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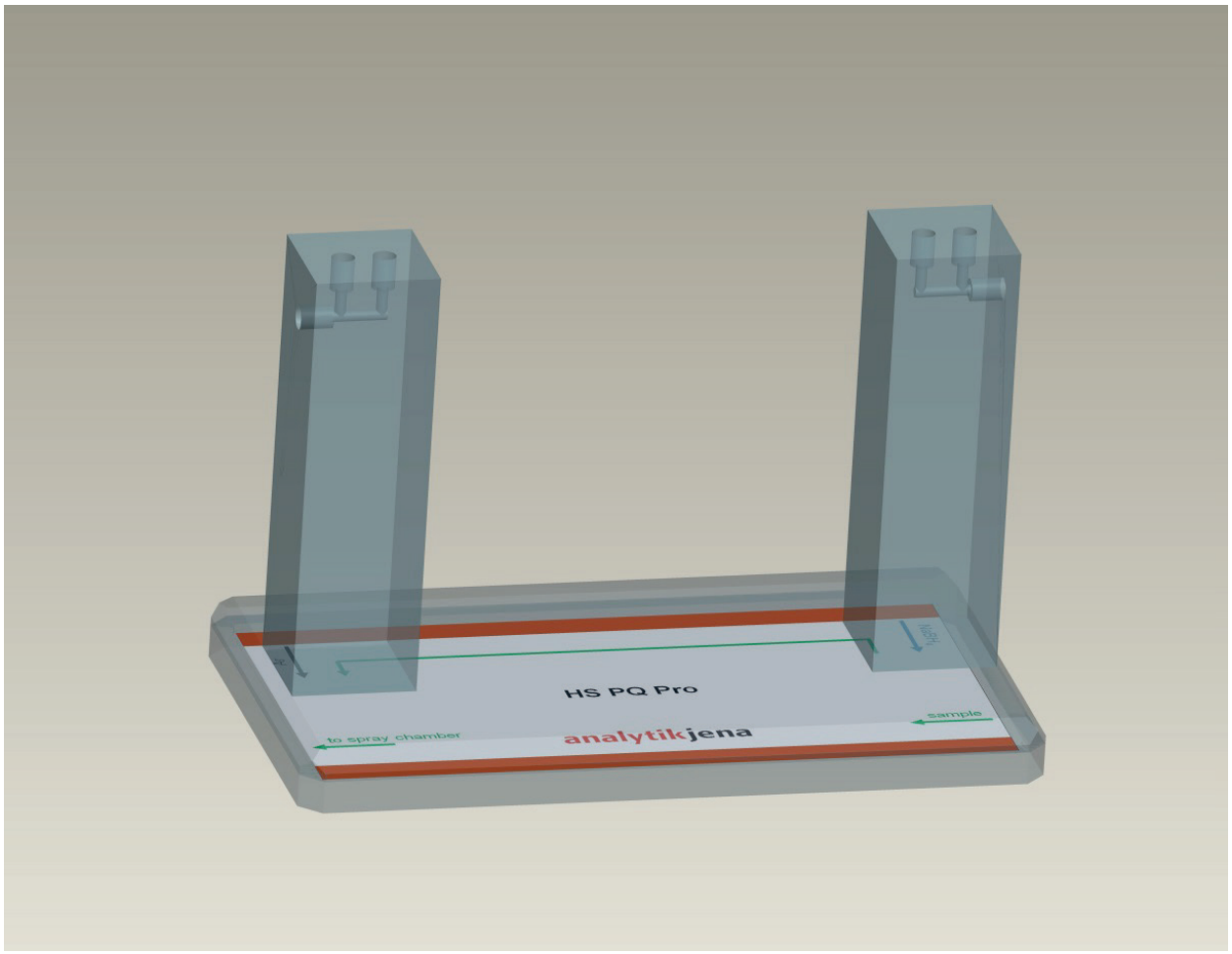
An Endress+Hauser Company

Operating Manual

HS PQ Pro
Hydride system for ICP-OES



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1 General

1.1 User manual notes

Content

The HS PQ Pro is a mercury/hydride system for ICP-OES for the determination of hydride-forming elements at superior detection limits. It is intended for operation by qualified specialist personnel observing this user manual.

The user manual informs about the design and function of the HS PQ Pro and provides the necessary know-how for the safe handling of the device and its components to personnel familiar with analysis. The user manual further includes notes on the maintenance and service of the equipment and potential causes and remedies of any faults.

Conventions

Instructions for action which occur in chronological order are numbered and combined into action units.

