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Operating Manual

HS 50

Mercury/Hydride System

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Contents

1 Safety notes

For your personal safety and for a trouble-free and safe operation of the HS50, read this chapter carefully before starting up the device.

Observe all safety notes given in this manual and all messages and notes displayed by the control software on the screen.

1.1 Symbols used in this manual

The following symbols are used in this manual to refer you to warnings and special advice:

Warning!

This symbol and the cue, "Warning", indicate a serious risk to life and limb, which may arise if the warning is not followed correctly.

Caution!

This symbol and the cue, "Caution", indicate a hazard to the instrument or instrument system, which may arise if the warning is not followed correctly.

Warning!

Hot surface!

Warning!

Dangerous electric voltage!

1.2 Intended use

The HS50 may only be used in combination with an atomic absorption spectrometer from Analytik Jena. Any departure from the intended use described in this manual will lead to restrictions in warranty and manufacturer's liability in the case of damage.

Non-observance of the safety notes given for the use of the HS50 is regarded as departure from intended use. Safety notes are given in particular on labels on the device, in Section 1.3 "Safety instructions" p. 6, and in the description of the required steps of operation.

1.3 Safety instructions

Local regulations

Observe the local safety regulations relevant to the operation of the device (e.g. occupational health and safety regulations, accident prevention regulations, environmental protection regulations).

References to potential hazards do not replace the occupational health and safety regulations to be observed.

Personnel

The HS50 may only be operated by qualified personnel who have received additional training for this type of work, which includes imparting the knowledge contained in this manual and that of the AAS device.

Installation and initial start-up

The HS50, if delivered in combination with the AAS device, is installed and started up by service technicians employed with or authorized by Analytik Jena. If the HS50 is retrofitted, it may also be installed and started up by the user. In this case, it is of particular importance that the user observes all relevant safety regulations! Any unauthorized tampering with the device puts the user at risk, endangers the functional safety of the device, and restricts the warranty.

Safety devices

Take care to ensure that the safety devices of the HS50 are always available and operative.

Operation allowed only with 50mm-slot burner and air/acetylene flame

Operate the HS 50 only with a 50mm-slot burner with air/acetylene flame. The operation with **nitrous oxide/acetylene flame is not allowed!**

Operating materials, dangerous substances

The operator is responsible for the selection of the substances used in the process and for their safe handling. This applies in particular to radioactive, infectious, toxic, caustic, combustible, explosive and other dangerous substances.

Make sure to observe the local regulations and guidelines when handling dangerous substances.

The operator is responsible for the collection and proper disposal of waste.

Always observe the warnings and advice given on the labels.

Use only labeled vessels, protective goggles and rubber gloves for handling the substances.

When used in combination with the AAS device, the HS50 may be operated only under an active **gas exhaust system**.

Cleaning with hydrofluoric acid and concentrated hydrochloric acid must be carried out in a **fume cupboard**.

When handling hydrofluoric acid and concentrated hydrochloric acid, make sure to wear a **rubber apron, rubber gloves and a facemask**.

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

Caution! Sodium tetrahydridoborate ($NaBH_4$) is strongly corrosive, hygroscopic and, in solutions, extremely aggressive. Avoid dripping and splashing of reductant solution.

Handle **biological samples** in compliance with local regulations for the use of infectious material.

Operation of pressurized gas cylinders and gas plants

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

The operation of pressurized gas cylinders and gas plants requires that the relevant local safety regulations and guidelines be fully complied with.

The operator must ensure that the type of connector used at the outlet side of the gas pressure regulators meets the relevant national requirements.

High-pressure tubes and pressure reducers may only be used for the gas for which they have been approved.

The operator must run monthly safety leak tests on all gas supplies and gas connectors including those on the device in order to detect any drop in pressure on pressurized, closed systems and supply lines. Leaks must be located and eliminated immediately.

High temperatures

High temperatures are generated by heating of the cell unit. Consider that the unit needs a cool-down time of one hour!

Do not touch the hot components during or immediately after the measurement.

