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FTPA2000-200 Series
Process FT-IR Spectrometers

User's Guide



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The only validated position to use the FTPA2000-200 Series spectrometer is at the horizontal position. Specifications are guaranteed for this position only. Although the spectrometer can be used in other orientations with good performances, specifications are not guaranteed. Consult your ABB service supplier if you need to install the spectrometer in another configuration than the one validated.



All servicing of the equipment is to be performed by Qualified Service Personnel only.

No user/operator adjustments inside the spectrometer are necessary or recommended by the manufacturer.

Customer support

ABB provides product support services throughout the world. To receive product support, either in or out of warranty, contact the ABB representative office that serves your geographical area, or the office shown below:

ABB Measurement & Analytics 3400, Rue Pierre-Ardouin Québec (Québec) G1P 0B2 CANADA	For U.S.A.: 1-800- HELP-365 email: ftirservice@us.abb.com For all other countries: email: ftirsupport@ca.abb.com Phone: 1-800-858-3847 (Canada) or 1-418-877-2944 (elsewhere)

You can also consult ABB's web site at:

http://www.abb.com/analytical

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Section 1 Safety

Class of equipment

The FTPA2000-200 Series Process FT-IR Spectrometers consist of an exposed metal chassis that is connected directly to earth via a power supply cord, and are therefore classified as Safety Class I equipments.



To avoid electrical shock, do not operate this equipment if it bears any sign of damage to any portion of its exterior surface.

Do not expose this equipment to any source of excessive moisture. Do not use it outdoors.

Do not use this equipment in an explosive atmosphere.

Certification

All ABB spectrometers and analyzers receive the following safety certifications:

cCSAus (Canadian Standards Association) for North America

CE (CE-test for the European Community)

Precautions



Failing to comply with any of the instructions, precautions or warnings contained in this manual is in direct violation of the standards of design, manufacture, and intended use of the equipment.

ABB assumes no liability for the user's failure to comply with any of these safety requirements.

The following precautions must be observed whenever the equipment is operated, serviced, or repaired.

Before operating the equipment:

- Do not use the equipment if any signs of damage are present. Contact ABB service personnel. Refer to Customer support on page ii.
- Read this manual thoroughly before using or operating this equipment. If you do not understand the content of this manuel, contact ABB service personnel. Refer to Customer support on page ii.
- Install the equipment as specified in the documentation provided (a separate site preparation guide and installation guide may be provided in some cases).
- Make sure the system is configured to use the available line voltage and that the correct fuse(s) for that voltage is (are) installed. Use only the type of fuse(s) specified as appropriate for this equipment (refer to Fuse type on page 3).
- Ensure that equipments and any devices or power cords connected to it are properly grounded.

While operating the equipment:

- Make sure the system is correctly purged for operation in hazardous locations.
- Do not operate the equipment in the presence of flammable gases, fumes or dust.
- Do not operate the equipment when its covers or panels have been removed.
- Do not interrupt the protective earthing connection (grounding). Any such action can lead to a potential shock hazard that could result in serious personnal injury.
- Do not operate the equipment if an interruption to the protective earthing is suspected. Ensure that the equipment remains inoperative.
- Do not use repaired fuses, and avoid any situations that could short-circuit the fuse.
- Unless absolutely necessary, do not attempt to a perform adjustments of any maintenance or repair procedure when the equipment is opened and connected to a power source at the same time. Any such procedure should only be carried out by a qualified service professional.

– Do not attempt any adjustment, maintenance, or repair procedure to the equipment if immediate first aid is not accessible.

Power connections

In accordance with international safety standards, each powered unit uses a three-wire power supply cord. When connected to an appropriate AC power receptacle, this cable grounds the chassis. A power supply cord, appropriate for the destination country, is supplied with each unit.



To avoid risk of injury or death, always observe the following precautions before operating the equipment:

Use only a power supply cord with a protective earthing terminal (grounding).

Connect the power supply cord only to a power outlet equipped with a protective earth contact. Never use an extension cord that is not equipped with this feature.

Fuse type

The main supply fuses used in the FTPA2000-200 Series Process FT-IR Spectrometers are rated as follows.

T2A/250V (120 V line) or T1A/250V (240 V line)

Symbols

The following symbols may be used in this manual or on the FTPA2000-200 Series Process FT-IR Spectrometer:

On the equipment

	Indicates the presence of a hot surface. Caution is required to avoid being burned.
	This symbol indicates the presence of laser radiations in the instrument. Caution is required during maintenance of the instrument

In this manual

Symbol	Meaning
	This symbol indicates a warning. Failure to comply with warnings can result in serious injury or loss of life. Ensure that all conditions necessary for safe handling and operation are met before proceeding.
	This symbol indicates information useful to the user.
	Follow instructions carefully to avoid damaging the equipment.

Moisture and dust

The FTPA2000-200 Series Process FT-IR Spectrometer is housed in a NEMA12 enclosure (intended for indoor use to provide a degree of protection against dust, falling dirt, and non-corrosive dripping liquids). It should not be exposed to excessive moisture or dust.

Laser and high voltage

Under normal operating conditions, the FTPA2000-200 Series Process FT-IR Spectrometer can be operated in complete safety. However, since the instrument contains a laser and uses high voltages (accessible only when the enclosure is open), observe the following warnings.



Opening the enclosure of the FTPA2000-200 Series Process FT-IR Spectrometer may result in exposure to laser radiation and high voltages. The enclosure is to be opened only by authorized ABB Inc. Service Personnel.

The equipement contains laser safety interlock device that turns the laser OFF when the protective housing is removed. Operation of an ABB laser with a defeated safety interlock is at operator's own risk and should be done by qualified personnel only

Laser type:	He-Ne
Laser class:	3B as per IEC-60825-1 and Class IIIa as per 21 CFR 1040.10
Output power:	4.5 mW (maximum) 500 mW (under faulty condition as per 3B class)
Wavelength:	632.8 nm



Use of controls or adjustments, or performance of procedures other than those specified herein may result in hazardous radiation exposure.



High voltage is present at the red wire connected to the laser tube inside the enclosure.

The voltage is approximately 7 kV at startup, and between 1200 V and 1400 V under normal operating conditions.

Because of the capacitors in the laser power supply, the high voltage may be present even when the power is OFF.

Location of Laser and Warning Labels

The following information describes the laser radiation and other warnings labels on the equipment along with their location.

Do not, under any circumstances, remove the warning and caution labels. Information must be available at all times for the security of the user.

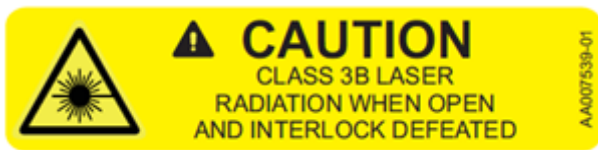


Figure 1- 1. Laser caution label

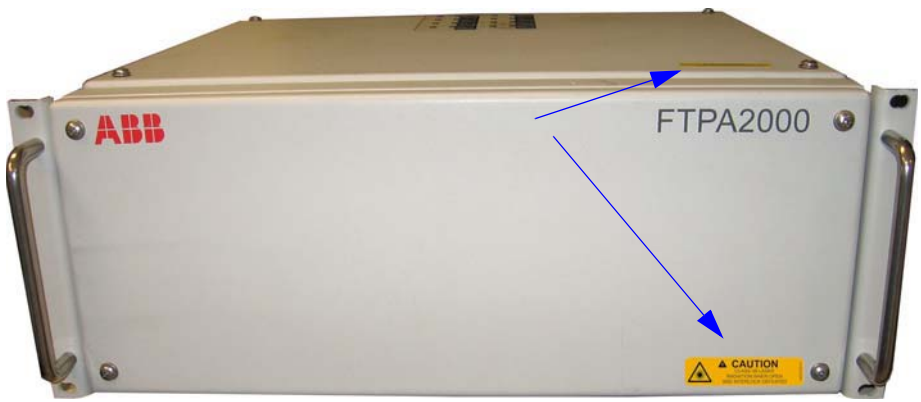


Figure 1- 2. Location of laser caution label



Figure 1- 3. Nameplate with Class 1 laser label



Figure 1- 4. Location of nameplate with Class 1 laser label



Figure 1- 5. Warning label



Figure 1- 6. Location of warning labels

Section 2 Introduction

Description

The FTPA2000-200 Series Process FT-IR Spectrometers are multi-channel Near Infrared FT-IR (Fourier Transform Infrared) spectrometers. They are designed for multi-point, real-time monitoring of continuous and batch processes. For each channel in use, a remote sampling accessory is connected to the Process FT-IR Spectrometer by optical fiber cables.

The FTPA2000-260 includes an eight-channel optical fiber launcher and a multi-detector module designed to support up to eight room-temperature detectors. The FTPA2000-263 has a 2-channel, high energy launcher and offers the same detector options as for the FTPA2000-260.

The FTPA2000-200 Series Process FT-IR Spectrometers can also be used with the TEC (Thermo-Electrically Cooled) Multi-Detector module. This module is designed to hold up to 8 thermo-electrically cooled detectors. Cooled detectors offer increased sensitivity and a very high degree of spectral response stability.

The FTPA2000-200 Series Process FT-IR Spectrometers are designed for fully automatic operation. All aspects of system operation, such as channel selection, sampling system control, sample analysis, data communication, and data archiving, are controlled by an automated analyzer software program that is specially configured for the application.

The FTPA2000-200 Series Process FT-IR Spectrometers are designed to be included in a complete system for FT-IR analysis referred as the “analyzer” (Refer to Appendix B, Glossary). This includes a personal computer, analyzer software, sampling accessories, and optical fiber cables. One sampling accessory and two optical fiber cables are required for each channel used. Each sampling accessory is usually incorporated into a sampling system that may include valves, filters, flow restriction systems, pumps, etc., some of which may be software controlled.

Calibration of the analyzer can be performed by personnel trained to use advanced chemometrics algorithms such as PLS. It can also be performed by ABB, ABB-qualified distributors, or by a qualified third party service company.

For information on FT-IR spectrometry and analyzer calibration, refer to the *FT-IR Reference Manual*, part number IMZ8557.

Parts identification

Figure 2- 1 shows the connection panel of the FTPA2000-200 Series Process FT-IR Spectrometer. The optical fiber inputs and outputs are mounted side-by-side for ease of connection. When the TEC Multi-Detector module is used, the TEC Multi-Detector Interface panel replaces the standard optical fiber input panel (refer to Figure 2- 2). No controls are provided for preamplifier gain, channel selection, and resolution as these are controlled by the analyzer software.

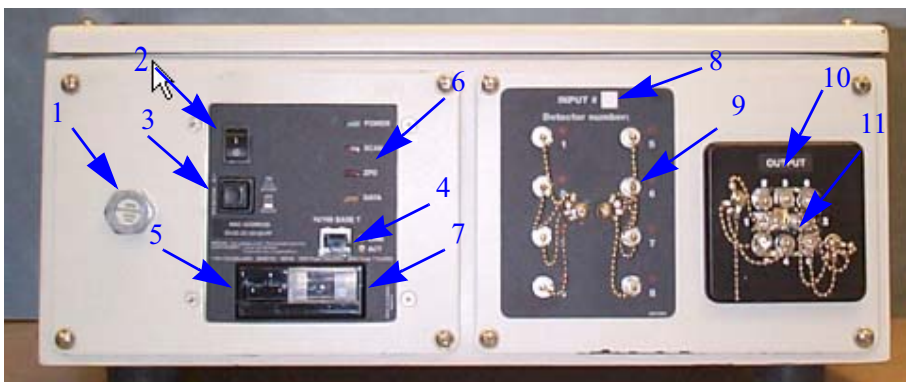


Figure 2- 1. Connection panels of the FTPA2000-260 Series Process FT-IR Spectrometer

1-Humidity indicator or purge inlet	7-Line-voltage configuration plate and fuse
2-Power switch	8-Optical input panel
3-Source breaker	9-Optical input connectors)
4-Ethernet connector	10-Optical output panel

1-Humidity indicator or purge inlet	7-Line-voltage configuration plate and fuse
5-Power input connector	11-Optical output connectors
6-Status LEDs	



Figure 2- 2. Connection panels on the TEC Multi-Detector module and the FTPA2000-200 Series Process. FT-IR Spectrometer

1-Optical input connector	5-Power input connector
2-Electrical link #1	6-Line-voltage configuration plate and fus
3-Electrical link #2	7-Electrical mate to (2)
4-Power switch	8-Electrical mate to (3)

Purge

The FTPA2000-200 Series Process FT-IR Spectrometer can be equipped with an optional purge inlet. Purging the FTPA2000-200 Series Process FT-IR Spectrometer with dry nitrogen on a continuous basis is useful when an application is sensitive to changes in air humidity, or when the sensitivity of the spectrometer is compromised by the absorption of CO_2 and H_2O found in normal concentrations in the ambient air. In cases where water vapor alone is to be eliminated, dry, oil-free instrumentation air can be used for purging.

When the FTPA2000-200 Series Process FT-IR Spectrometer is purged separately, the recommended purge flow rate is 4 to 5 L/min. The purge flow rate for a cabinet should be somewhat higher, depending on the size of the cabinet.

The purge inlet connector is a Swagelok male quick-connect type that fits into the threaded hole used by the humidity indicator. The purge connector, when installed, replaces the humidity indicator. The purge connector closes automatically when the female connector is disconnected. The female mating part is a Swagelok Part No. B-QC4-B-400 (brass), or Part No. SS-QC4-B-400 (stainless steel).

An automatic relief valve is installed in the spectrometer connection box, to prevent accidental over-pressurization of the enclosure. This relief valve opens if the internal pressure exceeds 1/3 psi. The purge option assembly number is SNL6700G.

Peripheral requirements

The following sections describe the principle requirements of the FTPA2000-200 Series Process FT-IR Spectrometer. Refer to Section 9, Technical Information.

Computer

Refer to the documentation supplied with the analyzer or the software for the minimal computer requirements.

Optical fiber cables

The FTPA2000-200 Series Process FT-IR Spectrometers are used with ultra-low OH-silica optical fiber cables. Depending on the model of your spectrometer, (260/263) either bundles of optical fiber cables or single core optical fibers can be used. Refer to Section 9, Technical Information. Using the inappropriate type of optical fiber cables will impair the spectrometer's performance.

Contact ABB for information on optical fiber quality and specifications.

When using cables longer than 25 m, the O-H stretch region at 7200 cm^{-1} (1.38 µm) may not be usable.



Optical fiber cables must be handled with great care. Contamination of the cable ends may result in signal loss or spectral artifacts. Before installing or removing optical fiber cables, refer to the Using optical fiber cables, part number IMZ8416.



Care must be taken to prevent excessive bending of fiber. This may cause the optical fiber to break.

The minimum bending radius is 600 times the core diameter of the fiber.

For example, when using fiber of 200 µm, the minimum bend radius is 0.12 meter (4.7 inches).

Fibers must be secured at cell junctions to prevent any movement that could disturb the optical performance.

Sampling system and accessories

The sampling system is the interface between the FTPA2000-200 Series Process FT-IR Spectrometer and the process. It is an important part of the system and must be designed to correctly sample the process and perform reference and zero acquisition procedures. The sampling system is manually actuated by the analyzer software via a form of I/O system.

The FTPA2000-200 Series Process FT-IR Spectrometer is often used with transmission cells for applications where it is easy to implement a process bypass

loop. Where this is not possible, an immersion probe can be used. Other types of cell, and probes can be acceptable, provided that they are fitted with a female SMA-905 fiber connector interface.

Refer to the *FT-IR Reference Manual* for more information on sampling systems.

Sampling accessories must be designed to withstand process specifications such as maximum temperature and pressure, and material compatibility.

For outdoor installations, the sampling accessories should be installed in a NEMA4 cabinet. Purging the cabinet may be necessary to avoid condensation and undesired vapors from interfering with measurements.

Section 3 Operation

Electrical panel

Figure 3- 1 shows the electrical panel of the FTPA2000-200 Series Process FT-IR Spectrometer.