Safety notes are indicated by a triangular warning sign and signal words. The type and source of the danger are stated together with notes on preventing the danger.

The elements of the control and analysis program ASpect PQ are indicated as follows:

- All elements, such as menu items, window names, buttons etc. are indicated with small caps (e.g. MODULES)
- Buttons are indicated by square brackets (e.g. [OK])
- Menu items in a command sequence are separated by an arrow (e.g. FILE ▸ OPEN)

Symbol and signal words

The user manual uses the following symbol and signal words to indicate hazards or instructions. The safety instructions are always placed before an action.

WARNING

Indicates a potentially hazardous situation which, unless avoided, may result in severe or fatal injuries.

1.2 Purpose

The HS PQ Pro must only be used in conjunction with an ICP-OES from Analytik Jena. Any deviation from the instructions for proper use described in this document may lead to warranty restrictions and reduced manufacturer liability in the case of damage.

If the safety instructions are not observed in handling the HS PQ Pro, this is taken to be a use which deviates from the intended purpose. Safety instructions are to be found on the equipment itself, in section "Safety instructions" and in the description of the relevant work steps.

1.3 Warranty and liability

The warranty duration and liability comply with the legal requirements and the provisions in the general terms and conditions of Analytik Jena.

Deviations from the intended use described in this user manual result in limitations of warranty and liability during a damage event. Damage to wearing parts or breakage of glass is not included in the warranty.

Warranty and liability claims are excluded for personal injury and property damage due to one or several of the following causes:

- Use of the HS PQ Pro other than intended
- Improper commissioning, operation and service of the HS PQ Pro
- Modifications of the HS PQ Pro without prior consultation with Analytik Jena
- Operation of the device with faulty safety equipment or improperly fitted safety and protection equipment
- Inadequate monitoring of the equipment components subject to wear
- Use of other than original spare parts, wearing parts or consumables
- Improper repairs
- Faults due to the non-observance of this user manual

2 Safety instructions

2.1 General notes

For your own safety and to ensure error-free and safe operation of the HS PQ Pro, please read this chapter carefully before commissioning.

Observe all safety notes listed in this user manual and all messages displayed by the control and analysis software on the monitor.

Besides the safety instructions in this user manual and the local safety regulations that apply to the operation of the device, the general applicable regulations regarding accident prevention, occupational health and safety and environmental protection have to be observed and complied with.

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

2.2 Requirements for the operating personnel

The device must only be operated by qualified specialist personnel instructed in the use of the device. The instructions also include the contents of this user manual and the user manuals of the connected system components.

In addition to the safety instructions in this user manual the generally applicable safety and accident prevention regulations of the respective country of operation must be observed and adhered to. The operator must ascertain the latest version of the regulations.

The user manual must be accessible to the operating and service personnel.

2.3 Safety instructions: Transport

Observe the following notes:

- Prior to transport, the HS PQ Pro and its pump and metering tubing must be flushed with distilled water and fully drained to prevent reducing solution or acid from dripping out. The solutions are aggressive and attack clothing.
- Only ship the HS PQ Pro in its original packaging.

2.4 Safety instructions: Operation

General

Observe the following notes:

- The operator of the HS PQ Pro must make sure before each commissioning that the condition of the device is sound.
- The tubing must be checked prior to use. Pump tubing that is no longer flexible or shows signs of heavy abrasion must be replaced. Tubing used for transferring samples and reducing agent must be replaced if deposits have formed.

Handling of samples and reagents

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

When handling hazardous substances the locally applicable safety instructions and/or instructions in the EC safety data sheets from the manufacturer of the auxiliary and operating materials must be complied with.

The following chemicals are used as reducing agent or for sample preparation when working with the HS PQ Pro:

- Sodium borohydride
- Sodium hydroxide
- Hydrochloric acid
- Nitric acid
- Bromide/bromate mixture

Sodium borohydride ($NaBH_4$) and sodium hydroxide (NaOH) are strongly corrosive, hygroscopic and, in solution, extremely aggressive. Concentrated hydrochloric acid (HCl, 37 %) is highly corrosive. Concentrated nitric acid (HNO_3, 65 %) is highly corrosive and oxidizing. Bromide/bromate mixtures have been classified as carcinogen. Care is required during the handling and disposal of these hazardous substances.

Wear appropriate personal protection equipment (safety goggles, protective gloves, protective clothing) when handling the above-named substances.

Waste disposal of sodium borohydride

Danger of oxyhydrogen reaction!

Hydrogen is released by the reaction of sodium borohydride with acids. An oxyhydrogen reaction may occur. Never dispose of sodium borohydride in the waste container for acids!

