analytikjena
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Operating Manual

mercur Duo plus
Mercury Analyzer

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For a proper and safe use of this product follow the instructions.
Keep the operating manual for future reference.

General information

http://www.analytik-jena.com

Documentation number

170:101.23

Edition

A (12/2020)

Implementation of the Technical Documentation

Analytik Jena

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1 Introduction

1.1 The mercur DUO plus

The mercur DUO plus is an excellent instrument for the determination of mercury using atomic fluorescence or atomic absorption. The mercur Duo plus is a fluorescence analyzer with additional absorption module for selection of atom fluorescence or atom absorption as analytical method and including two gold collectors for mercury enrichment.

The measuring range extends over the ng/L and µg/L ranges. The mercur DUO plus is a single-beam instrument with a mercury low-pressure lamp as exciting light source -and a photo-multiplier to record the fluorescent radiation and/or absorbtion of the sample.

The mercur DUO plus is used to examine liquid and dissociated samples. The instrument is especially suitable for water and waste water laboratories and for environmental analysis. The measurements are made with manual feeding of samples in discontinuous operation or with an autosampler in fully automatic operation.

Mercury is released using stannous II chloride, $SnCl_2$ x 2 H_2O, as reducing medium and transported in atomic form. The released mercury can be measured directly or it can be enriched with a gold collector. The enrichment improves the detection limit and separates mercury from other gases. Other gases can suppress the fluorescence signal or lead to unspecific absorption Mercury desorbed from the gold collector can either be transferred directly to the absorption cell and detected or transferred to a second gold collector beforehand. With the second gold collector, the device meets the EPA standard of the USA.

The mercur DUO is equipped with a fluorescence module, an absorption module and an enrichment unit.

The device software WinAAS controls the instrument itself, the sample peripherals and the recording and evaluation of the measurements.

1.2 Notes Regarding This Manual

This manual provides information about the installation and function of the mercur DUO plus for users familiar with mercury analysis and is a guide for operating the device and its components.

A separate Manual WinAAS is available for WinAAS control software.

Conventions

Instructions for actions which occur in chronological order are numbered and combined into action units. Safety instructions are indicated by a pictograph and a signal word. If necessary, the danger is named. The pictographs are explained in the Section below.

On-screen buttons are indicated by square brackets, e.g., **[OK]**.

Menu and option sequences in the software are separated by vertical strokes.

Symbols Used

The following symbols for warnings and system messages are used in this instruction manual:

Danger!
Notes of this kind must be observed, in order to prevent harm or physical injury to people.

Danger! Hot Surface!
Physical contact with a hot surface may cause skin burns.

Caution!
Notes of this kind must be observed, in order to prevent damage to instrument/equipment parts.

Danger! Dangerous Contact Voltage!

Emerging UV Radiation!

Warning of Caustic Substances!

Warning of Biohazards!

Note
Designates a note to be followed, in order to obtain correct measuring results.

2 Safety Instructions

For your own safety and to ensure error free and safe operation of the mercur DUO plus, please read this chapter carefully before using the appliance for the first time or before working on it.

Comply with all safety instructions in the manual and pay careful attention to all messages and notes which are displayed on the screen by the control software.

Use for the intended purpose

The mercur DUO plus is intended to be used for fluorescence spectrometry and atom absorption spectrometry of mercury.

Any departure from the instructions in this manual for proper use may lead to warranty restrictions and reduced manufacturer liability in the case of damage.

2.1 General Safety Instructions

Local codes

Pay attention to local safety codes which apply to the use of this appliance (e.g. work protection regulations, accident prevention regulations, environmental guidelines).

References to potential dangers do not replace the work protection regulations which must be observed.

Personnel

The mercur DUO plus may only be operated by qualified personnel who have received additional training for this type of work. Conveying the contents of this manual constitutes a part of the training.

Any work on electrical equipment may only be carried out by qualified electricians.

Installation, initial use and repairs

The mercur DUO plus may only be set-up, installed and repaired by the customer service of Analytik Jena or its appointed service companies. Any unauthorized operation puts the user in danger, endangers the function of the device and may void the warranty.

Switching off

The mercur DUO plus can only be shut off using the mains switch on the left side of the equipment. The mercur DUO plus and the PC components together can be switched off using the mains switch of the socket strip. Place the socket strip so that it within easy reach.

Electric shock

The mercur DUO plus is supplied with electrical voltage. **Extremely dangerous electrical voltages** are present in various parts of the system.

The mercur DUO plus may only be connected to a properly installed grounded socket. It may only be connected to power sources whose nominal voltage is the same as that on the name plate of the equipment.

Connect the mercur DUO plus and the PC together via the distribution strip supplied.

Do not connect any further devices to the distribution strip, otherwise the maximum permissable current may be exceeded.

The mercur DUO plus **must** be switched off and the mains plug pulled out before the instrument is opened up.

UV radiation

The mercury low-pressure lamp produces ultraviolet radiation. While in operation, the front plate of the mercur DUO plus must be closed (turned up).

If during service or maintenance operations the lamp must be operated uncovered, avoid direct exposure of the eyes to the UV radiation, i.e. wear UV safety goggles.

Operating substances, dangerous substances

The operator is responsible for the selection of substances used in the process as well as for their safe handling. This affects particularly radioactive, infectious, poisonous, corrosive, combustible, explosive and other dangerous substances.

When handling dangerous substances, local safety codes and guidelines must be observed.

Warnings on the labels must be always observed.

Use only vessels that are labeled.

When measuring **cyanide-containing material**, ensure that **prussic acid** cannot be generated in the waste bottle.

Biological samples have to be handled according to local guidelines regarding the handling of infectious material.

The operator is responsible for ensuring that **waste materials**, e.g., used active carbon filters or acids are disposed off in an environmentally responsible manner and according to local regulations.

Operating pressurized gas cylinders and gas plants

The inert gas is taken from gas cylinders or from a local pressurized gas plant.

For gas cylinder or gas plant operation, the safety instructions and guidelines which are apply at the operating location must be strictly complied with.

High-pressure hoses and pressure-reducers may only be used for the specified gases.

Leak testing of all gas connections must be carried out monthly.

Ventilation

The mercur DUO plus is ventilated downwards through the baseplate. Be careful to ensure that the warm air under the device can escape. Covered ventilation equipment may cause the device to break down or cause damage to it.

In cases of extreme contamination – for example, resulting from false dilution of reference solutions or samples – the mercur DUO plus may become unfit for further ultra-trace determination jobs.

Procedures for cold vapour generation from liquid samples are among the strongest detection methods applied in ultra-trace determination of elements using atom spectrometry. Their detection power ranges from only a few ng/L to a few sub-ng/L in some cases. In some other cases, blank values in reagents and vessels impose restrictions regarding detection power. All reaction paths and valves have been optimized for this operating range in terms of chemical stability and cleanness. However, if solutions in the mg/L range are allowed to flow through the reaction unit, there may be contamination inside of hoses, valves or reaction vessels of a kind that cannot be removed even by intensive flushing/purging.

Cleaning and Maintenance

The exterior of the mercur DUO plus may only be cleaned with a damp, **but not dripping,** cloth. Do not use any aggressive chemicals, cleaning agents or organic solvents.

Decontamination in case of biological contamination

The operator is responsible for carrying out suitable decontamination should the device be contaminated externally or internally with dangerous substances.

Spots, drops or larger spillages should be removed and cleaned using an absorbent material such as cotton wool, laboratory wipes or cellulose. Wipe the affected area with a suitable disinfectant such as Incidin Plus solution. Then, wipe the cleaned area dry.

Before using a cleaning or decontamination procedure other than that prescribed by the manufacturer, the user is required to check with the manufacturer that the intended procedure will not damage the device.

Sensitive Electronics

Only electrically connect and disconnect components to the mercur DUO plus when they are switched off.

Build-up of Foam in the Hg Cold Vapor Technique

If the sample shows a lot of foam building up, change the sample preparation method or add a few drops of defoaming agent.

Allowed are the following:

- ❑ Dow-Corning DB110A
- ❑ Silicon defoamer

Transport

The mercur DUO plus weighs 37 kg. Since it does not have carrying handles, the device must be gripped firmly with both hands at the lower end for carrying or lifting.

The guide values and statutory limits for lifting and carrying loads without auxiliary equipment must be observed and adhered to.

2.2 Safety labeling

Follow all warning labels that are affixed on the mercur DUO plus!

On the mercur DUO plus lamphouse, the following warning labels can be found:

Danger! UV Radiation!
Do not look directly – or indirectly via a mirror – into the UV lamp beam. Lamp radiation exposure may damage the retina or, in the event of extended skin contact, damage your skin! Please note that the front plate must be closed for operation (tilted up).

Hazardous Electrical Voltage!
There is electrical voltage present in various places inside the lamphouse. Use the main power switch to turn power supply off and pull the power plug from its socket before you open the mercur DUO plus!

The following warning symbol is attached to the front of the device next to the tube pumps:

Danger of Crushing!
During operation, there is a risk of crushing at the tube pumps. Long hair and baggy clothing can become caught in the pumps and drawn in. Wear suitable hair protections and tight-fitting clothing.

The following notice sign is attached to the rear of the device:

Unlock power cable before opening!

3 Specifications

3.1 Technical Data

Measurement Principle

- ❑ Atomic Fluorescence: Detection of the mercury fluorescence radiation at the 90° angle to the direction of the exciting radiation
- ❑ Atomic Absorption: Detection of absorption of lamp radiation energy
- ❑ Exciting and fluorescence or atomic absorption on the 253.7 nm wavelength
- ❑ D.C. light method, one-beam operation

Radiation Source

- ❑ Hg low-pressure lamp UVU5 with beaker electrode

Measurement Cell (Atomic Fluorescence)

- ❑ Flow-through fluorescence cell of quartz glass with inlet and outlet ports on the end faces
- ❑ Inner dimensions 10 x 10 x 32 (mm x mm x mm)
- ❑ Outer dimensions 12.5 x 12.5 x 40 (mm x mm x mm)
- ❑ The cell has an mirror-finish on the outside on two neighboring walls.

Measuring cell

- ❑ Continuous-flow absorption cell of quartz glass with quartz windows located on facial sides with preceding (up-line) inlet and outlet connector pieces.
- ❑ Length 235 mm, Light path length 250 nm
- ❑ Inner diameter 4 mm, outer diameter 6 mm
- ❑ The cell is provided with a protective jacket (black tube).

Detector

- ❑ Photomultiplier (PMT) 1P28, 9-stage

Photometer

- ❑ Atomic Fluorescence: Focusing of the exciting radiation on the measurement cell and the fluorescence radiation on the photomultiplier, each with a biconvex quartz lens
- ❑ Atomic Absorption: Direct beam path route from Hg lamp through absorption cell onto 9-stage 1P28 photomultiplier.

Function Groups

- ❑ 1-channel tube pump for the transport of the samples

Equipped with	Ismaprene tube 1.42 mm ID
Pump speed	4 levels
Capacity	5, 6, 8 or 11 mL/min

- ❑ 4-channel tube pump for the transport of reducing agent, acid and waste products

Equipped with	0.89 mm ID Ismaprene tube for reducing agent and acid 2.06 mm ID Ismaprene tube for waste products
Pump speed	constant, adapted to the speed of the sample pump
Capacity	Average of 2 mL/min

- ❑ Reactor of PEEK with 60° angle of incidence between sample/acid and reducing agent as well as between reaction products and transport gas stream
- ❑ Gas-liquid separator with small dead volume and reduced foam build-up
- ❑ Membrane dryer for drying the mercury-containing reaction gas using the counterflow principle
- ❑ Hg enrichment

Gold collector	0.5 gram gold-platinum alloy AuPt10 as a fine mesh
Clean out temperature	630°C, controlled
Cooling	Axial-flow ventilator

Operational Modes

- ❑ Continuous, with autosampler
- ❑ Discontinuous, without autosampler, manual
- ❑ Without enrichment
- ❑ With enrichment, with or without reload
- ❑ FBR method (fast baseline return)
  Once the peak maximum is reached, the cell is purged with a higher gas flow.

System Wash

- ❑ Acid alone
- ❑ Acid and reducing agent
  The soaking time for the reducing agent is variable.

Reagents

- ❑ Reducing agent
  Stannous chloride, $SnCl_2$ x 2 H_2O — 2 to 10 % in 3 % HCl
- ❑ Acid HCl — 1.5% conc.
- ❑ Consumed per measurement — 2 mL each

The reagents must be declared as low-in-mercury by the manufacturer!

Inert gas

- ❑ Argon or Helium

Purity	at least 99.999 Vol%, mercury-free
Inlet pressure, max.	700 kPa (7 bar)
Working pressure	200 kPa (2 bar)
Gas flow	max. 60 L/h

Operation Times. Name

- ❑ Sample load time — Time in which the sample pump fills the aspirating tube up to the double-valve group with sample.
- ❑ Reaction time — Time in which the sample pump pumps the sample to the reactor.
- ❑ Waiting time AZ — Time immediately before the stray light measurement (auto zero).
- ❑ Gas delay — Time between start of measuring and beginning of the measurement gas flow. Is employed in the FBR process.
- ❑ Purge time 1 ... 4 — Times for the transport of the reaction gas.
- ❑ Collector heating time
  Time in which the heating of the gold collector is switched on.
- ❑ Collector cooling time
  Time in which the ventilator of the gold collector is switched on.

Rating Parameters

- ❑ Carrier gas flow — typically 5 L/h or 10 L/h
- ❑ Cycle time — typically 40 sec (without enrichment, FBR process)
- ❑ Reaction time — typically 6 sec
- ❑ Dynamic range — 0.0001 to 1000 □g/L in 6 decades
- ❑ Sample size per measurement
  1 mL (for 6 sec reaction time)

Measured Value Processing

Analysis and display operating mode

- ❑ Fluorescence intensity — 0.0001 to 1.0000
- ❑ Extinction — 0.0001 to 1.0000
- ❑ Concentration — Value range: 5-digit (0.0001 to 99999 unit freely selectable)

Number of digits displayed	3, 4 or 5 selectable
Units of concentration	mg/L, µg/mL, ng/mL, µg/L, ng/L or user defined
Signal evaluation „Integration mode”	Peak height: Maximum value of the fluorescence intensity Integral value: time-integrated fluorescence intensity
Integration time	1 to 120 sec
Autozero (AZ measuring time)	1 to 120 sec
Delay	1 to 120 sec

Smoothing	Running average: over 0, 2, 4, 8, 12, 16 or 20 measured points Weighted average: over 0, 5, 11, 19 or 25 measured points (method of least squared error, according to Golay-Savitzky)
Results display window	Alphanumeric values Bar chart of integrated values (bar graph) Time-plot of the single peaks Overlaid peak plots Overview of peak plots
Special windows	Run Report Concentration values in curve Peak plots with variable integration limits
QC Window (Quality Check)	QC blank – blank QC chart QC control samples – mean chart – recovery chart QC duplicate measurement sample/matrix – Differences chart (Trend chart) – Range chart (Range chart) – Precision chart (SD chart) QC spike sample – percentage recovery chart
Statistical methods	Sigma statistics – mean value with standard deviation (SD) and – relative standard deviation (RSD) Median statistics – median value with range (R) and – relative range (R %)
Confidence interval	Can be selected: Absolute, relative or switched off Selectable confidence interval: 68.3% (1 σ) 90% (1.6 σ) 95.4 % (2 σ) 99% (2.6 σ) 99.7% (3 σ) 99.9% (3.6 σ)

Calibration

Calibration method	Standard calibration Bracketing calibration Recalibration Standard addition Method of additions calibration
Fit sample curve	Linear, variable weighting functions non-linear, variable weighting functions
Number of standards	1 to 30
Number of addition concentrations	1 to 30
Recalibration	Two-point recalibration with display of the recalibration factor

Power supply

Supply voltage Frequency	230 V ±10% 50/60 Hz Other voltages and frequencies on request
Mains fuse installation in the building	16 A
Power consumption	Average 90 VA Maximum value 600 VA
Overvoltage category	II according to DIN EN 61010-1
Contamination degree	2 according to DIN EN 61010-1
Protection class	I
Protection type	IP 20

Equipment Fuses

Instrument fuse fittings (5×20 mm² or 6.3 x 32 mm²) according to IEC 60127 / 230 V

Mains voltage Fuses F1 and F2	230 V T 3.15 A/H	110 V T 6.3 A/H

Ambient conditions

Working temperature	+10 °C to 35 °C
Humidity	max 90 % at +30°C
Storage temperature (drying agent)	-40 °C to +55 °C according to DIN 58390-2

Dimensions and Weights

Weight [kg]	37
Dimensions (W x H x D) [mm]	600 x 350 x 490

Control Computer Data

Computer (minimum requirements)	Processor: 1,6 GHz Dual Core CPU RAM: 2 GB RAM (32 Bit), 4 GB RAM (64 Bit) Hard drive space: min. 1 GB (SSD recommended) Graphic resolution: 1024 x 768 or higher Interfaces: min. 2 x USB 2.0 Keyboard, mouse
Operating system	Windows 7, 8 or 10 (32/64 Bit)

3.1.1 Technical Data on the Sampling Peripherals

Autosampler AS-F

Autosampler without dilution function, completely PC-controlled

Sample tray 139/15 Sample cups Special cups	 129 pieces, 15 mL 10 pieces, 50 mL
Sample tray 54/50 Sample cups	 54 pieces, 50 mL
Power supply	Via mercur DUO plus
Wash bottle	2 L
Mass	6,5 kg

Autosampler AS-FD

Autosampler with dilution function, completely PC-controlled

Sample tray 139/15 Sample cups Special cups	 129 pieces, 15 mL 10 pieces, 50 mL
Sample tray 54/50 Sample cups	 54 pieces, 50 mL
Dosing unit in the Fluidics module	5 mL
Power supply	Via mercur DUO plus
Wash bottle	2 L
Bottle for diluent	2 L
Mass (total) Autosampler Fluidics module	10.0 kg 6.5 kg 3.5 kg

3.2 Guidelines and Standards

Protection Class and Type

The mercur DUO plus belongs to protection class I.
The casing is of protection type IP20.