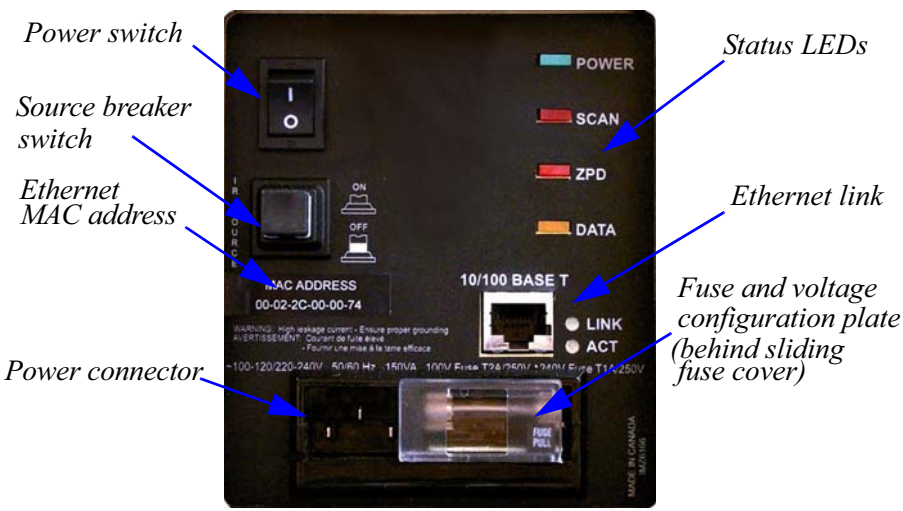


Figure 3- 1. Electrical panel

Data cables

Your computer and the spectrometer communicate via an Ethernet interface. You can either use a private connection (i.e. the spectrometer is connected directly to the computer) or use a local area Network (LAN).

Read the Safety information in Section 1, Safety before connecting the equipment.

Ethernet cables

Two Ethernet cables are supplied with the FTPA2000-200 series Process FTIR spectrometers, depending on the type of connection you need. Be sure to use the correct type of cable.

Private connection

A private (direct) connection from the spectrometer to the computer, usually requires a *crossover* cable. Refer to Figure 3- 2.



Figure 3- 2. Crossover cable

Connection trough a Network

A connection to a local area network will usually require a s*traight-pinned* cable. Refer to Figure 3- 3.



Figure 3- 3. Straight-pinned cable

The Ethernet cable must be connected to the RJ45 connector identified as “10/100 BASE T” on the electrical panel. The Ethernet MAC address is indicated on the electrical panel.

Two LEDs are associated with the Ethernet connector:

- LINK is ONwhen the instrument is properly connected. It flashes when any data is seen on the network.
- ACT flashes when a data connection has been opened by the PC FTIR application software.

Refer to Section 6, Checking communications to check the communication between the computer and spectrometer.

Start up

To start the analyzer, turn ON the FTPA2000-200 Series Process FT-IR Spectrometer, the computer, and all other powered components.

Checking the status LEDs

Immediately after turning ON the instrument, check if the sequence of status LEDs is as follows:

LED color	Identification	FTIR Initialization						Normal Operation
GREEN	POWER	ON	ON	ON	ON	ON	ON	ON
RED	SCAN	ON	ON	FLASH	FLASH	ON	OFF	OFF
RED	ZPD	ON	OFF	ON	FLASH	OFF	ON	OFF
YELLOW	DATA	ON	ON	ON	FLASH	ON	ON	BLINK

3- 1. Colored LED status

LED	Status	description	Normal Operation
LINK	ON	Ethernet cable connected to analyzer.	ON or Blinking
	OFF	Ethernet cable not connected to analyzer.	
	Blinking	Data transfer or activity present on connected network.	

3- 2. LED Status

LED	Status	description	Normal Operation
ACTivity	OFF	All connections closed.	Blinking
	Blinking	The PC FTIR application software is connected to the instrument. Will blink faster with each new opened connection.	

3- 2. LED Status

The above sequencing confirms the correct operation of the spectrometer module. During operation, the POWER LED should be ON and the DATA LED should be flashing. If you encounter problems, refer to Section 10, Troubleshooting.

Turning on the source

Set the source breaker-switch to ON (refer to Figure 3- 1).

After switching a source ON, allow a temperature stabilization time from 10 minutes to 4 hours, depending on your stability requirements.

Warm up

When turned on at room temperature, the spectrometer will need up to 4 hours to allow its infrared source and internal components to stabilize; for critical measurements, more time may be required. The instrument can be used immediately after being turned on, but the resulting spectra may not be within published specifications.

The spectrometer must be left ON at all times. Each time it is turned OFF then back ON, it can take several hours to become stable again.

Section 4 Detectors

Detectors

This section describes the detectors typically used with the FTPA2000-200 Series Process FT-IR Spectrometers.

Room temperature detectors

The FTPA2000-200 Series Process FT-IR Spectrometer includes an eight-channel optical fiber launcher and an internal multi-detector module designed to support up to eight room-temperature detectors. Different types of detectors can be used on different channels of the same spectrometer. Typical spectral ranges are shown below:

Detector type	Cutoff	Range
InGaAs 2.1RTA	2.1 µm	11 000 cm^{-1} to 4 800 cm^{-1}
InGaAs 2.6RTA	2.6 µm	9 000 cm^{-1} to 3 800 cm^{-1}

Table 4 - 1 Room temperature detectors

It is important to avoid using spectral features near these detectors' cut-off region because this region is highly affected by temperature variations.

Thermo-electrically cooled detectors

TEC (thermo-electrically cooled) detectors achieve a very high degree of spectral response stability because their temperature is controlled to a fraction of a degree. The low temperature reduces the noise level and thus provides increased sensitivity. These detectors are mounted in the TEC Multi-Detector module. Typical spectral ranges are shown below:

Detector type	Cutoff	Range
InGaAs21TE	2.1 µm	11 000 cm^{-1} to 4800 cm^{-1}
InGaAs26TE	2.6 µm	9 000 cm^{-1} to 3 800 cm^{-1}
InGaAs21RTB	2.1 µm	11 000 cm^{-1} to 4800 cm^{-1}
InGaAs26RTB	3.6 µm	9 000 cm^{-1} to 3 800 cm^{-1}
InNas30TE	3.0 µm	12 000 cm^{-1} to 3300 cm^{-1}

Table 4- 2. TE cooled detectors

TEC Multi-Detector module

The TEC Multi-Detector module is a 19-in. rack mount enclosure designed to hold up to 8 thermo-electrically cooled detectors. The module contains the electronic circuitry for temperature control and detector signal conditioning. Room-temperature detectors can also be mounted on this module for channels that do not require cooled detectors

Installation

The TEC Multi-Detector module produces heat and must therefore be mounted above the FTPA2000-200 Series Process FT-IR Spectrometer, as shown Figure 4- 1. Required when at least one TE-Cooled detector and for up to 8 TE-Cooled detectors are ordered.

Two cables (refer to Figure 4- 1), the control and signal cables, connect the FTPA2000-200 Series Process FT-IR Spectrometer and the TEC Multi-Detector module.

Before connecting or disconnecting the TE box from the spectrometer, make sure to turn the power OFF on the spectrometer and the TE box, **and** to disconnect both power cords. Failure to disconnecting both power cords may result in electrical damage to the detectors which is NOT covered by the warranty of the instrument.

.

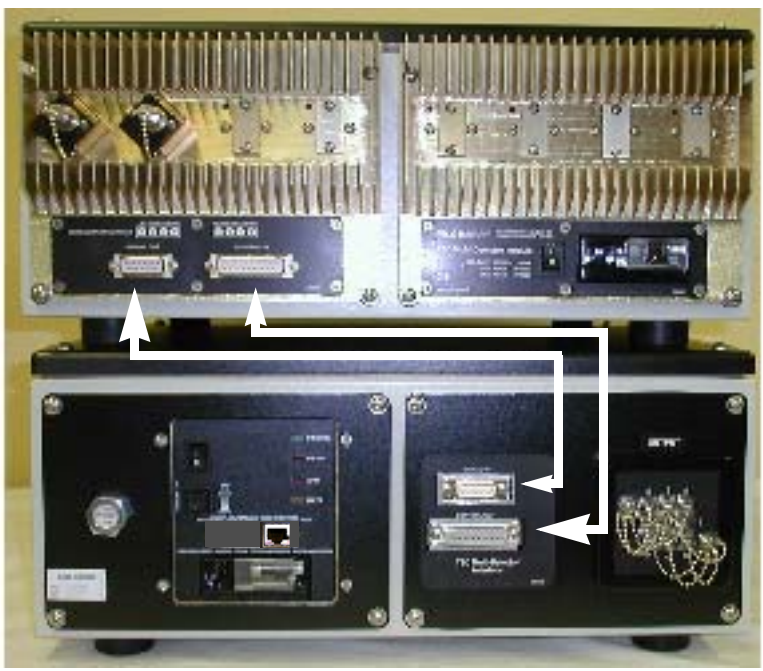


Figure 4- 1. Connections between TEC Multi-Detector module and FTPA2000 Series Process FT-IR Spectrometer

Be sure to connect and tighten the ground lug at each end of the signal cable (refer to Figure 4- 2).



Figure 4- 2. Ground lugs on signal cable

Section 5 Checking communications

Purpose

Your computer and the spectrometer communicate via an Ethernet interface. (cable). You can either use a private connection (i.e. the spectrometer is connected directly to the computer) or communicate through a network. This section shows how to check if the spectrometer communicates properly with the computer. Refer to Data cables on page 19 of this manual to choose the appropriate type of cable for your needs.



The computer delivered with your spectrometer comes with two Ethernet cables. One, labeled "*Cross-Over"* cable, is configured for a direct connection to the spectrometer. The other Ethernet cable labelled *Straight-pinned* cable connects to a network.

Checking the connection to the computer or to the network

Connect the spectrometer to the computer or the network (DHCP server). If you are using a private connection, the computer must be turned ON. When properly connected, the spectrometer Data LED will turn Green, when there is data activity it will be orange and flashing.



If the spectrometer green LINK indicator does not turn ON when it is connected to the other end, try with the other cable provided in the instrument<s package.

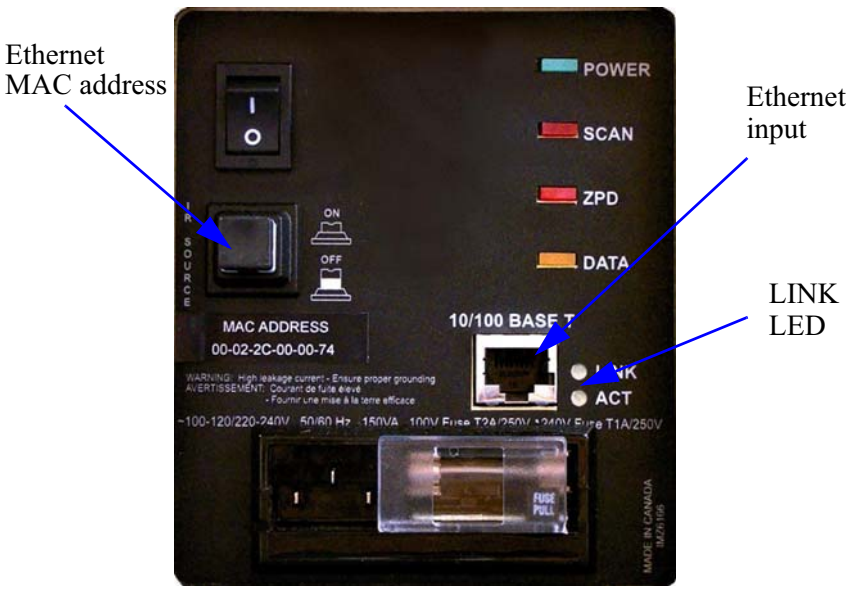


Figure 5- 3. Electrical panel

Please note the spectrometer MAC address is located on the Class 1 Laser label. (refer to) This is how the spectrometer will be identified by your computer or by the network connection.The MAC address might be required to check the connection if you have more than one instrument visible by the same PC.

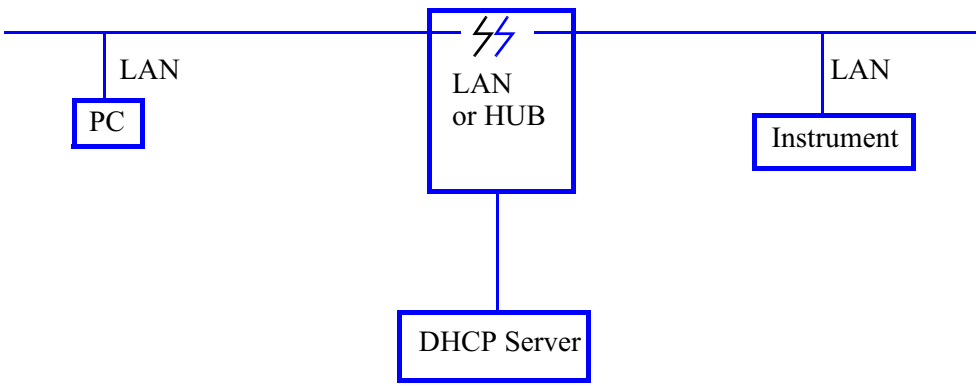
Setting up the Ethernet Connection

A successful connection requires both the PC and the instrument to be properly setup. There are, usually two setups possible:

- The instrument is not directly connected to the PC's Ethernet interface
- The instrument is directly connected to the PC's Ethernet interface

Not a direct connection

The instrument is not connected directly to the PC's Ethernet interface. Instead, both the instrument and the PC are connected to a LAN via an Ethernet switch, or hub.



In this setup, both the PC and the instrument will obtain their LAN configuration from the control DHCP server.

When first turned **ON**, your spectrometer will attempt to obtain automatically its LAN configuration from the DHCP server.

To ensure the DHCP server is properly detected, perform a power **OFF/ON** cycle after connecting properly the cable link in place (i.e. LINK LED must be **ON**).

To insure your PC Ethernet interface uses the DHCP server, perform the following procedure:

STEP 1 Open **Start >Settings> Network.**

STEP 2 In the **Network and Dial-up Connection** window, right-click **Local Area Connection** and select **Properties**. Refer to Figure 5- 4.

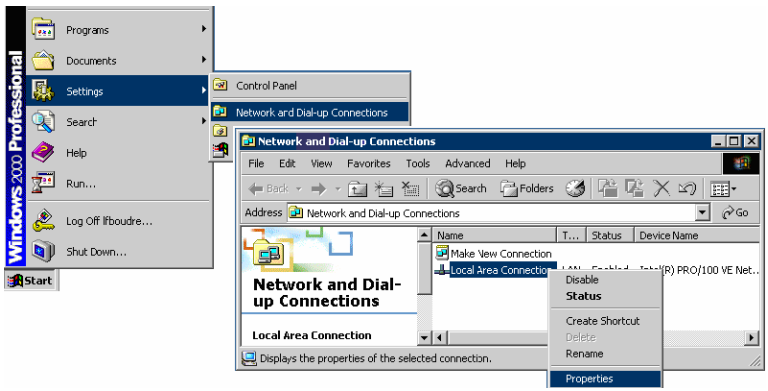


Figure 5- 4. Network and Dial-up Connection window

STEP 3 Select I**nternet Protocol (TCP/IP)** and click **Properties.**

STEP 4 In the Internet Protocol (TCP/IP) Properties window, the radio button **Obtain an IP address automatically** must be selected**.** Refer to Figure 5- 5.

