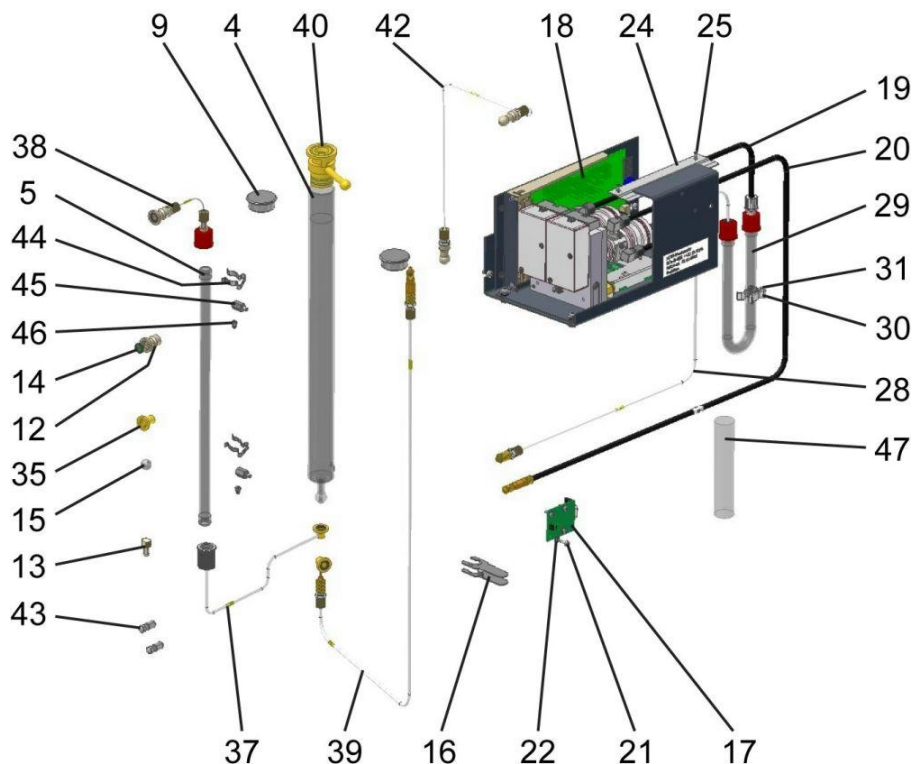
The following pictures show the upgrade kits with single NDIR detector and with dual NDIR detector:

Upgrade kit with single NDIR detector CO



Upgrade kit with dual NDIR detector CO/SO₂**Note:**

- The filled U-tube is only used for the exact SO₂ measurement but does not disturb the CO measurement, i.e., for O-operation a filled U-tube may stay in the gas way.
- The U-tube GL 14 with the corresponding holding clamps and tubings is also already installed.

**Legend:**

4 Pyrolysis tube	19 Tube no. 37	36 Hose seal 1/16"
5 Glass tube	20 Tube no. 29	37 Tube no. 46
9 Insulation plug	21 Screw M3x6	38 Tube no. 47
12 Pan UNF 1/4"	22 Serrated washer, 3.2	39 Tube no. 48
13 Blind plug UNF 1/4"	24 Guidance angle	40 Combustion tube flange
14 Quad ring, black	25 Screws M4x8	42 Tube no. 10
15 Ball	29 U tube	43 Ball (blind plug)
16 Ground-in clamp	30 Clamp	44 Clamp
17 RS 232 module	31 Screw M3x6	45 Spacer bolt
18 NDIR detector	35 Pan, closed	46 Screw M3x6
		47 Support rod

The following parts are also part of the kit but are not pictured.

- Sheath tube
- Ash crucible
- D-sub-adapter
- Software update CD.

**Safety instruction**

Strictly observe the safety instruction "Gas pressure" under **Warning notes during operation** (on page 13).

Process

The modification is divided into the following phases:

- Removal of components not needed
- Modification
- Installation of components necessary for the O operation
- bridge the adsorption column
- Installation of components necessary for the O operation, continued

Phase 1: Removal of components not needed

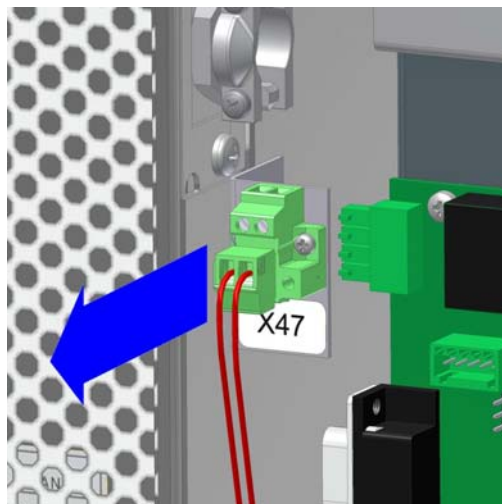


Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Turn off the instrument and pull the power supply plug.
- Open the right side door.
- Loosen the plug of the heating cartridge holder (X47) and close the right side door.



Note: For a modification to a mode with quartz glass bridge, the plug of the heating cartridge holder has to be plugged back into socket X47!

- Open the front door.

- Remove the heat protection below the furnace.



- If not already done, loosen all connections to the reaction tubes.
- Pull the furnace out of the instrument.
- Remove the ground-in clamps, the quartz glass bridge and the combustion tubes.
- Remove the O₂ supply tube and the reduction tube with the plug.

Phase 2: Modification



Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Open the left side wall.
- Unscrew the retaining screw (1) above the valve rack cover and remove the cold valve rack cover.

Loosen the plug of the cover!



The valve rack is now visible.

- Fasten the guidance angle (24) with screws M4x8 (25).



Loosely insert two screws M4x8 (25) into the tap holes, so that the distance between screw heads and sheet is still 2 mm.

- If the analyzer is operated with a single NDIR detector CO, go to step after next.
- Attach the clamp (30) in the gas insert by means of the screw (31). Fasten the filled U-tube (29) with the clamp (30).



- Mount the NDIR photometer (18) into the analyzer as displayed below: Push the two designated recesses over the loosely inserted screws (25) and then shift the photometer to the left up to the stop.



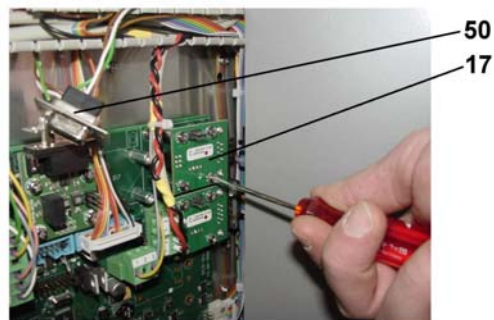
- Make sure the upper lug of the NDIR photometer will snap into the guidance angle.
- Now fasten the photometer by fixing both screws.
- Connect the photometer as follows:
 - (A) Cable #50 to RS232 module
 - (B) Cable #53 (internal IR)
 - (C) Cable #51 (power supply)

Connect the pre-installed cable no. 51 (C) with the double-pole plug on the IR board.

Connect the pre-installed data cable no. 50 (A) with the 9 pin D-SUB plug on the RS232 module of the IR photometer. In case the plug of the data cable does not fit to the RS232 module connector, use the enclosed "D-SUB adaptor" (part no. 05 001 961).



- Open the right side door.
- Attach the RS232 module (17) on the BCB board (JP5) by means of the four screws M3x6 and connect it (COM2).



- Connect the pre-installed data cable no. 50 to the RS232 module just installed.
- Remove the plugs from the rear wall.



- Remove the connecting piece of the measure gas outlet using a 7mm open jawed wrench.



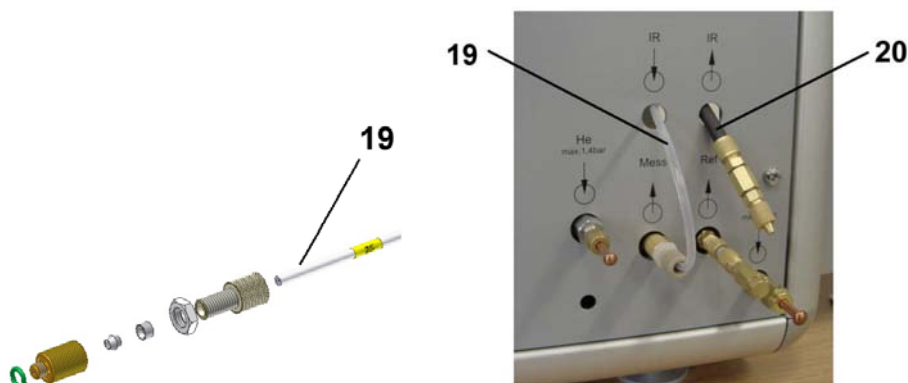
- Lead tube no. 37 (19) from inside to outside through the hole (IR inlet) and connect it to the measure gas outlet using a knurled reducing nipple.

When using a dual IR photometer connect the end of the hose line no. 25 (red cap) and hose line no. 28 (IR photometer inlet) to the U tube (29).

Lead the outlet hose line of the IR photometer no. 29 (20) from inside to outside through the hole (IR outlet).

The double nipple connector at the end of the hose line no. 29 (20) is used to connect the on-site waste gas line.

CAUTION: Follow the notes about discharging the waste gases into the open or into a vent in the vario MACRO cube main operating instructions!



Phase 3: Installation of components necessary for the O operation

Proceed as follows:

- Insert the pyrolysis tube which is filled and mounted with the combustion tube flange into the middle tube of the furnace.

Note:

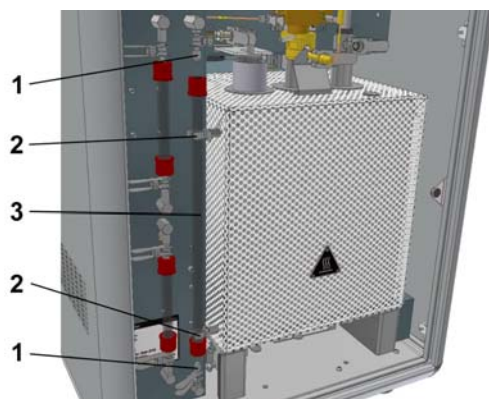
The top o-ring used for sealing of the bayonet catch has to be checked frequently for mechanical damages and replaced if necessary.

- Cover the left and the right heating tube of the furnace with an insulation plug.
- Remove the large drying tube from the instrument. Close the inlets at the instrument with the blind plugs (1).

Fasten the holding clamps (2) at the furnace sheet metal at the left side.

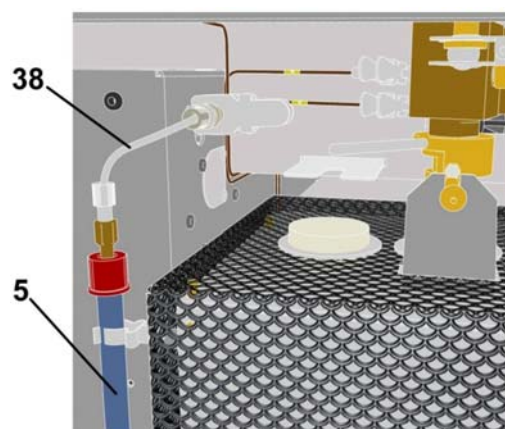
Replace the screws by the holding clamps.

Push carefully the filled absorption tube (3) into the clamps (2) located at the left side of the furnace. Observe that the NaOH layer is on the bottom (gas inlet).



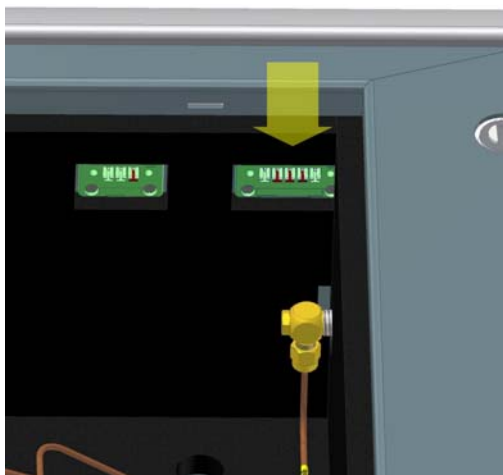
- Connect the pyrolysis tube outlet with the NaOH tube inlet by means of the tube No. 46.
- Push the furnace back into the instrument.
- Connect the outlet of the NaOH absorption tube (5) (top) with tube no. 47 (38). Connect the other end of the tube by means of the ground-in clamp to the ball of hose line no. 10 located at the instrument.

For that purpose the ball (of tube no. 10) has to be turned to 90° and pushed into the appropriate clamp.



- Close the open tube no. 8 with the provided blind ball and the open oxygen connection at the combustion tube flange with the closed pan (tube no. 27 is not used).
- Fasten the pyrolysis tube to the ball valve by means of the bayonet catch. The centering bolt has to be within the notch of the centering angle (lock against rotation).
- Remove the ball joint at the open end of tube no. 10 and replace it by the provided pan incl. quad ring.
- Loosen tube no. 110 from the angled screw coupling at valve MV 2.
- Now connect tube no. 110 and tube no. 10 by means of a ground-in clamp.

- Reinstall the cover of the valve rack. Insert the plug into socket X51.2.

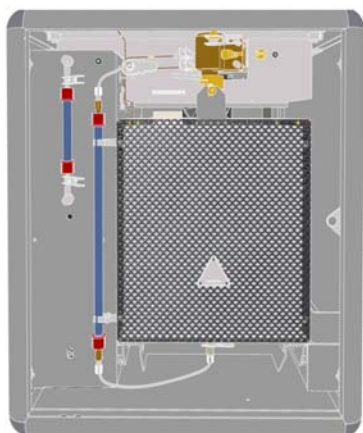


- Close the left side door.
- Remove the helium gas supply.
- Connect the forming gas supply.
- Set the intake pressure at the delivery point to show approx. 1150 mbar at the PC pressure display.

The modification has now been completed and the instrument is ready for the O determination in routine operation.

View after the modification has been completed

The following picture shows the oxygen mode after the modification has been completed.



Conditioning the pyrolysis tube

Introduction

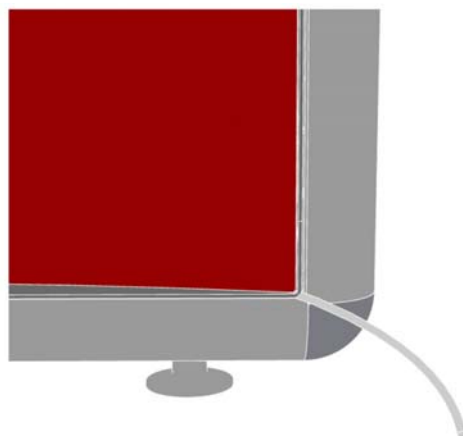
The following section describes in detail how to condition the pyrolysis tube.

Prior to routine analysis the pyrolysis tube has to be conditioned. For this purpose flush the carbon black filling for approx. 12 hours at 1,170°C under helium in the instrument; subsequently, analyze 5 samples polyethylene (weight 8 mg).

Conditioning the pyrolysis tube

Proceed as follows:

- Turn on PC and printer. Wait until the boot process has been finished.
- Switch on the instrument.
- The instrument performs now a reference run of the ball valve and autosampler.
- Switch on the operating gas. Set the intake pressure at the delivery point to 0.5 bar.
- Open the gas connection to the NaOH tube.
- Connect tube no. 48 (see upgrade kit part no. 39) with the outlet of the pyrolysis tube. Lead the end of the hose line through the crack in the door into the open. The front door has to be closed.



- Connect the end of tube no. 48 (see upgrade kit part no. 39) with the furnished black hose (Article No. 03 651 010, 25 m) and lead the gases resulting from conditioning (e.g. H₂S, water vapor) into an exhaust hood or into the open.
- Start the instrument software and select in the menu **System > Mode** the operation mode "O", option "IR" checked.
- Leave the mode menu by clicking **OK**; if necessary a new initialization of the instrument occurs.
- To heat up the furnace call the menu **Options > Settings > Parameters**. Set the temperature of oven 1 to 1170 °C.

Note: The modification of the instrument parameters is only possible with the appropriate access rights.

- After reaching the setpoint temperature (after approx. 1.5 hours) heat-out the pyrolysis tube for another 12 hours (over night).
- Remove hose line no. 38 (part no. 29).
- Connect the 25 m long exhaust hose (art. no. 03 651 010) with the outlet of the IR at the instrument rear.
- Close the gas connection at the NaOH tube and adjust the intake pressure at the delivery point until the PC displays a pressure of approx. 1.2 bar.
- Analyze 5 samples polyethylene each 8 mg (conditioning) and 10 samples benzoic acid each approx. 1.5 mg (stability test) after the flush process.
- Now the instrument is ready for the O determination in routine operation.

Note

Samples containing fluorine and phosphorus may cause false O results. Fluorine may cause damages in the instrument, particularly at the quartz parts. Alkaline, earth alkaline and sulfurous samples have to be loaded with a 1:1 mixture of hexamethylentetramine and ammonia chloride. When measuring heavy alkaline/earth alkaline samples the pyrolysis tube will corrode.

Changing of the pyrolysis crucible

Changing of the pyrolysis crucible

In addition to the common maintenance work, the replacement of the pyrolysis crucible for oxygen determination will be described here. The crucible has to be emptied after approx. 80 samples, if you work with the polyethylene additive.



Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Cool the furnace down to approx. 600°C.
- Open the front door.
- Initiate a pressure drop by clicking the menu command **Options > Maintenance > Replace parts**.
- After completion of the pressure drop procedure detach the ground-in clamp at the NaOH tube outlet.
- Open the bayonet catch at the ball valve.
- Pull the furnace out of the instrument.
- Pull the combustion tube flange out of the pyrolysis tube.
- Pull the sheath tube and the crucible with the tongs out of the pyrolysis tube.
- Empty the crucible.
- Install...
 - ... either the emptied crucible once again, or
 - ... a new crucible immediately after the filled crucible has been removed. This has to be conditioned by running 5 samples polyethylene (weight 8 mg). See **Conditioning the pyrolysis tube NDIR** (on page 62).
- Push the furnace into the instrument. Observe that the ball valve adaptor is centered in the bayonet catch.
- Close both the bayonet catch at the ball valve and the ground-in ball-and-socket joint at the NaOH tube.
- Leave the "Replace part" dialog by clicking **Finish**.
- Flush the apparatus for approx. 1 hour and set the furnace temperature back to 1,170 °C.
- Wait until the PC display of the baseline of the detector is stable.

The flushing time depends on the amount of atmospheric nitrogen penetrated into the apparatus during the replacement of the tube insert.

In unpropitious cases, the flushing procedure can last up to 45 minutes.

Establishing of the analysis readiness

Establishing of the analysis readiness

Proceed as follows:

- Turn on PC and printer and wait until the boot process has been completed.
- Switch on the instrument.
The instrument performs now a reference run of the ball valve and carousel.
- Switch on the operating gases.
- Launch the operating software.
- Open the "Analysis mode" dialog in the operating software by selecting **System > Mode**. Select the desired operation mode ("O" for oxygen).
- Set the detector mode to "IR".
- Leave the mode dialog by clicking **OK**; a re-initialization of the system takes place.

Defining test/standard substances

By means of the menu **Options > Settings > Standards** you can see whether the test substances to be used are stored there.

A description how to define a new and/or modify an existing standard is given under *Edit standard samples* in the vario MACRO cube operating instructions.

If no modifications have been carried out in the standard samples dialog, leave it by clicking **Close**, otherwise by clicking **Save** followed by **Close**.

Note:

If the value "0" stands for the element content percentage of a test substance, this test substance will be ignored for the respective element during calibration and/or during the calculation of the daily factor.

Routine operation

For a description of the particular software terms refer to *Menu and dialog descriptions* in the vario MACRO cube operating instructions.

Setting the furnace temperature

Proceed as follows:

- Open the "Device parameter" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Check and/or enter the following oven temperature (oven 2 is not needed here):
For operating mode O: Pyrolysis tube (oven 1): 1170 °C
- Leave the dialog by clicking **OK** (or by clicking **Cancel**). The modules are now re-initialized if necessary.

In the sataus view you can observe how the temperature of oven 1 increases.

The heat-up time takes approx. 60 minutes.

For an optimum lifetime of the instrument, the tubes and the consumables, we recommend to leave the instrument turned on.

Once the setpoint temperature has been reached the instrument is ready to measure.

Notes on performing calibration

Background

The calibration serves for creating a correlation between the measured peak area of the individual element and the concentration of the element in the sample.

This correlation is established via the so called calibration coefficients which are calculated from the calibration run.

Checking the calibration

Prior to the beginning of each series of measurements, it has to be checked if the instrument is calibrated.

Proceed as follows:

- Open the "Calibration coefficients" dialog in the operating software by selecting **Math. > Coefficients**.
- The coefficients dialog allows manual input of the calibration coefficients as well as of the limit values of the corresponding calibration range.

