IsoPrime100 Elemental Analyser User Guide

INTRODUCTION

ELEMENTAL ANALYSER MANUAL

This manual describes the detailed operation and maintenance for the Elemental Analyser when used in combination with an IsoPrime mass spectrometer. It must be used in conjunction with the following manuals:

- The Elemental Analyser manual supplied by Elementar Analysensysteme GmbH.
- The IsoPrime mass spectrometer manual supplied by Isoprime Ltd.
- The Reference Gas Injector manual supplied by Isoprime Ltd.
- The IonVantage User Interface manual supplied by Isoprime Ltd.
- The Microbalance manual supplied by the balance manufacturer.

This manual supplies additional information and assumes that the operator is familiar with the hardware and software described in the manuals listed above. Where required, brief descriptions and recommendations have been repeated from these manuals, but the relevant manuals will need to be consulted for complete descriptions.

If you have any comments or suggestions concerning this manual, please contact the Customer Service department at Isoprime Ltd, or your local Isoprime Ltd representative.

All information contained in this manual is believed to be correct at the time of publication. The publishers shall not be liable for errors contained herein nor for incidental or consequential damages in connection with the furnishing, performance or use of this material.

All product specifications, as well as the information contained in this manual, are subject to change without notice.

Isoprime Ltd. makes no warranty of any kind with regard to this material, including, but not limited to, the implied warranties of merchantability and fitness for a particular purpose.

SAFETY INFORMATION

Safety information concerning the Elemental Analyser can be found in the Elementar manual for the Analyser.

The IsoPrime mass spectrometer meets the following IEC (International Electrotechnical Commission) classifications:

- Safety Class 1
- Transient Overvoltage Category II
- Pollution Degree 2

This unit has been designed and tested in accordance with recognised safety standards and designed for use indoors.

If the instrument is used in a manner not specified by the manufacturer, the protection provided by the instrument may be impaired.

Whenever the safety protection of the IsoPrime is compromised, disconnect the instrument from all power sources and secure the unit against unintended operation.

Only suitably qualified personnel should perform maintenance procedures.

Substituting parts or performing any unauthorised modification to the instrument may result in a safety hazard.

Disconnect the mains supply before removing covers.

You must comply with all local and national requirements for electrical and mechanical safety.

If you require any additional information, please contact the Customer Service Department at:

Isoprime Ltd
Isoprime House
Cheadle Hulme
Cheadle
SK8 6PT
UK

or your local Isoprime Ltd representative.

SAFETY SYMBOLS

Warnings in the manual or on the instrument must be observed during all phases of service, repair, installation and operation of this instrument. Failure to comply with these precautions violates the safety standards of design and the intended use of the instrument.

Isoprime Ltd. assumes no liability for the customer’s failure to comply with these requirements

The following safety notices and symbols are used in the manual or on the instrument:

WARNING

Warnings are given to highlight situations or conditions where failure to observe the instruction could result in injury or death to persons.

CAUTION

Cautions are given to highlight situations or conditions where failure to observe the instruction could result in damage to the equipment, associated equipment or process.

Warning: This is a general warning symbol indicating that there is a potential health or safety hazard.

Warning: This symbol indicates that hazardous voltages may be present.

Warning: This symbol indicates that hot surfaces may be present

Warning: This symbol indicates that there is a danger from corrosive substances.

Warning: This symbol indicates that there is danger from toxic substances.

Caution: This is a general caution symbol, indicating that care must be taken to avoid the possibility of damaging the instrument or affecting its operation.

CONTENTS

SITE REQUIREMENTS

The site requirements, for the Elemental Analyser and interface to the mass spectrometer, are described in this section. The site requirements for the Isoprime100 mass spectrometer are detailed in the IsoPrime100.

BENCHTOP REQUIREMENTS

THE ELEMENTAL ANALYSER

The Elemental Analyser must be located as close to the IsoPrime mass spectrometer as possible as and not further than 1.5m. The bench top on which the IsoPrime mass spectrometer is installed must have sufficient space to accept the Elemental Analyser and be able to support the additional weight.

It must be level and free from vibrations.

The dimensions of the Elementar elemental analysers are shown in the following table:

Dimension	**vario MICRO cube**	**vario EL cube/ vario ISOTOPE cube**	**vario PYRO cube**
Width	480mm	480mm	480mm
Depth	550mm	550mm	550mm
Height	550mm	550mm	610mm
Weight	80kg	80kg	80kg

There must be clearance all around the Elemental Analyser to allow for comfortable maintenance. Allow at least 150 mm round the back of the unit for adequate air ventilation.

THE DILUTER

Dimensions of the Diluter:

Width: 23 cm

Depth: 30 cm

Height: 9 cm

Weight: 2 Kg

The Diluter will need to be fitted as near as possible to the reference gas injector.

THE MICROBALANCE

For high precision elemental analysis, it is strongly recommended to use a 6-figure microbalance capable of measuring down to 1µg. With less precise balances, it will not be possible to achieve the expected levels of precision of measurement for elemental composition.

ELECTRICAL REQUIREMENTS

- Electrical requirements for the IsoPrime mass spectrometer must comply with the specifications given in the IsoPrime manual.
- Electrical requirements for the Elemental Analyser must comply with the specifications given in the Elemental Analyser manual.
- Electrical requirements for the microbalance must comply with the requirements given in its own manual.

Electrical power is supplied to the Diluter via the communication cable to the mass spectrometer and there are no additional requirements.

Warning: Users should ensure that the provision of the Mains supplies described in this document is in accordance with any local regulations.

The table below summarises the electrical characteristics for each of the modules that may be in use:

System	Circuit	Source	Max. Current @ 110V 60Hz	Max. Current @ 230V 50Hz	Max. Fuse Rating	Approx. Heat Output	Transient Sensitive
IsoPrime	Mass spectrometer	Mains	7.2A	3.4A	10AT	600W	Yes
IsoPrime	Rotary pump	Mains	4.4A	2.4A	10AT	300W	No
Data system	Computer + printer	Mains	N/A	3A	10AT	500W	Yes
vario EA	Elemental analyser	Mains	N/A	8A	See vario EA Manual	1500 to 1800W	No

Note: Each line in the table represents an individual Mains connection and uses an individual Mains lead.

Note: Mains supply voltage fluctuations should not exceed ±10% of the nominal voltage.

COMPRESSED AIR

The IsoPrime and the Elemental Analyser require no compressed air but the Reference Gas Injector and the Diluter require a regulated compressed air supply of 55psi. If a compressed air line is not available, a compressor must be supplied.

The air supply should be oil, water and particulate free.

The airline connections on the reference gas injector module and sample preparation systems are 6 mm (OD) push-fit.

Warning: Compressed gas cylinders should be securely fastened to an immoveable structure or permanent wall. Compressed gasses should be stored and handled in accordance with relevant safety codes.

Warning: To avoid possible eye injury, wear eye protection when using compressed gas.

VENTING NOXIOUS GASES

Warning: Necessary precautions **MUST** be taken (Gas extraction hoods over the entire system and properly located gas alarm units, appropriate to the gas in use). It may also be necessary to obtain permission from local Health and Safety authorities if using the system to inject dangerous or toxic gases like H_2, CO, and SO_2.

The operator **MUST** ensure that they understand local regulations and that they comply with them.

Warning: The Elemental Analyser produces only small quantities of gases like H_2, CO, and SO_2, diluted in large flows of inert Carrier gas and offers no problem.

In the IsoPrime system, gases vent normally at two points: the rotary pump exhaust and the reference gas vents and open split in the Reference Gas Injector. An optional safety vent kit is available if noxious gases are being used with the Reference Gas Box.

The operator **MUST** ensure that they understand local regulations and that they comply with them.

It **MUST NOT** be overlooked that gases flow down gas lines and through a number of components like pressure regulators and valves, all of which are connected together with generally soft material ferrules to form gas tight seals. Leaks can develop at any of these connections, with the potential to leak out significant amounts of pure toxic or dangerous gas.

Warning: All gas, which enters the mass spectrometer, will leave via the rotary pump exhaust. The exhaust ports of the rotary pumps are fitted with oil mist filters, however you may need to connect to an exhaust line (15mm internal diameter) leading to a suitable exhaust point. Consult the rotary pump manufacturer’s manual for details of exhaust requirements.

The safe exhausting of these fumes **MUST** be given careful consideration when working with hazardous materials, like SO_2, CO and H_2.

SYSTEM DESCRIPTION

INTRODUCTION

The system comprises of:

- The IsoPrime mass spectrometer
- The Elemental Analyser
- The Reference Gas Injector
- The Diluter (optional)

The Elemental Analyser allows the preparation of 'real-life' samples into a form compatible with the IsoPrime mass spectrometer.

The mass spectrometer is designed to analyse simple gases like CO_2, N_2, CO, SO_2, and H_2. The Elemental Analyser transforms solid and liquid samples into these simple gases.

The Elemental Analyser converts samples into CO_2, N_2, SO_2 and H_2 (via H_2O) when used in Combustion mode.

Samples are converted into CO and H_2, when used in pyrolysis mode.

The Reference Gas Injector, mounted in parallel to the Elemental Analyser, allows the introduction of pure gases into the mass spectrometer for calibration purposes. A full description of this unit is given in the *Reference Gas Injector Manual.*

The Diluter is an optional unit that can be sited in between the Elemental Analyser and the IsoPrime mass spectrometer for the purpose of diluting some portions of the carrier flow from the Elemental Analyser. A description of this unit is given in this manual.

Warning: Provided the necessary precautions have been taken (Gas extraction hoods over the system and properly located gas alarm units appropriate to the gas in use) and, The system can be used with dangerous or toxic gases like H_2, CO, and SO_2,provided permission from local Health and Safety authorities has been granted and the necessary precautions have been taken (Gas extraction hoods over the system and properly located gas alarm units with the particular gases in use)

A safety vent kit is available as an option for use in assisting in venting noxious gases safely.

THE ELEMENTAL ANALYSER

The Elemental Analysers that can be interfaced to the IsoPrime mass spectrometer are the Elementar vario MICRO cube, vario EL cube, vario ISOTOPE cube and the vario PYRO cube.

Information concerning the setup, operation and any operational safety precautions for the elemental analysers can be found in their own respective manuals.

It is particularly important to set up the Elemental Analyser in accordance with the manufacturer's recommendations and carry out all the recommended preliminary tests, **BEFORE** it is used to make any isotopic measurements. Ensuring the EA is in full working order beforehand eliminates many potential problems after interfacing with the IsoPrime.

ELEMENTAL ANALYSER COMBUSTION

PRINCIPLE OF OPERATION

The solid or liquid sample is weighed into a small tin capsule (or silver capsule in the case of analysis by pyrolysis) and loaded into the carousel autosampler. Liquid samples can be encapsulated with the aid of a capsule sealing press. When an acquisition is initiated the autosampler moves the sample into a combustion tube that is heated to between 950 - 1150°C depending on the species of interest.

The sample and capsule melt in the combustion tube under an atmosphere that is temporarily enriched with oxygen. The tin boat promotes flash combustion. The combustion products are carried through on oxidation catalyst by a constant flow of helium. The oxidation products are then passed through a reduction reactor. Copper granules within the reduction reactor reduce nitrogen oxides (NO, N_2O & N_2O_2) to N_2, SO_3 to SO_2 and remove any excess oxygen from the combustion tube. Volatile halogen compounds are bound on a silver wool layer in the plug of the reduction tube.

The remaining CO_2, N_2 and SO_2 (if N and S were present in the original sample) pass into one or more desorption columns (mode and instrument dependent). The desorption column(s) physically absorb the measurable components in the analysis gas mixture. Each sample gas is then desorbed separately by controlling the temperature of the desorption column(s). Once released the gases sequentially pass through a Thermal Conductivity Detector (TCD) and are vented out of the instrument.

When used with the IsoPrime, this vent is connected via an Open Split to the inlet of the mass spectrometer. Carbon, nitrogen and sulphur isotope ratios can then be measured against a pulse of reference gas of known composition. The reference gas is introduced either from the Reference Gas Injector or the bellows of the Dual Inlet.

The EA can be configured in a large number of ways depending on the required analysis and optional kits (please refer to the appropriate EA or EA variants manuals for set up). The table below illustrates suitable modes for EA-IRMS analysis:

Mode	MICRO cube	EL cube	ISOTOPE cube	PYRO cube
Sequential NC Combustion	✓	✓	✓	Option[5]
Sequential NCS Combustion	✓	✓	✓	Option[5]
Sequential NCHS Combustion	×	Option[2]	Option[2]	×
Sequential NCH Combustion	×	Option[2]	Option[2]	×
O Pyrolysis 1170°C	Option[1]	Option[1]	Option[1]	×
O Pyrolysis 1450°	×	×	×	✓
H Pyrolysis 1350°	×	Option[3]	Option[3]	×
H Pyrolysis 1450°	×	×	×	✓
Sequential HO Pyrolysis High Temp	×	×	×	✓
H Reduction Chromium (liquid)	Option[4]	Option[4]	Option[4]	Option[4]

[1] Low temperature O pyrolysis kit

[2] H_2O – H_2 Conversion kit

[3] Low temperature H pyrolysis kit

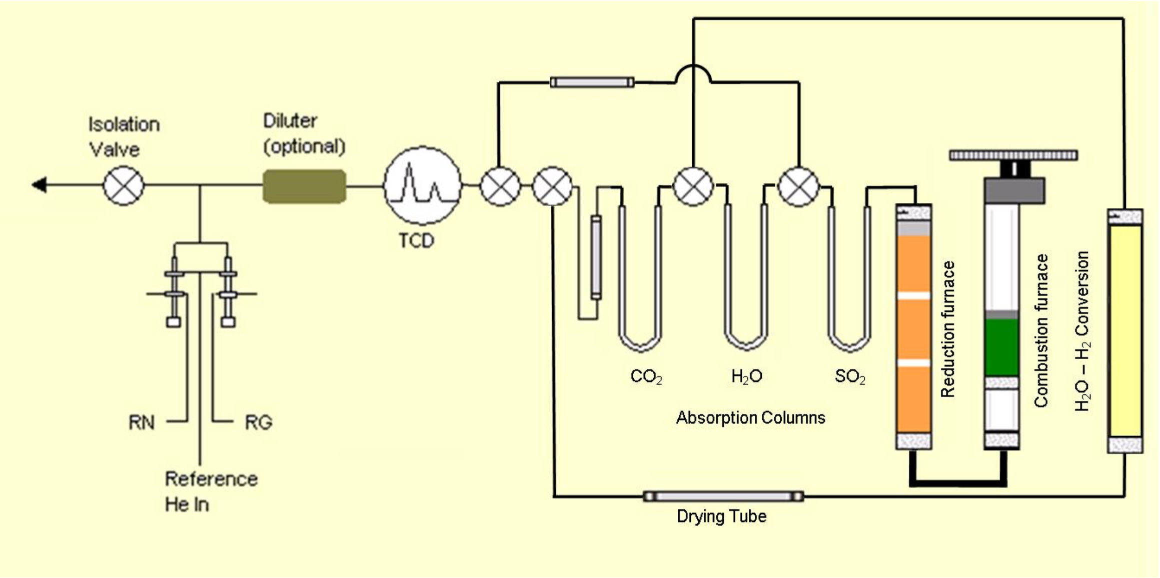
[4] Chromium reduction kit **AND** VLS (vario liquid sampler) kit

[5] NCS Upgrade kit

CONFIGURATION EXAMPLES

NCHS ANALYSIS

The diagram below describes the various components of the system used for CHNS analysis:

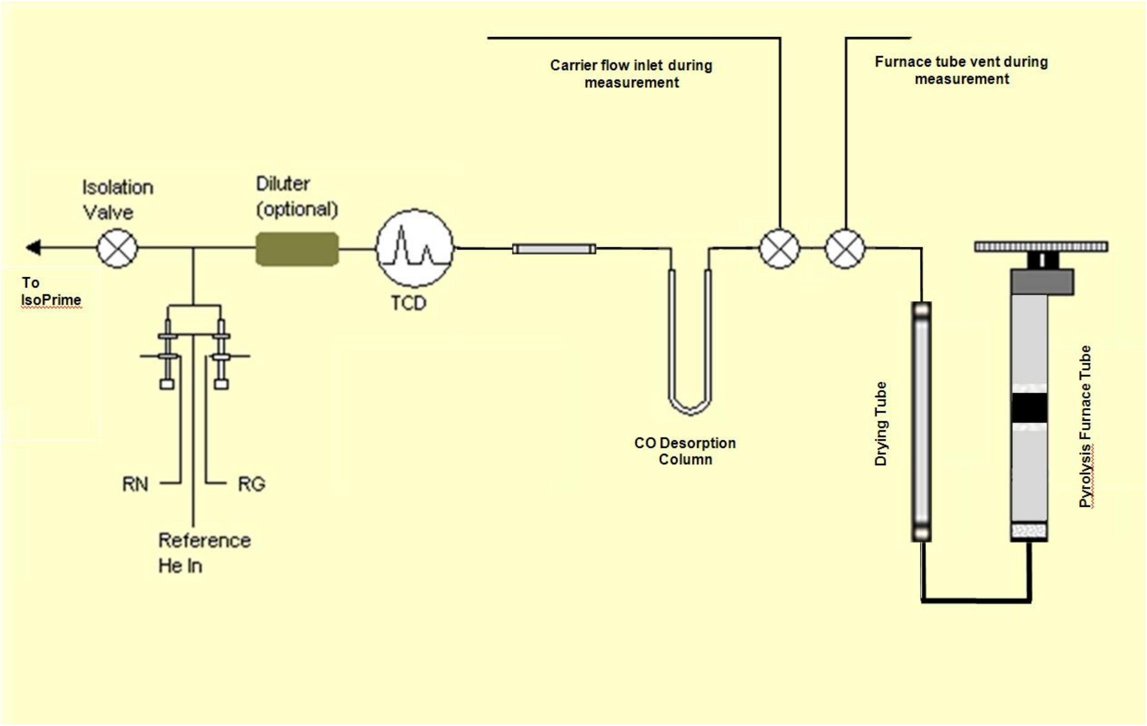


In the vario EL and ISOTOPE cubes a third furnace is fitted for CHNS analysis. This third tube is filled with a mix of magnesium, magnesium oxide and glassy carbon chips. When the water desorption column is heated, the valves in the EA switch to divert the flow through this tube where water is reduced to hydrogen.

The combustion and reduction furnace tubes are filled as for CNS analysis.

O PYROLYSIS

The diagram below illustrates the various components used for O analysis by pyrolysis, with back flush:

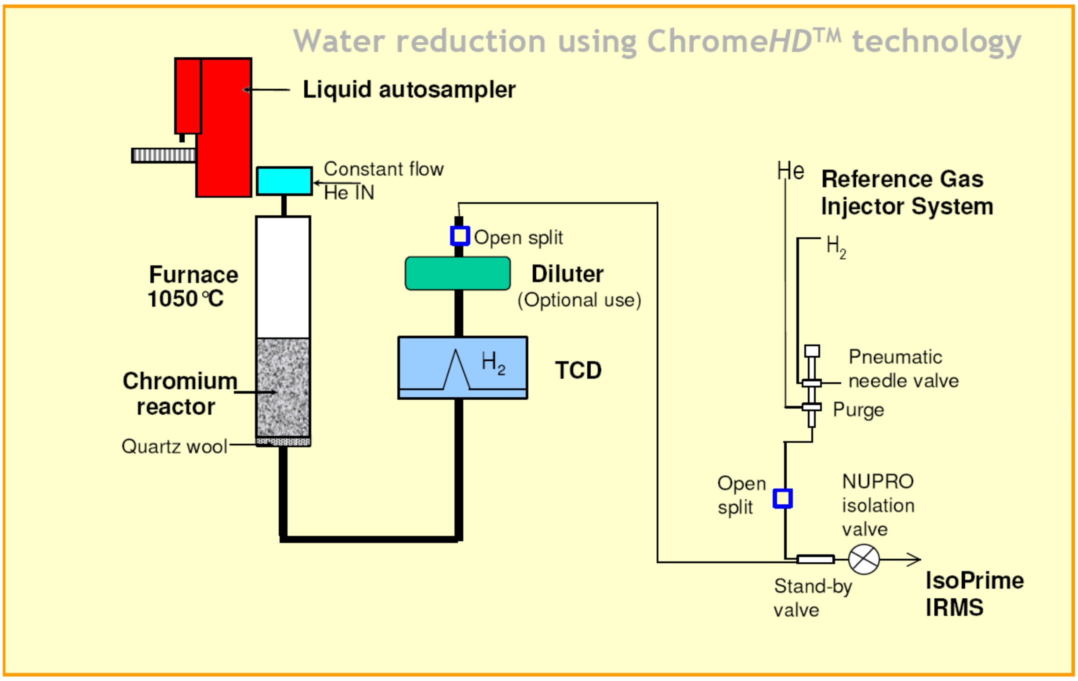


The pyrolysis tube is filled with carbon black. The vario ISOTOPE and PYRO cubes have the back-flush arrangement shown that delivers fresh helium to the desorption column during measurement. The vario EL cube does not have this back-flush arrangement.

Hydrogen pyrolysis or sequential HO pyrolysis has a similar set up, except that the furnace tube is filled with glassy carbon chips for hydrogen pyrolysis or an optimised mixture of glassy carbon chips and lamp black for sequential HO pyrolysis. Consult the appropriate EA variants manual for precise tube filling details.

H ANALYSIS (CHROME REDUCTION)

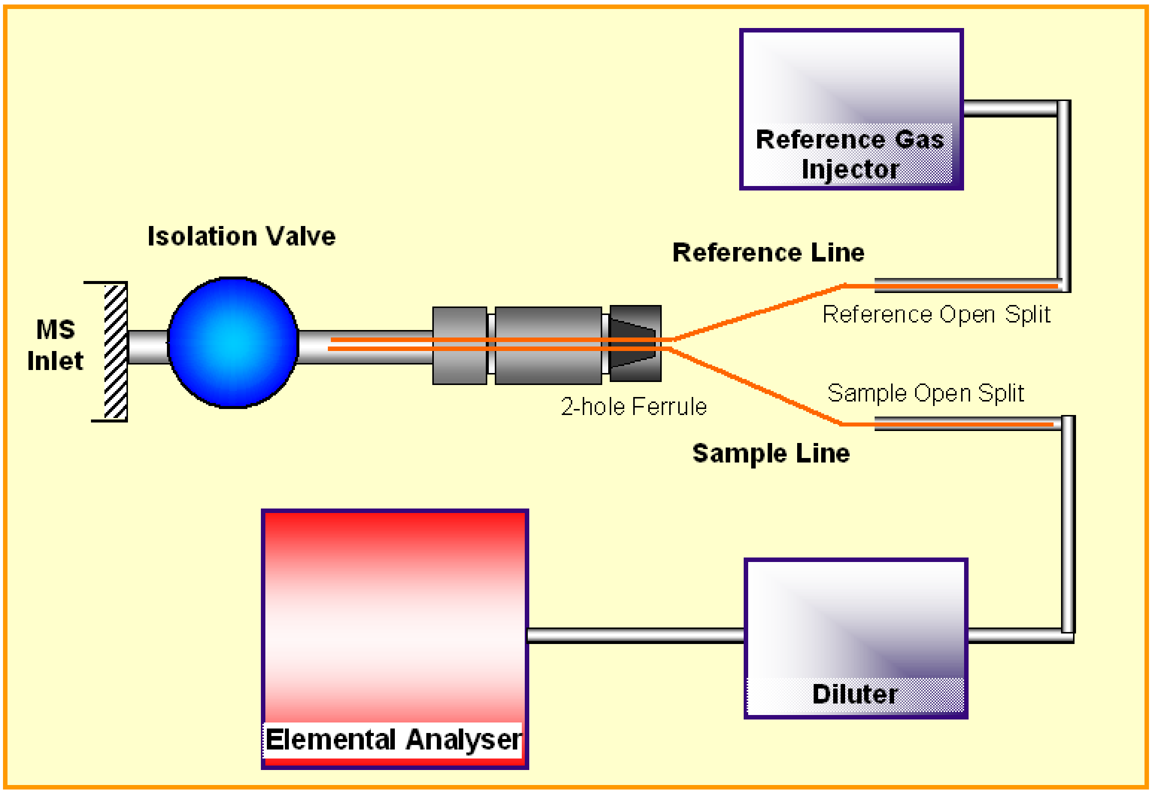
The diagram below illustrates the various components when used for H analysis by reduction with chromium:



Aqueous samples are injected through a septum into the furnace tube, and the water is reduced to hydrogen on the chromium.

INTERFACE GEOMETRY

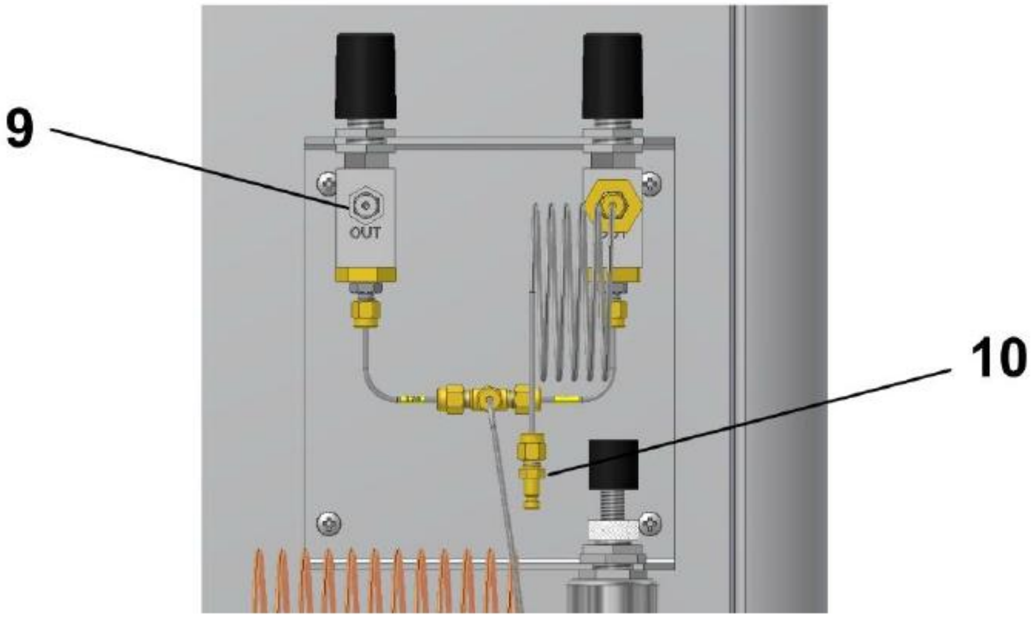
The Interface refers to the hardware, which is mounted between the mass spectrometer inlet and the Elemental Analyser.



The Interface consists of:

- An isolation valve mounted on the inlet of the mass spectrometer. Connected to this is a short piece of 1/16" stainless steel capillary that enters the Reference Gas Injector top panel. The isolation valve is a manual ON/OFF valve, closing this valve isolates the mass spectrometer from the external environment.
- A sample line of Vitreous Silica capillary (100 µm ID, length 1.5 m) is connected to the end of the SS capillary mentioned above. The other end of the sample line is inserted into a 1/16" SS capillary open split carrying the helium flow from the Elemental Analyser either directly from the analyser or via a diluter. . The sample line carries a portion of the sample gas in a helium carrier flow, from the Elemental Analyser to the ion source of the mass spectrometer. The remainder of the helium flow vents at the Sample Open Split.

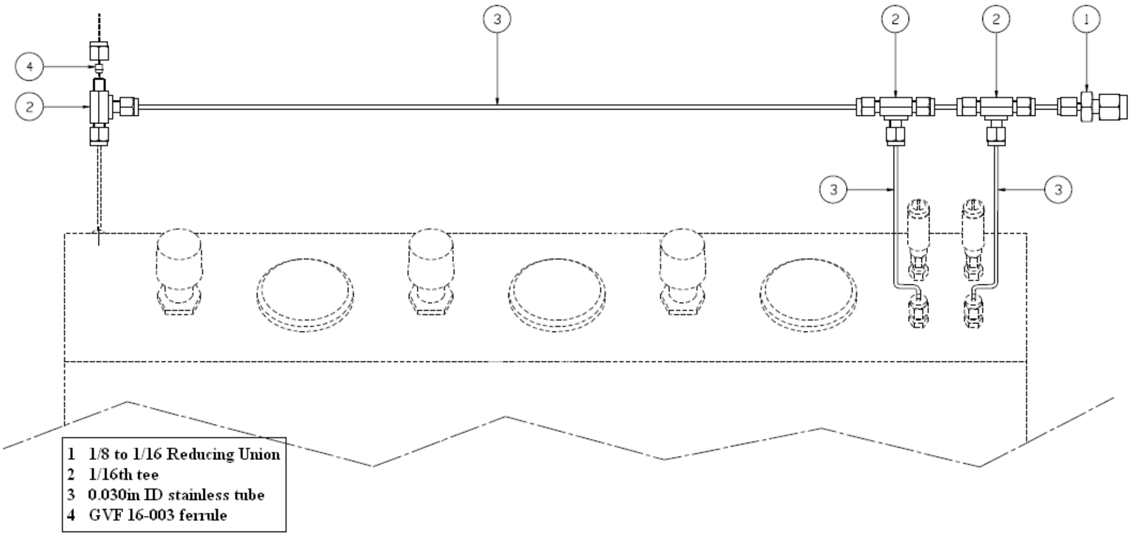
- A reference line of Vitreous Silica capillary (75µm ID, length 2 m) that is also connected to the end of the SS capillary mentioned above. The other end of the reference line is inserted into a 1/16” SS capillary carrying the helium flow from the Reference Gas Injector. The sample and reference line connect to the SS tube from the isolation valve via a two-hole graphitised vespel ferrule.
- Two needle valves on the rear of the EA. One is connected to the diluter via a length of 1/16” SS capillary and is normally set to provide a flow of approximately 100ml/min. The second is used to vent the remaining sample flow.



9	He-Meas	Measuring gas to the IRMS
10	He	Exhaust (vent)

SAFETY VENT KIT

On systems where H2, CO, or SO2 are being used as reference gases delivered through the reference gas box, a safety vent kit should be fitted to the reference gas box or boxes.



The open split point is sealed; the open split vent flow and the vent flows from the two gas supplies are carried out via 1/8th inch diameter tubing to the laboratory's extraction system.

THE DILUTER

GENERAL INFORMATION

The diluter is used when:

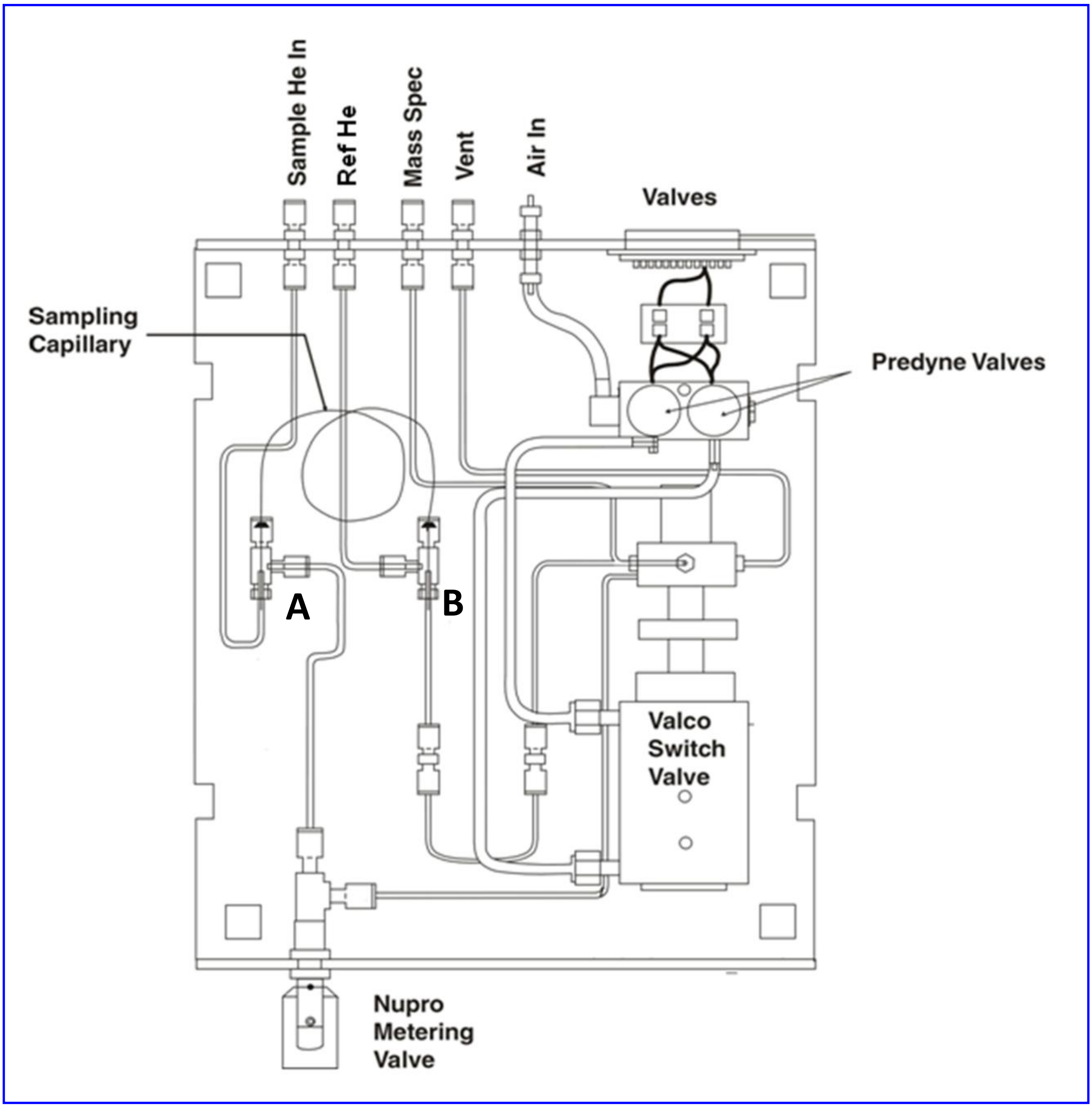
- A large amount of sample has to be processed by the Elemental Analyser to ensure homogeneity. This results in combustion or pyrolysis gases in such quantities that the ion currents produced exceed the normal measuring range of the Head Amplifiers. In this case the entire eluent from the Elemental Analyser is diluted during the acquisition.