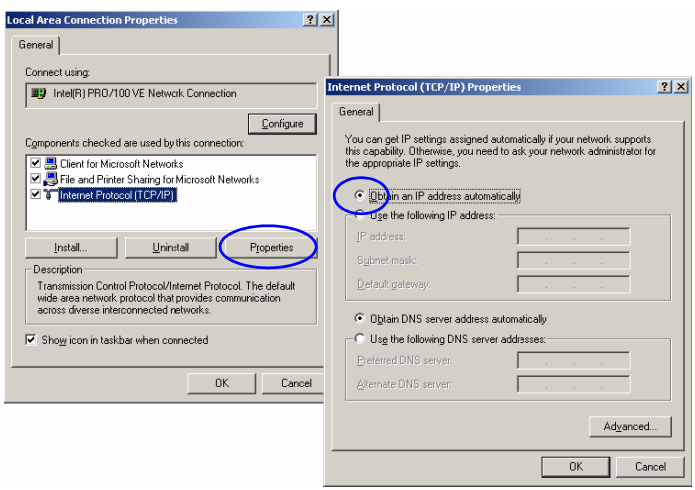
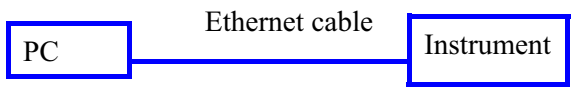


Figure 5- 5. Internet Protocol (TCP/IP) Properties dialog box

STEP 5 Then click **OK.**

Direct connection

The instrument is directly connected to the PC's Ethernet interface.



In this case, both the PC and the instrument will use a pre-configured LAN configuration parameters.

If, when first turned ON, the spectrometer can not detect a DHCP server, it will automatically use the following IP address:

10.127.127.127

The PC Ethernet interface should be configured to use a compatible set of LAN parameters, for example:

IP address: 10.127.127.127.1

Subnet Mask: 255.255.255.0

To ensure your PC Ethernet interface is properly set, perform the following procedure:

STEP 1 Open **Start> Settings> Network and Dial-up Connections.**

STEP 2 In the **Network Dial-up connections** window, right click **Local Area Connection** and select **Properties**. Refer to Figure 5- 4.

STEP 3 In the **Properties** dialog box, select **Internet Protocol (TCP/IP)**.

STEP 4 In the **Internet (TCP/IP) Properties** dialog box, select **Use the following IP address** and type the following information.

Type 10.127.127.1 in the IP address dialog box and 255.255.255.0 in the Subnet mask dialog box. Refer to figure Figure 5- 5.

Changing the computer or instrument IP address should be done with caution if one is not knowledgeable of Ethernet settings.

If you need to change the default IP address of your instrument (10.127.127.127) please refer to Advanced settings.

Checking the connection

The connection can be checked with the ABB FTIR Configuration Applet. To run the applet, go to the Windows Control Panel.

STEP 1 Click **Start>Settings > Control Panel** and double-click on the **ABB Bomem FTIR** icon. Refer to Figure 5- 6. .

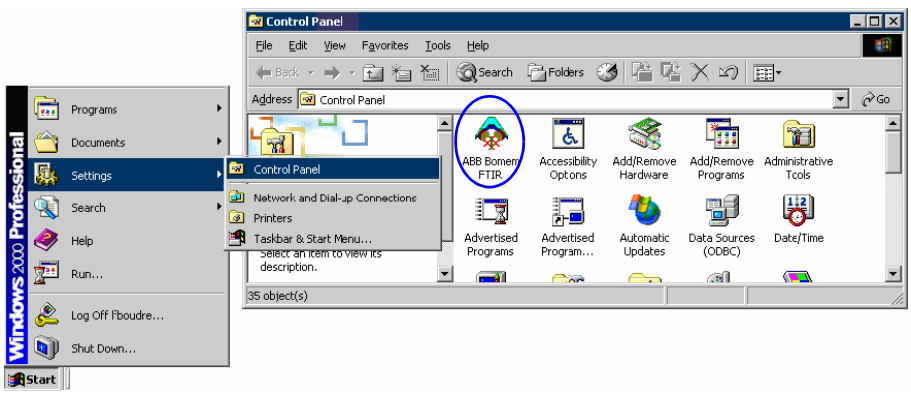


Figure 5- 6. ABB Bomem FTIR utility

STEP 2 The Applet will search the network for the presence of spectrometers. A message indicating that the Applet is detecting the presence of spectrometers

will appear. Then a list of all the spectrometers present on the Network will appear in the **ABB Bomem FTIR** window. Refer to Figure 5- 7.

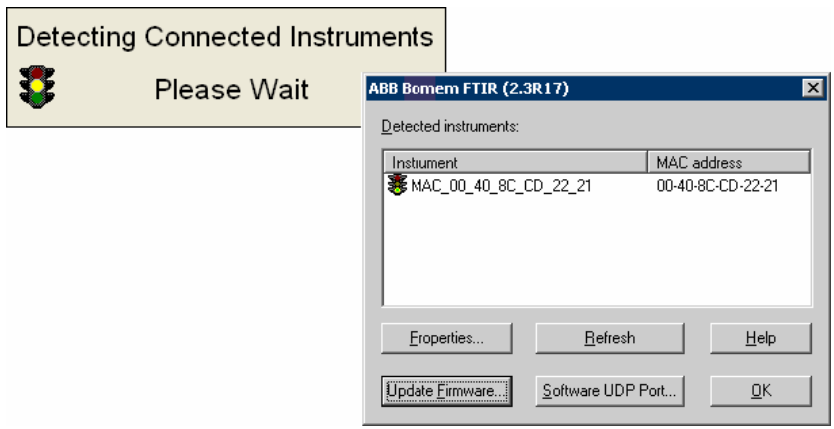


Figure 5- 7. Detecting connected instruments

If the MAC address of your spectrometer appears in the list, then the spectrometer's is connected.

If your spectrometer is not detected, refer to Section 10, Troubleshooting.

Section 6 User menu

Main Menu

To access the web page of the Main Menu of the analyzer follow this procedure.

STEP 1 Click **Start>Settings > Control Panel** and double-click on the **ABB Bomem FTIR** icon. Refer to Figure 6- 1.

.

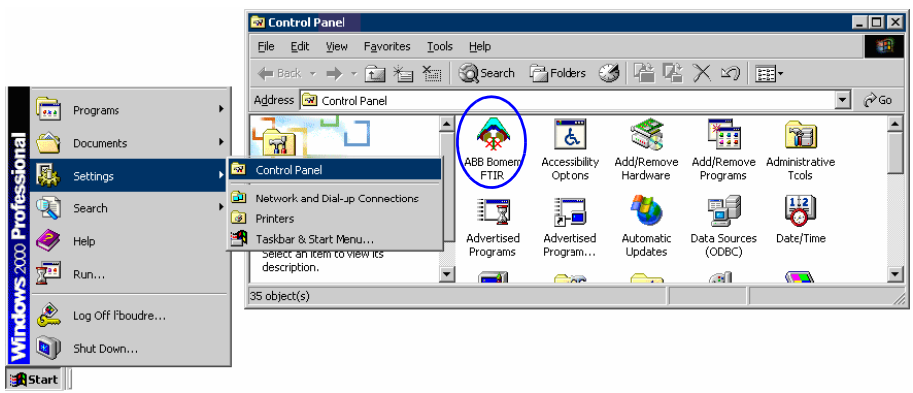


Figure 6- 1. ABB Bomem FTIR utility

STEP 2 The Applet will search the Network for the presence of spectrometers. A message indicating that the applet is detecting the presence of spectrometers

will appear. Then a list of all the spectrometers present on the Network will appear in the **ABB Bomem FTIR** window. Refer to Figure 6- 2.

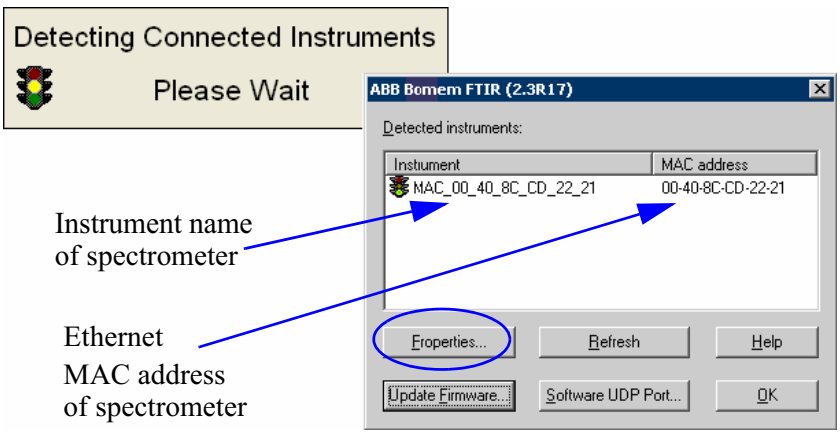


Figure 6- 2. Detecting connected instruments

STEP 3 Select the Ethernet MAC address of your spectrometer and click **Properties.** Refer to Figure 6- 2.

STEP 4 The web page of the main menu of your analyzer will be displayed. Refer to Figure 6- 3.

If your spectrometer is not detected, please refer to Section 8, Troubleshooting.

On the Main menu important information on the analyzer and software are provided.The Main menu also gives access to the User menu.

STEP 5 Click **User Menu** to access the User Menu.

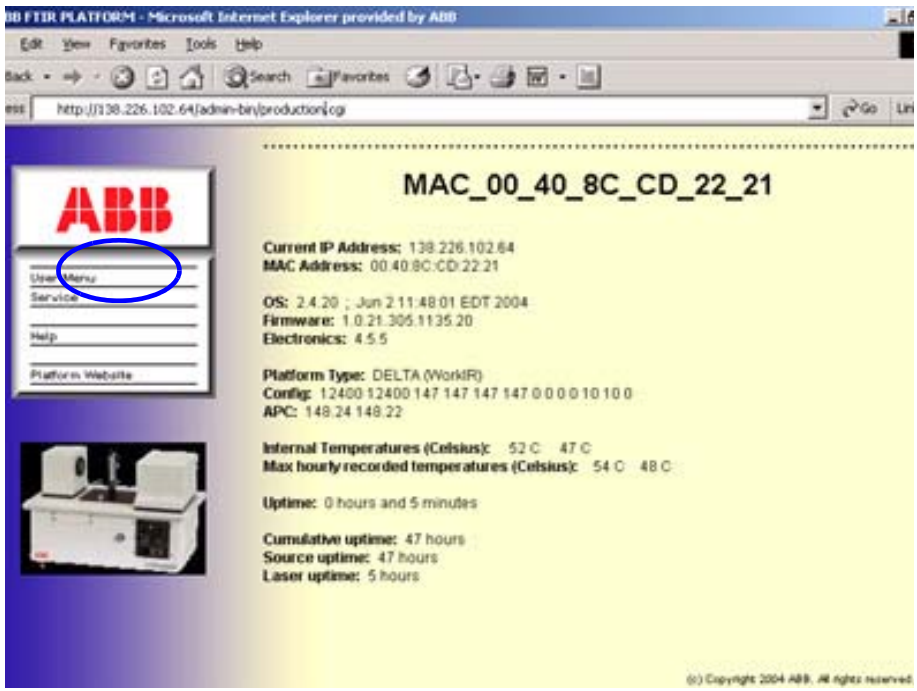


Figure 6- 3. Main menu of the analyzer Web page.

User Menu

The User menu offers options to the user that do not possess password protection by default. The default name for the spectrometer is the MAC address. If you need to change the name of the spectrometer, type the new name in the dialog box of the

User menu. If you need to change the IP parameter of the spectrometer such as the IP address, address mask, etc., click the Advanced button. Refer to Figure 6- 4.

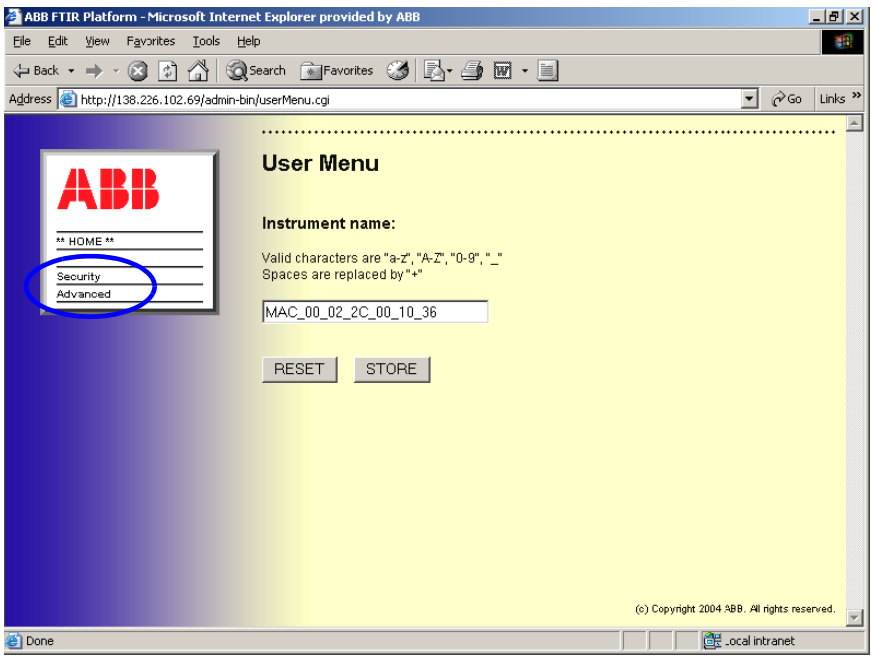


Figure 6- 4. User menu

Security menu

The security menu offers the possibility to the user to apply a password protection to limit the access to sensitive parameters such as IP address and instrument name that might render the device inaccessible if changed without control. This password will be applied for the user menu only.

STEP 1 In the **User menu** window click **Security,** refer to Figure 6- 4.

STEP 2 In the **Security** window, type a password in the new password dialog box, and retype the same password in the second dialog box for confirmation. Refer to Figure 6- 4.

If the password is lost, FTIR parameters will need to be factory resetted to recover access to the user menu. Call ABB service for more information.

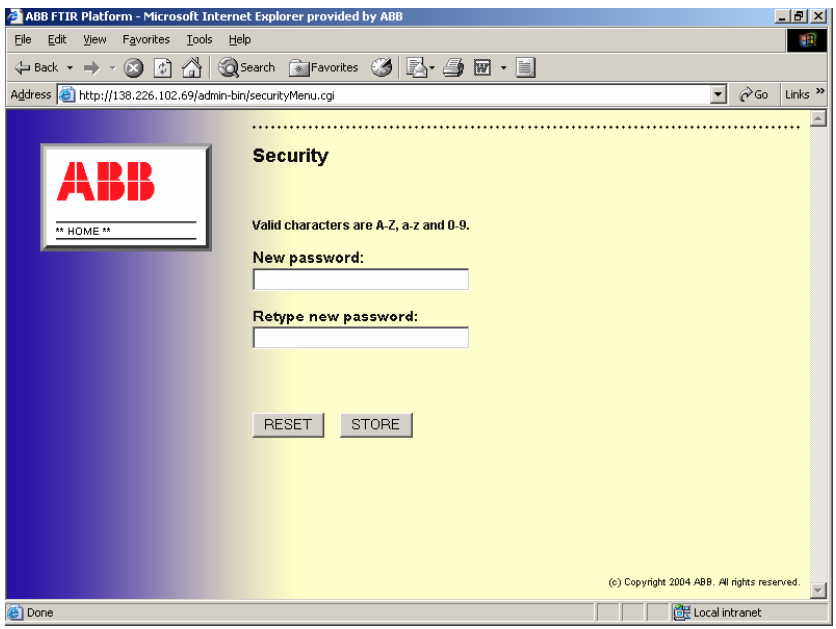


Figure 6- 5. Security menu

Advanced menu

The **Advanced Settings** window (refer to Figure 6- 6) provides access to define the IP parameters.

To access the **Advanced Settings** window, click the **Advanced** button of the **User Menu** (refer to Figure 6- 4.)