Sample weights

In practice, the following sample sequence has proven for a measuring range of 0.03 mg to 2.0 mg O:

- 10 conditioning samples of benzoic acid, approx. 2 -3 mg each for O conditioning
- 3 conditioning samples, 0.1-0.15 mg each
- 27 samples with sample weights as follows:
0.1 - 0.1 - 0.15 - 0.2 - 0.25 - 0.3 - 0.4 - 0.5 - 0.6 - 0.7 - 0.8 - 0.9 - 1.0 - 1.5 - 2.0 - 2.5 - 3.0 - 4.0 - 4.5 - 5.0 - 5.5 - 6.0 - 6.5 - 7.0 - 7.5 - 8.0 mg.

Thus, a measuring range up to 2 mg absolute oxygen will be covered.

Oxygen analyses in routine operation

Sample sequence

In routine operation, the following sample sequence is recommended:

- 3 x conditioning sample (approx. 2.0 mg benzoic acid)
- 4 x benzoic acid (approx. 2.0 mg) for the determination of the daily factor
- 20 real samples
- 3 x benzoic acid (approx. 2.0 mg) for the monitoring of the daily factor
- 20 real samples
- 3 x benzoic acid (approx. 2.0 mg) etc.

The sample weight values can be entered either directly from a connected balance or manually via the keyboard.

Parameter menu settings

The instrument has factory set analysis parameters for test substances defined in the standards menu (e.g. acetanilide, benzoic acid).

Note: The modification of the instrument parameters is only possible with the appropriate access rights.

Temperature parameters

The following table shows the pre-set temperatures and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Oven 1 (pyrolysis tube) in O mode	Pyrolysis tube	1,170 °C

Time parameters

The following table shows the pre-set times and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Flushing time	Time in which the blind hole of the ball valve is flushed, so the atmospheric oxygen will be removed.	10 s
Integrator reset delay peak O	This time comes into effect after the sample is fed and prevents the ensuing detector instabilities from being jointly integrated.	2 sec, operating mode O

Further process times and parameters are set via the "Method" dialog:

Parameter	Meaning	Factory setting
Autozero delay O	On starting up, the autozero alignment is carried out after the autozero delay.	2 sec, operating mode O
Peak anticipation O	The anticipation time comes into effect after the integrator reset. During this time the integrator waits for a measuring peak. If the measuring peak does not appear within this time, the integration is concluded and the next analysis is started.	150 s

Application notes for oxygen determination

Target group

Personnel with basic knowledge of chemistry and experience with laboratory work, e.g. chemistry laboratory workers.

Purpose

This section gives additional notes about the application for oxygen determination.

In this section

Pyrolysis temperature.....	69
Difficult matrices	69
Lifetime of the pyrolysis tube	70

Pyrolysis temperature

Pyrolysis temperature

The method provides correct results only, if the carbon black filling in the pyrolysis tube is operated at a temperature of at least 1120°C.

In order to set the correct pyrolysis temperature, some samples of benzoic acid (approx. 2,0 mg) are analyzed with different pyrolysis temperatures.

The optimum temperature value has been reached if the analysis results with the increase of temperature do no longer vary significantly (< 0.2 % absolute).

Difficult matrices

Organic substances

Samples hard to digest (crackable) may be digested by hydrogen containing, carbon containing and/or chlorine containing additives like graphite, polyethylene, hexamethylenetetramine or NH_4Cl .

The additives must be dry and must not contain any oxygen.

Substances containing fluorine

Substances containing fluorine react with the quartz glass forming silicon tetrafluoride and discharge oxygen which will be measured as CO .

Additives, containing blank values

Partially, the recommended additives are hygroscopic and therefore they will deliver a oxygen blank value.

This blank value has to be determined in order to be able to correct the analysis results.

Procedure example:

- 6 x analysis of 15 - 16 mg additive.
- If the results are stable, compute the mean value from samples 4, 5 and 6 and then subtract this value from all samples which have been weighed in with an additive. (Input in column "Blank")

Measuring alkaline/earth alkaline samples

When measuring alkaline/earth alkaline samples the pyrolysis tube will corrode and its lifetime will be shortened.

The system pressure will bloat the tube until it eventually bursts.

This may lead to destruction of the furnace.

It is recommended to check the tube regularly for bloatings and to replace it in time with original spare parts.

Notes on matrix dependency

Due to the nature of pyrolysis, differences in recovery may occur, depending on the molecular structure and bond type of the oxygen. This fact has to be considered when very precise measurements are required.

To guarantee the absolute accuracy of the measuring results, it is recommended to use standard substances for calibration and daily factor determination which have the same bond type like oxygen. For general measurements of unknown substances use the average daily factor of 2 measured standards.

The following table shows some examples for determining the daily factor and/or the calibration:

Analysis of ...	Calibration and/or daily factor substance
amino acids	Glutamic acid
nitrates	KNO ₃ , AgNO ₃
Coal	commercially available coal standard
general applications, unknown substance classes	calibration with benzoic acid; daily factor averaged from benzoic acid and acet anilide

Lifetime of the pyrolysis tube

Lifetime of the pyrolysis tube (and/or the carbon black filling)

Permanent flushing the tube with carrier gas has proven to be the most efficient procedure. The tube can be stored for example in an exsiccator during longer breaks, and then used again.

Note that under the existing measuring conditions the quality of the quartz glass is very important. Under the prevailing circumstances use only original spare parts from Elementar to avoid the destruction of the furnace.

If the pyrolysis tube is used again, a conditioning of the tube prior to the actual measurements shall be done.

- Flush for approx. 2 hours with carrier gas at 1170 °C
- Measurement of 5 samples polyethylene and 10 samples benzoic acid each approx. 2 mg.

Only if the carbon black filling in the pyrolysis tube has decreased significantly, the installation of a newly filled pyrolysis tube with subsequent flushing and conditioning is recommended.

Additional error messages in O mode

The following table lists possible error messages, explaining the causes of the errors and giving tips for troubleshooting:

Error	Possible causes	Corrective action
Wide peaks with test substances and peak end error	- Contaminated carbon black filling in the pyrolysis tube. - Used up carbon black filling in the pyrolysis tube. - Pyrolysis crucible contaminated.	Replace pyrolysis tube. Replace pyrolysis tube. Replace and/or empty crucible by more than 80 samples.
Wide peaks with samples	Indicates to uncompleted pyrolysis.	Add additives as described under Difficult matrices (on page 44).
Measuring values vary	- Contaminated carbon black filling in the pyrolysis tube. - Used up carbon black filling in the pyrolysis tube. - Pyrolysis crucible contaminated. - Leakages - Varying boat blank values.	Replace pyrolysis tube. Replace pyrolysis tube. Replace and/or empty crucible by more than 80 samples. Carry out leak test, eliminate leak if necessary. Run at least 20 blank samples with empty silver boats.
Peak end error	- Sample weight too high. - Oxygen content of sample too high.	Reduce sample weight.

CHAPTER 5

Chlorine determination with EC cell

Target group

Personnel involved with the instrument.

Purpose

This section describes the special features of the chlorine determination with EC cell.

In this chapter

Analytical characteristics and technical specifications.....	74
Substance digestion and functional diagram	74
Detection	76
Tube fillings	76
Notes on performing calibration.....	78
Chlorine analyses in routine operation	79
Notes on sensitivity and measuring range	80
Cross-sensitivity of the EC cells	81
Quantitative conversion from Cl to HCl.....	82
Maintenance of the HCl EC cells	82
Leak test.....	83
Modification to Cl operation	84

Analytical characteristics and technical specifications

Analytical characteristics

The following table explains the analytical characteristics:

Analytical characteristic	Comments
Analysis method	Chlorine determination by combustion, HCl detection with EC cell.
Detector	EC cell
Sample weight/sample volume	Approx. <1 to 30 mg (corresp. 1 to 30 µl) depending on the substance. For soil samples the weight can be increased up to 100 mg if required.
Working range (depending on kit and measuring mode)	15 - 70 µg Cl (EC cell 0 - 200 ppm HCl).
Precision / standard deviation	<5% rel., for homogeneous standards
Duration of analysis (depending on element content and sample weight)	approx. 7-10 min
Calibration	Linear and non-linear curve adjustment; total work range.
Data storage and data output	Storage on hard disk or external storage media. LIMS transfer possible. Data output to screen and printer.

Technical specifications

The following table contains the technical specifications of the gas supply:

Reference value	Technical specifications
Supply gases	Synthetic air.
Consumption of supply gases	Per analysis approx. 3.5 litres synthetic air. Due to the high gas consumption, the use of an economic air generator is recommended.

Substance digestion and functional diagram

Introduction

The following section explains:

- Which process occur in the reaction tubes of the furnace.
- How the reaction gas mixture is prepared for adsorption and separation into its constituents.

Processes during substance digestion and preparation of the reaction gas mixture

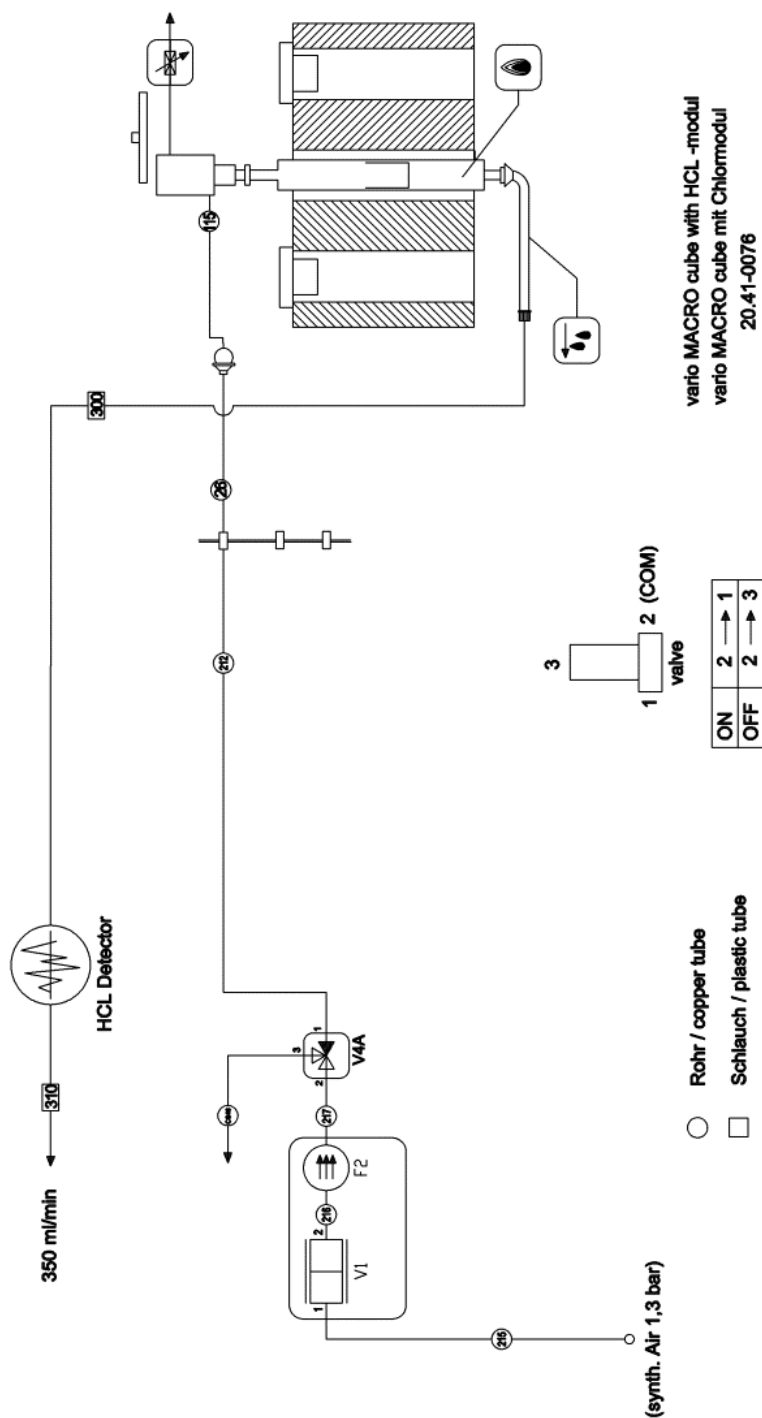
Substance digestion and preparation of the reaction gas mixture is divided into the following phases:

Phase	Process
1	The substance to be analyzed is digested in oxidative atmosphere at a temperature of approx. 1,150 °C by means of combustion.
2	For the digestion weigh in the sample into tin boats (for liquid samples tin capsules are available). The folded boat is thrown into the vertical quartz glass combustion tube by means of an autosampler.

- 3 The chlorine in the sample is quantitatively converted to HCl with hydrogen in the sample **and**, if necessary, with hydrogen in an additive.
- 4 Humidity / water is absorbed by a chemical drying substance (H_2SO_4 on carrier) which is downstream the combustion tube.
- 5 HCl and neutral combustion products (N_2 , CO_2 , etc.) are subsequently transported to the EC cell. The EC cell specifically reacts to HCl, thus, a gas separation is not necessary.

Notes

For a better understanding see also the following illustration (tubing diagram, chlorine determination).



Symbols

The following list names the functional and basic symbols:

	Two-way valve		Pressure sensor		Gas separation
	Three-way valve		Loop		Measuring cell
	Check valve		Heated tube		Sensor
	Throttle		Drying		Hose line
	Flow controller		Combustion		Copper tube
	Flow sensor		Post combustion		Reduction
	Pressure controller		Actuator		

Detection

Introduction

The HCl detection is done by means of an EC cell. The data of the EC cell are as follows:

- 0 - 200 ppm HCl, corresponds 15 to 70 µg Cl. For measurements of chlorine concentrations in the range of approx. 50 ppm up to approx. 4 %.

Note

The EC cell is slightly cross-sensitive to water vapor. Therefore, the measuring gas has to be dried.

A drying tube will be installed behind the combustion tube.

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.



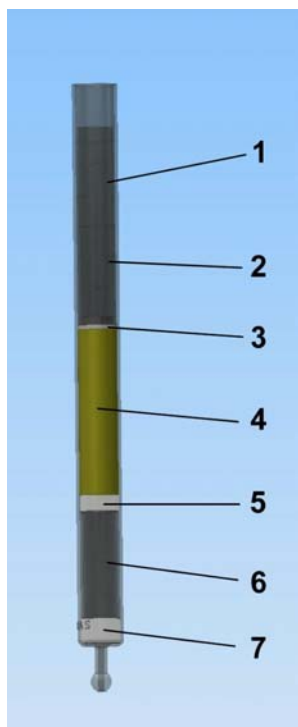
Safety instruction

- Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Filling of the quartz combustion tube for Cl determination

The arrangement of the filling must be carried out as shown in the following illustration.

The ash crucible in the inner part of the tube takes up the solid combustion residues (in particular ash and tin oxide) from the tin boat.



Legend:

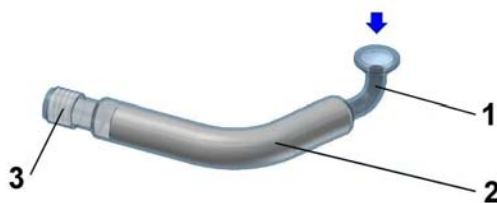
- 1 Sheath tube (empty ash finger, 60 mm)
- 2 Ash finger with bottom of Al_2O_3 wool
- 3 Corundum balls (3 mm)
- 4 WO_3 granulate (100 mm)
- 5 Quartz wool (10 mm)
- 6 Support tube (65 mm)
- 7 Quartz wool (15 mm)

Removal of traces of moisture and other contaminations from the carrier gas

For gas drying insert commercial cleaning cartridges between gas delivery point and instrument, if necessary.

Filling of the drying tube in the furnace area

The following picture shows the fillings of the drying tube:



Legend:

- 1 Quatz wool (in the bend)
- 2 Sicacide
- 3 Quartz wool (20 mm)

Proceed as follows:

- Close one end of the tube (pan side) with quartz wool.
- Fill the tube with Sicacide.
- Close the other end of the tube (thread side) with quartz wool.
- Insert the o-ring in the pan of the drying tube. Make sure the sealing surface is not soiled by quartz wool fibers.

Notes on performing calibration

Background

The calibration serves for creating a correlation between the measured peak area of the individual element and the concentration of the element in the sample.

This correlation is established via the so called calibration coefficients which are calculated from the calibration run.

Calculation of absolute element content

Calibration is performed by analyzing samples with known concentrations (standard samples) where the measured peak areas are correlated with the corresponding absolute element content.

For a standard sample, the following parameters are known:

- Element concentration
- Weight

Absolute element content is computed according to this formula:

$$a = \frac{w \cdot c}{100}$$

where:

a = absolute element content in [mg]

w = sample weight in [mg]

c = element concentration in [%]

Checking the calibration

Prior to the beginning of each series of measurements, it has to be checked if the instrument is calibrated.

Proceed as follows:

- Open the "Calibration coefficients" dialog in the operating software by selecting **Math. > Coefficients**.
- The coefficients dialog allows manual input of the calibration coefficients as well as of the limit values of the corresponding calibration range.

Sample weight/samples for the range of 15 - 70 µg Cl with usage of a oil standard

For this measuring range the following sample sequence is recommended (sample material e.g. oil standard Conostan with 0.5 % Cl):

- 3 Run-in samples with standard à 3 µl (approx. 0.87 mg)
- Standard samples with the following amounts:
3 µl - 3 µl - 3 µl - 3 µl - 5 µl - 5 µl - 7 µl - 7 µl - 10 µl - 10 µl - 15 µl - 15 µl

Note: The liquid standard samples will be filled in tin capsules and weighed in!! The volumetric measurement is not precise enough! Also note that the chlorine determination is not matrix independent. Thus, only standards should be used for the calibration which are similar to real samples.

Sample weight/samples for the range of 15 - 70 µg Cl with usage of a plant standard

For this measuring range the following sample sequence is recommended (sample material e.g. plant standard, BCR No. 100, Beech Leaves, 0.15 % Cl):

- 3 Run-in samples with standard à 30 mg (approx.)
- 3 Run-in samples with standard à 10 mg (approx.)
- Standard samples with the following amounts:
10 mg - 10 mg - 15 mg - 15 mg - 20 mg - 20 mg - 25 mg - 25 mg - 30 mg - 30 mg - 35 mg - 35 mg - 40 mg - 40 mg - 47 mg - 47 mg

Chlorine analyses in routine operation

Sample sequence

In routine operation, the following sample sequence is recommended:

- 3 x conditioning sample (standard, adjusted accordingly)
- 3 x standard for the determination of the daily factor
- 15 - 18 real samples
- 4 x standard for control of the daily factor
- 15 - 18 real samples
- 4 x standard etc.

Note: A sample series should consist of not more than 80 - 90 samples. Afterwards the EC cell should be replaced since otherwise the upper boundary of the measuring range will be decreased and the lower detection limit will be downgraded. See **Notes on sensitivity and measuring range** (on page 80).

The sample weight values can be entered either directly from a connected balance or manually via the keyboard.

Parameter menu settings

The instrument has factory set analysis parameters for test substances defined in the standards menu (e.g. HCl).

Note: The modification of the instrument parameters is only possible with the appropriate access rights.

Temperature parameters

The following table shows the pre-set temperatures and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Oven 1 (combustion tube) in Cl mode	Furnace right, combustion tube Cl	1150 °C

Time parameters

The following table shows the pre-set times and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Flushing time	Time in which the blind hole of the ball valve is flushed, so the atmospheric oxygen will be removed.	10 s
Integrator reset delay peak Cl	This time comes into effect after the sample is fed and prevents the ensuing detector instabilities from being jointly integrated.	2 s

Parameter	Meaning	Factory setting
Integrator reset delay peak Cl	This time comes into effect after the sample is fed and prevents the ensuing detector instabilities from being jointly integrated.	2 s

Further process times and parameters are set via the "Method" dialog:

Parameter	Meaning	Factory setting
Autozero delay Cl	On starting up, the autozero alignment is carried out after the autozero delay.	2 s
Peak Anticipation Cl	The anticiaption time comes into effect after the integrator reset. During this time the integrator waits for a measuring peak. If the measuring peak does not appear within this time, the integration is concluded and the next analysis is started.	300 s

Notes on sensitivity and measuring range

General

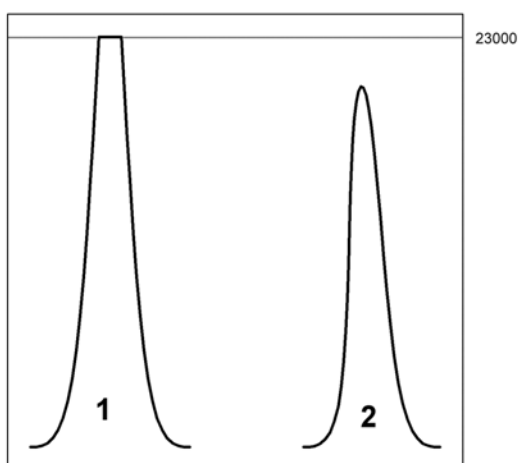
Due to the surface properties of the HCl gas the items described in the following have to be observed.