3 Technical description

3.1 Principle of operation

In the mercury/hydride system the acidified sample is mixed with a reducing agent (typically sodium borohydride). During this process, mercury is reduced to atomic Hg vapor, while arsenic, antimony, selenium, bismuth and tellurium form volatile hydrides.

(1) $BH_4^- + H^+ + 3\ H_2O \rightarrow H_3BO_3 + 8\ H$

(2) $Hg^{2+} + 2\ H \rightarrow Hg0 + 2\ H^+$

(3) $H_3AsO_3 + 6\ H \rightarrow AsH_3 + 3\ H_2O$

The formation of the volatile element hydrides depends to a large extent on the oxidation state of the analyte elements to be measured. For this reason it is essential that the analyte elements in standards and samples are available in the same oxidation state. A lower oxidation state in each case results in a higher measurement sensitivity. For this reason, samples and standards should be pre-reduced prior to the measurement to form the lower oxidation state or – if measurement in the higher oxidation state is desired, targeted oxidation should be performed.

3.2 Design of the HS PQ Pro

The HS PQ Pro is a mercury/hydride system for the dedicated determination of hydride-forming elements at superior detection limits.

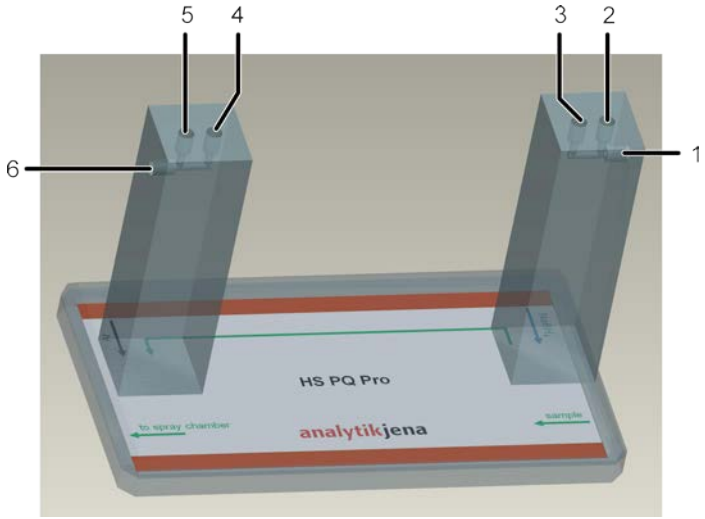


Fig. 1 Basic unit of the HS PQ Pro with mixing units

1 Sample feed "sample"
2 Reducing agent feed "NaBH4"
3 Reaction loop connection
4 Reaction loop connection
5 Argon connection "Ar"
6 Output to spray chamber "to spray chamber"

The basic unit of the HS PQ Pro accommodates the two mixing units. The acidified sample and the reducing agent are pumped to the first mixing unit and are mixed there. In the subsequent reaction loop, the sample is reduced and gaseous metal hydride or atomic Hg vapor is released.

In the second mixing unit, argon is added to the gas/fluid mixture and flushed into the spray chamber.

The flow diagram for the connection of the tubing set is located in the foot of the basic unit.

Tubing system

The tubing system comprises the following tubing

- Tubing for feeding samples and reducing agent
- Reaction loops of 200 and 800 mm length
- Argon tubing adapter with check valve
- Spray chamber connection with injector
- Adapter and connection tubing for waste
- Pump tubing (for supply of samples and reducing agent black – black, for waste purple – orange)

Spray chamber

A cyclonic spray chamber with a volume of 20 mL is used in the HS PQ Pro. The spray chamber has an inlet for the injector. The gas/fluid mixture is separated in the spray chamber. The measuring gas with the volatile hydrides or the atomic mercury is flushed into the plasma, while the fluid is pumped into the waste container.