Allow for a sufficient cool-down period before servicing or replacing the atomizer system.

Keep combustible materials away from the cell unit.

Cleaning and maintenance

Except for the operations described in Chapter 8, “Care and maintenance“, the HS50 may be opened and serviced only by service technicians employed with or expressly authorized by Analytik Jena. Non-observance involves the risk of misadjustment or damage of the device.

The HS60A/HS60 may be cleaned externally only with a slightly moistened, **not dripping** cloth.

Generation of hydrogen in hydride reactions

When sodium tetrahydridoborate reacts with the acid sample solution, hydrogen is liberated. The generation of hot, explosive hydrogen-air mixtures in the cell must be ruled out. The complete gas supply line from the reaction vessel to the cell outlet must be kept free of oxygen. To this end, take the following measures:

- Do not remove the reaction beaker during the reaction and measuring periods.
- Always close the cells gas-tightly with the windows. Replace the damaged cell even if it only shows minor chipping at its end faces.

Foaming in hydride and Hg cold vapor technique

If the sample is foaming strongly add a few drops of a defoaming agent, such as the following:

Dow-Corning DB110A, silicone defoaming agent and octanol

Determine the foaming of unknown samples in a test run, in which the reaction beaker is to be held under the pipette tip.

If, in too vigorous reactions, foam is carried along to the quartz cell, immediately stop the measurement process.

2 Techniques and overview of Hg / hydride systems

2.1 The hydride technique

The hydride technique allows the matrix-free determination of the hydride-forming elements As, Bi, Sb, Se, Sn and Te. It makes use of the fact that hydrogen, which is liberated when sodium tetrahydridoborate ($NaBH_4$) used as reactant reacts with the weakly to strongly acid sample solutions, forms gaseous metal hydrides with the metal ions present. The metal hydrides are conveyed by argon (carrier gas) and by liberated hydrogen to the heated quartz cell, where they are decomposed in steps by impact processes with gas particles and the silica glass wall at temperatures of 850°C to 1000°C (depending on the element) until free metal atoms have been generated. These absorb the primary radiation at the resonance line.

The advantage of hydride technique is that spectral interferences are virtually ruled out because only the element to be determined enters the atomizer as gaseous metal hydride.

2.2 The cold vapor technique

The cold vapor technique is used for the determination of mercury. In this technique, tin(II) chloride ($SnCl_2$) is used as reactant beside sodium tetrahydridoborate ($NaBH_4$). The reaction of the reactant with the acid sample solution directly leads to the liberation of atomic Hg vapor, which is carried by argon gas to the quartz cell. The free Hg atoms absorb the primary radiation at the resonance line. Heating of the cell from room temperature to 150°C reduces humidity-induced background interference.

2.3 The HydrEA technique

The HydrEA technique is the combination of the hydride or Hg cold vapor technique with the graphite-furnace technique. This technique allows the highly sensitive selective determination of the hydride-forming elements As, Bi, Sb, Se, Sn, and Te as well as Hg with the electrothermal atomizer.

The Hg/hydride system generates the gaseous metal hydrides or the atomic Hg vapor, which are conveyed by the argon carrier gas via the MPE 60 Micropipetting Unit to the graphite furnace, where they are enriched on the iridium-coated standard tube for wall atomization at a pre-heating temperature of 300°C. The metal hydrides or Hg atoms deposited on the precious metal iridium are atomized at 2,100°C or 800°C; the produced atomic vapor cloud absorbs the primary radiation at the resonance line of the element to be detected.

2.4 Overview of Hg / hydride systems

The range of Hg/hydride systems available extends from the most simple batch system for users with small sample batches and low performance requirements to the fully automatic continuous-flow mode device with batch system.