Device Safety

The mercur DUO plus satisfies the safety standards

- ❑ DIN EN 61010-1
- ❑ DIN EN 61010-2-061

EMC Compatibility

The mercur DUO plus has been tested for radio interference suppression and interference immunity. It fulfills the requirements stipulated by:

- ❑ EN 61326-1
- ❑ EN 55011 Class A

Directives for China

The device contains restricted substances (according to directive "Management Methods for the Restriction of the Use of Hazardous Substances in Electrical and Electronic Products"). Analytik Jena guarantees, that those hazardous substances may not leak out during the next 25 years when the device is used in accordance with its intended purpose.

EU Directives

The mercur DUO plus has been built and tested according to EU Directive 2014/35/EU and 2014/30/EU. It left the manufacturer in perfect and technically safe condition. To maintain this condition and to ensure safe operation, the operator must strictly observe the safety and operating instructions contained in this manual. The appropriate operating instructions should be referred to for accessories and system components from other manufacturers which have also been supplied.

4 Transportation & Installation Requirements

4.1 Transportation & Storage

For transportation and storage, the following ambient requirements must be fulfilled:

- Temperature range: -40 to +55 °C

4.2 Installation Requirements

The mercur DUO plus may only be set-up, installed and repaired by the customer service of Analytik Jena or their appointed service companies. Any unauthorized operation puts the user in danger, endangers the function of the device and may void the warranty.

During the installation a second person is required for some tasks.

When the installation is finished, the service personnel will test the device. The test results will be documented in the test protocol for the mercur DUO plus.

The user is responsible for everything that is not included in the original delivery, but is necessary for the operation of the mercur DUO plus. The operation of the mercur DUO plus demands certain local and system-specific requirements:

- ❑ Suitable place for setting up
  Space
  Ambient conditions
- ❑ Inert gas supply available
- ❑ Mains connection

Caution!
Pay attention to the safety instructions in Chapter „Safety Instructions” on page 7.
Observe work protection regulations. Warnings regarding potential danger do not replace valid work protection regulations!

Possible dangers when working with the mercur DUO plus are:

- ❑ Danger from electric current
- ❑ Danger when handling pressure cylinders
- ❑ Danger from toxic and chemically aggressive substances

4.3 Ambient Conditions

- ❑ The workspace of the mercur DUO plus should be free from dust, corrosive vapors and vibration.
- ❑ A separate room is recommended for sample preparation and storage of wet chemical substances.
- ❑ Temperature range during operation +10 °C to 35 °C
- ❑ Humidity during operation max. 90 % at 30 °C

4.3.1 Space Requirement and Weight

- ❑ Minimum size of worktable when the autosampler is standing next to the mercur DUO plus 1500 mm x 800 mm
  Select a height according from an ergonomic point of view.
- ❑ Carrying capacity of worktable: 80 kg
- ❑ Worktable surface wipe, scratch and corrosion resistant
  The tabletop must be proof against the absorption of moisture

Components	Width [mm]	Height [mm]	Depth [mm]	Weight [kg]
mercur DUO plus	600	350	490	37
AS-F	340	350	460	6.5
AS-FD				
Autosampler	340	350	460	6.5
Fluidics module	360	310	165	3.5

Table 4-1 Measurements and Weights of the Components of the mercur DUO plus

4.3.2 Power Supply

Warning!
During electrical installation, observe the VDE (German Association of Electrical Engineers) guidelines and local regulations!
The mains supply must be correctly grounded.
Do not use an adapter in the mains cabling.

The mercur DUO plus operates on single-phase alternating current. Optimum functioning of the device strongly depends on a correct mains connection.

The mercur DUO plus, PC and monitor are connected to the same phase using the distribution strip supplied with equipment.

To avoid sudden voltage fluctuations, do not connect the mercur DUO plus to the same electrical circuit as other power-intensive devices.

Connection Requirements

Voltage	230 V ±10% or different if specified in conditions and terms of supply
Frequency	50/60 Hz
Power consumption	up to 480 VA
Fusing	16 A

4.4 Gas Supply

The required inert gas serves as a transport medium for the mercury and as a purge gas for the system.

Caution!
If the inert gas is supplied by pressure cylinders, these must be secured to the wall in an upright position using cylinder holders.

Recommended Inert Gas	Inlet pressure	Consumption
Argon 5.0 or better, or Helium 5.0 or better Purity at least 99.999 Permitted constituents: Oxygen ≤ 2 ppm Nitrogen ≤ 5 ppm Humidity ≤ 5 ppm	max. 700 kPa (7 bar)	max. 60 NL/h

Table 4-2 Inert Gas

4.5 Waste Gas Disposal

The remaining gas containing mercury is passed through an active carbon filter in the mercur DUO plus that completely binds the mercury. The remaining gas leaving the mercur DUO plus can be released immediately to the surroundings or fed to an extraction plant. No special requirements are made on the extraction equipment.

5 Function and Construction

5.1 Configuration

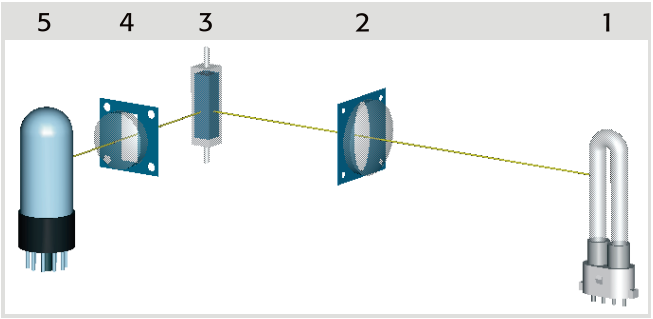
The mercur DUO is a fluorescence analyzer with additional absorption module for selection of atom fluorescence or atom absorption as analytical method and including two gold collectors for analysis performed with mercury enrichment

Fig. 5-1 mercur DUO plus PC with Autosampler AS-F

The mercur DUO plus can operate with or without autosampler. In all cases, sample, acid and reducing agent are aspirated by tube pumps. If there is no autosampler, each sample must be held ready for the measurement by hand. With autosampler, a larger number of samples can be analyzed fully automatically.

5.2 Working Principle of Atomic Fluorescence

5.2.1 The Principle of the Optics



1 Mercury low-pressure lamp
2 Quartz lens
3 Cell
4 Quartz lens
5 Receiver, PMT

Fig. 5-2 Schematic of the Optics

The radiation from a U-shaped mercury low-pressure lamp (1, Fig. 5-2) with beaker electrodes is focused by a biconvex quartz lens (2, Fig. 5-2) onto the fluorescence through-flow cell (3, Fig. 5-2). The mercury lamp emits mainly on the resonance wavelength of 253.7 nm.

Released mercury vapor flows through the cell with inlet and outlet ports on the end faces. Mercury atoms absorb the excitation radiation at the 253.7 nm wavelength and emit fluorescence radiation of the same wavelength in all directions.

The fluorescence radiation is decoupled at an angle of 90° from the excitation radiation and focused on a UV-sensitive photomultiplier (5, Fig. 5-2) by a second biconvex quartz lens (4, Fig. 5-2).

The cell has mirrored surfaces on two neighboring areas to increase the fluorescence yield. On the one hand, the mirroring reflects the excitation radiation, after it has passed though the cell once, back through the cell again in the reverse direction. On the other hand, fluorescence emitted in the opposite direction to that of the measuring device is reflected towards the radiation receiver.

Masks limit the size of the excitation and fluorescence beams. From the inner volume of the fluorescence cell (10 mm x 10 mm x 32 mm), a part-volume of 5mm x 5mm x 20mm is used for the fluorescence. This reduces considerably the amount of stray light reaching the PM

5.2.2 The Measurement Principle

The mercur DUO plus is a single-beam instrument that works according to the principle of D.C: light. This simple instrument idea was chosen because

- ❑ The mercury low-pressure lamp requires only a few minutes to run up to operating condition after switch-on and emits with very high stability after that.
- ❑ Before each fluorescence signal, a stray light value is measured, which records possible changes in lamp intensity.
- ❑ An optical filter in front of the quartz window of the absorption cell ensures that only the wavelength of 253.7 nm is used for measurement.

The pre-amplified measurement voltage from the photomultiplier is passed to an 18-bit analog-digital converter (ADC), of which 16 bits are used. The maximum ADC value of 65536 corresponds to 1.0 units of fluorescence.

The auto-zero value (AZ value) is measured in a gas phase in which no mercury has yet been released from the sample. Depending on the method, it records the level of the stray light of the fluorescence (a function of the photomultiplier voltage) or stray light value plus the blind value that arises from the acid and reducing agent contamination of the mercury.

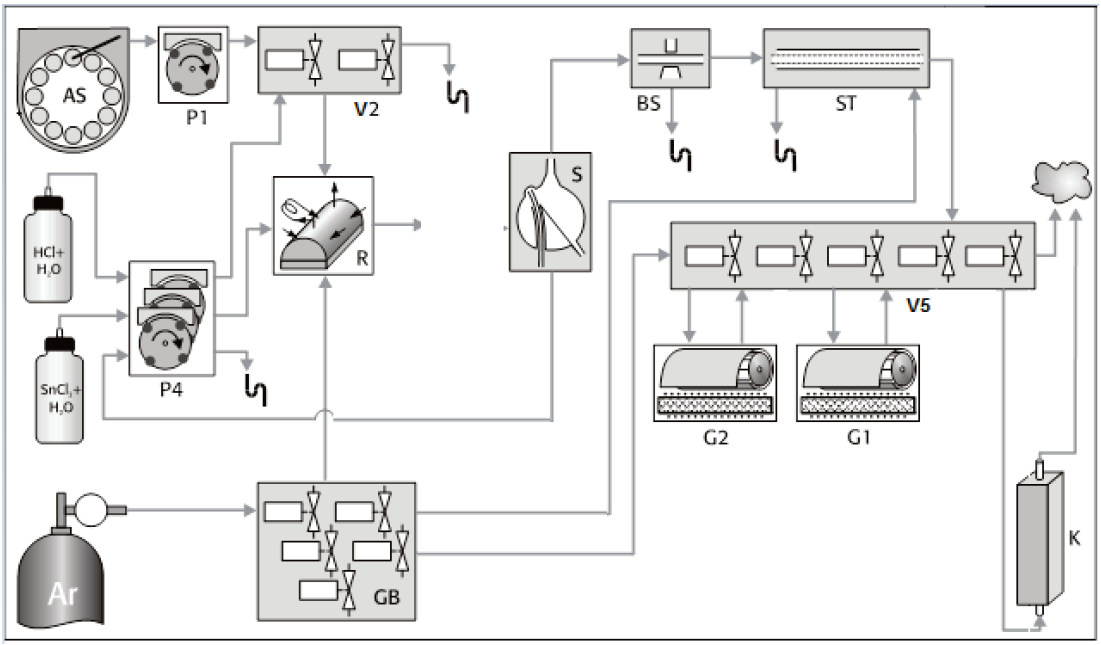
The stray light of the fluorescence cell is measured in the stationary gas state following a short gas purge at 50 L/h. It is displayed in percent of the ADC maximum value of 65536. The ratio of the current stray light value to the value ex-works is a measure of the cleanliness of the cell.

The A/R value (acid/reducing agent value) is the sum of the stray light value of the cell and the acid/reducing agent blind value of the system. It is measured as the acid flows via the sample intake path and the reagent flows directly to the reactor and the reaction products are transported to the cell with a gas flow of 15 L/hr via the gas-liquid separator. The A/R value is the reference value for the clean system and for the set point of the controlled system rinsing. The A/R value is recorded after a system rinsing.

5.2.3 The Reaction Principle

The mercur DUO plus works with stannous chloride, $SnCl_2$ x 2 H_2O, as reducing agent to minimize the release of gases that exert a quenching effect on the mercury fluorescence.

Helium or argon is used as carrier and purge gas, where helium brings not only a somewhat higher signal value but also a quicker drop-off in the fluorescence signal.



AS	Autosampler	S	Separator
P1	Sample pump	V4	5-valve group
V2	2-valve group	G1	Gold collector 1
BS	Bubble sensor	G2	Gold collector 2
ST	Membrane dryer	Ar	Gas cylinder, argon
P4	Reagent pump	GB	Gas box
R	Reactor	K	Cell

Fig. 5-3 Functional Diagram of mercur DUO plus

The sample solution is aspirated by a 1-channel tube pump (P1), acid and reducing agent by a 4-channel pump (P4). A 2-valve group (V2) switches either sample or acid to the reactor (R) as desired and the other component to waste. Sample and reducing agent meet in the reactor. The reaction product is carried by a flow of inert gas to the gas-liquid separator. In the reactor, the sample is reduced and atomic mercury released.

In the gas-liquid separator (S), the gas phase (mercury vapor and inert gas) and the liquid phase are separated from each other. The liquid is pumped off.

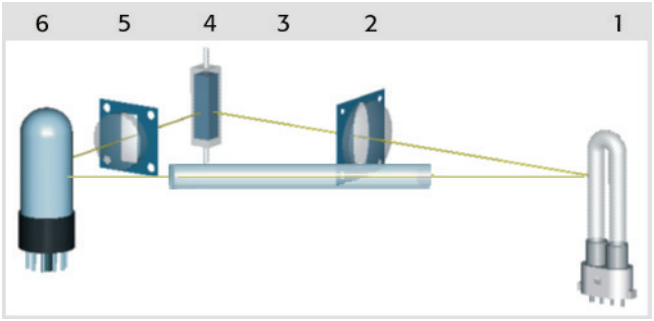
The separated gas is either led directly into the fluorescence cell and measured or onto a gold collector (G1) for mercury enrichment. The enriched gas mixture resulting from cleaning out the gold collector can be fed to the cell (K) to be measured or further to the second gold collector.

5.3 Working Principle of Atomic Absorption

The purpose of the absorption module is to allow extended mercur DUO plus application capabilities by adding atom absorption to the set of methods available for quantitative Hg-determination. It provides a more robust working tool where samples with complex matrices or higher Hg-content have to be handled.

5.3.1 Operating Principle

Optical diagram



1	Low-pressure mercury lamp	4	Fluorescence cell
2	Quartz lens	5	Quartz lens
3	Absorption cell	6	Receiver, PEM

Fig. 5-4 Optical beam Diagram with Atomic Fluorescence and Absorption

A U-shaped low-pressure mercury lamp with cup electrodes emits radiation that directly passes through the absorption cell to hit a detector (photomultiplier) surface. Preferentially, the low-pressure mercury lamp emits at the wavelength of 253.7 nm.

A stream of released mercury vapour is maintained through the continuous flow cell with inlet and outlet tube pieces which are arranged in front of the facial quartz windows. Mercury atoms absorb 253.7 nm radiations. The amount of radiation weakening is measured by a photomultiplier to be output to an evaluation module where it is displayed in extinction units.

5.3.2 Measuring principle

The absorption module relies on a single-beam arrangement which works with steady light.

This simple concept can be applied, because:

- the low-pressure mercury takes but a few minutes (from power available) to become operational and emit radiation with supreme stability
- an auto-zero value is measured before each absorption signal

Once pre-amplified, the photomultiplier voltage is transferred to an analog-digital converter (ADC).

The auto-zero value (AZ value) for baseline determination is measured following a short gas purge cycle performed at 50 L/h and with stationary gas conditions, i.e. while no mercury is released by the sample. It records those parts of the low-pressure mercury lamp's radiation energy which directly impinge on the photomultiplier. The result is indicated as a percentage value of the maximal ADC value (65536).