Peak shape

The maximum signal/noise ratio is achieved if the drying tubes and the ash finger are new or rarely used. Under these circumstances the lower detection limit is at its lowest value; however, due to the higher peak sharpness, the upper measure range limit is decreased.

The upper end of the measure range is at approx. 23000 scale units of the sensitivity scale (see pictures below). If the peak signal exceeds this threshold the upper parts of the peaks are cut off.

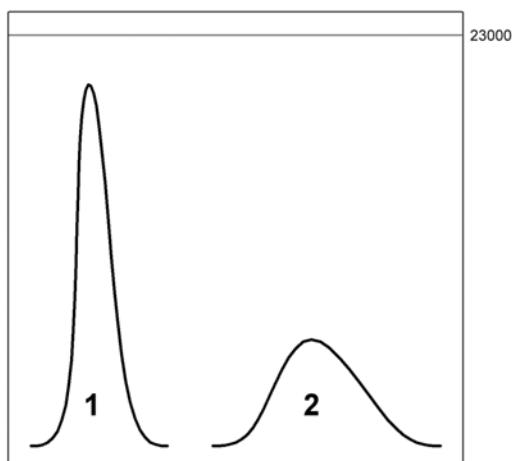
Example for unused components:



Legend:

- 1 Measure range exceeded
- 2 Measure range OK

Difference between new and used components:



Legend:

- 1 Drying/ash finger new
- 2 Drying/ash finger after 100 samples

Used components

Along with the usage of drying agent and ash finger, a gradual flattening of the peaks can be observed. With it and depending on the type of samples (due to anorganic residues) a loss of sensitivity is associated as well. Therefore it is recommended to measure 3 test standards after each 15 - 20 samples in order to correct the sensitivity drift.

The following table shows the relation between "drying agent/ash finger" and "sensitivity/measure range":

Drying tube/ Ash finger	Sensitivity	Upper measure range limit	Daily factor
unused	good	low	approx. 1.00
approx. 100 samples	approx. factor 2-3 worse	approx. factor 2-3 higher	approx. 1.20

Working with 2 EC cells alternately

Since the EC cells have to be regularly regenerated in a moisturized atmosphere (see **Maintenance of the HCl EC cells** (on page 82)) the system is delivered with two similar EC cells.

Due to fabrication tolerances, the sensitivity of both cells is not absolutely identical. However, experiences show that both cells can be operated with the same calibration - the tolerances can be compensated via the corresponding daily factor.

Cross-sensitivity of the EC cells

Background

The EC-cells are cross-sensitive to high concentrations of water vapor and to gases which arise during incomplete combustion (e.g. CO, CH₄ etc.). These gases will superimpose the HCl peak. Empirically, incomplete combustion occurs with organic substances with high sample weights. For samples up to 50 mg this should not occur.

Quantitative conversion from Cl to HCl

Background

To quantitatively convert the chlorine in the sample to HCl, the hydrogen in the samples is insufficient in some cases.

Exception:

- Mineral oils with approx. 15 % H and max. 5 % Cl.
- Organic samples with approx. 7 % H and max. 1-2 % Cl.

Recommendation

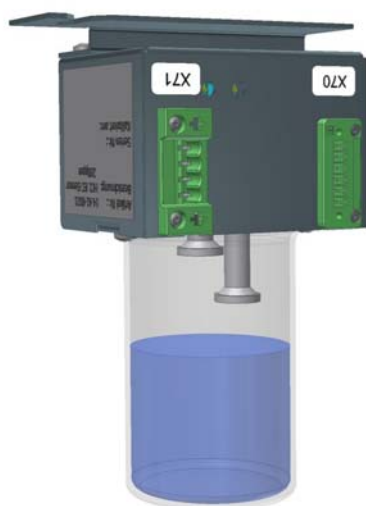
To guarantee the quantitative sample digestion and a quantitative HCl-formation in some cases it is useful to add stearic acid to the samples. The amount of the additive should be in a 1:1 ratio to the sample weight.

This applies particularly for organic compounds which have a disadvantageous H/Cl ratio (e.g. 5 % H, 17 % Cl) and inorganic compounds (e.g. ammonium chloride) as well.

Maintenance of the HCl EC cells

Maximum life time

A maximum of life time can be achieved if the EC cells are operated at an environment with natural humidity (at least 15 %, at most 90 % relative humidity). Since this is not possible during the analysis operation the cells have to be regularly exposed to either the atmospheric humidity or to an artificial moisturized atmosphere for regeneration. For this it is sufficient to store the EC cells with open gas connections (the connected gas hoses have to be removed). Alternatively, the EC cell can be put on a glass beaker (gas connections downwards) which is half-filled with water.



In order to ensure a continuous availability of the analyzer, two identical EC cells are included. Therefore, by turns one cell can be used for the measurement, the other one can be used for regeneration.

The following sequence has been well-proven:

- 1 - 2 days measurement
- 2 - 3 days regeneration

- and so on.

Note: To avoid a drying-out of the EC cells the carrier gas should be cut off after the end of an analysis run by means of the sleep function.

Note

Liquid water must under no circumstances reach the inside of the EC cell! Otherwise the cell would not be damaged, however, the HCl gas to be verified would be dissolved in the water and so a correct measurement would not be possible.

Leak test

Goal of the leak test

The leak test checks the instrument for leaks. Use the flow diagram for the chlorine mode as a help.

Performing a leak test

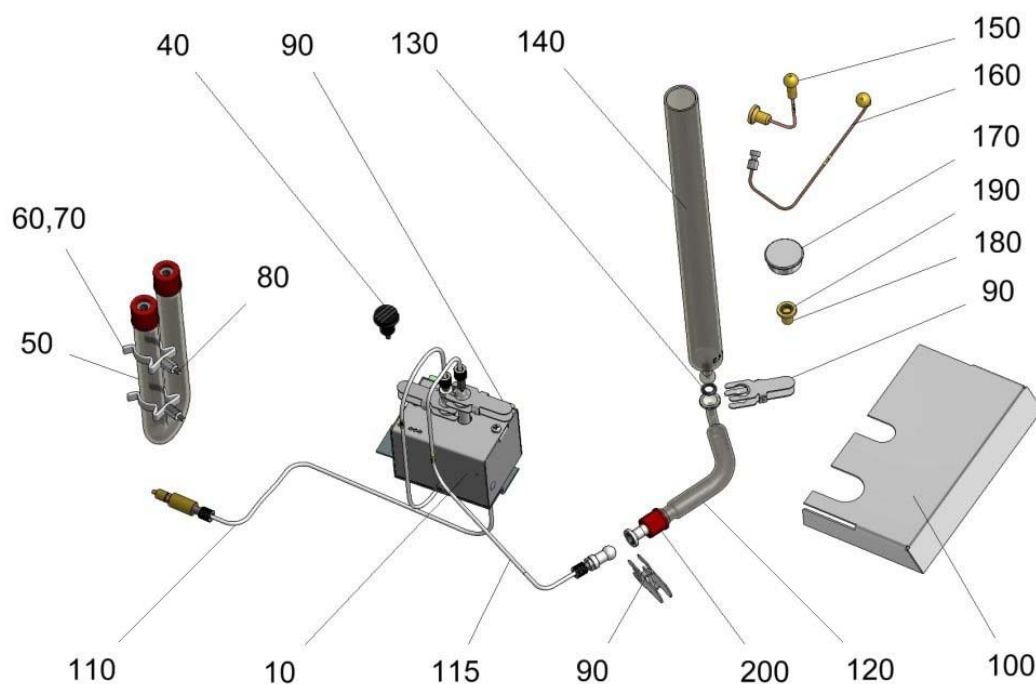
Proceed as follows:

- Shut off the pressure at the pressure reducer.
- Loosen the screw connection (tube 300) at the outlet of the drying tube.
- Close the outlet of the drying tube with the blind cap.
- Set the intake pressure to 1.3 bar at the pressure reducer.
- Observe the flow display of the flow meter.
- If the flow meter display shows a value between 0-3 ml/min during a time of 2 minutes, the instrument is leak free.
- If the flow display shows a value above 3 ml/min within this time, check all connections. Proceed according the principle of the steps previously described.
- After completed leak test, get the instrument back into the original condition of the chlorine mode. Use the flow diagram.

Modification to Cl operation

Scope of the upgrade kit for chlorine detection

All parts necessary for the tube modification are included in the upgrade kit for detecting chlorine and are labeled with numbers.



Legend:

10 CI detector with holding plate	100 Heat protection case	160 Tube no. 115
40 Mushroom-type screw M4x10	110 Tube no. 310	170 Blind plug
50 U tube	115 Tube no. 300	180 Pan, closed
60 Clamp for glass tube	120 Drying tube	190 Quad-ring
70 Screw M 3 x 6	130 O-ring	200 Adapter
80 Spacer bolt	140 Combustion tube	
90 Ground-in clamp	150 Tube no. 304	

Note: Item no. 150 is only required when operated with the VLS.

Phases of modification

The modification is divided into the following phases:

- Switching off the instrument
- Removal of components not needed
- Modifications at the furnace section
- Installing the EC cell and final work
- Gas connection

Phase 1: Switching off the instrument



Safety instruction

Strictly observe the safety instruction "Switching off the instrument" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Turn off the instrument after it has cooled down.
- Disconnect the power supply plug.
- Turn off the gas supply.

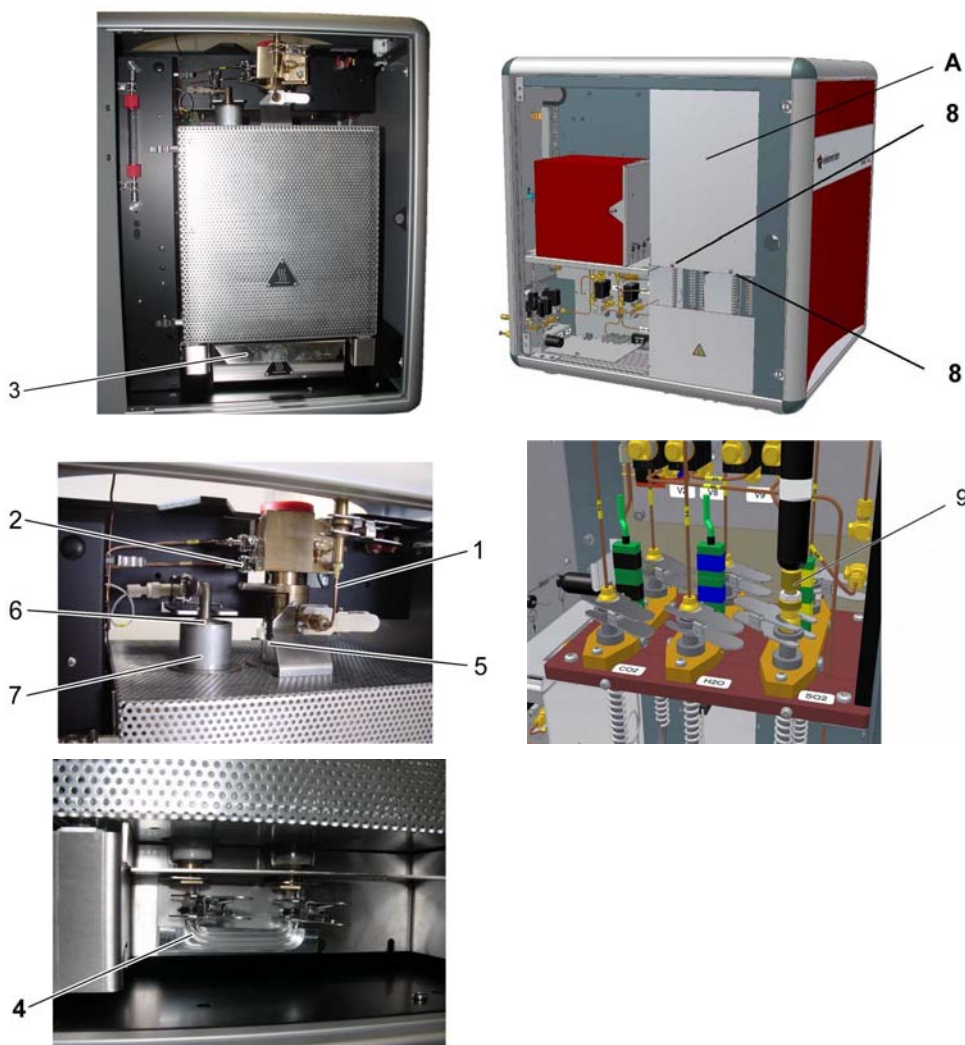
Note

To remove/install the tubes proceed as described in chapter *Removing standard reaction tubes* of the vario MACRO cube main operating instructions.

Phase 2: Removal of components not needed

Before starting the installation of the new components, certain components have to be removed. The removal is described in the following.

Pictures of the parts to be removed:



Legend:**Parts behind the front door**

- 1 Tube no. 27
- 2 Ground-in clamp for tube no. 5
- 3 Heat cover
- 4 Quartz glass bridge with clamps
- 5 Combustion tube with flange
- 6 Reduction tube with plug
- 7 Thermo tube

Parts behind the left side door

- A Fastening screws
- 8 Valve rack cover
- 9 Cable no. 61

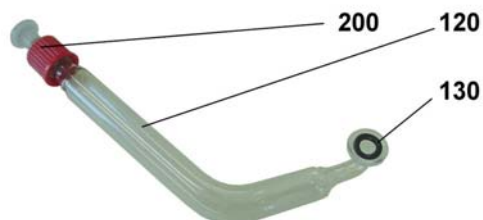
Proceed as follows:

- Open the front door.
- Remove parts 1 - 7.
- Open the left side wall.
- Unscrew the screws (A) of the valve area cover (8).
- Remove the valve area cover after it has cooled down.
- Pull the plug of the valve area cover.
Note: When re-installing the valve area cover has to be inserted again and the plug has to be re-connected.

Phase 3: Modifications at the furnace section

Proceed as follows:

- Insert the o-ring (130) in the pan of the filled absorber tube (120).
 If not done so far screw the adapter (200) onto the absorber tube.



- Insert the combustion tube (140) which is filled and mounted with the combustion tube flange into the right heater of the furnace. Connect the absorber tube pan (120) to the bottom connector of the combustion tube (140) and connect the adapter (200) to the hose line no. 300 (115) by means of ground-in clamps (90).
- Lay the hose line no. 300 as displayed in the pictures below (arrows):



- The free end of hose line no. 300 should be now located in the left area of the instrument.

- As displayed below, mount the seal with connection to the free end of the hose line no. 300 and connect the hose line to the inlet of the EC cell (10).



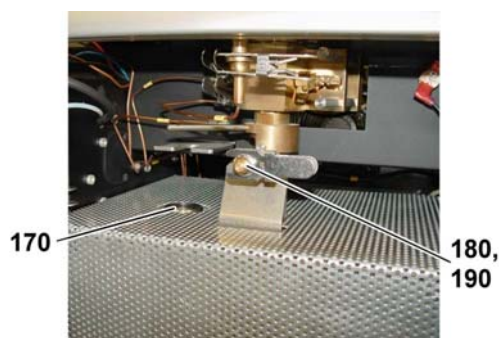
- Shift the heat protection case (100) over the absorber tube.



- Mount the tube no. 115 (160) between the pan (large) of the O₂ supply and the ball connector (small) of the ball valve.



- Push the furnace into the instrument and close the bayonet catch at the ball valve.
- Close the left heater of the furnace by means of the blind plug (170). Insert the quad ring (190) into the blind pan (180) and close the O₂ inlet with the blind pan.



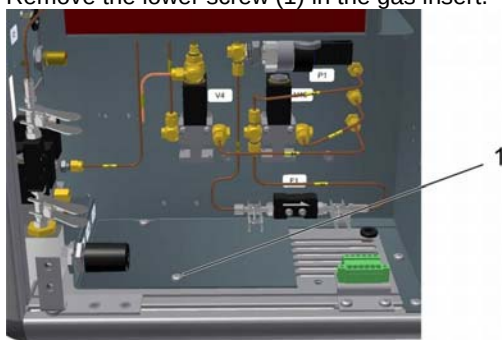
Phase 4: Installing the EC cell and final work

Proceed as follows:

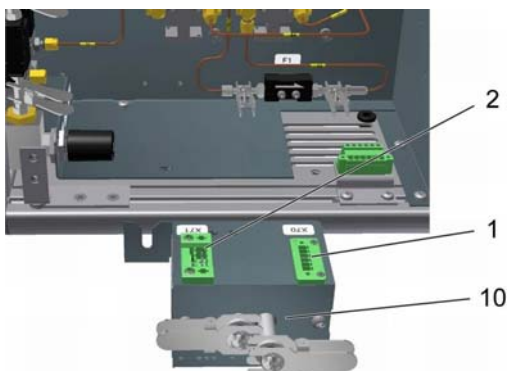
- The supply and signal cables for the HCl sensor are placed in the cable duct as displayed below. Remove the cover from the cable duct and lead cables no. 49 and 114 to the installation site of the HCl sensor.



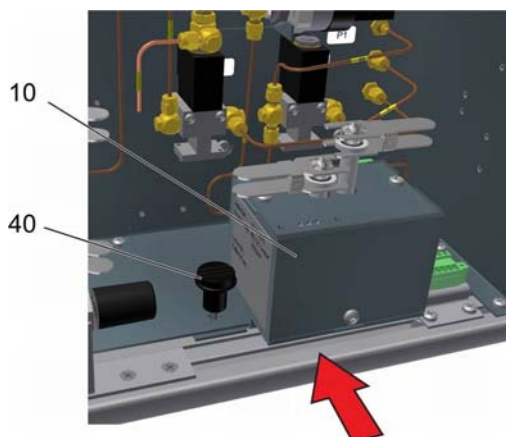
- Put the cover onto the cable duct again.
- Remove the lower screw (1) in the gas insert.



- Put the HCl sensor (10) in front of the gas insert and connect cable no. 49 to plug X 70 (1) and cable no. 114 to plug X 71 (2) of the HCl sensor.



- Push the HCl sensor (10) with its holder under the plate in the gas insert and fasten the HCl sensor by means of the mushroom-type screw (40).



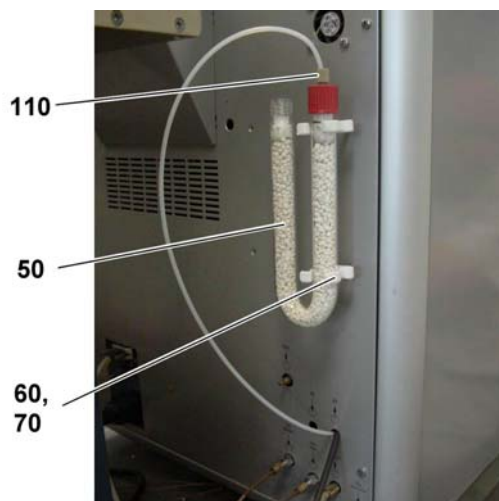
- Connect hose line no. 310 (110) to the outlet of the HCl sensor (10) and hose line no. 300 (115) to the inlet of the HCl sensor by means of ground-in clamps (90). Lead the opposite end of tube no. 310 (110) into the open through a free bore in the rear wall (remove the cover cap, if necessary).



- Connect the free end of tube no. 310 (110) outside the instrument back wall to the delivered waste gas tube (A, hose 5 x 1) and lead it into an exhaust hood.



- In case no exhaust hood is available, remove the adapter (B) and connect the free end of tube no. 310 (110) to the U tube (50) filled with soda lime. The U tube can be attached to the rear wall by means of the clamps and screws (60, 70) (drillings are available).



Note: Replacement interval of the adsorption agent (soda lime): Every 1000 samples. If not done so far, enter the replacement interval in the instrument software.

Phase 5: Gas connection

Proceed as follows:

- If not done so far connect the gas supply line to the delivery point (synthetic air).
- Open the gas supply at the delivery point and set the intake pressure there to 1.3 bar.
- Switch on the instrument.
- Launch the operating software.
- Open the left side wall of the instrument.
- Adjust the gas flow for chlorine determination with the needle valve accessible from the left: Setpoint 350 ml/min (PC display "Flow Air").
- Perform a leak test. The instrument is only ready to measure if the leak test was successful.

The modification is now completed.

CHAPTER 6

The TOC module

Target group

Personnel involved with the instrument.

Purpose

The section shows the construction of the TOC module.

In this chapter

Special features	92
Functional diagram	93
Tube fillings	94
Performing an analysis	96
Modification to TOC operation	97
TOC maintenance work	101

Special features

General

To work smoothly with the solid TOC mode of the vario MACRO cube requires a sound knowledge of the vario MACRO cube main operating instructions.

Reaction tubes

The TOC reaction tubes are placed in the furnace as follows:

- Combustion tube: central
- Post combustion tube: right
- Reduction tube: left

Combustion and post combustion tube will be filled according to the illustration. The filling and materials deviate from the standard filling requirements.

