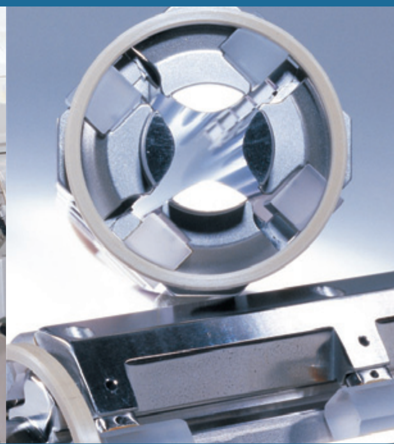
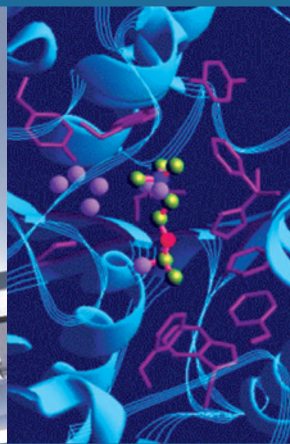
Thermo Fisher Scientific

Water Injection with TC/EA or Flash EA 1112/2000 HT

Revision A - 1250540





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Water Injection with TC/EA or Flash EA 1112/2000 HT

This manual outlines water injection using a TC/EA or a Flash EA 1112/2000 HT. It deals with the following topics:

Introduction

Liquids injected into the high-temperature conversion reactor are primarily purified waters, that is H_2O. Few other substances have been tested, some of which showed also reasonable results (ethanol, urine, blood plasma, for example). Operating conditions and statements about life time of the parts when analyzing other substances than water are expected to be similar. Specifications are only given for water. This document explains setup, operating conditions and methods to inject water.

Available Autosamplers

The following autosamplers are available:

- AS/AI 3000
- TriPlus
- GC PAL

All autosamplers are controlled by the Isodat software via COM port. For additional information, refer to the autosampler manuals as well.

AS/AI 3000

The AS/AI 3000 is a product of Thermo Fisher Scientific Italy and available in two different types:

- for GC and
- for EA.

The GC-type AS/AI 3000 is not readily applicable on an EA and vice versa as they contain different spare parts and brackets for mounting.

The AS/AI 3000 for EA is available:

- with an 8-position tray (Auto-Injector AI 3000, P/N 0723660) or
- with an 105-position carousel (AS 3000, P/N 0723670).

Using the AS/AI 3000 for liquid injections on a TC/EA or FlashEA 1112/2000 HT requires the *Kit for injection of water for TC/EA or FlashEA with AI/AS3000*. This kit contains the injector head, the special insert, an appropriate syringe, septa and other spare parts for a successful water analysis. The AS/AI 3000 is mounted on the TC/EA or the

FlashEA 1112/2000 HT using the brackets supplied with the autosampler. The recommended syringe is a 0.5 µL syringe. Refer to "Example Method for AS/AI 3000" on page 2-8.

TriPlus

The TriPlus is a product of Thermo Fisher Scientific Italy. Special brackets for mounting on a TC/EA or FlashEA 1112/2000 HT are required as well as the *Kit for injection of water for TC/EA or FlashEA with GC PAL* which contains the injector head, the special insert, an appropriate syringe, septa and some other spare parts.

GC PAL

The GC PAL autosampler is a product of CTC Analytics[1]. It is the successor of the A200S used for water injections previously. Special brackets for mounting on a TC/EA or FlashEA 1112/2000 HT are required as well as a *Kit for injection of water for TC/EA or FlashEA with GC PAL*. The kit contains the injector head, the special insert, an appropriate syringe, septa and some other spare parts. Setting of tray and syringe type and X, Y ,Z-position of tray and injector must be taken from the CTC Analytics manual. A 1.2 µL syringe is recommended.

Configuration in Isodat

A proper configuration of Isodat is necessary to ensure smooth operation between the AS and Isodat. All autosamplers must be operated by Isodat via RS232 ports (COM port). The corresponding COM port and the autosampler configuration as well as the syringe must be set as indicated in the autosampler properties of the Isodat Configurator.