5.3.3 Reaction principle

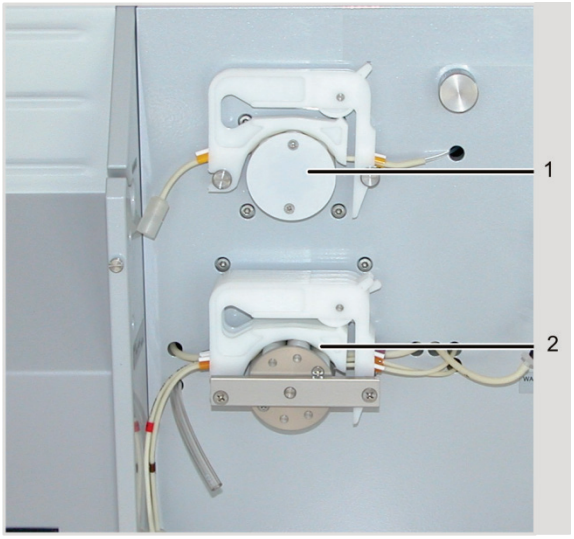
Cold vapour technology results in mercury to be set free inside the reactor. Once set free, the mercury vapour is separated from liquid reagents with the help of a carrier gas (argon or helium) and a down-line gas-liquid separator to be directly introduced into the absorption cell or be sent to a gold collector for mercury enrichment.

The gold collector is then baked out, which causes the gas mix to be enriched and finally forwarded to the absorption cell.

5.4 Main Function Groups

5.4.1 Tube Pumps

The mercur DUO plus is fitted with a 1-channel tube pump for the transport of the sample and a 4-channel tube pump for the transport of acid and reducing agent and for pumping off the liquid phase from the gas-liquid separator. Both tube pumps are fitted with adjustable snap-in cassettes.



1 Sample pump

2 Reagent and waste pump

Fig. 5-5 Tube Pumps

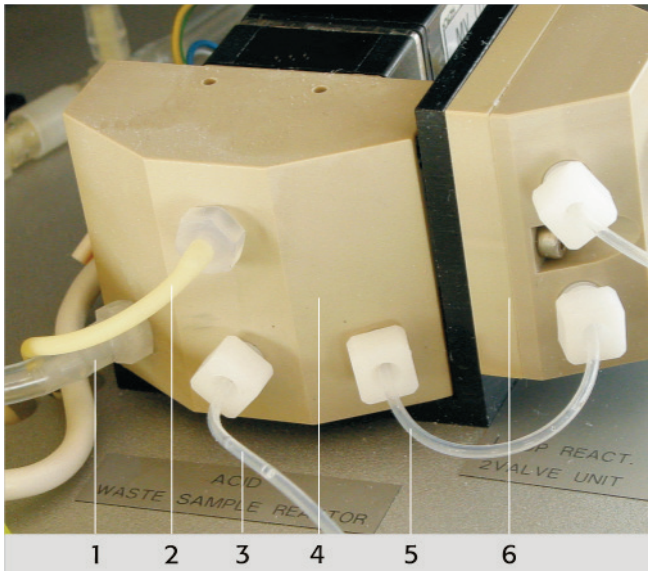
All pump tubes are made from Ismaprene. Each tube inside diameter is adapted channel-wise to the purpose of that channel, see the chapter „Technical Data”, from page 11.

The sample pump only runs during the load time and the reaction time. Four different speeds are selectable for the sample pump. The following pump flow rates correspond to the speed levels:

Speed Level	1	2	3	4
Pump flow rate in mL/min.	5 mL	6 mL/min	8 mL/min	10 mL/min

The 4-channel pump runs during the entire measurement cycle for measurements without enrichment; for measurements with enrichment, from the beginning of the measurement cycle to the end of purge time 1. The pump speed is set at a fixed value; is, however, adjusted internally during the reaction phase to the relevant speed level of the sample pump. The average delivery rate for acid and reducing agent is 2 mL/min.

5.4.2 The 2-Valve Group



1 To waste
2 Acid from the reagent pump
3 Sample from the sample pump
4 2-valve group
5 To the reactor
6 Reactor

Fig. 5-6 2-valve Assembly

The 2-valve group consists of two inerts solenoid valves on a PEEK base plate. It switches the sample stream to the reactor and the acid to waste during the reaction phase. Otherwise, the acid flow is switched to the reactor and the sample flows to waste when the sample pump is running.

5.4.3 Reactor

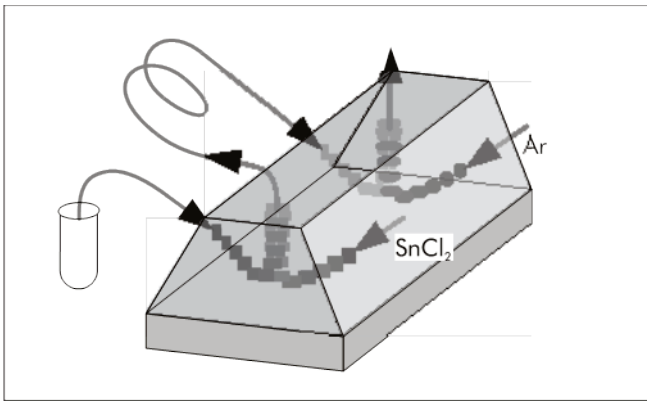
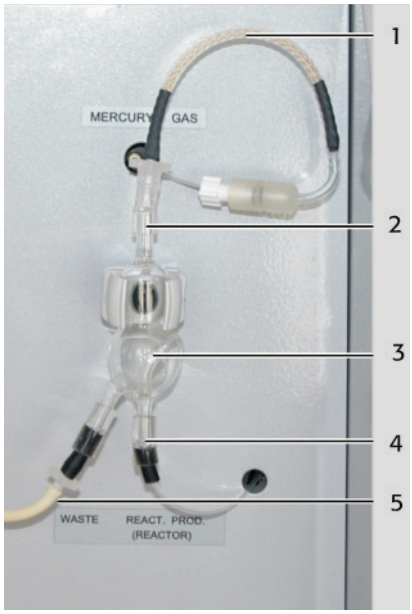


Fig. 5-7 Reactor

In the reactor made of PEEK, the sample or acid and reducing agent come together at an angle of 120° and react with each other. The reacting components are picked off at 60° to both inlets. The reaction continues in the 25 cm-long coiled MFA tube with 1 mm inside diameter. At a second collision point, the inert gas stream and the reaction products meet at an angle of 120° and are picked off at 60°. The reaction, i.e. the release of atomic mercury, is enclosed in the reactor.

5.4.4 Gas-Liquid Separator



1 Pre-dryer
2 Outlet, gas with mercury
3 Glass bead
4 Reaction product inlet
5 Liquid waste outlet

Fig. 5-8 Gas-Liquid Separator

The gas-liquid separator made of Duran glass is characterized by its low dead volume. The reaction products are fed in from below, the tube widens into a hemispherical bulge. This arrangement greatly reduces the formation of bubbles, even with foaming samples. The mercury vapor exits upwards with the carrier gas. This reduces the danger of droplets being entrained to a minimum. The liquid is pumped out from the floor of the gas-liquid separator.

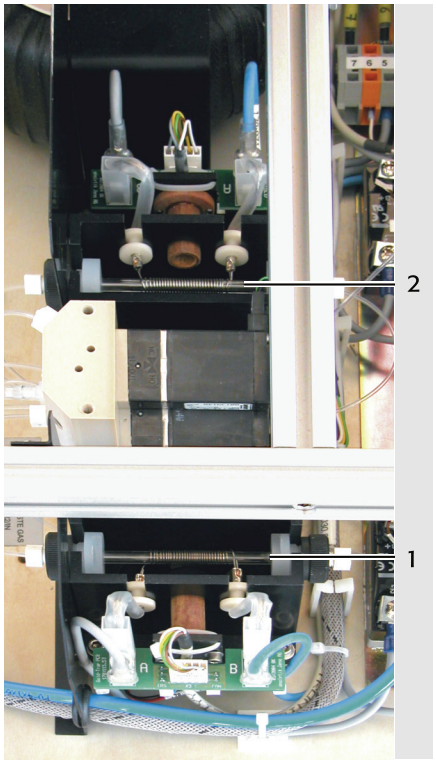
5.4.5 Bubble Sensor with Switchover Valve

The bubble sensor (BS, Fig. 5-3) follows immediately after the gas-liquid separator and detects the smallest bubbles and droplets in the MFA tubing. Bubbles and droplets cause a change in the refractive index in the MFA tubing that is detected by a light beam. If the bubble sensor reacts, the downstream solenoid valve switches over from direct through to waste and so prevents moisture penetrating into the sensitive modules in front of the cell.

5.4.6 Tube Membrane Dryer

In the tube membrane dryer (ST, Fig. 5-3), the reaction gas containing mercury is dried by moisture exchange on the counterflow principle. The tube membrane is surrounded by an outer tube through which dry inert gas flows – in counterflow with the reaction gas. From diffusion and specific chemical processes, the water content is extracted from the measurement gas. The membrane dryer connects the bubble sensor with the 5-valve group.

5.4.7 Mercury Enrichment Unit



1 Gold collector 1
2 Gold collector 2

Fig. 5-9 Gold Collectors

The mercur DUO plus is fitted with two enrichment units. An enrichment unit consists of:

- ❑ Gold collector: Fine gold-platinum mesh in ceramic tube with heating coil.
- ❑ Sensor for temperature monitoring of the gold collector when cleaning out (630 °C).
- ❑ Axial ventilator for cooling the gold collector after cleaning out.

5.4.8 Gas Purification

1 Active carbon filter

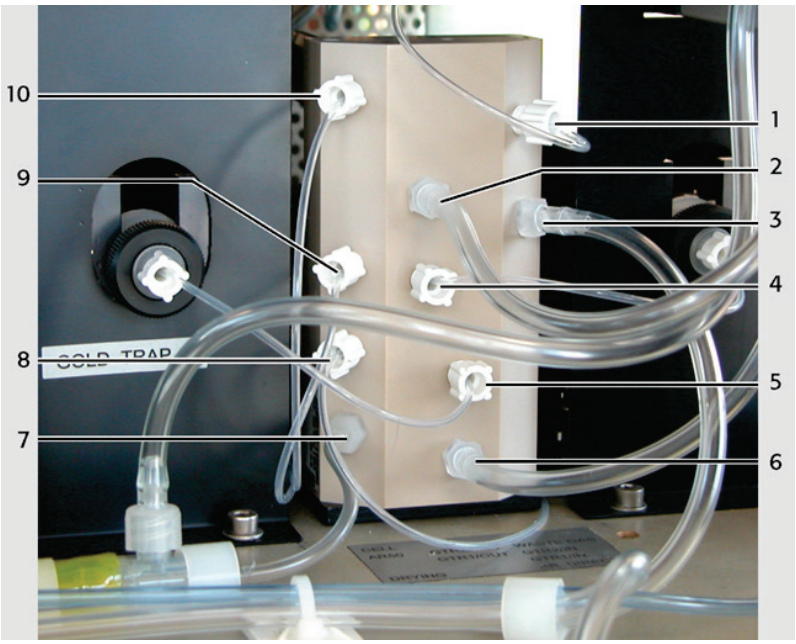
Fig. 5-10 Active Carbon Filter at Gas Inlet

Either argon or helium can be used as carrier gas (stripper gas).

The carrier gas is taken from a gas cylinder or from a locally available gas supply plant. Before entering the analysis instrument, traces of mercury and water that may be present are removed from the carrier gas by an active carbon filter. After this cleaning, the carrier gas is fed to the gas box.

A second active carbon filter is located after the measuring cell. After the measurement this has the effect that gas no longer needed is completely freed of contaminants so that it can be released to the atmosphere.

5.4.9 5-Valve Group



1	Outlet to fluorescence cell	6	Input of reaction gas from countercurrent dryer
2	50 L/h gas inlet	7	Inert gas inlet
3	Outlet to waste section	8	Input from gold collector 1
4	Outlet of gold collector 1	9	Input from gold collector 2
5	Outlet of gold collector 2	10	Outlet to absorption cell

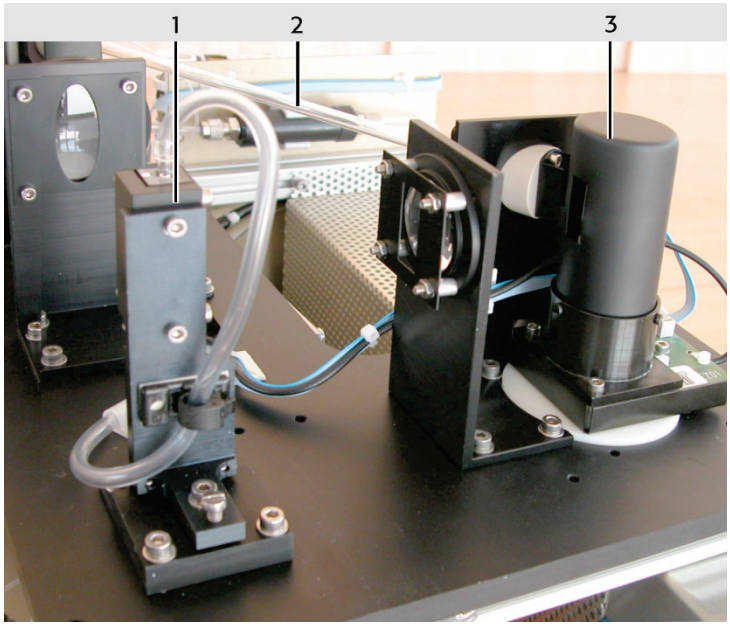
Fig. 5-11 5-valve Group

The 5-valve group consists of five inert gas solenoid valves mounted on a PEEK base body. It switches the flow path for reaction gas and carrier gas as follows:

- Reaction gas directly to absorption cell via dryer section
- Reaction gas directly to fluorescence cell via dryer section
- Reaction gas to waste gas section via dryer section
- Inert gas directly to absorption cell
- Inert gas directly to fluorescence cell
- Inert gas directly to waste gas section
- Reaction gas to waste gas section via dryer section and collector 1
- Inert gas to absorption cell via collector 1
- Inert gas to fluorescence cell via collector 1

- Inert gas to waste gas section via collector 1
- Inert gas to waste gas section via collectors 1 and 2
- Inert gas to absorption cell via collectors 1 and 2
- Inert gas to fluorescence cell via collectors 1 and 2
- Valve 2 of 50 L/h gas box linking directly to absorption cell will only be triggered if none of the other gas paths leads to the cell.
- Valve 2 of 50 L/h gas box linking directly to the fluorescence cell will only be triggered if none of the other gas paths leads to the cell.

5.4.10 Swing-Motion Drive of Photomultiplier



1 Fluorescence cell
2 Absorption cell (without protective jacket)
3 Photomultiplier on swing-motion drive

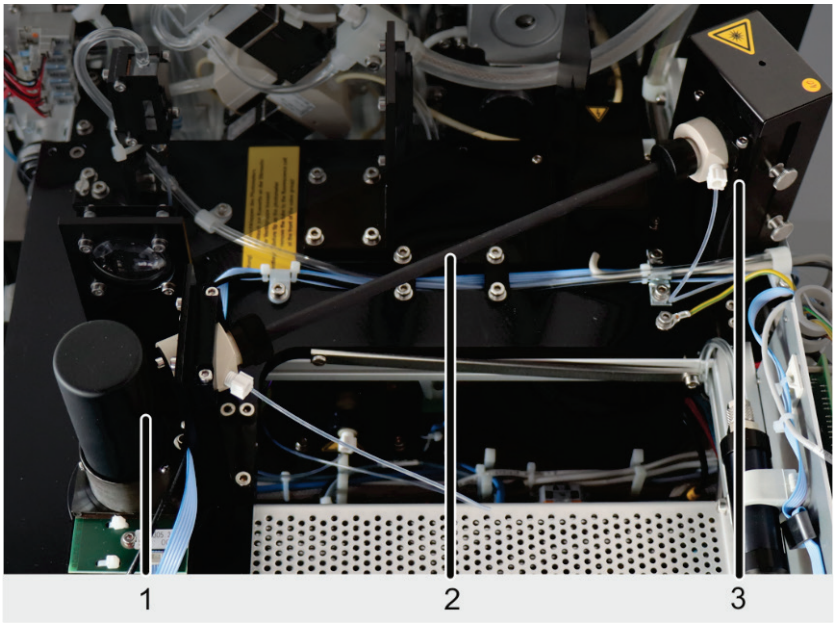
Fig. 5-12 Photomultiplier with swing-motion drive

A pneumatic swing-motion drive with electrically operated valve generates rotary motion of the photomultiplier between absorption cell position and fluorescence cell position.

Motion occurs between two adjustable stops that limit the motion length in absorption beam direction and fluorescence beam direction.

The photomultiplier's position will be automatically adjusted by the initialization routine, depending on the method that was selected on the preview screen.