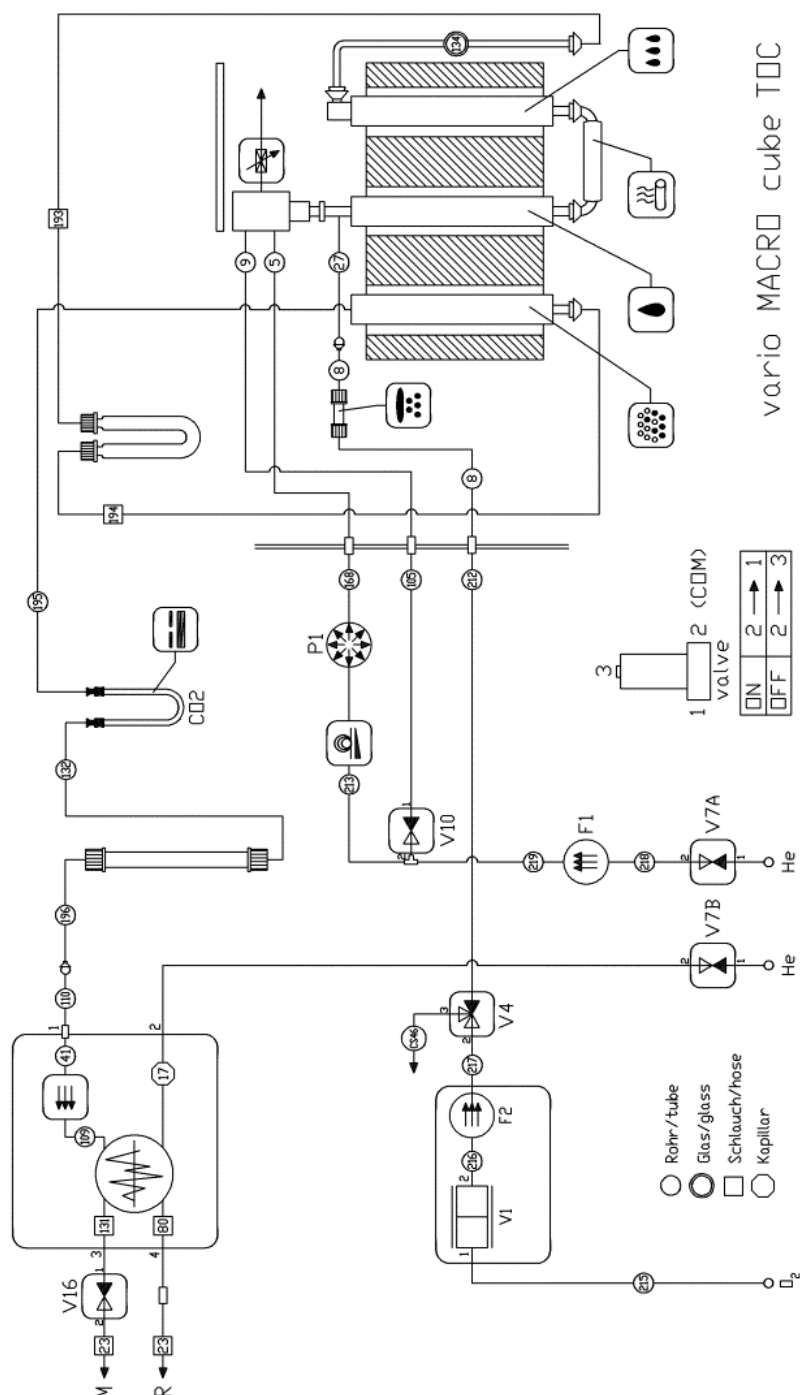
It shall be taken care to use quartz glass tubes. Steel tube would be destroyed due to possible acid residues in the samples.

The reduction tube will be filled like in CHN/CN mode. Please refer to the vario MACRO cube main operating instructions.

Functional diagram

Diagram

The following picture shows the flow diagram for the TOC mode:



Symbols

The following list names the functional and basic symbols:

	Two-way valve		Pressure sensor		Gas separation
	Three-way valve		Loop		Measuring cell
	Check valve		Heated tube		Sensor
	Throttle		Drying		Hose line
	Flow controller		Combustion		Copper tube
	Flow sensor		Post combustion		Reduction
	Pressure controller		Actuator		

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.

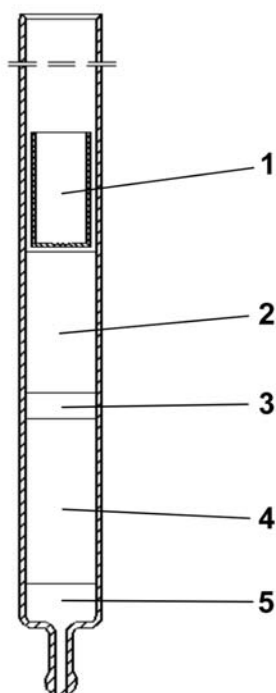


Safety instruction

Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Quartz combustion tube filling

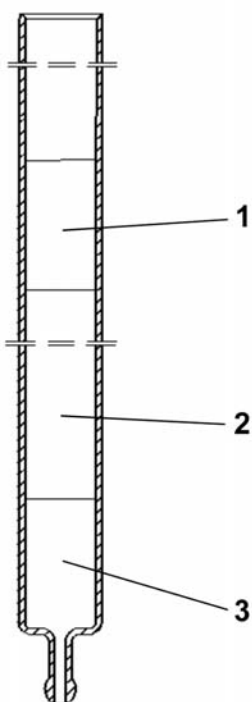
The following picture shows the fillings and filling heights of the combustion tube:

**Legend:**

- 1 Ash crucible, steel, 11.00-1363/4
- 2 Mixture 30 g cerium dioxide + 7 g corundum balls (55 mm)
- 3 Quartz wool (10 mm)
- 4 Corundum balls (65 mm)
- 5 Quartz wool (15 mm)

Quartz post combustion tube filling

The following picture shows the fillings and filling heights of the post combustion tube:

**Legend:**

- 1 Silver wool (50 mm)
- 2 Mixture 100 g copper oxide + 40 g corundum balls (200 mm)
- 3 Quartz wool (50 mm)

Further notes

- Use the furnished connection plugs for the combustion and post combustion tube.

- The filling of the reduction tube persists.
- As an ash container, use a steel crucible which is not identical to the steel crucible of the standard CHN/CN version.
- As oxygen lance, the O₂ lance 140 mm is recommended.
- Due to the high ash accumulation of this method we recommend an ash crucible exchange interval of 25 samples.
- For drying of the measuring gas, a drying tube has to be installed which will be between post combustion and reduction tube.
- Therefore, the installation of an additional module is required.
- Also the large drying tube in the instrument (front) has to be used. It is filled with Sicapent®.

Performing an analysis

Mode

For TOC determination the TOC mode is provided.

In order to activate the TOC mode open the dialog "Analysis mode" in the operating software by selecting **System > Mode** and choose the "TOC" option.

Device parameter

All required instrument parameters are factory set.

For acidified samples it is recommended to work with higher oxygen dosing due to the high amount of packing material.

The oxygen dosing will be defined in the instrument software in the "Methods" dialog via **Options > Settings > Methods**.

Temperature parameters

The following table explains the temperature parameters:

Parameter	Meaning	Factory setting
Furnace 1	Temperature of the combustion tube, furnace center	1,000 °C
Furnace 2	Temperature of the reduction tube, furnace left	830 °C
Furnace 3	Temperature of the post combustion tube, furnace right	900 °C
CO ₂ column	Desorption temperature of the CO ₂ column	240 °C

Preparing samples and performing an analysis

Proceed as follows:

- Punch squares of 40 mm length of cut silver foil into the shape of cylindric container by means of the form punch.
- Weigh approx. 250 mg samples (mineral soil: sample weigh of approx. 500 mg possible) into the beakers of formed silver foil.
- Acidify the sample weighed-in in silver foil with approx. 0.5 ml hydrochloric acid (3%) until no bubble formation is visible.
- Subsequently dry the acidified samples in a drying cabinet at 130 °C for 4 hours.
- For this phase a Teflon tray with recesses was designed where the silver beakers fit it and can be stored.
- After the drying time has elapsed insert the samples into the carousel.

- Enter the sample data (sample name, weight, method etc.) into the corresponding text fields of the instrument software.
- Start the analysis by clicking  (continuous operation) or  (single operation).

Modification to TOC operation

Requirements

Before starting work, the following requirements must be met:

Keep the following ready:

- Modification kit TOC module
- TOC module with tubing
- Tube no. 134, 193, 132, 194, 195, 196
- Leak search set
- Plugs for combustion tubes
- Oxygen lance 140 mm

Process

The modification is divided into the following phases:

- Allow instrument to cool down and disconnect from the mains
- Performing the modification.
- Conditioning new reaction tubes.
- Performing follow-up work and conditioning absorption tubes



Safety instruction

Strictly observe the safety instruction "Switching off the instrument" under **Warning notes during operation** (on page 13).

Phase 1: Allow instrument to cool down and disconnect from the mains

Proceed as follows:

- Open the "Device parameters" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Set the setpoint temperature of the furnaces to 0 °C and confirm by clicking **OK**.
- Wait 2–3 hours until the instrument has cooled down to at least 55 °C.
- Quit the operating software. Execute the following command: **File > Exit**.
- Switch off the analyzer and its peripherals.
- Disconnect the analyzer from the mains. Disconnect the power supply plug.



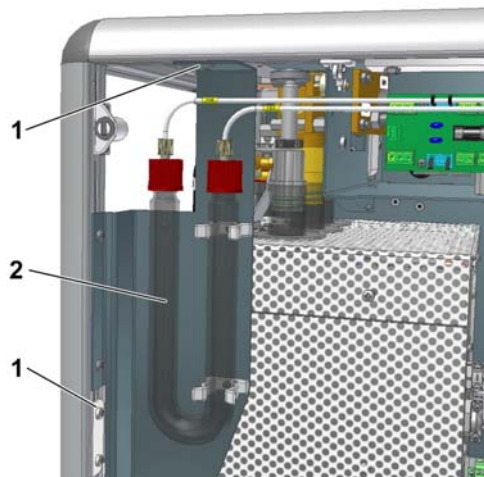
Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Phase 2: Performing the modification

Proceed as follows:

- Open the right side door.
 - Take the TOC (2) module and place it at the left and/or upper rack.
- Lead the groove nuts (1) into the groove of the rack and screw them tightly.



- Open the left side wall.
- Loosen the screws of the valve area cover and remove them.
- Open the front door.
- Loosen the bayonet catch.
- Loosen the ground-in clamp on the reduction tube.
- Dismount tube no. 27 (O₂ supply).
- Pull the furnace out of the instrument.
- Remove the reaction tubes from the instrument.
- If the instrument is currently configured for CHNS or CNS mode you have to modify the heating block with quartz glass bridge.

Install it to the position "combustion, post combustion tube" (right side).

The modification is described in the vario MACRO cube main operating instructions.

- Fill the combustion and post combustion tube as described under **Tube fillings** (on page 94).
- Fill the reduction tube for the CHN/CN mode as described in the vario MACRO cube main operating instructions.
- Install the new reaction tube for the TOC mode.
- If the instrument is currently configured for CHNS or CNS mode you also have to install the downholder for the post combustion tube.

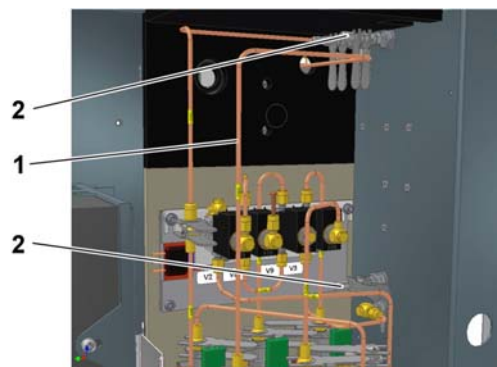
Screw the downholder to the designated position over the post combustion tube

Lead tube no. 134 (2) through the opening (furnace) in front of the post combustion tube. Fasten tube no. 134 at the post combustion tube by means of a ground-in clamp.



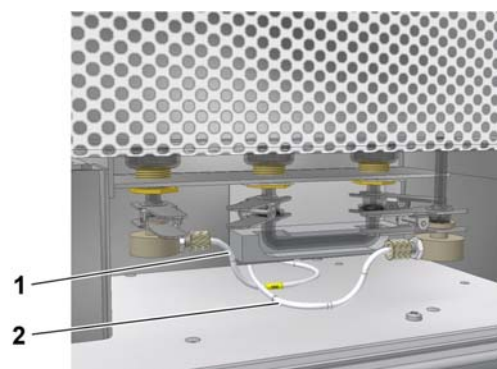
- Replace the tube connected to the reduction tube (outlet) by tube no. 195 (1). Connect it to the reduction tube and to the CO₂ column (front connector) by means of ground-in clamps. For that purpose loosen the existing tube from the CO₂ column and bend it slightly aside.

Close the ends of the upper small drying tube by means of the blind plugs (2).



- Connect tube no. 194 (1) coming from the drying tube of the TOC module to the reduction tube by means of a ground-in clamp.

Connect tube no. 193 (2) coming from the U tube of the TOC module to the glass tube no. 134 by means of a ground-in clamp. Previously, you should mount the connection piece to tube n. 193 if applicable.



- Connect the combustion and post combustion tube by means of the quartz glass bridge. The quartz glass bridge has to be in the heating block.

- Connect the CO₂ column (rear connector) to the large drying tube (bottom) by means of tube no. 132. For that purpose loosen the existing tube from the CO₂ column and bend it slightly aside. Fasten the tube with ground-in clamps.
- Connect the large drying tube (top) to tube no.110 (TCD inlet) by means of tube no. 196. Fasten the tube with ground-in clamps.
- Fill the U tube at the TOC module with Sicapent®. Proceed as described in the vario MACRO cube main operating instructions.
- Fill the large drying tube (front) with Sicapent®. Proceed as described in the vario MACRO cube main operating instructions.
- Close the right side door.
- Screw the valve cover back on.
- Close the left side door.
- Push the furnace back into the instrument.
- Close the bayonet catch at the ball valve.
- Connect tube no. 27.
- Connect tube no. 195 to the reduction tube.
- Fasten the post combustion tube with the downholder.
- Close the front door.



Safety instruction

Strictly observe the safety instruction "Changing mode" under **Warning notes during operation** (on page 13).

Phase 3: Conditioning new reaction tubes

Proceed as follows:

- Make sure the outlet of the last reaction tube is open, so the flush gas can properly flow through the reaction tubes.
- Plug the power supply plug of the analyzer into the socket.
- Turn on PC, monitor and printer and wait until the start process is completed.
- Switch the main instrument switch on. The instrument performs a reference run of the ball valve.
- Launch the operating software.
- Set the carrier gas intake pressure at the delivery point so that He flow at the PC displays approx. 200 ml/min.
- Change the operating mode. See **Performing an analysis** (on page 96).
- Open the "Device parameters" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Check whether the parameter set corresponds to the operating mode. Click **OK** to confirm your settings. The furnaces are heated.
- Flush the instrument with carrier gas during the heating phase.
- After reaching the required temperatures wait for the required conditioning time for the reaction tubes. For TOC mode the conditioning time for the combustion tube and the reduction tube is approx. 1.5 hours.
- Close all open ends of the reaction tubes again.
- Set the carrier gas intake pressure at the delivery point to show approx. 1200 mbar at the PC pressure display.

Phase 4: Performing the necessary follow-up work

Proceed as follows:

- Perform a leak test. If a leak test was passed, the instrument is ready for operation.
- Test the proper operation of the instrument with conditioning samples, blanks and standard samples.

TOC maintenance work

Maintenance work to be performed by the customer

The following maintenance work shall be performed by the user in regular intervals:

- Exchange of the Sicapent® filling and the cotton in the absorption tubes:
 - Open the front door and/or the right side door.
 - Loosen the hose connections and the screw caps.
 - Pull out the absorption tube.
- In addition, the maintenance of the basic instrument remain. Please refer to the vario MACRO cube main operating instructions.

CHAPTER 7

TIC solids module

Target group

Personnel with basic knowledge of chemistry and experience with laboratory work, e.g. chemistry laboratory workers.

Purpose

This chapter is meant to explain working with TIC solids module.

In this chapter

General information	104
Scope of delivery	104
Safety instructions	104
Technical specifications.....	105
Analytical characteristics	106
Functional diagram TIC module.....	107
The components.....	109
Tube fillings	109
Installation and initial start up of the TIC module	111
Selecting the operating mode	114
General measuring principle TIC	114
Analysis run	116
Defining custom standard substances	118
Maintenance work	118

General information

The TIC solids module

The TIC solids module is an auxiliary unit to the vario MACRO cube. The knowledge of the vario MACRO cube operating instructions is also prerequisite for the proper operation of the TIC solids module.

- The TIC module is exclusively suitable for the analysis of the TIC in solid or pasty samples which release CO₂ by adding diluted hydrochlorid acid.
- The analysis of aggressive chemicals or materials which may form gas mixtures of potentially explosive nature by adding acid is strictly prohibited. It may lead to serious damages of the instrument and injuries to the operating personnel.

Difficult applications

For the above mentioned and/or for difficult applications you may use the counseling service of our application lab in order to develop safe working instructions..

Scope of delivery

Scope of delivery

TIC module soliTIC

Additional attachment to vario MACRO cube instrument which allows TIC measurements in solids, suspensions or sludges.

Prod. No. 36.00-0000

You will find further order information for spares or consumables in the annex and in the current consumables catalog.

Safety instructions

General Notes

- The TIC module is exclusively suitable for the analysis of the TIC in solid or pasty samples which release CO₂ by adding diluted hydrochlorid acid.
- The analysis of aggressive chemicals or materials which may form gas mixtures of potentially explosive nature by adding acid is strictly prohibited. It may lead to serious damages of the instrument and injuries to the operating personnel.
- For the above mentioned and/or for difficult applications you may use the counseling service of our application lab in order to develop safe working instructions. and to use special parameters and/or instrument options, if necessary.

Set up / Initial operation

- The initial start-up, operation, maintenance and repairing must only be performed by qualified personnel authorized by Elementar Analysensysteme GmbH.
- The opening of the transport packaging may lead to loss of warranty! If visible damages of the delivered parts can be detected, please immediately inform the forwarder and the contractor.
- The installation site has to be well ventilated. The exhaust line has to be lead into the open and/or extractor hood since during operation toxic gases are formed from the samples and may leave the instrument. During permanent operation the accumulation of the corresponding gases in the air may be over the admissible WEL (=Workplace exposure limit).

- The end of the waste gas lines must discharge into the open at a location protected from the wind as pressure fluctuations, e.g. caused by wind, cause detector instabilities.
- The liquid residues of the TIC determination are partly strongly acidic and must only be lead into the canalization after neutralization. If the analyzed samples contained compounds hazardous to water, the liquid residues have to be disposed duly elsewhere.

Reagents

- Observe the safety instructions of the chemical manufacturer (on the label of the bottle or in the safety data sheet) when handling chemicals.
- Wear protective glasses and the protective gloves when handling Sicapent® (phosphorus pentoxide), NaOH (sodium hydroxide) and $Mg(ClO_4)_2$ (magnesium perchlorate)! **Caution! Danger of chemical burns!!**
- Wear the enclosed protective leather gloves when handling cold quartz and glass parts. **Caution! Risk of injuries due to broken glass!!**

Maintenance / Tube exchange

- The operational reliability of the SoliTIC module can only be guaranteed if original consumables and original spare parts from ELEMENTAR Analysensysteme GmbH will be used. When using other consumables or chemicals of insufficient quality injuries of the operating personnel or damages at the instrument may occur. Unsuitable spare parts lead to warranty loss and may falsify the analysis results.
- All maintenance intervals mentioned in this section are significantly depending on the particular sample matrix. They are only examples and by no means guarantee service life of consumables or wear and tear parts!
- The walls and doors of the instrument may only be opened by authorized personnel for the purpose of maintenance.
- Prior to opening the instrument rear wall all other instruments shall be disconnected from the mains by turning off the main switch and pulling the power supply plug. **Caution! Danger by electric shock - 110-230 Volt!!** Prior to reinitialisation, the casing has to be reinstalled properly (mind the protective conductor).
- Before and after the modification to the solids mode, remove the hydrochloric acid from the container and from the syringe for safety reasons.
- The IR detector and the TIC module must not be put under overpressure at any time. This may lead to damages at the components.

Technical specifications

Standardization

The instrument conforms to CE standards in accordance with EC Directives:

- EMC 89/336/EEC
- LVD 73/23/EEC

Control and data processing

The following table contains the technical specifications of the control and data processing system:

Reference value	Technical specifications
Control and evaluation unit	PC with operating system Windows 2000, Windows XP Professional or Windows 7 Printer (optional)
Software	German or English Menu-driven Status display during analysis Real-time graphics

Interfaces

USB, RS232 /V24, Safety low voltage as per DIN IEC 380/VDE 0806/08.81

Dimensions and weights

The following table contains dimensions and weight of the instrument:

Reference value	Technical specifications
Dimensions	250 mm x 200 mm x 440 mm (Width x Depth x Height)
Weight	approx. 5 kg

Electrical and gas supply

The following table contains the technical specifications of the electrical and gas supply:

Reference value	Technical specifications
Mains voltage	100–230 Volt AC $\pm$ 10 %; 50–60 Hz
Carrier gas	Consumption approx.