Fig. 2 Cyclonic spray chamber 20 mL

3.3 Rating plate

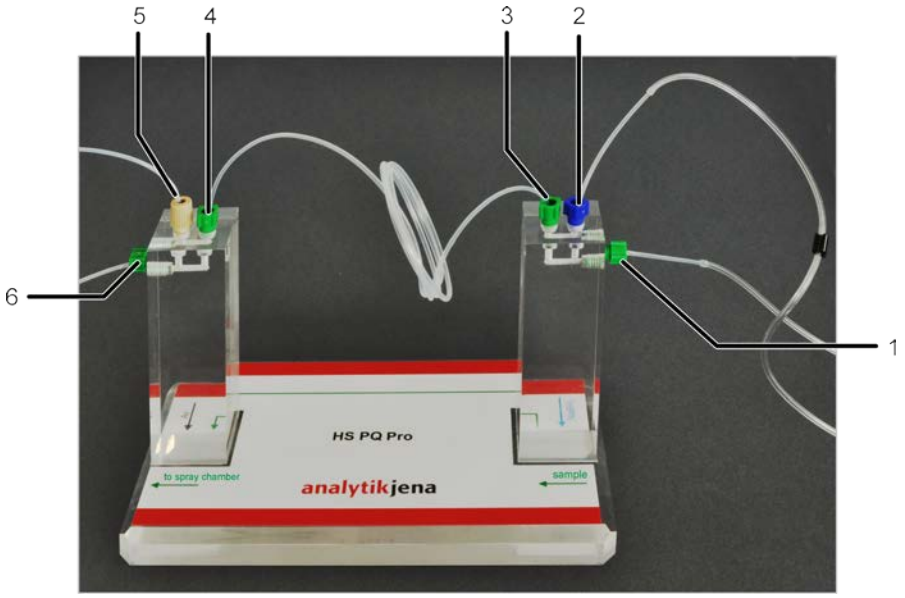
The rating plate is located on the bottom of the tripod and includes the following information:

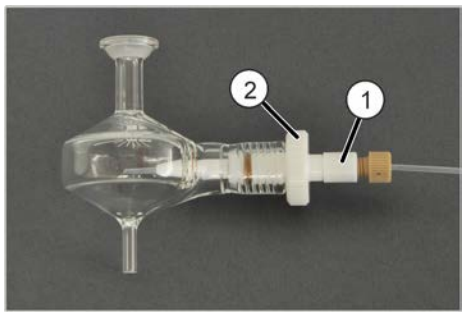
- Manufacturer address
- Name of the device type and model
- Serial number
- CE marking
- Instruction to pay attention to the user manual during operation
- Disposal instructions (Do not dispose of as domestic waste!)
- Year of manufacture

4 Installation

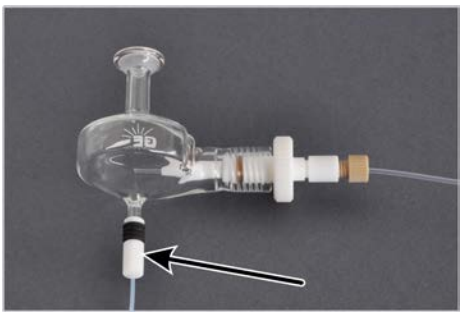
4.1 Installing the HS PQ Pro

1. Screw the tubing set into the basic unit. For connections in the basic unit see flow diagram on the basic unit:
   - Screw the sample tubing (1) into the 1st mixing unit. Connect with pump tubing (black – black) and sample capillary.
   - Screw the reducing agent tubing (2) (blue connector) into the 1st mixing unit. Connect with pump tubing (black – black) and reducing agent capillary.
   - Screw reaction loop (3 and 4) into the connections in both mixing units.
   - Screw argon connection tubing (5) with check valve into the 2nd mixing unit.
   - Screw the spray chamber connection with injector (6) into the 2nd mixing unit.





2. Plug the injector (1) into the spray chamber until the stop and tighten the plastic screw at the spray chamber (2) finger-tight.



3. Attach the waste tubing to the spray chamber. Attach the waste tubing to the pump tubing (purple – orange) using the adapter. At-tach thicker tubing to the other side of the pump tubing and guide into the waste container.

4. Place the basic unit of the HS PQ Pro in the sample chamber of the PlasmaQuant PQ 9000.
5. Attach the spray chamber to the torch of the PlasmaQuant PQ 9000 using the fork clamp.
6. Span the sample, reducing agent and waste pump tubing in the tubing pump of the PlasmaQuant PQ 9000. Note the pump direction!
7. Plug the argon connection of the PlasmaQuant PQ 9000 onto the argon connection tubing.
   ✓ The HS PQ Pro is now installed.

Check the system for leaks prior to starting work (see section "Checking the HS PQ Pro for leaks and igniting plasma" p. 17).

4.2 Notes on installation

To ensure the system tightness, the sealing rings on the tubing ends in front of the screw connectors must be seated correctly.