- Within a particular sample, sequential analysis is required on two or more gas species and one of the gas species is produced in large quantities when compared to the others. In this case, a portion of the sample flow from the Elemental Analyser is injected into a “reference” helium flow and passed to the mass spectrometer. The extra helium flow dilutes the amount of gas that would otherwise reach the mass spectrometer.

A typical example of this is the sequential analysis of N and C from organic molecules where the N/C ratio is small (typically less than 1:10). In order to obtain ion currents within the measuring range of the Head amplifiers for both gases (N_2 and CO_2), it is necessary to dilute the CO_2.

If a diluter is not available in such a situation, then sequential analysis of the same sample is not possible. In order to obtain measurements of both N and C, it becomes necessary to perform the analysis of two samples, a larger sample size is used for N and a smaller sample size is used for C.

DESCRIPTION AND PRINCIPLE OF OPERATION



The diluters principle of operation is as follows:

The sample and carrier flow from the Elemental Analyser flows into the Diluter at the inlet marked “**Sample He In**”. At the tee connector marked **A**, the flow divides into two lines, one line passes through the metering valve mounted on the front face of the Diluter, the second line, labelled “sampling capillary” consists of a Vitreous Silica capillary of length 30 cm and 150µm ID.

Opening and closing the metering valve will modify the portion of the carrier that will pass through the sampling capillary. If the metering valve is fully open, then all the flow passes through the metering valve and none through the Sampling capillary. If the flow through the metering valve is reduced, then the pressure at **A** increases and more of the carrier passes through the Sampling capillary. The metering valve can be thought of as a means to vary the pressure upstream of the valve: the higher the pressure at point A and the higher the flow through the Sampling capillary.

The flow from the metering valve is connected to port 2 of a Valco 2-way valve. Port 1 is connected to the outlet from the Diluter labelled “**Mass Spec**”.

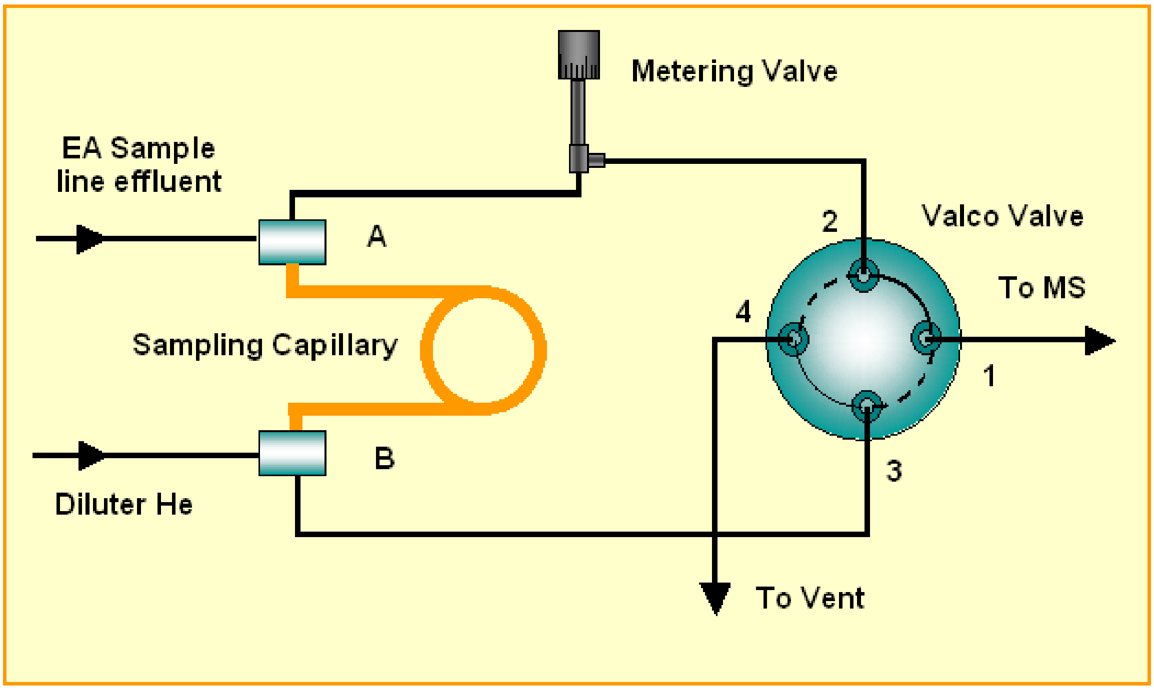
Ports 1 and 2 are connected in one position of the valve, allowing an undiluted flow from the Elemental analyser to pass to the mass spectrometer. The small portion of flow passing through the sampling capillary from the tee connector **A** enters a second Tee connector **B**, and meets an additional carrier flow of helium “Ref He” which dilutes the flow. This diluted eluent from the sampling capillary is connected to port 4 of the Valco valve. Port 3 is connected to the **Vent** outlet at the back of the Diluter. When ports 3 and 4 are connected, the diluted flow vents to atmosphere.

If the Valco valve is switched to its second state, port 3 will be connected to port 1, and the diluted flow will be directed towards the mass spectrometer. The undiluted carrier vents out to atmosphere.

In this manner it is possible to switch between diluted and undiluted carrier flow within the same sample run.

The additional flow of helium coming from the inlet labelled “**Ref He**” is regulated to approximately 40 ml/min by a crimp mounted on the 0.006” SS inlet capillary.

The flow paths are displayed on the image below:



CONNECTING THE DILUTER TO THE ELEMENTAL ANALYSER

Caution: Ensure the following instructions are followed connecting the diluter; failure to do so could damage the mass spectrometer.

- Ensure that the isolation valve at the mass spectrometer inlet is closed when connecting the Diluter to the elemental analyser. The flow of helium to the mass spectrometer will be temporarily interrupted during this operation.
- Connect the Helium supply to the Swagelok Plug Valve which is also fitted with the SS 0.006” capillary tubing. Adjust the capillary clamp to give a Helium flow of around 40ml/min (the plug valve must be open at this point). Once the flow has been set, connect this assembly to the rear of the Diluter at the port marked “Ref He In”. There should now be a Helium carrier flow which can be measured at the “Vent” outlet on the Diluter.
- Connect the compressed air line to the Inlet port marked “Air IN”.
- Connect the ribbon cable to the 25-way d-type on the rear of the diluter, and plug the other end into the breakout on the reference gas injector ribbon cable.
- Connect a length of (1/16” X 0.030” SS tubing long enough to reach the back of the diluter to the left hand needle valve at the rear of the EA, Fully open the left hand needle valve and then slowly Open the vent (right hand side) needle valve until a flow of 100 ml/min can be measured at the end of the SS tubing. Connect the tubing to “Sam He” port at the back of the diluter. Note that in order to measure the flows out of the two needle valves it will be necessary for EA to be operational.
- Connect a suitably long length of SS tubing (1/16” X 0.030”) to the outlet port labelled “Mass Spec” of the diluter and feed it through one of the grommets located at the rear of the reference gas Injector. Insert the sample line silica capillary (I.D. 100 µm).
- Make sure that the source is turned OFF in IonVantage and re-open the Isolation valve. Wait a few moments for the mass spectrometer pressure to fall to less than 5E-6 bar. Once the vacuum has dropped below the trip level the source may be turned back on.

Leak check the diluter lines with either a helium leak sensor or if Argon gas is available, peak jump to argon (As discussed in the isoprime100 manual) and leak check the diluter connections with a small flow of argon gas. Information about using the Diluter can be found in the “*System Operation*” section.

SYSTEM OPERATION

This chapter describes the procedure to set up and run t a list of samples and how to obtain results.

OVERVIEW OF SOFTWARE

Note: The software suites must be opened in a specific order to gain communication. Firstly, open the EA Vario software and wait for communication to the EA to initialise. Then open the MS IonVantage software.

The communication settings are normally preset but the following items in this section may have to be followed to gain full control of the EA-IRMS system.

The two suites of software, IonVantage and the appropriate vario EA software, communicate via a program within IonVantage called “variointerface.exe”. When an acquisition is initiated in IonVantage this interface transfers sample data information from the IonVantage sample list into the vario sample list, and then once analysis is complete, collects elemental analysis information from the vario software and imports it into the IonVantage sample reports.

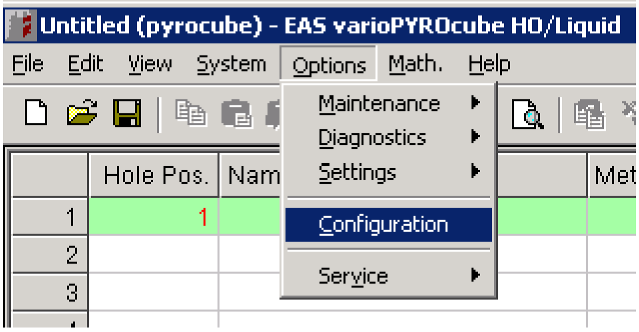
The interface also allows access to the EA methods and sample names within the vario software from the IonVantage sample list.

The vario software must have the “Remote” settings configured correctly for this to work and the vario software must be started before IonVantage so that the “variointerface” program can find the vario software when IonVantage is started.

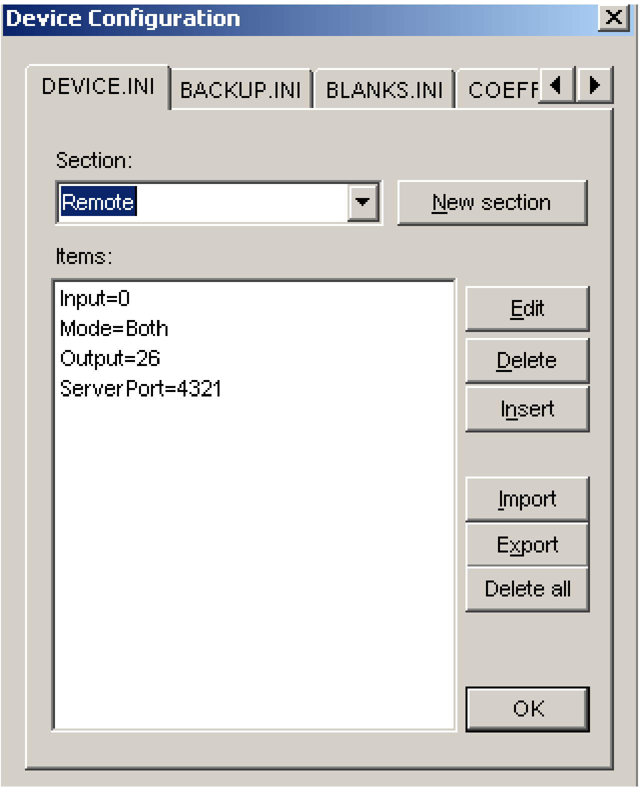
VARIO SOFTWARE CONFIGURATION

After the vario software has been installed, it must be configured to be able to communicate with IonVantage. This is done by defining appropriate “Remote” settings in the vario software.

To do this, select the “Configuration” item in the “Options” command line item:



In the “DEVICE.INI” tab Select “Remote” in the “Section” drop down menu. If “Remote is not in the drop down list, then, type “Remote” in the “Section” box, and press the “New section” button. Check that the 4 lines in the “items” box match those shown in the picture below. Use the “Edit” and “Insert” buttons If anything is missing or incorrect .



Section: Remote

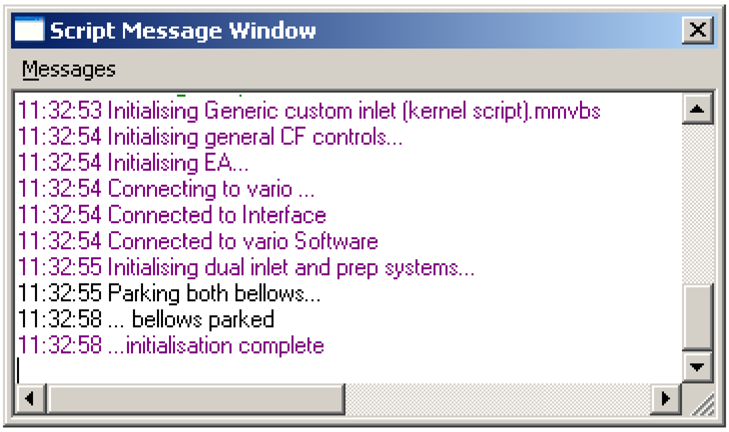
Items:

```
Input=0
Mode=Both
Output=26
ServerPort=4321
```

*Note that it is very important to get the case of the letters correct, so for example “ServerPort” has upper case S, upper case P and there is **no** space between Server and Port.

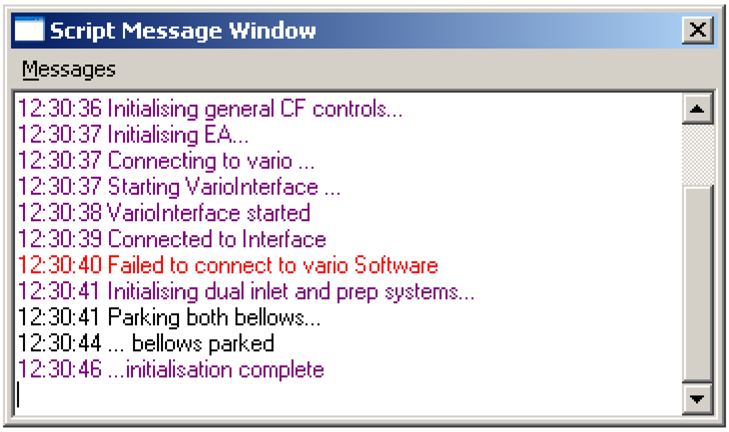
If the interface has been configured correctly the following messages should be present in the “Script Message Window” s

“... Connected to Interface” and
“... Connected to vario Software” are present:



```
11:32:53 Initialising Generic custom inlet (kernel script).mmvbs
11:32:54 Initialising general CF controls...
11:32:54 Initialising EA...
11:32:54 Connecting to vario ...
11:32:54 Connected to Interface
11:32:54 Connected to vario Software
11:32:55 Initialising dual inlet and prep systems...
11:32:55 Parking both bellows...
11:32:58 ... bellows parked
11:32:58 ...initialisation complete
```

If communication between the two suites of software failed, then a communication failure message is returned:

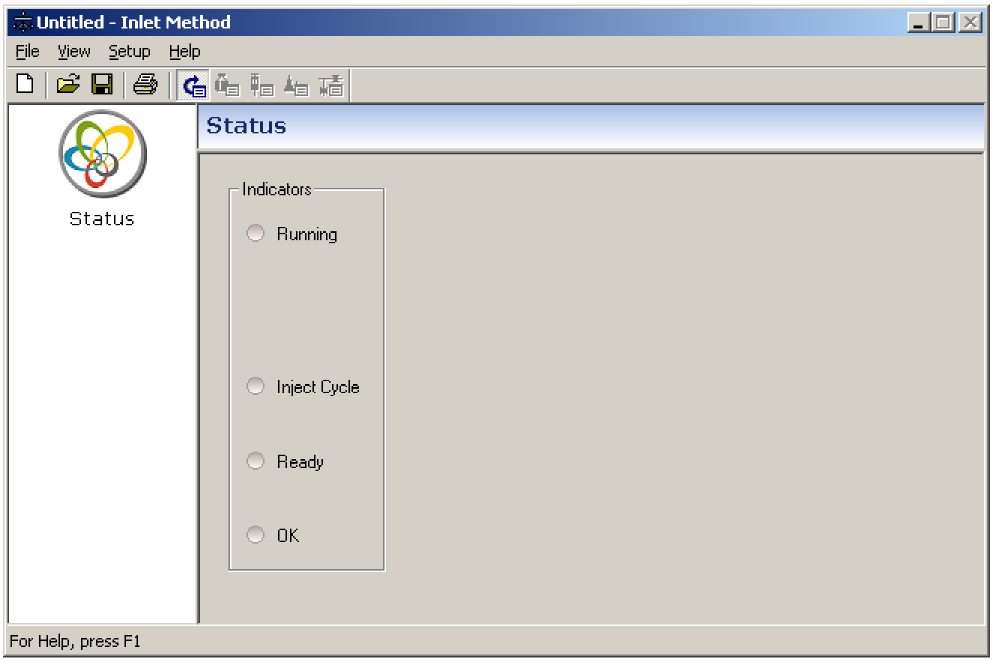


```
12:30:36 Initialising general CF controls...
12:30:37 Initialising EA...
12:30:37 Connecting to vario ...
12:30:37 Starting VarioInterface ...
12:30:38 VarioInterface started
12:30:39 Connected to Interface
12:30:40 Failed to connect to vario Software
12:30:41 Initialising dual inlet and prep systems...
12:30:41 Parking both bellows...
12:30:44 ... bellows parked
12:30:46 ...initialisation complete
```

THE EA CUSTOM INLET

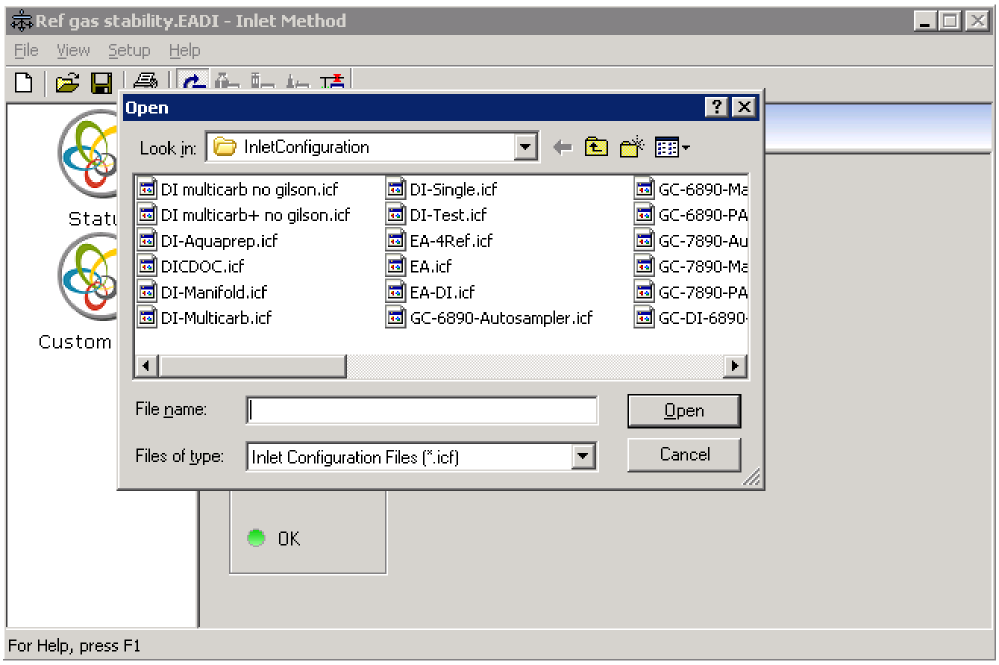
SELECTING A CUSTOM INLET

To use the Elemental Analyser continuous flow software, the correct custom inlet must be loaded. To open the default inlet, press the inlet button in the IonVantage sample list page (if not already open). The default inlet editor is shown below:



The actual appearance depends on the settings in the pc’s “Display Properties”, accessed by right clicking on an empty part of the desktop and selecting the “Properties” option.

To open the EA inlet, select “Setup”, “Open”:



The three options EA-4Ref.icf, EA.icf and EA-DI.icf cover most of the inlet configurations that include the EA. EA.icf is used for those instances when only a single reference gas box is available EA-4Ref.icf is used when two reference gas boxes are used (In both cases a standby valve will be displayed automatically if fitted to the instrument). EA-DI.icf is used when the EA is used with an isoprime100 dual inlet system.

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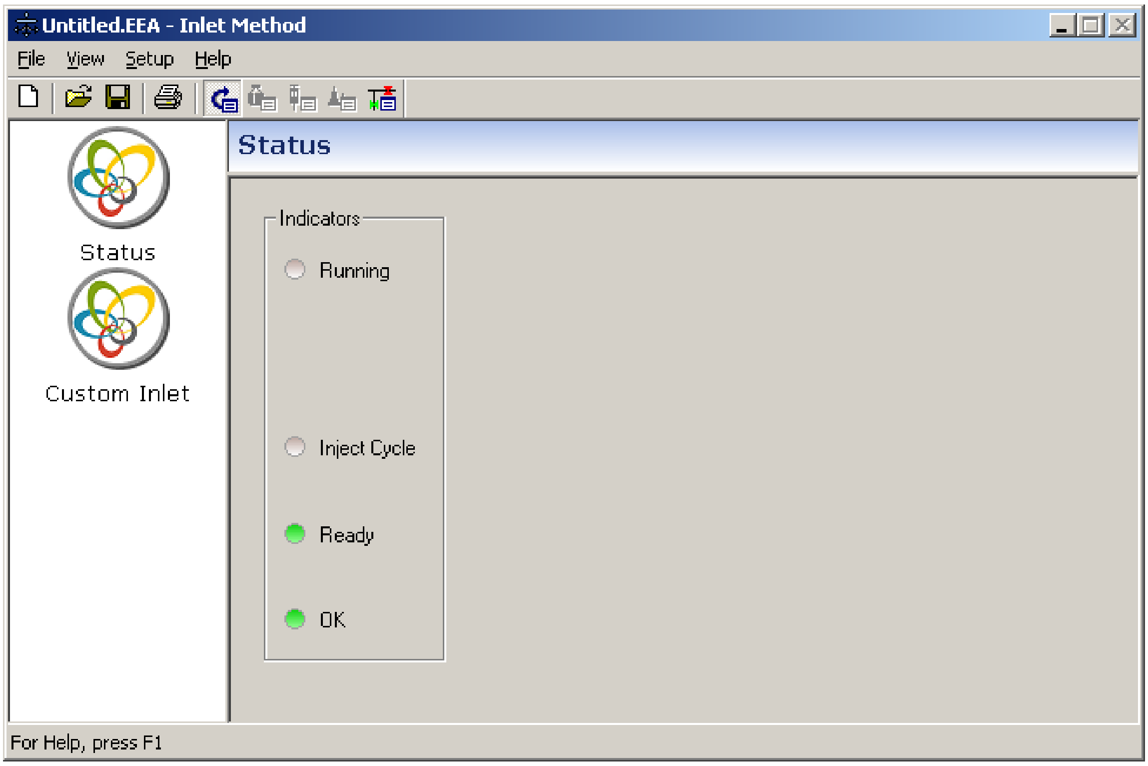
During the loading of the inlet, two green indicators will appear in the “Indicators” box, as shown below:



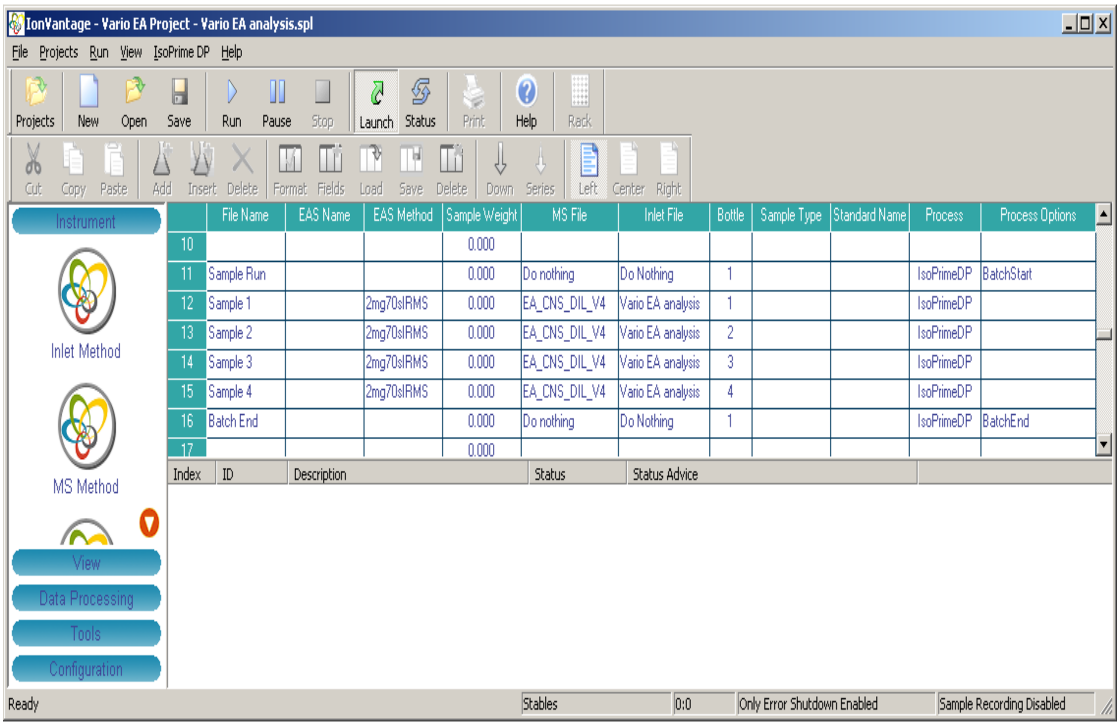
If the 2 green ready lights do not appear on the inlet status page the EA has not configured properly. This is normally due to the inlet kernel losing communications with the inlet page. Restarting the IonVantage software should fix the communication problem. Once the EA is successfully configured the system is ready to run.

CREATING AN IONVANTAGE SAMPLE LIST

OVERVIEW

To create an IonVantage EA sample list, each sample entry must be linked to an appropriate custom inlet, method file, EA method file and data processing program.

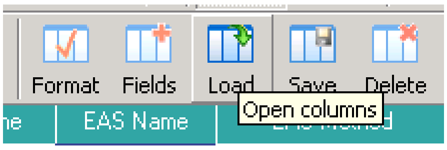
A typical example is shown below. In this sample list “Sample 3” (index number 14) is set up to be analysed using an inlet file named “Vario EA analysis”, a mass spectrometer method named “EA_CNS_DIL_V4” (column entitled “MS File”), an EA method named “2mg70sIRMS” (column entitled “EAS Method”), and processed using the option “IsoPrimeDP” (column entitled “Process”).

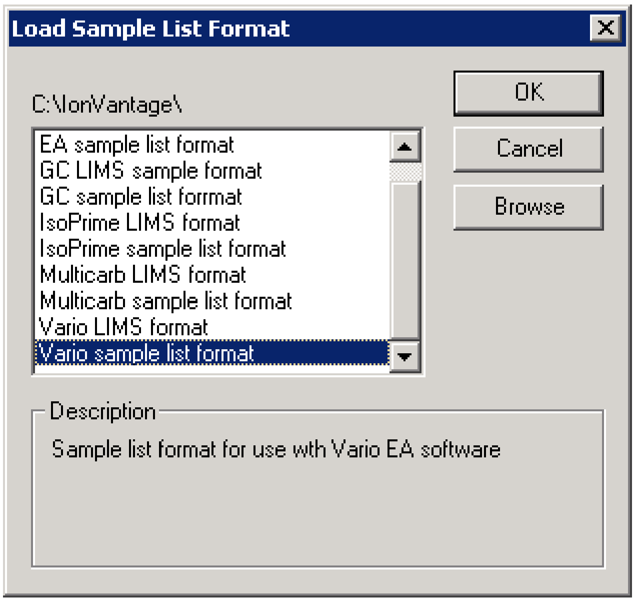


	File Name	EAS Name	EAS Method	Sample Weight	MS File	Inlet File	Bottle	Sample Type	Standard Name	Process	Process Options
10				0.000							
11	Sample Run			0.000	Do nothing	Do Nothing	1			IsoPrimeDP	BatchStart
12	Sample 1		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	1			IsoPrimeDP	
13	Sample 2		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	2			IsoPrimeDP	
14	Sample 3		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	3			IsoPrimeDP	
15	Sample 4		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	4			IsoPrimeDP	
16	Batch End			0.000	Do nothing	Do Nothing	1			IsoPrimeDP	BatchEnd
17				0.000							

The “Inlet File” controls mass spectrometer operations before and after data is acquired. The “MS File” controls mass spectrometer operations during data acquisition; the “EAS Method” controls EA operations during the sample analysis and the “Process” option, in this instance, will ensure data processing takes place on the raw data obtained.

If the EAS Name and EAS Method columns are missing they can be loaded by clicking the “Load column format” button and selecting the “Vario sample list format”.





C:\IonVantage\

- EA sample list format
- GC LIMS sample format
- GC sample list format
- IsoPrime LIMS format
- IsoPrime sample list format
- Multicarb LIMS format
- Multicarb sample list format
- Vario LIMS format
- Vario sample list format

Sample list format for use with Vario EA software

Inlet Files, MS Files and EAS Methods are selected by double clicking a cell in the appropriate column of the sample list. This opens a drop down menu showing all currently saved files – Note that it takes a short while for the EAS methods to appear as these are read directly from the current mode of the vario software. “IsoPrimeDP” should always be selected in the “Process” column. Optionally, an “EAS Name” can be entered for each sample in the sample list. These are read from the current list of standards and keywords in the vario software. If an “EAS Name” is selected, then this name, rather than the sample name, is transferred to the vario software when analysis starts. This is useful for allowing standards and blanks to be defined in the vario list..

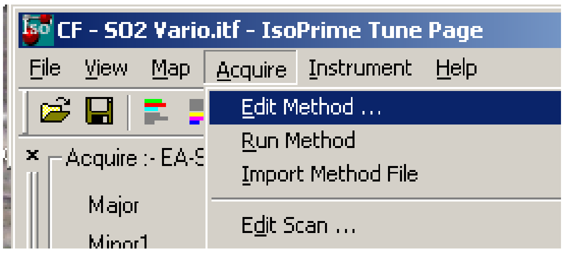
MS METHOD FILES

Method files are used to control valves on the custom inlet and to define Peak Jumping timings. Unlike scripting files, method sequences are loaded into the firmware of the IsoPrime from the PC. The advantages of this are:

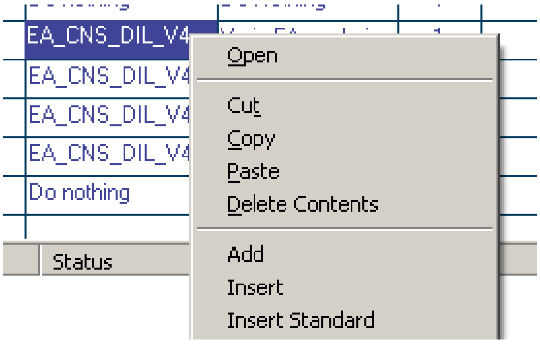
It permits the more accurate internal clock of the IsoPrime to activate time critical functions

It locks control of the inlet, preventing the operator from changing a valve setting during an analysis.

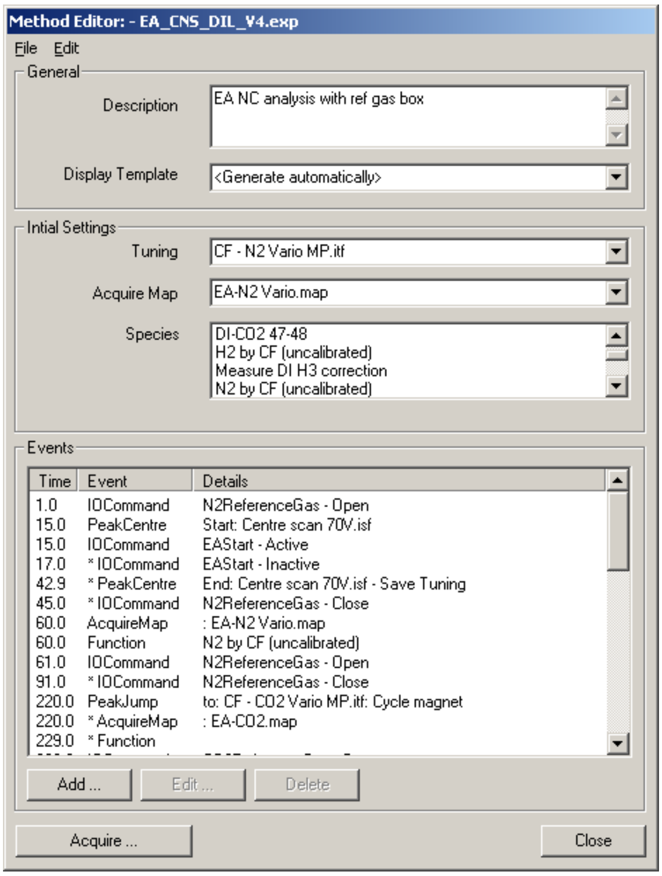
Consequently, a method file is typically used to control the inlet during data acquisition, whilst the scripting is used to control the inlet (or other software) before and after data acquisition has commenced. Unlike scripting files, method files are not written in visual basic but are defined through the tune page. To access the method editor select “Edit Method” in the “Acquire” menu.