Ambient conditions

The following table contains the technical specifications of the ambient conditions:

Reference value	Technical specifications
Protection class	Protection class I, protective conductor connection
Mode of protection	IP20, installation in dry rooms only
Noise level	55 dB (A), as per DIN 45635 section 1
Permissible ambient temperature	Maximum: + 35 °C, minimum: + 15 °C

Analytical characteristics

Analytical characteristics

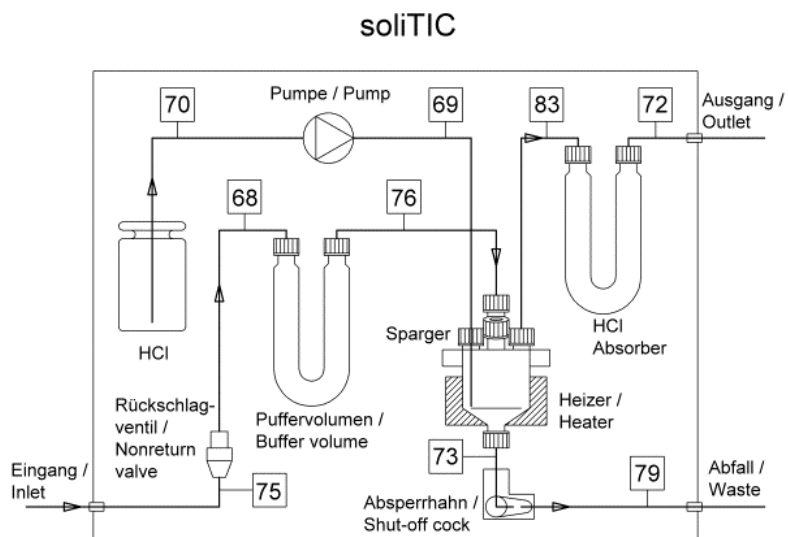
The following table explains the analytical characteristics:

Analytical characteristic	Comments
Operation modes	TIC solids
Working range	TIC
Calibration	linear and/or polynomial
Standard deviation	< 1 % rel. for 6-fold determination
Sample weight	max. 2 g, depending on sample density
Duration of analysis	8 - 15 Min depending from digestion behaviour, sample weight and TIC content of the sample
Sample digestion	Acid at 50 °C
Data storage and data output	Storage on hard disk or external storage media. LIMS transfer possible. Data output to screen and printer.

Functional diagram TIC module

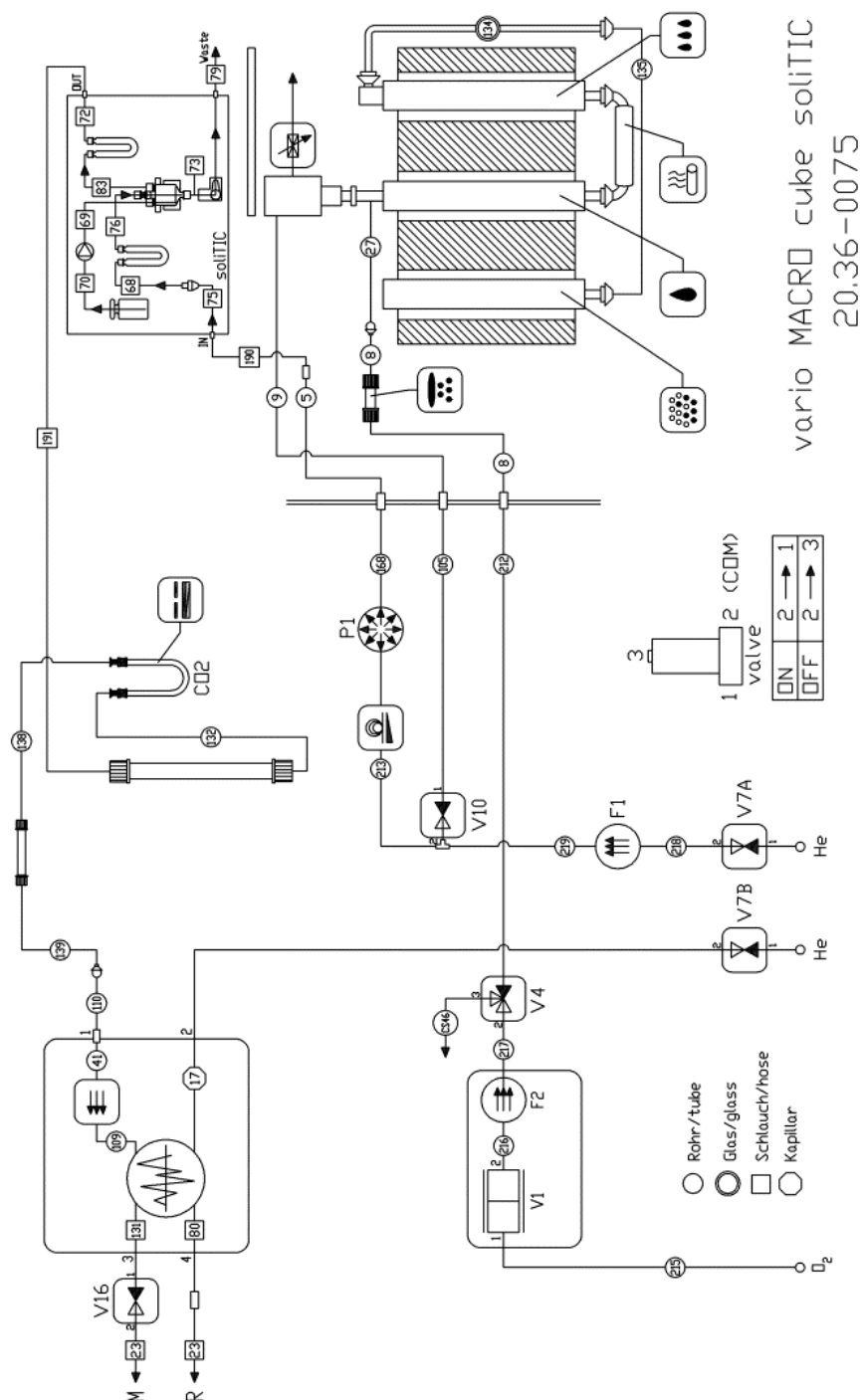
Functional diagram TIC module soliTIC

The following picture shows the functional diagram of the TIC module soliTIC.



Funktional diagram coupling TIC module with vario MACRO cube basic instrument

The following picture shows the coupling of the TIC module (soliTIC) with the vario MACRO cube basic instrument.



Symbols

The following list names the functional and basic symbols:



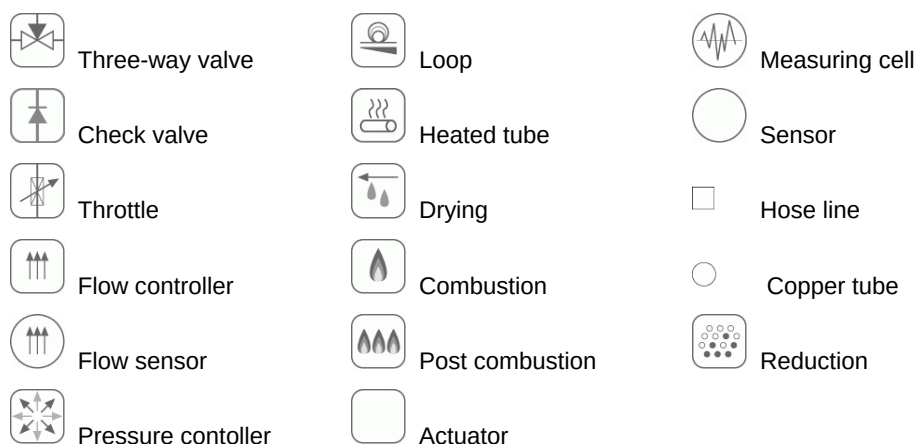
Two-way valve



Pressure sensor



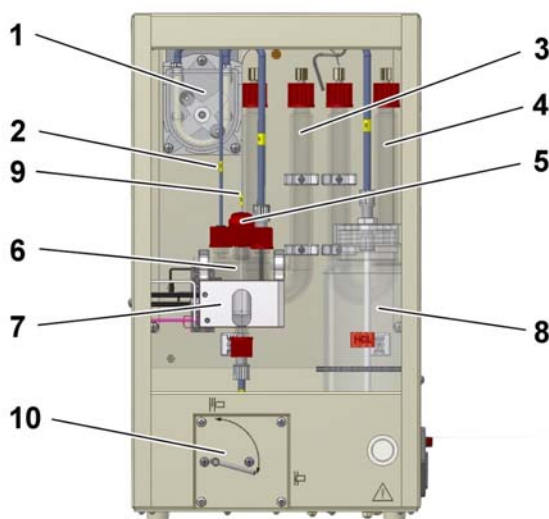
Gas separation



The components

The components

The following picture shows the TIC module in detail:



Legend:

- 1 Acid dosing
- 2 Measuring outlet
- 3 Buffer volume (U-tube)
- 4 HCl absorber (U-tube)
- 5 Sample inlet
- 6 TIC reactor
- 7 Heater
- 8 Acid container
- 9 Gas supply
- 10 Changeover gas/waste

Not visible: H₂O absorber (U tube, attached at the rear wall).

Tube fillings

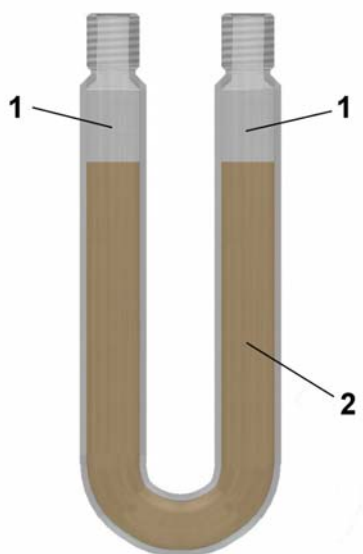
Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.

Filling of the HCl absorber tube

The following picture shows the fillings of the HCl absorber tube:

**Legend:**

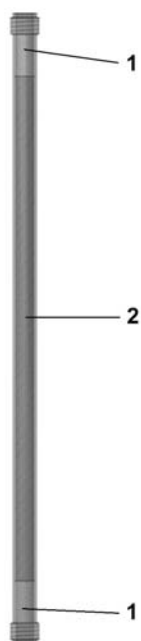
- 1 Silver wool (20 mm)
- 2 Copper

Proceed as follows:

- Fill in copper (2). To do so, tap the tube wall with a piece of wood or cork so as to prevent cavities.
- Close the tube ends with silver wool (1).

Drying tube filling

The following picture shows the fillings of the drying tube:

**Legend:**

- 1 Filter, 03 002 399 (20 mm)
- 2 Sicapent®

Proceed as follows:

- Insert the filter material (1) at one end of the tube.

- Fill in the Sicapent® (2). To do so, tap the tube wall with a piece of wood or cork so as to prevent cavities.
- Close the other tube end with filter material (1).

Installation and initial start up of the TIC module

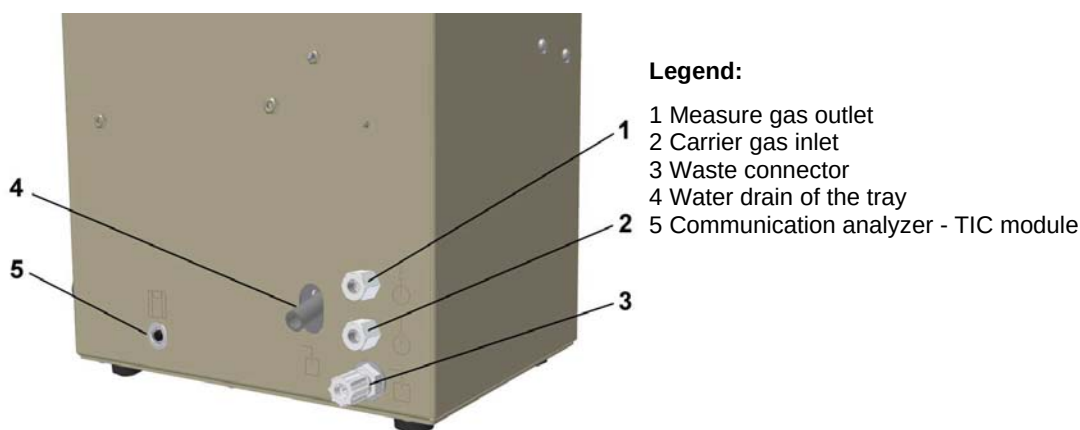
Phases of installation and initial start up

Installation and initial start up of the TIC module is divided into the following phases:

- Preparing the TIC module for the connection to the analyzer.
- Modifications in the analyzer.
- After the modification.

Connections at the rear of the TIC module

The following picture shows the connections of the TIC module:



Phase 1: Preparing the TIC module for the connection to the analyzer.

Proceed as follows:

- Connect the waste connector (3) with the waste gas line and the water drain connector (4) with the waste water line. Observe the proper laying of the waste gas line as described under **Safety instructions** (on page 104).
- Connect the communication cable No. 5 to the plug (5).

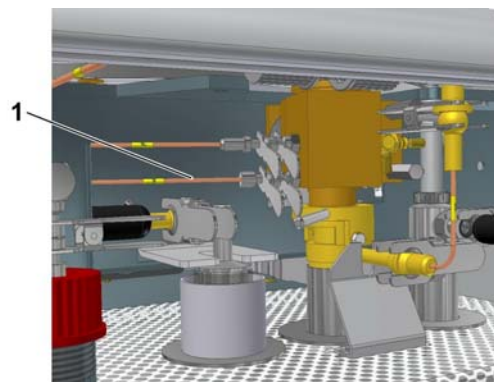
Phase 2: Modifications in the analyzer

It is not necessary to turn off the vario MACRO cube instrument.

Proceed as follows:

- The furnaces will not be used during the TIC operation. Set the furnace temperature via **Options > Settings > Parameter** to 0 °C.
- Shut off the gas supply into the vario MACRO cube instrument (carrier gas and O₂).
- Wait until the system pressure has dropped down to 0 bar.
- Turn on the operation mode "TIC solids" in the software under **System > Mode**.
- Open the front and the left side door.

- Loosen tube no. 5 (1) from the ball valve block and connect tube no. 5 to the hose line no. 190.

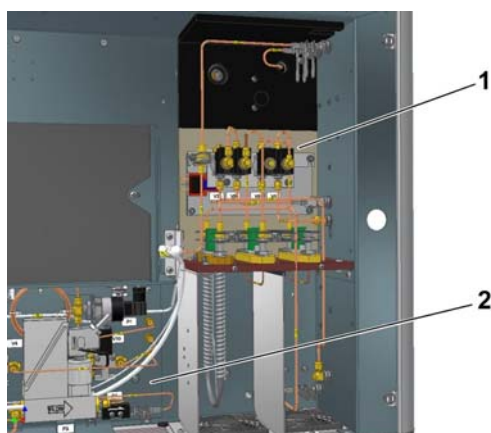


- Also remove the valve rack cover.
- Lead the hose line no. 190 through the valve area and the gas rack to the TIC outlet (2) at the rear wall of the instrument.

Lead the hose line no. 191 from the TIC inlet (1) at the rear wall of the instrument through the gas rack and the valve area to the large drying tube (top).



The following picture shows the valve area (1) and the gas rack (2):



- Connect hose line no. 191 to the large drying tube (top).
- Connect the CO₂ column (rear connector) to the large drying tube by means of tube no. 132.
- Connect the CO₂ column outlet (front connector) to the upper small drying tube (bottom connector) by means of tube no. 138.

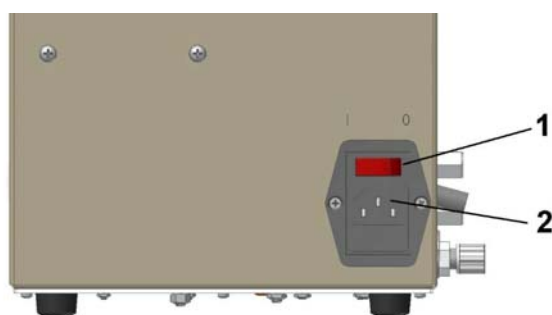
- Connect the upper small drying tube (top connector) to tube no.110 (TCD inlet) by means of tube no. 139.
- Attach the valve rack cover again.
- Close the left side door.
- Now connect both lines which come out from the rear wall of the analyzer to the rear of the TIC module (the designations shown in parentheses refer to the illustration above "Connections at the rear of the TIC module"):
 - Hose line no. 191 to measure gas outlet TIC module (1).
 - Hose line no. 190 to carrier gas inlet TIC module (2).
- Connect the communication cable No. 5 to the "TIC" plug (1) of the analyzer.



Phase 3: After the modification

Proceed as follows:

- Now place the TIC module next to the analyzer, preferably on its left side.
- If not done so far insert the filled U tube into the TIC module. See **Tube fillings** (on page 109) and **The components (TIC module)** (on page 109).
- Fill 4-5% HCl into the acid container in the TIC module. See **The components (TIC module)** (on page 109).
- Open the gas supply at the delivery point.
- Create maintenance intervals for the absorber tube and for the acid container, if necessary. See "Defining maintenance intervals in the software" in the main operating instructions.
- Connect the power supply cable (2) and switch on the instrument. The On/Off switch (1) is located on the right side of the TIC module.



- Decide:
If...
 - ... approximately the same flow and pressure values as prior to maintenance work are displayed: The instrument is ready to measure again.
 - ... distinctly different flow and pressure values to those displayed prior to maintenance work are displayed: Perform a leak test. The instrument is only ready to measure when the leak test is successful.

Selecting the operating mode

Essential condition

Before switching operating modes, you must have performed all refitting work required for the new operating mode.



Safety instruction

Strictly observe the safety instruction "Changing mode" under **Warning notes during operation** (on page 13).

Selecting the operating mode

Proceed as follows:

- Perform all refitting work required for the new operating mode.
- Execute the command **System > Mode** in the instrument software. A message window appears which requests you to confirm the change of the operating mode once more.
- Click **Yes** if you want to continue. The "Analysis mode" dialog is displayed.
- Here, check the option "TIC Solid (with soliTIC module)". Then click **OK**.
- The "Change to new mode" dialog is displayed. If not done so far, follow here the instructions for the modification.
- Click **OK** if you have refitted the instrument. The operating mode is changed.

General measuring principle TIC

General measuring principle TIC

The following steps show the measuring principle:

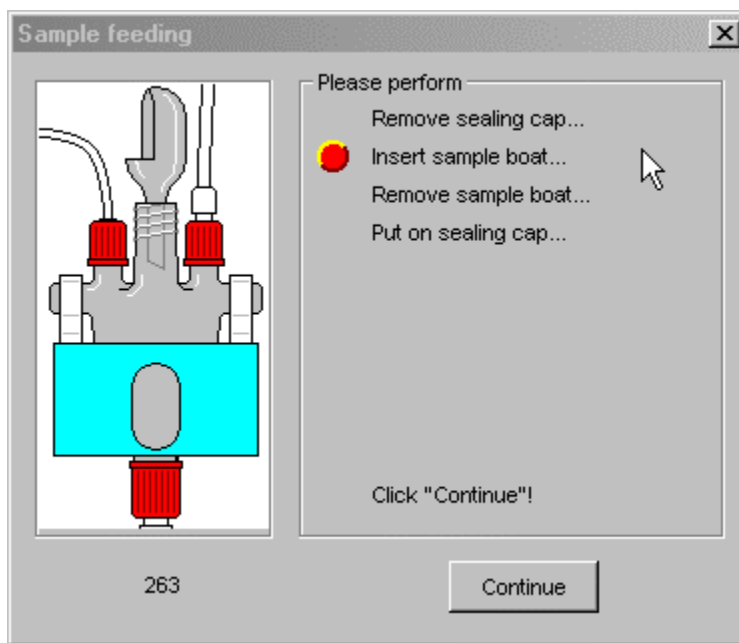
- For the determination of the TIC, the sample to be measured has to be homogenized first and weighed-in into the furnished boat.
- The weight will be entered in the instrument software. The analysis will be started by clicking the **Single** symbol.
- After auto-zero of the detector and after turning off the carrier gas the boats are put on the TIC reactor and the sample is flushed into the reactor by means of little water.
- After confirmation of the feeding hydrochloric acid will be automatically dosed and the carrier gas started. The sample will be heated up to 50°C.
- The carrier gas flows through different drying and absorption steps and will be subsequently analyzed in the detector for CO₂.
- The TIC concentration will be calculated from the integral value of the measurement by means of the calibration coefficient.