Note The GC PAL is best operated using the driver of the A200S. The driver for the AS/AI 3000 is only installed during an Isodat installation following the setup with XCalibur support. See Figure 1. ▲

[1] www.ctc.ch

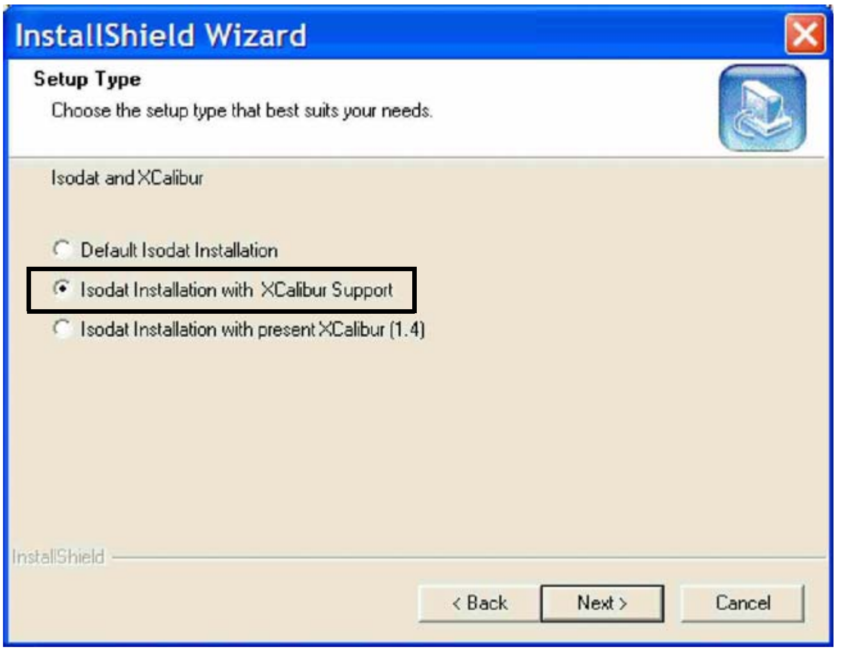


Figure 1. Isodat installation with XCalibur suport

The driver can be installed afterwards by re-installing the current service pack in use. The properties of all autosamplers can be changed in the Configurator. Access is possible via the tab of pre-defined Elemental Analyzer Sets for ConFlo IV. See Figure 2.

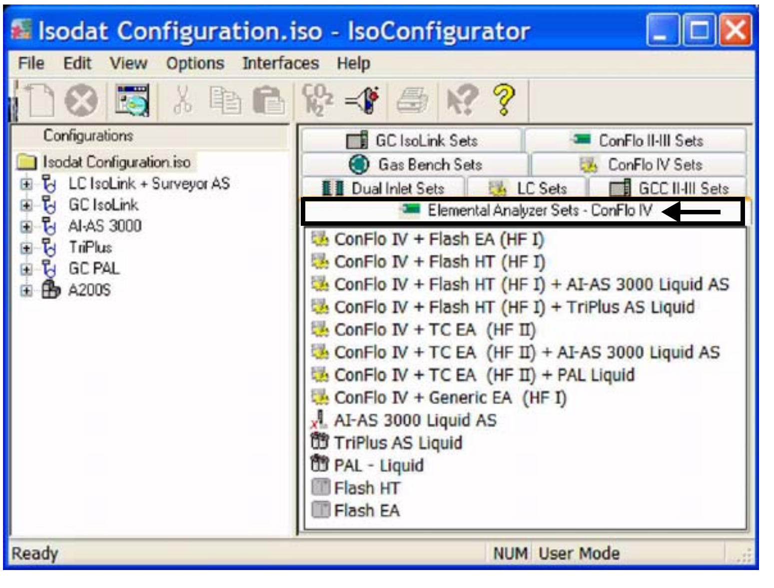


Figure 2. Access to autosampler properties in Configurator

The AS/AI 3000 driver must be configured in the Configurator using this device. Right- click on the icon.

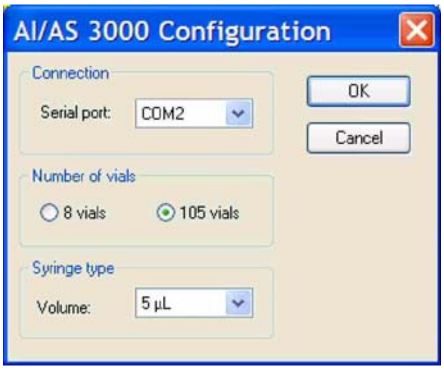


Figure 3. Serial port and settings for connecting AI/AS 3000 to computer

Check the serial port for the connection of the autosampler to the computer. Select the correct number of vials. When working with the 0.5 µL syringe, the set volume should be 5 µL. See Figure 3.