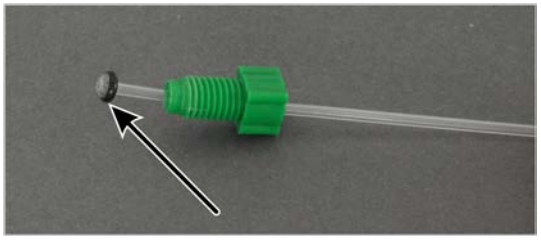
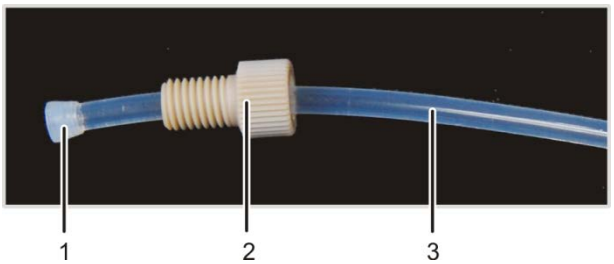


Fig. 3 Sealing rings at tubing end of a screw connection

In the argon connection in the mixing unit, a ferrule seals the connection in the screw connection. The conical side of the ferrule must point toward the banjo bolt.



1 Ferrule
2 Banjo bolt
3 Tubing

Fig. 4 Position of the ferrule in the argon connection of the mixing unit

5 Operation

5.1 Preparing reagents and samples

WARNING

Danger of oxyhydrogen reaction!

Hydrogen is released by the reaction of sodium borohydride with acid. An oxyhydrogen reaction may occur. Never dispose of sodium borohydride in the waste container for acids!

WARNING

Safety goggles, protective gloves and protective clothing must be worn when handling chemicals used in the analysis. The safety notices on the labels must be observed.

Provide the reducing agent and rinse solution when beginning the analysis and prepare the samples.

Reducing agent

- Weigh 3 g $NaBH_4$ and 1 g NaOH into the reducing agent container. Fill with 1 L demineralized water.
  - ✓ The prepared solution can be kept at room temperature for approx. 12 h.
- Alternatively:

  Weigh 30 g $NaBH_4$ and 10 g NaOH into a 1000 mL volumetric flask. Fill with 1 L demineralized water. Dilute to final concentration (1:10) every day a measurement is performed.
  - ✓ The concentrated solution can be kept at 4 ± 3 °C for approx. 7 days.

Samples

- Analysis of metal hydrides:

  Samples must contain at least 3% HCl. Prereduce the samples depending on the analyte element.
- Analysis of mercury:

  In addition, mix samples with HCl, HNO_3 or bromide/bromate mixture.

For sample preparation see section "Preparing samples and standards" p. 18.

Rinsing solution

- Mix 1 L demineralized water with 5 mL HNO_3 and 15 mL HCl

5.2 Performing measurements

5.2.1 Creating a method for analysis with the HS PQ Pro

1. Turn on the ICP-OES device and start the ASpect PQ program.
2. Create a new method and select the analysis wavelengths.

   Note:
   Not all element combinations can be measured simultaneously using the same method (see section "Analyzing multiple elements from one sample solution" p. 19).

   The following analysis wavelengths are recommended:

Element	Analysis wavelengths
Se	196,0280 nm
As	193,6980 nm
Sb	217,5810 nm
Te	214,2814 nm
Bi	223,0608 nm
Hg	253,6519 nm

   ✓ The default settings are loaded in the method.

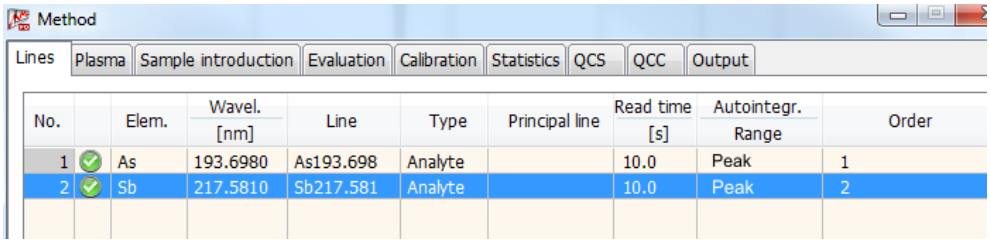
3. For analysis using hydride technique, enter the below settings in the method parameters.
4. Save the method under an individual name.

   ✓ The method can be used for the subsequent analysis.