5.4.11 Absorption Cell



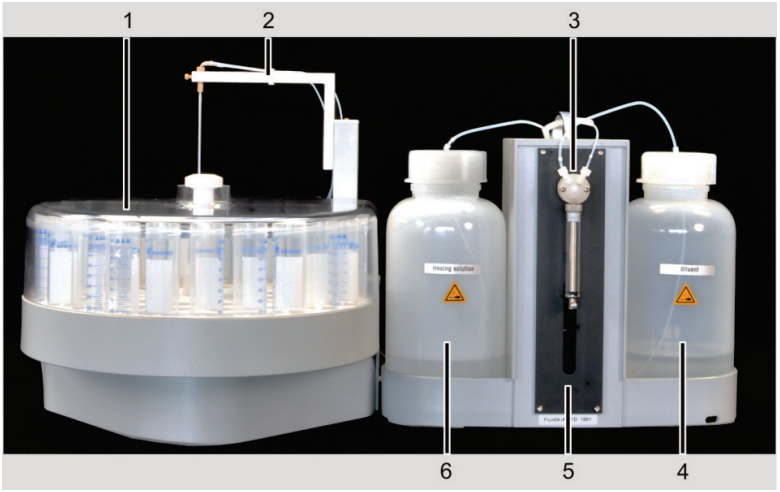
1 Receiver (photomultiplier) side
2 Absorption cell (with protective jacket)
3 Low-pressure mercury lamp

Fig. 5-13 Absorption Cell

A quartz tube of 4 mm inner diameter, 6 mm outer diameter and a length of 235 mm has been selected as absorption cell. This quartz tube is sealed by quartz glass windows on its facial ends. Its optical wavelength is 250 mm. In order to prevent stray-light effects, the absorption cell is fitted with a black jacket shield.

5.5 Autosampler AS-F / AS-FD

The mercur DUO plus can ooperate with manual or automatic feed of the samples. The use of an autosampler makes automatic operation possible.



1 Sample tray with cover
2 Autosampler arm
3 dosing unit (5000 µL)
4 Storage bottle for diluent
5 Fluidics module
6 Storage bottle for rinsing solution

Fig. 5-14 Autosampler AS-FD with separate Fluidics module

Autosamplers suitable for the mercur DUO plus are

- ❑ Autosampler AS-F, an automatic autosampler
- ❑ Autosampler AS-FD, with additional dilution function

For both autosamplers, there are two types of trays available with different numbers and sizes of sample cups.

139 positions	Sample tray with 129 sample positions for 15 mL Sarstedt cups on the outer track and 10 sample positions for 50 mL Sarstedt cups on the inner track
54 positions	Sample tray with 54 positions for 50 mL Sarstedt cups

Both sample trays have the same outer diameter. The most suitable tray should be selected according to the requirements of the sample analysis:

- ❑ Available sample quantity
- ❑ Number of repeat measurements per sample

The software controlled autosampler arm reaches all the positions intended for sample-taking. The dipping depth into the sample and the special cups is preset, however, it can be adjusted via the control software.

The mercur DUO plus supplies the autosamplers with operational voltage. Tray and autosampler arm are driven by stepping motors. The tray is rotated. The autosampler arm is rotatable and can be lowered by 120 mm.

On the top of the autosampler AS-F there is a wash cup with overflow next to the sample tray. In the autosampler AS-FD the wash cup is located in a plastic block together with a mixing cup. A diaphragm pump delivers the rinsing solution from the storage bottle into the wash cup – this action cleans the dipped canula by washing it inside and out. Excess washing liquid flows through the overflow into the waste receptacle, which is under the table during the wash cycle.

The autosampler AS-FD features an extra Fluidics module with a dosing unit (5000 µL). The Fluidics module is electrically connected to the autosampler and is supplied with operating voltage via the mercur DUO plus. Standards or samples are diluted in the mixing cup by first placing the concentrate into the mixing cup. Then the diluent is added at a high dosing speed (max. volume: V = 20 mL). A fixed waiting time ensures complete mixing. A second diaphragm pump extracts the residual liquid that has not been taken up by the mercur DUO plus.

The autosampler AS-FD with dilution function features the following advantages:

- ❑ Preparation of standards for the calibration by diluting one or several stock standards in the mixing cup
- ❑ Dilution of the sample if its concentration is too high, i.e., its element content is higher than 110 % of the calibration standard with the highest concentration
- ❑ Dilution of all samples at freely selectable dilution ratios up to a ratio of 1:400

5.6 Measurement Sequences: Fluorescence Absorption

5.6.1 Direct Measurement

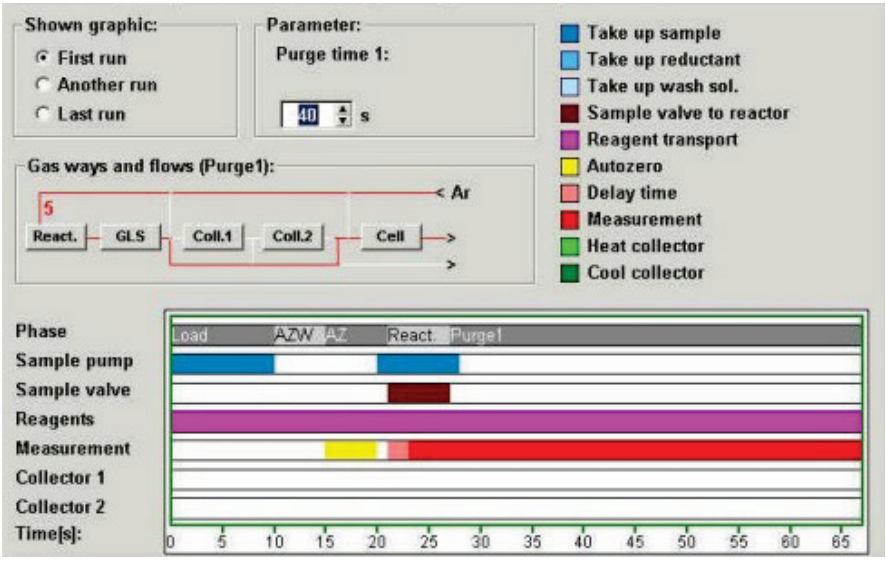


Fig. 5-15 Direct Measurement (without enrichment), Time Schematic

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the auto-zero waiting time (**AZW**), reagents are delivered from the 4-channel pump. With a constant gas flow, constant measurement conditions are set up in the cell. The stray light value is then recorded (**AZ**).

During the reaction time (**React.**), the double-valve group releases the sample to the reactor, the sample pump runs. The measurement is started at the same time as the reaction begins. Reaction time and pump speed determine the sample quantity that is converted.

During the following purge time (**Purge1**), the constant gas flow continues to purge released mercury from the cell till the system is finally clear.

5.6.2 Direct Measurement with FBR (fast baseline return)

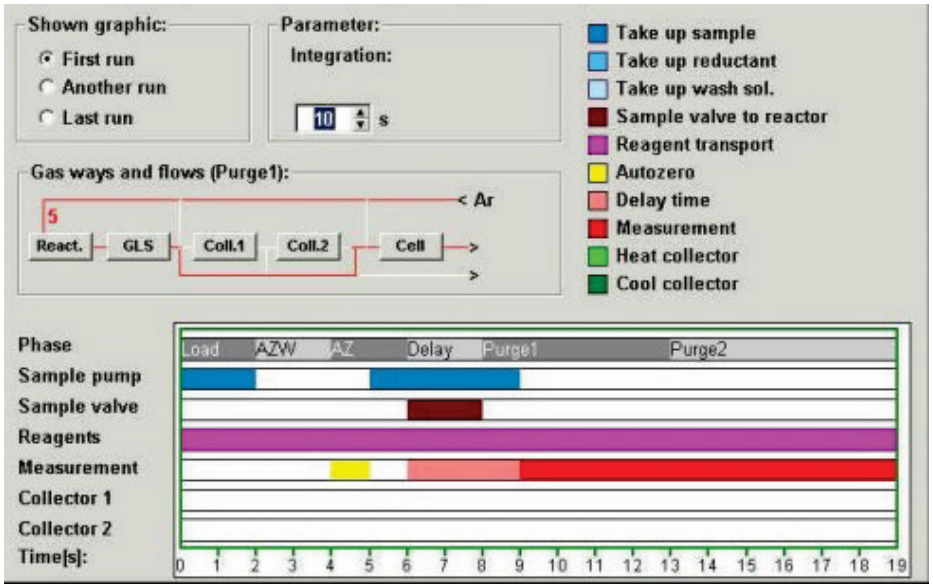


Fig. 5-16 Direct Measurement with FBR, Time Schematic Chart

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the auto-zero waiting time (**AZW**), gas flows through the cell with 50 L/hr, released by valve 2 of the gas box. The gas stream creates the same conditions for the subsequent recording of the stray light value (**AZ**) as for the breaking off of the signal. During the auto-zero waiting time, the 4-channel pump delivers reagents and the gas flows through the reaction section to waste gas.

During the reaction time, the double-valve group releases the sample to the reactor. Reaction time and sample pump speed determine the sample quantity that is converted. The gas flow of 50 L/hr is interrupted. The gas flow through the reaction section can be delayed relative to the simultaneous reaction and measurement starts in order to increase the peak height of the fluorescence signal.

During the purge time 1 (**Purge1**), the gas flow is kept constant through the reaction section.

During the purge time 2 (**Purge2**), the gas flows again with 50 L/hr through the cell and uses the cell to be quickly purged, so rapidly returning the signal to the baseline (fast baseline return, FBR). The freely selectable gas stream through the reaction section flows during purge time 2 to waste gas and purges the system.

5.6.3 Measurement with Enrichment (without reload)

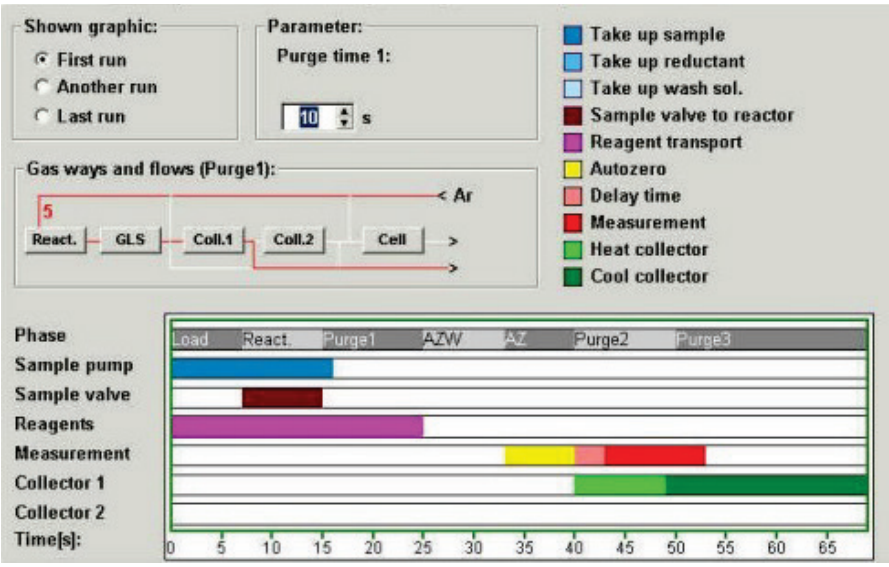


Fig. 5-17 Measurement with Enrichment, Time Schematic Chart

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the reaction time (**React.**), the sample pump continues to run and the double-valve group releases the sample to the reactor. At the same time, the 4-channel pump delivers reagents. Reaction time and sample pump speed determine the sample quantity that is converted. The gas flow through the reaction section carries the released mercury during the reaction time and the subsequent purge time 1 to the gold collector 1, where it is enriched. The carrier gas that has been freed of mercury flows to waste gas. The 4-channel pump runs to the end of purge time 1.

During the auto-zero waiting time (**AZW**), fresh gas is fed directly to the cell via the gold collector. It creates constant conditions for the stray light measurement.

The cleaning out of the gold collector, the purge time 2 and the measurement are started simultaneously. The transport gas stream flows with other freely selectable flow rates; it transports the mercury released in collector 1 to the cell.

The cooling back down of the gold collector to room temperature follows on after the cleaning out process.

The purge time 3 follows the purge time 2, the same fresh gas flows as during the auto-zero waiting time and the AZ phase. Cell and gold collector are purged with fresh gas; the measurement signal comes to an end on the baseline.

5.6.4 Measuring with Enrichment and FBR

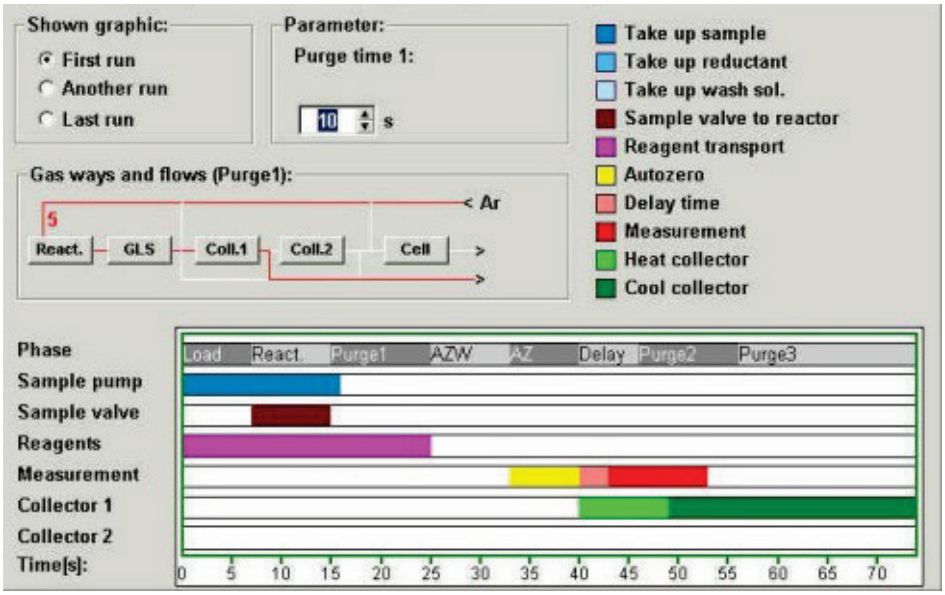


Fig. 5-18 Measurement with Enrichment and FBR, Time Schematic Chart

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the reaction time (**React.**), the sample pump continues to run and the double-valve group releases the sample to the reactor. At the same time, the 4-channel pump delivers reagents. Reaction time and sample pump speed determine the sample quantity that is converted. The gas flow through the reaction section carries the released mercury during the reaction time and the subsequent purge time 1 (**Purge1**) to the gold collector 1, where it is enriched. The carrier gas that has been freed of mercury flows to waste gas. The 4-channel pump runs to the end of purge time 1.

During the auto-zero waiting time (**AZW**), inert gas flows through the cell with 50 L/hr, released by valve 2 of the gas box. The gas stream creates the same conditions for the subsequent recording of the stray light value (**AZ**) as for the breaking off of the signal. The 4-channel pump delivers reagents and the gas flows through the reaction section to waste gas.

The measurement is started at the same time as the cleaning out of the gold collector. The fresh gas flow through the gold collector 1 can be delayed relative to the start of the cleaning out and simultaneous measurement start in order to increase the peak height of the fluorescence signal. The 50 L/hr gas stream is stopped when the stream of fresh gas is released. The carrier gas transports the released mercury from the gold collector 1 to the cell. The cooling back down of the gold collector to room temperature follows on after the cleaning out process.

During the purge time 3, the FBR gas flows with 50 L/hr through the cell and quickly purges this free. Th signal quickly returns to the baseline (fast baseline return).

At the same time, a freely selectable transport gas quantity flows through the gold collector 1 to waste gas.