The TriPlus driver must be configured in the Configurator using this device. Right- click on the icon.

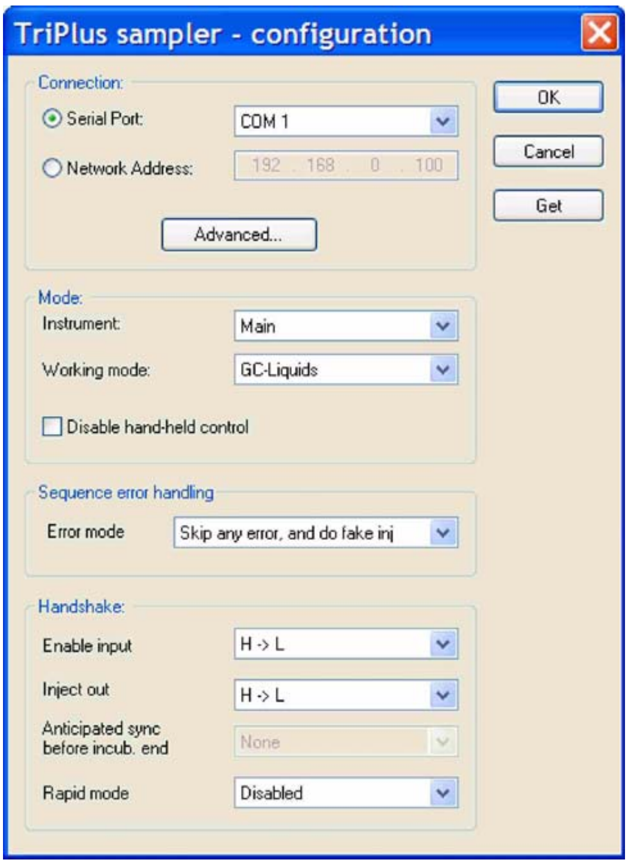


Figure 4. Settings for connecting TriPlus to computer

The GC PAL driver must be configured in the Configurator using this device. Right- click on the icon.

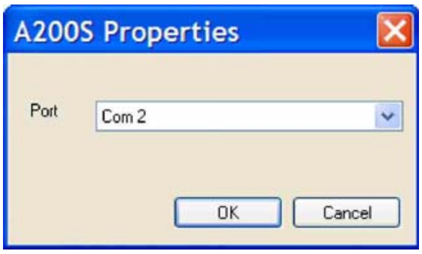


Figure 5. Port for connecting GC PAL to computer

Choose the correct COM port. See Figure 5. The syringe type must be set in the GC PAL. For detailed information, refer to the GC PAL manual.

Elemental Analyzer Setup

Water injections can be performed on the FlashEA 1112/2000 HT or on the TC/EA by using the high-temperature conversion reactor. Reactor temperatures should be 1400 °C. Commonly, column temperature is 90 °C. The carrier flow is set to 100 mL/min.

Age and condition of the reactor and the separation column may require adjustments of flow and GC temperature to achieve sufficient separation of the H_2 and CO peak.

Note The fan on top of the TC/EA should not be used to maintain a high temperature of the injector head. ▲

Reactor Setup

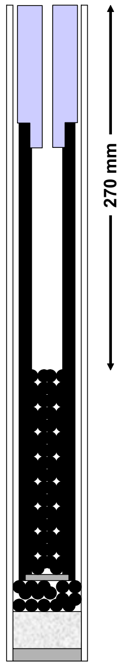


Figure 6. Reactor for liquids

The reactor for liquids differs from the setup for solids. Any graphite must be removed, and it must be taken care that the water vapor is transferred quickly into the hot zone without contacting the ceramic tube. See Figure 6.

This is achieved by the special stainless steel insert. The insert must preferably be on a level with the rim of the ceramic tube. This way, the needle tip introduces deeply into the special insert. Together with the carrier flow, this prevents contact with the ceramic tube after the rapid expansion of the water. The space usually filled by the crucible is now filled with glassy carbon granules to avoid fast consumption of the glassy carbon tube by providing another carbon source in the reaction zone.

Syringes

Table 1 lists the volumes of syringes together with their part numbers.