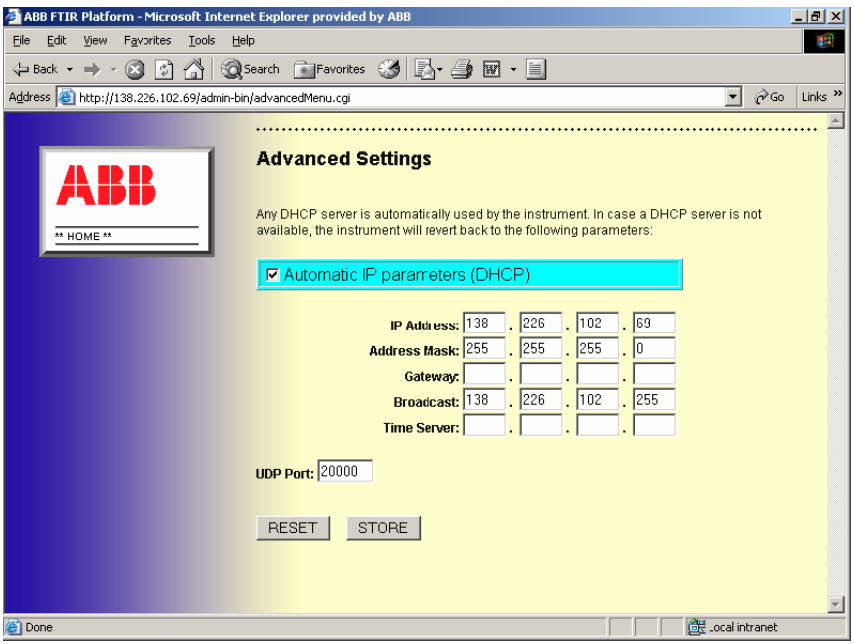


Figure 6- 6. Advanced settings

Care must be taken when changing any of the parameters of the **Advanced Settings** menu (Figure 6- 6) as it may render the device to be inaccessible.

the default ABB UDP Port value is 20000.

Section 7 Firmware update

Introduction

the instrument's firmware is a computer program stored inside the instrument's electronics and which controls all aspects of the instrument's behavior.

Firmware updates van be made available by ABB in order to improve the instrument's performances, or to correct discrepancies in the instrument's behavior.

Contact our service department for any questions regarding the availability of firmware updates.

The firmware is easily updates via the Ethernet link by using the ABB Bomem FTIR control panel.

Firmware version

Before performing the update of your firmware, check the version of your firmware to make sure you have an earlier version that requires updating.

Version information is available on the Web page of the analyzer.

If you know the IP address of your analyzer:

STEP 1 Open Internet Explorer.

STEP 2 Type the IP address of your analyzer as the Web address.

STEP 3 In the Main menu of your Analyzer's Web page check the version of your firmware. Refer to Figure 7- 1

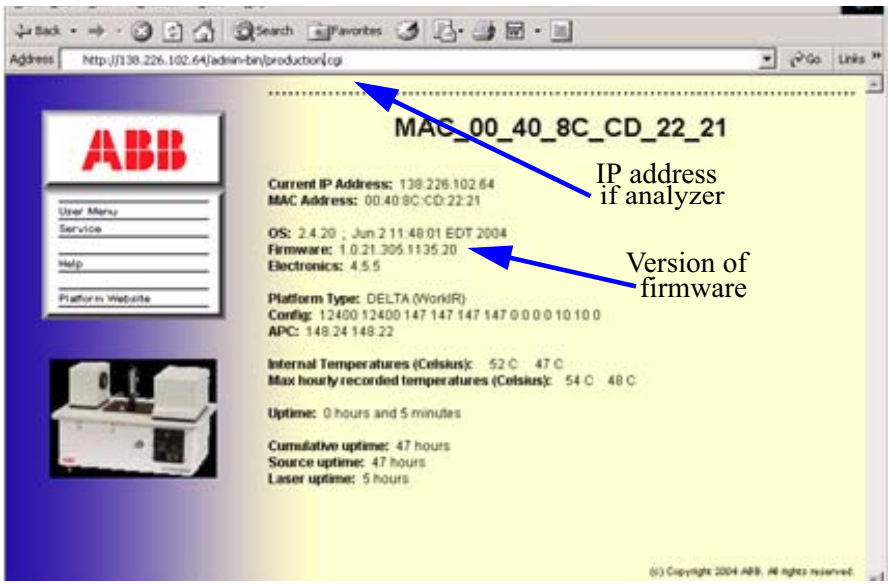


Figure 7- 1. Main menu of the Analyzer's web page.

If you do not know the IP address of you analyzer

STEP 1 Click **Start>Settings > Control Panel** and double-click on the **ABB Bomem FTIR** icon. Refer to Figure 7- 2.

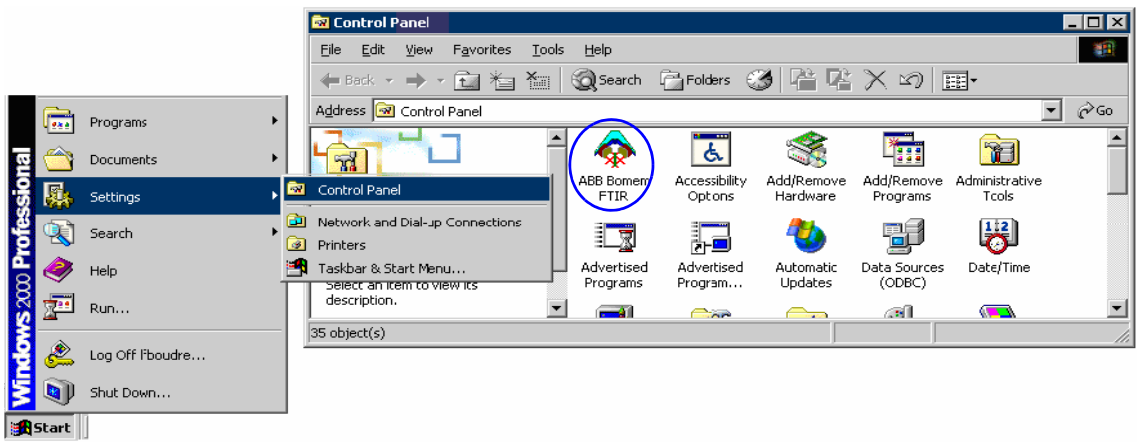


Figure 7- 2. ABB Bomem FTIR Applet

STEP 2 The ABB Bomem FTIR applet will search the network for the presence of analyzers. A message indicating that the applet is detecting the presence of analyzers will appear. Then a list of all the analyzers present on the Network will appear in the **ABB Bomem FTIR** window. Click the name of your

analyzer (MAC address of your analyzer) and Select Properties. Refer to Figure 7- 3.

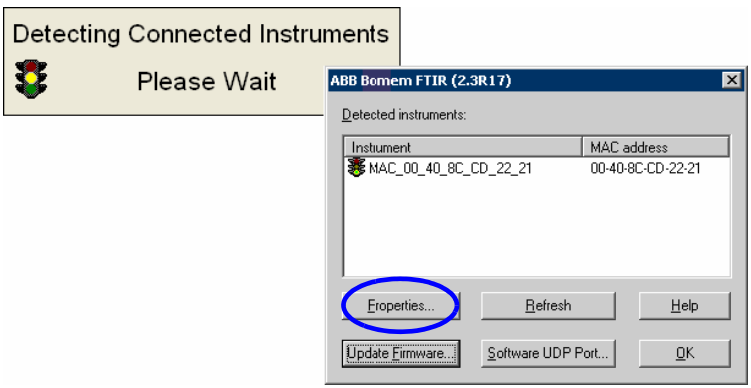


Figure 7- 3. ABB FTIR dialog box

STEP 3 In the WEB page, locate your firmware version. Refer to Figure 7- 1.

Firmware Update

The Ethernet connection allows easy update of the instrument's firmware.The update is done via the ABB FTIR Configuration Applet.

STEP 1 Click **Start>Settings > Control Panel** and double-click on the **ABB Bomem FTIR** icon. Refer to Figure 7- 2.

STEP 2 The ABB Bomem FTIR applet will search the network for the presence of analyzers. A message indicating that the applet is detecting the presence of

analyzers will appear. Then a list of all the analyzers present on the Network will appear in the **ABB Bomem FTIR** window. Refer to Figure 7- 3.

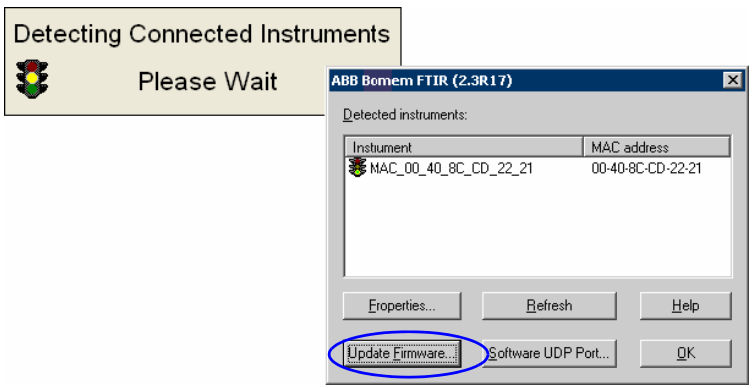


Figure 7- 4. ABB FTIR dialog box

STEP 3 In the **ABB Bomem FTIR** dialog box, select the instrument corresponding to the analyzer's MAC address and click on **Update Firmware**. Refer to Figure 7- 4.

STEP 4 In the **Firmware Upload** dialog box, select **Select File** and select the update file located on the floppy disk or CD. Refer to Figure 7- 5.

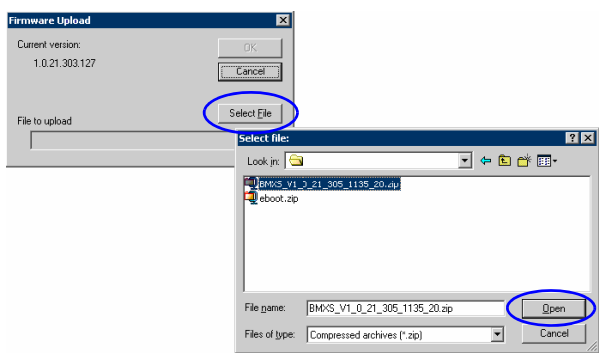


Figure 7- 5. Selecting Update file

STEP 5 Click **OK** to launch the updating process. This may take up to 5 minutes. At the end you will get a message that the instrument is rebooting.Refer to Figure 7- 6

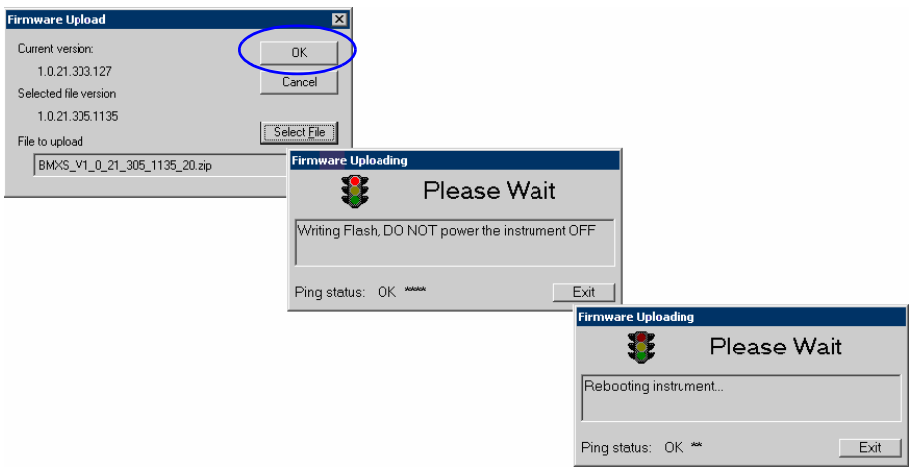


Figure 7- 6. Uploading Firmware

STEP 6 The update will conclude with the confirmation screen. Refer to Figure 7- 7.

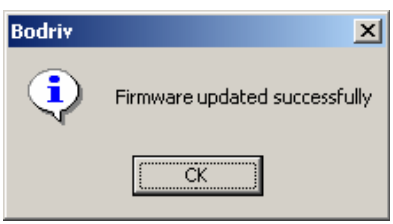


Figure 7- 7. Firmware updated confirmation dialog box

Section 8 Maintenance

Maintenance must be done by trained and qualified personnel only.

High voltage is present at the red wire connected to the laser tube.

The voltage is approximately 7 kV at startup, and between 1200 V and 1400 V under normal operating conditions.

Because of the capacitors in the laser power supply, the high voltage may be present even when the power is off.

After making any modification to the analyzer software or hardware, such as the loading of a new software version, realignment of optics, source replacement, laser replacement, preamplifier gain adjustment, etc., the OQ (Operation Qualification) tests must be repeated.

Maintenance schedule

The FTPA2000-200 Series Process FT-IR Spectrometer is a permanently aligned instrument and should not require realignment during its life span. ABB recommends that an ABB trained Service Engineer performs all servicing of the instrument. The following preventive maintenance schedule is recommended:

Maintenance operation	Frequency
source replacement	every 6 months
laser replacement	every 3 years

Table 8 - 1 Maintenance Frequency

.



Laser replacement must be done by an ABB trained Service Engineer personnel only.

Removing the FTPA2000-200 Series Process FT-IR Spectrometer

It may be necessary to remove the FTPA2000-200 Series Process FT-IR Spectrometer from its mounting rack or panel if the mounting configuration does not provide enough room for the following procedures. In this case, the FTPA2000-200 Series Process FT-IR Spectrometer must be placed horizontally on a stable surface. Before reconnecting the optical fiber cables, refer to Section Optical fiber cables on page 16.

Connecting optical fiber cables

Refer to Using Optical Fiber Cables reference guide to perform any maintenance on optical fiber cables (part number IMZ8416).



Before mating an optical fiber cable to a connector, make sure that the cable tip and the connector are clean and dry. The presence of contaminants may damage the cable tip and the sampling accessory.

Tightening SMA connectors

When connecting an SMA connector, first tighten it by hand. Then, with a torque wrench, further tighten the connector. A torque of 50 oz.-in. is recommended. If a torque wrench is not available, carefully tighten the connector using a small wrench after it has been tightened by hand.



Over-tightening an SMA connector may damage the cable tip and may put the sampling accessory out of alignment.

Securing optical fiber cables

Once a permanent installation is made, it is important to secure the optical fiber cables to a fixed surface to prevent the SMA connectors from loosening with time due to mechanical vibrations. Loose SMA connectors may cause inaccurate analytical results.

Source replacement



To avoid damaging the electronic components, use a properly grounded anti-static bracelet. If this is not available, touch the metal case frequently with your fingers to discharge static electricity.

Touching the NIR source lamp with your fingers will shorten the life span of the source module.

Do not touch the optical parts with your fingers as this may affect the performance of the spectrometer.

To replace the source, use the following procedure.

STEP 1 Turn the FTPA2000-200 Series Process FT-IR Spectrometer OFF and unplug the power cord.

STEP 2 Remove the 4 top screws and remove the top panel of the FTPA2000-200 Series Process FT-IR Spectrometer enclosure. Refer to Figure 8- 1.