5.6.5 Measuring with Enrichment and Reload

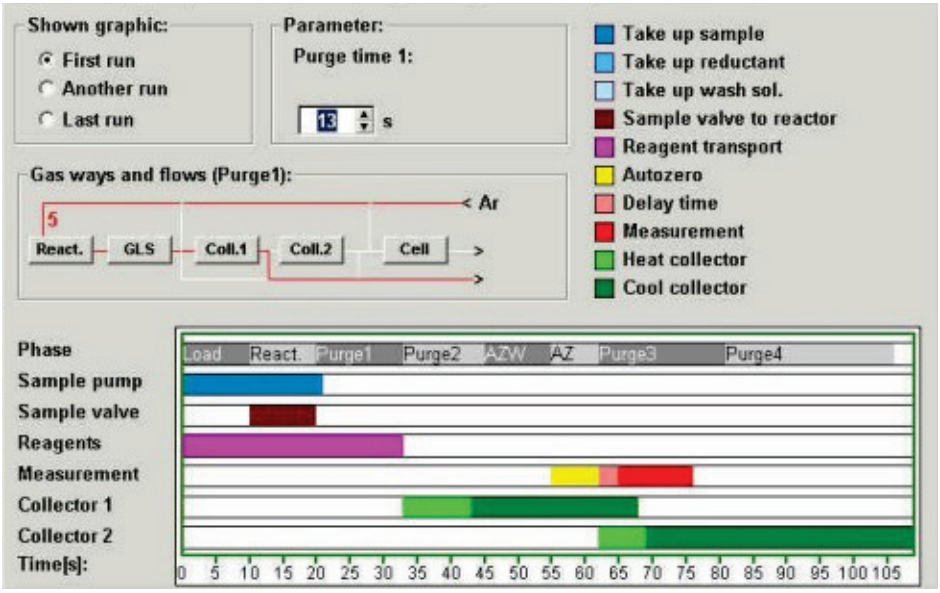


Fig. 5-19 Measurement with Enrichment and Transfer, Time Schematic Chart

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the reaction time (**React.**), the sample pump continues to run and the double-valve group releases the sample to the reactor. At the same time, the 4-channel pump delivers reagents. Reaction time and sample pump speed determine the sample quantity that is converted. The gas flow through the reaction section carries the released mercury during the reaction time and the subsequent purge time 1 to the gold collector 1, where it is enriched. The carrier gas that has been freed of mercury flows to waste gas. The 4-channel pump runs to the end of purge time 1.

The cleaning out of the gold collector 1 and the purge time 2 begin simultaneously. The fresh gas transports the released mercury from gold collector 1 to gold collector 2. In gold collector 2, the mercury is stored again; the transport gas flows mercury-free to waste gas.

The cooling back down of the gold collector 1 to room temperature follows on after the cleaning out process.

During the auto-zero waiting time (**AZW**), a freely selectable quantity of fresh gas flows directly over the gold collectors 1 and 2 to the cell and creates constant conditions there for the stray light measurement (**AZ**).

The cleaning out of the gold collector 2, the purge time 3 and the measurement begin simultaneously. The transport gas flows directly through the gold collectors 1 and 2. It delivers the mercury released from collector 2 to the fluorescence cell.

The cooling back down of the gold collector 2 to room temperature follows on after the cleaning out process.

In the purge time 4, the same gas stream flows as during auto-zero waiting time and the AZ phase – direct through the gold collectors 1 and 2 to the cell and lets the measurement signal run out to the baseline.

5.6.6 Measuring with Enrichment, Reload and FBR

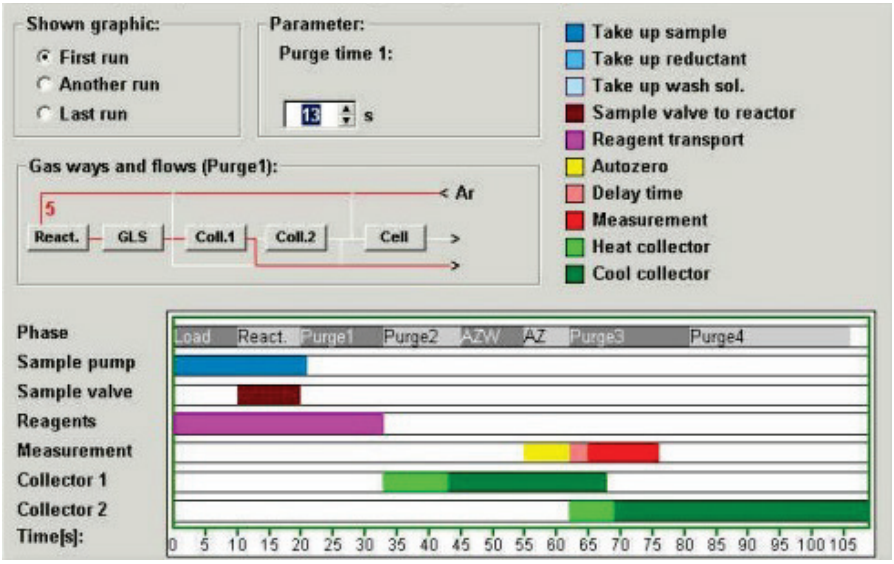


Fig. 5-20 Measurement with Enrichment, Transfer and FBR, Time Schematic Chart

Before the first measurement of a statistic block, the measurement section is filled up to the double-valve group with sample (**Load**). This phase does not apply in the case of further measurements.

During the reaction time (**React.**), the sample pump continues to run and the double-valve group releases the sample to the reactor. At the same time, the 4-channel pump delivers reagents. Reaction time and sample pump speed determine the sample quantity that is converted. The gas flow through the reaction section carries the released mercury during the reaction time and the subsequent purge time 1 to the gold collector 1, where it is enriched. The carrier gas that has been freed of mercury flows to waste gas. The 4-channel pump runs to the end of purge time 1.

The cleaning out of the gold collector 1 and the purge time 2 begin simultaneously. The fresh gas transports the released mercury from gold collector 1 to gold collector 2. In gold collector 2, the mercury is stored again; the transport gas flows mercury-free to waste gas.

The cooling back down of the gold collector 1 to room temperature follows on after the cleaning out process.

During the auto-zero waiting time (**AZW**), gas flows through the cell with 50 L/hr, released by valve 2 of the gas box. The gas stream creates the same conditions for the subsequent recording of the stray light value (**AZ**) as for the breaking off of the signal. During this period, no gas flows through the gold collectors.

The measurement is started at the same time as the cleaning out of the gold collector 2. The transport gas flow can be delayed relative to the simultaneous reaction and measurement starts in order to increase the peak height of the fluorescence signal. The 50 L/hr gas stream is stopped when the transport gas is released. The transport gas flows directly through both gold collectors and delivers the mercury released from collector 2 to the cell.

The cooling back down of the gold collector 2 to room temperature follows on after the cleaning out process.

During the purge time 4, the FBR gas flows with 50 L/hr through the cell and quickly purges this free. Th signal quickly returns to the baseline (fast baseline return).

At the same time, a stream of cleaning gas flows through the gold collector 1 to waste gas.

5.6.7 System Wash

Depending on the measuring task, the system wash can

- ❑ take place after each sample
- ❑ be set as action in the sample table
- ❑ be carried out when the concentration is exceeded

The system wash takes place, depending on the pre-selection, only with acid or with reducing agent and acid.

When **washing with acid**, the auotsampler dipps the canula with the sample intake tube into the wash cup; the wash pump delivers acid from the storage bottle into the wash cup. When working without autosampler, the sample aspiration tube is dipped into an acid storage bottle by hand (after being shown how to do this). The system wash is then started. During the first half of the wash time, the double valve group switches the acid delivered by the sample pump to waste and to the reactor during the second half.

The **wash with reducing agent and acid** begins with the reducing agent.

The sample aspiration tube is dipped into a sample vessel containing reducing agent; automatically from the autosampler, manually when there is no autosampler (after instruction). The system wash is then started. During the first half of the reducing agent wash time, the double valve group switches the reducing agent delivered by the sample pump to waste and to the reactor during the second half of the wash time.

Once the reducing agent wash time is completed, the soaking time of several tens of seconds to several minutes can follow. During this time, the sample tube, the double-valve group, reactor and gas-liquid separator are all exposed to the effect of the reducing agent solution.

After the period of exposure, the sample aspiration tube is dipped in acid. Again during the first half of the wash time, the double valve group switches the acid delivered by the sample pump to waste and to the reactor during the second half.

The sample pump and the 4-channel pump are running during the wash times.

5.7 Measurement Sequences: Atomic Absorption

Analytical procedures are identical with the measurement sequences described for fluorescence operation.

Typical system time values for direct measurement:

Sample loading time:	10 s
AZ waiting time:	5 s
Zero balancing:	5 s
Reaction time:	6 s
Purge time 1:	34 s
Integration time:	40 s

6 Installing and Using for the First Time

6.1 General Notes

Caution!
Any unauthorized operation puts the user in danger, endangers the function of the device and may void the warranty.

The mercur DUO plus may only be set-up, installed and repaired by the customer service of Analytik Jena or their appointed service companies.

For a smooth installation and a disruption free operation of the mercur DUO plus ensure, that:

- ❑ All safety notes according to the manual are adhered to.
- ❑ All warnings and notes on the device are adhered to.
- ❑ Any notes output by the control program are observed.
- ❑ The operating conditions according to Chapter „Installation Requirements” on page 18 are adhered to.

6.2 Equipment Arrangement

Recommended: Set up the PC, monitor, keyboard and mouse on the right, next to the mercur DUO plus.

If the work table is sufficiently deep, it is best to set up the autosampler in front of the mercur DUO plus. This gives the shortest distance for the tube between the autosampler and the mercur DUO plus.

The autosampler can also stand on the left, next to the mercur DUO plus or on top of it – depending on the space available. Pay particular attention to keep the tube connections short to the mercur DUO plus.

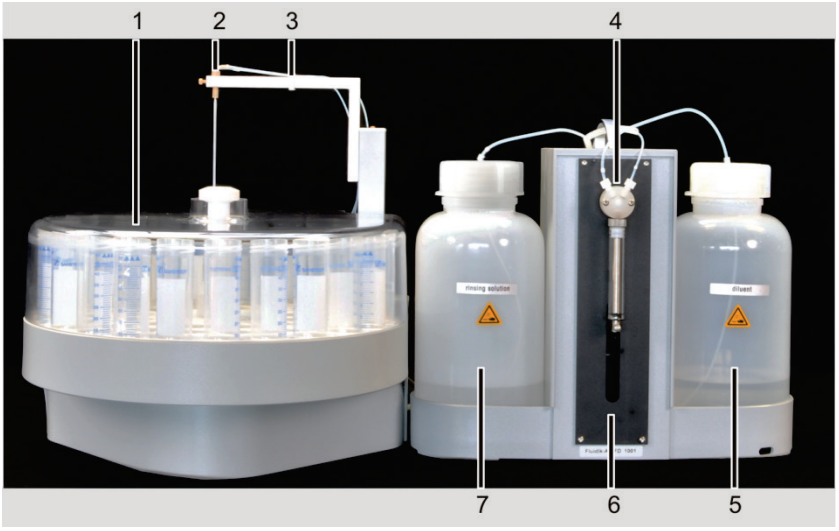
6.3 Supply and Control Connections

The supply and control connections are located on the rear side of the mercur DUO plus.

1 Mains voltage input, fuses
2 Active carbon filter (gas input)
3 Connection PC
4 Autosampler (connection sampler)
5 Gas outlet, waste gas

Fig. 6-1 mercur DUO plus, Rear Side

6.4 Install the Autosampler



1 Sample tray
2 Canulas with guide
3 Autosampler arm with tube guide disk
4 Dosing unit (5000 µL)
5 Storage bottle for the diluent
6 Fluidics module
7 Storage bottle for rinsing solution

Fig. 6-2 Autosampler AS-FD with Fluidics module

Caution! Risk of Damage of the electronics!

Switch off the mercur DUO plus prior to any installation!

Connecting or disconnecting electrical contacts might damage the sensitive electronics of the mercur DUO plus.

1. Place the autosampler in front of the mercur DUO plus, left to it or on top of the device.
2. Place the Fluidics module (for AS-FD) or storage bottle for rinsing solution (for AS-F) next to the autosampler.
3. Plug the control cable for connecting the autosampler to the mercur DUO plus into the connection on the rear of the autosampler and lock it in place (2, Fig. 6-3).
4. Plug the control cable into "sampler" connection on the rear of the mercur DUO plus (5, Fig. 6-1) and lock it in place.
5. In the AS-FD plug the control cable for connecting the Fluidics module to the autosampler into the connection on the rear of the autosampler and lock it in place (1, Fig. 6-3).
6. Attach the outlet tube to the outlet connector of the autosampler (3, Fig. 6-3). Attach the outlet tube to the connector or the corresponding opening in the lid of the collection bottle.
   Note: Position the outlet tube at a constant incline. If necessary, shorten the tube. Tube must not dip in the liquid.
7. Screw the wash tube to the rear of the autosampler (4, Fig. 6-3). In the AS-F introduce the other end of the tube into the storage bottle for rinsing solution.
   Note: In the AS-FD the tubes for connecting the autosampler and the Fluidics module are attached to each other by encasing and are numbered. Marking wash tube "2".

1 Fluidics module connection
2 mercur DUO plus connection
3 Connector for outlet tube
4 Screw for wash tube

Fig. 6-3 Autosampler AS-FD, Rear Side

8. Slide the tube guide disk (3, Fig. 6-2) on to the autosampler arm.
9. Put the canula(s) (2, Fig. 6-2) with guide into the autosampler arm and fix in place.
10. In the AS-FD feed the dosing tube for the diluent (marking "1") through the tube guide disk at the autosampler arm and plug it onto the thicker canula of the autosampler arm.
    Note: The autosampler arm can be moved manually when switched off.

11. Plug the sample intake tube from the mercur DUO plus through the tube guide disk onto the thin canula of the autosampler arm.
(For installation of sample intake tube onto mercur DUO plus see chapter „Check and Replace Pump Tubes” on page 50)
12. Place the sample tray onto the autosampler housing, make sure it latches.
Note: The controller does not start the autosampler or stops automatically if no sample tray has been placed.
13. Place the sample cover until it sits in the guide rail.

Preparing the Fluidics module (for AS-FD)

1 Storage bottle for rinsing solution
2 Diluent connection
3 Dosing tube connection (to AS-FD)
4 Dosing syringe, consisting of piston and glass cylinder
5 Dosing syringe with attachment screw
6 Storage bottle for diluent

Fig. 6-4 Fluidics module with Dosing Unit

1. If necessary, fit the dosing syringe to the dosing unit (→ Section "Replace Dosing Syringe" on page 64).
2. Place the storage bottles for the rinsing solution (left) and diluent (right) into the bottle holders of the Fluidics module.
3. Immerse the short tube (marking "3") into the storage bottle for the diluent. Screw the second tube end to the valve (2, Fig. 6-4).
4. Screw the dosing tube for the diluent (encased, marking "1") to the second connection of the valve (3, Fig. 6-4).
5. Immerse the hose for the rinsing solution (marking "2") into the storage bottle.

6.5 Install and Start WinAAS Program

Installation and start of the WinAAS program necessary for the control of the mercur DUO plus are described in the WinAAS manual.

6.5.1 Additional Software Settings for Atomic Absorption Analysis

Energy balancing

The Int.-Parameters/Levels tab includes an **Energy** field for absorption mode.

This field displays the currently set PEM voltage (photomultiplier voltage with the related energy as a percentage value.

On pressing of the **[Zero Balance]** button, the PEM voltage will take on such a level that the photomultiplier will receive 70% of primary radiation.

Regardless of that, settings for photomultiplier voltage can also be made manually.

On subsequent actuation of the **[Update]** button, the pertaining energy value will come on display.

Mit der zusätzlich eingeführten Schaltfläche **[Energie-Scan]** ist es möglich, über längere Zeitabschnitte den Energielevel zu beobachten.

Error test

A pseudo LED to check for correct swing-drive motion state has been added to the **Error test** tab.

If the swing drive is found to be in one of the two defined beam directions (absorption / fluorescence), the green LED will light.

If the swing drive is found to be in any other than the defined beam directions, the red LED will light to signal an error situation.

6.6 Prepare for Manual Working

1. Fill the storage bottle for reducing agent with stannous chloride solution; dip the aspiration tube in the liquid.
2. Fill the storage bottle for acid with HCl; dip the aspiration tube in the liquid.
3. Snap in the tube cartridges, check the snap-in position or adjust to the correct position.
4. Open the inert gas supply, set the outlet pressure.
5. Place the outlet tube for residual liquid in the collection bottle.
6. Place the sample cups ready.
7. Switch on the device.

6.7 Prepare for Automatic Operation with Autosampler

1. Fill the storage bottle for reducing agent with stannous chloride solution; dip the aspiration tube in the liquid.
2. Fill the storage bottle for acid with HCl; dip the aspiration tube in the liquid.
3. Snap in the tube cartridges, check the snap-in position or adjust to the correct position.

4. Open the inert gas supply, set the outlet pressure.
5. Place the outlet tube for residual liquid in the collection bottle.
6. Fill the storage bottles for rinsing solution and diluent (in the AS-FD).
7. Lead the sample tube from the mercur DUO plus through the tube guide disk on the autosampler arm and plug it into the thin canula.
8. Attach the outlet tube to the outlet connector of the autosampler (rear side, 3, Fig. 6-3) and place the end in the collection bottle. Choose a length and position the outlet tube at a constant incline.
9. Place the sample tray onto the autosampler housing, make sure it latches.
   Note: The controller does not start the autosampler or stops automatically if no sample tray has been placed.
10. Fit out the tray.
11. Place the sample cover until it sits in the guide rail.
12. Switch on the device.

7 Service and Maintenance

Safety Instructions

The operator may not undertake any care or maintenance to this device and its components, other than those specified and described in this chapter.