Method settings

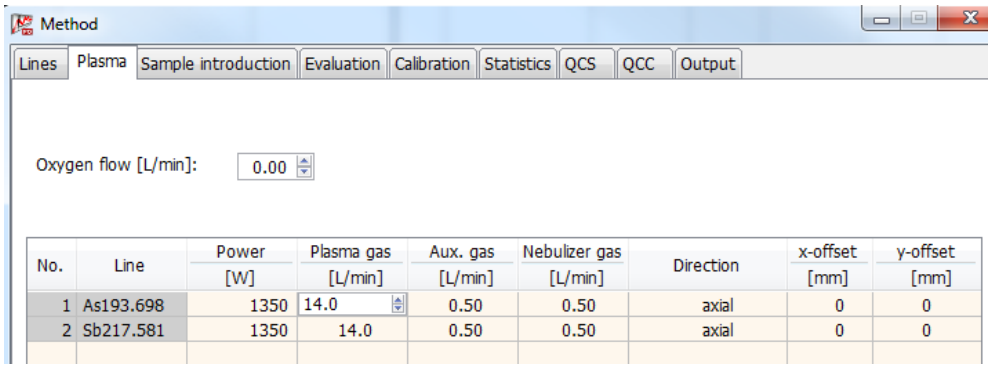
- LINES method tab:

Parameter	Settings
AUTOINTEGR. RANGE	PEAK
READ TIME	10 s



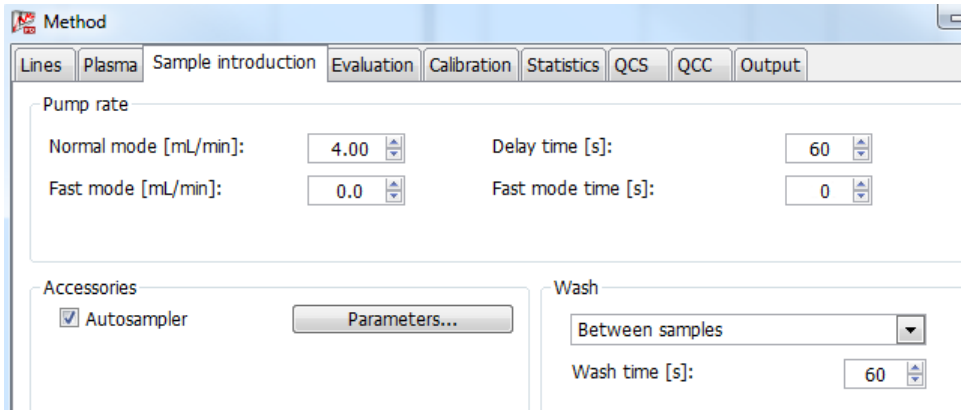
- PLASMA method tab:

Parameter	Settings
POWER	1350 W
PLASMA GAS	14 L/h



- SAMPLE INTRODUCTION method tab:

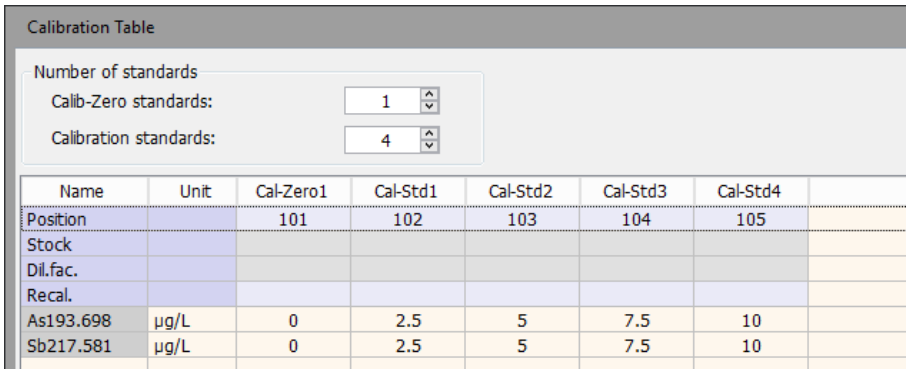
Parameter	Settings
NORMAL MODE [mL/min]	4
FAST MODE [mL/min]	0
DELAY TIME [s]	40 – 70
FAST MODE TIME [s]	0
WASH TIME [s]	40 – 70



Note:
The delay and wash times depend on the corresponding analyte, the use of the sampler and the use of a long or short reaction loop.

- CALIBRATION method tab:

Enter the standard concentrations to be measured.



- QCS method tab:

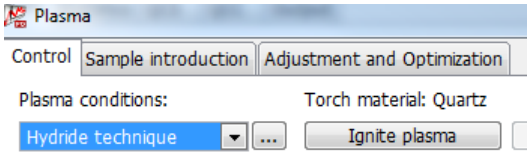
Enter control standards and recoveries.

5.3 Setting the plasma ignition conditions

ASpect PQ versions 1.2.1 and higher

For ASpect PQ program versions 1.2.1 and higher, the optimized plasma conditions for hydride operation are already stored.

