H/Device

Operating Manual



H/Device

Table of Contents

Chapter Page 1. Principle of the H/Device 2 - 1 2. 3. 31 Compressed air connection from valve 11 3 - 2 3.2 H/Device software installation 3 - 6 3.3 Autosampler A200S 4 - 1 4. 4.1 4.2 Before starting an analysis 5 - 1 5. 5.1 5.2 5.3 6.

1. Introduction

The H/Device is a novel preparation system for hydrogen from water and volatile organic compounds. It is based on a reduction reaction with hot chromium. It connects directly to the dual inlet system of the IRMS and can be fully automated using a 200position autosampler.

2. Principle of the H/Device

Fig. 2 - 1



Chromium quantitatively reduces water and other compounds to hydrogen gas at temperatures > 700°C, simultaneously binding other elements of the sample to thermally stable compounds like nitrides, carbides, oxides and halides:

$$2Cr+3H_2O \rightarrow Cr_2O_3+3H_2$$

The sample water or volatile organic compounds are flash evaporated from a gas tight syringe and reduced by contact with hot chromium.

The reaction tube is directly coupled to the dual inlet system of the mass spectrometer. The coupling of the furnace to the IRMS is arranged such that the hydrogen gas enters into the sample side of the dual inlet system of the mass spectrometer in a stepwise procedure. From the reactor it is first equilibrated into an intermediate volume. Then the reactor is closed off and the gas is allowed into the variable volume.

The reaction furnace is developed for small samples (~1 μ l liquid). The reactor is a quartz tube of special design. It is filled with 50-100 g chromium powder and a layer of quartz wool at both ends. Depending on the reactor size 100-200 reduction reactions are possible with a single reactor.

On top of the vertically positioned furnace, an injector unit is mounted and sealed to atmosphere with a layered septum (see figure 3-1).

The reaction system is connected to the IRMS using a 1/4" Cajon Ultratorr adapter. It is evacuated directly via the IRMS vacuum system.

Depending on the nature of the sample the optimum reaction temperature can vary. For water and aqueous samples, it lies between 800 and 900 °C. For methane, higher temperatures (~1000 °C) are required.

3. Components of the H/Device

The following parts are delivered together with an H/Device:

- installation diskette : H/Device.wrk
- quartz wool
- Chromium
- two 2 µl syringes (gastight)
- 10 quartz reactors
- 25 septa (Auto/Sep TM 11 mm; Part No.: 041872 from SGE)
- a glass funnel and a connecting hose
- a compressed air connecting hose
- a 230 Volts mains power cord
- a stainless steel hose connection to the dual inlet of the IRMS

optional:

In case the H/Device is connected to an Autosampler A200S, an additional 230 Volts cable connection and the interface cable connection to the computer will be delivered.

3

Fig. 3 - 1 H/Device with Autosampler



3.1 Installation of the H/Device

- 1. Remove the lower front panel of the H/Device (see fig. 3 6 Reactor installation) and adjust the Cajon adapter unit to the oven. To unscrew the unit, turn it clockwise and pull it off. Put it back again by turning counter clockwise. In case an O-ring needs replacement pull off the Cajon adapter unit to gain access to the Cajon nut.
- 2. Compressed air connection from valve 11 of the dual inlet system

The reactor inlet valve takes the logical position of valve 11 in the dual inlet system. This is done by moving the compressed air hose from valve 11 to the reactor inlet valve. The physical valve 11 is normally open when no pressure is applied.

- After switching valve 11 to open (i.e. remove compressed air from it) remove the pressure connection from valve 11 and connect it to the valve inside the H/Device.
- Connect the stainless steel connecting hose from the H/Device' output to the dual inlet of the mass spectrometer, sample side (left).
- Check for leak tightness using the inlet system control program.
- 3. Connect the 230 Volt cable to the power supply.

<u>NOTE:</u> All MS peripheral units should be connected via the MS power supply to avoid ground loops.

4. Setup of the JUMO temperature controller

The temperature controller is located at the front panel of the H/Device (see fig. 3 - 1).