Alternatively right click on a method file in the IonVantage sample list:



Select “Open”, this will open a window showing the selected method file:



Method Editor: - EA_CNS_DIL_V4.exp

General

Description: EA NC analysis with ref gas box

Display Template: <Generate automatically>

Intial Settings

Tuning: CF - N2 Vario MP.itf

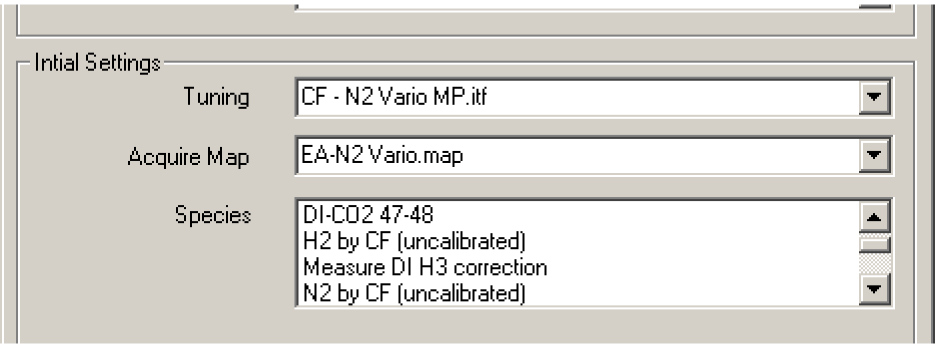
Acquire Map: EA-N2 Vario.map

Species:
DI-CO2 47-48
H2 by CF (uncalibrated)
Measure DI H3 correction
N2 by CF (uncalibrated)

Events

Time	Event	Details
1.0	IOCommand	N2ReferenceGas - Open
15.0	PeakCentre	Start: Centre scan 70V.isf
15.0	IOCommand	EAStart - Active
17.0	* IOCommand	EAStart - Inactive
42.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
45.0	* IOCommand	N2ReferenceGas - Close
60.0	AcquireMap	: EA-N2 Vario.map
60.0	Function	N2 by CF (uncalibrated)
61.0	IOCommand	N2ReferenceGas - Open
91.0	* IOCommand	N2ReferenceGas - Close
220.0	PeakJump	to: CF - CO2 Vario MP.itf: Cycle magnet
220.0	* AcquireMap	: EA-CO2.map
229.0	* Function	

The method file can be edited to define the desired valve and peak jump timings Some experimentation is required to define a perfect list for the MS. It is recommend that when creating a new method, the operator runs a sample using only the elemental analyser first to give some indication of the timing of sample peaks. .



Intial Settings

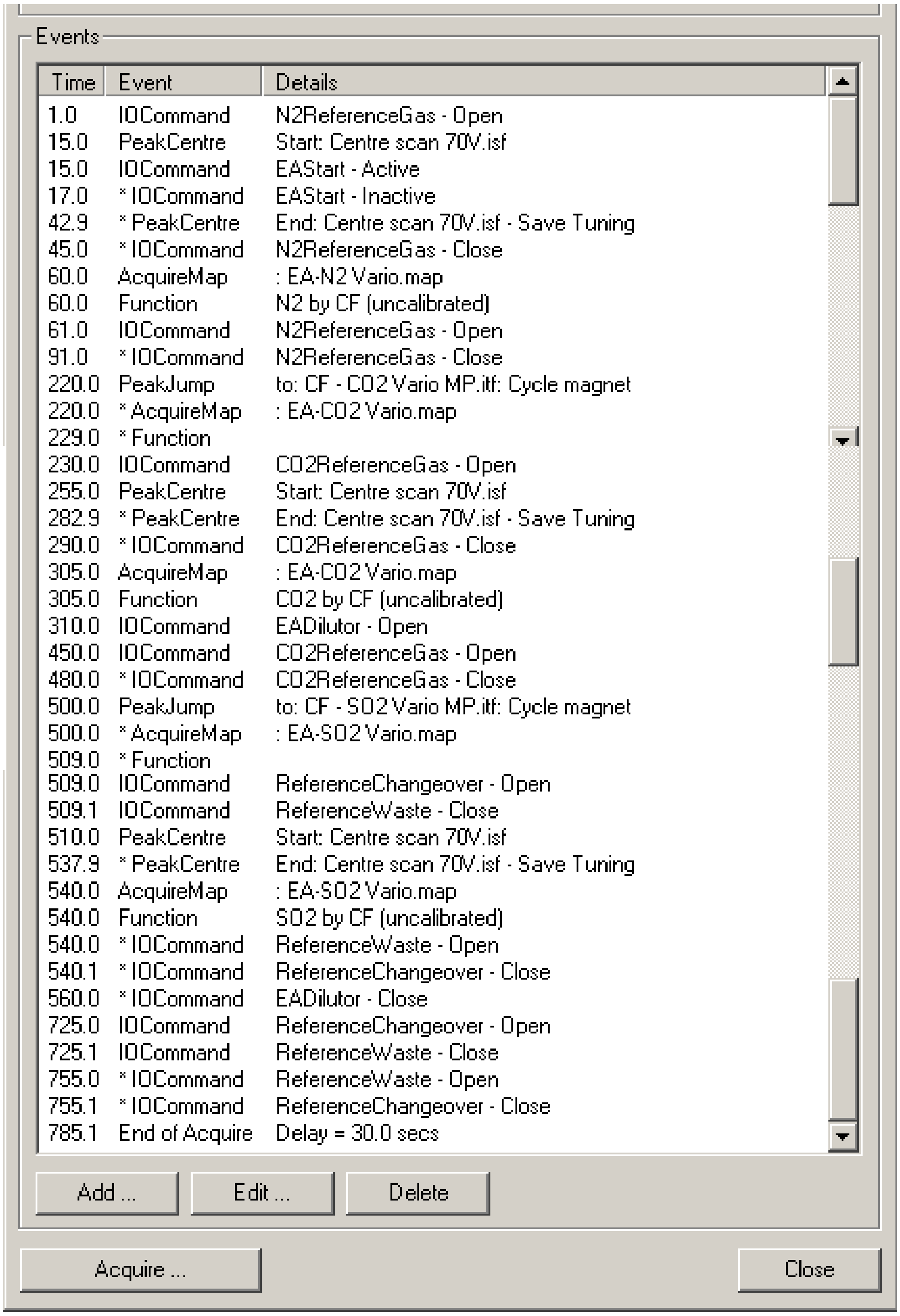
Tuning: CF - N2 Vario MP.itf

Acquire Map: EA-N2 Vario.map

Species:
DI-CO2 47-48
H2 by CF (uncalibrated)
Measure DI H3 correction
N2 by CF (uncalibrated)

The initial settings indicate how the mass spectrometer will be set up before the acquisition starts. An initial tuning file is defined, in this example “CF – N2 Vario MP.itfalong with an acquire map (the labels attached to the various signals measured or calculated) . Notice that the N2 species is not highlighted for this initial part of the acquisition, because in this method, the first part of the sequence is to perform a peak centre scan to locate the nitrogen beam accurately.

The picture below shows the complete “Event” list for the “EA_CNS_DIL_V4” method above, and the table below that briefly explains the steps:



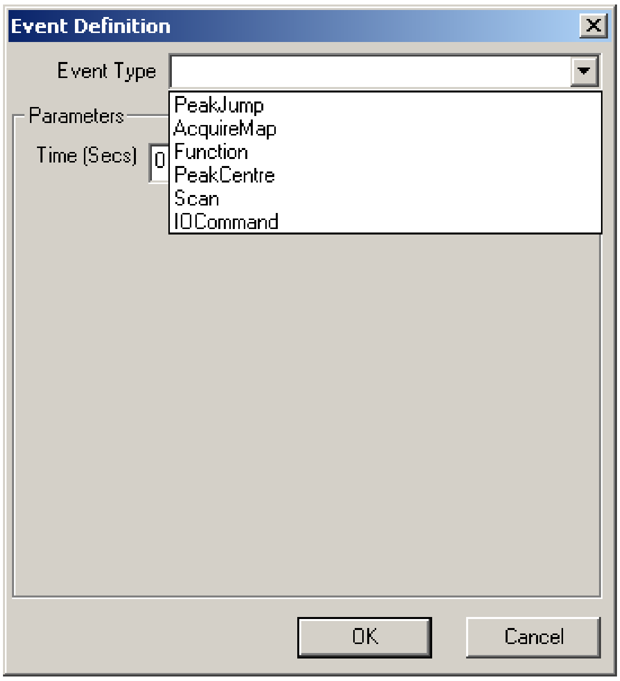
Time	Event	Details
1.0	IOCommand	N2ReferenceGas - Open
15.0	PeakCentre	Start: Centre scan 70V.isf
15.0	IOCommand	EAStart - Active
17.0	* IOCommand	EAStart - Inactive
42.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
45.0	* IOCommand	N2ReferenceGas - Close
60.0	AcquireMap	: EA-N2 Vario.map
60.0	Function	N2 by CF (uncalibrated)
61.0	IOCommand	N2ReferenceGas - Open
91.0	* IOCommand	N2ReferenceGas - Close
220.0	PeakJump	to: CF - CO2 Vario MP.itf: Cycle magnet
220.0	* AcquireMap	: EA-CO2 Vario.map
229.0	* Function	
230.0	IOCommand	CO2ReferenceGas - Open
255.0	PeakCentre	Start: Centre scan 70V.isf
282.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
290.0	* IOCommand	CO2ReferenceGas - Close
305.0	AcquireMap	: EA-CO2 Vario.map
305.0	Function	CO2 by CF (uncalibrated)
310.0	IOCommand	EADilutor - Open
450.0	IOCommand	CO2ReferenceGas - Open
480.0	* IOCommand	CO2ReferenceGas - Close
500.0	PeakJump	to: CF - SO2 Vario MP.itf: Cycle magnet
500.0	* AcquireMap	: EA-SO2 Vario.map
509.0	* Function	
509.0	IOCommand	ReferenceChangeover - Open
509.1	IOCommand	ReferenceWaste - Close
510.0	PeakCentre	Start: Centre scan 70V.isf
537.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
540.0	AcquireMap	: EA-SO2 Vario.map
540.0	Function	SO2 by CF (uncalibrated)
540.0	* IOCommand	ReferenceWaste - Open
540.1	* IOCommand	ReferenceChangeover - Close
560.0	* IOCommand	EADilutor - Close
725.0	IOCommand	ReferenceChangeover - Open
725.1	IOCommand	ReferenceWaste - Close
755.0	* IOCommand	ReferenceWaste - Open
755.1	* IOCommand	ReferenceChangeover - Close
785.1	End of Acquire	Delay = 30.0 secs

Times	Event	Description
0 & 45	N2Reference-Open/Close	A pulse of reference gas is injected to give a signal for the instrument to centre on
15 & 42.9	PeakCentre	A peak centre scan is performed, and the results saved to the current tuning file – “CF – N2 Vario MP.itf” here.
15 & 17	EAStart – Active/Inactive	The start signal for the EA acquisition. With vario EAs, this is a software command (script operation “VarioAnalyse” in script file “EA inlet control.mmvbs”), with other EAs, a contact closure in the IsoPrime electronics (script operation “Analyse”)
60	EA-N2 Vario acquire map	Defines labels for the data about to be acquired in the immediately following function
60	N2 by CF function	The data collected in this function will be processed according to the parameters defined in the “N2 by CF (uncalibrated)” species
61 & 91	N2Reference-Open/Close	A further injection of reference gas for comparison with the sample signals
220 & 229	PeakJump	To CO_2, using the tuning file “CF – CO2 Vario MP.itf, labelling the data as defined in the acquire map “EA-CO2 Vario.map”. Again, no species is specified in the function, because a peak centre is the next but one event
230 & 290	CO2Reference-Open/Close	A pulse of reference gas is injected to give a signal for the instrument to centre on
255 & 282.9	PeakCentre	A peak centre scan is performed, this time for CO_2, and the results saved to the current tuning file “CF – CO2 Vario MP.itf”
305	EA-CO2 Vario acquire map	Defines labels for the data about to be acquired in the immediately following function
305	CO2 by CF function	The data collected in this function will be processed according to the parameters defined in the “CO2 by CF (uncalibrated)” species
310 & 560	EADiluter – Open/Close	The diluter valve being switched to dilute the CO_2 signal from the sample. The times should be arranged to

		coincide with autozero delays on the EA, where possible
450 & 480	CO2Reference-Open/Close	A further injection of reference gas for comparison with the sample signals
500 & 509	PeakJump	To SO_2, using the tuning file “CF – SO2 Vario MP.itf, labelling the data as defined in the acquire map “EA-S509.0O2 Vario.map”. Again, no species is specified in the function, because a peak centre is the next but one event
509, 509.1 & 540, 540.1	ReferenceChangeover/ Waste – Open/Close	A pulse of reference gas is injected to give a signal for the instrument to centre on, but the commands are more complicate in this instance because the SO_2 is being delivered from the reference bellows of a dual inlet
510 & 537.9	PeakCentre	A peak centre scan is performed, this time for SO_2, and the results saved to the current tuning file “CF – SO2 Vario MP.itf”
540	EA-SO2 Vario acquire map	Defines labels for the data about to be acquired in the immediately following function
540	SO2 by CF function	The data collected in this function will be processed according to the parameters defined in the “SO2 by CF (uncalibrated)” species
725, 725.1 & 755, 755.1	ReferenceChangeover/ Waste – Open/Close	A further injection of reference gas for comparison with the sample signals
785.1	End of acquire delay	To give time for the reference gas signal to dissipate before the next analysis

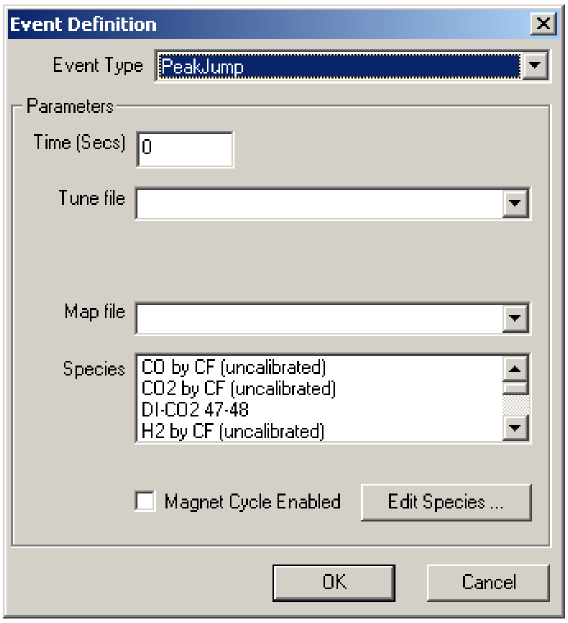
MS METHOD EVENTS

There are many events that can be inserted into a method file. Pressing the “Add” button in the “Method Editor” opens an “Event Definition” window, and the “Event Type” drop down menu reveals a set of types.



The menu in the “Parameters” frame is context sensitive, allowing information appropriate to the event type to be entered. The various event types are listed below:

PEAKJUMP

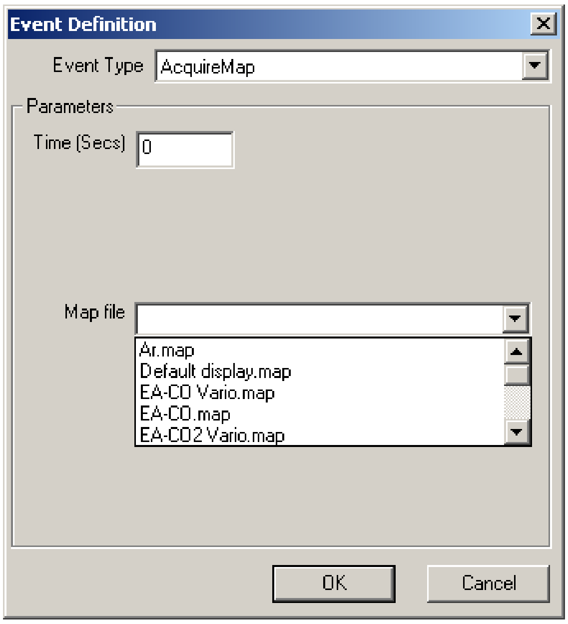

Event Type: PeakJump

Time (Secs): 0

The peak jump event allows the user to switch between tuning file, map file and species. This is useful when analysing more than one gas from the same sample. When creating a method that incorporates peak jumping it is important to make sure that the tuning file has been recently checked for the gas of interest.

Cycling the magnet is recommended to minimise the effects of magnet hysteresis.

AcquireMap



Event Definition

Event Type: AcquireMap

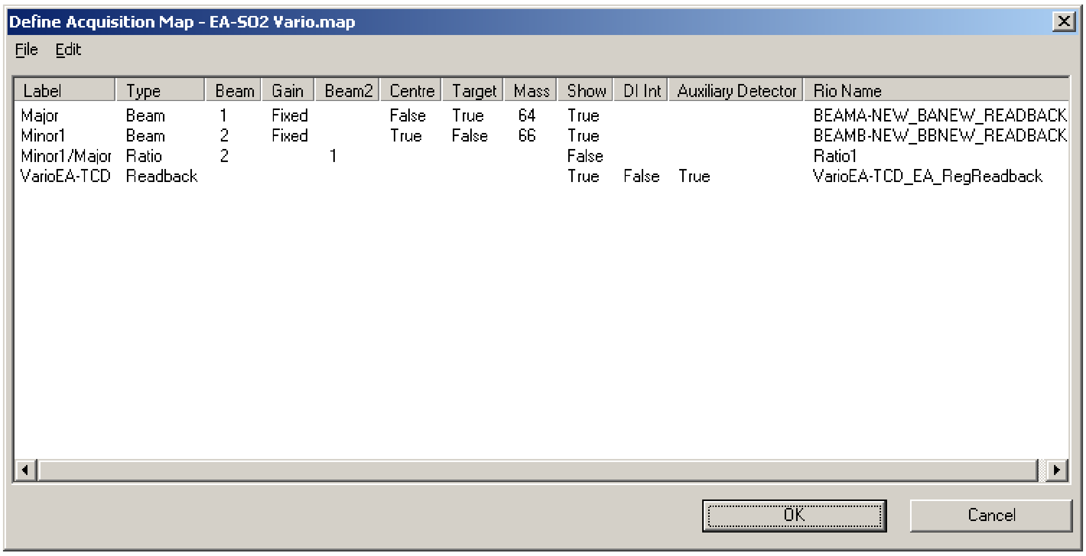
Parameters

Time (Secs): 0

Map file:

- Ar.map
- Default display.map
- EA-CO Vario.map
- EA-CO.map
- EA-CO2 Vario.map

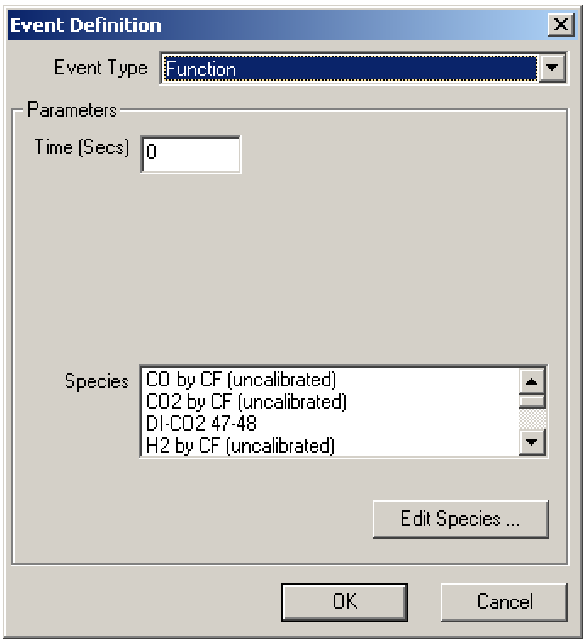
The acquire map event (which can be edited in the tune page) is used to define a name and mass to the data that is retained for data processing. It is also used to identify which beams are displayed in the tune page window and which are used as target for the peak centre tuning function. The example below shows the “EA-SO2 Vario.map”,



Define Acquisition Map - EA-SO2 Vario.map

Label	Type	Beam	Gain	Beam2	Centre	Target	Mass	Show	DI Int	Auxiliary Detector	Rio Name
Major	Beam	1	Fixed		False	True	64	True			BEAMA-NEW_BANEW_READBACK
Minor1	Beam	2	Fixed		True	False	66	True			BEAMB-NEW_BBNEW_READBACK
Minor1/Major	Ratio	2		1				False			Ratio1
VarioEA-TCD	Readback							True	False	True	VarioEA-TCD_EA_RegReadback

FUNCTION

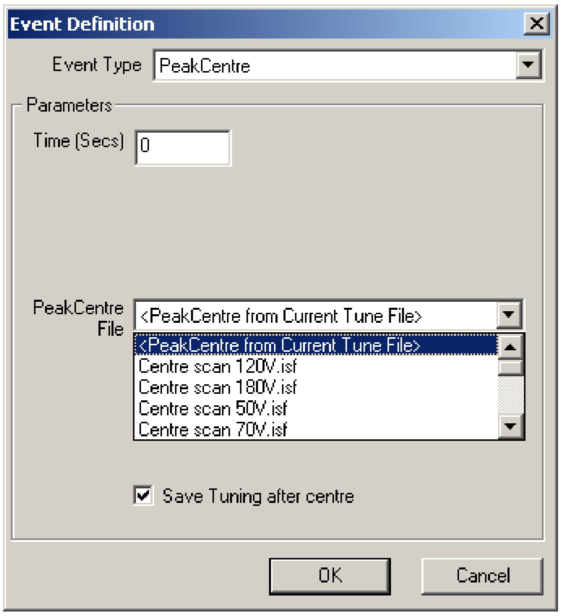


Event Type: Function

Time (Secs): 0

The “Function” event defines which species information is used for processing data. The species information consists of integration parameters, reference gas values, correction factors and calculation templates to produce a final results sheet.

PEAKCENTRE



Event Type: PeakCentre

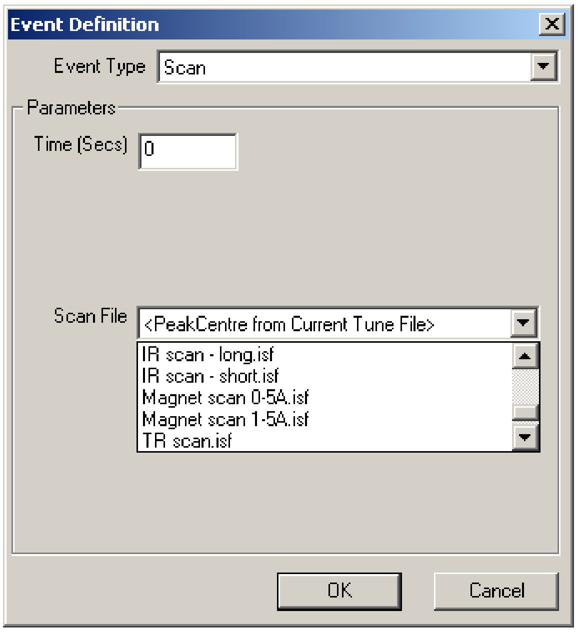
Time (Secs): 0

PeakCentre File: <PeakCentre from Current Tune File>

☑ Save Tuning after centre

The PeakCentre event initiates a peak centre scan at the time specified during the data acquisition. The default setting “<PeakCentre from Current Tune File>” - will ensure that the usual peak centre scan for any particular gas is used. If the “Save Tuning after centre” check box is checked, then the updated accelerating voltage is saved in the tuning file ready for the next sample data acquisition. It is important to note that this function does not replace the necessity to check the tuning of any gases before setting a sample list running.

SCAN



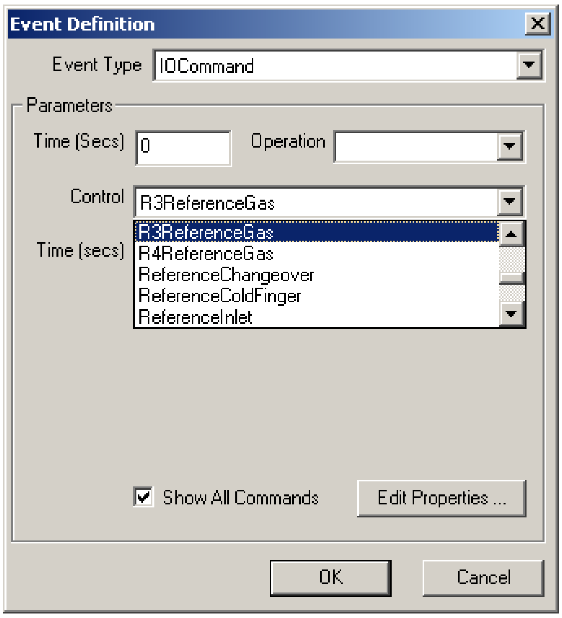
Event Type: Scan

Time (Secs): 0

Scan File: <PeakCentre from Current Tune File>

The “Scan” function allows any of the scan files that have been generated in the tune page menus to be run in the experiment. This allows a full record of the tuning parameters to be recorded if desired.

IOCOMMAND



Event Type: IOCommand

Time (Secs): 0

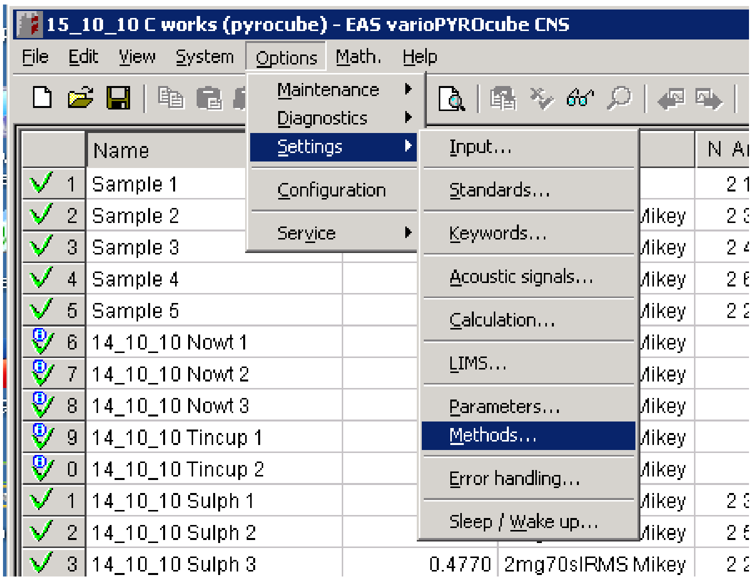
Control: R3ReferenceGas

☑ Show All Commands

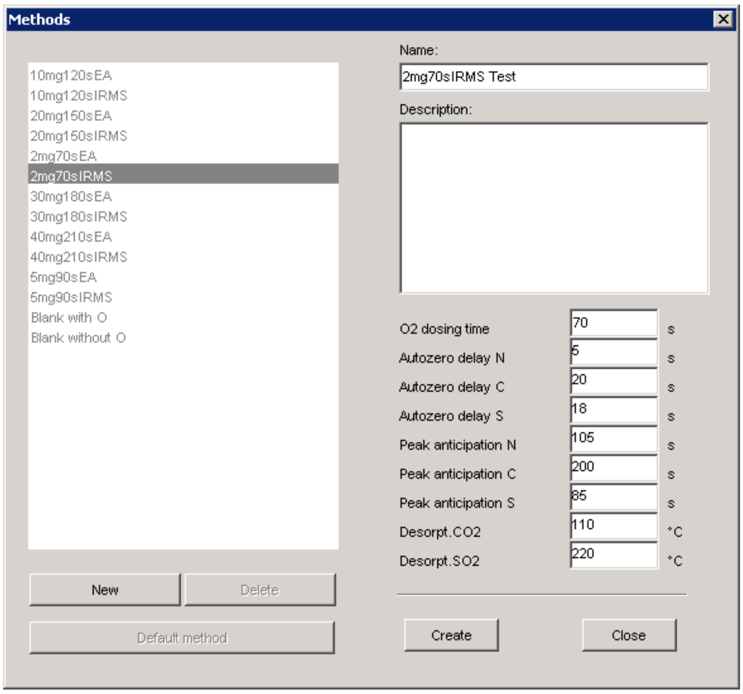
The IOCommand event type includes all the valve switching operations and other events where an on/off,or similar, command isused. This command is essential to most method files as it is used to define when an EAstart command is sent, the timing and duration of reference gas pulses and diluter timings.

EA METHOD FILES

In addition to the MS method an appropriate EA method must also be selected. The methods window in the Vario software is selected by clicking on options > settings > methods.



There are a set of pre-defined methods for each operational mode which aim to cater for a selection of sample sizes and oxygen dosing times. New methods can be created using the New button, which clears all the parameter entries, or, alternatively if working from an existing method, by clicking on the method and then typing a new name in the name field. Once the desired parameters have been set the new method can be saved by pressing the "Save"/"Create" button. An example of the method window is shown below:



Name: 2mg70sIRMS Test

Description:

O2 dosing time 70 s
Autozero delay N 5 s
Autozero delay C 20 s
Autozero delay S 18 s
Peak anticipation N 105 s
Peak anticipation C 200 s
Peak anticipation S 85 s
Desorpt.CO2 110 °C
Desorpt.SO2 220 °C

The method parameters are described in the EA manual. There are a number of points to note:

- "Peak anticipation" times are the minimum times the EA will spend integrating a particular element peak. If a peak is found during the peak anticipation time window, then, at the end of the anticipation time the EA will move onto the next step in the analysis. If not, the integration will continue for that element until either a peak end does occur, or the software times out (600s in most cases).

- The anticipation times used in EA methods for EA-IRMS are generally much longer than required for EA analysis alone, to allow sufficient time for any peak jumping and reference gas pulses that may be required before the next gas is evolved from the EA desorption columns.

- For the varioISOTOPE and varioPYROCUBE EAs, the desorption temperature for CO2 is set lower for use with the IsoPrime than when used as a standalone EA. This is to slow down the speed at which the gas comes off the adsorption column. If left a higher temperature it would result in a very fast, intense CO2 peak that would not be accurately integrated by the mass spectrometer. The long autozero delay times for CO2 and SO2, to allow time for diluter valve switching without the EA attempting to integrate pressure change signals on the TCD.

The preloaded methods are designed to be used for sample weights up to that mentioned in the method name, so for example it is not advisable to use a 2mg 70s IRMS method with 5 mg samples as it is unlikely that complete sample combustion would be achieved .The appropriate EA method can be selected in IonVantage in the EAS method window

Sample list BOTTLE NUMBER

A bottle number must be specified in the “bottle” column for all samples. This is normally the position of the samples in any autosampler being used.

- The EA autosampler carousel in solids modes only works sequentially and does not reference this number, however filling it out correctly can act as a useful point of reference when loading samples into the autosampler.
-
- The Vario Liquid Sampler (VLS) samples directly from the position specified, so the correct bottle number must be specified in liquid modes.

SAMPLE SEQUENCE

For best results, the Sample list should be constructed according to the recommendations below:

- Recommended sample sequence:

Batch start and batch end at the end of the sample list.
At least 3 Blanks
At least 2 Dummy samples for conditioning purposes
At least 3 Standards
No more than 30 unknown samples
At least one Standard material
Subsequently, place at least one Standard material after every 15 unknown samples. If this Standard is declared as an unknown sample, it can be used as an accuracy check throughout the batch.

- Each unknown sample should be analysed at minimum in triplicate.

The recommended sequence assumes that the reproducibility of Blanks has been checked beforehand. Fairly large Blank areas (up to 1% of sample area) can be tolerated, but variations in their sizes cannot. Blank reproducibility is essential.

MANAGING SAMPLE MEMORY EFFECTS

Inter sample memory for isotopic enrichments can be a problem, the elimination of memory can be difficult and unpredictable. The general guidelines for system cleanliness and optimised combustion conditions are not always sufficient to eliminate this effect completely. Furthermore, the extent of the effect is dependent on the sample type and the element under consideration. The sample list must therefore be constructed to minimise these effects, if they are observed:

- Ensure that the Blanks are measured at the beginning of the batch, while the residual memory is at natural abundance. Blanks placed at the end of the AutoRun will not result in any valid isotopic correction, unless several dummy materials have been acquired after the final sample and until natural enrichment has been fully recovered, before attempting to measure a Blank.
- Place samples in order of increasing enrichments to minimise the enrichment gaps between each sample type
- Never introduce Dummy samples or Wash samples in the middle of such a Run because it will serve only to increase the step in enrichment to the next sample.
- It may be necessary to analyse a larger number of each sample type than usual, such that the first result(s) can be ignored from the final calculations

PREPARING SAMPLES AND USING THE MICRO BALANCE

The Microbalance must:

- Be able to measure down to 1µg and be used correctly in order to obtain good reproducible data.
- Be placed on a solid table, isolated from vibrations and draughts and must be carefully levelled by adjusting the levelling screw legs.
- Be calibrated in accordance with the manufacturer's procedure.