HS 50:	Simple batch system with pneumatic operating principle. The quartz cell is heated by an acetylene-air flame.
HS 55:	Batch system with electrically heated cell unit, but without Hg enrichment unit. The reductant used is metered by a single-channel peristaltic pump.
HS 55A:	Same as HS55, but with gold collector for the enrichment of Hg
HS 60:	Hg hydride system for continuous and batch mode with electrically heated cell unit and automatic gas path selector, but without Hg enrichment unit
HS 60A:	Same as HS 60, but with gold collector for Hg enrichment

For the essential modules such as the cell unit, the control circuit board, the batch module, the single-channel peristaltic pump and the Hg enrichment unit, an optimized standard solution is available for the respective device models.

The Hg / hydride systems can be used for the techniques described above independent of the scope of equipment.

2.5 The HS50 Hg/hydride system

Fig. 2-1 HS 50 installed in novAA 300

The HS 50 Hg/hydride system is a purely pneumatically operating batch system for manual operation. The reductant is conveyed pneumatically; the quartz cell is heated by the flame.

The HS50 is designed for users with small sample batches and moderate demands on the reproducibility of the measurements (around 5%).

The HS50 consists of the batch unit and the cell holder with quartz cell.

The batch unit is hung up in the flame sample compartment. The cell holder is attached to the 50-mm single-slot burner. The quartz cell is heated by the air/acetylene flame for the determination of the hydride-forming elements.

The batch module and the dispensing bottle for the reductant are located at the bottom of the batch unit and well accessible.

The HS 50 is time-controlled in a simple way by AAS software.

3 Specifications

Techniques:	Hydride technique Hg cold vapor technique without enrichment	
Operating modes:	Discontinuous flow (batch mode)	
Detectable elements:	As, Bi, Hg, Sb, Se, Sn, Te	

Reagents

Reductant (R):	Sodium tetrahydridoborate ($NaBH_4$) with sodium hydroxide (NaOH) at a ratio of 3:1 Tin(II) chloride ($SnCl_2$) as alternative to Hg determination
Approximate concentration values:	$NABH_4$: 1% / 0.33% $SnCl_2$: 5%

Main functional modules

Reaction unit	Batch module: PTFE beaker with tapered bottom	
Dispensing bottle	300 mL	
Cell holder	Fitted to 50-mm single slot burner	
Quartz cell	Length: 140mm, waisted in the middle section ID 16 / 8 mm with detachable quartz windows	

Heating: Air/acetylene flame

Hydride formers	Acetylene/air ratio	0.15
	Temperature	940 °C
Mercury	Acetylene/air ratio	0.09
	Temperature	Room temperature or low-fuel flame

Inert gas: Argon

Purity	At least 99.999Vol%	
Inlet pressure	3 - 6 bar	
Operating pressure	0.5 bar	
Gas flows	F1 = 15 L/h F2 = 12 L/h	(TRANSPORT GAS) (PURGE GAS)

Ambient conditions

Corrosion protection:	Device is corrosion-proof against the samples to be analyzed
Operating temperature:	+10°C ... +35°C
Humidity:	Max. 90% at +30°C
Storage and transport temperature:	-40°C ... +50°C according to DIN 58390-2

Dimensions (W x H x D) [mm]	Batch unit	270 mm x 210 mm x 190 mm
	Cell holder	160 mm x 120 mm x.50 mm
Weight:	Batch unit	2 kg
	Cell holder	0.25 kg

Standards and directives	Protection Type	The casing of the HS50 provides protection acc. to IP44.
	Device safety	The HS50 complies with the standards IEC61010-1 and IEC61010-2-061.
	EC Directives	The HS50 was produced and tested in compliance with the following EC directives: 73/23/EEC and 89/336/EEC

4 Installation and transport conditions

In general, service technicians employed with or authorized by Analytik Jena will install the Hg/hydride system together with the AAS device. If the hydride system is supplied later, it may also be installed by the operator's personnel.

The operator is responsible for everything that is not included in the scope of supply, but necessary for the operation of the hydride system. The operation requires definite local utilities and supplies. Therefore, carefully read the Chapter "Installation Requirements" of the user's manual of your AAS device.

Caution! Corrosive substances!