To program the temperature controller proceed as follows:

 Turn on the power supply. The red flashing numbers on the temperature controller display indicate that the controller is not programmed yet (see figure)

Fig. 3 - 2 Temperature controller



H/Device

- Press the ENTER key and hold it while pressing the PGM key in addition. The programming will start with the information: Al. 1000 on the lower display.
- Select the following values to program the temperature controller:

AI.	1150
Pb.	5
d.t	2
r.t	12
су.	0.5
Hys.	1
у.	0
rA.Sd	60

Selection is made using the \checkmark and \checkmark keys on the front panel of the temperature controller.

- moves the active position one to the left
 - increases the value by one

Each selection has to be saved with ENTER.

- After all selections are made restart the programming and jog through the menu until y. is displayed again
- Press the ENTER and PGM key together again to yield the submenu:
 - C1114001C1120010SP.L0SP.H910OFFS0
- End programming with pressing ENTER to save all values
- After a while, the temperature set for the reactor is displayed. The lower green numbers show the actual reactor temperature e.g. 50 °C. The LED on the right hand side indicates the heating action. The rate of heating is fixed by the parameters given above programming. Heat the system in steps of ~100 °C to the final temperature.

Setting a new temperature value:

- Press 'PGM' only
- 'sp' is displayed
- Select a new temperature using the arrow keys
- when finished press 'ENTER', then 'PGM'

H/Device

Hint: In case the heating is not working correctly, remove the side panel and check the cable connections to the heating element. Turn around the orange and white cable connection and try heating again (see figure 3 - 3, Temperature controller, rear connections).

Fig. 3 - 3 Temperature controller, rear connections

More information on the temperature controller is provided on the instructions leaflet provided by the manufacturer of the controller, Juchheim KG, Fulda.



5. Programming of the microprocessor temperature controller of Jumo iTRON 16.

3

- Press the "P" key and hold it two seconds
- Change values with up and down arrows
- Select the following values to program the temperature controller:

Pb.1	10
Pb.2	1
d.t.	2
r.t.	12
CY.1	2.0
CY.2	2.0
db	0
HyS.1	1
HyS.2	1
Y.0	0
Y.1	100
Y.2	0
d.F	0.9
rA.Sd.	100

- After all selections are made restart the programming and skip through the menu until "Y.0".
- Press "P" key and hold it two seconds

C 111	044
C 112	0
C 113	33
C 115	1
C 116	0
SP.L	0
SP.H	910
OFFS	0

Fig. 3 - 4 Temperature controller Jumo iTRON 16



3.2 Reactor installation

a. Preparation

3

<u>NOTE:</u> Working with chromium powder may be hazardous to your health. Thus, reactor filling should be carried out under special ventilation conditions. Please read the instructions on the package.

For filling the oven, proceed as follows:

Fig. 3 - 5 Reactor filling



- Take a very small amount of glass wool and stuff it into the reactor tubes end with the smaller diameter. Use a fused silica capillary or a clean syringe.
- Put an elastic cap on top of the prepared reactor side.
- Connect the glass funnel to the other end of the reactor tube and fill it with chromium powder. While filling, tap against the outer walls of the reactor tube to concentrate the powder. This will ensure homogeneity of the reactor filling.

<u>NOTE:</u> Chromium powder should be present only in the large diameter portion of the reactor (see figure 3 - 5 Reactor filling).

3

- Take a pair of tweezers and stuff the other reactor end with small amounts of quartz wool. Repeat the stuffing three times to remove chromium particles from the inner side of the reactor tube.
- Clean the reactors outside and remove the cap.
- The reactor is ready to be inserted into the H/Device.

b. Installation of the reactor

Fig. 3 - 6 Reactor installation 1



 To install the reactor into the H/Device, remove the lower front panel to get access to the reactor connections (see figure reactor installation 1).

Fig. 3 - 7 Reactor installation 2



Remove the reactors cover and the septum in the injector block on top of the H/Device.

Fig. 3 - 8 Reactor cover



- Insert the reactor tube into the heating unit and connect it to the Cajon connector at the bottom.
- Tighten the connector nut and put the cover back on top.
- Try to move the reactor tube a little bit with your fingers in order to check for a tight fit. The reactor tube should stick out of the injector block bottom by 0.5 to 1 mm for a good fit with the septa.

Fig. 3 - 9 Injector



— Tighten the injector block again.