The weighing area and all tools (tweezers, micro spatula, tin capsule holder, sample trays, balance weighing pan) used for the weighing procedure must be kept clean, to avoid sample contamination.

Wear gloves when handling tin or silver capsules to avoid contamination from the natural greases on hands.

Weighing procedure:

- Place a new tin capsule on the balance pan and close the balance door.
- Wait for the balance to settle completely and press the TARE button.
- Remove the tin capsule from the balance pan and place a small amount of sample into the capsule.
- Weigh the sample. Do not forget to close the balance window. If necessary, adjust the weight by adding or removing some sample material.
- Place the sample on the top surface of the tin capsule holder.
- Using the tweezers, close the top of the capsule tightly and fold over.
- Fold several times in all directions and compress the capsule into a tightly packed ball

To avoid potential sample loss take care not to damage the tin foil when folding.

- The resulting ball should be tightly packed to ensure that the sample is well sealed inside the capsule and evenly surrounded by tin foil, to optimise the combustion process.

The final geometry should be as spherical as possible to prevent any jamming inside the autosampler.

STARTING AN ANALYSIS

The full system comprises a number of different modules which should be checked individually and collectively prior to real sample analysis.

PRECISION AND ACCURACY WITH REFERENCE MATERIALS

Before proceeding with the analysis of real samples, the external precision of measurement, together with the accuracy of measurement must be evaluated.

This is achieved by using “reference” materials with known elemental and isotopic compositions. The nature of this material must be as close as possible to the type of real samples that will need to be analysed.

Each laboratory is encouraged to build up a library of such reference materials. The reference materials used, should be:

- Stable
- Non-hygroscopic
- Non-volatile
- Homogeneous
- Available in large quantities so stock will be available for a long period
- Inexpensive so that extensive use can be made without cost consideration.

The reference material can also be incorporated within the same batch when analysing real samples. This will serve as quality evaluation and as a Standard material aiding calibration in the calculations of both elemental and isotopic compositions of the unknown samples.

CHECK LIST TO PREPARE FOR SAMPLE ANALYSIS

Below is a systematic checklist before attempting to analyse real samples:

All the gas connections are made, with gases of the correct purity and with the correct supply pressures. (Refer to the *Gas requirements* sections of the manuals for the various modules).

All communication cables have been connected correctly. (Refer to the relevant sections of the manuals for the various modules).

All electrical connections have been made and modules have been switched ON. (Refer to the relevant sections of the manuals for the various modules).

The Elemental Analyser is configured correctly according to the type of analysis and samples to be analysed.

The reactors in the Elemental Analyser have been filled with catalysts suitable for the type of analysis. (Refer to the relevant sections of the EA manual).

The catalysts in the Elemental Analyser are in good condition.

The mass spectrometer is at the correct operating pressure.

The mass spectrometer backgrounds are below the recommended levels. Refer to isoprime100 manual.

All separate modules in the system such as the MS, EA, Diluter and Reference Gas Box have been leak checked. (Refer to the relevant sections of the manuals for these various modules).

The Peak shapes for the gases of interest are correct and there is coincidence of the ion beams at the collectors. (Refer to the manual for the Reference Gas Injector).

The source parameters are optimised and fine-tuned. (Refer to the manual for the Reference Gas Injector).

The mass spectrometer is stable. (Refer to the manual for the Reference Gas Injector).

The mass spectrometer is linear. (Refer to the manual for the Reference Gas Injector).

The method parameters for the Elemental Analyser have been optimised to yield the best chromatographic quality.

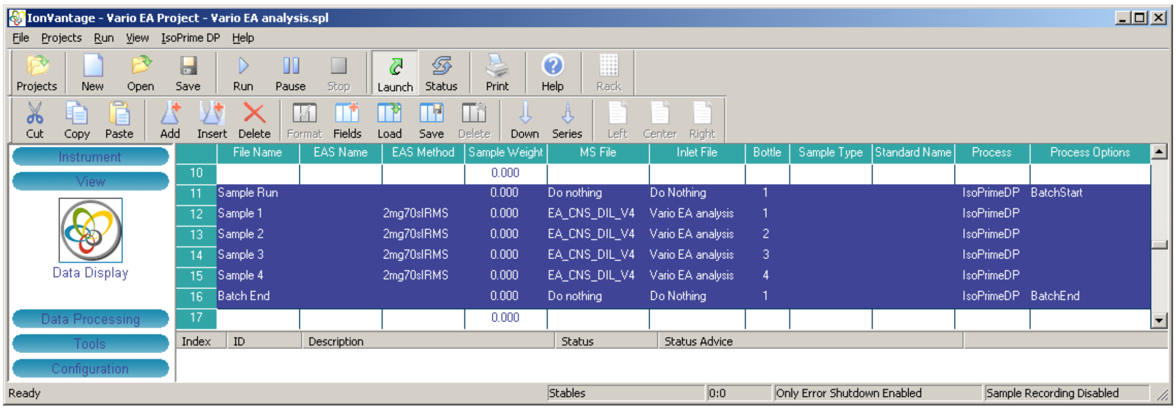
Precision and accuracy of measurement have been checked for both isotopic and elemental results using suitable known standard.

Only after this is the system is ready to analyse samples.

STARTING THE SAMPLE LIST

Once an Ionvantage sample list has been created with appropriate **File Name**, **EAS Name** (if required)**, Sample weight, EAS Method, MS File**, **Inlet File** and **Process file** selected for each entry, the following steps should be carried out to start the analysis

- Select the samples list by pressing in the appropriate numbered cells of the very first column. This will highlight the entire line of each selected sample. In the sample list shown below, samples 11 to 16 have been selected for analysis:



	File Name	EAS Name	EAS Method	Sample Weight	MS File	Inlet File	Bottle	Sample Type	Standard Name	Process	Process Options
10				0.000							
11	Sample Run			0.000	Do nothing	Do Nothing	1			IsoPrimeDP	BatchStart
12	Sample 1		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	1			IsoPrimeDP	
13	Sample 2		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	2			IsoPrimeDP	
14	Sample 3		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	3			IsoPrimeDP	
15	Sample 4		2mg70sIRMS	0.000	EA_CNS_DIL_V4	Vario EA analysis	4			IsoPrimeDP	
16	Batch End			0.000	Do nothing	Do Nothing	1			IsoPrimeDP	BatchEnd
17				0.000							

Index	ID	Description	Status	Status Advice

Ready
Stables
0:0
Only Error Shutdown Enabled
Sample Recording Disabled

Either press **Run** on the sample list toolbar, or select **Run Start** from the menu. Both actions result in the display of the **Start Sample List Run** window.

- S Press **OK** to start the run. An arrow next to the in the sample list indicates the sample currently being analysed.

REPROCESSING DATA

INTRODUCTION

Once samples have been acquired, the reprocessing facilities allow the user to access the raw data for reprocessing if required.

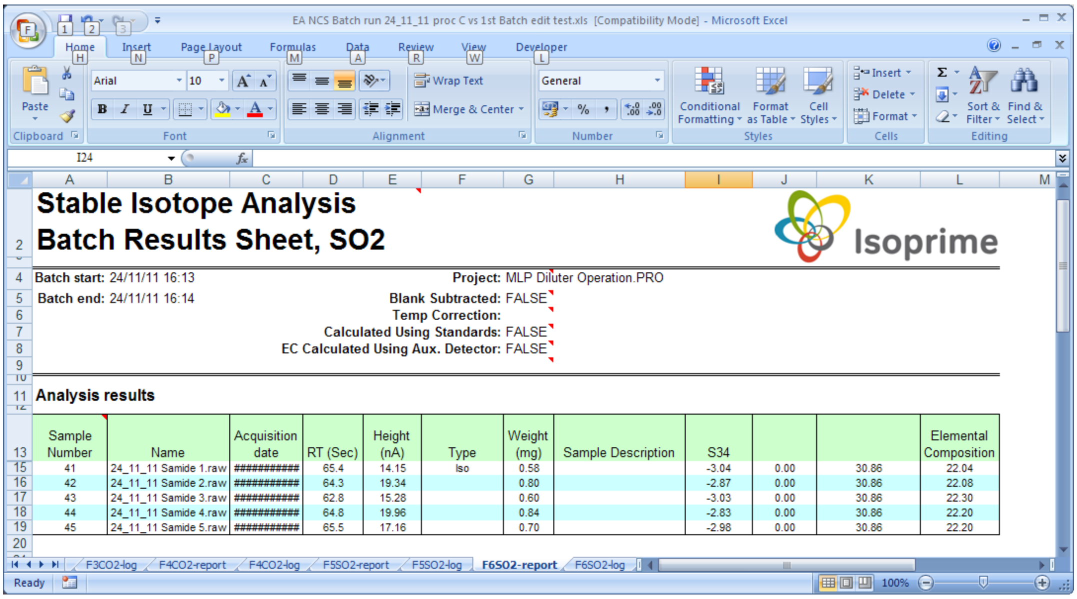
With this facility it is possible to modify:

- Any of the sample integration parameters: integration window, zeros, and peak detection parameters
- Any of the reference gas integration parameters: integration window, gas calibration parameters
- Any of the TCD integration parameters: integration window, zeros, and peak detection parameters.

BATCH REPROCESSING

Many user-defined variables can be modified and applied to an entire batch. Modifying the setting for the batch will recalculate the data for each sample. It is possible to enable or disable blank calculation and enable or disable isotopic standards calculations from the batch report.

The example, below shows how to apply isotopic standards to the batch for sulphur isotope δ^{34}S measurements.



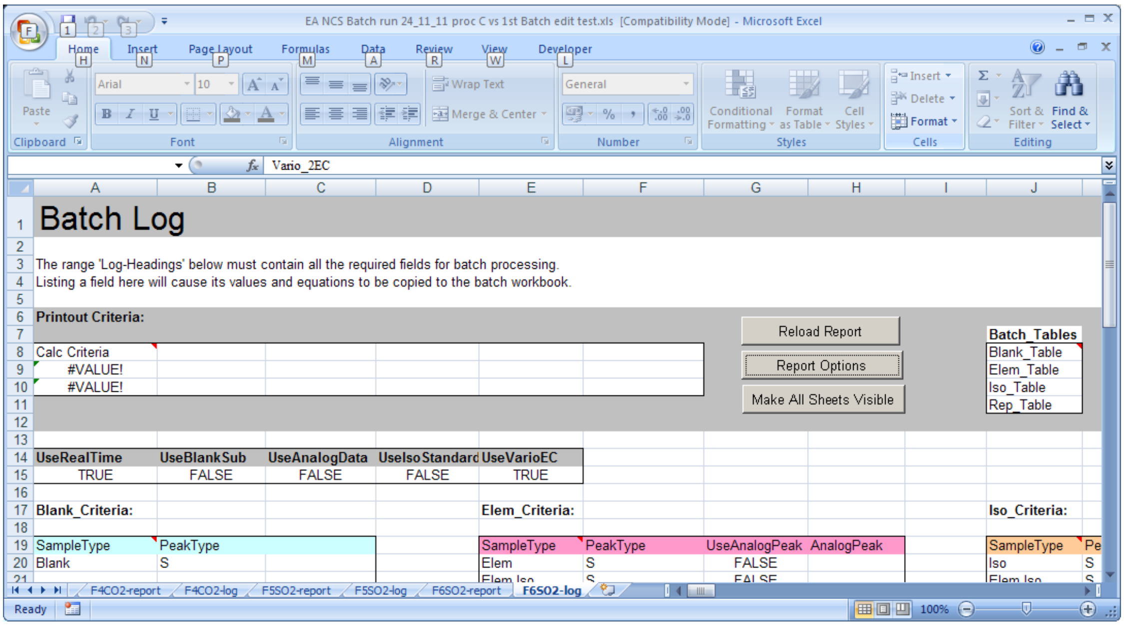
Stable Isotope Analysis
Batch Results Sheet, SO2

Batch start: 24/11/11 16:13
Batch end: 24/11/11 16:14
Project: MLP Diluter Operation.PRO
Blank Subtracted: FALSE
Temp Correction:
Calculated Using Standards: FALSE
EC Calculated Using Aux. Detector: FALSE

Analysis results

Sample Number	Name	Acquisition date	RT (Sec)	Height (nA)	Type	Weight (mg)	Sample Description	S34			Elemental Composition
41	24_11_11 Samide 1.raw	###########	65.4	14.15	Iso	0.58		-3.04	0.00	30.86	22.04
42	24_11_11 Samide 2.raw	###########	64.3	19.34		0.80		-2.87	0.00	30.86	22.08
43	24_11_11 Samide 3.raw	###########	62.8	15.28		0.60		-3.03	0.00	30.86	22.30
44	24_11_11 Samide 4.raw	###########	64.8	19.96		0.84		-2.83	0.00	30.86	22.20
45	24_11_11 Samide 5.raw	###########	65.5	17.16		0.70		-2.98	0.00	30.86	22.20

The summary data at the top of the sheet shows the "Calculated Using Standards" option set to FALSE, It also shows that sample 41 has been declared as an "Iso" standard. Clicking on the log tab for the report (F6SO2-LOG) opens up the following page:



Batch Log

The range 'Log-Headings' below must contain all the required fields for batch processing.
Listing a field here will cause its values and equations to be copied to the batch workbook.

Printout Criteria:

Calc Criteria
#VALUE!
#VALUE!

Reload Report
Report Options
Make All Sheets Visible

Batch_Tables
Blank_Table
Elem_Table
Iso_Table
Rep_Table

UseRealTime	UseBlankSub	UseAnalogData	UseIsoStandard	UseVarioEC
TRUE	FALSE	FALSE	FALSE	TRUE

Blank_Criteria:

SampleType	PeakType
Blank	S

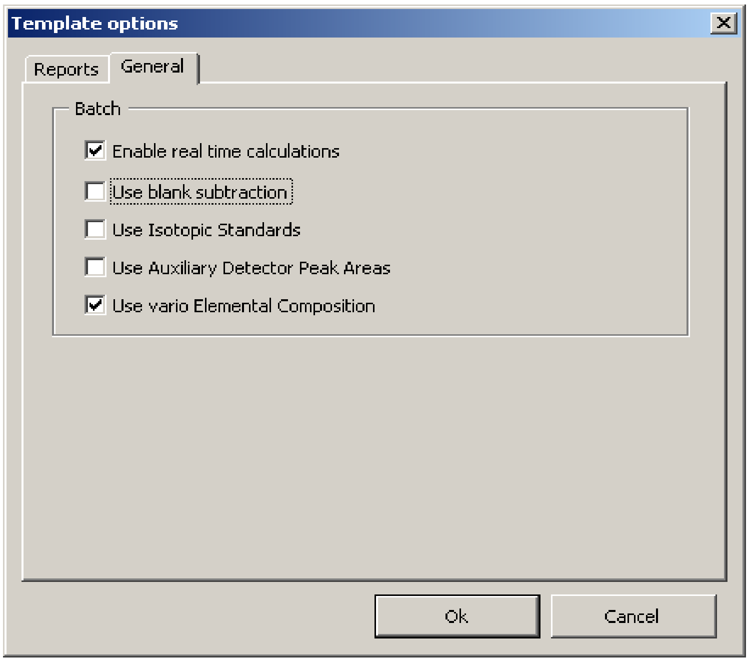
Elem_Criteria:

SampleType	PeakType	UseAnalogPeak	AnalogPeak
Elem	S	FALSE	

Iso_Criteria:

SampleType	Pe
Iso	S

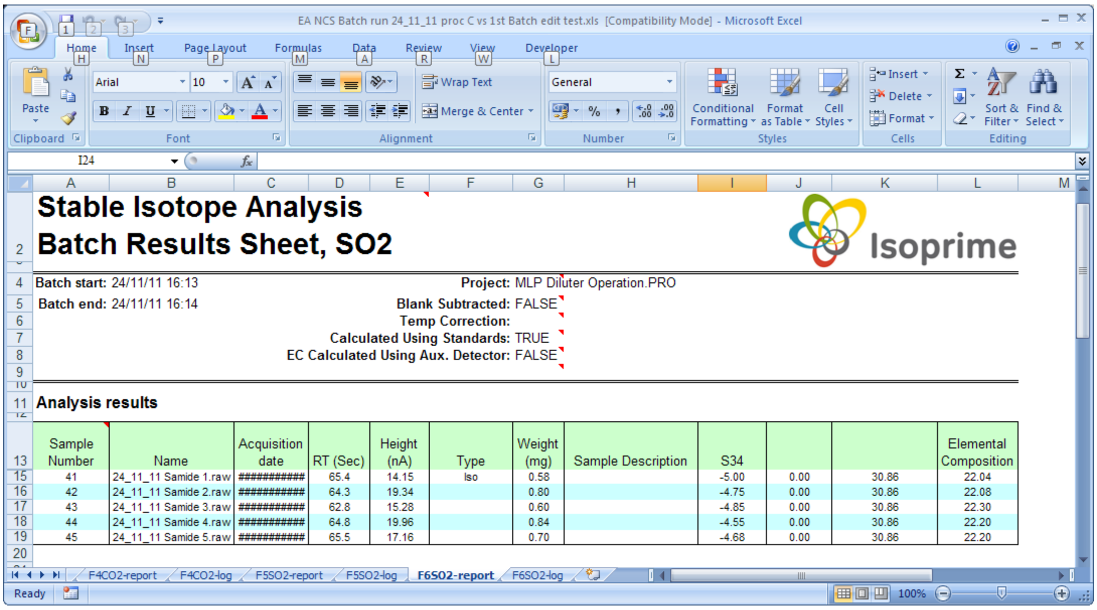
Click on the Report options button to open the "Template options" window:



Batch
☑ Enable real time calculations
☐ Use blank subtraction
☐ Use Isotopic Standards
☐ Use Auxiliary Detector Peak Areas
☑ Use vario Elemental Composition

Select the "Use Isotopic Standards" checkbox. Note that the "Use vario Elemental Composition" checkbox is ticked. This causes IonVantage to collect and report the data from the EA for the elemental composition.

Pressing ok at this point will cause the sample nominated as iso to be defined as a standard and the batch will recalculated correcting the following data against the standards delta value.



Stable Isotope Analysis
Batch Results Sheet, SO2

Batch start: 24/11/11 16:13
Batch end: 24/11/11 16:14

Project: MLP Diluter Operation.PRO
Blank Subtracted: FALSE
Temp Correction:
Calculated Using Standards: TRUE
EC Calculated Using Aux. Detector: FALSE

Analysis results

Sample Number	Name	Acquisition date	RT (Sec)	Height (nA)	Type	Weight (mg)	Sample Description	S34			Elemental Composition
41	24_11_11 Samide 1.raw	###########	65.4	14.15	Iso	0.58		-5.00	0.00	30.86	22.04
42	24_11_11 Samide 2.raw	###########	64.3	19.34		0.80		-4.75	0.00	30.86	22.08
43	24_11_11 Samide 3.raw	###########	62.8	15.28		0.60		-4.85	0.00	30.86	22.30
44	24_11_11 Samide 4.raw	###########	64.8	19.96		0.84		-4.55	0.00	30.86	22.20
45	24_11_11 Samide 5.raw	###########	65.5	17.16		0.70		-4.68	0.00	30.86	22.20

Note that the “Calculated Using Standards” flag is now set to TRUE.

SINGLE SAMPLE BATCH REPROCESSING

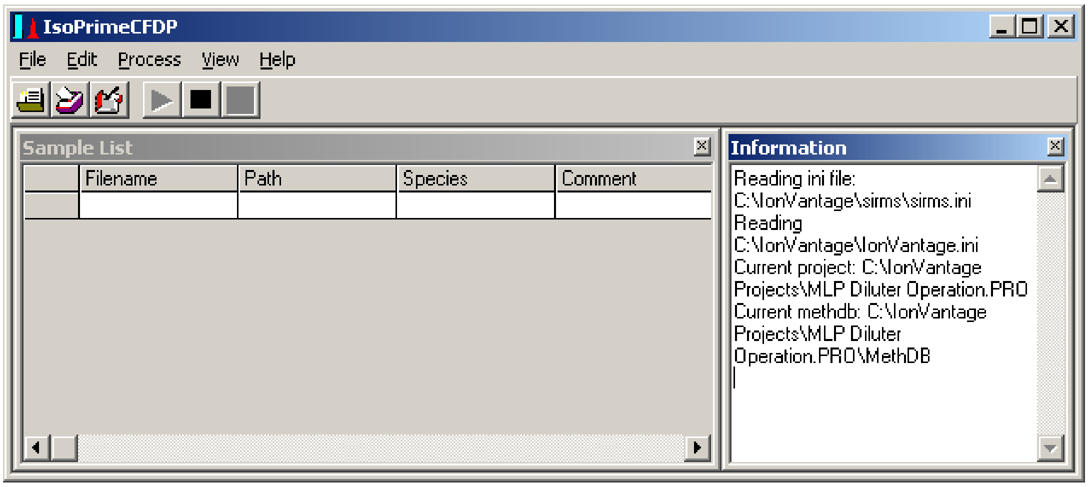
Reprocessing facilities can be accessed in two different ways:

- From the CFDP facility
- From the Sample List

These two routes are discussed in the rest of this section.

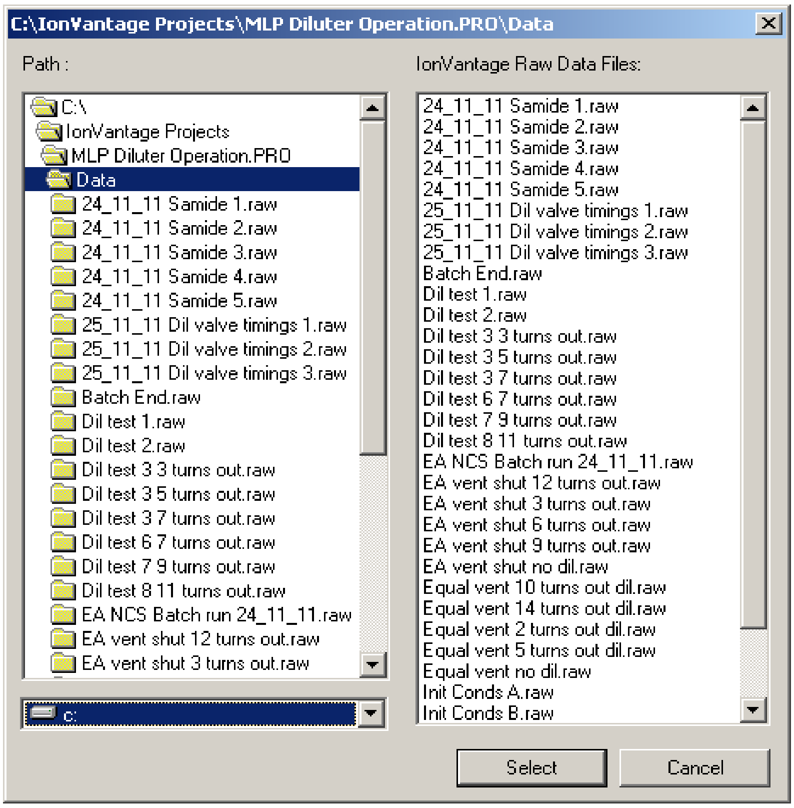
ACCESS VIA CFDP

To access the CFDP facility (Continuous Flow Data Processing), double click the CFDP icon on the deskto.



Reading ini file:
C:\IonVantage\sirms\sirms.ini
Reading
C:\IonVantage\IonVantage.ini
Current project: C:\IonVantage Projects\MLP Diluter Operation.PRO
Current methdb: C:\IonVantage Projects\MLP Diluter Operation.PRO\MethDB

- The list of **IonVantage Projects** can be accessed by clicking on the **File** menu and then **Open IonVantage Raw File**. Select a **Project** name and open its **Data** file:

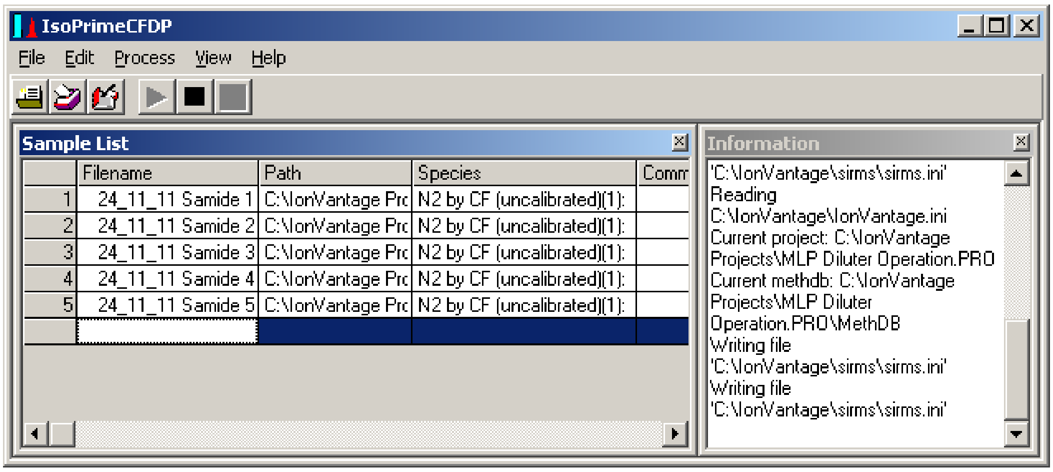


C:\
IonVantage Projects
MLP Diluter Operation.PRO
Data
24_11_11 Samide 1.raw
24_11_11 Samide 2.raw
24_11_11 Samide 3.raw
24_11_11 Samide 4.raw
24_11_11 Samide 5.raw
25_11_11 Dil valve timings 1.raw
25_11_11 Dil valve timings 2.raw
25_11_11 Dil valve timings 3.raw
Batch End.raw
Dil test 1.raw
Dil test 2.raw
Dil test 3 3 turns out.raw
Dil test 3 5 turns out.raw
Dil test 3 7 turns out.raw
Dil test 6 7 turns out.raw
Dil test 7 9 turns out.raw
Dil test 8 11 turns out.raw
EA NCS Batch run 24_11_11.raw
EA vent shut 12 turns out.raw
EA vent shut 3 turns out.raw

24_11_11 Samide 1.raw
24_11_11 Samide 2.raw
24_11_11 Samide 3.raw
24_11_11 Samide 4.raw
24_11_11 Samide 5.raw
25_11_11 Dil valve timings 1.raw
25_11_11 Dil valve timings 2.raw
25_11_11 Dil valve timings 3.raw
Batch End.raw
Dil test 1.raw
Dil test 2.raw
Dil test 3 3 turns out.raw
Dil test 3 5 turns out.raw
Dil test 3 7 turns out.raw
Dil test 6 7 turns out.raw
Dil test 7 9 turns out.raw
Dil test 8 11 turns out.raw
EA NCS Batch run 24_11_11.raw
EA vent shut 12 turns out.raw
EA vent shut 3 turns out.raw
EA vent shut 6 turns out.raw
EA vent shut 9 turns out.raw
EA vent shut no dil.raw
Equal vent 10 turns out dil.raw
Equal vent 14 turns out dil.raw
Equal vent 2 turns out dil.raw
Equal vent 5 turns out dil.raw
Equal vent no dil.raw
Init Conds A.raw
Init Conds B.raw

The **Data** folder consists of all the acquisition files contained in this particular **Project**

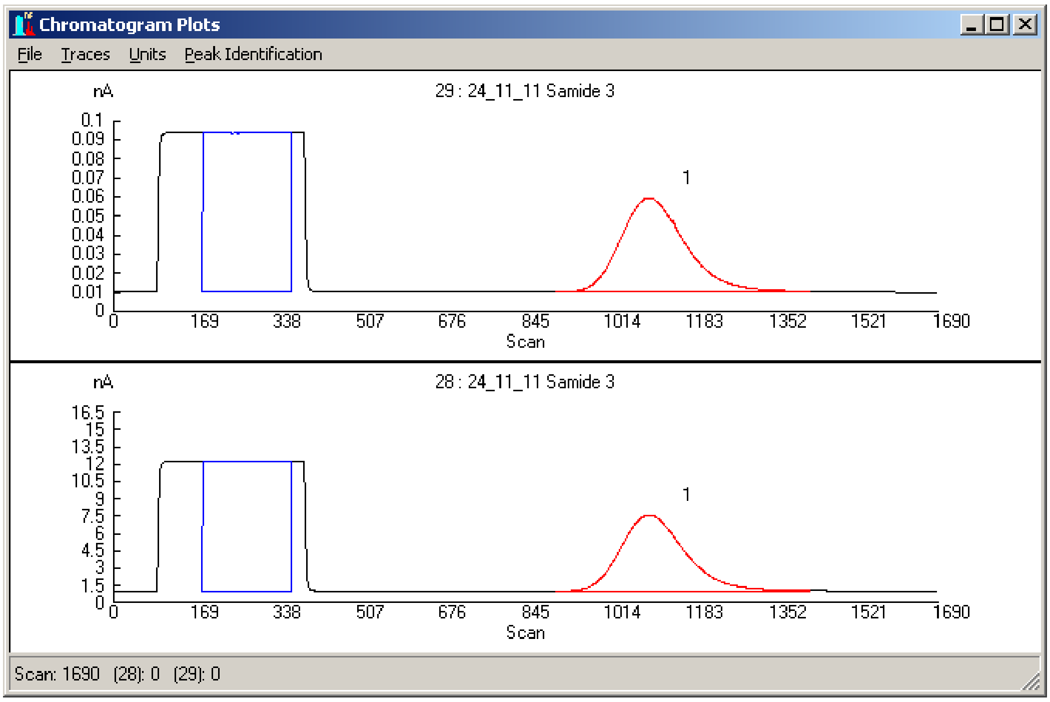
- Highlight the full set of files of interest from the **right hand frame** and click on the **Select** button. This causes the selected file to appear in the IsoPrime CFDP window.



	Filename	Path	Species	Comr
1	24_11_11 Samide 1	C:\IonVantage Prc	N2 by CF (uncalibrated)(1):	
2	24_11_11 Samide 2	C:\IonVantage Prc	N2 by CF (uncalibrated)(1):	
3	24_11_11 Samide 3	C:\IonVantage Prc	N2 by CF (uncalibrated)(1):	
4	24_11_11 Samide 4	C:\IonVantage Prc	N2 by CF (uncalibrated)(1):	
5	24_11_11 Samide 5	C:\IonVantage Prc	N2 by CF (uncalibrated)(1):	

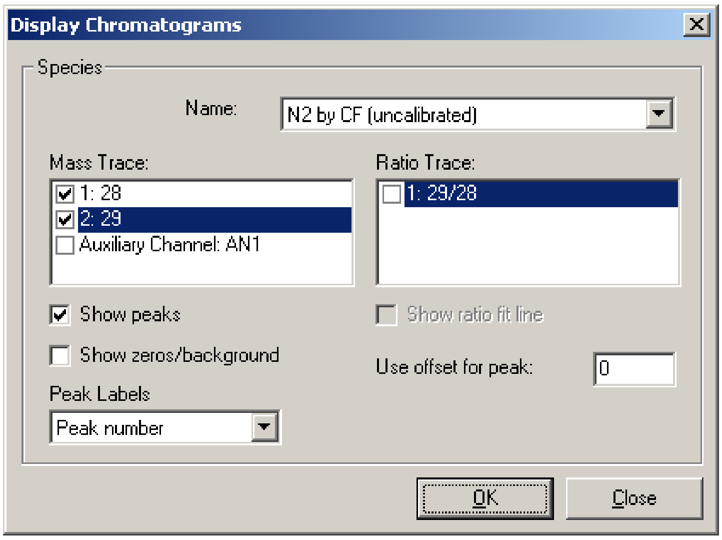
```
'C:\IonVantage\sirms\sirms.ini'
Reading
C:\IonVantage\IonVantage.ini
Current project: C:\IonVantage
Projects\MLP Diluter Operation.PRO
Current methdb: C:\IonVantage
Projects\MLP Diluter
Operation.PRO\MethDB
Writing file
'C:\IonVantage\sirms\sirms.ini'
Writing file
'C:\IonVantage\sirms\sirms.ini'
```

Each chromatogram can be examined by highlighting the particular row and then opening **Display Data** in the **Process** menu:



Scan: 1690 (28): 0 (29): 0

The displayed chromatogram trace can be changed by selecting the **View Traces** option in the **Traces** menu



Name: N2 by CF (uncalibrated)

Mass Trace:
☑ 1: 28
☑ 2: 29
☐ Auxiliary Channel: AN1

Ratio Trace:
☐ 1: 29/28

☑ Show peaks
☐ Show zeros/background
☐ Show ratio fit line

Use offset for peak: 0

Peak Labels: Peak number

The list of available traces, both mass and ratio, is shown in the two **Trace** text boxes. Each trace can be selected by ticking the appropriate check boxes. Options include showing peaks, the zero line and ratio fit line.

Acquisitions with more than one species included in the run (EA-NC analysis for example) feature each species on individual chromatogram plots.