Table 1. Syringes

Volume [µL]	P/N
0.5	36504045
1.2	1087760
10	1198440[1]

[1] gas tight; alternatively (not delivered)

To ensure reproducible volumes, the amount of liquid injected using a syringe should be at least a tenth of the syringe volume. Any volume above 0.2 µL requires dilution (managed by the interface) to obtain amplitudes in a reasonable range.

The maximum injected volume is 1 µL. Larger volumes lead to an uncontrollable expansion when the water passes into the gas phase. The 0.5 µL syringe is used with the AS/AI 3000. The 1.2 µL syringe is used with the GC PAL (CTC Analytics).

Autosampler Methods

This section outlines example methods for several autosamplers.

General Remarks

Slow sample uptake is recommended to avoid gas bubbles. Syringes with plungers down to the needle tip (plunger-in-needle) require fast injection (pre injection delay zero). Capillary forces inside the needle may contribute to memory effects. All syringes should be kept in the reactor, so that the sample is entirely evaporated (post injection delay 10-16 s). Another step of cleansing is performed by rinsing the syringes with the sample prior to the injection (plunger strokes or rinses). Recommended autosampler methods will be outlined below.

Example Method for AS/AI 3000

This section describes an example method when using the AS/AI 3000 for water injection. See Figure 7.

The default syringe size set in the Configurator is 5 µL. The sample volume of 1 µL as shown in the method accounts for a sample volume of 0.1 µL.

Alternatively, rinses can be used to avoid cross contamination of samples. Rinses are deposited in the waste container of the autosampler while plunger strokes rinse the syringe in the sample vial. Sample depth can be set to Center when using micro inserts.

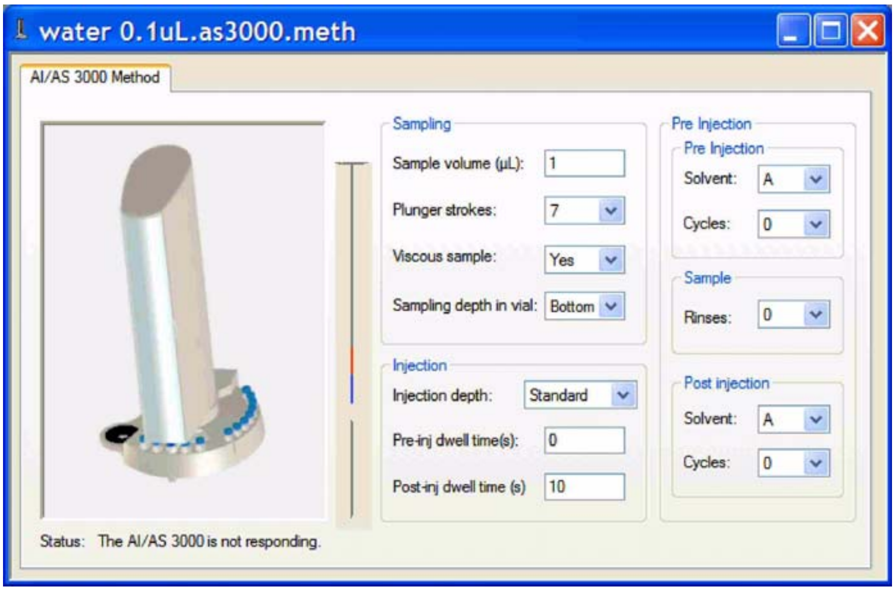


Figure 7. AS/AI 3000 method

Example Method for TriPlus

This section describes an example method for the TriPlus using a 10 µL syringe. See Figure 8.