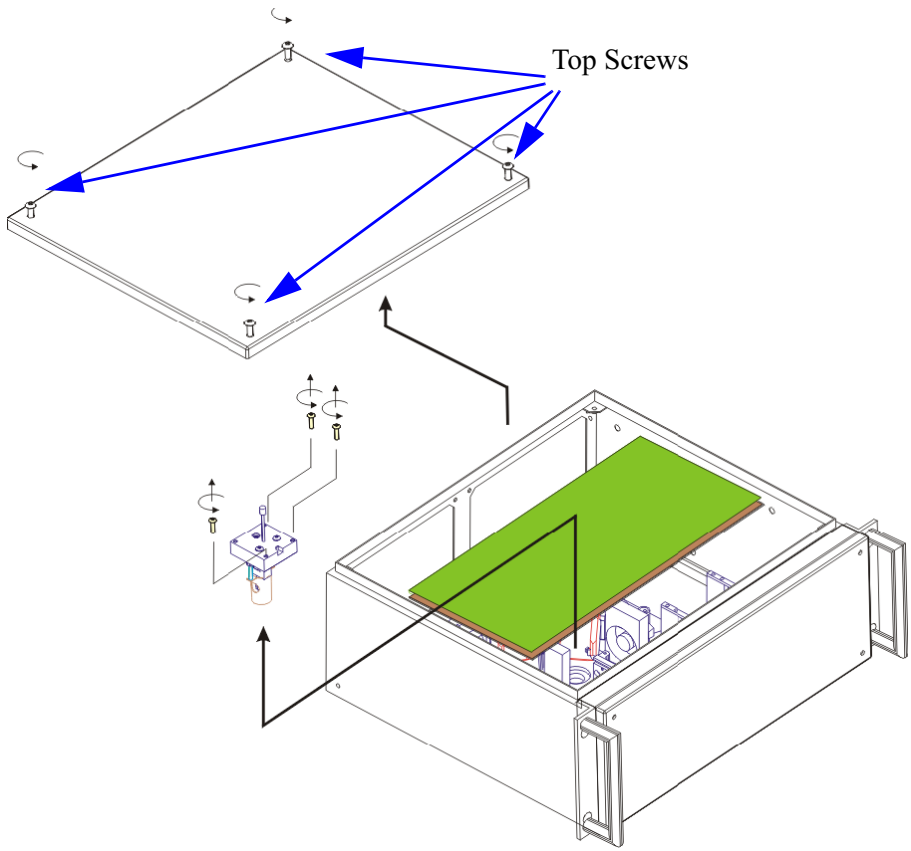


Figure 8- 1. Source replacement

High voltage may be present at the red wire connected to the laser tube, even when the power is off.

STEP 3 Unplug the power connector from the source module.

STEP 4 Unscrew the 3 captive Phillips screws that hold the source module on its holder. The 3 Phillips screws will remain in their mounting holes after being unscrewed.

STEP 5 Carefully remove the source module.

The source module is very close to the data board.If you have trouble removing the source module, contact ABB's service department.

STEP 6 Install the new source module and tighten the 3 Phillips screws.

The source module is pre-aligned. The 4 security hexagonal screws are used for alignment. Any modification of this adjustment will affect the performance of the spectrometer.

DO NOT touch adjustment screws.

STEP 7 Connect the power connector to the source module.

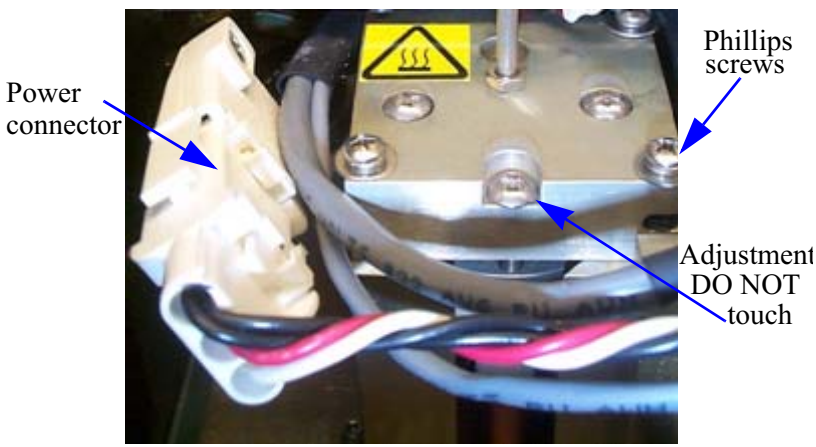


Figure 8- 2. Source module

STEP 8 Make sure there are no wires in front of any optical part.

STEP 9 Connect the power cord and turn the FTPA2000-200 Series Process FT-IR Spectrometer ON.

STEP 10 Make sure the source is lit.

STEP 11 Shut OFF the spectrometer.

STEP 12 Replace the top panel of the FTPA2000-200 Series Process FT-IR Spectrometer enclosure and install the 4 screws removed at Step 2. Refer to Figure 8- 1.

STEP 13 Allow the FTPA2000-200 Series Process FT-IR Spectrometer to warm up before using it.

Fuse replacement

To replace the fuse of the FTPA2000-200 series FTIR spectrometers, refer to the following procedure.

STEP 1 Move the sliding fuse cover to the left to reveal the fuse. Refer to Figure 8- 3.

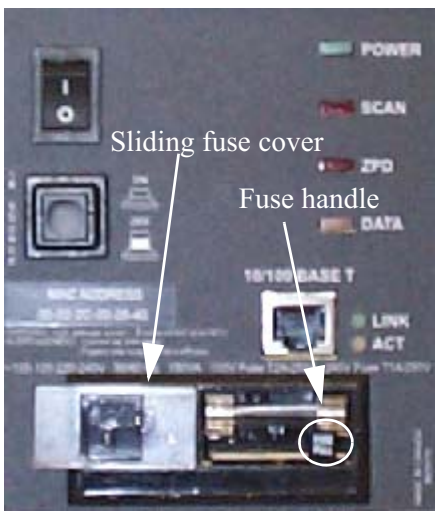


Figure 8- 3. Sliding fuse cover

STEP 2 Pull the Fuse handle to release the fuse. Pulling will be easy, then some force will be required to eject the fuse holder. Do not twist the fuse handle. Refer to Figure 8- 4.

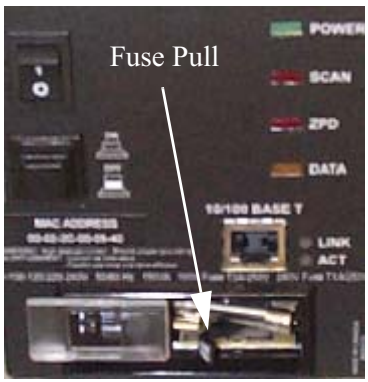


Figure 8- 4. Fuse pull, pulled

STEP 3 Remove the fuse from the fuse holder.

STEP 4 Install a new fuse into the fuse holder.

STEP 5 Push the fuse pull to the right to reinsert the fuse holder into place.

STEP 6 Move the sliding fuse cover over the fuse.

Make sure to use slow blow fuses. Refer to Section 9, Technical Information.

Humidity indicator

The indicator works as follows: four numbers (20, 30, 40, and 50) are visible on the indicator. The numbers are printed on a blue background. The background color turns from blue to white when the humidity (expressed in percent) inside the unit exceeds the level indicated by the numbers.

For example: when the background color of all 4 numbers is blue, the humidity level is less than 20%, when the background color of the number 20 starts to turn

white, the humidity level is between 20 and 30%, and when both the 20 and 30 start to turn white, the humidity level is between 30 and 40%.

Section 9 Technical Information

Specifications

Specifications are given in the following tables. Make sure that the electrical power supply and environmental conditions of the installation site meet all specifications. All values are nominal. Refer to the test report provided with your spectrometer for validated spectral specifications.

Unless otherwise specified, technical information is for the FTPA2000-260 and FTPA2000-263 models.

Electrical

Rated line voltage	100-120 VAC or 220-240 VAC (manually selectable)
Line voltage fluctuation:	Not to exceed 10% of the nominal line voltage
Rated frequency:	50-60 Hz
Rated power consumption:	150 VA
Fuse type:	T2A/250V (120 V line) T1A/250V (240 V line)

Mechanical

Enclosure:	Painted NEMA12 steel box
Overall dimensions (W×D×H):	17 in. × 16 in. × 7 in. (44 cm × 41.5 cm × 17.5 cm)
Additional clearance:	1 ft. (30 cm) in the back for optical fiber cable.
Mechanical interface:	Refer to Appendix A, Mechanical Interface
Weight:	42 lb. (19 kg)

Environmental

In order for the FTPA20000-200 series spectrometer to meet its specifications, it must be operated under the following conditions:

Storage temperature range:	0ºC to 30ºC, stable within ±5ºC
Operating temperature range:	10ºC to 30ºC Spectrometer specifications are met when temperature is maintained within ±5ºC
Optimal operating range	Room temperature
Humidity range:	5% to 95% non-condensing
Pollution degree:	2
Altitude	6560 ft. (2000 m) maximum
CSA installation category	II

Pollution is any addition of foreign matter, solid, liquid, or gaseous (ionized gases), that may produce a reduction of dielectric strength or surface resistivity. Pollution degree 2 is normally only non-conductive pollution. However, a temporary conductivity caused by condensation must be expected occasionally.

Spectrometer

Resolution:	1 to 128 cm^{-1} in increments of 2 ×
Spectrometer spectral range:	3800 to 14000 cm^{-1} Spectrometer can cover this range, however the choice of detector will determine the effective scanning range.
Scanning speed:	1 cm/s , 2cm/s
Purge (optional):	4-5 L/min
Computer interface:	Ethernet link, 10/100 Mbps
Stabilization time:	Approximately 4 hours after power-up (8 hours is preferable)

Data Cables

Data cables	Private connection: Cross over cable
	Network connection: Straight pinned cable

Optical fiber cables

Analyzer model:	FTPA2000-260		FTPA2000-263
Fiber type:	Ultra-low OH Silica		Ultra-low OH Silica
Spectral range (10 m length):	11 100 – 4750 cm^{-1} (0.9 – 2.1 µm)		11 100 – 4750 cm^{-1} (0.9 – 2.1 µm)
Numerical aperture:	.22		0.22
Core diameter:	300 µm		2mm diameter composed of 54-200 µm fibers
Minimum bending radius:	12 cm (4.7 in.)	30 cm (11.8 in.)	12 cm (4.7 in.)
Jacketing:	PVC or stainless steel		Stainless steel
Maximum length: PVC: Stainless steel:	 200 m 75 m		 Na 50 m
Connectors:	SMA-905		SMA-905



Care must be taken to prevent excessive bending of fiber. This may cause the fiber to break.

The minimum bending radius is 600 times the core diameter of the fiber.

For example, when using fiber of 200 µm, the minimum bending radius is 0.12 meter (4.7 inches).

Fibers must be secured at cell junctions to prevent any movement that could disturb the optical performance.

Interferometer

Spectrometer:	**FTPA2000-260**	**FTPA2000-263**
Ports:	4-port optical design	

Principle:	Patented Michelson-type with 2 corner-cube retro reflectors mounted on wish-bone swing arm	
Beamsplitter material:	BK7	
Number of Channels	8	2
Retro reflectors precision:	2-arc sec. corner-cubes	
Internal reference:	He-Ne laser	

Performance

For performance information on the FTPA2000-260 and FTPA2000-263 spectrometers, refer to the Technical Data Sheets.

Section 10 Troubleshooting

Troubleshooting

This chapter presents several troubleshooting information either for LED, software or connection troubleshooting.

	The equipement contains laser safety interlock device that turns the laser OFF when the protective housing is removed. Operation of an ABB laser with a defeated safety interlock is at operator's own risk and should be done by qualified personnel only.



Opening the enclosure may result in exposure to laser radiation and high voltages.

The enclosure is to be opened only by authorized ABB Service Personnel.

Laser type: He-Ne
Laser class: 3B
Wavelength: 632.8nm (vacuum)
Beam diameter: 0.75 mm ±0.05 mm
Beam divergence: ≤ 1.2 mrad
Output power at laser tube :2-4.5 mWatt
Wavelength:632.8 nm
Power output according to 3B class: 5-500 MW (under faulty condition)

High voltages are present inside the enclosure. Always proceed with care when the enclosure is opened.

Upon power-up: Normal State

Upon power up, the following LED sequence should occur.

LED color	Identification	FTIR Initialization						Normal Operation
GREEN	POWER	ON	ON	ON	ON	ON	ON	ON
RED	SCAN	ON	ON	FLASH	FLASH	ON	OFF	OFF
RED	ZPD	ON	OFF	ON	FLASH	OFF	ON	OFF
YELLOW	DATA	ON	ON	ON	FLASH	ON	ON	BLINK

Table 10 1. Colored LED status

LED	Identification	Status	description	Normal Operation
GREEN	Link	ON	Ethernet cable connected to analyzer between instrument and Ethernet card of analyzer PC.	ON or blinking
		Blinking	Data transfer or activity present on connected network.	
YELLOW BLINKING	ACTivity	OFF	All connections closed.	Blinking
		Blinking	A data connection is made to the FTIR instrument. Will blink faster with each new simultaneously opened connection.	

10- 2. LED Status

Troubleshooting table

For problems that are encountered during use, refer to the following table and to the following flow charts:

Problem	Possible cause	Solution
GREEN POWER LED Off	Power switch not ON.	Turn power switch ON. Refer to Electrical panel on page 19.
	Power cable not connected.	Make sure the power cable is connected.
	Fuse blown.	Check the voltage configuration plate and the fuse rating, and then replace the fuse. Refer to Fuse replacement on page 54.
	Power outlet dead.	Test outlet.
	Internal problem.	Contact ABB. Refer to Customer support on page ii.
LED sequence incorrect (on start up)	Internal problem.	Contact ABB. Refer to Customer support on page ii.
DATA LED not flashing (after start up)	Internal problem.	Contact ABB. Refer to Customer support on page ii.
No light at optical output panel (Flatline spectrum)	Spectrometer problems	Contact ABB. Refer to Customer support on page ii.
	Source breaker switch is OFF or tripped.	Set source breaker switch to ON.Refer to Figure 3- 1.
	Source failure.	Replace the source as shown in Source replacement on page 51.
LINK LED is off	Ethernet cable not connected.	Check connection between analyzer and PC or Network.
DATA LED is off	Data connection closed, No data is transferred.	Check connection, make sure PC software is running.

10- 3. Troubleshooting table

Troubleshooting Diagram

Figure 10- 1 presents the first troubleshooting to perform when a problem occurs with your analyzer. Each time you end up performing an action to solve a situation, repeat the troubleshooting from the beginning. If you have performed each step of the troubleshooting diagram, proceed to software troubleshooting.

Each time you perform an action to correct a problem, reboot the analyzer by switching the Power switch from ON to OFF.

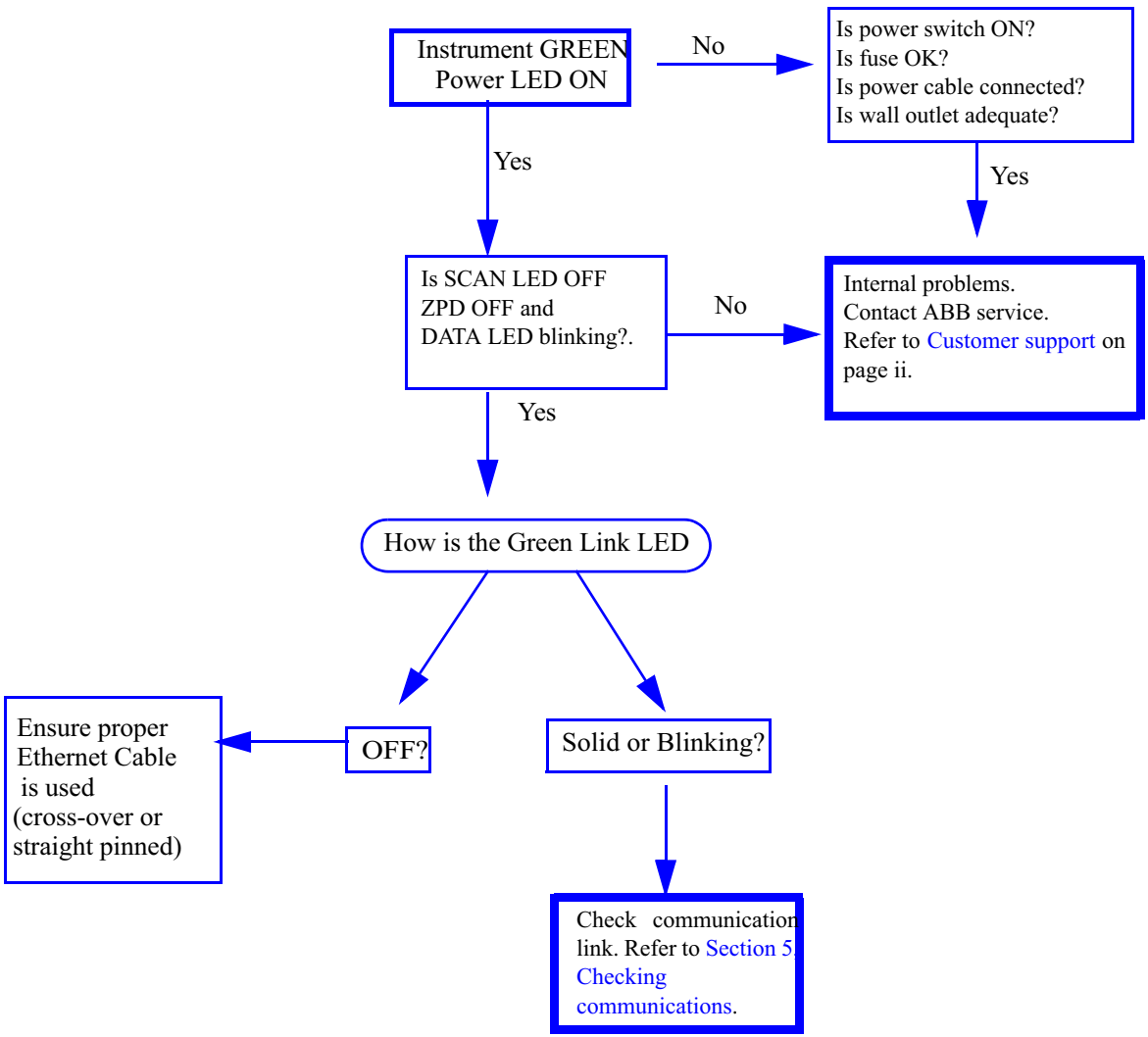


Figure 10- 1. Start-up troubleshooting diagram

After performing LED troubleshooting and Startup troubleshooting, refer to your software user guide to perform software troubleshooting.