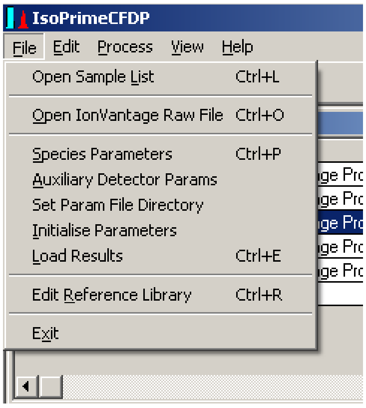
The first species analysed in the method file is the default-displayed peak. In EA-NC mode this will be nitrogen.

To view other species:

- Click on the drop down menu **Name**: in the display chromatogram window.
- Select required species, **N2 by CF (uncalibrated)** in the example shown above.
- The species will now update to display the masses and ratios for the selected species.

INTEGRATION PARAMETERS

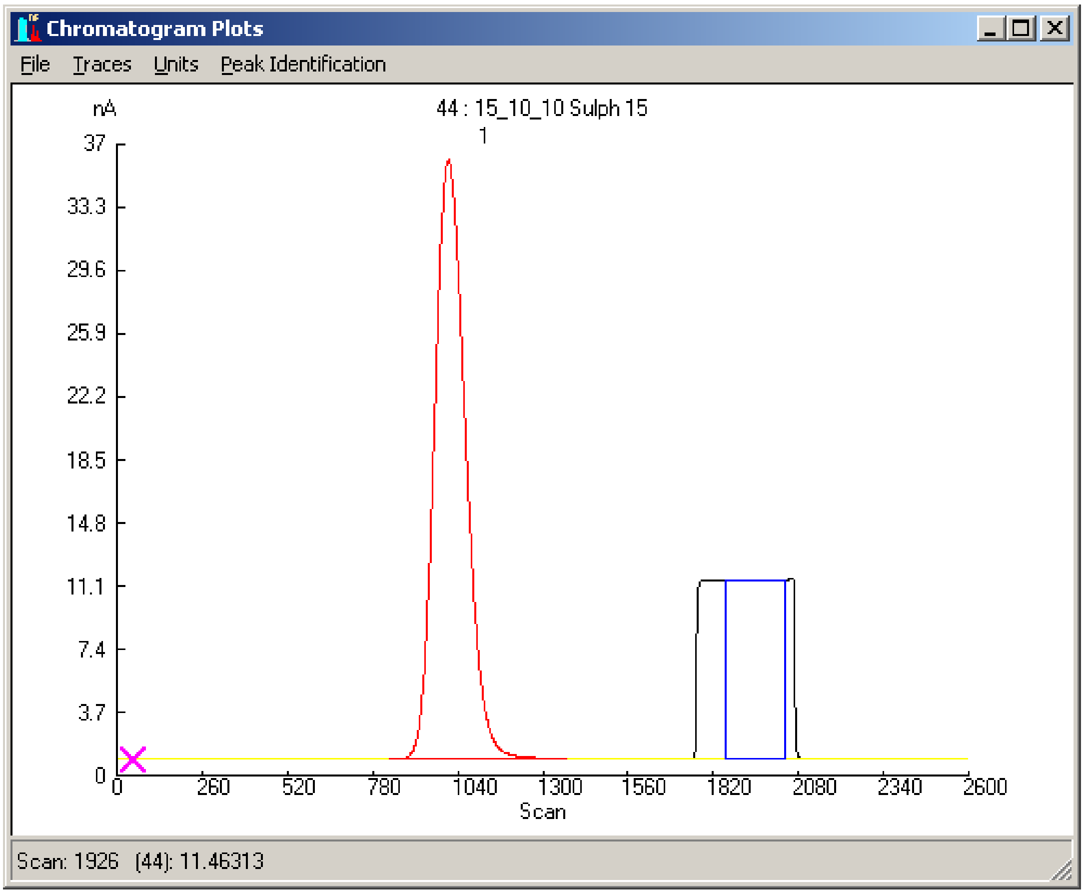
The main IsoPrimeCFDP window includes options to change integration parameters; this can be accessed via the **File** parameters option:



- **Species Parameters** gives access to all parameters relating to the Sample and Reference peaks acquired from the mass spectrometer.
- **Auxiliary Detector Params** gives access to all the parameters relating to the TCD.
- **Edit Reference Library** gives access to the library of Standards, from which information relating to Standards can be edited and new Standards can be added and defined.

CHANGING THE ZERO POSITION

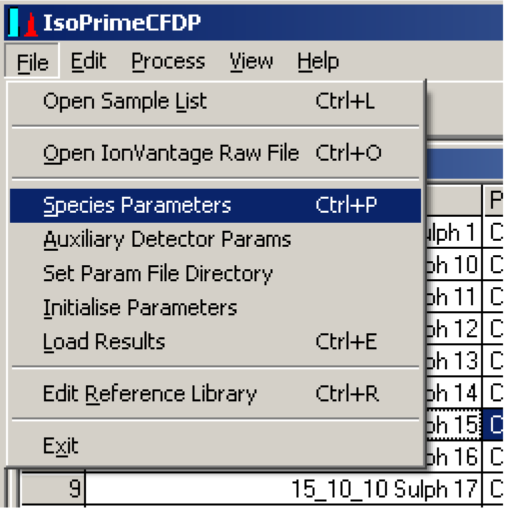
It may be necessary to change the point at which the zeros are measured in the processing. For example the trace below shows the acquisition of CO_2 for which the zero had been specified at the beginning:



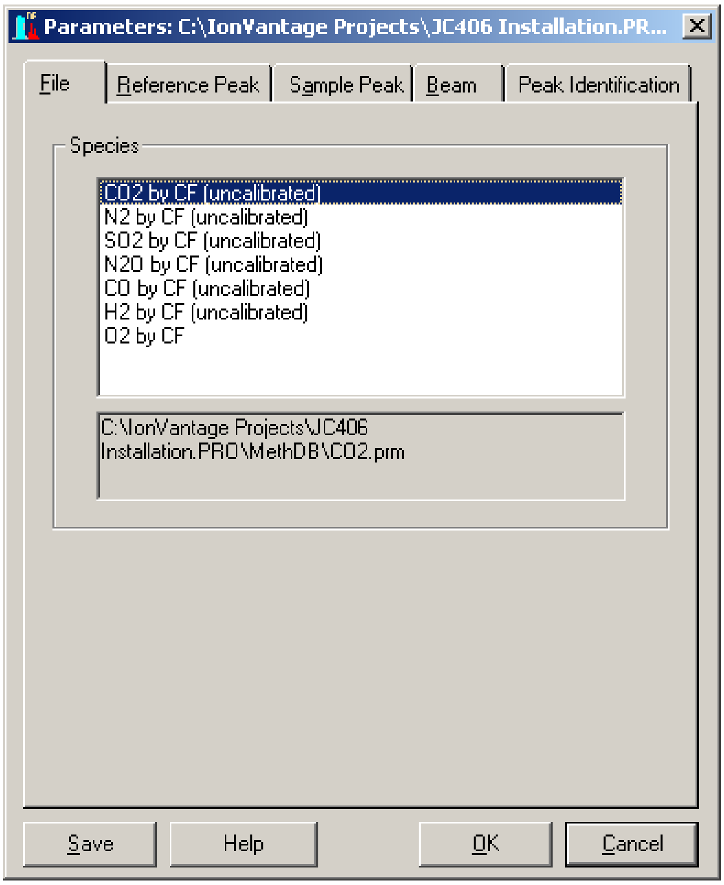
The Zero Point is currently situated before the sample peak is eluted by the EA. If the instrument has just peak jumped from nitrogen, it is possible there may be some interference on the instrument background.

The zero position would therefore be better placed after the reference peak

- Open the Species Parameters window



- Select the correct gas species, in this example CO_2.



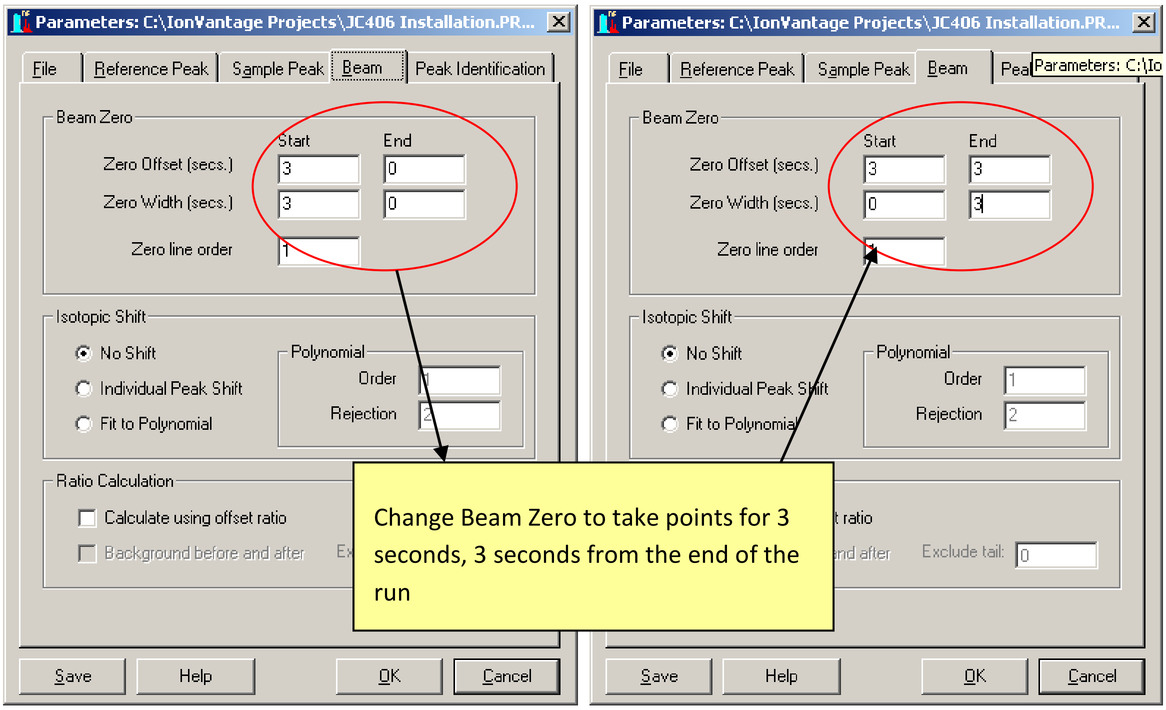
Parameters: C:\IonVantage Projects\JC406 Installation.PR...

Species

CO2 by CF (uncalibrated)
N2 by CF (uncalibrated)
SO2 by CF (uncalibrated)
N2O by CF (uncalibrated)
CO by CF (uncalibrated)
H2 by CF (uncalibrated)
O2 by CF

C:\IonVantage Projects\JC406 Installation.PRO\MethDB\CO2.prm

- Open the **Beam** Page of the **Parameters** window and make the relevant change as shown below:



Parameters: C:\IonVantage Projects\JC406 Installation.PR...

Beam Zero

	Start	End
Zero Offset (secs.)	3	0
Zero Width (secs.)	3	0
Zero line order	1	

Isotopic Shift

● No Shift
○ Individual Peak Shift
○ Fit to Polynomial

Polynomial
Order 1
Rejection 2

Ratio Calculation

☐ Calculate using offset ratio
☐ Background before and after

Parameters: C:\IonVantage Projects\JC406 Installation.PR...

Beam Zero

	Start	End
Zero Offset (secs.)	3	3
Zero Width (secs.)	0	3
Zero line order	1	

Isotopic Shift

● No Shift
○ Individual Peak Shift
○ Fit to Polynomial

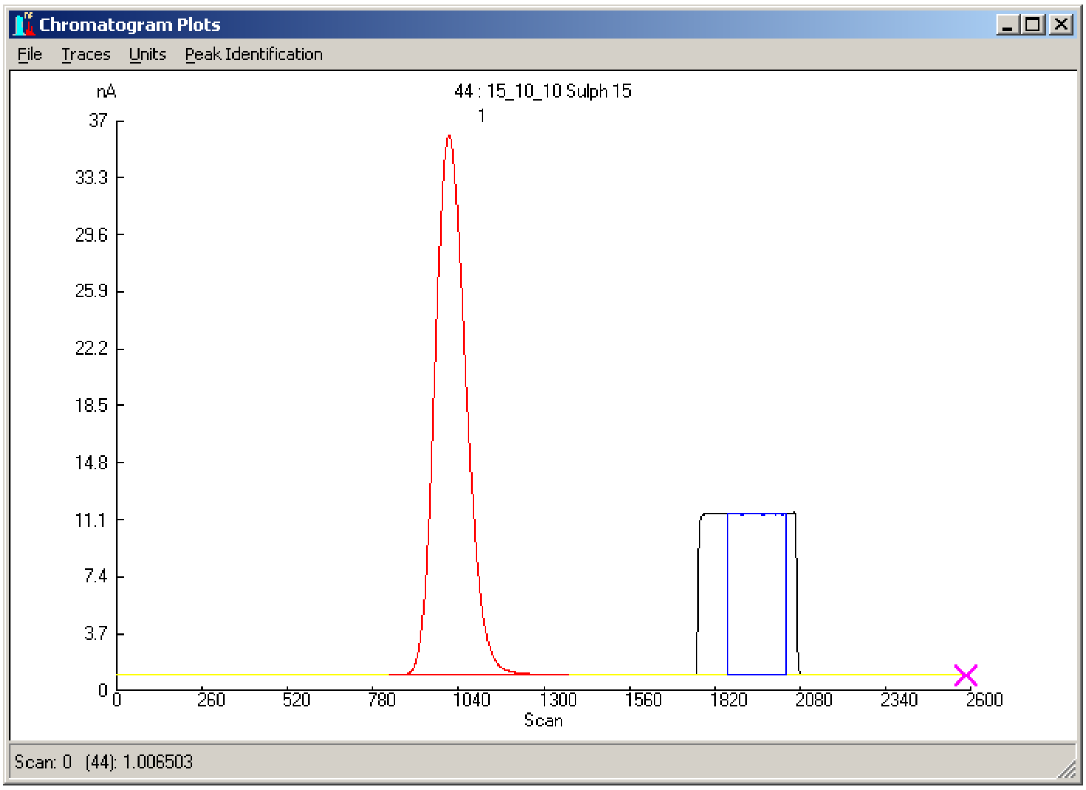
Polynomial
Order 1
Rejection 2

Exclude tail: 0

Change Beam Zero to take points for 3 seconds, 3 seconds from the end of the run

- Click **OK** the accept the changes, Reprocess the file and re-open the trace

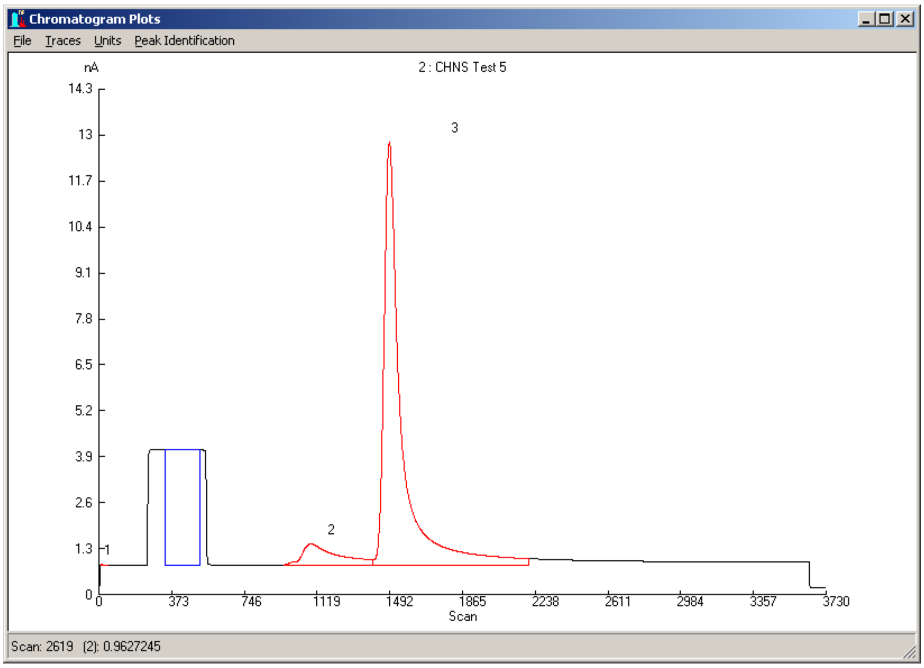
The zero is now in a more suitable position:



Scan: 0 (44): 1.006503

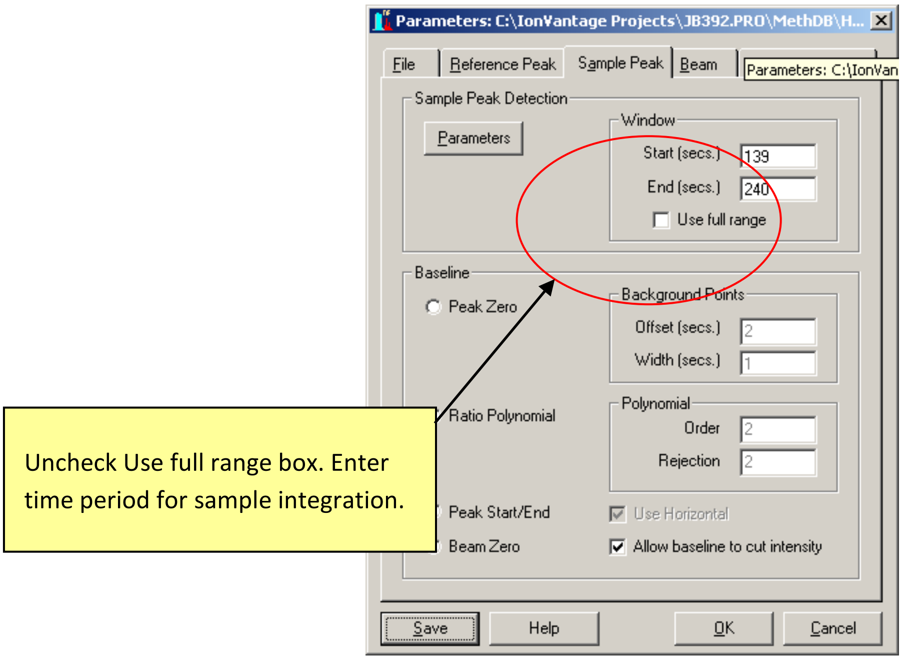
DEFINE SAMPLE INTEGRATION WINDOW

The user also has the option of defining the sample integration window for each sample peak, this can be used to limit what the processing integrates to only the major peak. In the example below shows the chromatogram of the mass 2 signal measured from a sample of Sulphanilamide run in NCHS mode. . It includes a large H_2 peak and a much smaller peak before it due to valve switching in the EA. It also includes a very tiny peak at the start of the function due to the source supplies settling after the peak jump from the previous function.



Scan: 2619 (2): 0.9627245

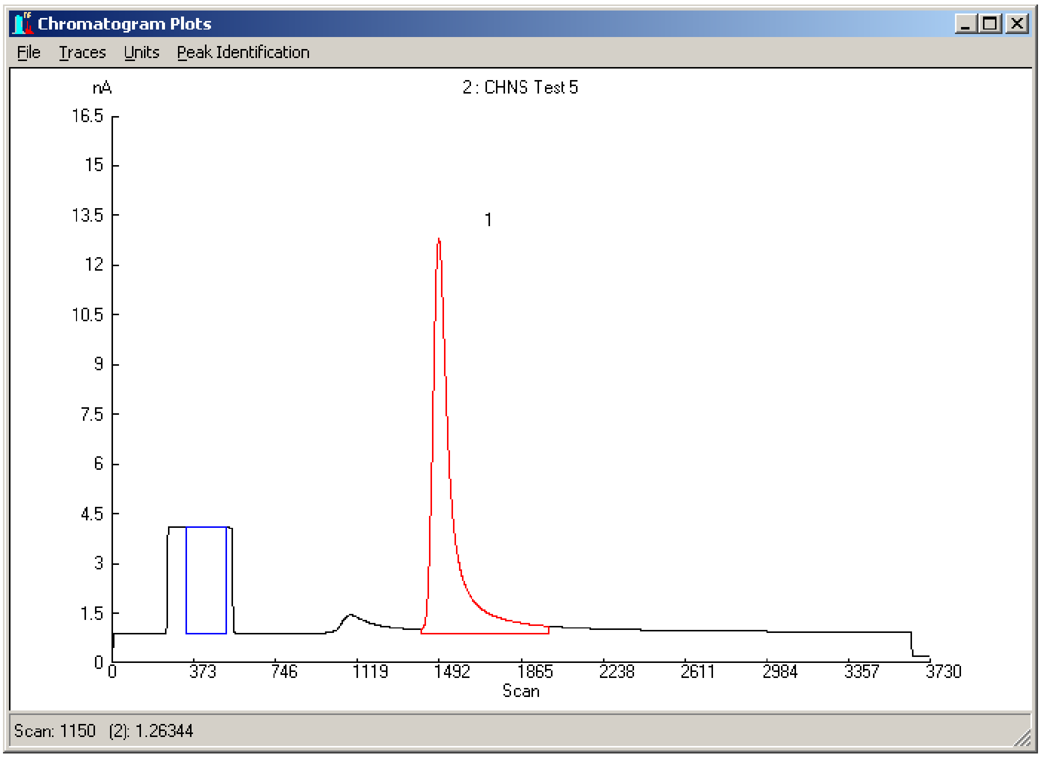
If the integration window is defined for the entire range, then all three peaks will be integrated. The parameters to define **Sample windows** are found on the **Sample Peak** page of the **Parameters** window. This window is accessed from the main CFDP window by clicking on **File, species parameters.** Select the required species and go to the Sample Peak Tab. In the *Window* frame, uncheck the box labelled *Use full range* and define the required Start and End time for the integration period.



Start (secs.) 139
End (secs.) 240
☐ Use full range
Offset (secs.) 2
Width (secs.) 1
Order 2
Rejection 2
☑ Use Horizontal
☑ Allow baseline to cut intensity

Uncheck Use full range box. Enter time period for sample integration.

In the example above, inspection of the trace shows that the sample peak can be found in the interval from 195 to and 240 seconds. The trace below shows the integration area with these timings defined for that period



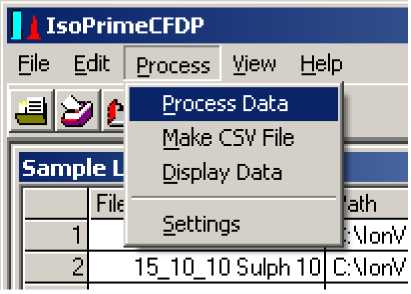
In this manner the two unrequired peaks will not be found and therefore not integrated.

REPROCESSING AFTER MAKING CHANGES

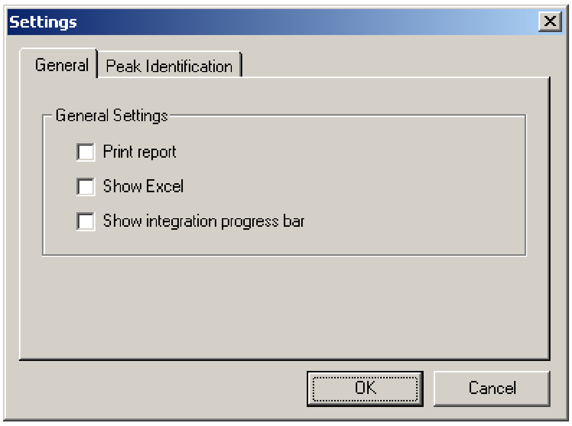
REPROCESSING OF A SINGLE CHROMATOGRAM

When all the desired changes have been made to the parameters, the single data file can be reprocessed in the manner described below:

- From the **IsoPrimeCFDP** window, highlight the Data file that needs to be reprocessed.
- Click on **Process Data** in the **Process** menu:



The file will be reprocessed using the new parameters and a Printout of the results will be printed. To change the printing preferences go to **Process, Settings** in the main CFDP window. The following window appears. Select the preferred option and press **OK.**



The reprocessed data can be found in the same file as the original.Reprocessing of an entire batch

When all the desired changes have been made and checked for one or more individual chromatograms, the entire batch of samples can be re-processed using the new parameters

- From the **IsoPrimeCFDP** window, highlight the full set of Data files included in the batch. Click on **Process Data** in the **Process** menu. This will reprocess each sample in the sample list.

Note that although it is possible to reprocess data using IsoPrime CFDP, batch reporting is unavailable because the facility to set up a batch start and end doesn't exist in IsoPrime CFDP. To reprocess a sample list into a new batch, data reprocessing must take place within the sample list of IonVantage.

DATA PROCESSING IN THE SAMPLE LIST

It is also possible to reprocess data through the Sample List window. In this manner it is possible to make all the changes described previously and in addition it is possible to make changes to the Sample List. These additional changes include:

- Modifying the values for weights.

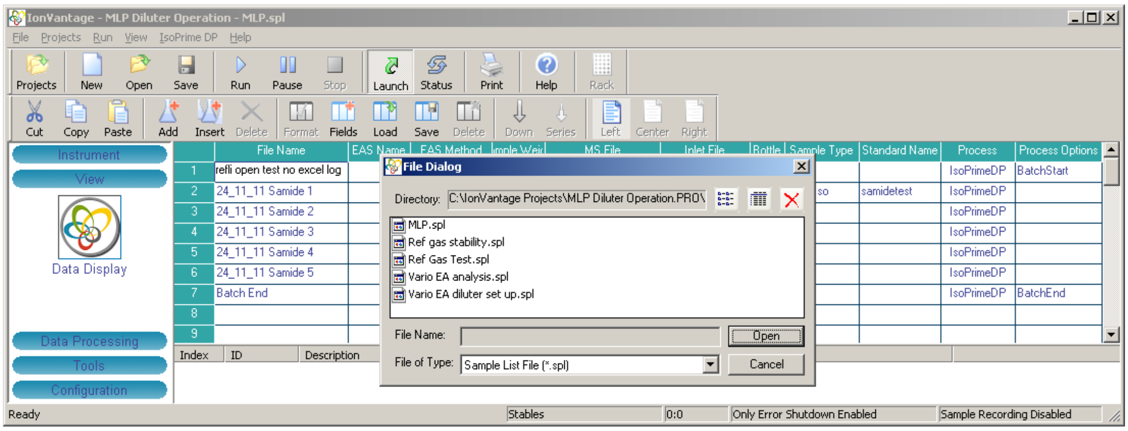
This is useful if the mass spectral peak intensity data is being used to calculate elemental composition, which is often the case with EAs other than the Elementar vario cube range.

- Modifying the Sample Type definition.

It is useful to be able to re-define the Sample Type so that results can be evaluated either with or without blank correction, or against different standards in the run, particularly as a quality control check.

To access the desired batch for reprocessing:

- From the Projects Menu of the Sample List window, select the appropriate Project and Sample List



	File Name	EAS Name	EAS Method	mple Weig	MS File	Inlet File	Bottle	Sample Type	Standard Name	Process	Process Options
1	refli open test no excel log									IsoPrimeDP	BatchStart
2	24_11_11 Samide 1							so	samidetest	IsoPrimeDP	
3	24_11_11 Samide 2									IsoPrimeDP	
4	24_11_11 Samide 3									IsoPrimeDP	
5	24_11_11 Samide 4									IsoPrimeDP	
6	24_11_11 Samide 5									IsoPrimeDP	
7	Batch End									IsoPrimeDP	BatchEnd
8											
9											

Index	ID	Description

Directory: C:\IonVantage Projects\MLP Diluter Operation.PRO\

MLP.spl
Ref gas stability.spl
Ref Gas Test.spl
Vario EA analysis.spl
Vario EA diluter set up.spl

File Name:

File of Type: Sample List File (*.spl)

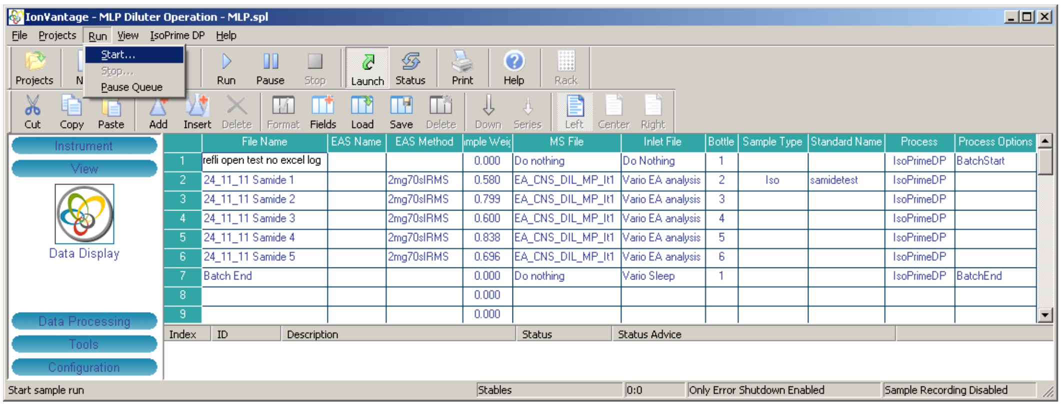
Ready | Stables | 0:0 | Only Error Shutdown Enabled | Sample Recording Disabled

- Make the appropriate changes to the **Sample List**, defining elemental and isotopic standard types as required, and inserting standard names

- Note that It is advisable to give the “BatchStart” sample a new name so that the original batch report isn’t overwritten – changes to integration parameters, for example, may make substantial differences to the results in the batch file. If the changes aren’t recorded and the batch file is overwritten it may be difficult to recover the original batch results (though the individual raw data folders automatically keep all copies of reprocessed sample data)

The batch is now ready for reprocessing.

To reprocess, highlight the rows in the sample list required (generally from the BatchStart to the BatchEnd inclusive), go to the **Run** menu and select **Start** (or press the ▷ Run button):



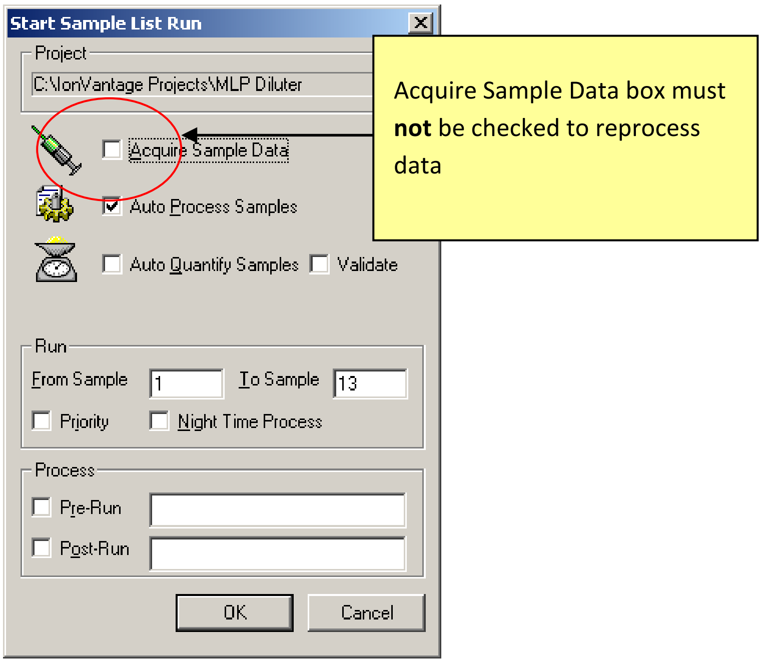
	File Name	EAS Name	EAS Method	imple Weig	MS File	Inlet File	Bottle	Sample Type	Standard Name	Process	Process Options
1	refli open test no excel log			0.000	Do nothing	Do Nothing	1			IsoPrimeDP	BatchStart
2	24_11_11 Samide 1		2mg70sIRMS	0.580	EA_CNS_DIL_MP_It1	Vario EA analysis	2	Iso	samidetest	IsoPrimeDP	
3	24_11_11 Samide 2		2mg70sIRMS	0.799	EA_CNS_DIL_MP_It1	Vario EA analysis	3			IsoPrimeDP	
4	24_11_11 Samide 3		2mg70sIRMS	0.600	EA_CNS_DIL_MP_It1	Vario EA analysis	4			IsoPrimeDP	
5	24_11_11 Samide 4		2mg70sIRMS	0.838	EA_CNS_DIL_MP_It1	Vario EA analysis	5			IsoPrimeDP	
6	24_11_11 Samide 5		2mg70sIRMS	0.696	EA_CNS_DIL_MP_It1	Vario EA analysis	6			IsoPrimeDP	
7	Batch End			0.000	Do nothing	Vario Sleep	1			IsoPrimeDP	BatchEnd
8				0.000							
9				0.000							

Index	ID	Description	Status	Status Advice

Start sample run | Stables | 0:0 | Only Error Shutdown Enabled | Sample Recording Disabled

This will open up the Start Sample List Run window.

Caution: Be sure that the acquire sample data box is **NOT** checked before proceeding with the reprocess. Failing to do so could overwrite sample data already acquired.