3.3 H/Device software installation

The ISODAT H/Device Software is provided on a separate diskette (Hdevice.wrk) together with the delivery of your H/Device unit. The diskette includes a number of executable files and corresponding resource files in addition to those used by the standard ISODAT software.

Requirements: Successfully installed ISODAT software with at least one unused ISODAT configuration (e.g. C).

Exit the ISODAT program:	Press <alt> and simultaneously type: 'quit' on the</alt>
	keyboard

You are returned to the root directory. [CA(root)]. Switch to the subdirectory ISOTST: [cd\isotst] and activate the installation program: type: 'install' <ENTER> The ISODAT Installation Menu is displayed.

3

Activate the corresponding submenus:

Type: 5 for Peripheral Type Installation Menu Type: 3 for H/Device Installation

After copying files and creating backups, the program will ask in a dialog for technical details of the H/Device equipment.

Please answer exactly and pay attention to the type of parameters to be entered, select an unoccupied configuration to install H/Device.

numeric (0,1 etc) or alpha-numeric (Y,N etc)

<u>CAUTION:</u> There is no check of entered parameters. Wrong input may cause a faulty system installation. After the installation is completed, return to the main menu and exit the installation program. Start the ISODAT software system by booting.

4. Autosampler A200S

4.1 Installation

4

Install the Autosampler to COM1 or COM2 of your computer. If you are working with ISODAT leave ISODAT with <ALT QUIT> first. Call C:\>SETUP The SETUP program of the REAL 32 operating system will welcome you.

Move to submenu: STATIONS AND MULTIPORTS and

select 3 COM(SERIAL) PORTS (INTERNAL DRIVER) and make your choice of the COM (Serial) Port

Serial configuration for COM

Baud rate	9600
Parity	none
Data bits	8
Stop bits	1

To save your selection:

Write configuration information to system file

Following the installation of the Autosampler, move to ISODAT Configuration D, Edit environment. Call the <SYSTAB EDITOR> program.

The Editor always comes up with Jump Record 30, WORDS.

Select Record 37 by pointing the <Select Rec> function with the mouse cursor and clicking.

Type the desired record number and click the right mouse button.

In record 37, switch to BYTES by pointing the <Pg Up> function with the mouse cursor and clicking.

Set: BYTE 0:1, enter and save.

H/Device

OPERATING MANUAL

4

Fig. 4 - 1

>>> SYSTEM TABLE <<< >>> Record Nr.: 37

	BYTE	WORD	LONGINTEGER	LONGREAL
0:	1	0	0	0.600000
1:	0	60	0	0.000000
2: 3:	0	3 0	0	0.000000 0.000000
3:	U	0	0	0.000000
4:	0	0	0	0.000000
5: 6:	0 0	0 2	0	0.0000000 0.0000000
7:	0	0	õ	0.0000000
8:	0	0	0	0.000000
9:	õ	õ	0	0.000000
0 :	1	0	0	0.000000
1:	0	0	0	0.00000000000
12:	1	0	0	0.00000000000
13:	0	0	0	0.00000000000
14:	0	0	0	0.00000000000
15:	0	0	0	0.0000000000
16:	0	0	0	0.00000000000
17: 18:	0	0	0	0.00000000000
19:	õ	0	0	0.0000000000000000000000000000000000000
20:	0	0	0	0.00000000000
21: 22:	0	0	0	0.0000000000000000000000000000000000000
23:	0	0	0	0.000000000000
24:	0	0	0	0.00000000000
?5: .46:	0	0	0	0.0000000000000000000000000000000000000
27:	0	0	0	0.000000000000
28:	0	0	0	0.00000000000
29: 30:	0 0	0	0	0.0000000000000000000000000000000000000
30:	0	0	0	0.000000000000
	U	0	U U	0.0000000000000000000000000000000000000
SS 0:: SS 1::				
SS 2::				
SS 3::				
SS 4::				
SS 5::				
SS 6::				
SS 7::				
LS 0::				
LS 1::				
LS 2::				

4.2 Preparing the autosampler to work with the H/Device:

An injection method is needed to specify the injection cycle of the autosampler A200S. The autosampler is controlled by a microprocessor. Nine different injection methods are available. The method to be used is selected in STANDBY or SINGLE INJECT state by setting the METH value at the end of the programming procedure. The autosampler screen will display the information: FST LST CNT METH

1...9

Fig. 4 - 2Autosampler control panel

4



Individual parameters of the selected method are checked or changed by pressing the MET key. The different injection parameters are displayed. Use the MET key to leave the method editor mode and save all changes. Use the CLR key to discard all changes. The MET LED and the CLR LED will flash to indicate the valid keys for leaving the edit mode.