- After completion of the analysis the result can be saved.

Analysis steps

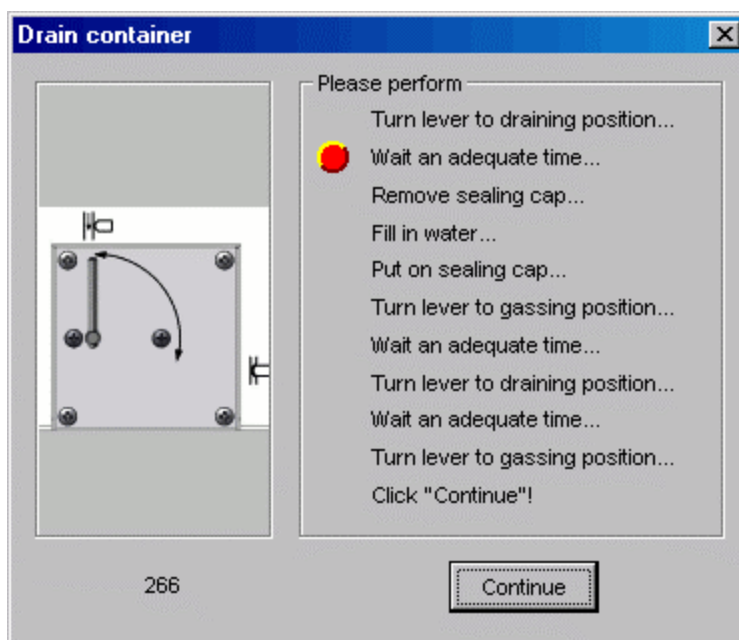
The following pictures show the analysis steps:

- Start of the single measurement
- Inserting the sample



- Drain and flush container. The following steps are to be performed:
 - For draining turn lever upwards and wait for an adequate time.
 - Remove sealing cap.
 - Fill water into the container by means of a wash bottle.
 - Put on the sealing cap again.
 - For gassing turn lever downwards (4 o'clock position) and wait for an adequate time.
 - For draining turn lever upwards and wait for an adequate time.

- For gassing turn lever downwards (4 o'clock position).



Analysis run

Note

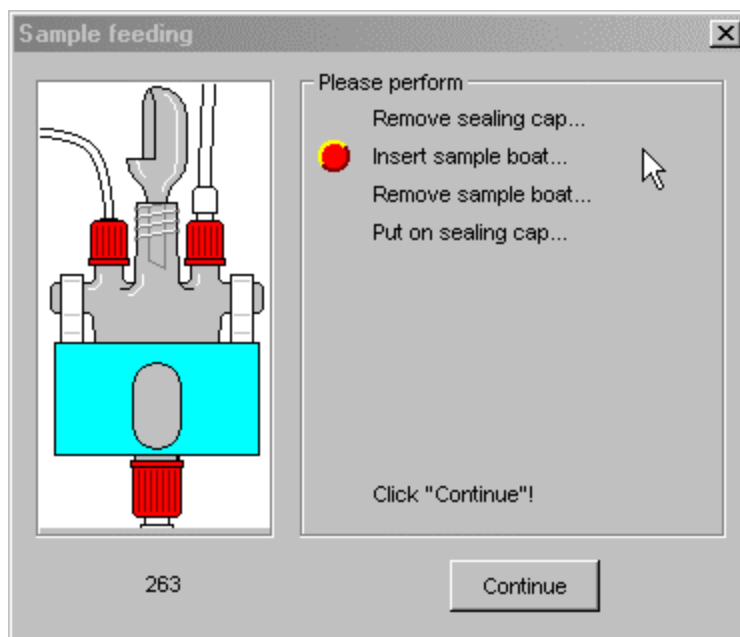
For feeding it is recommended to weigh-in the samples into the furnished boats. It shall be taken care that the TIC reactor of the module is closed.

Performing an analysis

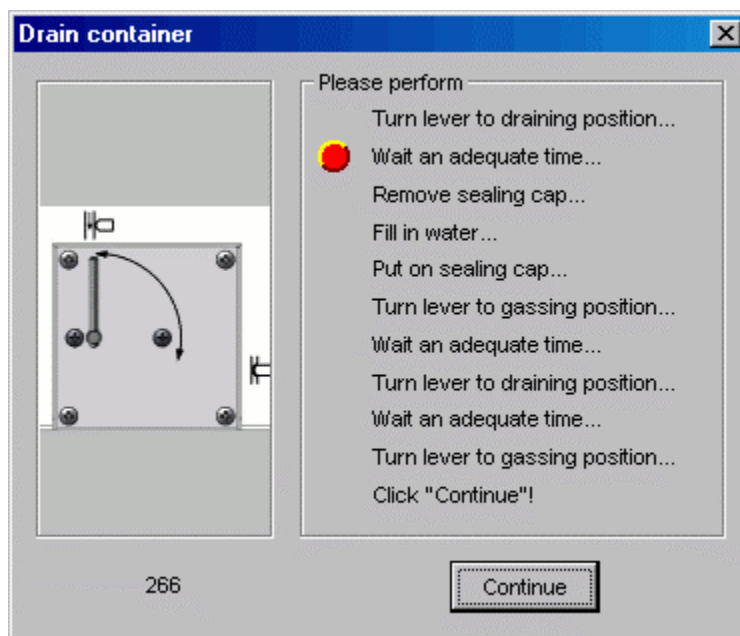
Proceed as follows:

- Enter sample name, sample weight and measuring method into the corresponding text field of the instrument software.
- Start the measuring process by clicking the **Single** start button, .

- After the autozero and baseline recording you will be asked by the dialog to feed the TIC module. The following dialog appears:



- Unscrew the front screwing of the TIC reactor, put on the boat and flush the sample into the reactor with some UP water. After this the reactor has to be closed again.
- Click **Next**. Now the feeding will be displayed in the software. Now the acid is automatically dosed and the carrier gas started.
- After completion of the peak recording the user will be requested to empty the system. The following dialog appears:



- To empty the container turn the lever at the casing front to the vertical position.
- Wait an appropriate time until the container is completely empty.

- To avoid subsequent measurement errors the container must be flushed once again. Unscrew the front screwing of the TIC reactor and fill some UP water into the reactor by means of a wash bottle.
- Close the container with the front screwing again.
- Then turn the lever back to its original position and wait for an adequate time until pressure has built up again in the container.
- To remove the flushing water from the container turn the lever at the casing front to the vertical position again.
- Wait an appropriate time until the container is completely empty.
- Now turn the lever back into the horizontal position. The instrument is ready for the next analysis.

Make sure that air gets into the TIC container during the flushing process. This air produces an "interference peak" in the detector which occurs approx. 2-3 minutes after closing the lever.

Prior to a new analysis start monitor the detector signal in the status display of the PC whether it is stable at zero or near at zero.

Defining custom standard substances

Defining custom standard substances

Proceed as follows:

- Open the "Standard samples" dialog in the operating software by selecting **Options > Settings > Standards**.
- Click **New**. The input boxes on the right area are now empty. Enter the data of the standard sample to be newly defined.
- For the substance, enter...
 - ... the name of the substance in the "name" field.
 - ... the theoretical element content in percent in the "Conc. [%]" fields (or in ppm in the "Conc. [ppm]" fields respectively). If you enter 0 for the theoretical element content of a substance element, the element is ignored in the calculation.
 - ... the permissible tolerance for each element in the "Tolerance [%]" fields (usually 5%).
- Click **Create**. Your new standard sample will now be included in the list in the left area of the dialog.
- You have now defined the standard substance.
- Click **Close** to close the dialog.

Maintenance work

Note

The following maintenance work shall be performed by the user in regular intervals.

Exchange of the peristaltic hose at the hose pump

Proceed as follows:

- Remove the front plate (unscrew retaining bolt).
- Remove the cover of the hose pump.
- Remount the covers again after exchange of the pump hose.

Cleaning of the TIC reactor

Proceed as follows:

- Loosen the screwings at the reactor on top and bottom.
- Remove the reactor from the holding.
- Clean the reactor with diluted HCl (1.6%) and UP water.
- Drying the reactor is not necessary.
- Push the reactor back in.

Renewal of the filling of the HCl absorption tube

The copper filling and the silver wool get black by consumption. Renew the filling of the HCl absorption tube accordingly.

Filling the acid container

Refill the acid container.

Renewal of the drying tube filling in the vario MACRO cube instrument.

The Sicapent® filling gets blue by consumption. Accordingly replace the drying tube filling in the vario MACRO cube instrument.

CHAPTER 8

CHNS determination with the liquid autosampler vario LS

Target group

Personnel involved with the instrument.

Purpose

This chapter describes the special features of the CHNS determination in liquid mode with the liquid sampler vario LS.

Note

The removal of the liquid sampler vario LS is described in detail in the vario LS operating instructions. Read the corresponding sections there.

In this chapter

CHNS determination with vario LS	122
Tube fillings	125
Selecting the operating mode	127
CHNS routine operation	127
Setting device parameters	128
Defining custom standard substances	130
Defining custom methods	131
Modification into CHNS liquid mode	131
Calibration	133
View of the analytical results	135
Check list, prior to the analysis run	136
Shut-down for measuring breaks	136

CHNS determination with vario LS

General

The CHNS analysis process is based on the oxidation digestion method. The CHNS analysis process allows measurements with an injection volume of up to 50 µl.

The measuring principle:

The measuring principle is divided into the following phases:

- The substance to be analyzed will be digested by means of oxidative combustion. The quantitative substance digestion is based on the principle of explosive combustion in oxygen containing helium atmosphere in a combustion tube which is filled with WO_3 at a temperature of approx. 1150°C.
- For the digestion the sample will be injected into quartz wool (approx. 400°C) and quantitatively mobilized so that it will be quantitatively oxidized at the following WO_3 in connection with the added oxygen.
- The oxidized combustion of the elements C, H, N and S produces the combustion products CO_2 , H_2O , NO_2 , SO_2 - except of molecular nitrogen - as well as volatile halogen compounds, if the sample contains halogens.
- A copper contact (reduction tube) daisy-chained reduces the nitric oxides and SO_3 at 850 °C to molecular nitrogen and SO_2 and bounds the excess oxygen. Helium serves as carrier and flush gas.
- After the copper contact the halogen compounds will be chemically bound by means of a suitable absorber (e.g. with silver wool) and thus removed from the gas stream.
- The remaining gas mixture of helium, CO_2 , H_2O , SO_2 and N_2 and components will be subsequently lead into a separation and measuring system.

Measuring start

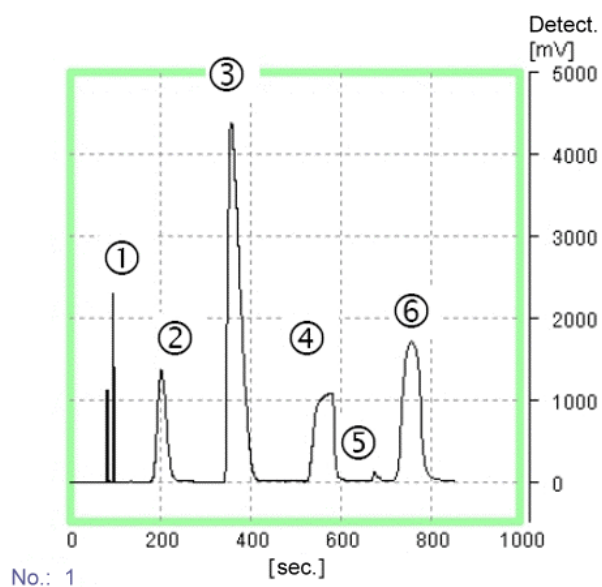
The samples will be filled in 1.5 ml vials with septum screw caps and placed on the tray of the VLS. The sample volume to be injected can be adjusted by selecting the corresponding method.

An analysis will be processed as follows.

- Enter the data of the sample to be analyzed, like "Hole pos", "Name", "Density" and "Method".
- Equip the tray with the vials corresponding to the data input.
- Start the vario MACRO cube by clicking the  "Single" or  "Auto" symbol.
- After completion of the Auto Zero Adjust the VLS gets a start signal and the syringe will be flushed several times with the current sample to be analyzed and filled with the injection volume. Subsequently, the O_2 dosing into the combustion tube starts.
- The VLS gets into the injection position and injects the sample through the septum free injection valve into the combustion tube.

Integration

The following picture shows the integration course:

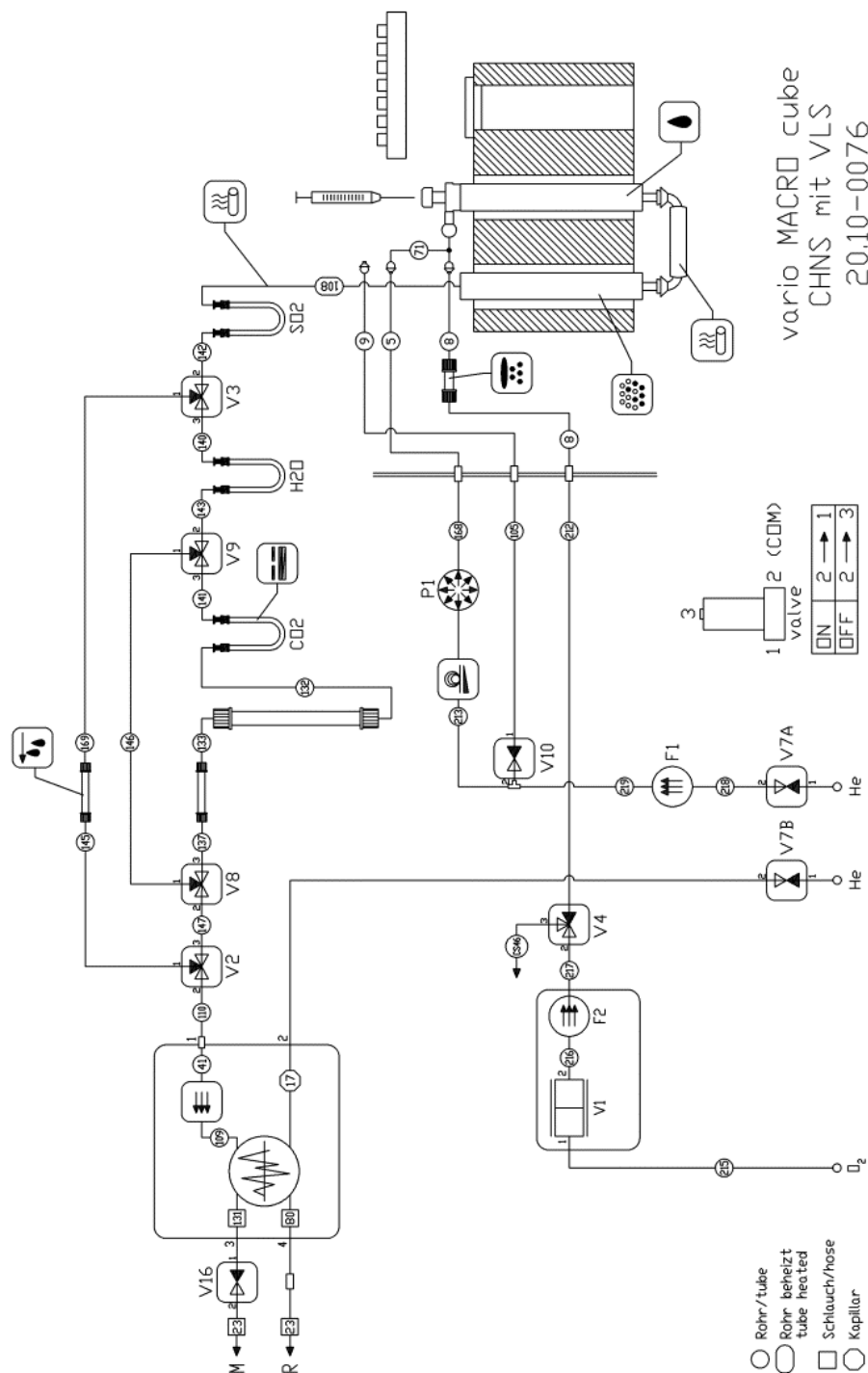


Legend:

- 1 Detector fluctuations during sample feeding, auto zero
- 2 N₂ peak
- 3 CO₂ peak
- 4 H₂ peak
- 5 Foreign gases of the SO₂ column
- 6 SO₂ peak

Functional diagram

The following picture shows the functional diagram of the CHNS mode with VLS.



Symbols

The following list names the functional and basic symbols:



Two-way valve



Pressure sensor



Gas separation

	Three-way valve		Loop		Measuring cell
	Check valve		Heated tube		Sensor
	Throttle		Drying		Hose line
	Flow controller		Combustion		Copper tube
	Flow sensor		Post combustion		Reduction
	Pressure controller		Actuator		

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.

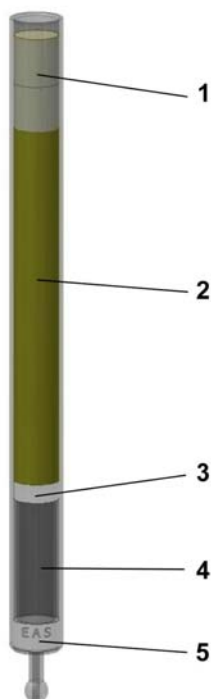


Safety instruction

Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Combustion tube filling

The following picture shows the fillings and filling heights of the combustion tube:

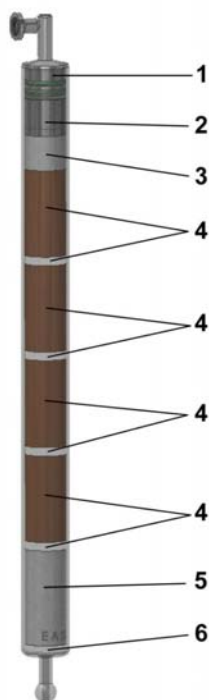


Legend:

- 1 Quartz wool (50 mm)
- 2 Tungsten oxide (WO_3 , 200 mm)
- 3 Quartz wool (10 mm)
- 4 Support tube (65 mm)
- 5 Quartz wool (15 mm)

Reduction tube filling

The following picture shows the fillings and filling heights of the reduction tube:



Legend:

- 1 Plug with o-ring
- 2 Silver wool (25 mm)
- 3 Corundum balls (55 mm)
- 4 Copper (4 x 50 mm, separated by quartz wool)
- 5 Corundum balls (55 mm)
- 6 Quartz wool (5 mm)

Note

All drying tubes will be filled according to the regular CHNS/CNS operation. Please refer to the vario MACRO cube main operating instructions.

Selecting the operating mode

Essential condition

Before switching operating modes, you must have performed all refitting work required for the new operating mode.

The installation of the liquid sampler vario LS is described in detail in the vario LS operating instructions. Read the corresponding sections there.



Safety instruction

Strictly observe the safety instruction "Changing mode" under **Warning notes during operation** (on page 13).

Selecting the operating mode

Proceed as follows:

- Perform all refitting work required for the new operating mode.
- Execute the command **System > Mode** in the instrument software. A message window appears which requests you to confirm the change of the operating mode once more.
- Click **Yes** if you want to continue. The "Analysis mode" dialog is displayed.
- Select the desired analysis mode "CHNS". Select also the feeding mode "VLS". Then click **OK**.
- The "Change to new mode" dialog is displayed. If not done so far, follow here the instructions for the modification.
- Click **OK** if you have refitted the instrument. The operating mode is changed.

CHNS routine operation

Sample sequence

In routine operation, the following sample sequence is recommended:

- 3 x Run-in samples (Hexadecane+Pyridine+Di-Octylsulfide)
- 3 x Factor samples (Hexadecane+Pyridine+Di-Octylsulfide)
- 20 real samples, 3 fold determination
- 3 x Hexadecane+Pyridine+Di-Octylsulfide
- 20 real samples, 3 fold determination
- 3 x Hexadecane+Pyridine+Di-Octylsulfide etc.

Setting device parameters

About instrument parameters

You need to know the following about instrument parameters:

- The instrument parameters listed here are average values.
- The optimized instrument parameters from initial start-up are stored on the enclosed installation CD. The user can optimize them for special applications or extraordinary demands.
- In every operating mode, the instrument parameters required for the analysis process are saved under **Options > Settings > Parameters**.

The "Device parameter" dialog

The dialog shows the device parameters currently set. It is opened via **Options > Settings > Parameters**. The left field of the dialog lists the parameter categories. By clicking the corresponding category the associated parameters will appear in the right area of the dialog.