Project: C:\IonVantage Projects\MLP Diluter

☐ Acquire Sample Data

☑ Auto Process Samples

☐ Auto Quantify Samples ☐ Validate

From Sample: 1 To Sample: 13

☐ Priority ☐ Night Time Process

☐ Pre-Run

☐ Post-Run

Acquire Sample Data box must **not** be checked to reprocess data

Press **OK** and the reprocessing will begin.

Note: As well as renaming the batch start function it is advisable also to run the batch end to prevent copies of excel remaining open. These can be viewed within the PC Task Manager program.

TROUBLESHOOTING

OVERVIEW

This section aim is to help the operator diagnose the source of a fault, should a problem be encountered. It is designed to be a guide rather than a complete description of all situations that may arise as the instrument is used.

Additional information may be found in the IsoPrime manual, the IsoPrime Reference Gas Box manual and the appropriate vario EA manual.

It is important to remember that many problems have a simple cause like leaks or a need for maintenance. The cure for these problems is reasonably straightforward. It is worthwhile spending some time checking that the cause of a problem has been correctly diagnosed before dismantling any part of the system. It must also be remembered that breaking and re-making connections can introduce additional faults (Leaks, over-tightening of ferrules, incorrectly engaged capillaries in fittings); it is therefore worthwhile minimising the number of interventions to what is strictly needed to cure the original problem observed.

It is also worthwhile keeping an instrument log book; repeat problems can be solved very quickly if the cause has been seen previously. If it is felt that any information gathered in this way is of general interest and should be included in future versions of this manual, please, contact the customer service department at Isoprime Ltd.

OPERATING PRESSURES CANNOT BE OBTAINED

This is normally caused by leaks. The first step is to identify the area of the leaking site: mass spectrometer, reference gas injector, diluter, elemental analyser or interface.

Isolating the IsoPrime by closing the Nupro isolation valve is a very quick test to check if an instrument peripheral is causing the problem.

Normally the last action before the problem is the cause.

- Changing EA tubes/traps can often cause high operating pressures if not fitted correctly.
- Fused Silica is fragile and can easily be broken.
- If needed, refer to the *Reference Gas Injector* manual, to identify the leaking area.
- Refer to the maintenance section and EA manual to identify a leakage within the EA using the rough and fine leak test functions..
- Check that the EA is not in Sleep Mode

Cure all leaks before attempting to make any measurement.

THE RECOMMENDED BACKGROUNDS CANNOT BE REACHED

ARGON AND NITROGEN

This is usually caused by leaks. Follow the steps above to diagnose and fix the leak.

Note that High temperature EA analysis using ceramic furnace tubes and carbon filled glassy carbon tubes can cause high 28 backgrounds. Be careful not to mistake this for a leak, in this situation check the argon background to confirm the leak; cooling the EA slightly may also prove that the high 28 background is caused by the tube.

FOR THE REFERENCE GAS

The most likely cause is in the Reference Gas Injector, where the reference gas injection valve is not closing correctly. If this is the case, changing the reference gas pressures should change the size of the “leak”. Refer to *the Reference Gas Injector* manual for details on repairing the valve.

THE RECOMMENDED BLANK LEVELS CANNOT BE ACHIEVED

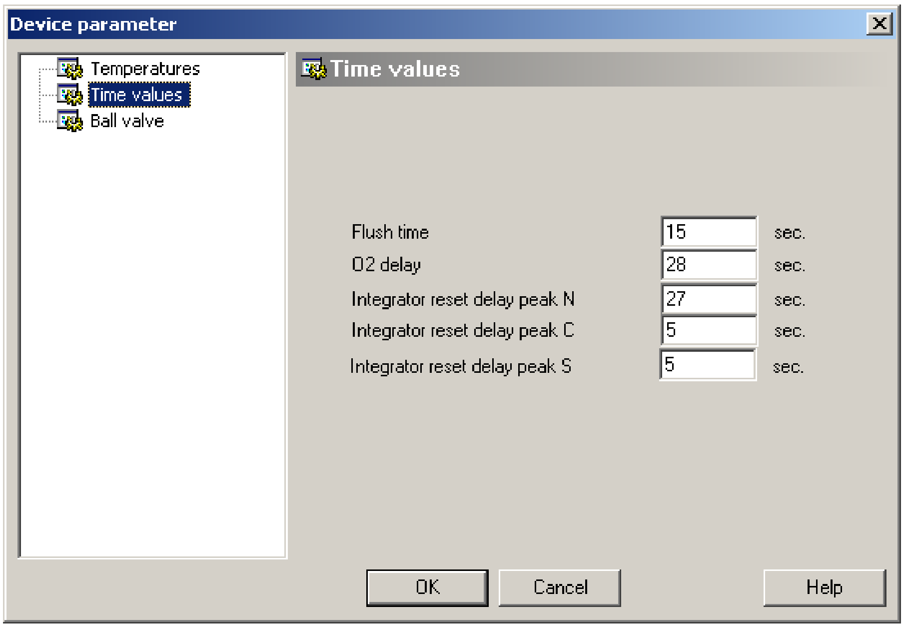
NITROGEN

This is usually caused by one of the following faults:

- Check that the ball valve on the autosampler is working correctly. Use the EA software to perform a leak check of the EA. If the valve has become loose or sample cups have been trapped within it, leaks may be introduced into the system.

- Ensure that the correct grade of oxygen is being used to combust the samples. Poor quality gas can introduce unacceptable blank levels in the instrument. Performing a blank test without the introduction of oxygen will prove if this is the problem.

- Check the flow rate and timing of the “flush flow” on the EA. The flush time can be set in “Options”, “Settings”, “Parameters” on the “Time values” tab page:



Flush time 15 sec.
O2 delay 28 sec.
Integrator reset delay peak N 27 sec.
Integrator reset delay peak C 5 sec.
Integrator reset delay peak S 5 sec.

- The flush flow rate can be checked and adjusted at the outlet of the throttle valve on the ball valve assembly.

OTHER GASES

Possible causes for poor blanks on the other gases include:

- Contaminated sample cups – check blank runs with and without an empty sample cup being combusted.
- Contaminated gases – run a set of “Blank with O” and “Blank without O” methods, say 5 of each. Discard the results of the first one or two “Blank with O” runs, as they may be combusting remnants of previous samples. The difference in the remaining two sets of blanks may give an indication if the oxygen is contaminated, or the lack of a difference may indicate helium contamination.
- Contaminated desorption traps, especially with moisture. This is often a problem if the EA has been shut down for a length of time. The traps can be conditioned either by using the “Column heat out” methods in “Options”, “Maintenance”, or by using the “System test” menu in “Options”, “Diagnostics

POOR PRECISION OF MEASUREMENT

Ensure that the system is both stable and linear, using the stability and linear tests described in the *Reference Gas Injector* manual.

If the instrument is stable and linear the most probable causes are:

- Leaks.
- The elemental analyser combustion/reduction tubes may need regenerating or replacing.
- The Drying Tubes may be exhausted.
- The combustion tube may contain too much ash. Remove ash finger and empty.
- The tin capsules may contain variable amounts of organic contaminants
- The combustion conditions may not be correct and the combustion is not complete.
- The method file timings are not optimum. Check that:

The reference gas pulses are well separated from the sample peaks.

The peak jump timing or the diluter valve actions occur well outside the start or finish of any sample peaks and preferably during “autozero delay” periods in the EA acquisition.

The total acquisition time is not long enough for complete elution of sample peaks and reference pulses.

There is enough time between two acquisitions for a complete return to baseline, before the start of the next acquisition.

- The zeros may not have been taken at suitable times. Check that zeros are taken away from any peak tail, disturbance to baselines caused by valve actions or peak jumping.
- The flush time and flow rate for the ball valve may need to be adjusted.

POOR LINEARITY

Ensure that the mass spectrometer is both stable and linear, using the stability and linear tests described in the *Reference Gas Injector* manual.

Non-linearity of sample results is usually caused by:

- Unsuitable blank subtraction: Check if blank subtraction was performed and whether the results for blanks are stable and have a reasonable size.
- Incomplete combustion: Check chemicals, ash in the combustion reactor. Remove and empty ash finger.
- Incorrect integration parameters, in particular check the sample window.
- The method file timings are not optimum. Check as described above for poor precision.

POOR ACCURACY

THE INACCURACY IS CONSTANT ACROSS A VARIETY OF STANDARDS

- Check the reference gas calibration.
- Check that there are no leaks.
- Check that the reference gas is not contaminated and is flowing continuously through the reference gas purge. If no flow is recorded then purge the reference gas line with a high flow initially, and then reduce this flow to approximately 5 ml/min as described in the *Reference Gas Injector* manual.
- Check for possible contamination in the elemental analyser and all interfacing lines.
- Check that the combustion is complete.
- Check that the water traps are in good condition.

THE INACCURACY IS RANDOM ACROSS A RANGE OF STANDARDS

- Check for possible contamination in the elemental analyser and all interfacing lines.
- Check that the combustion is complete.
- Check that the combustion reactor is in good condition and that excessive ash has not built up.
- Check that the water trap is in good condition.

POOR SENSITIVITY

Ensure that the sensitivity is acceptable for reference gas pulses and that poor sensitivity is observed only for sample peaks.

If the Diluter is being used, check that the dilution is set at a reasonable level.

If the above is true then the most likely cause is:

- Leaks within the Elemental Analyser.
- Check that the flow rates for the split at the rear of the EA are balanced correctly, particularly if the reference helium supply to the diluter has been set at a higher flow rate than specified, and the poor sensitivity is occurring in a dilution step.
- Check that the absorption column temperature ramps are set correctly

THERE IS NO SAMPLE PEAK

Ensure that the reference gas pulse is seen at the mass spectrometer.

- Check the TCD display to see if there are any peaks displaying. If there is nothing on the TCD there will be nothing on the IsoPrime.
- Check that the **Start** signal to the elemental analyser is functioning correctly. This can be checked by filling a line in the EA sample list with a sample name, weight and method, then double clicking the

"StartEA" button on the EA tab page of the inlet page of IonVantage, and a few seconds later double clicking it again to de-activate the EAStart. Check that the initiation sequence of the EA commences.

- Check that the autosampler is dropping samples into the Combustion reactor. It is worth watching a sample drop into the ball valve to be sure it will enter the EA.
- Check that the Vitreous Silica sample line has not become blocked (This would result in a very low base pressure at the mass spectrometer < 1E-6 mbar) or is not broken (This would result in a very high base pressure at the mass spectrometer > 1E-5 mbar)

THERE ARE MEMORY EFFECTS

Memory effects can usually be attributed to:

- Incomplete combustion of samples, resulting in the mixing of residues from a previous sample. It is essential to optimise the combustion process by ensuring that sufficient oxygen at an adequate injection pressure is used and that the arrival of the sample at the combustion site coincides with the arrival of the oxygen pulse.
- It is also essential that the samples are not dropped into the combustion reactor on top of a large build-up of ash from previous combustions. Sample like soils contain non-combustible material that will quickly build up and affect the combustion site. Regular cleaning of the combustion reactor to eliminate ash and residues from the combustion site is essential. Using the Ash Finger and emptying it out regularly can help prevent this type of problem.
- Combustion gas residues lingering at active sites. The carrier lines and connectors between the combustion reactor and all the way to the mass spectrometer inlet must be kept clean. Absorption trap contamination may also be the source of active sites.

Recommendations for minimising memory effects that cannot be avoided:

- On the autosampler, load samples in increasing order of isotopic enrichment and ensure that you measure Blanks and reference materials at the beginning of the batch, when residual memory is at natural abundance.
- Do not introduce dummy or wash samples in between real samples, as this will usually increase the step in enrichment to the next real sample. Use sample material itself to act as a dummy or a wash sample.

- In severe cases of memory effects, it may be necessary to increase the number of replicate analysis for each sample and discard the first few replicates until steady isotopic measurement is obtained for each sample material. This may be needed in the event of enriched samples, but should never be required for samples at normal natural abundances.

CALIBRATION OF THE DILUTER

Check that the Diluter is connected correctly, as described in the subsection entitled "*The Diluter*" of the "*System Description*" section.

Check that all the connections at the Diluter are leak tight. Take care that the diluter valve is in its open state if you are leak checking the "dilution" portion of the circuit and in its closed state when leak checking the "no-dilution" portion of the circuit.

In order to calibrate the Diluter, it is best to use Urea. Urea combusts to form roughly the same amount of N_2 and CO_2 gases. The dilution factor can thus be established without having to weigh samples.

For a particular sample, the N_2 gas is allowed to pass to the mass spectrometer undiluted and the CO_2 gas is diluted. An approximate value of the dilution factor can be obtained by observing the ratios for the heights of N_2 and CO_2.

- Prepare a "NC diluter" run with peak jumping and the diluter valve opening for the CO_2 portion of the run.
- Turn the knob of the metering valve to the position 0 on the vernier scale. This position corresponds to the MINIMUM dilution possible.
- Run the sample. From the display traces, note the ratio for the heights of N_2 and CO_2. Convert this ratio as X_0: 1. For example, if the N_2 peak height is 5 times the CO_2 peak height, the dilution would be approximately 5 times because in the case of no dilution of the CO_2 peak, the peak heights would be of similar size.
- Repeat acquisitions for the metering valve knob set to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 turns.
- For each acquisition, obtain a dilution ratio X_n: 1 where n = number of turns on the vernier scale.
- Plot a graph of X_n on the vertical axis against the number of turns, n on the horizontal axis.

It is worthwhile keeping the calibration curve obtained. It can be re-used as long as the diluting flow is not changed. There is of course no real reason for changing the flow, unless the desired dilution level cannot be achieved.

MAINTENANCE

The maintenance section describes a procedure for changing gas cylinders, and an alternative method of leak checking the EA that may help in locating a leak more quickly than the methods described in the EA manual. For detailed information on maintenance of the mass spectrometer and the EA, consult the appropriate instrument manuals.

CHANGING GAS CYLINDERS

HELIUM

Caution: Helium **MUST** be kept flowing continuously through the entire system as long as the TCD is switched ON and the isolation valve to the mass spectrometer is open, with the ion source on.

Failure of the helium flow may cause damage to the TCD filaments and to the mass spectrometer.

If helium stops flowing, air will enter at the open splits and flow into the mass spectrometer. The source filament may be damaged, and moisture may settle on the surfaces inside the vacuum enclosure. It may take several days for the surfaces to lose the moisture.

It is strongly advised to carefully monitor the amount of gas remaining in the helium cylinder, in particular before leaving at night and at weekends.

PROCEDURE

- Close the isolation valve
- Turn the ion source OFF
- Switch the Elemental Analyser to Standby
- Close the gas tap at the top of old the gas cylinder.
- Wait for pressures to decay completely
- Close the second stage pressure regulator at the gas cylinder
- Remove the two stage pressure regulator
- Mount the regulator securely on the new gas cylinder

- Open the gas tap at the top of the gas cylinder
- Set the second stage regulator to 4 bar.
- Using Snoop or an electronic Leak detector, check that there is no leak at the connection you have undone whilst changing the cylinder.
- Wait for several minutes to purge atmospheric gases out of the gas lines.
- Switch the Elemental Analyser out of standby
- Open the Isolation valve
- Wait for the mass spectrometer vacuum to fall below 5E-6 mbar.
- Turn the Source back ON
- Wait at least 15 minutes for the mass spectrometer to settle down, before using the reference gas injector.
- Wait for the necessary length of time for the Elemental Analyser to be back in the Ready state.

REFERENCE GAS

Unlike the replacement of helium, it is not necessary to switch the Elemental Analyser to the standby state or to close the isolation valve at the mass spectrometer inlet, whilst changing the reference gas bottles.

After the bottle has been changed, the entire gas lines must be purged to eliminate all traces of atmospheric gases. This is best achieved by fully opening the appropriate purge needle valve on the reference gas injector module.

Leave the needle valve fully open for a few minutes, and then reduce the flow to between 2 and 5 ml min^{-1}.

PROCEDURE TO FOLLOW:

- Close the reference gas valve from the Inlet window of the IonVantage User Interface.
- Close the isolation valve on the top of old the gas cylinder.

- Wait for pressures to decay completely.
- Close the second stage pressure regulator at the gas cylinder.
- Remove the two-stage pressure regulator.
- Mount the regulator securely on the new gas cylinder.
- Open the gas tap at the top of the gas cylinder.
- Set the second stage regulator to 4bar.
- Using Snoop or an electronic Leak detector, check that there is no leak at the connection you have undone whilst changing the cylinder.
- Open fully the needle valve that controls the flow of gas at the reference gas vent on the reference gas injector module.
- Wait for several minutes to purge atmospheric gases out of the gas lines.
- Reduce the vent flow between 2 and 5 ml min^{-1}.

RECOMMENDATIONS

No damage to the instrument will result if the reference gas supply runs out. However, if this occurs during an acquisition it will not be possible to obtain an enrichment calculation with respect to the reference gas. Enrichment can be obtained by reprocessing the data relative to a known sample.

Additionally, as a cylinder becomes empty, the gas has a tendency to modify its isotopic composition. If this occurs, accuracy of measurements will be lost.

Some gases like carbon dioxide are usually stored in pressurised reservoirs in the liquid phase, This can make it difficult to monitor the amount of gas remaining in the bottle, as the pressure stays the same until there is very little gas left and the contents become gaseous, at which stage the pressure starts to fall.

As a rule of thumb, it is wise to change the CO_2 reference gas cylinder as soon as the cylinder pressure starts to fall.

For other gases that are not stored in the liquid phase, the cylinder must be changed as soon as the outlet pressure of 4bar cannot be maintained, or **before** if it is suspected that isotopic composition of the gas is beginning to change.

OXYGEN GAS

Oxygen gas is only connected to the Elemental Analyser . The oxygen cylinder can therefore be exchanged without closing any MS valves or switching any of the electrical supplies off.

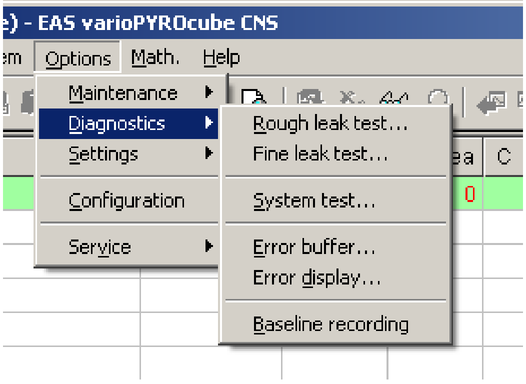
Full purging of the oxygen supply lines must be carried out before attempting to use the Elemental Analyser and the cleanliness of the oxygen must be tested.

This is fully described in the appropriate vario EA manual in the chapter "*Using the instrument*" under the section" *performing measurement work.*

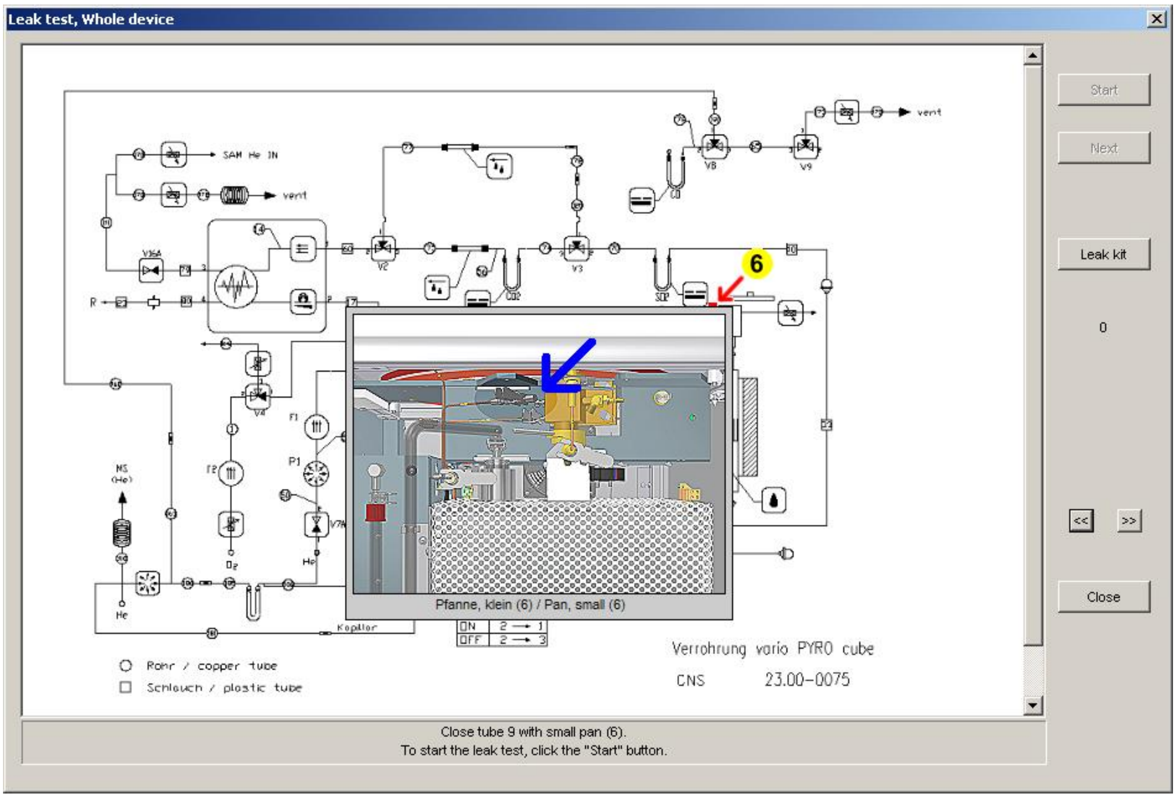
LEAK CHECKING THE ELEMENTAL ANALYSER

INTRODUCTION

The EA can be leak checked using either of two routines in the vario software, Both the "rough" and "fine" leak test are accessed through the diagnostics menu:



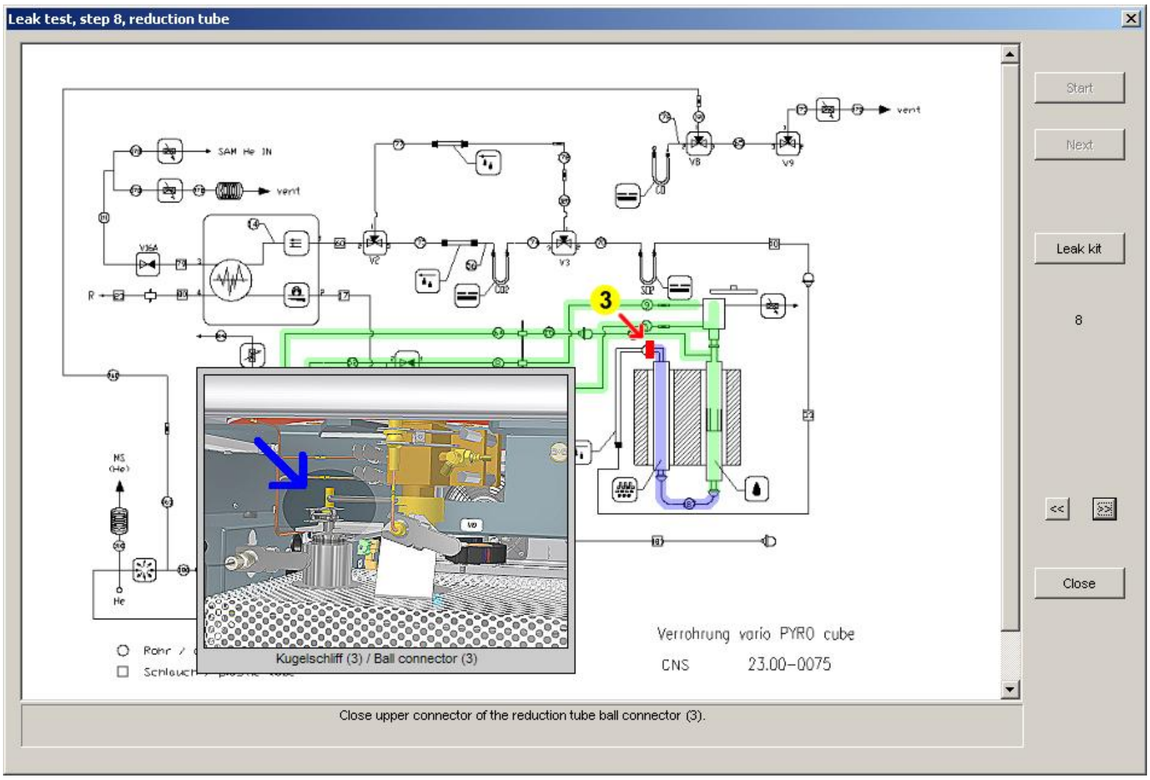
When either of these options is selected, a map of the EA system is displayed in a "Leak test" window. The "rough" leak check version conducts a leak check by pressurising the system, closing the inlet and outlet valves, waiting a short period for pressure stabilisation and then monitoring the pressure drop in the system over a period of time depending on instrument type and mode. The first step of the fine leak test is similar to the rough leak test, but the pressure drop is monitored for a much longer period of time, and so is a much more stringent test. For EA-IRMS work .If a leak is found when monitoring the pressure drop, the fine leak test routine takes the user through a stepwise sequence designed to identify were the leak might originate from. The interface, has a numeric counter for each step in the sequence and an active "forward" "backward" and "next" button n. The schematic gives an indication of where to block the system using the Elementar leak check kit and when the identifying number is hovered over with the cursor, a picture appears indicating how to block the point in question:



Close tube 9 with small pan (6).
To start the leak test, click the "Start" button.

, the system should pass the fine leak check.

Depending on the result of each step, the software will select the next leak check step to narrow down on the leak point. As each step concludes successfully, the succeeding picture of the EA map indicates which portions have been successfully tested and which are under test in that step. For example, step 8 of the fine leak check procedure for a PYRO cube in CNS mode shows the gas inlet, ball valve and combustion furnace have previously been found leak tight (shaded green), and that the quartz bridge and reduction furnace tube are currently under test (shaded blue):



Leak test, step 8, reduction tube

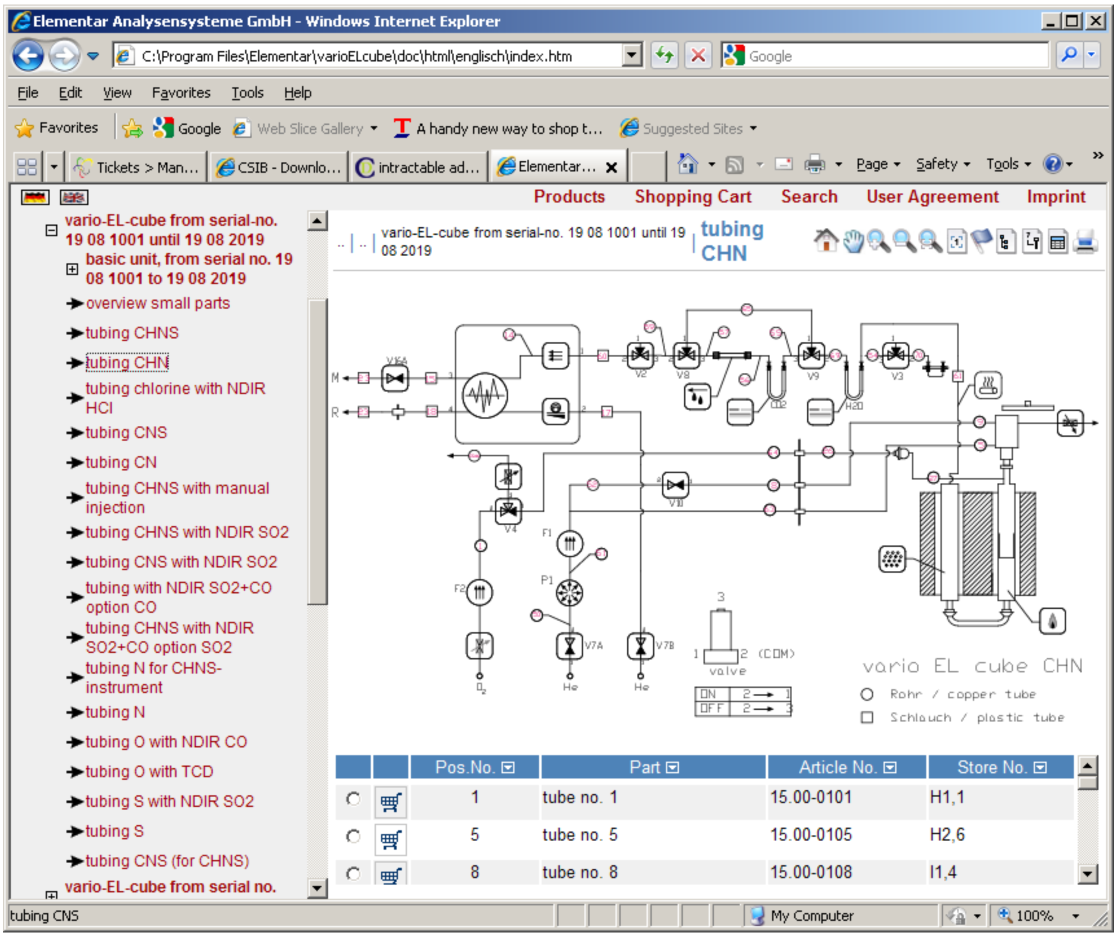
Kugelschliff (3) / Ball connector (3)

Close upper connector of the reduction tube ball connector (3).

QUICK LEAK CHECK OF EA

Sometimes leak checking the EA using the above routines can be a little difficult and time consuming, considering that the most common locations for leaks are where the combustion, reduction tubes have been replaced, or on the ball valve, and that these areas among the last tested areas of the fine leak check process, an alternative method may be employed to speed the process up.

The general procedure involves stopping the carrier flow, introducing a blockage, and starting the carrier flow up again, and looking for the “Flow-He” readback to fall to zero. The method is particularly straightforward if reference is made to a flow schematic of the EA. This can be found either in the manual (in the sections describing mode changes) or in the “Documentation” package by double clicking on the icon, allowing the blocked content as required, and using the menu tree in the left hand pane to find the tubing diagrams.



vario-EL-cube from serial-no. 19 08 1001 until 19 08 2019
- basic unit, from serial no. 19 08 1001 to 19 08 2019
  - overview small parts
  - tubing CHNS
  - tubing CHN
  - tubing chlorine with NDIR HCl
  - tubing CNS
  - tubing CN
  - tubing CHNS with manual injection
  - tubing CHNS with NDIR SO2
  - tubing CNS with NDIR SO2
  - tubing with NDIR SO2+CO option CO
  - tubing CHNS with NDIR SO2+CO option SO2
  - tubing N for CHNS-instrument
  - tubing N
  - tubing O with NDIR CO
  - tubing O with TCD
  - tubing S with NDIR SO2
  - tubing S
  - tubing CNS (for CHNS)

vario-EL-cube from serial no.

.. | .. | vario-EL-cube from serial-no. 19 08 1001 until 19 08 2019 | tubing CHN

		Pos.No.	Part	Article No.	Store No.
○	🛒	1	tube no. 1	15.00-0101	H1,1
○	🛒	5	tube no. 5	15.00-0105	H2,6
○	🛒	8	tube no. 8	15.00-0108	I1,4

The following instructions describe the sequence of events necessary to perform the alternative leak check:

- In the “Options”, “Maintenance” menu, click “Replace parts”
- Press OK on the message concerning hot parts, and when the pressure has dropped, fit a blank ball on the outlet of the reduction furnace tube
- Press the “Finish” button
- Watch the “Flow-He” readback.

Blocking the outlet of the reduction furnace separates the drying tubes (which are often changed) and the furnace tubes/ball valve which also are often changed – so this corresponds to a point roughly half way along the flow in terms of common leakage areas.

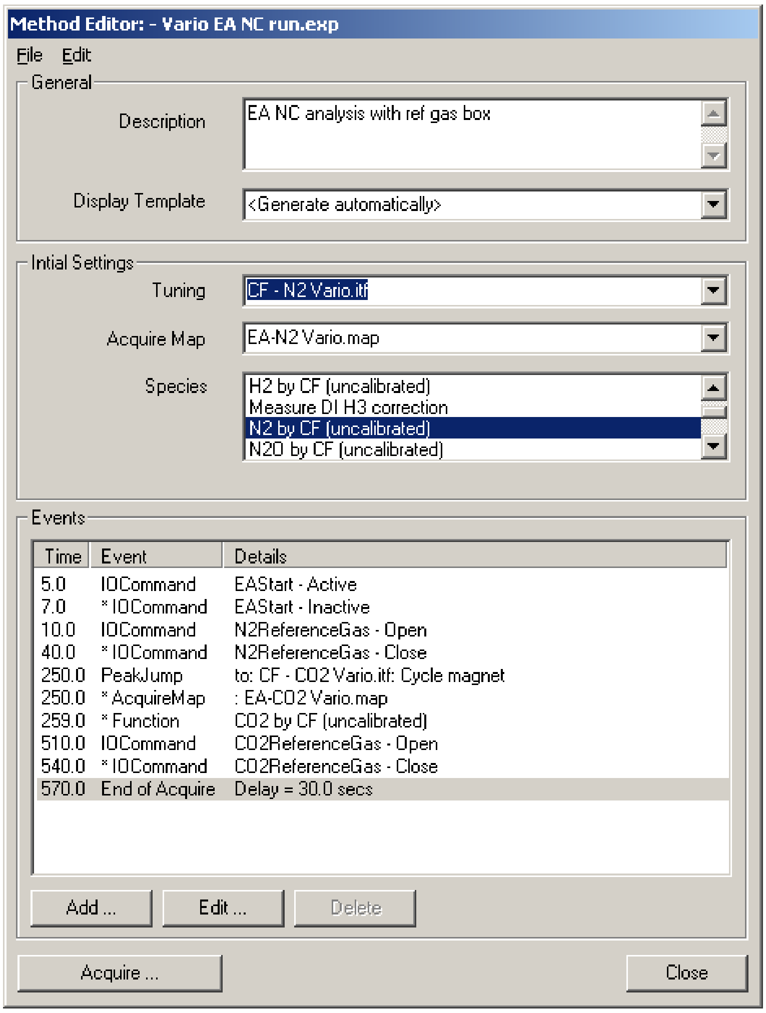
- If the “Flow-He” readback falls to zero (this may take a good 2 minutes or so), this indicates the furnace tubes and ball valve are leak tight, and the apparent leak must be after the blockage point.
- If the “Flow-He” readback doesn’t fall to zero, this indicates the leak is before the blockage point.
- Depending on what happens to the “Flow-He” readback, choose another point to block the flow.