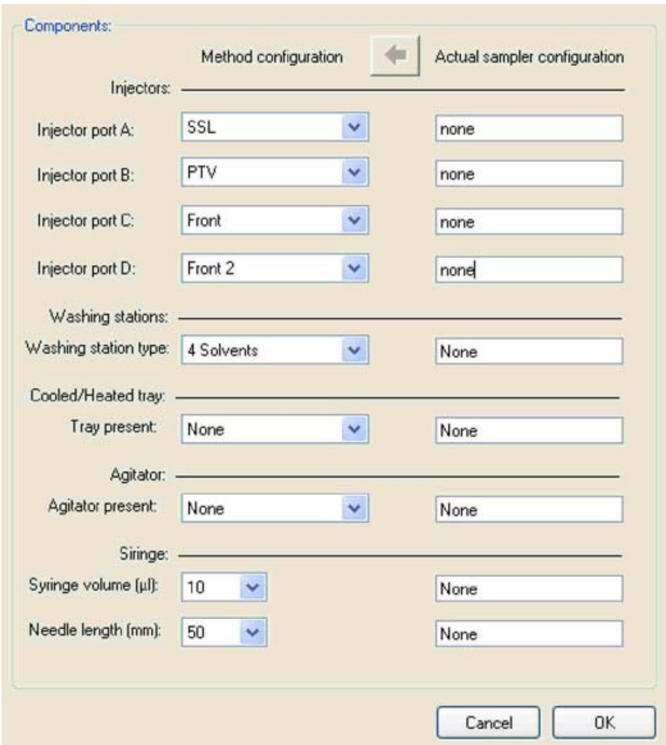


Figure 8. TriPlus method

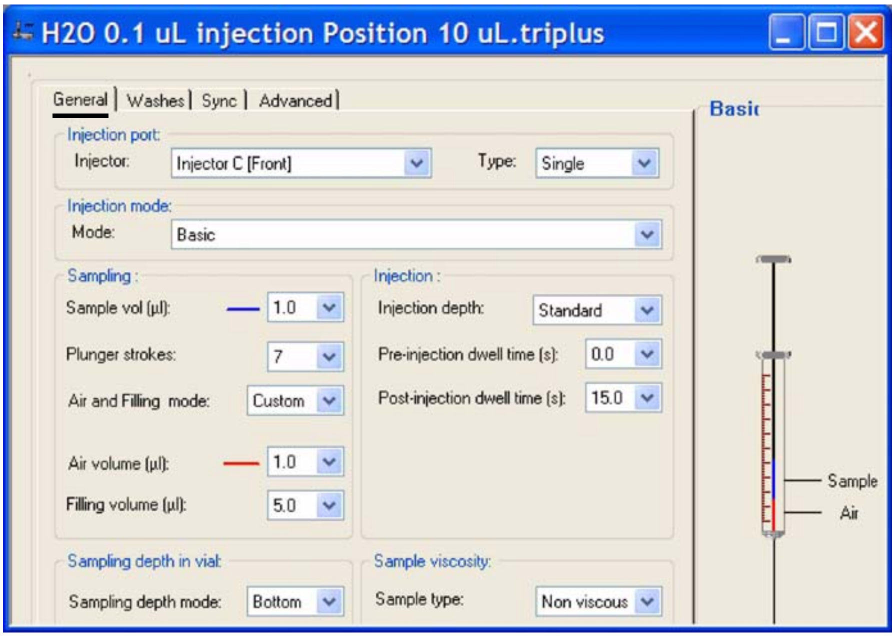


Figure 9. TriPlus method - General tab

Figure 9 shows the General tab of the TriPlus method.