Before any relocation of the device, purge all tubes thoroughly to ensure that neither sample liquids and reductant solutions or acid can leak from the aspirating tubes, nor residual liquids from the waste tube. The above-mentioned liquids are aggressive and attack clothing.

5 Function and design of the HS50

5.1 Operating principle

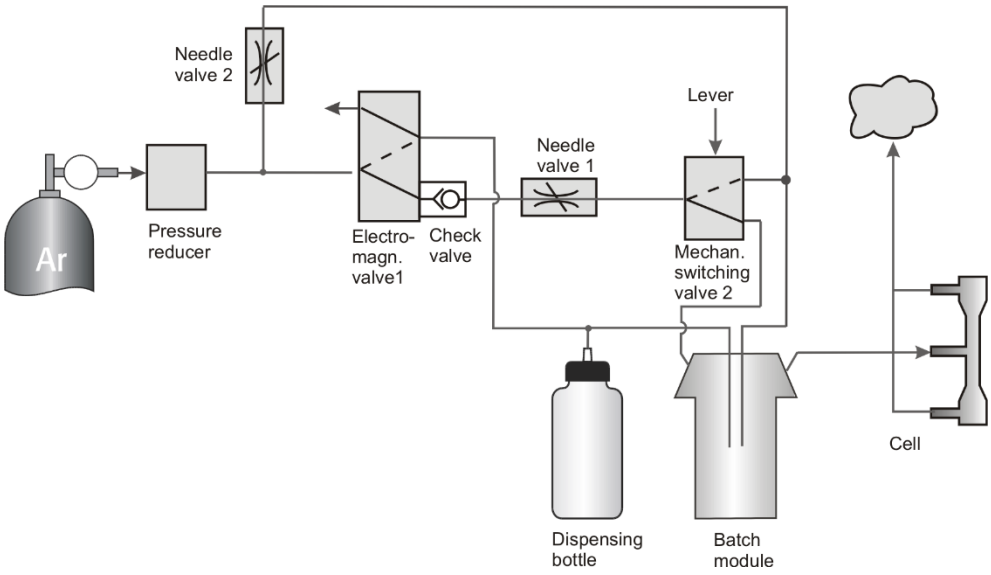


Fig. 6-1 Functional diagram of HS 50

In general, the HS60/60A works with sodium tetrahydridoborate ($NaBH_4$) as reductant; for Hg determination it is also possible to use tin(II) chloride ($SnCl_2$). The carrier and purge gas used is argon.

As soon as the argon supply is opened, there are two gas flows through the device:

Gas flow F1 "TRANSP. GAS"	15 L/h as purge and transport gas flow through the reaction beaker
Gas flow F2 "PURGE GAS"	12 L/h through the metering tip of the batch module to the bottom of the reaction beaker supporting the reaction.

The gas flows are fixedly adjusted by needle valves.

The sample is pipetted into the reaction beaker (max. 30 mL), which is clamped in the head of the batch module.

The reaction beaker is purged free of air by an argon flow. As soon as the electromagnetic valve is energized, it will switch and thus allow flow F1 to flow into the dispensing bottle. There, a pressure is built up pressing the reductant into the beaker. The reaction liberates gaseous metal hydride or atomic Hg vapor. These are conveyed into the quartz cell by the argon flow and hydrogen, which is liberated as well. If the valve is no longer energized, it will return to its initial state. Then, F1 will flow again through the reaction beaker and purge it free. At the same time, the dispensing bottle is aerated and the reductant flow breaks off.
After the measurement procedure, the reaction beaker is to be removed, purged and charged with the next sample.

Switching to $SnCl_2$

When using $SnCl_2$ as reductant for the determination of Hg, it is necessary to switch the manual valve to position "$SnCl_2$". In this position, gas flow F1 is forced through the metering tip to the bottom of the reaction beaker in addition to F2. Both gas flows are bubbling through the sample supporting their reaction with $SnCl_2$.