Temperature parameters

The factory-set temperatures are optimized for best possible sample combustion and separation of the measuring components. The following table shows the pre-set values in section **Temperature** and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Furnace 1	Temperature of the combustion tube, furnace center	1150 °C
Furnace 2	Temperature of the reduction tube, furnace left	850 °C

Time parameters

The factory-set time parameters of the analyzer are selected in order to provide optimum evaluation of the measuring signal under normal application conditions. The following table shows the pre-set values in section **Times** and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
O ₂ delay	Defines the time to wait after loading before beginning O ₂ dosing.	1 s
Maximum O ₂ dosing time	Defines the maximum duration of the O ₂ dosing.	300 s
Integrator reset delay, peak N	Defines the time after which the integrator is reset to zero before beginning actual integration.	1 s
Integrator reset delay, peak C	See description of integrator reset delay, peak N.	1 s
Integrator reset delay, peak H	See description of integrator reset delay, peak N.	5 s
Integrator reset delay, peak S	See description of integrator reset delay, peak N.	1 s

Parameters for the liquid sample feeder

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Add-on volume	Additional sample amount in [µl] which is not injected.	1
Flush intake (G1)	Suction speed during flushing.	30
Flush eject (G2)	Ejection speed during flushing.	120 (100 µl-syringe) 60 (10 µl-syringe)
Prepare intake (G3)	Suction speed during preparation for injection.	3

Prepare eject (G4)	Ejection speed for removal of bubbles.	120 (100 µl-syringe) 60 (10 µl-syringe)
Dose intake (G5)	Suction speed of the actual sample.	3
Dose eject (G6)	Injection speed into the furnace.	120 (100 µl-syringe) 60 (10 µl-syringe)
Num. of prep. cycles	Number of preparation cycles.	2
Number Flushing procedure	Number of flushing processes with the new sample.	3
Motor current	Maximum motor current for torque limitation.	60

Explanations regarding the syringe parameters:

- The syringe volume in the info header corresponds to the syringe size. Selecting or setting of the syringe volume will be performed under **System > Feeding**.
- The syringe parameters are individually saved for each syringe size.
- The add-on volume can be = 0 for most cases, required for certain applications.
- The sample volume injected into the furnace can be set under **Options > Settings > Methods**
- Also the syringe parameters can be individually defined for each method.

Flows

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Flow helium	Carrier gas flow in [ml/min].	600

Integration time

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Max. integration time	Defines the maximum duration of the peak integration.	600 s

Limit temperatures

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Limit temp. Comb. tube	If the combustion tube temperature exceeds this value a safety shutdown of the combustion unit will be performed.	1,200 °C
Reduction tube	See Comb. tube	1,200 °C
CO ₂ column	See Comb. tube	300 °C
H ₂ O column	See Comb. tube	300 °C
SO ₂ column	See Comb. tube	300 °C

Peak recognition TCD baseline

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
Number of measuring values per mean value group	20
Number of successful mean value groups	3
Number of unsuccessful mean value groups	10
Baseline constant	3

Baseline factor in ‰	10
admissible baseline difference	15

Peak Recognition TCD Peak End

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
Peak max. limit sens./insens.	1500
Peak insens. End threshold	800
Peak sens. end constant	800
Activate Relative Peak End	no
Peak relative end threshold	800

Peak recognition TCD amplification

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
TCD amplification level	2
TCD amplification level N	4
TCD amplification level dummy	1

Defining custom standard substances

Defining custom standard substances

Proceed as follows:

- Open the "Standard samples" dialog in the operating software by selecting **Options > Settings > Standards**.
- Click **New**. The input boxes on the right area are now empty. Enter the data of the standard sample to be newly defined.
- For the substance, enter...
 - ... the name of the substance in the "name" field.
 - ... the theoretical element content in percent in the "Conc. [%]" fields (or in ppm in the "Conc. [ppm]" fields respectively). If you enter 0 for the theoretical element content of a substance element, the element is ignored in the calculation.
 - ... the permissible tolerance for each element in the "Tolerance [%]" fields (usually 5%).
- Click **Create**. Your new standard sample will now be included in the list in the left area of the dialog.
- You have now defined the standard substance.
- Click **Close** to close the dialog.

Defining custom methods

View and define methods

In the "Methods" dialog you can view existing methods or define new methods.

View existing methods

Proceed as follows:

- Open the "Methods" dialog in the operating software by selecting **Options > Settings > Methods**.
- In the left field, select the appropriate method. In the fields at the right side the parameters of the selected method are now displayed.
- Click **Close** to close the dialog again.

Defining custom methods

Proceed as follows:

- Open the "Methods" dialog in the operating software by selecting **Options > Settings > Methods**.
- Click **New**. The input boxes on the right of the dialog are now empty. Enter the parameters of the method to be newly defined:
- Enter the following:
 - Enter the name of your method in the "ID" field.
 - Enter the purpose of the method, for example, in the "Description" field.
 - Input the corresponding method parameters in the other boxes.
- Click **Create**. Your new method will now be included in the list in the left area of the dialog. You have now defined the method.
- Click **Close** to close the dialog.

Modification into CHNS liquid mode

Modification of the basic instrument

For modifying the basic instrument the following steps shall be completed one after the other.

Basic is the CHNS mode.

Requirements

Before starting work, the following requirements must be met:

Keep the following ready:

- Installing the vario LS autosampler + accessories.

Process

The section is divided into the following phases:

- Switching off the instrument.
- Installing the vario LS autosampler.
- Modifying the furnace part.
- Conditioning new reaction tubes.

- Performing follow-up work.

Phase 1: Switching off the instrument



Safety instruction

Strictly observe the safety instruction "Switching off the instrument" under **Warning notes during operation** (on page 13).

Phase 2: Installing the vario LS autosampler

Proceed as follows:

- Mount the liquid sample onto the vario MACRO cube according to the operating instructions of the vario LS.
- Connect tube no. 5 and tube no. 8 with the furnished tube no. 71.
- Connect tube no. 71 to the combustion tube connector.
- Close tube no. 9 with a blind plug.

Phase 3: Modifying the furnace part



Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Open the front door.
- Pull the furnace out of the instrument. Loosen the screw at the guiding of the combustion tube and push the bolt to the right.
- Fill the combustion and reduction tube for the CHNS mode in liquid operation.
- Fill the absorption tube for the CHNS mode.
- Remove the old combustion and reduction tube, if necessary.
- Install the new combustion and reduction tube, if necessary. Leave the outlet of the reduction tube open for a later conditioning.
- Place the combustion tube plug with septum onto the combustion tube.
- Push the furnace back into the instrument.
- Push the bolt to the left and tighten the screw at the guiding of the combustion tube.
- Connect tube no. 71 to the combustion tube connection.
- Connect the combustion and post combustion tube by means of the quartz glass bridge.
- Close the front door.

Phase 4: Conditioning new reaction tubes



Safety instruction

Strictly observe the safety instruction "Installing and conditioning the reaction tubes" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Plug the power supply plug of the analyzer into the socket.
- Turn on PC, monitor and printer and wait until the start process is completed.
- Switch the main instrument switch on.
- The instrument performs a reference run of the VLS.
- Launch the operating software.
- Set the intake pressure at the delivery point so that He flow at the PC displays approx. 200 ml/min.
- Change the operating mode.
- Open the "Instrument parameters" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Check whether the parameter set corresponds to the operating mode. Click **OK** to confirm your settings. The furnaces are heated.
- Flush the instrument with helium during the heating phase.
- After reaching the required temperatures wait for the required conditioning time for the reaction tubes. For CHNS mode the conditioning time for the combustion tube and the reduction tube is 1.5 hours.
- Close all open ends of the reaction tubes again.
- Set the Helium intake pressure at the delivery point to show approx. 1200 mbar at the PC pressure display.

Phase 5: Performing follow-up work

Proceed as follows:

- Perform a leak test. If a leak test was passed, the instrument is ready for operation.
- Test the proper operation of the instrument with conditioning samples, blanks and standard samples.

Calibration

General

The vario MACRO cube has a calibrated set of coefficients which can be used. This is already calibrated in solids mode or may be generated here. If a different procedure is requested, Elementar suggests the following calibration for CHNS in liquid operation.

Please make sure to have the necessary standards available prior to the calibration.

The elemental analyzer vario MACRO cube + vario LS is no absolute measuring instrument. Therefore, the correlation between CHNS content and CHNS measuring values [Integrals] has to be obtained by means of a calibration. Factory set test substances with a known CHNS content and different sample weights will be analyzed.

Note:

The density of a sample has to be known in order to obtain a calibration in mg absolute vs. the peak area.

The software automatically calculates the calibration functions (four polynomes 4th order).

A proper calibration in the selected operation mode which includes the required working range for each element, is vital for the accuracy of the results. Calibrations therefore have to be performed with special diligence.

The knowledge of the vario MACRO cube operating instructions and the technical possibilities of the instrument are prerequisite for a successful calibration.

Experience has shown that the calibration of the vario MACRO cube elemental analyzer remains stable for at least 6 months. Recalibration is recommended if the daily correction factor lies outside a range of 0.9 - 1.1 or if components which may influence the results have been exchanged (e.g. detector).

Prior to a calibration series, the filling of the combustion and reduction tube have to be renewed and the instruments has to be checked for leaks.

Recommended calibration

For CHNS the following is recommended:

- Mixture of Hexadecane, Pyridine and Di-Octysulfide.
 - Hexadecane:
d = 0.773 mg/μl; 84.87 % C; 15.13 % H
 - Pyridine:
d = 0.978 mg/μl; 17.71 % N; 75.92 % C; 6.37 % H
 - Di-Octysulfide:
d = 0.842 mg/μl; 74.34 % C; 13.26 % H; 12.40 % S
- For a calibration range of fill exactly the following amounts into a 100 ml volumetric flask:
 - 84.0 ml Hexadecane
 - 8.0 ml Pyridine
 - 8.0 ml Di-Octysulfide

The data for the standard solution are as follows:

d = 0.79492 mg/μl; 83.098 % C, 14.108 % H, 1.744 % N, 1.050 % S.

These data have to be saved under **Options > Settings > Standards**.

By weighing-in the different substances in a 100 ml volumetric flask a better accuracy of the percentage can be reached. (Temperature dependency of the density etc.).

Numerical example

In the following a numerical example is given which should clarify the data of the standard solution mentioned above.

Calculation of the weights from the individual volumes:

Volumetric flask (empty):	79.945 g		
+ 84 ml Hexadecane:	144.877 g	= net:	64.932 g
+ 8 ml Pyridine:	152.701 g	= net:	7.824 g
+ 8 ml Di-Octysulfide:	159.437 g	= net:	6.736 g
Σ = 100 ml mixture		Σ	79.492 g

Calculation of absolute element contents:

64.932 g Hexadecane	=	55.108 g C	+	9.824 g H	
7.824 g Pyridine	=	5.940 g C	+	0.498 g H	+ 1.385 g N
6.736 g Di-Octylsulfide	=	5.008 g C	+	0.893 g H	+ 0.835 g S
79.492 g mixture		66.056 g C		11.215 g H	1.385 g N 0.835 g S

Calculating the percentages of the test substance (mixture):

$$\% \text{ C} = \frac{66.056 \text{ g C} \cdot 100}{79.492 \text{ g}} = 83.098 \%$$

$$\begin{array}{rcl}
 & 79.492 \text{ g} & \\
 \% \text{ H} = & \frac{11.215 \text{ g H} \cdot 100}{79.492 \text{ g}} & = 14,108 \% \\
 \\
 \% \text{ N} = & \frac{1.385 \text{ g N} \cdot 100}{79.492 \text{ g}} & = 1,742 \% \\
 \\
 \% \text{ S} = & \frac{0.835 \text{ g S} \cdot 100}{79.492 \text{ g}} & = 1,050 \% \\
 \\
 & \Sigma & = 100 \%
 \end{array}$$

Calculating the density of the test substance:

$$\text{Density} = \frac{79.492 \text{ g}}{100 \text{ ml}} = 0.79492 \text{ g/ml}$$

The following sample series is recommended:

- 4-fold (6-fold) determination of "Run-in" samples, Hexadecane + Di Octysulfide + Pyridine, sample volume μl
- 4-fold (6-fold) determination of "Run-in" samples, Hexadecane + Di Octysulfide + Pyridine, sample volume μl

View of the analytical results

Display

The analytical results will be displayed in two different ways:

- Real calculation of the measured integral values, determined from N%, C%, H% and S%.
- Analysis results from the sum of N% + C% + H% + S% = 100% standardized will be displayed as N%_{norm}, C%_{norm}, H%_{norm}, S%_{norm}.
The advantage of this method is that the analytical results are correct, even if the density is unknown or dosing of the sample was not correct (inclusions of air in the syringe, samples with low boiling point).

The mathematical procedure is as follows:

$$F = (N\% + C\% + H\% + S\%) / 100$$

$$N\%_{\text{norm}} = N\% \cdot F$$

$$C\%_{\text{norm}} = C\% \cdot F$$

$$H\%_{\text{norm}} = H\% \cdot F$$

$$S\%_{\text{norm}} = S\% \cdot F$$

Note

The standardized calculation assumes that the samples only contain C, H, N and S. The calculation is incorrect, if the samples contain O in addition. However, traces of that component in the range of some ppm do not have any influence.

Check list, prior to the analysis run

Prior to the analysis run

Prior to starting an analysis run, the following points shall be completed:

- Maintenance intervals observed?
- Operation mode set?
- Gas on?
- Pressure on?
- Lecktest passed?
- Absorption tube filled and installed?
- Detector signal stable?
- Sample name, method and standard samples edited and assigned?

Shut-down for measuring breaks

Maintenance work to be performed by the customer

The following maintenance work shall be performed by the user in regular intervals:

- Exchange of the Sicapent® and the cotton in the absorption tubes.
- Exchange of the septum for injection.
- Exchange of the combustion tubes.

In addition, the maintenance of the basic instrument remain. Please refer to the vario MACRO cube main operating instructions.

Note

We recommend to determine the maintenance intervals via **Options > Maintenance > Intervals** in the instrument software in order not to forget any maintenance work

CHAPTER 9

CHN determination with the liquid autosampler vario LS

Target group

Personnel involved with the instrument.

Purpose

This chapter describes the special features of the CHN determination in liquid mode with the liquid sampler vario LS.

Note

The removal of the liquid sampler vario LS is described in detail in the vario LS operating instructions. Read the corresponding sections there.

In this chapter

CHN determination with vario LS.....	138
Tube fillings	141
Selecting the operating mode.....	143
CHN routine operation.....	143
Setting device parameters.....	144
Defining custom standard substances.....	146
Defining custom methods	146
Modification into CHN liquid mode.....	147
Calibration	149
View of the analytical results	151
Check list, prior to the analysis run.....	151
Shut-down for measuring breaks.....	152

CHN determination with vario LS

General

The CHN analysis process is based on the oxidation digestion method. The CHN analysis process allows measurements with an injection volume of up to 50 µl.

The measuring principle:

The measuring principle is divided into the following phases:

- The substance to be analyzed will be digested by means of oxidative combustion. The quantitative substance digestion is based on the principle of explosive combustion in oxygen containing helium atmosphere in a combustion tube which is filled with CuO in the lower range and with silver wool at a temperature of approx. 950°C.
- For the digestion the sample will be injected into quartz wool (approx. 400°C) and quantitatively mobilized so that it will be quantitatively oxidized at the following CuO in connection with the added oxygen.
- The oxidized combustion of the elements C, H and N produces the combustion products CO₂, H₂O, NO, NO₂, SO₂ - except of molecular nitrogen - as well as volatile halogen compounds, if the sample contains sulfur and halogens.
- SO₂ and SO₃ are actively absorbed at silver wool.
- A copper contact (reduction tube), daisy-chained, reduces the nitric oxides at 600 °C to molecular nitrogen and bounds the excess oxygen. Helium serves as carrier and flush gas.
- After the copper contact the halogen compounds will be chemically bound by means of a suitable absorber (e.g. with silver wool) and thus removed from the gas stream.
- The remaining gas mixture of helium, CO₂, H₂O and N₂ and components will be subsequently lead into a separation and measuring system.

Measuring start

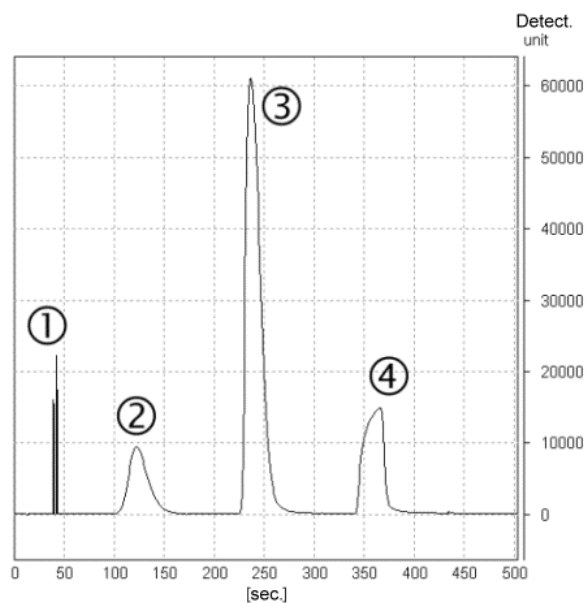
The samples will be filled in 1.5 ml vials with septum screw caps and placed on the tray of the VLS. The sample volume to be injected can be adjusted by selecting the corresponding method.

An analysis will be processed as follows.

- Enter the data of the sample to be analyzed, like "Hole pos", "Name", "Density" and "Method".
- Equip the tray with the vials corresponding to the data input.
- Start the vario MACRO cube by clicking the  "Single" or  "Auto" symbol.
- After completion of the Auto Zero Adjust the VLS gets a start signal and the syringe will be flushed several times with the current sample to be analyzed and filled with the injection volume. Subsequently, the O₂ dosing into the combustion tube starts.
- The VLS gets into the injection position and injects the sample through the septum free injection valve into the combustion tube.

Integration

The following picture shows the integration course:

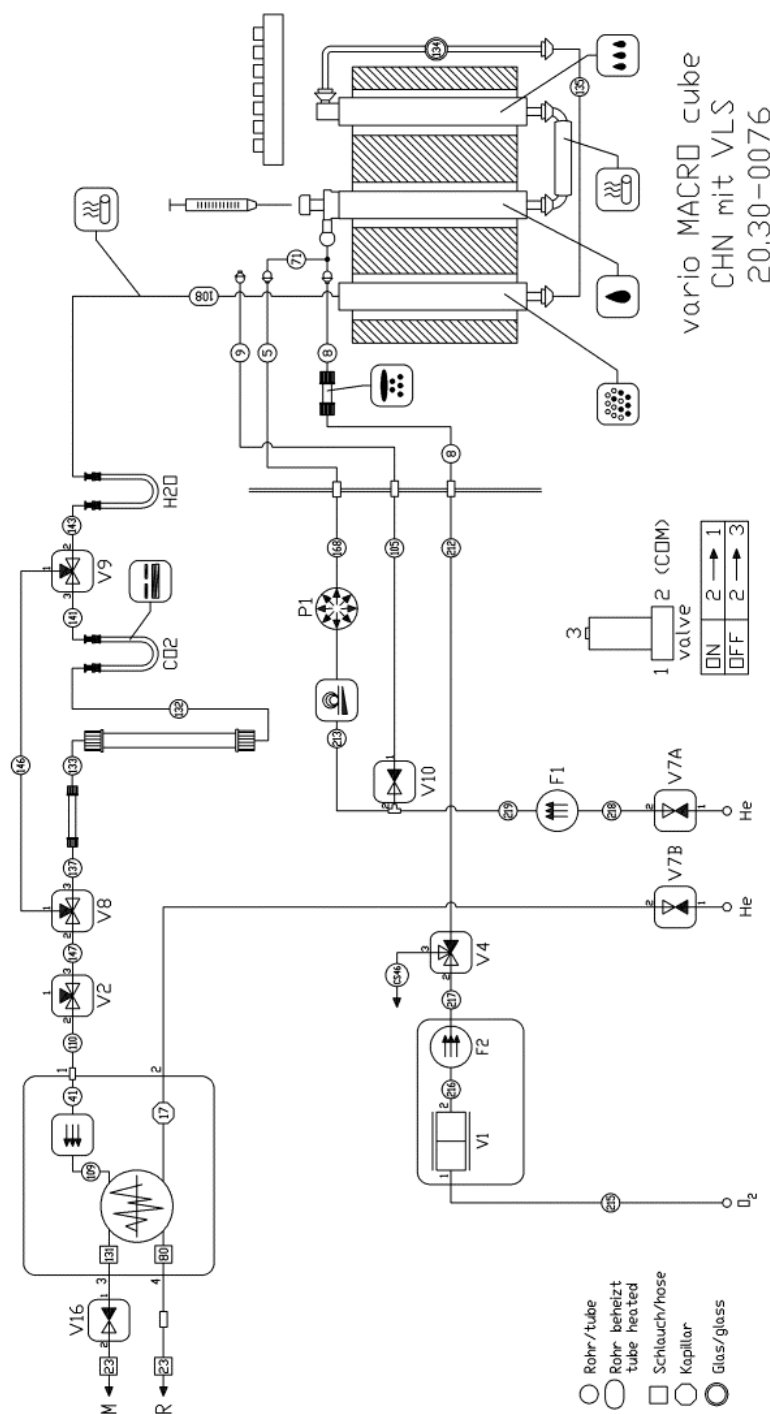


Legend:

- 1 Detector fluctuations during sample feeding, auto zero
- 2 N₂ peak
- 3 CO₂ peak
- 4 H₂ peak

Functional diagram

The following picture shows the functional diagram of the CHN mode with VLS.