<u>NOTE:</u> If the method edit mode is not terminated by pressing either the MET or CLR key within one minute, editing is automatically aborted and any changes are discarded.

Start editing the method by pressing: MET

First, a state information will be given: Injection Mode Normal Injection

Method parameters are displayed on several screens:

- Move to the next parameter by pressing the horizontal arrow keys:
- Set the parameter values by using the vertical arrow keys:

Proceed editing the method to run with the H/Device in the following way:

H/Device	OPERATING	MANUAL	
Screen : FST LST	CNT METH 9		Set to : 9
► Injection Mode Normal Injection			
VOLUME SAMPLAIR x 0.1 I 000 000			SAMPL: 60 AIR:0
► PREINJ SOLVENT CLEAN 00			SOLVENT: 0
► PREINJ SAMPLE CLEAN 00			SAMPLE: 0
► FILLING VOL CNT x 0.1 µI 001 00			VOL: 60 CNT: 3
SYR PULLUP DELAY x 0.1 sec 00			DELAY: 10
▶ PLSPD FILL INJ x 1 µl/s 01 01			FILL: 4 INJ : 55
► INJECTION POINT OUTER			No Change
► SPLITTER PRE PST x 1.0 sec 000 000			PRE: 000 PST : 000

H/Device

► INJDELAY PRE PST x 0.1 sec 000 000

4

PRE: 000 PST: 100

PSTINJ SOLVENT CLEAN 00

SOLVENT: 00

► INJECTION MODE NORMAL INJECTION

At this point, press MET to leave the method editor and save the changes. The program will ask you:

SAVE AS METHOD

Select method value 9 and press MET again to save the method.

The autosampler A200S should now be working with a proper injection method for H/Device measurements. For further information on the A200S functions, please refer to the corresponding A200S Manual.

5. Before starting an analysis

5.1 Heating the Reactor:

 Move to the ISODAT Configuration A / Support-A environment and call the <INLET CTRL> program.

5

- Close valve 39 and notice the forevacuum pressure value (e.g. 20 µbar).
- Open valve 39, 13 and 11 (see figure 5 1) to evacuate the reactor and wait until the forevacuum pressure approaches the previous value.
- In case this value is not reached after some minutes, leak-check the system.
- Start heating the reactor oven to 100 °C by pressing PGM: sp. Enter 100 and press PGM again to finish the procedure. The LED K1 indicates the heating action.
- Move to the INLET SYSTEM CONTROL and watch the forevacuum pressure stabilize.
- Repeat the heating procedure in a 100 °C steps until a temperature of 700 to 850 °C is reached.
- In case the forevacuum is in the desired range after heating the reactor, open valve 40 to reach high vacuum.



Fig. 5-1 Inlet Control

5.2 Preparing the Mass Spectrometer for H/D measurement

- Connect a hydrogen gas to port A2 (reference side, figure 5-1) and introduce about 50 mbar gas into the bellows system. The signal intensity may be checked via the <INSTR.CONTROL> program in the ACON-D/CNF-D environment. Change the cup configuration to HD by pointing the <CUP CFG> function with the mouse cursor and activate the function by mouse-click. The hydrogen signal should be 4 to 5 Volts.
- Determination of the H₃⁺ factor: To yield precise hydrogen measurements, the ion source must be tuned to give a small and stable H₃⁺ - factor. For the various Thermo Finnigan mass spectrometers the H₃⁺ - factor should be as follows:

MAT 252	< 10 ppm/nA
delta S	< 15 ppm/nA
DELTA ^{plus}	< 10ppm/nA

5

To determine the H_3^+ - factor, move to the ACON-D/CONFIG-D environment and call the <H3-FACTOR> program. Follow the instructions on the screen or consult your ISODAT manual.

<u>NOTE:</u> To guarantee reproducibility, the H_3^+ -factor should be measured a number of times, with a deviation of 0.1 units at most.