Only service engineers from Analytik Jena, or technical personnel authorized by Analytik Jena may carry out repairs to the mercur DUO plus.

Please observe all guidelines, standards and safety instructions when doing any maintenance work as specified in Chapter „Safety Instructions” page 7.

To guarantee perfect and safe functioning, the mercur DUO plus should be inspected on an annual basis by service engineers from Analytik Jena.

Only use original replacement parts from Analytik Jena . Laboratory parts required for routine operation, can be ordered from Analytik Jena.

7.1 Daily Maintenance

7.1.1 Tasks for the Daily Start-Up

1. Hang the tube cartridges in place and check or set the pressure of the pump tubes by setting the snap-in position.
2. Load the system with reducing agent and acid: Place the ends of the aspiration tubes in the liquids in the respective storage bottles.

7.1.2 Tasks before Switching Off at the End of the Day

1. Rinse the sample, reducing agent and acid tubes with distilled or weakly acidic water.
2. Pump the tubes empty.
3. Relax the pump tubes by disconnecting the tube cartridges.

7.2 Cleaning

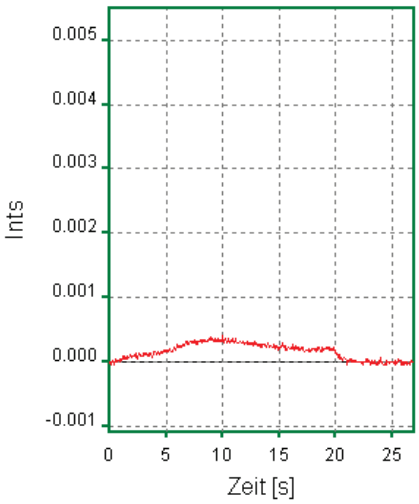
7.2.1 Determine Reason for/or Place of Contamination/Clogging

Sample intake tube

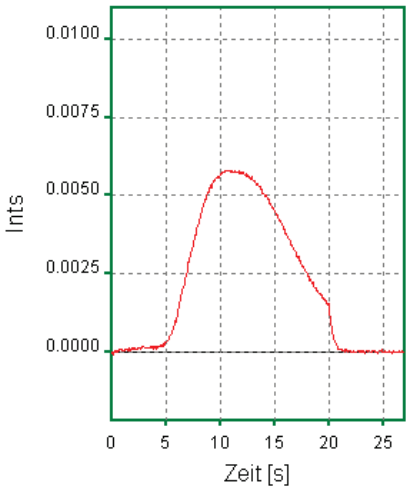
1. Load method „Without enrichment/ FBR/ 0...5 µg/L“.
2. Trigger repeated measurement cycles with an acidified blank solution (e.g. 2 mL HCl *Hg-free* + 1 mL HNO_3 in 100 mL of distilled water).

With conditions selected as described above, the approximate blank value reading should be from 0.0003 and a maximum of 0.001 Int. for a system to be considered clean. The intake tube must be assumed to be contaminated if the intensity vale is clearly increased, the signal gets smaller with each measurement, but rises again after a short down-time of the system.

Signals



Blank value



Contamination

Intake canula of autosampler

1. Check blank value as described above, once with only the sample intake tube alone connected and once combined with the autosampler's intake canula (e.g. deinstalled).

If an increased blank value is obtained for intake tube combined with intake canula and if it is found to get smaller as more measurements are performed, the capillary is contaminated.

Reactor group

To check the reactor group for potential clogging, draw in water and air alternately for each of the three aspiration tubes.

Watch this process with the front shield somewhat open.

1. Trigger sample pump and components pump operation in WinAAS program, than let distilled water draw in only by the sample tube at first.
   Water will be pumped to the sample valve and on to the waste section.
2. Switch sample valve („Sample to Reactor“).
   Water will now be transported through the small connecting tube to the reactor group, will then pass through the reaction loop and a transfer tube to arrive at the gas-liquid separator.
3. Let pumping continue until tube is completely empty.
4. Repeat this whole process with the acid tube.
   Water will be transported to the sample valve and on to the waste section.
5. Switch sample valve („Sample to Waste“).
   Water flows through reactor group, reaction loop and is forwarded to the gas-liquid separator.
6. Once the tube has been completely emptied, let water be drawn in through the reductant tube.
   As you do this, the water will flow directly to the reactor group, transit the reaction loop and the transfer tube and enter the gas-liquid separator.

A clogging situation must be assumed if the water does not flow in the manner as described above.

5-valve group and gas path

1. Load method „Without enrichment/ FBR/ 0...5 µg/L“.
2. Lower all three aspiration tubes into distilled water volume.
3. Trigger repeated measurement cycles.

On completion of several repeat cycles, the signal should be found to virtually coincide with the baseline. An increased signal, which shows a marked drop directly after zero-compensation, suggests contamination in a gas path (of the 5-valve group).

Cell

A clearly raised light-scattering value (e.g. PEM = 600 V 80 %) suggests contamination of the cell.

1. Perform lamp test in WinAAS program.
2. Compare latest light-scattering value with previous recorded readings in History.

To directly determine the current level of light scattering, you may use the „Light Scatter Values“ function in Win-AAS.

3. Set PEM voltage to 600 V.
4. Trigger light scatter measurement.
5. Compare currently measured reading with „Value after Factory Setting“ that is displayed immediately above.

7.2.2 Remove Contamination / Clogging

Sample intake tube

1. Perform repeated system purging with different solutions:
   - using 1 mL HNO_3 and 2 mL HCl in 100 mL of distilled water or
   - using identical solution with addition of 0.25 mL of bromide-bromate solution according to EPA 1631 (or work instructions for installation)
2. You may also run a number of measurement cycles instead of system purging.

Another option is to purge the intake tube using reductant ($SnCl_2$ x 2 H_2O).

3. Open the mercur DUO plus window. Change to the tab Parameters.
4. Select **System cleaning / at actions / Cleaning with reductant+acid** in WinAAS program and trigger **system cleaning**.
5. Perform repeated purge cycles of the system using only diluted (e.g. 3%) HCl, until reductant residues have been completely removed from the sample intake tube.
6. Check on the progress of cleaning state by performing blank value measurements (including with longer wait intervals in between).

Intake canula of autosampler

Same as sample intake tube

Reactor group

To remove pockets of clogging or contamination, the reactor group must be detached, opened and cleaned (see chapter „Clean/Replace Reactor” on page 52).

Gas-liquid separator

Visible yellowish encrustation on the inner wall surface of the G-L separator consisting of tin stone should be removed at regular intervals

Deinstall and clean the gas-liquid separator (see chapter "Clean/Replace Gas-Liquid Separator„ on page 51).

5-valve group and gas path

Pockets of contamination along the gas path can be removed by extensive purging with argon.

1. Select **mercur DUO plus / Control**, then turn on **Valve 3** and **Valve 4** in WinAAS program.
2. Let argon flow through “**Dry Section->Cell**“ gas path for at least 30 minutes then let it flow through ”**Gas->Cell**“ cell for another 30 minutes.
3. Check for absence of contamination as described on page 48 and repeat this process if necessary.

Fluorescence cell

Minor contamination

Trigger repeated lamp test cycles in WinAAS program.
The fluorescence cell will be purged with fresh argon for one minute each time.

Major contamination

Deinstall and clean the fluorescence cell (see chapter "Clean/Replace the Fluorescence Cell„ on page 56).

7.3 Maintenance on Demand

7.3.1 Change Fuse

Warning!
Ensure the mercur DUO plus is switched off and the mains unplugged before changing the fuse!

The mains input fuses are located at the rear of the device (see Fig. 6-1) and are marked.

Fuse Number	Fuse Type for 230 V	Fuse Type for 110 V
F1	T 3.15 A/H	T 6.3 A/H
F2	T 3.15 A/H	T 6.3 A/H

7.3.2 Check and Replace Pump Tubes

Caution!
Corrosive liquid hazard! Wash and pump out the tubes before replacing.

Carry out a regular visual inspection of the pump tubes for wear and any changes in shape.

Use the Second Usage Area

The pump tubes for reducing agent and acid have two usage areas. Usually the area between first and second stopper in the tube cartridge is laid in. When this area is worn out by the pump movement, the tube can be laid between the second and third stopper in the tube cartridge:

1. Take out the tube cartridges.
2. Lay the unused section of tube between the second and third stoppers in the tube cartridges.
3. Replace the tube cartridges and press them on.

Replace the sample intake tube

If there is any change in shape on the pump section or irreversible contamination, replace the sample tube as follows:

1. Pull off the sample tube from the canula on the dipping arm.
2. Take out the tube cartridge, remove the sample tube.
3. Unfasten the front plate and fold down.
4. Disconnect the sample tube at the double-valve group and pull through the front plate.
5. Screw on the new sample tube to the double-valve group and put through the front plate.
6. Fold the font plate back up and fasten.
7. Lay the pumping section in the tube cartridge, paying attention to pumping direction (!).
8. Replace the tube cartridge and press it on.
9. Lead the sample tube to the autosampler and stick on the intake canula.

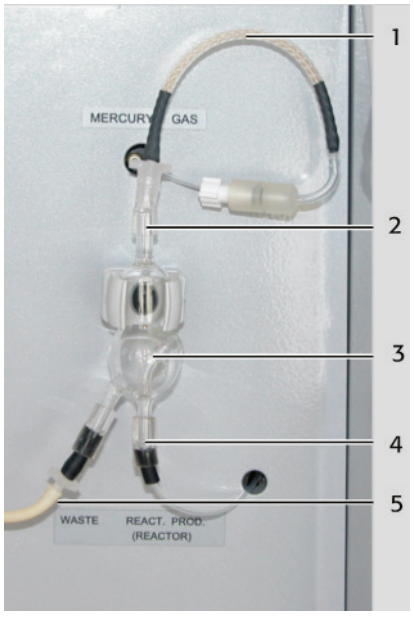
Replace the aspiration tubes for reducing agent and acid

If at least one pump tube shows signs of wear in both pumping sections, replace both tubes as follows:

1. Remove the aspiration tubes from the storage bottles.
2. Take out the tube cartridges, remove the pump tubes.
3. Unfasten the front plate and fold down.
4. Pull off the pump tubes from the double-valve group and from the reactor.
5. Stick new aspiration tubes onto the double-valve group and reactor.
6. Stick the aspiration tubes through the front plate.
7. Lay the aspiration tubes in the tube cartridges, hang the tube cartridges back in and press in place.
8. Place the aspiration tube for acid (from the double-valve group) in the corresponding storage bottle.
9. Place the aspiration tube for reducing agent (from reactor) in the storage bottle.
10. Fold the font plate back up and fasten.

7.3.3 Clean/Replace Gas-Liquid Separator

Try first to remove solid deposits in the gas-liquid separator by cleaning. If this is not successful, replace the separator.



1 Pre-dryer
2 Outlet, gas with mercury
3 Glass bead
4 Reaction product inlet
5 Liquid waste outlet

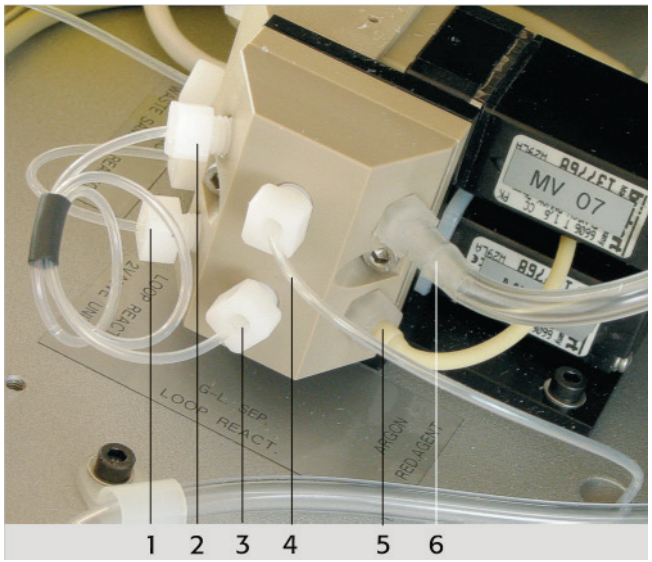
Fig. 7-1 Gas-Liquid Separator

1. Pull off the tubes from the gas-liquid separator:
   - Pumping out tube, bottom left
   - Tube coming from reactor, bottom
   - Gas outlet tube, top
2. Pull the gas-liquid separator out of the clamp.

3. Place separator into an ultra-sonic bath for treatment with diluted NaOH (about 5 pellets in approximately 50 mL of distilled water) for several minutes.
   Typically, this will fully remove any encrustation.
4. Carefully rinse with distilled water and allow drying.
5. Place the cleaned or new gas-liquid separator into the clamp.
6. Stick the tubes onto the nozzles of the gas-liquid separator.
   - Pumping out tube, bottom left
   - Tube from reactor, bottom
   - Gas tube onto the outlet nozzle, top.

7.3.4 Clean/Replace Reactor

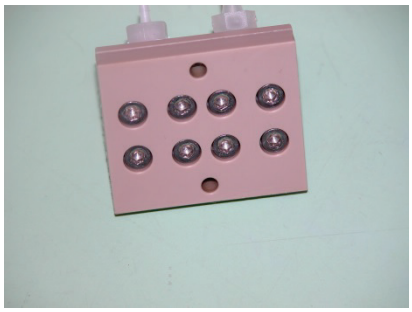
The reactor must be cleaned or replaced when non-reproducible peak signals occur or the peak signals are absent or seriously reduced delivery rates appear.



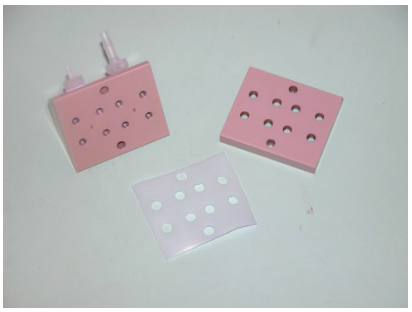
1	Sample inlet (or acid)
2; 3	Connections, tube bridge, reactor tube
4	Reaction products outlet
5	Reduction agent inlet
6	Inert gas inlet

Fig. 7-2 Reactor, Connections

1. Perform system purging in WinAAS program. Do this with all three aspiration tubes drawing in distilled water.
2. Unfasten the front plate and fold down
3. Unscrew or pull off the tubes from the reactor
   - Pump tube for reducing agent (5, Fig. 7-2)
   - Sample/acid tube coming from the double-valve group (1, Fig. 7-2)
   - Tube bridge (2 and 3, Fig. 7-2)
   - Gas inlet tube (6, Fig. 7-2)
   - Tube to gas-liquid separator (4, Fig. 7-2)
4. Unscrew the reactor.
5. Unscrew eight screws in baseplate of reactor group so they can be taken apart into its baseplate, Teflon seal and top part (Fig. 7-3).



Bottom view of reactor group



Top part, Teflon foil and baseplate of reactor group

Fig. 7-3 Reactor Group taken apart

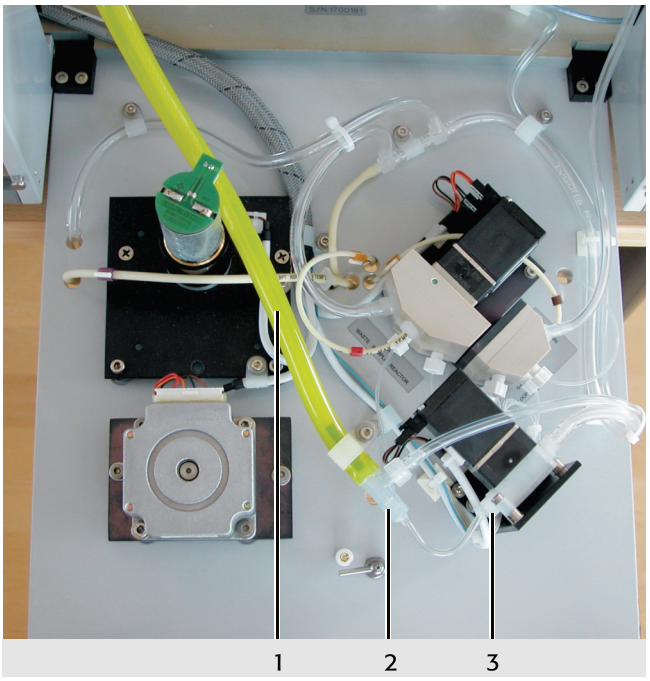
6. Clean the channels in the upper part with a cleaning wire.
7. Clean the threads with a round brush.
8. For cleaning, submerge the top part into an ultra-sonic bath and expose it to 3% HCL for some minutes.
   You may also use pressurized air to remove pockets of clogging inside of ducts.
9. Use a wipe to remove sedimentation (if any) from the Teflon foil.
   To remove spots of Hg-contamination, place the foil into bromide-bromate solution (1 mL in 100 mL of distilled water according to EPA 1631 or work instructions for installation).
10. Rinse top part and foil thoroughly with distilled water, then allow drying. Reassemble reactor group.
11. Install reactor. First screw the reactor together outside, alternating diagonally, then inside – also diagonally. Note: Firmly retighten the baseplate screws, always proceeding **cross-wise**.
12. Screw the tube bridge and screw-in connector into the reactor.
13. Screw on the cleaned/new reactor.
14. Screw the tubes into the reactor or onto the nozzles of the reactor.
    - Pump tube for reducing agent
    - Sample/acid tube coming from the double-valve group
    - Gas inlet tube
    - Tube to the gas-liquid separator
15. Fold the front plate back up and latch.