5.2 Main functional modules

5.2.1 Batch module

The batch module consists of:

- Head with:
  - Gas supplies: “TRANSPORT GAS“ (F1 = 15 L/h) and “PURGE GAS“ (F2 = 12 L/h)
  - Gas outlet “TO TUBE“
  - Flange gasket for reaction beaker
  - Metering tip
- Reaction beaker with tapered bottom for sample volumes of 1 to 30 mL.

Reductant and gas flow F2 are led through the metering tip down to the bottom of the reaction beaker. The reaction with the sample starts from the bottom; it is accelerated by the liberated reaction gas and gas flow F2. Gas flow F1 enters the reaction beaker at the top and serves for conveyance.

5.2.2 Dispensing bottle

If screwed on, the 300-mL dispensing bottle for the reductant is closed gas tight. When argon is introduced into the bottle, an overpressure builds up, which forces the reductant through the metering tube into the reaction beaker.

5.2.3 Pneumatic system

The pneumatic system consists of:

- Pressure reducer for the adjustment of the operating pressure
- 2 needle valves for limiting gas flows F1 and F2
- Electromagnetic valve 1: Switches gas flow F1 from batch module to dispensing bottle and vice versa and aerates the dispensing bottle
- Mechanical switching valve 2 with lever: Serves to switch gas flow F1 to the metering tip in Hg determination with $SnCl_2$.

5.3 Measurement requirements

Caution! Use air/acetylene flame!

Only use the air/acetylene flame of the 50-mm single-slot burner for heating the cell.

1. Under "AASini" and "Available techniques", select the "HS50" option. ("AASini" becomes accessible by simultaneously pressing "ALT" and "." while the starting screen is being displayed.)
2. The hydride forming elements are determined with the cell being heated.
3. It is recommended to use an acetylene/air ratio of 0.15 for the flame. If the acetylene/air ratio is > 0.16, the cell already starts getting sooted on the bottom. The soot deposits hinder heat transfer.
4. **Caution!** To ignite the flame, make sure to remove the cell holder with the cell from the burner. Then, while the flame is burning, attach the cell holder quickly to prevent the flame sensor from responding because of the interruption of flame emission.
5. Hg determination is performed at room temperature or with a low-fuel flame. For the operation at room temperature conditions, burner, cell holder and cell must have cooled down.

5.4 Measurement procedure

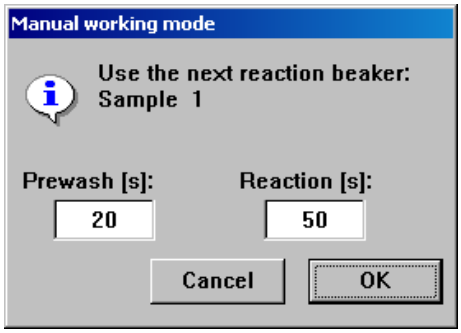
The AAS device must be run in flame mode with peak area or peak height integration. Autosampler and injection switch are deactivated. The integration time selected must be long enough to ensure that the total signal is captured. A delay can be included in the process before, if necessary.

The measurement process comprises the following sections: Purging – zero adjustment – reaction/integration.

During the purge period, air is removed from the reaction beaker. The purging step is skipped in Hg determination, as the argon flow already purges Hg from the sample.

During the reaction period, the reactant is forced into the reaction beaker. Reaction time and integration start at the same time.

On starting the measurement process by "Start Abs", "Start Conc." or "Measure row", the following window will appear:



In this window, you can freely select purge time and reaction time. For Hg determination, the purge time must be set to "0". After having positioned the new reaction beaker as prompted, the operation must be immediately confirmed by a click on [OK], as the argon flow is already purging the beaker. The purge time is counted down in the window.

The purging process is followed by zero adjustment over the AZ time entered under "Integration".

When this has been done, the electromagnetic valve switches, thus releasing the transport of reductant. At the same time, the integration time is started and the signal curve recorded.

When the reaction period is over, the valve switches back, thus stopping the reductant flow.

The measurement process is finished, when the integration time is over and the signal has dropped again to zero level.