Fig. 5 - 2 ACON H_3^+ - FACTOR DETERMINATION

- **TIP:** 1. In case the H₃⁺-factor is not stable, check the peak mid setting. Move to <INSTR.CONTROL> and call the <SHAPE> program by activating <MEASURE>. The program will show, whether the selected middle of the peak is ok (see figure).
 - In case the H₃⁺-factor is not small enough, try to tune the ion source again. The linearity mode should yield the best H₃⁺-factor. Please note that the stability of the H₃⁺-factor is by far more important for a good measurement than its value.



Fig. 5 - 3 H_3^+ - factor

5.3 Defining an H/D experiment:

5

Just like other ISODAT supported MS experiments, the H/Device experiment is defined via a method consisting of the three method parts (Experiment, Process and Format) with most of the method parameters described in the corresponding manuals. For the H/Device experiment only the Process parameters differ and therefore are described in the following:

a. FOREVAC THRESHOLD [µbar]: e.g. 80 see example

This parameter represents the forevacuum threshold, which will prompt an error message if not reached after 60 seconds. The system then stops automatically. The parameter differs for all MS Instruments and therefore has to be defined empirically. Define the Forevac Threshold by watching the pressure on the Instrument Control panel: Close valve 39 and notice the pressure value after the system has stabilized. Add about 20 units as a safety margin.

<u>NOTE:</u> In case the reactor is exhausted, the Forevac Threshold value will not be reached in a minutes' time and water may enter the inlet system.

b. FV PUMP SAMPLER [sec]: e.g. 5 sec

When the forevacuum threshold is reached, the system pumps for another 5 seconds before closing valve 39.

c. HV PUMP TIME SAMPLER [sec]: e.g. 60

Simultaneous with the closing of valve 39, valve 40 is opened and the system is pumped with High Vacuum for one minute.

<u>NOTE:</u> — Pump Time Sampler is used for the H/Device — Pump Time Bellow is used for the sample side — Standard gas is introduced manually

d. REACTION TIME [sec]:

Time for the injected substance to react with chromium. Reaction time differs from substance to substance. H_2O only needs 20 to 60 seconds to react whereas organic compounds need longer time (to be determined empirically).

NOTE: Valve 11 must be closed!

e. EQUILIBR.TIME [sec]:

Valve 11 is opened and the gas mixture is allowed to expand into the intermediate or expansion volume (connecting metal hose plus valve body)

An equilibration time of 30 seconds is recommended for 800 to 850 °C. For other temperatures, this needs to be tested empirically.

f. TRANSFER TIME [sec]:

Time for the gas to expand from the expansion volume into the variable volume (bellow).

H/Device

Fig. 5 - 4

METHOD : H/DEVICE >>> E X P E R I M E N T <<< COMMENT COMMENT : GAS : HD GASNAME CUP # 7 CUP # 8 : 2.0 : 3.0 CUP # 0 : 0.0 RATIO 1 X/Y RATIO 2 X/Y : 3.0 2.0 : 0.0 0.0 1 CHANGEOVER : VAR. VOLUME 1 COV PORT #1 : VAR. VOLUME 2 COV PORT #2 COV PORT #3 : COV PORT #4 : : 2 STANDARD PORT # : 1 SAMPLE PORT # MEASURE : P/M6 ORDER IDLE TIME [SEC] : 16 INTEGRATION TIME [SEC] : 8 BACKGROUND [SEC] : 30 [SEC] : 16 IDLE TIME INTEGRATION TIME DELAY TIME [SEC] : 2.0 PEAKCENTER : 2.0 [SEC] : 1.0 MASS DELAY TIME PRESS ADJUST MASS : 2.0 MASTER LEVEL [V] : 6.0 [SEC] : 1.0 DELAY TIME INTERFERING MASS GASNAME : HD : 2.0 : 3.0 CUP # 7 CUP # 8 CUP # 0 : 0.0 INTERFERING MASS IDLE TIME [SEC] : 0 MASS 1 PORT : CUP# :0 INT. TIME [SEC] : 0 : 0.0 : 0 : 0.0 :0 2 : 3 : 0.0 :0 : : : 0.0 4 :0 : : : 0.0 :0 : 5 : :0 : 6 : 0.0 : : 0 7 : 0.0 :0 : : 0 8 : 0.0 :0 : : 0.0 9 :0 : 0 : : 0.0 : 0 :0 10 : >>> P R O C E S S <<< MODE : -FOREVAC THRESHOLD FV PUMP TIME SAMPLER [uBAR]: 30 [SEC] : 5 HV PUMP TIME SAMPLER FV PUMP TIME BELLOW HV PUMP TIME BELLOW REACTION TIME [SEC] : 60 [SEC] : 5 [SEC] : 30 [SEC] : 60 [SEC] [SEC] [SEC] EQULIBRATION TIME TRANSFER TIME : 60 <<< MODE : FORMAT >>> FORMAT EVALUATION : S1 OUTLIER TEST PRINTER LIST TYPE GRAPHICS : LONG : NO REPORT ALPHA (CO3) CORRECTION ALPHA (H2O) CORRECTION ATOM% / APE REPORT NO NO : : NO