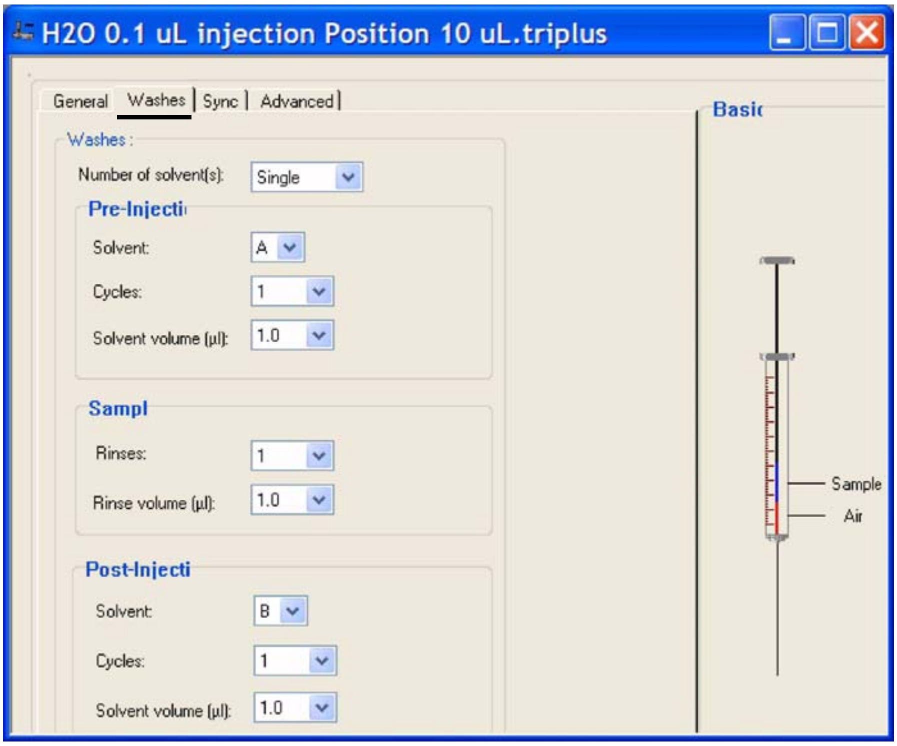


Figure 10. TriPlus method - Washes tab

Figure 10 shows the Washes tab of the TriPlus method.

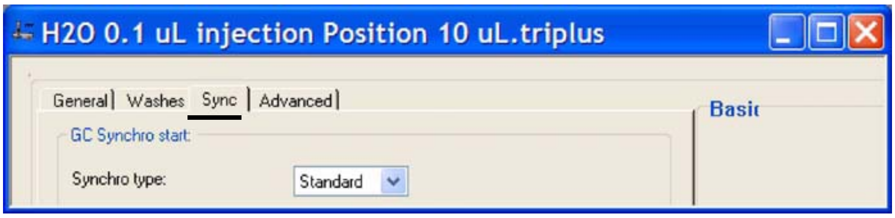


Figure 11. TriPlus method - Sync tab

Figure 11 shows the Sync tab of the TriPlus method.

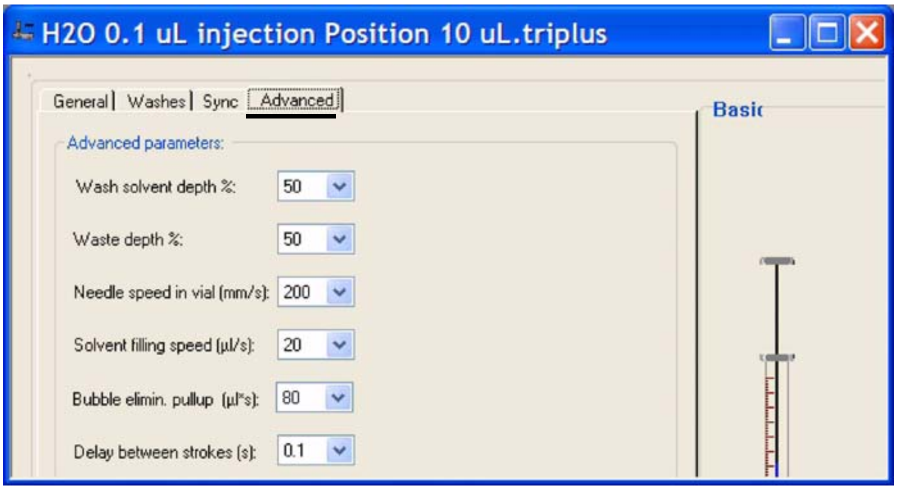


Figure 12. TriPlus method - Advanced tab

Figure 12 shows the Advanced tab of the TriPlus method.

Example Method for GC PAL

This section describes an example method for the GC PAL. The actual syringe size must be set in the GC PAL.

Note The recommended 1.2 µL syringe cannot be chosen. Define the 2.0 µL syringe instead. The syringe size in the method (see Figure 13) and in the GC PAL must be identical. ▲

The size and the corresponding sample volume are used to define the plunger height which is then used when uploading the method to the autosampler.

Figure 13. GC PAL method

Alternatively, a method can be created using the GC PAL. Refer to the GC PAL manual.

Using the PAL loader software (on a CD in the autosampler box) a setup for water injections can be uploaded. This setup can be found in the Isodat folder at C:\Thermo\Isodat NT\Global\Help Files\PAL. The appropriate file is EA water_080310.sss or HDevice 040203.sss. These files contain a method saved as method no. 9. The method is used by selecting Internal No 9 in the sequence. See Figure 16.