7.3.5 Replace Membrane Dryer

Replace membrane dryer

The membrane dryer (tube dryer) remains functioning so long as the bubble sensor with downstream valve functions correctly, i.e. does not let moisture in liquid form pass.

If the membrane dryer becomes contaminated, do not attempt to clean it, but replace it once the bubble-sensor is again in a functioning state.



1 Tube dryer
2 T-piece
3 Connection on the solenoid valve of the bubble sensor

Fig. 7-4 Membrane Dryer

1. Unfasten the front plate and fold down.
2. Disconnect the tubes for gas inlet and outlet of the counterflow drying at both T-pieces (2, Fig. 7-4) of the drying tube.
3. Disconnect the tube dryer at the outlet of the single valve (3, Fig. 7-4) and at the 5-valve group.
4. Stick a new tube dryer onto the free end of the single valve and the free connection on the 5-valve group.
5. Stick tubes for gas inlet and outlet of the counterflow drying onto both free T-piece connections of the drying tube. Take note of the counterflow directions.
6. Fold the font plate back up and fasten.

Replace pre-dryer

The pre-dryer is located at the gas outlet of the gas liquid separator (1, Fig. 5-8). It must be exchanged if it does not keep the humidity away from the system anymore. This one is recognizable at the signal of the bubble sensor. The pre-dryer also must be exchanged if the recovery of QC samples is bad or the signal amplitude is too little. Humidity in the fluorescence cell causes quenching.

1. Release hollow-core bolt.
2. Detach hose from gas outlet piece of gas-liquid separator.
3. Screw on new pre-dryer.
4. Slide hose over gas-liquid separator.

7.3.6 Replace Tubes

If the path of the tube from the double-valve group up to the fluorescence cell is contaminated and a longer wash phase with reducing agent and acid as well as gas purge bring no noticeable lowering in the stray light level, the following tubes must be replaced:

- ❑ Tube from the double-valve group to the reactor
- ❑ Reactor tube
- ❑ Tube from the reactor to the gas-liquid separator
- ❑ Tube from the gas-liquid separator to the bubble sensor
- ❑ Tube dryer
- ❑ Tubes between the 5-valve group and both gold collectors
- ❑ Cell tube (from the 5-valve group to the cell)

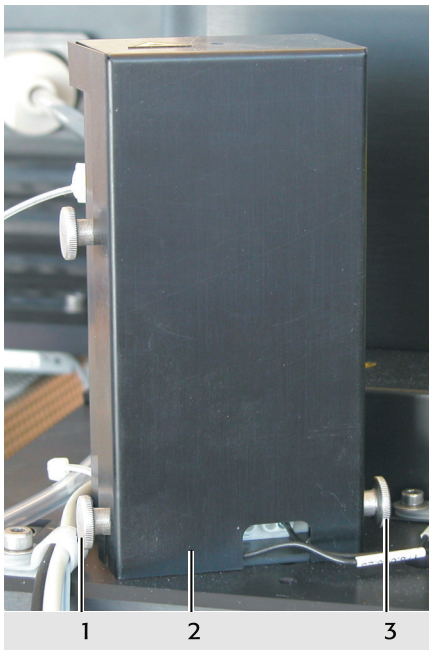
1. Unfasten the front plate and fold down.
2. Screw out the affected tube or pull off from the nozzle.
3. Screw in a new tube with a hollow screw or push onto the nozzle.
4. When all tubes have been replaced, fold up the front plate and fasten.

7.3.7 Replace Mercury Low-Pressure Lamp

When the fluorescence intensity for known standard - and reference solutions distinctly fall off and contamination in the system can be excluded as a cause, then the mercury lamp must be replaced.

There are parts in mercur DUO plus carrying mains voltage!
Switch off the mercur DUO plus, pull out the mains plug.

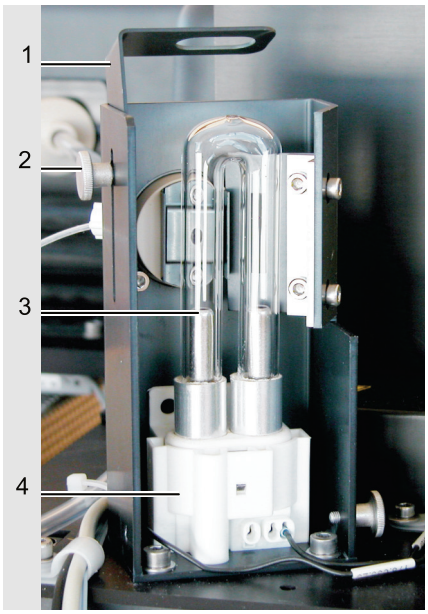
1. Switch off the mercur DUO plus. Pull out the mains plug.
2. Undo the four screws accessible from below at the corners of the instrument (key for internal hex socket 5 mm) and lift off the cover of the device.



1 & 3 Knurled thumb screws

2 Lamphouse

Fig. 7-5 Lamphouse



1 Mech. Hg lamp locking fixture

2 Knurled thumb screw

3 Hg lamp

4 Lamp socket

Fig. 7-6 Lamphouse open

3. Remove cover shield (2, Fig. 7-5), release knurled thumb screw (1 &. 3, Fig. 7-5) to do this.
4. Loosen knurled thumb screws of (2, Fig. 7-6) Hg lamp locking fixture and push fixture (1, Fig. 7-6) up.
5. Pull Hg lamp (3, Fig. 7-6) out of socket.
6. Insert new Hg lamp into socket.
7. Push Hg lamp locking fixture down and clamp fixture.
8. Mount cover shield and clamp shield with knurled thumb screws.
9. Replace instrument cover and screw on from below.
10. Insert the mains plug.

7.3.8 Clean/Replace the Fluorescence Cell

If the stray light level is much higher than normal and cannot be lowered by gas purging, the fluorescence cell must be wet-chemical cleaned or replaced.

There are parts in mercur DUO plus carrying mains voltage!
Switch off the mercur DUO plus, pull out the mains plug.

1. Switch off the mercur DUO plus. Pull out the mains plug.
2. Undo the four screws accessible from below at the corners of the instrument (key for internal hex socket 5 mm) and lift off the cover of the device.

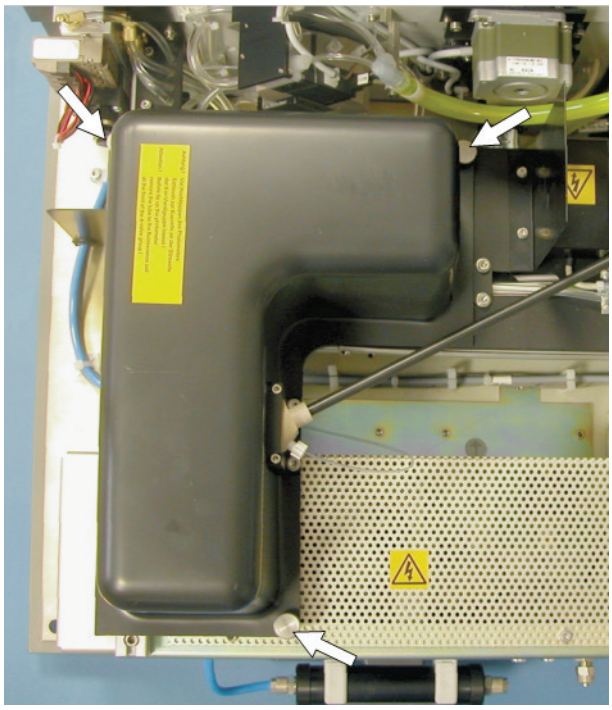
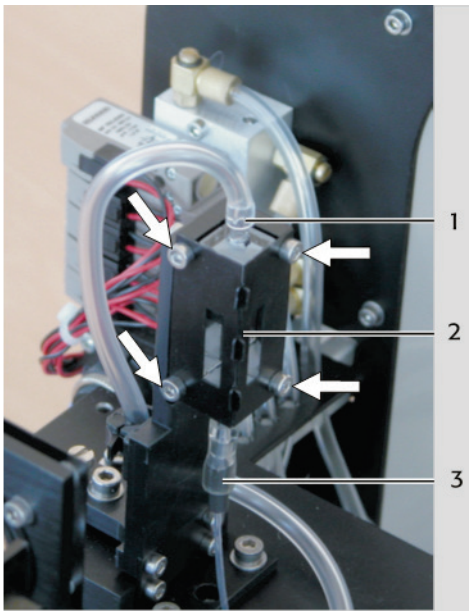


Fig. 7-7 Knurled thumb screws for mech. fixing of photometer top cover

3. Loosen three knurled thumb screws (arrows, Fig. 7-7) that clamp the photometer top cover. Remove photometer top cover (Fig. 7-7).



1 Outlet hose
2 Cell cage
3 Supply hose

Fig. 7-8 Fluorescence Cell

4. Carefully detach hoses (1 and 3, Fig. 7-8) from lower and upper tube piece of cell.
5. Loosen all four Allen screws (arrows, Fig. 7-8) at cell cage (3, Fig. 7-8).
6. Pull the cell upwards out of the holder. Remember to hold the cell **only by its gas terminals** as you do this, in order to protect the cell's glass surfaces.
7. Use warm distilled water with addition of 0.5 g cleaning substrate in 500 mL to clean the cell.
   Use a spray bottle with a suitable tube to force the cleaning solution through the measurement cell (see Fig. 7-9).

Caution!
Do not use aggressive chemicals (such as hydrofluoric acid) for cleaning. Substance of this kind will destroy the surface and reflective coating of the cell.

8. Perform several post-rinse cycles using distilled water.
9. To clean, let clean gas (for example, N_2 or Ar) slowly flow through the cell space, slightly heating the cell at the same time.
   Hold the measurement cell in downward-inclined position, in order to be able to spot a salt film that may be forming in this place (see Fig. 7-9). In this case rinse the cell until no more salt film can be seen.

Cleaning of Cell

Drying of Cell

Fig. 7-9 Cleaning and drying of fluorescence cell

10. Clean (fluff-free) the unmirrored outer surface of the cell.
11. Set the cleaned or new cell in the holder and fix evenly in place.
12. Stick the hoses onto the cell nozzles.
13. Replace the photometer cover and fix in place with the knurled screws.
14. Replace instrument cover and screw on from below.
15. Insert the mains plug.

7.3.9 Replace Active Carbon Filters

The active carbon filter in the waste gas path has to be replaced every one or two years. The active carbon filter at the gas inlet has to be changed preventatively every 5 years at the latest.

A replace of the filter at the gas inlet also can be required if the blank value (with intake tube into air) measured repeatedly is too high.

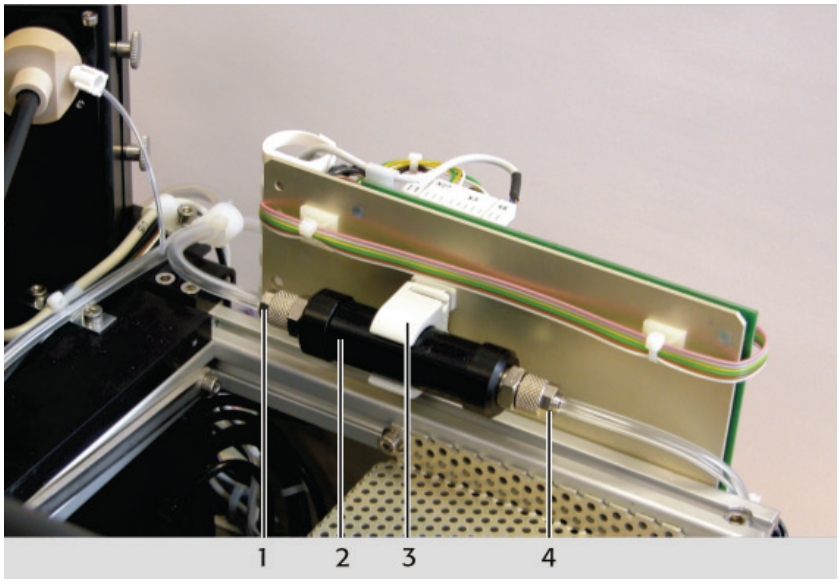
Before Replacement of the filters exclude other contaminations:

- ❑ Choose reagents that are classified as mercury free.
- ❑ Rinse the system with distilled water.
- ❑ Carry out the cleaning steps according to the previous sections (gas liquid separator, reactor, fluorescence cell …).

- ❑ Replace tubes and tube dryers.

Active Carbon Filter in the Waste Gas Path

There are parts in mercur DUO plus carrying mains voltage!
Switch off the mercur DUO plus, pull out the mains plug.



1;4 Hose connectors 3 Holder

2 Active carbon filter

Fig. 7-10 Active Carbon Filter in Waste Gas Path

1. Switch off the mercur DUO plus. Pull out the mains plug.
2. Undo the four screws accessible from below at the corners of the instrument (key for internal hex socket 5 mm) and lift off the cover of the device.
3. Loosen union nuts and detach hoses (1 and 4, Fig. 7-10) from filter.
4. Pull exhausted active carbon filter (2, Fig. 7-10) out of holder (3, Fig. 7-10), then insert new active carbon filter.
5. Reconnect the hoses to the filter.
6. Replace instrument cover and screw on from below.
7. Insert the mains plug.

The active carbon filter adsorbs the mercury in the remaining gas. If you don´t replace the filter, the remaining gas has to be carried to a fume extractor or immediately to atmosphere.

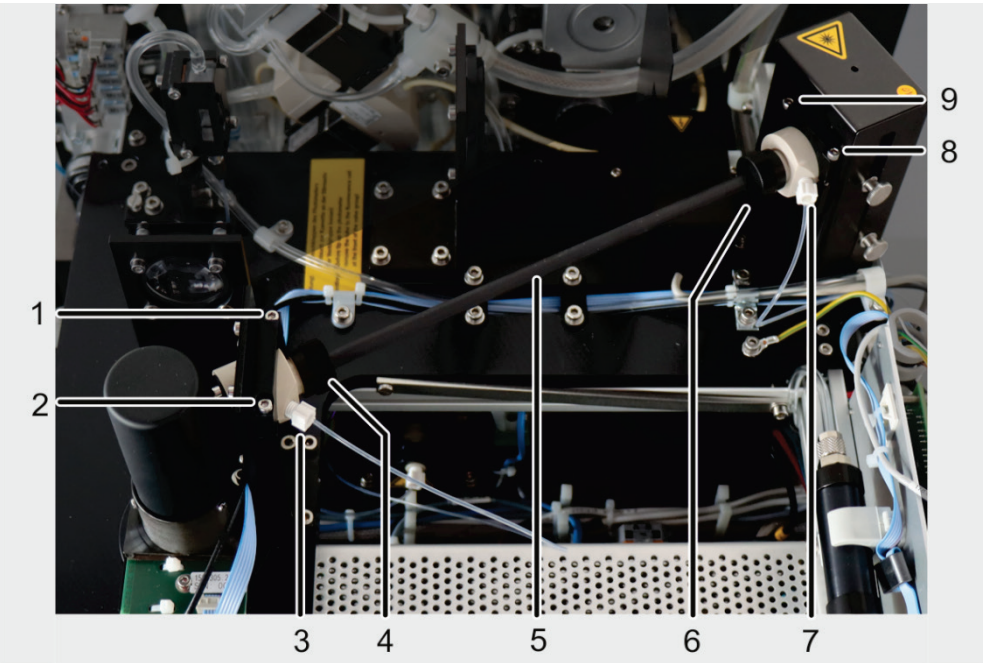
Active Carbon Filter in the Gas Inlet

1. Unscrew the tubes from the filter (2, Fig. 5-10 p.28).
2. Take the used filter out of the holder and snap a new active carbon filter into the holder.
3. Reconnect the tubes to the filter.