Contacting ABB

Before calling ABB Bomem service department

In this section is described the information you need to have ready, before contacting ABB Bomem service department.



If a phone line is connected, via a modem, to the computer, an ABB Bomem service engineer can connect to the computer and gather this information for you. Supply the phone line number to that service engineer and the time slot in which to connect. At all time, ABB Bomem representative will request your authorization to connect to the system.

Preparing troubleshooting files.

If after performing the troubleshooting procedures (tables and diagram) you are unable to solve a problem, contact ABB customer support. Refer to Customer support on page ii. Before contacting ABB, select the files you need (refer to table Table 10- 4) and send them in a zipped format to ABB.

	File type (refer to following list)					
Console State	**1**	**2**	**3**	**4**	**5**	**6**
Alarm/Warning	x	x	x	x		x
Fault			x		x	x

10- 4. Choosing the required files

1. Generate a report for each report configuration for the period during which problems occurred. Refer to the **Tools screen** in the User's guide of your FTSW100 software.
2. Export the Last Good Reference spectrum and any suspect spectrum. Refer to the **History screen** of the User's guide in your FTSW100 software.

3. Export the Events over the time frame where the problem occurred. Refer to the **Event Log** screen in the User's guide of your FTSW100 software.
4. Include all the files located in the C:\Bomem\Persistence folder.
5. Use the **Windows Event Viewer** to save the Windows Application and System Logs. Refer to the Troubleshooting section in the User's guide of your FTSW100 software.
6. Export the latest committed version of your FTSW100 Application. Refer to the User's guide of your FTSW100 software.

Send the files to FTIRSupport@ca.abb.com with a brief description of the problem. Use the following subject format

– "Your company name" FTSW100 problem.

Appendix K Principles of Operation

This chapter briefly explains how the analyzer operates.

The interaction of light with matter

The analyzer analyses a product by means of transmitting **infrared** (IR) light through the product. Infrared light is light whose wavelengths are longer than those of visible light (see Figure A-1). The infrared region of the spectrum can be divided into the near-, mid-, and far-infrared (NIR, MIR, and FIR, respectively) regions.

The terms in boldface type are defined in the Glossary.

In IR spectrometry, the **wavenumber** is often used instead of the wavelength. The wavenumber is the reciprocal of the wavelength. The unit of the wavenumber is 1/cm or cm^{-1}.

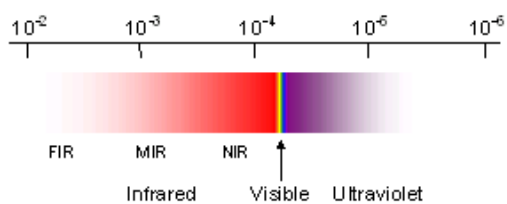


Figure 11- 2. Light spectrum (wavelenghts in cm3)

The analyzer makes use of the fact that different substances in the sample (the product being analyzed) absorb infrared light at certain specific wavelengths but not at others. Water and protein, for example, both absorb infrared light, but not at the same wavelengths. This allows the analyzer to differentiate between them.

The mathematical relationship between the amount of the substance and the amount of light absorbed is known as **Beer-Lambert's law.**

The amount of infrared light absorbed by a substance depends on the amount of that substance in the light beam — the more substance there is, the more light is

absorbed. This allows the analyzer to determine what quantity of water, protein, etc. is in the sample.

It is therefore the interaction of infrared light with the sample that allows the spectrometer to determine various properties of the sample. Measuring this interaction precisely and interpreting the results requires complex mathematical calculations. These are performed automatically by the software, making the analyzer easy to use.

The sample cell

Figure A- 2 shows how the light passes through the sample in the sample cell.

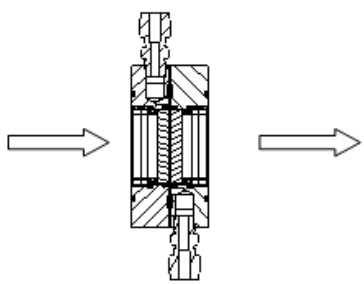


Figure 11- 3. Sample Cell cross section

During acquisition of a sample spectrum, sample liquid from the process stream is routed by the sampling handling system into the sample cell. The sample flows through the cell from bottom to top to prevent the formation of bubbles.

The infrared light from the spectrometer travels along the transfer optics (optical fiber cables) to the sample cell where it passes through the sample. The distance that the light travels through the sample is called the **path length**. The path length is one of the parameters in Beer-Lambert's law.

After passing through the cell, then the light returns to the spectrometer cabinet where it strikes the **detector**. A detector is a sensitive device that converts the light into an electrical signal whose voltage is proportional to the intensity of the light. The spectrometer sends this signal to the computer.

Appendix A Mechanical Interface



Figure 12- 1. FTPA2000-200 Series Process FTIR Spectrometer front view

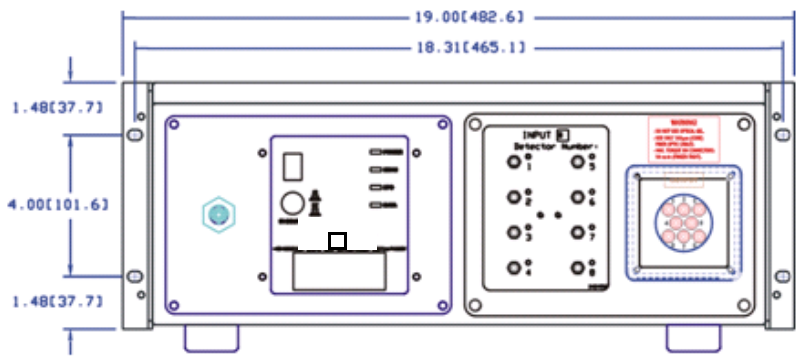


Figure 12- 2. FTPA2000-200 Series Process FTIR Spectrometer rear view

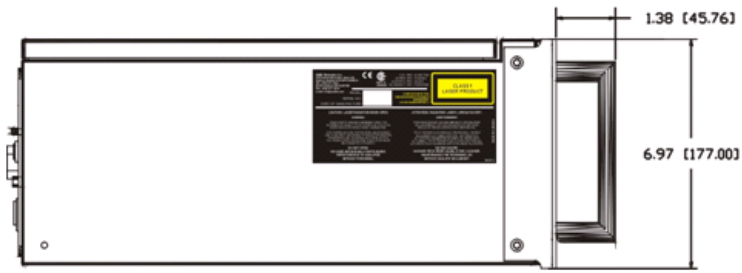


Figure 12- 3. FTPA2000-200 Series Process FTIR Spectrometer lateral view

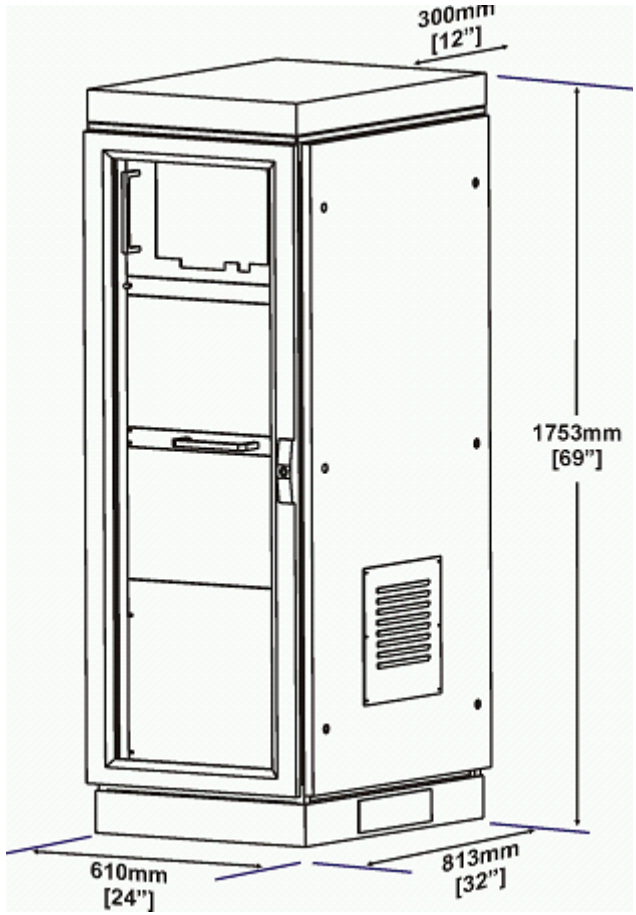


Figure 12- 4. Cabinet dimension for FTPA2000-200 Series Process FTIR Spectrometer

Appendix B Glossary

The following terms are defined as they are used in ABB manuals. Some may not apply to your analyzer.

absorbance (also called optical density or extinction)

A measure of the amount of light absorbed as it passes through a sample.

The absorbance A is the logarithm of the ratio of the intensity I0 of the light striking the sample to the intensity I of the light which passes through the sample.

$$A = \log_{10} \frac{I_0}{I} = \log_{10} \frac{1}{T}$$

The absorbance is equal to the logarithm of the reciprocal of the transmittance T.

absorbance spectrum

The absorbance of a sample as a function of the frequency or wavelength over a given spectral range.

The absorbance spectrum is calculated point-by-point from the sample and reference spectra as follows:

$$Absorbance = -\log_{10}\left(\frac{sample}{reference}\right)$$

ADC

Analog-to-digital converter

agreement

The error between the analyzer result and the result obtained with a laboratory primary method. This is often expressed as accuracy.

analyzer

A complete system for FT-IR or FT-NIR analysis.

Background spectrum (see reference spectrum)

beamsplitter

A semi-reflecting mirror in the interferometer used to divide the radiation from the infrared source into two beams, and to recombine the two beams into a single beam.

Beer-Lambert's law

An equation relating the absorption of light by a sample to the absorption coefficient of the sample, the path length, and the concentration.

$$A_\lambda = \varepsilon_\lambda \times b \times C$$

where A_λ is the sample's absorbance value at a specific wavelength ()

ε_λ is the absorption coefficient of the material at that wavelength ($\ell \cdot mol^{-1}\ cm^{-1}$).

b is the path length through the sample (cm)

C is the concentration of the analyte ($mol \cdot \ell^{-1}$)

BK7

A high quality optical glass.
BK7 is not hygroscopic. Its refractive index is 1.50 at 8000 cm^{-1}. Its spectral range is from 25000 cm^{-1} to 3700 cm^{-1}.

blank sample

A sample that does not absorb infrared radiation within the spectral range where the measurement is performed.

calibration

The process of aligning analyzer measurements to agree with reference measurements obtained using a primary method.

calibration (or model or calibration model)

The set of equations that represents the relationship between the absorbance spectra of a set of samples and the properties of the samples.

Some common types of models are peak height, peak ratio, PLS and autosubtract models.

calibration set (or training set)

In spectrometer calibration, a set of standard samples used in calibration model development. The calibration set covers the expected ranges of property values, as well as any other variations that may affect the spectra, such as temperature. When there is more than one property, the calibration set must include independent variations of each property.

CAN (Controller Area Network)

CAN (Controller Area Network) is a local serial bus system especially suited to interconnect smart devices such as sensors and actuators in automated equipment.

CAN is used in ABB analyzers for distributed I/O. This is used for controlling sampling system valves, accepting inputs from external sensors, and for sending analysis results to control systems (4-20 mA current loop analog outputs and open/close digital outputs).

CANopen

A network protocol that allows direct peer-to-peer data exchange between nodes on a CAN network (CANbus).

channel

An optical channel on the spectrometer. Each channel is associated with one sampling accessory and one detector.

The FTPA2000-200 Series Process FT-IR Spectrometer, for example, has multiple channels. Each channel can be connected to a sampling cell by a fiber-optic cable. This allows one FTPA2000-200 Series Process FT-IR Spectrometer to do the same job as several single-channel spectrometer.

It is possible to have more than one sampling point on a channel. This is accomplished using valves to direct the sample from different sampling points into the sampling cell. In most cases, however, there is only one sampling point per channel and the two terms can be used interchangeably.

channel spectrum

A spectral artifact caused by reflections in the gap between two optical surfaces, for example, between parallel window surfaces or at the coupling point between optical fiber ends. Also called Fabry-Perot interference.

To avoid channel spectrum in transmission cells with a small optical pathlength, a wedge in the sample path is used to prevent parallelism of the two windows.

coadded spectrum

The spectrum resulting from averaging, on a point-by-point basis, a number of spectra or interferograms. Co addition is used to increase the signal-to-noise ratio of a spectrum.

DCS

Distributed control system.

desiccant

A substance used as a drying agent.

detector

A device in a spectrometer that produces an electrical signal that is proportional to the intensity of the light striking it.

detector cut-off

The frequency or wavelength at lower end of the spectral range.

detector saturation

A condition of the detector whereby an increase in the light intensity striking it no longer produces a linearly proportional change in the output signal. This is a nonlinear condition and can cause Fourier stray light.

D-star (D*)

A value used to designate the specific detectivity. This is a performance measure independent of detector size. The higher is the D* value, the better is the detector.

$$D^* = (A \times \Delta f)^{1/2} D$$

where	A	is the sensitive area
	Δf	is the bandwidth frequencies
	D	is the reciprocal of noise equivalent power (NEP)

factor

In analysis using the PLS algorithm, one of a series of synthetic spectra which represent the most common variations in a given set of spectra (also known as latent vectors, characteristic vectors, spectral loadings, loading vectors, principal components, or variation spectra.).

Fast Fourier transform (FFT)

A mathematical algorithm for efficient calculation of the Fourier transform.

Fourier transform

A mathematical function that transforms the time-dependent information contained in the interferogram into the corresponding optical spectrum.

F-ratio

An indicator of spectral residual after modeling that can help detect whether an abnormal condition has occurred during analysis. The F-ratio should normally be low (typically less than 10, depending on the application). An F ratio higher than average may indicate that the wrong material is being analyzed or that there is a problem with the system.

FTE

Fourier transform embedded software handling input and output.

FT-IR (or FTIR)

Fourier transform infrared.

FT-MIR

Fourier transform mid-infrared.

FT-NIR

Fourier transform near-infrared.

grab sample

A sample taken from the process at the precise time that a spectrum is recorded. Laboratory analysis of the grab sample using a primary method is used to validate or improve the analyzer calibration.

GRAF

Gas retrieval algorithm for Fourier Transform spectrometer.

hygroscopic

Able to absorb moisture from the atmosphere.

hygroscopic optical component

An optical component made of hygroscopic material. Such optical components can be damaged if exposed to humidity because they can absorb moisture from the atmosphere.

infrared

A region of the electromagnetic spectrum between visible light and radio waves where the wavelengths are longer than those of red light.

initial (or first) reference (or zero)

The first reference spectrum collected when the system was commissioned. This is used as a base to monitor changes in the analyzer response over time.