Note The sss-file does not contain proper x,y,z entries for tray and injector position! These positions must be changed and adjusted to your system setup. Refer to the GC PAL manual for detailed description of how to change the positions. ▲

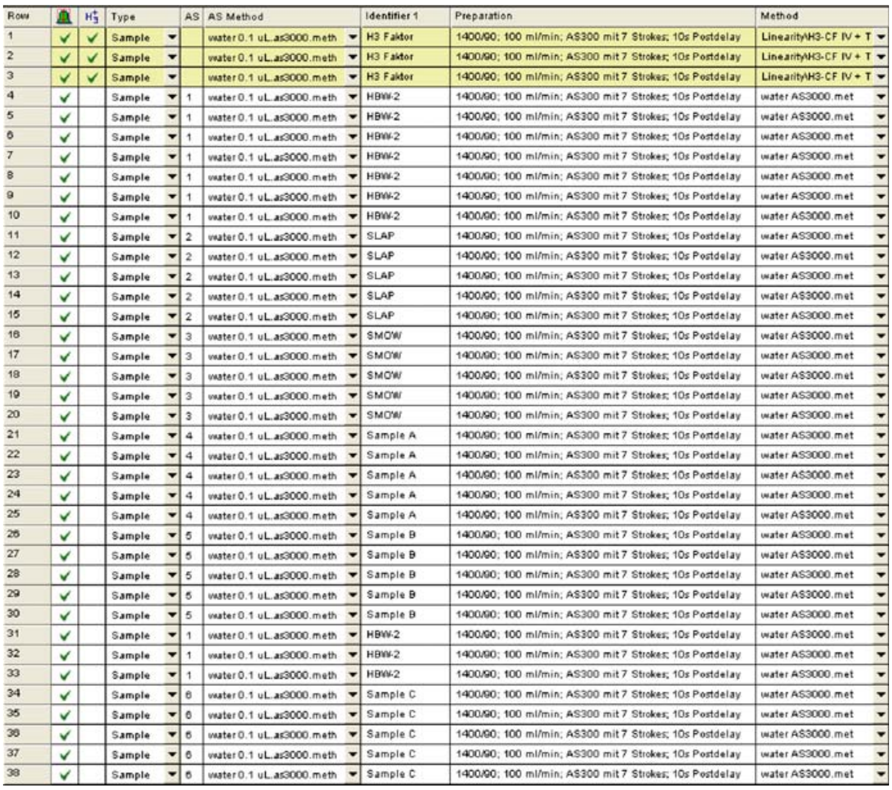
Sequence Setup

Sequences can be set up as shown in Figure 14. Samples can be injected five times to discard the first two results, if affected by memory. This is only necessary, if the samples vary considerably in their isotopic difference. It is recommended to use standards for post-evaluation. Common procedures are described in the literature, for example:

- Coplen T (1988): Normalization of oxygen and hydrogen isotope data. Chem. Geol. **72**: 293-297.
- Nelson ST (2000): A simple, practical methodology for routine VSMOW/SLAP normalization of water samples analyzed by continuous flow methods. Rapid Comm. Mass Spectrom. **14**: 1044-1046.

Example Sequence Using AS/AI 3000

Figure 14 shows an example sequence for water injections using an AS/AI 3000 in Isodat 3.0.