Recommended settings:

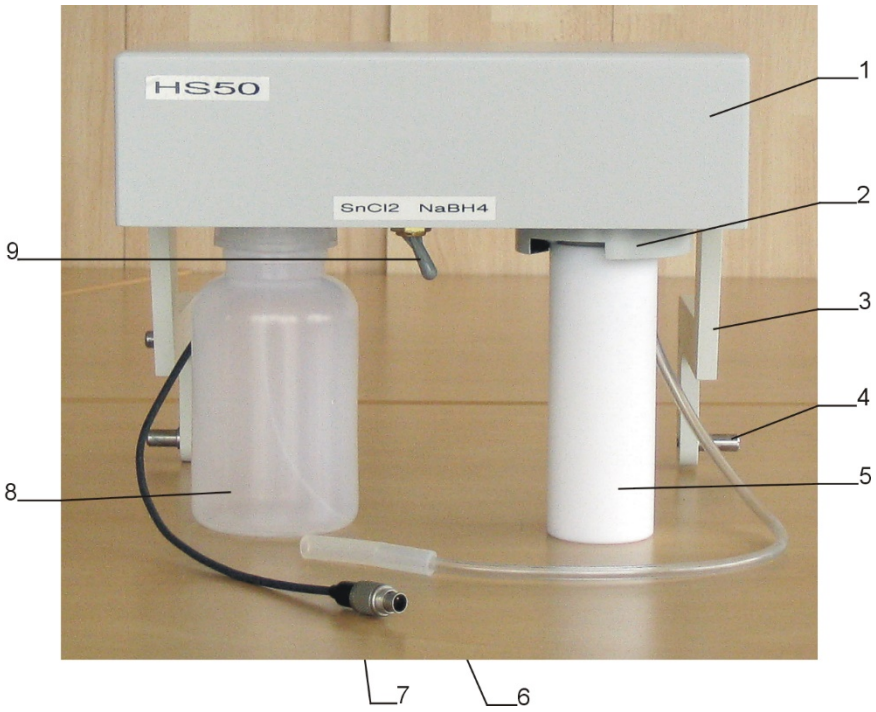
Integration type	Integral value
Smoothing	Golay-Sawitzky with 25 points
Integration time	45 s (Te: 25 s)
AZ time	2 s
Autosampler	No
Injection switch	Off

Hydride parameters:

Element	Purge time	Reaction time	Conc. $NaBH_4$	Acid
As	40 s	8 s	1%	3% HCl
Bi	15 s	5 s	1%	3% HCl
Hg	0	5 s	1%	3% HNO_3
Sb				
Se	40 s	10 s	1%	3% HCl
Te	30 s	15 s	1.5%	3% HCl

6 Installation and start-up

6.1 Installation of batch unit



1	Cover	6	Gas tube to quartz cell
2	Bayonet mount with reaction beaker	7	Cable with two-pole connector
3	Hook-up angle plate	8	Reductant dispensing bottle
4	Hook-up bolt	9	Reductant switching lever
5	Reaction beaker		