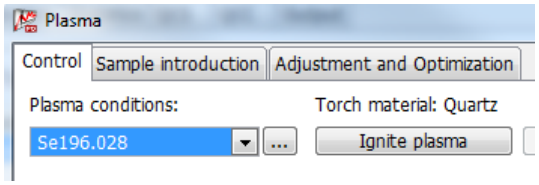
- In the PLASMA / CONTROL window, select the HYDRIDE TECHNIQUE option in the PLASMA CONDITIONS list.



ASpect PQ versions below 1.2.1

In ASpect PQ program versions with a version number below 1.2.1, the ignition conditions must be saved manually:

1. Open saved hydride method.
2. Open the PLASMA window.
3. In the PLASMA / CONTROL window, select one of the lines from the method in the PLASMA CONDITIONS list.

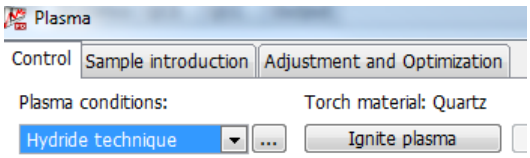


✓ The method settings for the plasma are transferred to the PLASMA window.

4. Click [...] next to the PLASMA CONDITIONS list.
5. Select the SAVE CURRENT PLASMA PARAMETERS option and name the ignition condition "Hydride technique".

✓ The settings saved in the method are saved as ignition conditions.

During future work with the HS PQ Pro you can load these settings for plasma ignition in the PLASMA CONDITIONS list in the PLASMA / CONTROL window.



5.3.1 Checking the HS PQ Pro for leaks and igniting plasma

Before igniting the plasma, the installed HS PQ Pro must be checked for leaks.

1. Immerse reducing agent capillary and sample tubing with manual aspirating capillary in demineralized water.
2. Open the PLASMA window.
3. On the CONTROL tab in the PLASMA CONDITIONS list, select the ignition conditions HYDRIDE TECHNIQUES for the HS PQ Pro (see also section "Setting the plasma ignition conditions" p. 16).
4. Start the gas flows at the plasma by selecting [SET].
   - ✓ This generates the counter pressure for the conveyed amount of water and residual oxygen is expelled from the system.
5. On the SAMPLE INTRODUCTION tab, set the PUMP RATE value to 4 mL/min.
6. Start pump with [SET].
7. Check tubing system for bubbles.

   No bubbles may form in the tubing system including the reaction loop. Gas bubbles may only be present in the transfer tubing to the spray chamber.
8. Remove leaks in the system. Check seat of the seals in the tubing connectors.
9. Immerse suction cannula for reducing agent in the $NaBH_4$ solution.
10. Ignite the plasma.
11. Wait approx. 3 min and then start the analysis.

6 Notes on application

6.1 Preparing samples and standards

6.1.1 Reduction of arsenic (V) to arsenic (III)

For drinking and surface water

- Mix 5 mL sample with 5 mL concentrated HCl.
- Add 1 mL reducing agent (5% potassium iodide/ 5% ascorbic acid) and let the mixture sit at room temperate for at least 45 minutes.
- Fill the solution to the same volume (e.g. 50 mL).

$H_3AsO_4 + 3I^- + 2H_3O^+ \rightarrow H_3AsO_3 + I_3^- + 3H_2O$

For digestion solutions that contain excess oxidizing acids, hydroxylammonium chloride or sulfamic acid must be added prior to the reduction.

6.1.2 Oxidation of arsenic (III) to arsenic (V)

For measuring arsenic (V), samples and standards must be oxidized with HNO_3 prior to measurement.

For drinking and surface water

- Mix 5 mL sample with 1 mL concentrated HNO_3.
- Warm the mixture slightly and let it sit for 30 min.
- Then add 5 mL concentrated HCl.
- Fill the solution to 20 mL.

6.1.3 Pretreatment of antimony

The reduction and oxidation of samples to analyze antimony corresponds to the pretreatment processes described for arsenic.

6.1.4 Prereduction of selenium

As selenium (VI) does not form any volatile hydrides, the element must be available in tetravalent form for measurement. This is achieved by heating it with half-concentrated hydrochloric acid.

- Mix 5 mL sample with 5 mL concentrated HCl and heat to 90 °C for 45 min in a closed container.
- Depending on the sample matrix, it may be necessary to prevent a reverse reaction caused by the formed chlorine by adding some sulfamic acid.