Symbols

The following list names the functional and basic symbols:



Two-way valve



Pressure sensor



Gas separation

	Three-way valve		Loop		Measuring cell
	Check valve		Heated tube		Sensor
	Throttle		Drying		Hose line
	Flow controller		Combustion		Copper tube
	Flow sensor		Post combustion		Reduction
	Pressure controller		Actuator		

Tube fillings

Requirements:

Before starting work, the following requirements must be met:

- All quartz and glass components must be cleaned before their usage. Clean the tubes from fingerprints by means of a suitable solvent (e.g. acetone) before installing. Otherwise there is a risk of crystallization which will lead to premature ageing of the quartz.
- Use chemicals necessary for the tube fillings only in the appropriate quality. Delivery directly from the instrument manufacturer.

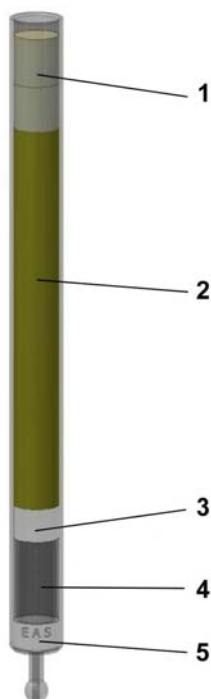


Safety instruction

Strictly observe the safety instruction "Filling reaction tubes" under **Warning notes during operation** (on page 13).

Combustion tube filling

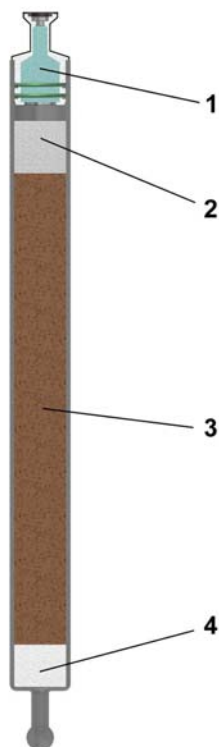
The following picture shows the fillings and filling heights of the combustion tube:

**Legend:**

- 1 Quartz wool (50 mm)
- 2 Copper oxide (CuO)
- 3 Quartz wool (20 mm)
- 4 Silver wool (50 mm)
- 5 Quartz wool (20 mm)

Reduction tube filling

The following picture shows the fillings and filling heights of the reduction tube:

**Legend:**

- 1 Plug with o-ring
- 2 Silver wool (20 mm)
- 3 Copper
- 4 Quartz wool (25 mm)

Note

All drying tubes will be filled according to the regular CHN/CN operation. Please refer to the vario MACRO cube main operating instructions.

Selecting the operating mode

Essential condition

Before switching operating modes, you must have performed all refitting work required for the new operating mode.

The installation of the liquid sampler vario LS is described in detail in the vario LS operating instructions. Read the corresponding sections there.



Safety instruction

Strictly observe the safety instruction "Changing mode" under **Warning notes during operation** (on page 13).

Selecting the operating mode

Proceed as follows:

- Perform all refitting work required for the new operating mode.
- Execute the command **System > Mode** in the instrument software. A message window appears which requests you to confirm the change of the operating mode once more.
- Click **Yes** if you want to continue. The "Analysis mode" dialog is displayed.
- Select the desired analysis mode "CHN". Select also the feeding mode "VLS". Then click **OK**.
- The "Change to new mode" dialog is displayed. If not done so far, follow here the instructions for the modification.
- Click **OK** if you have refitted the instrument. The operating mode is changed.

CHN routine operation

Sample sequence

In routine operation, the following sample sequence is recommended:

- 3 x Run-in samples (Hexadecane+Pyridine)
- 3 x Factor samples (Hexadecane+Pyridine)
- 20 real samples, 3 fold determination
- 3 x Hexadecane+Pyridine
- 20 real samples, 3 fold determination
- 3 x Hexadecane+Pyridine.... etc.

Setting device parameters

About instrument parameters

You need to know the following about instrument parameters:

- The instrument parameters listed here are average values.
- The optimized instrument parameters from initial start-up are stored on the enclosed installation CD. The user can optimize them for special applications or extraordinary demands.
- In every operating mode, the instrument parameters required for the analysis process are saved under **Options > Settings > Parameters**.

The "Device parameter" dialog

The dialog shows the device parameters currently set. It is opened via **Options > Settings > Parameters**. The left field of the dialog lists the parameter categories. By clicking the corresponding category the associated parameters will appear in the right area of the dialog.

Temperature parameters

The factory-set temperatures are optimized for best possible sample combustion and separation of the measuring components. The following table shows the pre-set values in section **Temperature** and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Furnace 1	Temperature of the combustion tube, furnace center	950 °C
Furnace 2	Temperature of the reduction tube, furnace left	600 °C

Time parameters

The factory-set time parameters of the analyzer are selected in order to provide optimum evaluation of the measuring signal under normal application conditions. The following table shows the pre-set values in section **Times** and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
O ₂ delay	Defines the time to wait after loading before beginning O ₂ dosing.	1 s
Maximum O ₂ dosing time	Defines the maximum duration of the O ₂ dosing.	300 s
Integrator reset delay, peak N	Defines the time after which the integrator is reset to zero before beginning actual integration.	1 s
Integrator reset delay, peak C	See description of integrator reset delay, peak N.	1 s
Integrator reset delay, peak H	See description of integrator reset delay, peak N.	5 s

Parameters for the liquid sample feeder

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Add-on volume	Additional sample amount in [µl] which is not injected.	1
Flush intake (G1)	Suction speed during flushing.	30
Flush eject (G2)	Ejection speed during flushing.	120 (100 µl-syringe) 60 (10 µl-syringe)
Prepare intake (G3)	Suction speed during preparation for injection.	3

Prepare eject (G4)	Ejection speed for removal of bubbles.	120 (100 µl-syringe) 60 (10 µl-syringe)
Dose intake (G5)	Suction speed of the actual sample.	3
Dose eject (G6)	Injection speed into the furnace.	120 (100 µl-syringe) 60 (10 µl-syringe)
Num. of prep. cycles	Number of preparation cycles.	2
Number Flushing procedure	Number of flushing processes with the new sample.	3
Motor current	Maximum motor current for torque limitation.	60

Explanations regarding the syringe parameters:

- The syringe volume in the info header corresponds to the syringe size. Selecting or setting of the syringe volume will be performed under **System > Feeding**.
- The syringe parameters are individually saved for each syringe size.
- The add-on volume can be = 0 for most cases, required for certain applications.
- The sample volume injected into the furnace can be set under **Options > Settings > Methods**
- Also the syringe parameters can be individually defined for each method.

Flows

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Flow helium	Carrier gas flow in [ml/min].	250

Integration time

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Max. integration time	Defines the maximum duration of the peak integration.	600 s

Limit temperatures

The following table shows the pre-set values and explains the meaning of the parameters:

Parameter	Meaning	Factory setting
Limit temp. Comb. tube	If the combustion tube temperature exceeds this value a safety shutdown of the combustion unit will be performed.	1,200 °C
Reduction tube	See Comb. tube	1,200 °C
CO ₂ column	See Comb. tube	300 °C
H ₂ O column	See Comb. tube	300 °C

Peak recognition TCD baseline

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
Number of measuring values per mean value group	20
Number of successful mean value groups	3
Number of unsuccessful mean value groups	10
Baseline constant	3
Baseline factor in %	10

admissible baseline difference | 15

Peak Recognition TCD Peak End

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
Peak max. limit sens./insens.	1500
Peak insens. End threshold	800
Peak sens. end constant	800
Activate Relative Peak End	no
Peak relative end threshold	800

Peak recognition TCD amplification

The following table shows the pre-set values of the parameters:

Parameter	Factory setting
TCD amplification level	2
TCD amplification level N	4
TCD amplification level dummy	1

Defining custom standard substances

Defining custom standard substances

Proceed as follows:

- Open the "Standard samples" dialog in the operating software by selecting **Options > Settings > Standards**.
- Click **New**. The input boxes on the right area are now empty. Enter the data of the standard sample to be newly defined.
- For the substance, enter...
 - ... the name of the substance in the "name" field.
 - ... the theoretical element content in percent in the "Conc. [%]" fields (or in ppm in the "Conc. [ppm]" fields respectively). If you enter 0 for the theoretical element content of a substance element, the element is ignored in the calculation.
 - ... the permissible tolerance for each element in the "Tolerance [%]" fields (usually 5%).
- Click **Create**. Your new standard sample will now be included in the list in the left area of the dialog.
- You have now defined the standard substance.
- Click **Close** to close the dialog.

Defining custom methods

View and define methods

In the "Methods" dialog you can view existing methods or define new methods.

View existing methods

Proceed as follows:

- Open the "Methods" dialog in the operating software by selecting **Options > Settings > Methods**.
- In the left field, select the appropriate method. In the fields at the right side the parameters of the selected method are now displayed.
- Click **Close** to close the dialog again.

Defining custom methods

Proceed as follows:

- Open the "Methods" dialog in the operating software by selecting **Options > Settings > Methods**.
- Click **New**. The input boxes on the right of the dialog are now empty. Enter the parameters of the method to be newly defined:
- Enter the following:
 - Enter the name of your method in the "ID" field.
 - Enter the purpose of the method, for example, in the "Description" field.
 - Input the corresponding method parameters in the other boxes.
- Click **Create**. Your new method will now be included in the list in the left area of the dialog. You have now defined the method.
- Click **Close** to close the dialog.

Modification into CHN liquid mode

Modification of the basic instrument

For modifying the basic instrument the following steps shall be completed one after the other.

Basic is the CHN mode.

Requirements

Before starting work, the following requirements must be met:

Keep the following ready:

- Installing the vario LS autosampler + accessories.

Process

The section is divided into the following phases:

- Switching off the instrument.
- Installing the vario LS autosampler.
- Modifying the furnace part.
- Conditioning new reaction tubes.
- Performing follow-up work.

Phase 1: Switching off the instrument



Safety instruction

Strictly observe the safety instruction "Switching off the instrument" under **Warning notes during operation** (on page 13).

Phase 2: Installing the vario LS autosampler

Proceed as follows:

- Mount the liquid sample onto the vario MACRO cube according to the operating instructions of the vario LS.
- Connect tube no. 5 and tube no. 26 with the furnished tube no. 71.
- Connect tube no. 71 to the combustion tube connector.
- Close tube no. 9 with a blind plug.

Phase 3: Modifying the furnace part



Safety instruction

Strictly observe the safety instruction "Hot instrument parts" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Open the front door.
- Pull the furnace out of the instrument. Loosen the screw at the guiding of the combustion tube and push the bolt to the right.
- Fill the combustion and reduction tube for the CHN mode in liquid operation.
- Fill the absorption tube for the CHN mode.
- Remove the old combustion and reduction tube, if necessary.
- Install the new combustion and reduction tube, if necessary. Leave the outlet of the reduction tube open for a later conditioning.
- Place the combustion tube plug with septum onto the combustion tube.
- Push the furnace back into the instrument.
- Push the bolt to the left and tighten the screw at the guiding of the combustion tube.
- Connect tube no. 71 to the combustion tube connection.
- Connect the combustion and post combustion tube by means of the quartz glass bridge.
- Close the front door.

Phase 4: Conditioning new reaction tubes



Safety instruction

Strictly observe the safety instruction "Installing and conditioning the reaction tubes" under **Warning notes during operation** (on page 13).

Proceed as follows:

- Plug the power supply plug of the analyzer into the socket.
- Turn on PC, monitor and printer and wait until the start process is completed.

- Switch the main instrument switch on.
- The instrument performs a reference run of the VLS.
- Launch the operating software.
- Set the intake pressure at the delivery point so that He flow at the PC displays approx. 200 ml/min.
- Change the operating mode.
- Open the "Instrument parameters" dialog in the operating software by selecting **Options > Settings > Parameters**.
- Check whether the parameter set corresponds to the operating mode. Click **OK** to confirm your settings. The furnaces are heated.
- Flush the instrument with helium during the heating phase.
- After reaching the required temperatures wait for the required conditioning time for the reaction tubes. For CHN mode the conditioning time for the combustion tube and the reduction tube is 1.5 hours.
- Close all open ends of the reaction tubes again.
- Set the Helium intake pressure at the delivery point to show approx. 1200 mbar at the PC pressure display.

Phase 5: Performing follow-up work

Proceed as follows:

- Perform a leak test. If a leak test was passed, the instrument is ready for operation.
- Test the proper operation of the instrument with conditioning samples, blanks and standard samples.

Calibration

General

The vario MACRO cube has a calibrated set of coefficients which can be used. This is already calibrated in solids mode or may be generated here. If a different procedure is requested, Elementar suggests the following calibration for CHN in liquid operation.

Please make sure to have the necessary standards available prior to the calibration.

The elemental analyzer vario MACRO cube + vario LS is no absolute measuring instrument. Therefore, the correlation between CHN content and CHN measuring values [Integrals] has to be obtained by means of a calibration. Factory set test substances with a known CHN content and different sample weights will be analyzed.

Note:

The density of a sample has to be known in order to obtain a calibration in mg absolute vs. the peak area.

The software automatically calculates the calibration functions (three polynomes 4th order).

A proper calibration in the selected operation mode which includes the required working range for each element, is vital for the accuracy of the results. Calibrations therefore have to be performed with special diligence.

The knowledge of the vario MACRO cube operating instructions and the technical possibilities of the instrument are prerequisite for a successful calibration.

Experience has shown that the calibration of the vario MACRO cube elemental analyzer remains stable for at least 6 months. Recalibration is recommended if the daily correction factor lies outside a range of 0.9 - 1.1 or if components which may influence the results have been exchanged (e.g. detector).

Prior to a calibration series, the filling of the combustion and reduction tube have to be renewed and the instruments has to be checked for leaks.

Recommended calibration

For CHN the following is recommended:

- Mixture of Hexadecane and Pyridine.
 - Hexadecane:
d = 0.773 mg/μl; 84.87 % C; 15.13 % H
 - Pyridine:
d = 0.978 mg/μl; 17.71 % N; 75.92 % C; 6.37 % H
- For a calibration range of 0.14 mg N abs., max. 6.6 mg C abs., max. 1.1 mg H abs. fill exactly the following amounts into a 100 ml volumetric flask:
 - 92.0 ml Hexadecane
 - 8.0 ml Pyridine

The data for the standard solution are as follows:

d = 0.7894 mg/μl; 83.98 % C; 14.26 % H; 1.754 % N.

These data have to be saved under **Options > Settings > Standards**.

By weighing-in the different substances in a 100 ml volumetric flask a better accuracy of the percentage can be reached. (Temperature dependency of the density etc.).

Numerical example

In the following a numerical example is given which should clarify the data of the standard solution mentioned above.

Calculation of the weights from the individual volumes:

Volumetric flask (empty):	79.945 g		
+ 92 ml Hexadecane:	151.061 g	= net:	71.116 g
+ 8 ml Pyridine:	158.885 g	= net:	7.824 g
Σ = 100 ml mixture		Σ	78.940 g

Calculation of absolute element contents:

71.116 g Hexadecane	=	60.356 g C	+	10.760 g H	
7.824 g Pyridine	=	5.940 g C	+	0.498 g H	+ 1.385 g N
78.940 g mixture		66.296 g C		11.258 g H	1.385 g N

Calculating the percentages of the test substance (mixture):

$$\% \text{ C} = \frac{66.296 \text{ g C} \cdot 100}{78.940 \text{ g}} = 83,982 \%$$

$$\% \text{ H} = \frac{11.258 \text{ g H} \cdot 100}{78.940 \text{ g}} = 14,261 \%$$

$$\% \text{ N} = \frac{1.385 \text{ g N} \cdot 100}{78.940 \text{ g}} = 1,754 \%$$

$$\Sigma = 100 \%$$

Calculating the density of the test substance:

$$\text{Density} = \frac{78.940 \text{ g}}{100 \text{ ml}} = 0.7894 \text{ g/ml}$$

The following sample series is recommended:

- 4-fold (6-fold) determination of "Run-in" samples, Hexadecane + Pyridine, sample volume 8 µl
- 4-fold (6-fold) determination of Hexadecane + Pyridine, sample volume 10 µl, 8 µl, 6 µl, 2 µl, 1 µl.

View of the analytical results

Display

The analytical results will be displayed in two different ways:

- Real calculation of the measured integral values, determined from N%, C% and H%.
- Analysis results from the sum of N% + C% + H% = 100% standardized will be displayed as N%_{norm}, C%_{norm}, H%_{norm}.
The advantage of this method is that the analytical results are correct, even if the density is unknown or dosing of the sample was not correct (inclusions of air in the syringe, samples with low boiling point).

The mathematical procedure is as follows:

$$F = (N\% + C\% + H\%) / 100$$

$$N\%_{\text{norm}} = N\% \cdot F$$

$$C\%_{\text{norm}} = C\% \cdot F$$

$$H\%_{\text{norm}} = H\% \cdot F$$

Note

The standardized calculation assumes that the samples only contain C, H and N. The calculation is incorrect, if the samples contain O and S in addition. However, traces of these components in the range of some ppm do not have any influence.

Check list, prior to the analysis run

Prior to the analysis run

Prior to starting an analysis run, the following points shall be completed:

- Maintenance intervals observed?
- Operation mode set?
- Gas on?
- Pressure on?
- Lecktest passed?
- Absorption tube filled and installed?
- Detector signal stable?
- Sample name, method and standard samples edited and assigned?

Shut-down for measuring breaks

Maintenance work to be performed by the customer

The following maintenance work shall be performed by the user in regular intervals:

- Exchange of the Sicapent® and the cotton in the absorption tubes.
- Exchange of the septum for injection.
- Exchange of the combustion tubes.

In addition, the maintenance of the basic instrument remain. Please refer to the vario MACRO cube main operating instructions.

Note

We recommend to determine the maintenance intervals via **Options > Maintenance > Intervals** in the instrument software in order not to forget any maintenance work

Index

A

About this document - 11
Additional error messages in O mode - 46, 71
Analysis run - 116
Analytical characteristics - 106
Analytical characteristics and technical specifications - 26, 48, 74
Application notes for oxygen determination - 43, 68

C

Calibration - 133, 149
Changing of the pyrolysis crucible - 37, 64
Check list, prior to the analysis run - 136, 151
Chlorine analyses in routine operation - 79
Chlorine determination with EC cell - 73
CHN determination with the liquid autosampler vario LS - 137
CHN determination with vario LS - 138
CHN routine operation - 143
CHNS determination with the liquid autosampler vario LS - 121
CHNS determination with vario LS - 122
CHNS routine operation - 127
Conditioning the pyrolysis tube - 36, 38, 62, 64
Cross-sensitivity of the EC cells - 81

D

Defining custom methods - 131, 146
Defining custom standard substances - 118, 130, 146
Detection - 29, 52, 76
Difficult matrices - 44, 46, 69, 71
Display conventions - 12

E

Establishing of the analysis readiness - 38, 65

F

Functional diagram - 17, 93
Functional diagram TIC module - 107

G

General - 9
General information - 104
General information on the operating instructions - 12
General measuring principle TIC - 114

I

Installation and initial start up of the TIC module - 111

L

Leak test - 83
Lifetime of the pyrolysis tube - 45, 70

M

Maintenance of the HCl EC cells - 81, 82
Maintenance work - 118
Modification into CHN liquid mode - 147
Modification into CHNS liquid mode - 131
Modification to CI operation - 84
Modification to O Mode - 31, 54
Modification to S operation - 19
Modification to TOC operation - 97

N

Notes on performing calibration - 39, 66, 78
Notes on sensitivity and measuring range - 79, 80
Notes regarding modification - 13

O

Oxygen analyses in routine operation - 40, 66
Oxygen determination with NDIR - 47
Oxygen determination with TCD - 25

P

Performing an analysis - 96, 100
Pyrolysis temperature - 44, 69

Q

Quantitative conversion from CI to HCl - 82

R

Revision history - 10

S

Safety instructions - 104, 111
Scope of delivery - 104
Selecting the operating mode - 114, 127, 143
Separation of the reaction gases - 29
Setting device parameters - 128, 144
Shut-down for measuring breaks - 136, 152
Special features - 16, 92
Substance digestion and functional diagram - 26, 48, 74
Sulfur determination with NDIR - 15

T

Technical specifications - 105
The components - 109, 113
The TOC module - 91

TIC solids module - 103
TOC maintenance work - 101
Tube fillings - 30, 52, 76, 94, 98, 109, 113, 125, 141

V

View of the analytical results - 135, 151

W

Warning notes during operation - 13, 30, 32, 38, 52,
55, 56, 57, 64, 76, 85, 94, 97, 100, 114, 125, 127,
132, 141, 143, 148
Working with the operating instructions - 12