Fig. 7-1 HS50 batch unit

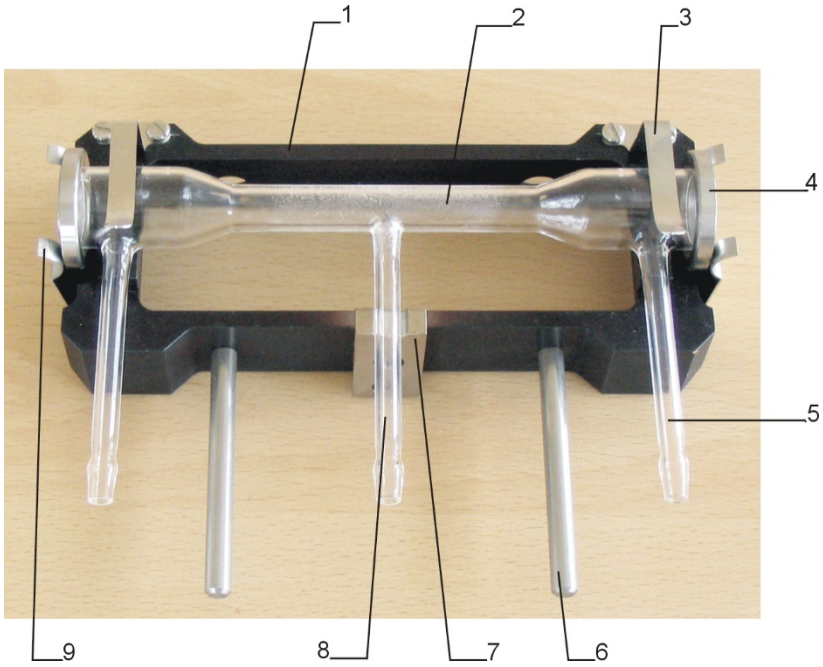
1. Hang up batch unit in flame sample compartment.
2. Plug cable of batch unit onto the two-pole connector "SFS 6" of the injection switch in the sample compartment:

novAA 300	Left-hand sample compartment wall
novAA 400	Swivel arm
Zeenit 700 / contrAA® 300 / contrAA® 700	Right-hand sample compartment wall

3. Connect the argon tube on the bottom of the batch unit.
4. Plug the gas tube to the cell onto the middle tube connector of the cell.
5. Fill the dispensing bottle with reactant solution:
   $NaBH_4$ for hydride formers and mercury
   $SnCl_2$ as alternative reductant for mercury
   Caution! Avoid changeover between $NaBH_4$ and $SnCl_2$.

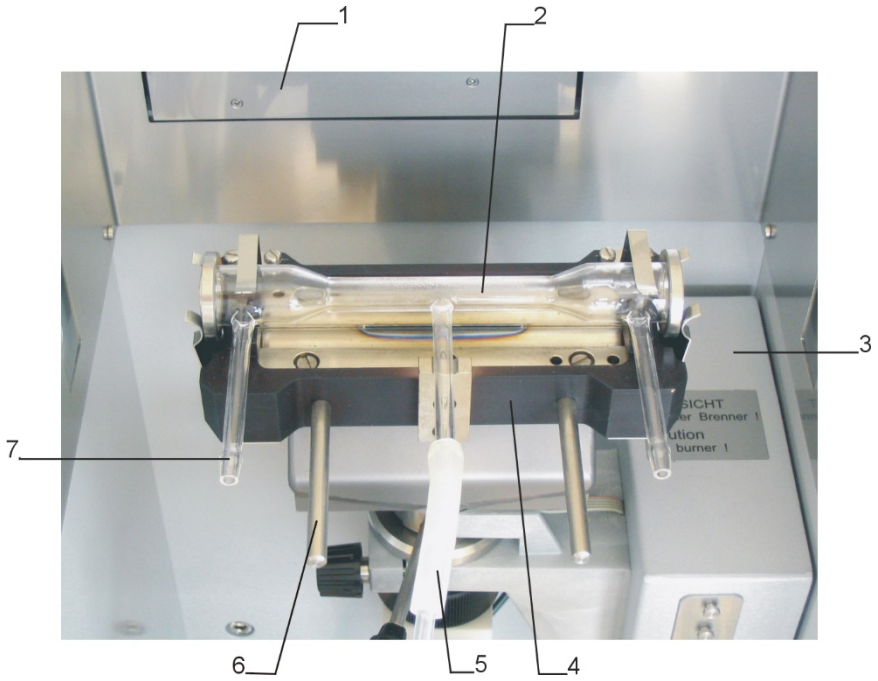
6. **For Hg determination with SnCl2 used as reductant:**
   Make sure to switch the lever on the bottom of the unit from $NaBH_4$ to $SnCl_2$.