7.4 Absorption Module

7.4.1 Clean/Replace the Absorption Cell

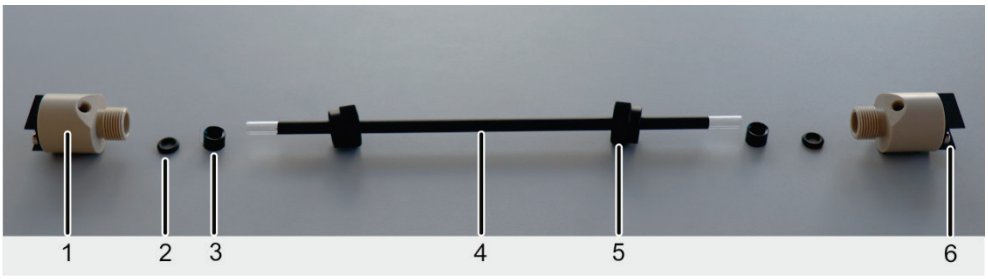
The absorption cell holder is designed for easy removal and replacement of the cell. For cell replacement, unscrew the fixing screws in the screw-mount locations and remove the cup-shaped holder halves at either end of the cell. The cell can then be removed from the top.



1;2	Allen screws	6	Union nut
3	Absorption cell holder with hose connector for gas inlet (at photomultiplier)	7	Absorption cell holder with hose connector for gas outlet (at lamphouse)
4	Union nut	8,9	Allen screws
5	Absorption cell in jacket hose		

Fig. 7-11 Replacement of Absorption Cell

1. Turn mercur DUO plus off. Pull mains plug.
2. Loosen four corner-position screws which are accessible from the bottom (using 5 mm Allen wrench), then take top part off.
3. Loosen knurled thumb screw (arrows, Fig. 7-7, S.57) for clamping of photometer top. Take photometer top off.
4. Turn out hose connectors from the right and the left holder of the absorption cell (3 and 7, Fig. 7-11).
5. Loosen right screws (1,2 and 8;9, Fig. 7-11) to be able to remove right and left cup-shaped holder.
6. Take absorption cell out. Loosen the black union nuts and pull both cell holders off in lateral direction.
7. Clean absorption cell using dilute acid (HCl or HNO_3, 3 %) and distilled water. If necessary, replace absorption cell.



1	Absorption cell holder with hose connector	4	Absorption cell with jacket hose
2	Sealing ring	5	Union nut
3	Sleeve (with conical end)	6	Optical aperture

Fig. 7-12 Absorption cell, disassembled

8. Re- mount the absorption cell: Put the two black union nuts, the sleeves and the sealing rings one after the other on the absorption cell. Orient the conical side of the sleeves towards the sealing rings.
9. Mount both cell holders onto the absorption cell and screw them with the black union nuts. Align the two apertures parallel to each other. Aim both hose connections forward.
10. Place the absorption cell into its designated holder.
    Note: The two holders are not identical. The holder with a quartz glass window (transparent) on the front side faces the photomultiplier. The holder with an optical filter (non-transparent) points to the lamphouse.
    The two apertures should shield the lamp output and the input of the photomultiplier as well as possible. At the same time, the photomultiplier must be able to rotate freely on the swing motion drives.
11. Re-mount right and left cup-shaped holders and tighten holders.
12. Screw hose connectors back into both cell holders.
13. Put on photometer top and screw photometer top on with knurled thumb screws.
14. Mount top cover and screw cover on from the bottom.
15. Insert mains plug.

7.5 Maintenance Work on the Autosampler

7.5.1 Clean Wash Cup

1. Clean wash cup with a swab soaked in alcohol.

Rinse several times thoroughly with distilled and lightly acidic water:

2. In the Window **Autosampler** call up Tab **Function tests**.
3. Select **Pumps / Wash pump**. With **[Start]** start the rinsing of the wash cup.
4. With **[Stop]** stop the pump.

Note
If strongly coloured samples are analyzed, the colours may stain the wash cup.

7.5.2 Wash Mixing Cup (AS-FD)

Should the autosampler be out of operation for longer periods, wash the mixing cup several times with distilled and lightly acidic water before taking it out of operation.

1. In the Window **Autosampler** call up Tab **Function tests**.
2. Pipette acidic water into the mixing cup. Observe volume capacity: 20 mL.
3. Select **Pumps / Mix cup pump**.
4. With **[Start]** start the mixing cup pump and allow it to run until the mixing cup is emptied (noticeable by a distinctive change in the sound).
5. With **[Stop]** stop the pump.
6. Alternatively use the shortcut key **[Wash mix cup]** in the Window **Autosampler**.

7.5.3 Clean after Cup Overflow

If during the process the overflow of the wash cup or the mixing cup (with AS-FD) has over spilled, immediately interrupt the process and clean the device.

1. Stop the measuring process immediately.
2. Take up the liquid with cellulose wadding or cloth. Wipe the surface dry.
3. Washing cup: Ensure that the outlet can be drained, i.e., remove any sharp bends in the draining tube or make sure that the draining tube does not dip into the liquid in the waste bottle.
4. Mixing cup (only for AS-FD): With **[Start]** start the mixing cup pump and allow it to run until the mixing cup is emptied. With **[Stop]** stop the pump (see chapter „Wash Mixing Cup (AS-FD)”).

7.5.4 Clean Dosing Tube (AS-FD)

The Dosing tube (marking „1”) has to be cleaned when the sample is spread out in the tube.

Diluted Acid (HNO_3 / HCl, 10 %) is recommended as a cleaning solution.

1. Fill the diluted acid into the storage bottle for the diluent.
2. Use the shortcut key **[Wash mix cup]** in the Window **Autosampler**. Rinse the system as often as is necessary.

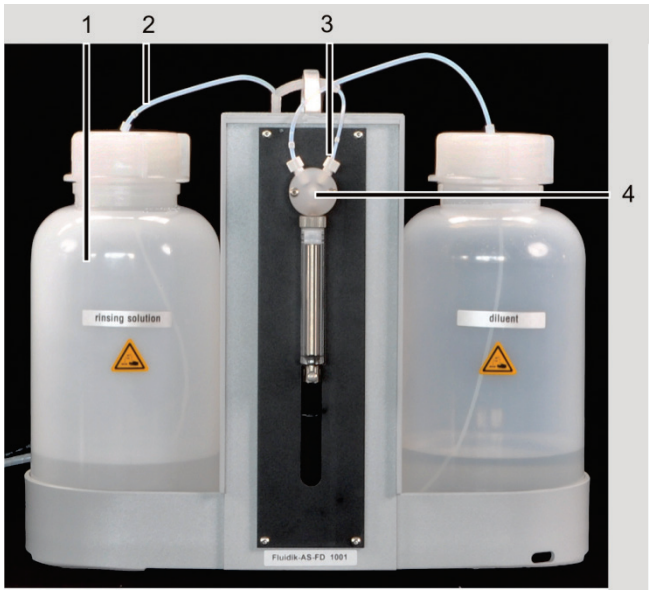
7.5.5 Wash Dosing Unit prior to period of decommissioning (AS-FD)

If salts were added to the diluent, the dosing unit and the dosing tube must be washed with distilled water prior to long periods of decommissioning. Otherwise scaling and blocking may occur.

1. Fill the storage bottle for the diluent with distilled water.
2. Use the shortcut key **[Wash mix cup]** in the Window **Autosampler**. Rinse the system several times.

7.5.6 Replace Tube Set for Diluent and Rinsing Solution (AS-FD)

1. Pull the dosing tube for diluent off the thicker canula at the autosampler arm and feed it through the tube guide disk.
2. Detach the tube for the rinsing solution at the rear of the autosampler (4, Fig. 6-3).
3. Pull the encased tubes out of the attachment lug at the rear of the autosampler.
4. Pull the tube for the rinsing solution off the storage bottle (1 and 2, Fig. 7-13).
5. Unscrew the dosing tube from the valve (3 and 4, Fig. 7-13).
6. Screw the new tube set with dosing tube (marking "1") to the valve.
7. Insert the tube with the marking "2" into the storage bottle for the rinsing solution.
8. Attach the encased tubes with the attachment lug to the rear of the autosampler.
9. Screw the tube for the rinsing solution to the rear of the autosampler.
10. Slide the other end of the dosing tube through the tube guide onto the thicker canula of the autosampler arm.



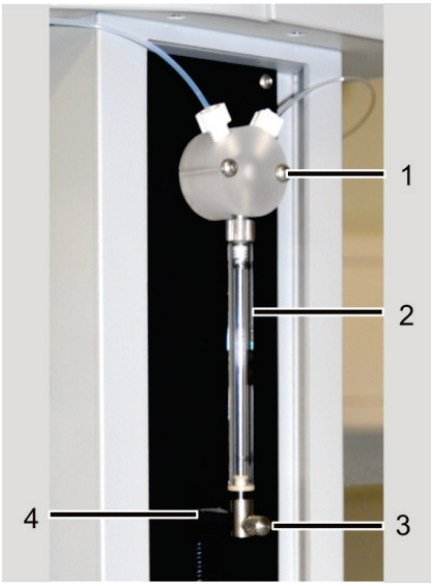
1 Storage bottle for the diluent
2 Tube for diluent
3 Connection of dosing tube (to AS-FD)
4 Valve

Fig. 7-13 Fluidics module of AS-FD

7.5.7 Replace Sample Intake Tube

If there is any change in shape on the pump section or irreversible contamination, replace the sample tube as described in chapter „Check and Replace Pump Tubes” on page 50.

7.5.8 Replace Dosing Syringe (AS-FD)



1 Valve
2 Dosing syringe, consisting of piston and glass cylinder
3 Attachment screw
4 Drive rod

Fig. 7-14 Dosing Unit at AS-FD

1. In the Window **Autosampler,** Tab **Function tests**, enter the pipetting volume 3000µL.
2. Activate the Button **[Take up]**: The piston for the dosing device is moved down (according to the aspirating procedure).
3. Unfasten the attachment screw (3, Fig. 7-14).
4. Unscrew the dosing syringe (2, Fig. 7-14) from the valve and remove it.
5. Screw the new syringe to the valve.
6. Carefully pull the piston down until the eyelet at the piston end is aligned with the hole in the drive rod.
7. Screw the attachment screw for the piston finger tight to the drive rod.
   Caution: Do not apply too much force! The material may be damaged!
8. Activate the Button **[Initialize]**: The piston of the dosing syringe returns to the initial state.
9. Use the shortcut key **[Wash mix cup]** in the Window **Autosampler** to rinse the dosing syringe until all air is removed from the glass cylinder.

7.5.9 Replace Canulas of Autosampler Arm

The canula for aspirating the sample (thinner canula for AS-F and AS-FD) and the canula for aspirating the diluent (thicker canula, AS-FD) have to be replaced if they are clearly contaminated.

1. Pull the tubes from the canulas (only one canula and tube for AS-F).
2. Loosen the fixing screw on the autosampler arm (2, Fig. 7-15).
3. Pull the canula guide upwards and out (3, Fig. 7-15).
4. Introduce the new canula guide with the canulas into the dipping arm and hold in place with the locking screw. Set the canula height for them to terminate 1-2 mm above the wash and mixing cup.

5. Stick the tubes on the canulas as before: sample intake tube from the mercur DUO plus on the thinner canula, dosing tube for the diluent on the thicker canula.

1 Sample intake tube and dosing tube
2 Fixing screw
3 Canula(s) with guide

Fig. 7-15 Replacement of Canulas

8 Instructions on Methods

8.1 Important Note Regarding Sample Concentration

In cases of extreme contamination – for example, resulting from false dilution of reference solutions or samples – the cold vapour system may become unfit for further ultra-trace determination jobs.

Procedures for cold vapour generation from liquid samples are among the strongest detection methods applied in ultra-trace determination of elements using atom spectrometry. Their detection power ranges from only a few ng/L to a few sub-ng/L in some cases. In some other cases, blank values in reagents and vessels impose restrictions regarding detection power. All reaction paths and valves have been optimized for this operating range in terms of chemical stability and cleanness. However, if solutions in the mg/L range are allowed to flow through the reaction unit, there may be contamination inside of hoses, valves or reaction vessels of a kind that cannot be removed even by intensive flushing/purging.

8.2 Notes on Operation Mode

For each of the six operation modes

- ❑ Without enrichment
- ❑ Without enrichment, with FBR method
- ❑ With enrichment
- ❑ With enrichment and FBR method
- ❑ Enrichment with reloading
- ❑ Enrichment with reloading and FBR method

is stored as a complete dataset in the method memory and can cope with many measurement tasks. These datasets encompass operation times (run times), gas flows, pump speed, integration and AZ time, smoothing and statistical parameters – amongst many others.

Sample solutions with high acid content or with components which release fluorescence-extinguishing gases such as hydrogen, oxygen or nitrogen on reacting with stannous chloride must be measured with enrichment.

The FBR method (fast baseline return) is recommended when the peak value of the fluorescence signal is evaluated. For this, a fast signal break-off after passing the fluorescence peak by purging the cell with a greater gas flow is justified.

The system wash can

- ❑ Take place after each sample
- ❑ Be set as action in the sample table
- ❑ Only be carried out when the concentration is exceeded.

The wash can be reduced in terms of the use of acid and reducing agent as well as of the particular wash time and the soaking time of the reducing agent.

8.3 Importance of Stray Light Measurement

Additional stray light measurements outside the measurement routines are used as an indicator that stability of the mercury low-pressure lamp after running-in is adequate and as a check on system contamination.

The stray light value of the unused system at 600 V PMT voltage is stored in **Mercur / Int.-Parameter/Level** as **ex-factory setting** and is available at any time as a comparison. It is given in percent of the maximum ADU value and is a maximum of 40 % depending on the characteristics of the instrument (cleanliness of the fluorescence cell, sensitivity of the photomultipliers)

The current stray light level can be checked at any time with **Mercur / Int.-Parameter/Level / Measuring**; it is entered Current Value. If the value at the moment is twice as high as the ex-factory setting, the system is contaminated. The system must be thoroughly washed, replacement of components may even be necessary.

Under **Mercur / Int. Parameter / Level / History**, the current stray light value is entered in a chart; the x-values are the measurement days. If several stray light measurements are made on the same day, the previous value of the same day is overwritten so that at the end of the working day it is always the last value measured that is entered in the chart. The chart shows the variation of stray light value with time.

The mercury lamp is ready for carrying out measurements about 10 minutes after being switched on. The lamp can be tested under **Mercur / Int.-Parameter/Level / Lamp Testing** , in that a repeating stray light measurement in the stationary system at 600V PMT voltage over 60 x 1 sec is triggered. The first stray light value is compared with the last one. If the deviation is <0.2 %, the lamp is taken as run-in and the LED lights up green.

8.4 Reagents

Use only stannous chloride and concentrated hydrochloric acid with proven low mercury content in preparing the reagents for the mercury analysis.

You can further lower the mercury content of your reagent preparations by „blowing out”: Feed mercury-free argon (120 L/hr, for 30 minutes – EN 13506 standard) into the liquid down as far as the floor of the vessel.

Stannous chloride solution is relatively unstable under the influence of oxygen. Extend the storage life of the reducing agent solution by storing it in gas-tight bottles (with screw cap).

8.5 Cups for Samples and Special Samples

For the mercury ultratrace analysis, cup materials are required that are proven for long life, for example made of borosilicate glass, quartz glass or FEP/PFA.

Clean the cups very thoroughly before use.

Clearly mark the cups. Always use the same cup for the same purpose (standards, blank solution, QC samples).

9 Waste Disposal

It is mostly liquid waste that accumulates in fluorescence spectrometry. This contains metal ions or heavy metal ions, but mostly various mineral acids which are used during sample preparation. For safe disposal of this waste, all solutions must be neutralized, for example with a dilute sodium hydroxide solution.

The neutralized waste must be brought to the appropriate waste disposal center for expert disposal according to the appropriate legal guidelines.

Used active carbon filters in the mercur DUO plus contain mercury. Dispose of these as poisonous waste according to the legal and local regulations.

The mercur DUO plus can be returned to Analytik Jena for proper disposal. Please contact the customer service department.

10 Terminology

Analysis line	A spectral line determined by a set of analysis instructions.
Analyte	The element to be defined.
AZ	Autozero for the flame technique
Detection limit	The mass (concentration) of the element to be analyzed, which can be detected with a preset confidence level.
FBR Method	Fast baseline return. Process for the fast return of the measurement signal to the baseline.
Methods	A method contains all parameters which are required for analysis of samples of a specific element, i.e., spectrometer, atomizer, calibration, sample, autosampler and QC settings, if necessary, also the settings for the QC charts and the results windows (provided these parameters have been considered in the method). Methods can be saved and reloaded. When changing from one method to another, all WinAAS settings may be changed over directly to a new analysis task.
Quenching effect	Fluorescence extinguishing quality
PMT	Photomultiplier
Sample solution	Solution which originates after treating the sample to be analyzed according to the analysis instructions.
Statistical series	For calculating the statistical accuracy of an analysis, the individual sample is analyzed for the current element several times in a row. This sample analysis series is defined as a statistical series in this manual.
Stock solution	Solution of a suitable composition (diluent, acid type, acidic content, etc.) which contains the analyte in high and known concentrations. The stock solution is used for making standard solutions.

11 Index