$HSeO_4^- + 3H^+ + 2Cl^- \rightarrow H_2SeO_3 + Cl_2 + H_2O$

6.1.5 Prereduction of tellurium

The prereduction of tellurium corresponds to the prereduction for analysis of selenium.

6.1.6 Prereduction of bismuth

In hydrochloric solutions, bismuth is present in trivalent form. For this reason, an additional prereduction of the solutions is not necessary.

6.1.7 Sample preparation for mercury

Mercury (I) is prone to disproportionation. The atomic mercury formed in this process volatilizes easily. For this reason it is necessary for this element to mix samples and standards with oxidizing agents to keep the element in bivalent form. Depending on the application, different DIN methods are available for this purpose.

DIN 16772

- Stabilize 100 mL sample with 2.1 mL HCl and 0.7 mL HNO_3.

DIN EN 13506

- Mix 30 – 40 mL sample with 2.5 mL HCL conc. and 1 mL KBr-$KBrO_3$ reagent (595 mg KBr / 139 mg $KBrO_3$ in 50 mL demineralized water).
- Let it sit at room temperature for at least 30 min.
- Add 50 µL NH_2OH*Cl (12%) (hydroxylammonium chloride).
- Fill with demineralized water to 50 mL.

6.2 Analyzing multiple elements from one sample solution

Due to a similar or identical sample pretreatment it is feasible to analyze multiple elements from one sample solution, such as e.g. As III and Sb III. However, it is also possible to measure these elements with lower sensitivity at the higher oxidation level and to combine it with the analysis of selenium.

Examples

Analyte combination	Sample pretreatment	Reduction loop
Se IV, Te IV, Bi III	See chapter 6.1.4 - 6.1.6	short
As III, Sb III	See chapter 6.1.1, 6.1.3	short
Sb V, As V, Se IV, Te IV	Oxidize sample with HNO_3 (6.1.2), then mix with conc. HCl at 1:1 ratio and reduce selenium, as described in chapter 6.1.4	long

7 Maintenance and care

7.1 Replacing the tubing path

If the tubing path of the HS PQ Pro is contaminated and if a longer wash process with reducing agent solution and acid does not reduce the blank values, the following tubings incl. the corresponding pump tubing must be replaced:

- Sample tubing
- Reaction loop
- Transfer tubing to mixing chamber

1. Unscrew tubing from the mixing unit.
2. Screw new tubing into mixing unit with banjo bolt. Ensure that the seals are seated correctly.
3. Loosen the plastic nut at the spray chamber and pull out the injector.
4. Push the new injector into the spray chamber as far as possible and tighten the plastic screw finger-tight.

See also section "Installation" p. 11.

7.2 Cleaning the spray chamber

As a first step, remove deposits in the spray chamber by cleaning it. If this does not render successful results, replace the spray chamber.

WARNING

The cleaning solution (concentrated hydrochloric acid) is highly corrosive. The vapors irritate the respiratory paths. Wear gloves, protective clothing and safety goggles and work under an extractor!

1. Open the fork clamp at the torch and detach the spray chamber.
2. Remove the waste tubing connection from the connector.
3. Slightly loosen the plastic nut at the spray chamber and pull the injector out of the spray chamber.
4. Clean the spray chamber with concentrated hydrochloric acid (37 %). Allow the acid to act for several hours.
5. Then flush the spray chamber with distilled water.
6. Reinsert the cleaned or new spray chamber (see section "Installation" p. 11).

8 Troubleshooting

Problem	Possible cause	Measure
Poor measurement sensitivity or no signal	Reducing agent not fresh or already decomposed	Prepare fresh reducing agent
	Analyte is not available in correct oxidation state	Prereduce sample and standard according to the instructions
	Axial cone window not clean	Remove and clean the window of the PlasmaQuant PQ 9000
Poor reproducibility	The waste solution is pumped out unevenly	Optimize the pressure of the pump tubing, replace pump tubing if necessary (see PlasmaQuant PQ 9000 user manual)
Poor recovery of an added standard	Different kinetics of release of the volatile hydride	Adaption of the amount of acid in samples and standard solutions
Non-linear calibration function despite small measured values / curvilinear increase of the calibration function	Carry-over effect of the analyte	Increase wash and delay times

9 Technical data

Designation/type	HS PQ Pro / mercury/hydride system for ICP-OES
Basic unit dimensions (W x H x D)	approx. 180 x 100 x 120 mm
Weight of the basic unit	approx. 500 g
Basic unit material	PMMA
Reaction loop short	200 mm
Reaction loop long	800 mm
Spray chamber	Cyclonic spray chamber with 20 mL volume