6.2 Completing and installing the cell holder



1	Cell holder	6	Handle of cell holder
2	Quartz cell	7	Support for middle cell connector
3	Cell body retaining clip	8	Inlet connector (middle cell connector)
4	Mount with quartz window	9	Window mount retaining clip
5	Outlet connector		

Fig. 7-2 Cell holder with cell



1	Ignition arm in sample compartment	5	Gas tube from batch module
2	Quartz cell on cell holder	6	Handle of cell holder
3	Vertical adjustment	7	50-mm single-slot burner
4	Cell holder		

Fig. 7-3 Cell holder attached to burner

1. Put the quartz cell into the cell holder and secure it in position with the retaining clips.
2. Plug the mounts with quartz windows onto the cell ends and secure them in position with the corresponding retaining clips.
3. Put the 50-mm single-slot burner onto the burner neck and clamp it.
4. For the determination of hydride formers:
   Ignite the flame.
5. Attach the cell holder with the quartz cell to the burner.

7 Care and maintenance

7.1 Safety notes

Do not carry out any care and maintenance work on the HS50 other than that specified in this chapter.

The device may be repaired only by service technicians employed with or authorized by Analytik Jena.

When you do any maintenance, observe all guidelines, standards and safety advice given in Chapter 1 “Safety notes”.

To ensure proper and safe functioning of the HS50, it should be checked once a year by Technical Service of Analytik Jena.

Only use spares that have been supplied by Analytik Jena. Laboratory parts required for routine operation can be ordered from Analytik Jena.

7.2 Daily maintenance after conclusion of measurements

1. Rinse the metering tube with deionized/redistilled water or diluted hydrochloric acid. To this end, immerse the tube in the bottle containing the wash solution and start the procedure. Finally purge the tube until it is empty.
2. Rinse reaction beaker and metering tip using deionized/redistilled water or diluted hydrochloric acid.
3. Store the reductant solution in the refrigerator.

Stability	$NaBH_4$	2 - 3 weeks
	$SnCl_2$	3 - 7 days

7.3 Inspecting, cutting and replacing the metering tube

1. Loosen the clamp screw on the batch module and pull out the PTFE metering tube.
2. Inspect the tube ends. Cut the tube end off if it shows crystalline deposits.
3. Inspect the entire tube. Install a new PTFE tube if the used tube shows creases and sections with restricted cross-section. Fasten the clamp screw tightly.

Note

The end of the tube must be slipped approximately 10 mm over the metering tip.

7.4 Inspecting and replacing the flange gasket in the batch module

After longer operation, the gasket at the flange may loose its elasticity and thus the sealing effect. Then, it must be changed.

1. With a single turn, remove the reaction beaker from the flange.
2. Inspect the gasket at the flange. Remove it if it is worn, and replace it by a new one.
3. Push the reaction beaker onto the flange and lock it in place by a turn.

7.5 Cleaning cell window and cell

Risk of burns!

Before removing the cell windows and the cell, allow the cell unit to cool down.

Cell windows cleaning

Take care not to contaminate the cell windows!

Do not touch the cell windows. Fingerprints will burn in.

Wear rubber gloves!

1. Push the cell window retaining clips back and remove the windows with their mounts.
2. Wash the cell windows with diluted hydrochloric acid.
3. Rinse the cell windows with distilled water and allow them to dry.

Cell cleaning

Highly corrosive and toxic substances!

Hydrofluoric acid is highly corrosive and toxic.
Work should be carried out in a fume cupboard.
Wear rubber gloves, rubber apron and a facemask.

1. Release the cell retaining clips.
2. Remove the cell and disconnect the tubes.
3. Bathe the cell in cold 40% hydrofluoric acid for a period of 5 to 10 minutes.
4. Remove any peeled off film from the inside of the tube by intensive brushing with a suitable round brush under running water.
5. Rinse the cell with distilled water and let it dry.

Check the end faces of the cell for intactness!

Stop using damaged cells and replace them!

6. Put the cell into its holder and clamp it with the retaining clips.
7. On both ends, attach the cell windows with mount and clamp them in place by means of the corresponding retaining clips.

Note

Verify that the cell windows are correctly located at the cell!