Row		H_3^+	Type	AS	AS Method	Identifier 1	Preparation	Method
1	✓	✓	Sample		water 0.1 uL.as3000.meth	H3 Faktor	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	Linearity\H3-CF IV + T
2	✓	✓	Sample		water 0.1 uL.as3000.meth	H3 Faktor	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	Linearity\H3-CF IV + T
3	✓	✓	Sample		water 0.1 uL.as3000.meth	H3 Faktor	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	Linearity\H3-CF IV + T
4	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
5	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
6	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
7	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
8	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
9	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
10	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
11	✓		Sample	2	water 0.1 uL.as3000.meth	SLAP	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
12	✓		Sample	2	water 0.1 uL.as3000.meth	SLAP	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
13	✓		Sample	2	water 0.1 uL.as3000.meth	SLAP	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
14	✓		Sample	2	water 0.1 uL.as3000.meth	SLAP	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
15	✓		Sample	2	water 0.1 uL.as3000.meth	SLAP	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
16	✓		Sample	3	water 0.1 uL.as3000.meth	SMOW	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
17	✓		Sample	3	water 0.1 uL.as3000.meth	SMOW	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
18	✓		Sample	3	water 0.1 uL.as3000.meth	SMOW	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
19	✓		Sample	3	water 0.1 uL.as3000.meth	SMOW	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
20	✓		Sample	3	water 0.1 uL.as3000.meth	SMOW	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
21	✓		Sample	4	water 0.1 uL.as3000.meth	Sample A	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
22	✓		Sample	4	water 0.1 uL.as3000.meth	Sample A	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
23	✓		Sample	4	water 0.1 uL.as3000.meth	Sample A	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
24	✓		Sample	4	water 0.1 uL.as3000.meth	Sample A	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
25	✓		Sample	4	water 0.1 uL.as3000.meth	Sample A	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
26	✓		Sample	5	water 0.1 uL.as3000.meth	Sample B	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
27	✓		Sample	5	water 0.1 uL.as3000.meth	Sample B	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
28	✓		Sample	5	water 0.1 uL.as3000.meth	Sample B	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
29	✓		Sample	5	water 0.1 uL.as3000.meth	Sample B	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
30	✓		Sample	5	water 0.1 uL.as3000.meth	Sample B	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
31	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
32	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
33	✓		Sample	1	water 0.1 uL.as3000.meth	HBW-2	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
34	✓		Sample	6	water 0.1 uL.as3000.meth	Sample C	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
35	✓		Sample	6	water 0.1 uL.as3000.meth	Sample C	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
36	✓		Sample	6	water 0.1 uL.as3000.meth	Sample C	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
37	✓		Sample	6	water 0.1 uL.as3000.meth	Sample C	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met
38	✓		Sample	6	water 0.1 uL.as3000.meth	Sample C	1400/90; 100 ml/min; AS300 mit 7 Strokes; 10s Postdelay	water AS3000.met

Figure 14. Sequence for water injections using AS/AI 3000

The sequence shows repetitive analysis of a lab standard (HBW-2) and of the international calibration standards V-SMOW and SLAP, respectively.

Note The column for automatic H_3 factor analysis is only available with ConFlo IV and Isodat 3.0 or higher. ▲

Example Sequence Using GC PAL

Figure 15 shows an example sequence for water injections using a GC PAL (as A200S).

Row			H_3^+	Amount	Type	AS	AS Method	Identifier 1	Preparation	Method
1	✓		✓		Sample		AS\water 1.2 uL.A200S	H3-Factor		Linearity\H3-CF IV + 1
2	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
3	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
4	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
5	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
6	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
7	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
8	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
9	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met
10	✓				Sample	1	AS\water 1.2 uL.A200S	HBW-2		water GC-Pal.met

Figure 15. Sequence for water injections using GC PAL - (1)

The autosampler method was edited in Isodat and saved as water 1.2 uL.A200S. Alternatively, the method can be edited in the GC PAL and saved as Internal No. 9. See Figure 16.

Note The column for automatic H_3 factor analysis is only available with ConFlo IV and Isodat 3.0 or higher. ▲

Row			H_3^+	Amount	Type	AS	AS Method	Identifier 1	Preparation	Method
1	✓		✓		Sample		>Internal No 9	H3-Factor		Linearity\H3-CF IV + 1
2	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
3	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
4	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
5	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
6	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
7	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
8	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
9	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met
10	✓				Sample	1	>Internal No 9	HBW-2		water GC-Pal.met

Figure 16. Sequence for water injections using GC PAL - (2)

Troubleshooting

Table 2 lists common sources of problems and recommendations to resolve them.

Table 2. Common sources of problems

Characteristics	Likely cause	Action to be taken
Double peak of H_2	syringe defect	Replace syringe
High standard deviation for both isotopes	septum particles or sample particles are introduced into reactor during injection	Replace sample. Replace syringe. Replace septum
High standard deviation of H_2	wrong H_3 factor	Determine new H_3 factor
High standard deviation of CO	bad separation of H_2 and CO	Bake out separation column at maximum temperature under helium flow (190 °C for two days in FlashEA HT, 300 °C over night in TC/EA)
	varying background determination	Recalibrate jump calibration in Instrument Control of Isodat
Tailing of H_2	high restriction in glassy carbon tube, adsorption	clean reactor, use coarse granulate in glassy carbon tube
Tailing of H_2 and CO	adsorption/desorption effects	clean reactor, exchange ceramic and glassy carbon tube
High mass 30	dirty separation column	bake out at maximum temperature FlashEA HT: 190 °C, 48 h TC/EA: 300 °C, 4-5 h

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