Initial Qualification (IQ)

A procedure used to ensure that an instrument has been correctly installed.

interferogram

A representation of the electrical signal from the detector of a FT-IR spectrometer. The interferogram is a graph of the voltage at the output of the detector as a function of the position of interferometer scan mechanism. The spectrum is calculated from the interferogram using a Fourier transform.

interferometer

The device in an FT-IR spectrometer that modulates the infrared beam coming from the source.

The interferometer splits the infrared beam into two beams, introduces a continuously varying optical path difference (OPD) between the two beams, and recombines the beams. When the beams are recombined, interference caused by the OPD modulates the beam.

least-squares regression

A regression procedure used to establish a parameter value derived from multiple absorbance values such that the sum of the squares of the differences between the model absorbances and the actual absorbances is minimized.

MODBUS®

A protocol widely used to establish master-slave communication between intelligent devices. A MODBUS message sent from a master to a slave contains the address of the slave, the command, the data, and a check sum.

The MODBUS protocol is independent of the underlying physical layer. It is traditionally implemented using RS232, RS422, or RS485 serial link over a variety of media (e.g. wire pair, fiber, radio, etc.). MODBUS TCP/IP uses TCP/IP and Ethernet to carry the MODBUS messages.

model (see calibration model)

ModV

A proprietary protocol for communication with Dow DCS systems over a serial link.

monitoring (sampling) point

A monitoring point is a point in a process stream where the material in the process (the sample) is analyzed (see Channel).

monitoring (sampling) system

A system used to direct a sample from a process stream to the gas cell. The monitoring system may include software-controlled valves, pumps, and other devices.

NEMA

National Electrical Manufacturers Association

nonlinearity

A deviation from the normally linear relation between the output and the input of a device. Non-linearity occurs when the output of a device does not vary in direct proportion to the input, for example, when saturation occurs.

OPC (OLE for Process Control)

OPC, or OLE (Object Linking and Embedding) for Process Control, is a software standard for connecting Windows-based process control applications to industrial programmable controllers and control systems. Devices use OPC to exchange digital, analog, and text data.

OPC is based on Microsoft's COM (Component Object Model) technology, which defines how individual software components can interact and share data under Windows.

open beam

A condition in which there is no sample in the gas cell.

open-beam spectrum

A spectrum acquired in the open-beam condition.

Operation Qualification (OQ)

A test procedure used to ensure that an instrument is operating within specifications.

optical density (see absorbance)

outlier (or outlier sample)

A sample in a set of samples for which a predicted property value or spectral structure lies significantly outside the main cluster of the corresponding property values or structures for that set.

Outliers can be caused by several different factors including unexpected variations in the property value, inconsistent sample handling, or changes in the performance of the instrument.

path length
The distance that light travels through the sample during analysis.

PLC
Programmable logic controller.

predict
In spectroscopy, to obtain the value for a specific property of a sample from its spectrum by using one or more calibration models.

prediction
In spectroscopy, the value obtained from predicting a property.

preprocessing
Mathematical treatment applied to a spectrum before the calibration model is applied to it. There are a number of standard preprocessing algorithms commonly used in spectroscopy.

primary method
The accepted standard laboratory technique for measuring the properties of samples. When developing a calibration model, the "known" property values of the training set samples are determined by measurement using the primary method.

property
A single, measurable characteristic of a sample, whether it be a physical property such as temperature or a chemical property such as concentration.

raw spectrum
A spectrum that has not undergone any mathematical alterations.

reference spectrum(also called background spectrum or zero spectrum)
A single-beam spectrum that only contains information about the analyzer, including the gas cell and the air present in any part of the modulated beam optical path. This is required in order to obtain a transmittance or absorbance spectrum of the sample.
A reference spectrum is obtained by removing the sample from the sample accessory or by filling the sample accessory with a blank sample and acquiring a spectrum.

repeatability

The precision of repeated measurements on the same instrument.

reproducibility

The precision of repeated measurements on different instruments.

resolution

The smallest frequency interval that can be distinguished over a spectral range. The lower the resolution setting on the spectrometer, the more data points there are in the spectrum.

Lowering the resolution setting on the spectrometer yields spectra with a "higher" resolution, since there are more data points covering the same spectral range.

sampling or monitoring accessory (gas cell)

A device that permits interaction of the modulated light beam from the spectrometer with the sample, for the purpose of obtaining a transmittance, absorbance, or reflectance spectrum of the sample.

Flow-through cells and immersion probes are commonly used sampling accessories.

sampling point

A sampling point is a point in a process where the material in the process (the sample) is analyzed (see Channel).

saturation (see detector saturation)

scan

With the ABB FT-IR spectrometer, a forward and a reverse sweep of the interferometer scan mechanism.

A single scan results in two interferograms, one for the forward sweep and one for the reverse sweep (see Coadded spectrum).

sequence

In FTSW100, a sequence defines the order in which streams are analyzed. Although a number of different sequences can be defined, only one sequence can run at a time.

single-beam spectrum

The spectrum that results from performing a Fourier transform on the interferogram obtained from a spectrometer.

The single-beam spectrum contains information not only about any sample present in the sample compartment or sampling accessory, but also about the instrument

(the source, all the optical components, the ambient air, as well as any contamination there may be in the optical path).

spectral range

The range of frequencies (or wavelengths) over which the amplitude of a spectrum is above the acceptable noise level. It is application dependent.

spectrometer

An instrument for producing a spectrum and measuring the wavelengths, energies, etc. involved.

An FT-IR spectrometer has a photoelectric detector and produces a spectrum that shows how the transmittance, absorbance, or reflectance of the sample varies with wavelength. Such instruments are also called spectrophotometers.

spectrum

A range of electromagnetic energies arrayed in order of increasing or decreasing wavelength.

A distribution of transmission or absorbance levels over a range of wavelengths, arrayed in order of increasing or decreasing wavelength.

stray light

Apparent optical energy, caused by nonlinearity, in a spectral region where no energy is expected (Fourier stray light).

Modulated light reaching the detector without having passed through the sample.

stream

A current or flow of material in a process.

A stream is analyzed using a gas cell connected to the analyzer. One gas cell is used for each analyzed stream unless the monitoring system is set up for stream switching.

training set (see calibration set)

transmittance

A measure of the amount of light that passes through the sample, often expressed as a percentage.

The transmittance T is the ratio of the intensity I of the light which passes through the sample to the intensity I_0 of the light striking the sample.

$$T = \frac{I}{I_0} \qquad \%T = 100T$$

transmittance spectrum

The percent transmittance of a sample as a function of the frequency or wavelength over a given spectral range.

The transmittance spectrum is calculated point-by-point from the sample and reference spectra as follows:

$$\%Transmittance = \frac{sample}{reference} \times 100$$

Trigger

A trigger represents a signal (usually a digital input) used to activate operations in Enablir. When a trigger is switched from off (0) to on (1), the associated action is performed. Examples of triggers are an external signal from a DCS or other device, a software parameter whose value can be changed by the user, and a timer.

validation

Tests used to establish that an analyzer is providing results within the expected degree of agreement. This can include predictions with known samples and diagnostics on the reference and sample spectra.

wavelength

The distance (λ) between successive points of equal phase in a wave.

In FT-IR spectrometry, wavelength is usually expressed in micrometers (μm) or nanometers (nm).

wavenumber

The number (σ) of cycles of a wave in unit length. The wavenumber is the reciprocal of the wavelength:

$$\sigma = \frac{1}{\lambda}$$

The unit of the wavenumber is 1cm or cm^{-1}.

zero spectrum (see reference spectrum)

ZPD (Zero Path Difference)

The point where the scan mechanism of a FT-IR Spectrometer is positioned so that the two beams from the beamsplitter travel exactly the same distance before being recombined.



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ABB Measurement & Analytics
3400, Rue Pierre-Ardouin
Québec (Québec) G1P 0B2
Canada

For America: 1-800- HELP-365
email: ftirservice@us.abb.com
For North America: 1-800 858-3847
For all other countries: +1-418-877-2944
email: ftirsupport@ca.abb.com

Introduction to On-line PLS Calibration

Reference Manual



IMZ8314
Revision B October 2015

ABOUT THIS MANUAL

Purpose of this manual

This manual provides an introduction to developing and maintaining on-line calibrations for the FTPA2000-200 series using PLS. It requires that the user be already familiar with a PLS calibration development tool such as PLS/IQ™ or PLSPlus™ from Thermo Galactic Products.

Note: Where possible, the terms used in this manual are coherent with those used in documents published by Thermo GalacticProducts..

Audience

This manual is intended for people who will be involved in developing or maintaining calibrations on the FTPA2000-200. It is designed to be useful to people with basic knowledge in spectroscopy.

How this manual is organized

This manual is divided into an *Introduction*, and three parts:

- Part 1, *FTPA2000-200 Calibration*, provides practical information required to develop, control, and maintain a calibration.
- Part 2, *On-Line Calibration Procedure*, provides a procedure for qualifying a FTPA2000-based system, as well as an example of a procedure used to develop a toluene calibration in a para-xylene process plant.
- Part 3, *Spectrometer Calibration*, provides basic information about calibration which applies to all spectrometers. People with little experience in spectrometer calibration should read this part first.

Supplementary information about some topics is provided in the margin.

This manual includes a number of terms shown in **boldface** type. These are explained in the Glossary.

Some information of a technical or mathematical nature is provided in shaded sidebars. Reading this information is optional.

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1. INTRODUCTION

1.1 FTPA2000-200

FTPA2000-200 is a multi-point, multi-stream FT-NIR analyzer. It is designed for remote, real-time monitoring of continuous and batch processes through fiber-optic cables. The FTPA2000-200 is used for quality monitoring and process control in refining, petrochemicals, polymers, plastics, chemicals, pharmaceutics, foods, and other industries.

The FTPA2000-200 makes use of the near-infrared (NIR) spectrum for analysis. This spectrum is particularly well suited for the quantitative analysis of organic compounds containing C-H, O-H, or N-H bonds, as is common in the above mentioned industries. In addition, it is easy to transmit the near-infrared spectrum through fiber-optic cables.

The FTPA2000-200 has eight fiber optic channels. Each channel can be connected to a remote *sampling accessory* (e.g. flow-through sampling cell or immersion probe). The acquisition of spectra is performed sequentially, one channel after another.

Typically, a high precision measurement of a clean liquid such as xylene, toluene, etc., can be performed by the FTPA2000-200 in approximately one minute, once a reference has been acquired. If liquids from different process streams are compatible, it is possible to use the same sampling cell for different streams. In this case, valves are used to select the stream to be sampled.

The recommended calibration algorithm for the FTPA2000-200 is PLS[a]. All comments and examples in Parts 1 and 2 of this manual are based on the use of PLS.

[a]PLS (Partial Least Squares) is a multivariate technique used in developing calibrations for spectrometers. Several chemometrics software programs are available which use this technique.

For general information on calibration development including PLS, refer to Part 3 of this manual.

The main advantage of PLS is that, when developing the calibration, it is not necessary to know all of the properties of the training set samples, but only of those which will actually be measured by the calibration. (A property can be concentration, temperature, OH value, octane number, cloud point, etc.) However, all products which will be present in the process must be included in the training set samples, and their relative properties must cover all the variations that will be present in the process.

1.2 Reference documents

For information on installing and verifying the FTPA2000-200, refer to the *FTPA2000-200 User's guide* (Part No. IMZ9782).

Before handling or installing fiber-optic cables, be sure to read *Using fiber-Optic Cables* (Part No. IMZ8416).

PART 1: FTPA2000-200 CALIBRATION

2. SAMPLING ACCESSORIES

The sampling accessories most commonly used with the FTPA2000-200 are the flow-through sampling cell and the immersion probe. Flow-through cells are used in a ***process bypass loop*** whereas immersion probes are immersed directly into the process. The type of sampling accessory used depends on a number of factors, such as:

- the temperature, viscosity, and reactivity of the sample
- the frequency at which the sampling accessory must be zeroed, and the use of automatic zeroing and flow control
- the complexity of installing a process by-pass loop, and the type of piping or vessel used in the process

2.1 Flow-through cells

One technique used to sample a process is to install a ***sampling system*** in a process bypass loop, as shown in Figure 2-1.

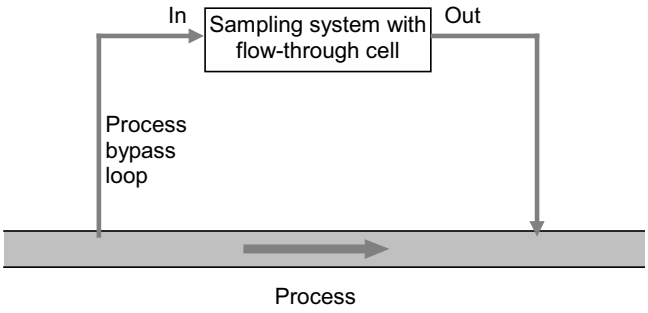


Figure 2-1. Process bypass loop

The sampling system includes a flow-through sampling cell connected to the analyzer by fiber-optic cables. The process bypass loop provides a parallel flow for sampling that can be completely isolated from the process for maintenance or repair. Details of the sampling system are shown in Figure 2-3.

Figure 2-2 shows a typical flow-through cell used with the FTPA2000-200.

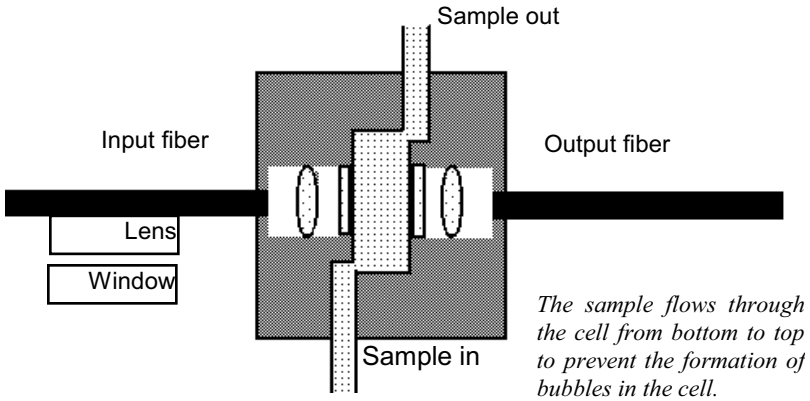


Figure 2-2. Flow-through cell

[a]*Refer to Part 3 of this manual for information on the operation of the interferometer and the detector.*

The sample (the liquid extracted from the process for analysis) flows through the cell from the bottom to the top. This prevent the formation of bubbles in the cell. The optical beam modulated by the FTPA2000-200 ***interferometer***[a] enters the cell through the input optical fiber, passes through the sample, and is returned to the ***detector***[a] through the output fiber.

2.1.1 The sampling system

[b]*Before performing analyses, it is necessary to obtain a spectrum called a reference, or zero, spectrum. See Chapter 3 for information on the use of the reference spectrum.*

Figure 2-3 shows a typical sampling system using a flow-through sampling cell, for analyzing a clean liquid sample such as para-xylene, toluene, benzene, etc. In this example, nitrogen gas is used to purge the cell to obtain a **reference**[b], or **zero**[b], **spectrum**.

For applications where the sample contaminates the cell windows, it may be necessary to inject a cleaning fluid into the cell before it is purged with dry nitrogen. The layout will then be different. Some applications may require a zero fluid instead of dry nitrogen for the reference spectrum.