0

0

0

Fig. 5 - 5

>>> S E Q U E N C E T A B L E : H_DEVICE

PORT NUMBER	METHOD STANDARD IDENT	SAMPLE IDENT ACTION		
>16/9	H/DEVICE oztech-62.25	smow	/	/
>16/9	H/DEVICE oztech-62.25	smow	1	/
>16/9	H/DEVICE oztech-62.25	smow	/	/
>16/9	H/DEVICE oztech-62.25	smow	/	1
>17/9	H/DEVICE oztech-62.25	SLAP	1	/
>17/9	H/DEVICE oztech-62.25	SLAP	1	/
>17/9	H/DEVICE oztech-62.25	SLAP	1	/
>17/9	H/DEVICE oztech-62.25	SLAP	1	1
>18/9	H/DEVICE oztech-62.25	GISP	/	/
>18/9	H/DEVICE oztech-62.25	GISP	/	/
>18/9	H/DEVICE oztech-62.25	GISP	/	/
>18/9	H/DEVICE oztech-62.25	GISP	/	1
> 1/9	H/DEVICE oztech-62.25	sample#1	/	/
>1/9	H/DEVICE oztech-62.25	sample#1	/	/
>1/9	H/DEVICE oztech-62.25	sample#1	/	/
>1/9	H/DEVICE oztech-62.25	sample#1	/	/
>2/9	H/DEVICE oztech-62.25	sample#2	/	/
> 2/9	H/DEVICE oztech-62.25	sample#2	/	/
>2/9	H/DEVICE oztech-62.25	sample#2	/	/
>2/9	H/DEVICE oztech-62.25	sample#2	/	/
>3/9	H/DEVICE oztech-62.25	sample#3	1	/
>3/9	H/DEVICE oztech-62.25	sample#3	/	,
>3/9	H/DEVICE oztech-62.25	sample#3		,
>3/9	H/DEVICE oztech-62.25	sample#3	/	/
>4/9	H/DEVICE oztech-62.25	sample#4	/	/

6. Preparing a sequence and starting the measurement:

To start a measurement with the H/Device move to the <SEQUENCE EDITOR> and define a sequence first.

6

Start by pressing F8 (CREATE). Enter your sequence table name and the number of 'lines', which refers to the number of samples to be measured. Edit each line and fill out the fields with the appropriate entries like

		here, 1 is the sample number and 9 is the autosampler method
—	Sample ident 1-3	put in a sample identifier scheme of your choice. Each of the en-
		tries is searchable for retrieving the data
—	Method	Put in a valid method name that defines the measurement pa-
		rameters for this sample
—	Standard	Use a valid standard name.
—	Action	No action is required. You may put in a reference refill (RR) or a
		buffered reference (BR) if appropriate
—	Sample size	not required. Normally, 1 µl of sample is injected, determined by the method of the autosampler

For further information on sequence editing, refer to the ISODAT Manual.

As usual, the measurement is started from the <SEQUENCE ACQ>uisition editor screen by pressing F5 (='MEASURE').

<u>NOTE:</u> The H/Device acquisition module does not include a <SINGLE ACQ>uisition option. All measurements must started using <SEQUENCE ACQ>uisition.

Thermo Finnigan MAT GmbH Barkhausenstr. 2 28197 Bremen Germany