- Use the “Replace parts” option to stop the carrier flow again, block the flow at the new position, and retest by clicking the “Finish” button in the “Replace parts” menu.

A2 MODE DEPENDENT MS METHOD FILES

The following composite pictures show suggested MS method files for use with the EA in various modes. The methods can be used as a starting point, and then adjusted to suit particular applications.

NC WITH PEAK JUMP AND NO DILUTION



Method Editor: - Vario EA NC run.exp

General

Description: EA NC analysis with ref gas box

Display Template: <Generate automatically>

Intial Settings

Tuning: CF - N2 Vario.itf

Acquire Map: EA-N2 Vario.map

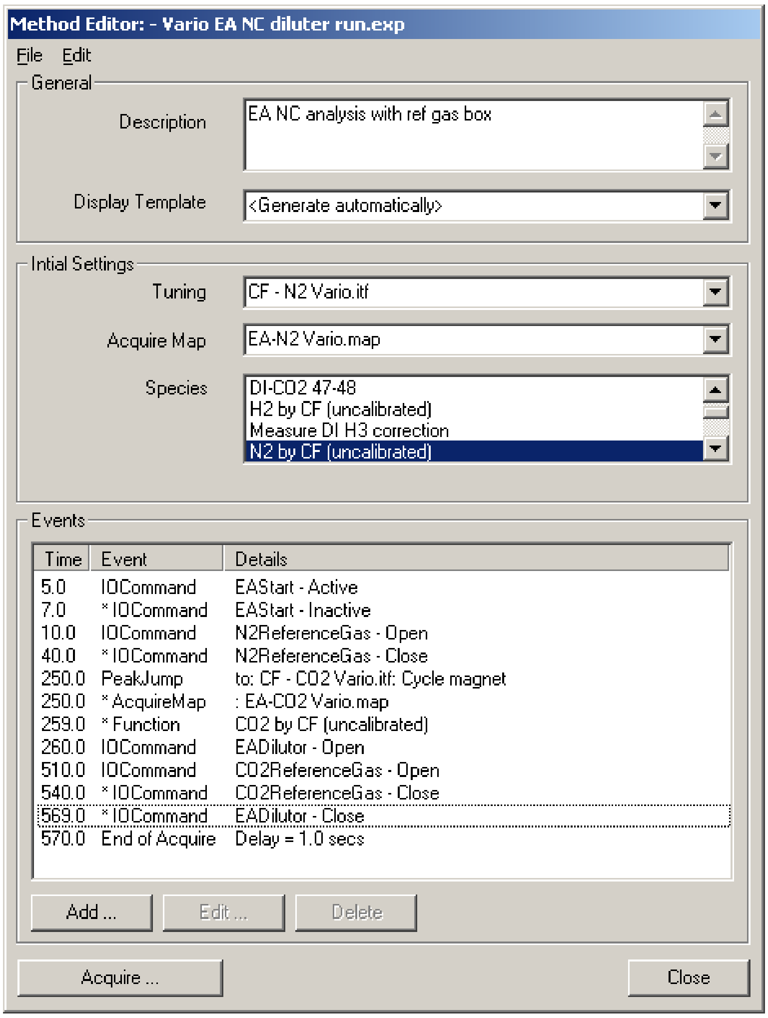
Species:
H2 by CF (uncalibrated)
Measure DI H3 correction
N2 by CF (uncalibrated)
N2O by CF (uncalibrated)

Events

Time	Event	Details
5.0	IOCommand	EAStart - Active
7.0	* IOCommand	EAStart - Inactive
10.0	IOCommand	N2ReferenceGas - Open
40.0	* IOCommand	N2ReferenceGas - Close
250.0	PeakJump	to: CF - CO2 Vario.itf: Cycle magnet
250.0	* AcquireMap	: EA-CO2 Vario.map
259.0	* Function	CO2 by CF (uncalibrated)
510.0	IOCommand	CO2ReferenceGas - Open
540.0	* IOCommand	CO2ReferenceGas - Close
570.0	End of Acquire	Delay = 30.0 secs

This method can be used with the vario MICRO, EL, ISOTOPE and PYRO cubes in NC mode.

NC WITH PEAK JUMP AND DILUTION



Method Editor: - Vario EA NC diluter run.exp

Description: EA NC analysis with ref gas box

Display Template: <Generate automatically>

Tuning: CF - N2 Vario.itf

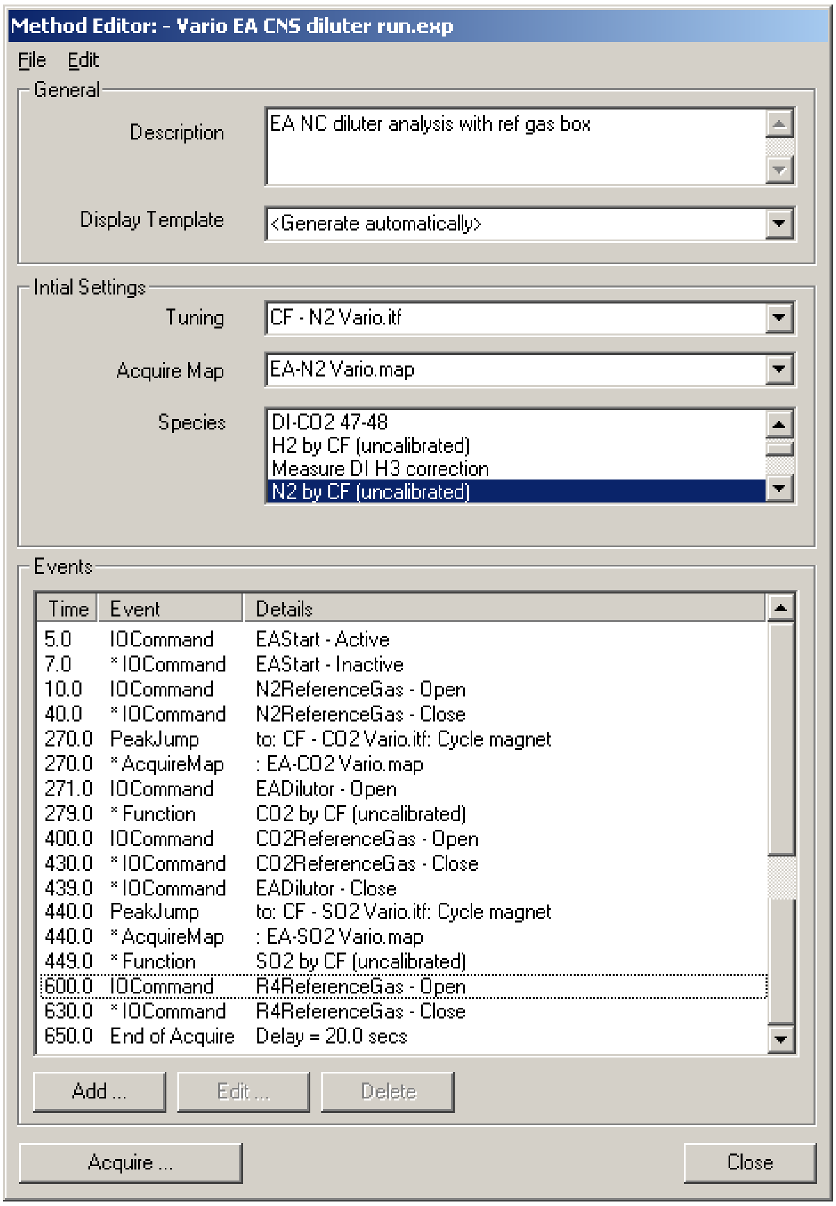
Acquire Map: EA-N2 Vario.map

Species:
- DI-CO2 47-48
- H2 by CF (uncalibrated)
- Measure DI H3 correction
- N2 by CF (uncalibrated)

Time	Event	Details
5.0	IOCommand	EAStart - Active
7.0	* IOCommand	EAStart - Inactive
10.0	IOCommand	N2ReferenceGas - Open
40.0	* IOCommand	N2ReferenceGas - Close
250.0	PeakJump	to: CF - CO2 Vario.itf: Cycle magnet
250.0	* AcquireMap	: EA-CO2 Vario.map
259.0	* Function	CO2 by CF (uncalibrated)
260.0	IOCommand	EADilutor - Open
510.0	IOCommand	CO2ReferenceGas - Open
540.0	* IOCommand	CO2ReferenceGas - Close
569.0	* IOCommand	EADilutor - Close
570.0	End of Acquire	Delay = 1.0 secs

For best results, the EADiluter-Open command should be timed to coincide with an autozero delay period in the EA method. This is to prevent the EA software integrating spikes in the TCD signal that might occur due to instantaneous pressure changes as the diluter valve is switched. The EADiluter-Close command should be timed after the EA integration has finished. This method is suitable for all four of the vario EAs in CN mode.

NCS WITH PEAK JUMP AND DILUTION FOR C



Description: EA NC diluter analysis with ref gas box

Display Template: <Generate automatically>

Tuning: CF - N2 Vario.itf

Acquire Map: EA-N2 Vario.map

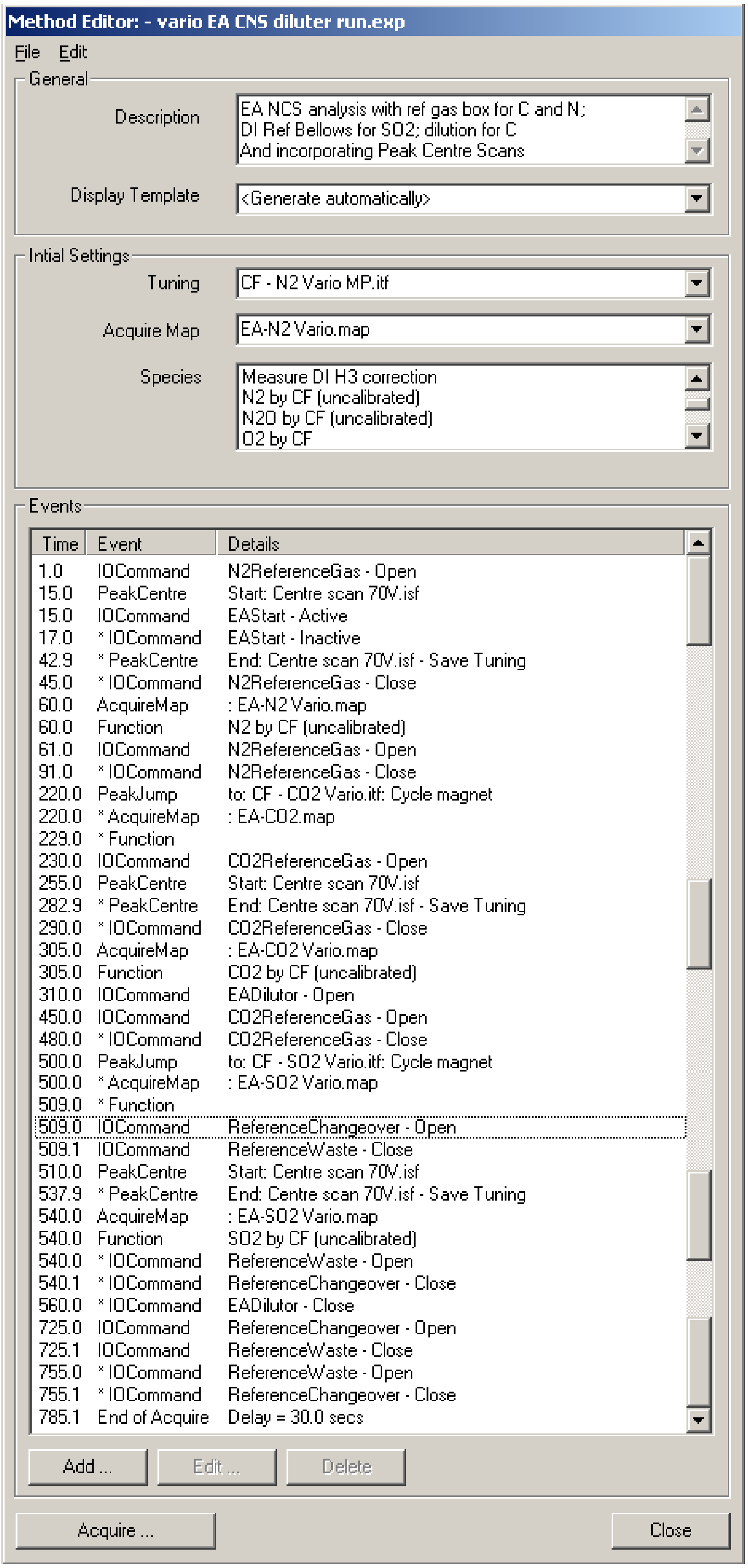
Species:
DI-CO2 47-48
H2 by CF (uncalibrated)
Measure DI H3 correction
N2 by CF (uncalibrated)

Time	Event	Details
5.0	IOCommand	EAStart - Active
7.0	* IOCommand	EAStart - Inactive
10.0	IOCommand	N2ReferenceGas - Open
40.0	* IOCommand	N2ReferenceGas - Close
270.0	PeakJump	to: CF - CO2 Vario.itf: Cycle magnet
270.0	* AcquireMap	: EA-CO2 Vario.map
271.0	IOCommand	EADilutor - Open
279.0	* Function	CO2 by CF (uncalibrated)
400.0	IOCommand	CO2ReferenceGas - Open
430.0	* IOCommand	CO2ReferenceGas - Close
439.0	* IOCommand	EADilutor - Close
440.0	PeakJump	to: CF - SO2 Vario.itf: Cycle magnet
440.0	* AcquireMap	: EA-SO2 Vario.map
449.0	* Function	SO2 by CF (uncalibrated)
600.0	IOCommand	R4ReferenceGas - Open
630.0	* IOCommand	R4ReferenceGas - Close
650.0	End of Acquire	Delay = 20.0 secs

For best results, adjust the timing of the diluter valve to coincide with the extended autozero delays on the EA run. This method is suitable for all four of the vario EAs running in NCS mode.

NCS WITH PEAK JUMP, DILUTION FOR C AND PEAK CENTRE

A more complicated analysis can be created that ensures the mass spectrometer is perfectly centred on the beams of interest as each gas species in turn passes into the mass spectrometer. In this example, the SO_2 is delivered from the reference bellows of a dual inlet. A similar pattern of DI valve operations can be used for gas being delivered from the sample bellows. Again, the diluter valve times should correspond to autozero delay times on the EA. This method is suitable for the vario EL, ISOTOPE and PYRO cubes in NCS mode.



Method Editor: - vario EA CNS diluter run.exp

General

Description: EA NCS analysis with ref gas box for C and N; DI Ref Bellows for SO2; dilution for C And incorporating Peak Centre Scans

Display Template: <Generate automatically>

Intial Settings

Tuning: CF - N2 Vario MP.itf

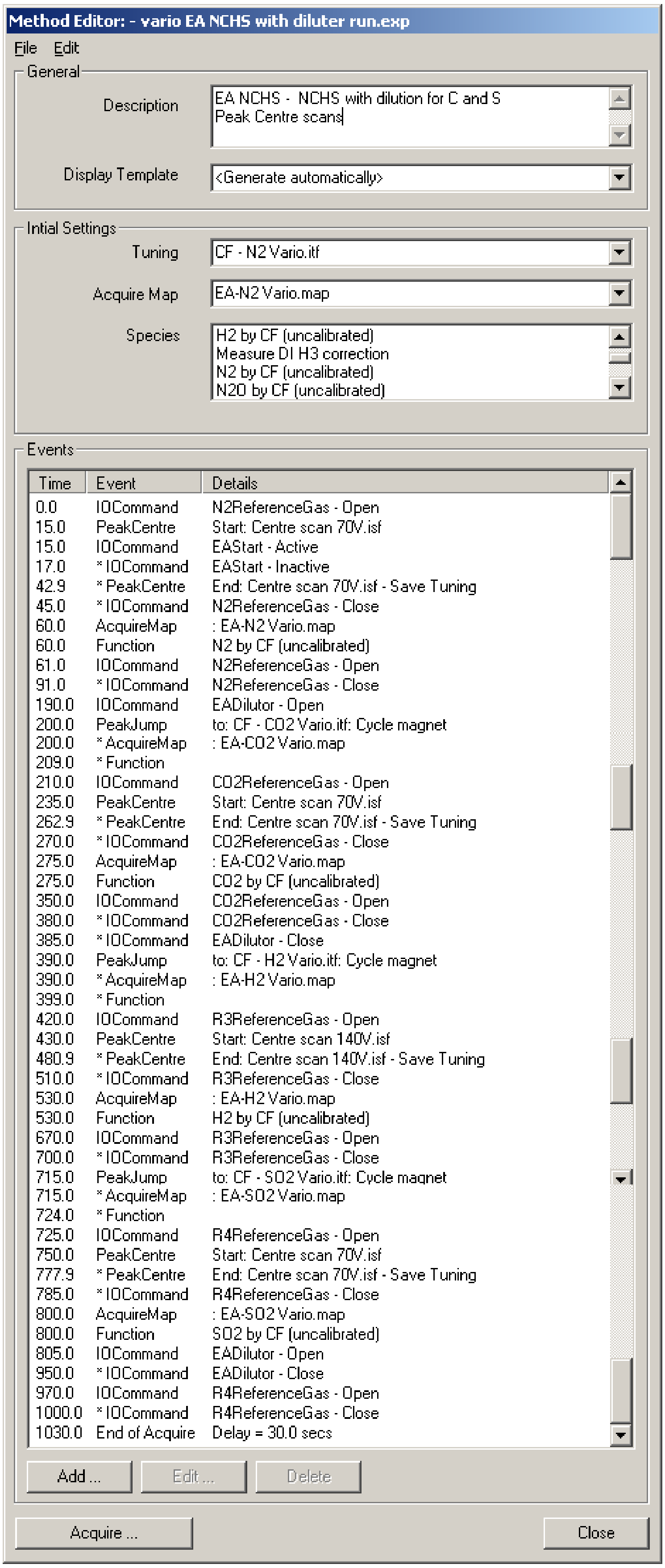
Acquire Map: EA-N2 Vario.map

Species:
Measure DI H3 correction
N2 by CF (uncalibrated)
N2O by CF (uncalibrated)
O2 by CF

Events

Time	Event	Details
1.0	IOCommand	N2ReferenceGas - Open
15.0	PeakCentre	Start: Centre scan 70V.isf
15.0	IOCommand	EAStart - Active
17.0	* IOCommand	EAStart - Inactive
42.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
45.0	* IOCommand	N2ReferenceGas - Close
60.0	AcquireMap	: EA-N2 Vario.map
60.0	Function	N2 by CF (uncalibrated)
61.0	IOCommand	N2ReferenceGas - Open
91.0	* IOCommand	N2ReferenceGas - Close
220.0	PeakJump	to: CF - CO2 Vario.itf: Cycle magnet
220.0	* AcquireMap	: EA-CO2.map
229.0	* Function	
230.0	IOCommand	CO2ReferenceGas - Open
255.0	PeakCentre	Start: Centre scan 70V.isf
282.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
290.0	* IOCommand	CO2ReferenceGas - Close
305.0	AcquireMap	: EA-CO2 Vario.map
305.0	Function	CO2 by CF (uncalibrated)
310.0	IOCommand	EADilutor - Open
450.0	IOCommand	CO2ReferenceGas - Open
480.0	* IOCommand	CO2ReferenceGas - Close
500.0	PeakJump	to: CF - SO2 Vario.itf: Cycle magnet
500.0	* AcquireMap	: EA-SO2 Vario.map
509.0	* Function	
509.0	IOCommand	ReferenceChangeover - Open
509.1	IOCommand	ReferenceWaste - Close
510.0	PeakCentre	Start: Centre scan 70V.isf
537.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
540.0	AcquireMap	: EA-SO2 Vario.map
540.0	Function	SO2 by CF (uncalibrated)
540.0	* IOCommand	ReferenceWaste - Open
540.1	* IOCommand	ReferenceChangeover - Close
560.0	* IOCommand	EADilutor - Close
725.0	IOCommand	ReferenceChangeover - Open
725.1	IOCommand	ReferenceWaste - Close
755.0	* IOCommand	ReferenceWaste - Open
755.1	* IOCommand	ReferenceChangeover - Close
785.1	End of Acquire	Delay = 30.0 secs

NCHS WITH PEAK CENTRE AND DILUTION FOR C AND S



Description: EA NCHS - NCHS with dilution for C and S
Peak Centre scans

Display Template: <Generate automatically>

Tuning: CF - N2 Vario.itf

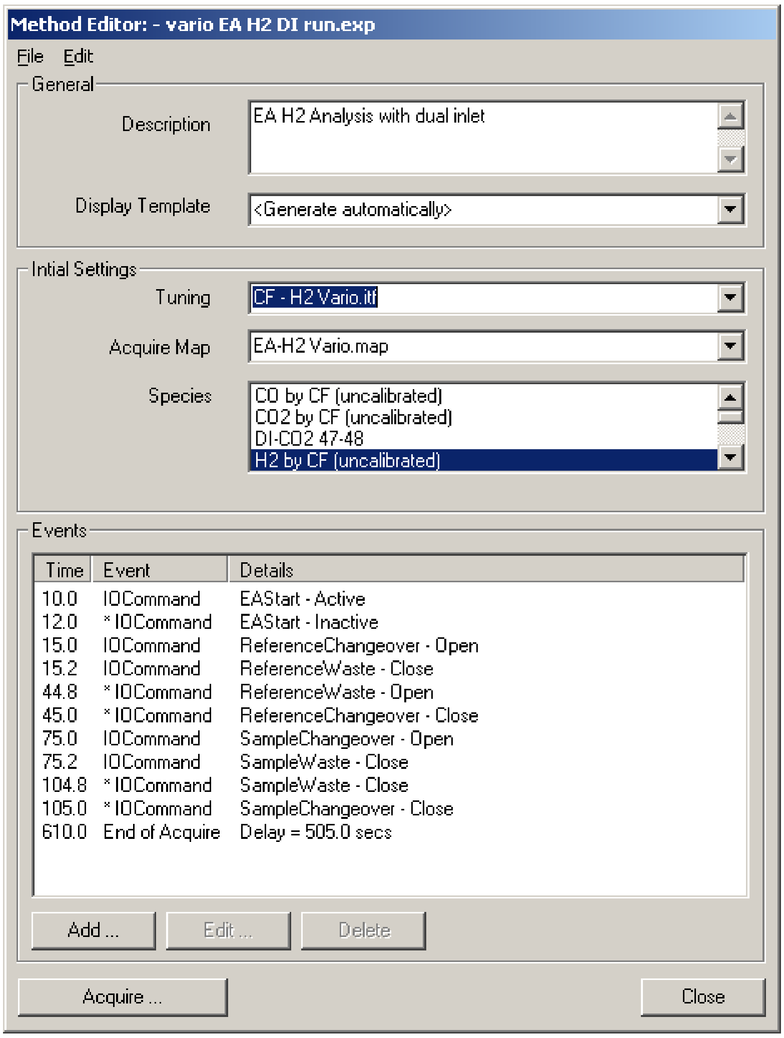
Acquire Map: EA-N2 Vario.map

Species:
H2 by CF (uncalibrated)
Measure DI H3 correction
N2 by CF (uncalibrated)
N2O by CF (uncalibrated)

Time	Event	Details
0.0	IOCommand	N2ReferenceGas - Open
15.0	PeakCentre	Start: Centre scan 70V.isf
15.0	IOCommand	EAStart - Active
17.0	* IOCommand	EAStart - Inactive
42.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
45.0	* IOCommand	N2ReferenceGas - Close
60.0	AcquireMap	: EA-N2 Vario.map
60.0	Function	N2 by CF (uncalibrated)
61.0	IOCommand	N2ReferenceGas - Open
91.0	* IOCommand	N2ReferenceGas - Close
190.0	IOCommand	EADilutor - Open
200.0	PeakJump	to: CF - CO2 Vario.itf: Cycle magnet
200.0	* AcquireMap	: EA-CO2 Vario.map
209.0	* Function	
210.0	IOCommand	CO2ReferenceGas - Open
235.0	PeakCentre	Start: Centre scan 70V.isf
262.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
270.0	* IOCommand	CO2ReferenceGas - Close
275.0	AcquireMap	: EA-CO2 Vario.map
275.0	Function	CO2 by CF (uncalibrated)
350.0	IOCommand	CO2ReferenceGas - Open
380.0	* IOCommand	CO2ReferenceGas - Close
385.0	* IOCommand	EADilutor - Close
390.0	PeakJump	to: CF - H2 Vario.itf: Cycle magnet
390.0	* AcquireMap	: EA-H2 Vario.map
399.0	* Function	
420.0	IOCommand	R3ReferenceGas - Open
430.0	PeakCentre	Start: Centre scan 140V.isf
480.9	* PeakCentre	End: Centre scan 140V.isf - Save Tuning
510.0	* IOCommand	R3ReferenceGas - Close
530.0	AcquireMap	: EA-H2 Vario.map
530.0	Function	H2 by CF (uncalibrated)
670.0	IOCommand	R3ReferenceGas - Open
700.0	* IOCommand	R3ReferenceGas - Close
715.0	PeakJump	to: CF - SO2 Vario.itf: Cycle magnet
715.0	* AcquireMap	: EA-SO2 Vario.map
724.0	* Function	
725.0	IOCommand	R4ReferenceGas - Open
750.0	PeakCentre	Start: Centre scan 70V.isf
777.9	* PeakCentre	End: Centre scan 70V.isf - Save Tuning
785.0	* IOCommand	R4ReferenceGas - Close
800.0	AcquireMap	: EA-SO2 Vario.map
800.0	Function	SO2 by CF (uncalibrated)
805.0	IOCommand	EADilutor - Open
950.0	* IOCommand	EADilutor - Close
970.0	IOCommand	R4ReferenceGas - Open
1000.0	* IOCommand	R4ReferenceGas - Close
1030.0	End of Acquire	Delay = 30.0 secs

The diluter valve timings should be set to coincide with the extended autozero delays in the EA method.. In this method, H_2 and SO_2 reference gases are introduced using a second reference gas box. This method is suitable for use with the vario EL and ISOTOPE cubes running in NCHS with H_2O to H_2 conversion mode.

HD RUN



Method Editor: - vario EA H2 DI run.exp

Description: EA H2 Analysis with dual inlet

Display Template: <Generate automatically>

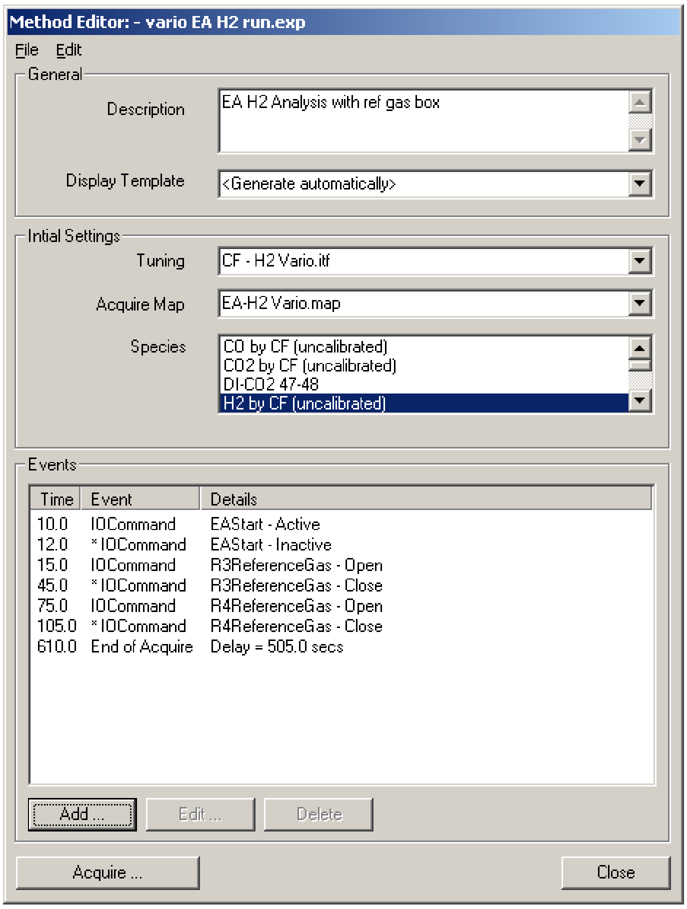
Tuning: CF - H2 Vario.itf

Acquire Map: EA-H2 Vario.map

Species:
CO by CF (uncalibrated)
CO2 by CF (uncalibrated)
DI-CO2 47-48
H2 by CF (uncalibrated)

Time	Event	Details
10.0	IOCommand	EAStart - Active
12.0	* IOCommand	EAStart - Inactive
15.0	IOCommand	ReferenceChangeover - Open
15.2	IOCommand	ReferenceWaste - Close
44.8	* IOCommand	ReferenceWaste - Open
45.0	* IOCommand	ReferenceChangeover - Close
75.0	IOCommand	SampleChangeover - Open
75.2	IOCommand	SampleWaste - Close
104.8	* IOCommand	SampleWaste - Close
105.0	* IOCommand	SampleChangeover - Close
610.0	End of Acquire	Delay = 505.0 secs

This method is a suitable starting point for HD analysis by either the chromium reduction method, or by pyrolysis of liquid or solid samples on the vario EL, ISOTOPE or PYRO cubes. The method shown above is used with a dual inlet having different pressures of H_2 in the sample and reference bellows of the DI. If a reference gas box is used, the DI valve commands are replaced with R3 and R4 reference gas valve commands as shown below.



Description: EA H2 Analysis with ref gas box

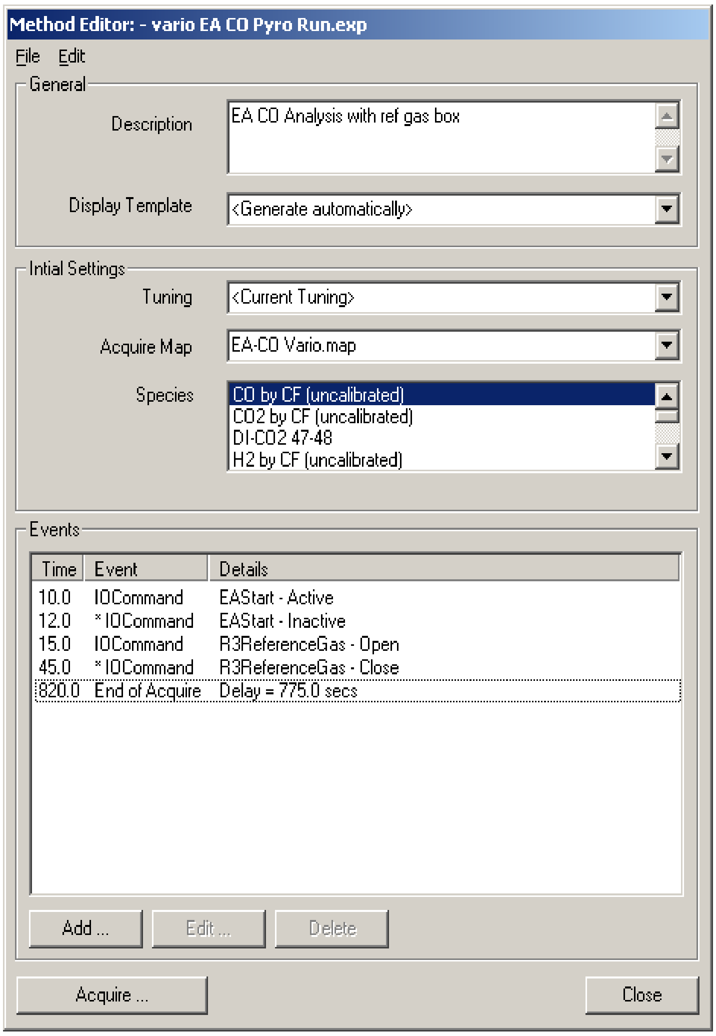
Display Template: <Generate automatically>

Tuning: CF - H2 Vario.itf

Acquire Map: EA-H2 Vario.map

Species:
- CO by CF (uncalibrated)
- CO2 by CF (uncalibrated)
- DI-CO2 47-48
- H2 by CF (uncalibrated)

Time	Event	Details
10.0	IOCommand	EAStart - Active
12.0	* IOCommand	EAStart - Inactive
15.0	IOCommand	R3ReferenceGas - Open
45.0	* IOCommand	R3ReferenceGas - Close
75.0	IOCommand	R4ReferenceGas - Open
105.0	* IOCommand	R4ReferenceGas - Close
610.0	End of Acquire	Delay = 505.0 secs



Description: EA CO Analysis with ref gas box

Display Template: <Generate automatically>

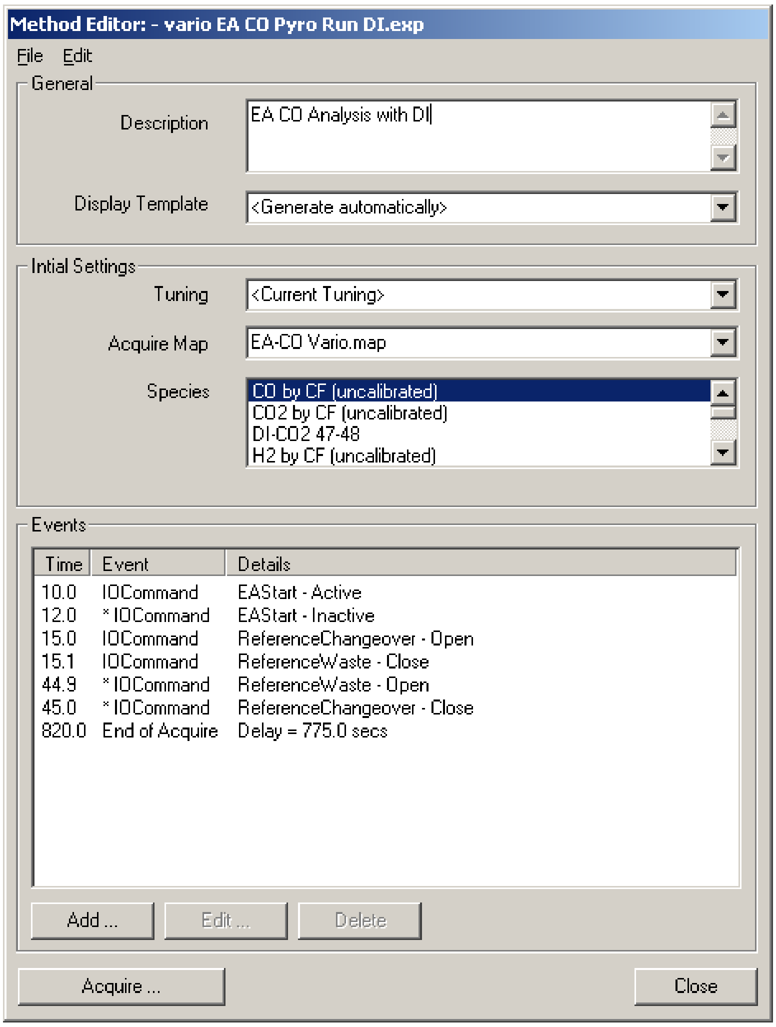
Tuning: <Current Tuning>

Acquire Map: EA-CO Vario.map

Species: CO by CF (uncalibrated)
CO2 by CF (uncalibrated)
DI-CO2 47-48
H2 by CF (uncalibrated)

Time	Event	Details
10.0	IOCommand	EAStart - Active
12.0	* IOCommand	EAStart - Inactive
15.0	IOCommand	R3ReferenceGas - Open
45.0	* IOCommand	R3ReferenceGas - Close
820.0	End of Acquire	Delay = 775.0 secs

This method is a suitable starting point for pyrolysis runs using the vario EL, ISOTOPE or PYRO cubes. The method shown uses a reference gas box to introduce CO reference gas to the mass spectrometer – the open splits in the system must be vented safely. A dual inlet can be used to deliver the reference gas instead, and the R3 valve commends would be replaced by a series of DI valve commands as below:



Method Editor: - vario EA CO Pyro Run DI.exp

General

Description: EA CO Analysis with DI

Display Template: <Generate automatically>

Intial Settings

Tuning: <Current Tuning>

Acquire Map: EA-CO Vario.map

Species:
- CO by CF (uncalibrated)
- CO2 by CF (uncalibrated)
- DI-CO2 47-48
- H2 by CF (uncalibrated)

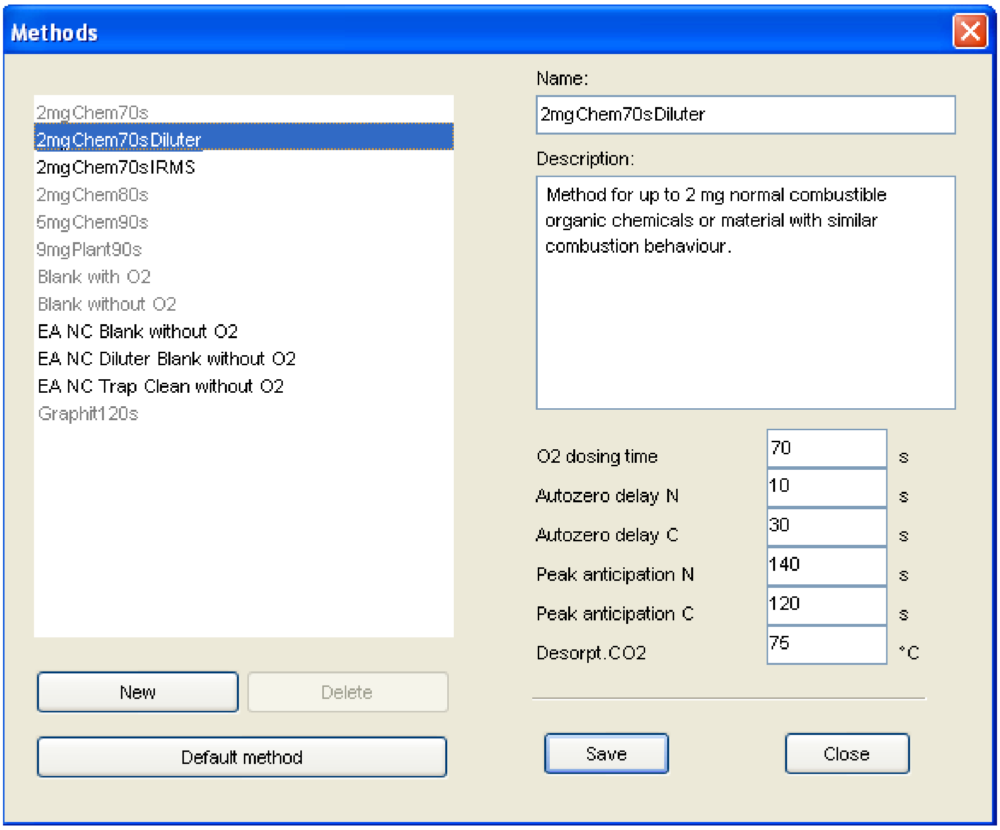
Events

Time	Event	Details
10.0	IOCommand	EAStart - Active
12.0	* IOCommand	EAStart - Inactive
15.0	IOCommand	ReferenceChangeover - Open
15.1	IOCommand	ReferenceWaste - Close
44.9	* IOCommand	ReferenceWaste - Open
45.0	* IOCommand	ReferenceChangeover - Close
820.0	End of Acquire	Delay = 775.0 secs

A3 MODE DEPENDENT EA METHOD FILES

The following pictures show suggested EA methods for use in the various modes. The methods can be used as a starting point, and then adjusted to suit particular applications.

NC METHODS



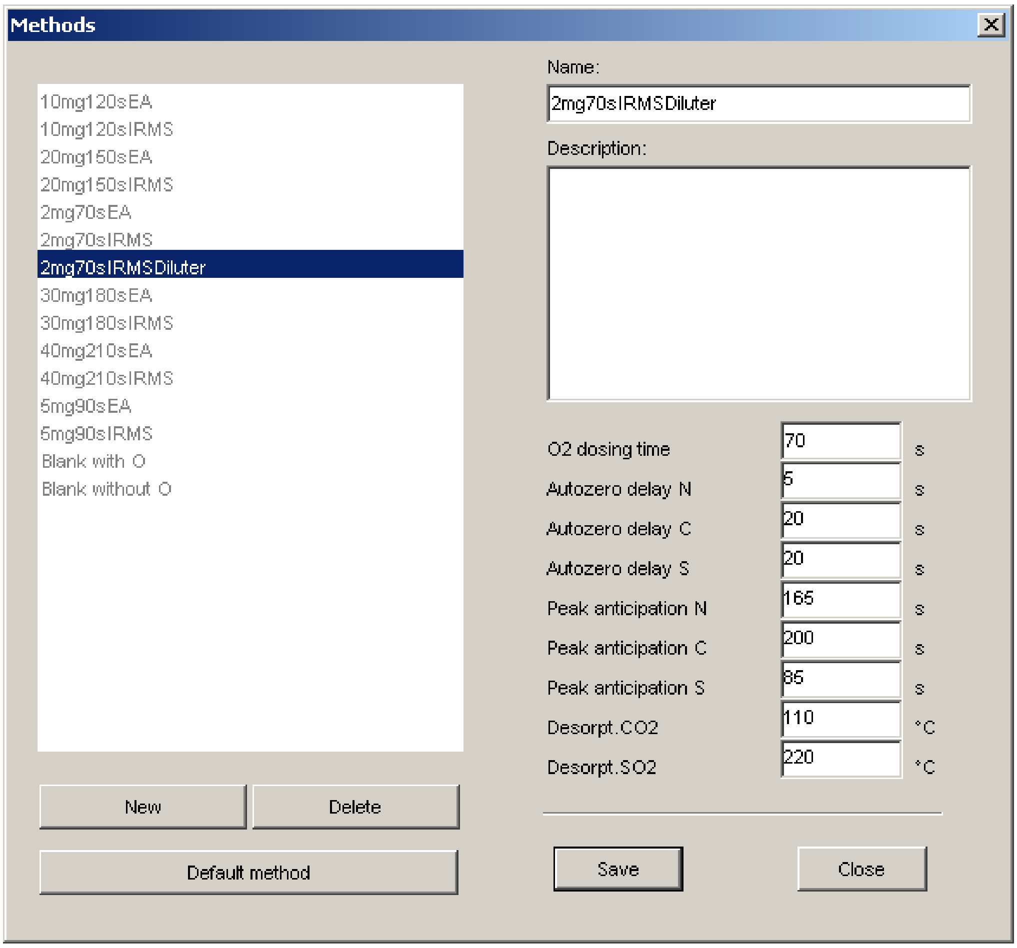
Name: 2mgChem70sDiluter

Description: Method for up to 2 mg normal combustible organic chemicals or material with similar combustion behaviour.

O2 dosing time	70	s
Autozero delay N	10	s
Autozero delay C	30	s
Peak anticipation N	140	s
Peak anticipation C	120	s
Desorpt.CO2	75	°C

Note the long autozero delay time for C, during which time the diluter can be switched. This method is also suitable without dilution. The desorption temperature for CO_2 is that used with the vario MICRO; the vario EL, ISOTOPE and PYRO cubes should have the desorption temperature set to 110°C

NCS METHODS



10mg120sEA
10mg120sIRMS
20mg150sEA
20mg150sIRMS
2mg70sEA
2mg70sIRMS
2mg70sIRMSDiluter
30mg180sEA
30mg180sIRMS
40mg210sEA
40mg210sIRMS
5mg90sEA
5mg90sIRMS
Blank with O
Blank without O

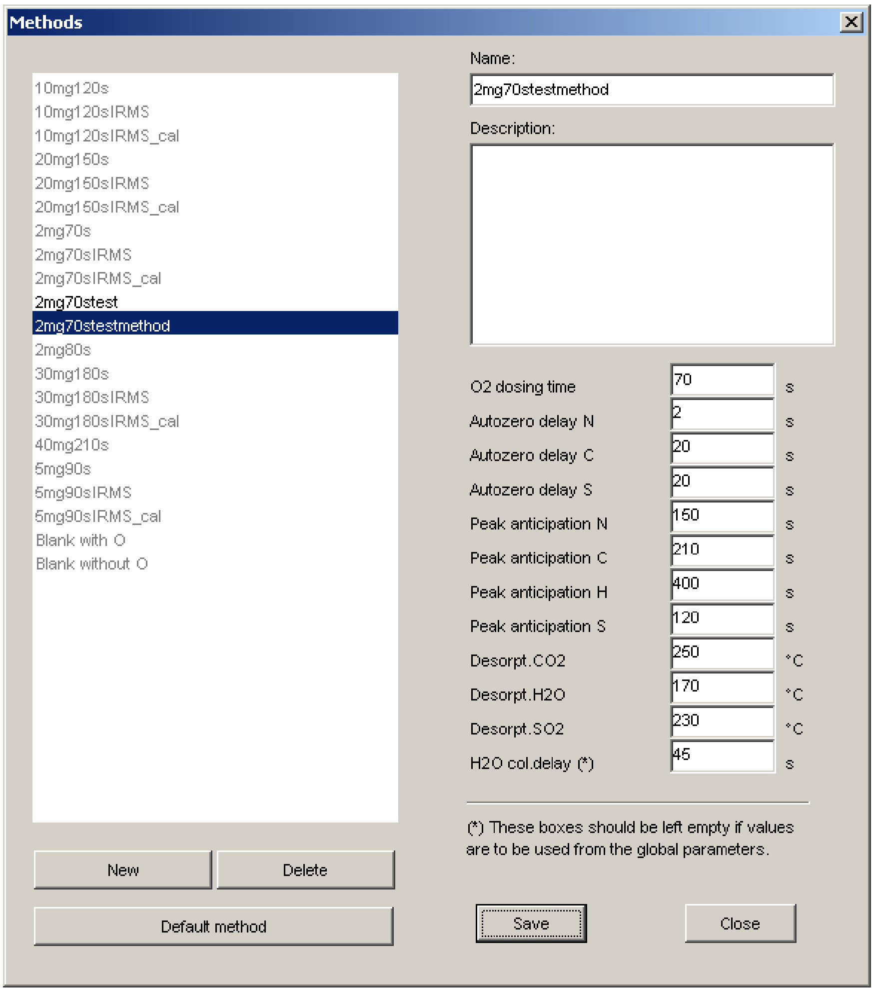
Name: 2mg70sIRMSDiluter

Description:

O2 dosing time	70	s
Autozero delay N	5	s
Autozero delay C	20	s
Autozero delay S	20	s
Peak anticipation N	165	s
Peak anticipation C	200	s
Peak anticipation S	85	s
Desorpt.CO2	110	°C
Desorpt.SO2	220	°C

This method is used for CNS analysis with either the vario EL, ISOTOPE or PYRO cubes. Note that the SO2 desorption column standby temperature is set to 110°C on the EL and ISOTOPE, while for the PYROCUBE, a temperature of 60°C is used.

NCHS METHODS



Name: 2mg70stestmethod

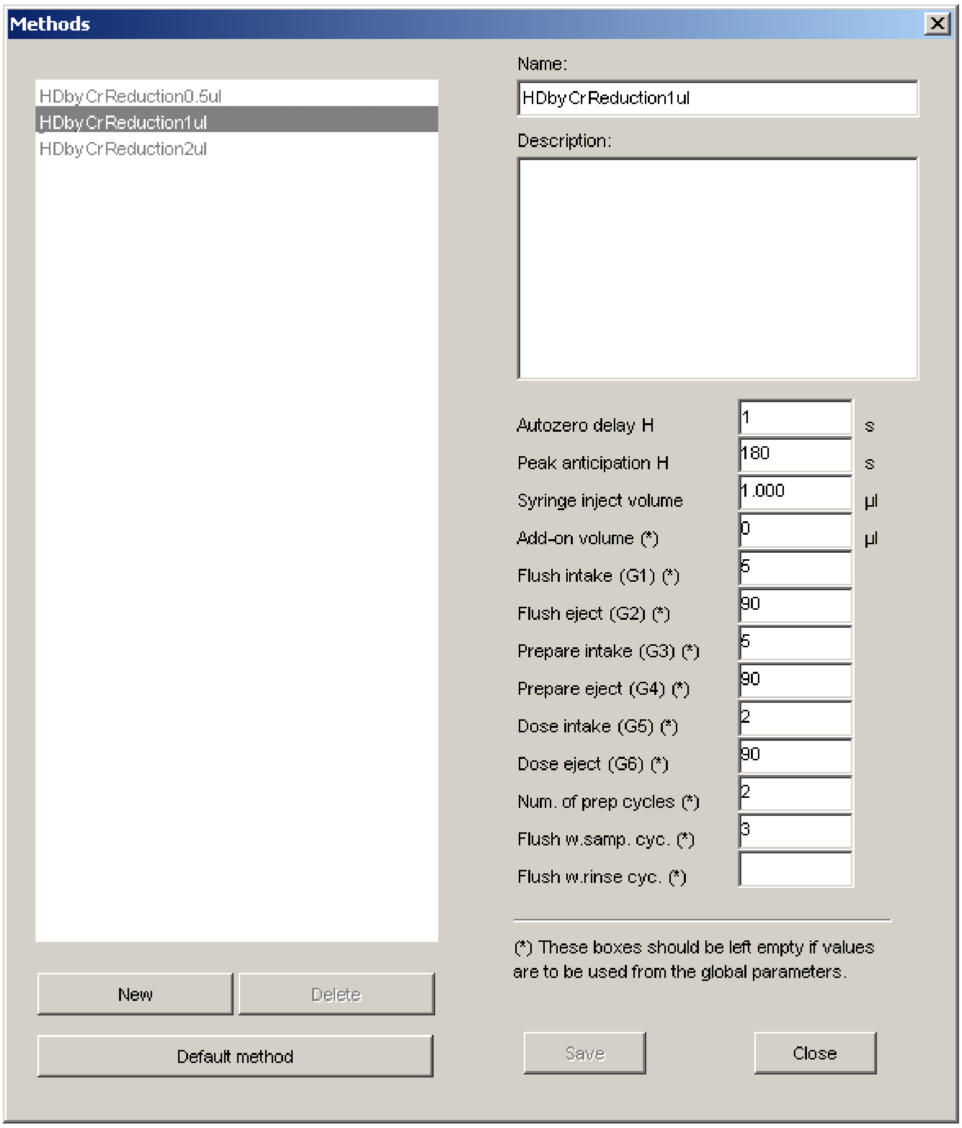
Description:

O2 dosing time	70	s
Autozero delay N	2	s
Autozero delay C	20	s
Autozero delay S	20	s
Peak anticipation N	150	s
Peak anticipation C	210	s
Peak anticipation H	400	s
Peak anticipation S	120	s
Desorpt.CO2	250	°C
Desorpt.H2O	170	°C
Desorpt.SO2	230	°C
H2O col.delay (*)	45	s

(*) These boxes should be left empty if values are to be used from the global parameters.

The NCHS method above (suitable for the vario EL and ISOTOPE cubes) includes extended autozero delay times to provide a window to switch the diluter valve. There is also a parameter “H2O col delay”. At the start of this time period, two valves in the EA are switched to pass the carrier gas flow from the main path after the H_2O desorption column, through the water reduction furnace (where fitted) to allow deuterium ratio measurement in the mass spectrometer. The desorption trap is not heated until the end of this time period, allowing the carrier gas to flush the reduction loop of any air that may have entered in the period the loop was closed off. This parameter can also be set in the main “parameters” section of the EA software.

HD BY CHROMIUM REDUCTION



HDbyCrReduction0.5ul
HDbyCrReduction1ul
HDbyCrReduction2ul

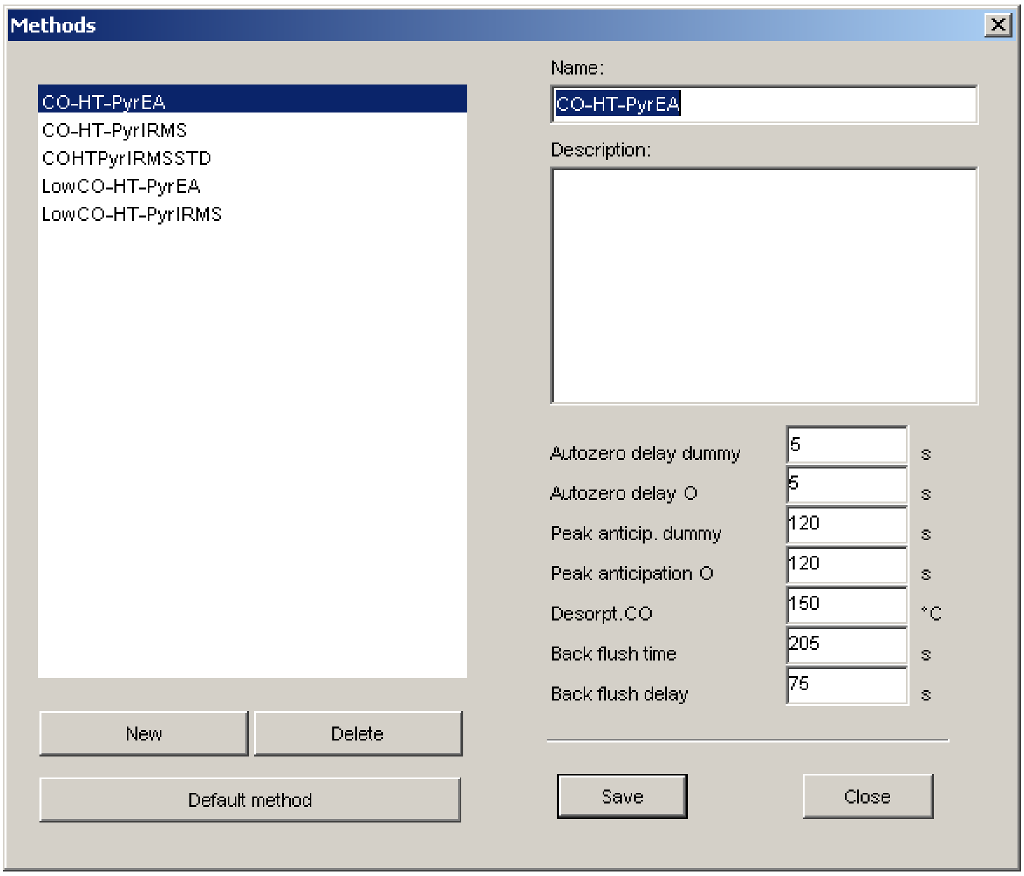
Name: HDbyCrReduction1ul

Description:

Autozero delay H	1	s
Peak anticipation H	180	s
Syringe inject volume	1.000	µl
Add-on volume (*)	0	µl
Flush intake (G1) (*)	5	
Flush eject (G2) (*)	90	
Prepare intake (G3) (*)	5	
Prepare eject (G4) (*)	90	
Dose intake (G5) (*)	2	
Dose eject (G6) (*)	90	
Num. of prep cycles (*)	2	
Flush w.samp. cyc. (*)	3	
Flush w.rinse cyc. (*)		

(*) These boxes should be left empty if values are to be used from the global parameters.

This method requires the use of the Vario Liquid Sampler (VLS), and most of the parameters are involved with speed of plunger movements during various operations with the syringe. Complete information is available in the VLS manual.



Name: CO-HT-PyrEA

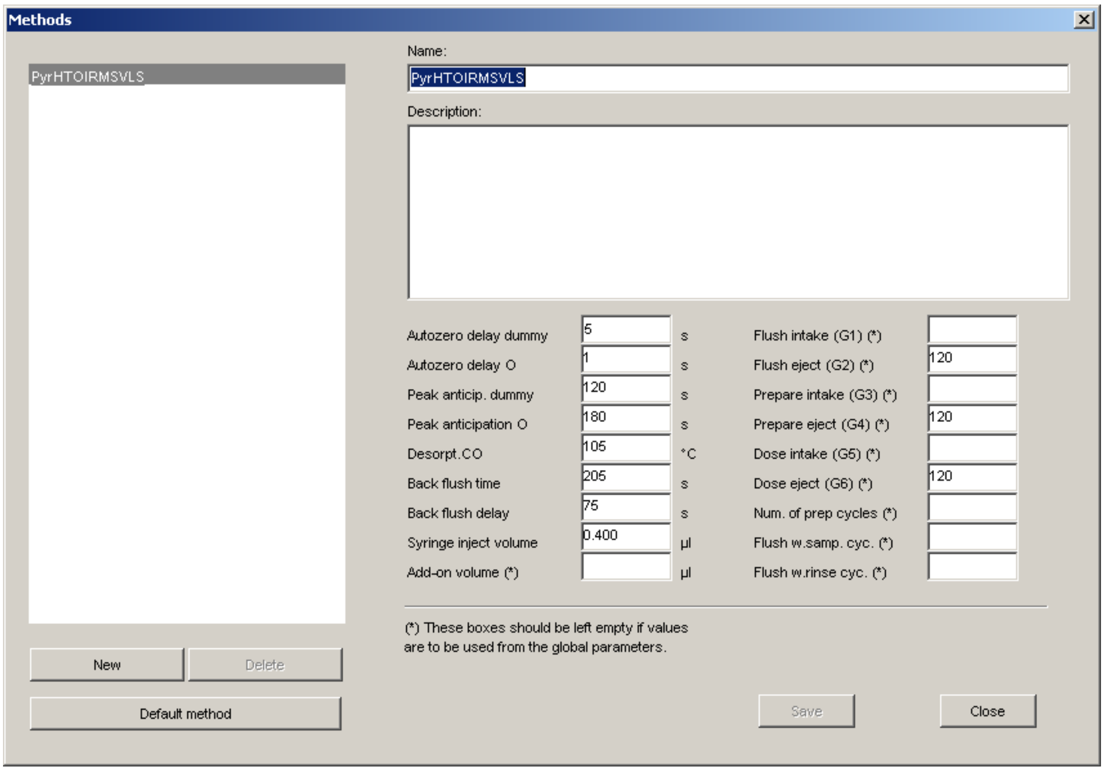
Description:

Autozero delay dummy	5	s
Autozero delay O	5	s
Peak anticip. dummy	120	s
Peak anticipation O	120	s
Desorpt.CO	150	°C
Back flush time	205	s
Back flush delay	75	s

This method is suitable for the vario EL, ISOTOPE and PYRO cubes, though there are slight differences between the parameters available. The vario EL does not have back flush capability.

The “Dummy” parameters define the part of the run where the CO produced by pyrolysis of the sample is held on the CO desorption trap whilst any atmosphere introduced in the sampling process (for example the small amount of nitrogen remaining in the capsule during sample preparation) is flushed through the EA.

The pyrolysis methods are also useable with the VLS, when a set of parameters for driving the injection are included as shown below



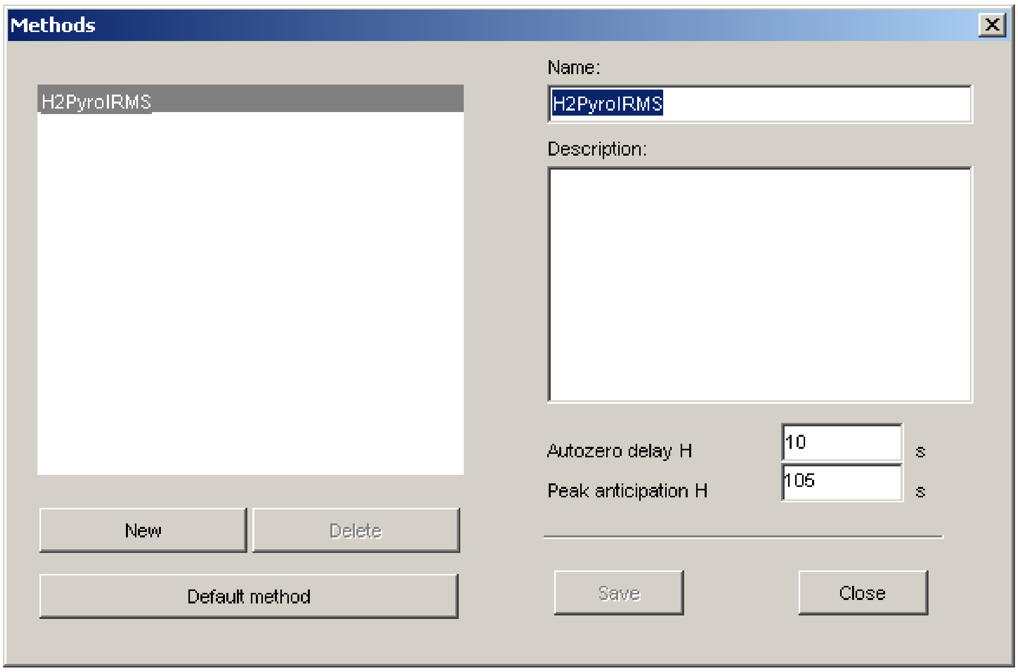
Name: PyrHTOIRMSVLS

Description:

Autozero delay dummy	5	s	Flush intake (G1) (*)	
Autozero delay O	1	s	Flush eject (G2) (*)	120
Peak anticip. dummy	120	s	Prepare intake (G3) (*)	
Peak anticipation O	180	s	Prepare eject (G4) (*)	120
Desorpt.CO	105	°C	Dose intake (G5) (*)	
Back flush time	205	s	Dose eject (G6) (*)	120
Back flush delay	75	s	Num. of prep cycles (*)	
Syringe inject volume	0.400	µl	Flush w.samp. cyc. (*)	
Add-on volume (*)		µl	Flush w.rinse cyc. (*)	

(*) These boxes should be left empty if values
are to be used from the global parameters.

H BY HIGH TEMPERATURE PYROLYSIS

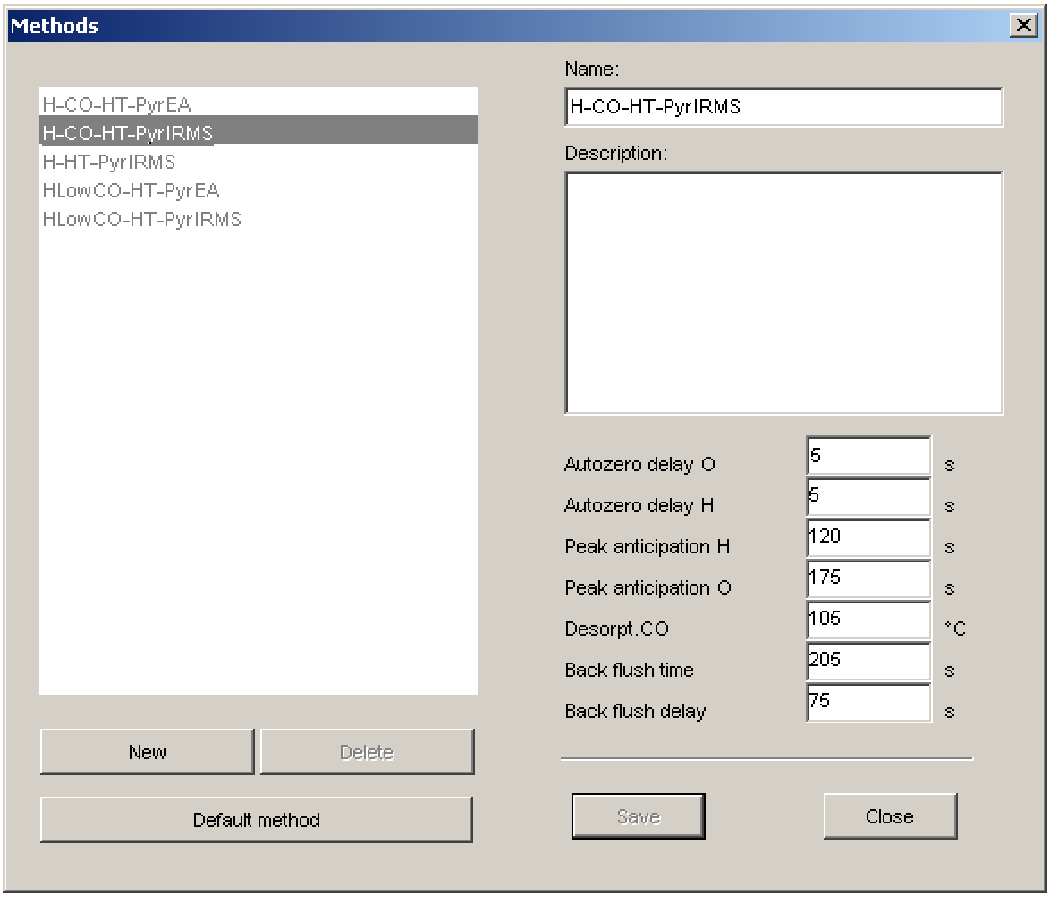


Name: H2PyroIRMS

Description:

Autozero delay H	10	s
Peak anticipation H	105	s

This EA method is particularly simple as there is no retention of any gases on desorption traps. The sample is injected, and some time later hydrogen comes out of the vent.



Name: H-CO-HT-PyrIRMS

Description:

Autozero delay O	5	s
Autozero delay H	5	s
Peak anticipation H	120	s
Peak anticipation O	175	s
Desorpt.CO	105	°C
Back flush time	205	s
Back flush delay	75	s

This method allows H and O to be determined in the same pyrolysis run