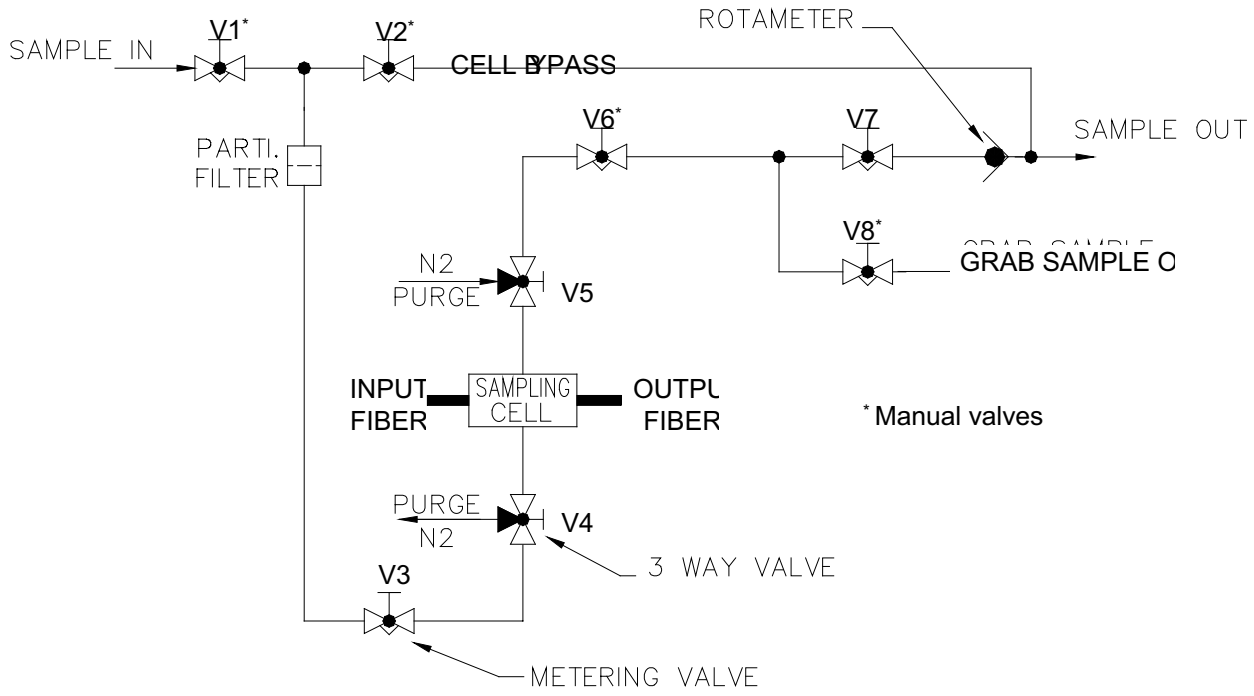


Figure 2-3. Sampling system for a flow-through cell

The sample enters the sampling system through V1.

When a reference spectrum is required, V3 and V7 are closed and the sample bypasses the cell through V2 and the cell bypass. Before and during the acquisition of the reference spectrum, V4 and V5 are set to let nitrogen flow through the cell. V4 and V5 are three-way valves.

After the reference spectrum is acquired, V4 and V5 are set to let the sample flow through the cell. Then, V3 and V7 are opened.

In the case where automatic zeroing and flow control is used, V3, V4, V5, and V7 in Figure 2-3 are computer controlled. V1, V2, V6, and V8 are manual valves.

V1 is used to adjust the flow through the entire sampling system, and can be closed for maintenance purposes. V2 is adjusted so that enough pressure is generated through the cell. V6 is adjusted for a sampling flow of about 3 L/min, as indicated by the rotameter. V8 remains closed during normal operation; it is only used to manually grab samples for on-line calibration development and maintenance.

Note: The flow rate through the sampling cell should be approximately 3 L/min in order to have laminar flow inside the cell.

It is important to have sufficient flow in the cell bypass at all times. This ensures that the liquid in the sampling system is always fresh and accurately represents the liquid in the process.

Experience has shown that cell flow should be between 25% and 100% of the cell bypass flow. This means that the flow rate in the cell bypass should be between approximately 3 and 12 L/min.

It is also important that the grab sample output be as close as possible to the sampling cell. During calibration, each time a spectrum is acquired of the liquid in the sampling cell, a sample is grabbed manually. It is essential that the grab sample accurately represent the liquid in the cell at the time of spectral acquisition.

If the above conditions are not met, the accuracy of the calibration, and of the analyses, may be reduced considerably.

2.1.2 Problems to avoid

2.1.2.1 Air bubbles in the cell

It is very important to prevent the formation of air bubbles in the cell, because these diffuse light and produce measurement errors.

Figure 2-4 shows an example of signal loss due to such light-diffusing phenomena. Here, phenol and acetone are being measured in a mixture containing a small quantity of water as an emulsion.

In this example, the emulsion has raised the base line to 1 ***absorbance unit***. This means that only 10% of the light is getting through the cell. Since all frequencies are equally attenuated, we can conclude that the non-homogeneities are much larger than the wavelength of the near-infrared beam.

A higher absorbance means that less light is transmitted through the cell.

The emulsion prevents light from reaching the output fiber. This raises the measured absorbance.

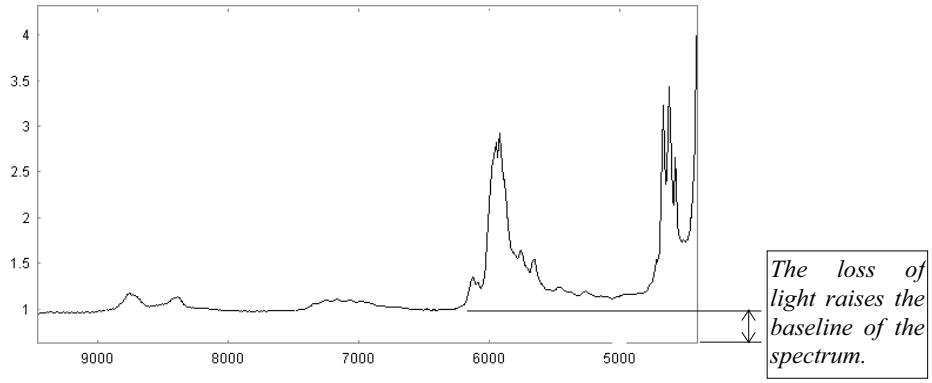


Figure 2-4. Signal loss due to air bubbles

2.1.2.2 Deposits on the cell windows

Some samples may leave a deposit on the surface of the two windows that are in contact with the liquid. In this case, the cell must be cleaned and a new reference spectrum obtained fairly frequently. When frequent zeroing is required, it can be automated and controlled by software.

In some cases, the cell must be cleaned with a cleaning fluid before it is purged with the zero liquid or gas. In other cases, the zero liquid used will also clean the cell windows.

2.1.2.3 Particles in the sample

Any particles or particle-like material in the sample will diffuse or absorb light when present in the optical path of the cell. This causes conditions where the signal-to-noise ratio is poor, which in turn reduces the precision of the calibration, and may even prevent the calibration from working. Filters must be used in any sampling system that samples a flow containing particles or particle-like emulsions such as air bubbles, water emulsion, etc. We recommend stainless steel filters with a particulate retention of 0.1µ to 1µ as the final filtering step before the sampling cell.

2.1.2.4 Ambient gas

An ambient gas signature may be included in the PLS calibration. If a high precision calibration is required, or if the training set does not contain an ambient gas signature, the sample and reference spectra must be free from contamination from the ambient air. This can be accomplished by purging the spectrometer, as well as the fiber-optic connections to the sampling cell, with dry nitrogen.

Figure 2-5 shows the configuration of a flow-through sampling cell with purge caps. The caps are mounted where the input and output optical fibers are connected. These caps are purged through the purge inputs. Vent holes located at the top of the caps prevent pressure buildup inside the cap.

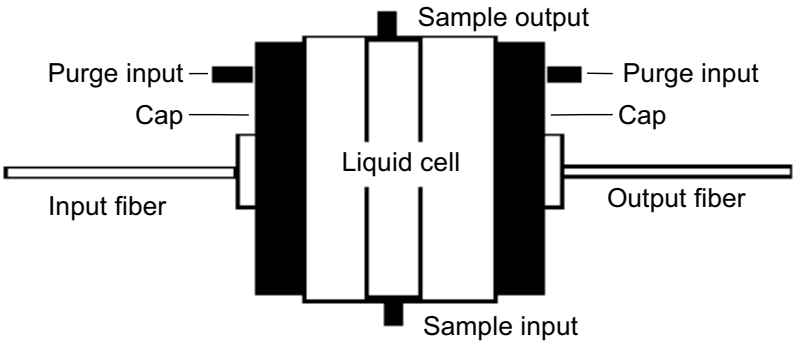


Figure 2-5. Flow-through cell with purge caps

Purging the caps reduces the time required to carry out the calibration since it removed all water vapor around the fiber connectors. Purging the caps is also useful when the cell environment may be contaminated with a gas (e.g. volatile hydrocarbon gas) that could be detected by the spectrometer.

Note: If the calibration is developed with spectra which are free from water vapor, then all analyses must be performed under the same conditions. Therefore, if a purge is used for calibration, it must be also used for sample analysis.

If water vapor was not present in the reference spectrum, and it is later found that the spectra acquired during analysis contain water lines, it is possible to add a water signature to the calibration spectra to correct the method. This must be done with great care since some spectra may be used many times in the calibration training set, and this may end up modeling part of the noise.

The same approach can be used to add information about sample temperature, fiber temperature, and base line variations. This works best when the required precision is relatively low.

2.2 Immersion probes

For some applications, it is not possible to use a process bypass loop and a flow-through cell for sampling. It may not be possible, for example, to withdraw a sample from the process, or the sample may be too viscous to use a flow-through cell.

In cases like these, it is possible to immerse a probe directly into a process line or a tank. This simplifies the measurement, but may make it difficult to implement an automatic periodic reference spectrum acquisition.

Figure 2-6 shows an immersion probe mounted on a flange to adapt it to the process line. It is equipped with a mechanism that retracts the probe out of the sample in order to acquire a reference spectrum without having to stop the flow in the process line.



Figure 2-6. Immersion probe

Figure 2-7 shows a drawing of a typical probe with the input and output fibers, the sample gap, and the reference chamber. The size of the sample gap can be adjusted as required by the analysis.

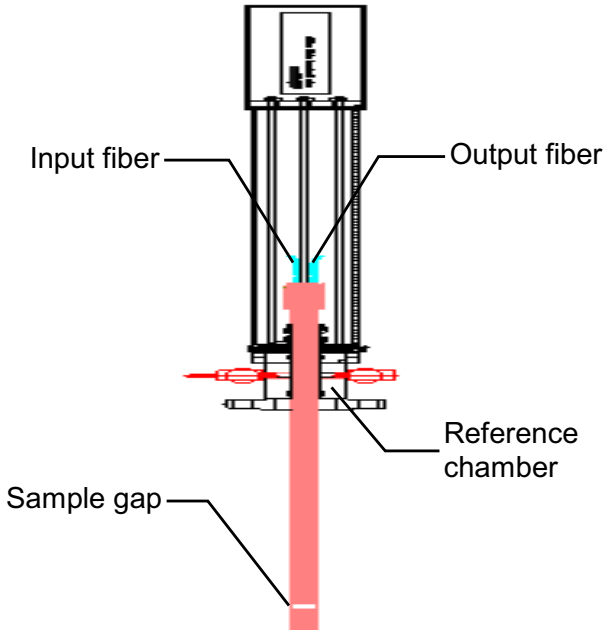


Figure 2-7. Immersion probe

The modulated light from the interferometer is sent to the probe through the input fiber. Inside the probe, a lens directs the light across the sample gap. It is then reflected back across the sample gap by a mirror. The lens gathers the reflected light, which has passed twice through the liquid in the sample gap. The output fiber returns this light to the analyzer.

2.2.1 Retraction of probe for referencing

It is important to be able to acquire a reference spectrum without having to stop the flow in the process line. A reference spectrum is acquired using either dry nitrogen or a zero liquid in the sample gap.

Figure 2-8 shows a detailed drawing of the probe assembly installed in a process line. When a reference spectrum is needed, the probe is retracted manually with the handle. Once the probe is in the reference chamber, a ball valve is closed to isolate the probe tip from the process stream. Then the probe tip, including the sample gap, is cleaned with a solvent. After cleaning, the reference chamber is purged with dry nitrogen or zero liquid until no trace of any spectral signature is detectable. Then the reference spectrum is acquired.

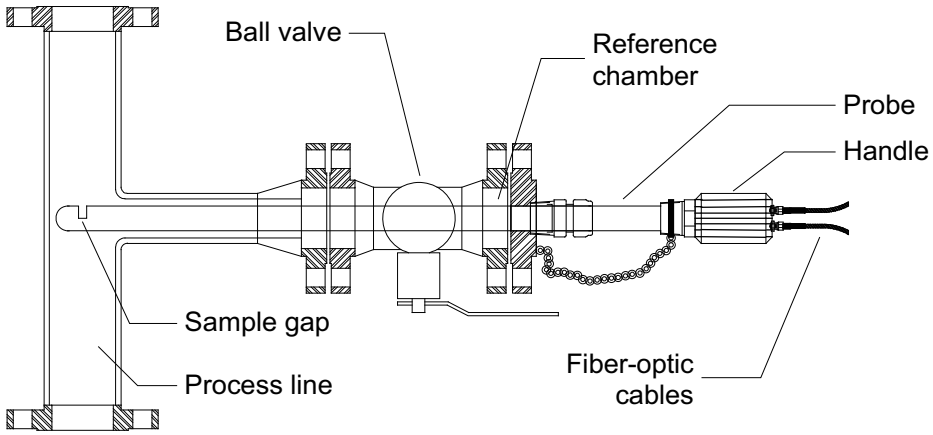


Figure 2-8. Typical immersion probe assembly

3.2 Examining the reference spectrum

The reference spectrum can yield a great deal of information about the analyzer. The reference spectrum, can indicate, for example, if ***nonlinearity*** is present in the system, and can give an indication of the suitability of the sampling accessory being used. It is good practice to examine the reference spectrum when the system is commissioned and after maintenance interventions.

3.2.1 Nonlinearity

Nonlinearity can occur when an electrical component becomes overloaded. Figure 3-2 shows the ***stray light*** that nonlinearity in the detector or preamplifier can induce. This stray light can be seen in low frequency regions below the active part of the spectrum. If this is observed, the gain adjustment of the detector preamplifier should be reduced to eliminate the nonlinearity.

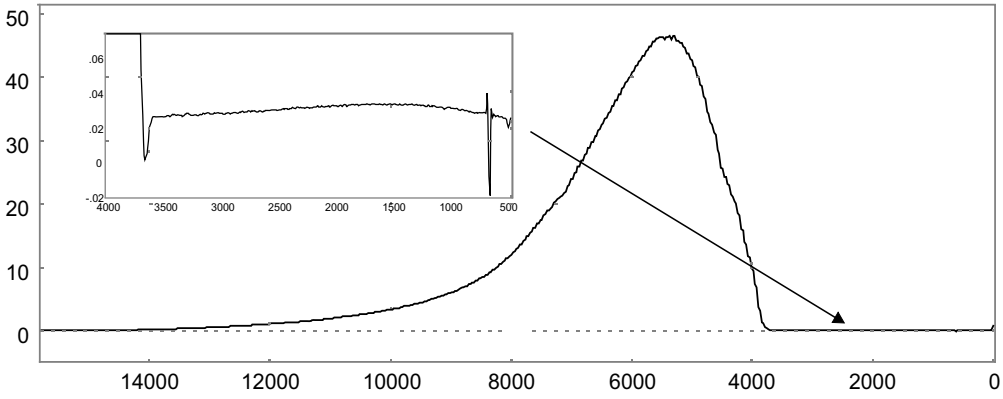


Figure 3-2. Non-linearity stray light

3.2.2 Suitability of the sampling accessory

A close look at the reference spectrum can also show whether the appropriate sampling cell has been chosen. Figure 3-3 shows the transmission of two flow-through cells that can be used with the FTPA2000-200.

The "Extended Near-IR" version of the IR Link™ High Pressure Liquid Cell (cell B) is so called because its range is extended into the mid-IR region (toward the right on the horizontal scale). This is not apparent in the figure because the detector (InGaAs extended range) limits the range in this direction to approximately 4000 cm^{-1}.

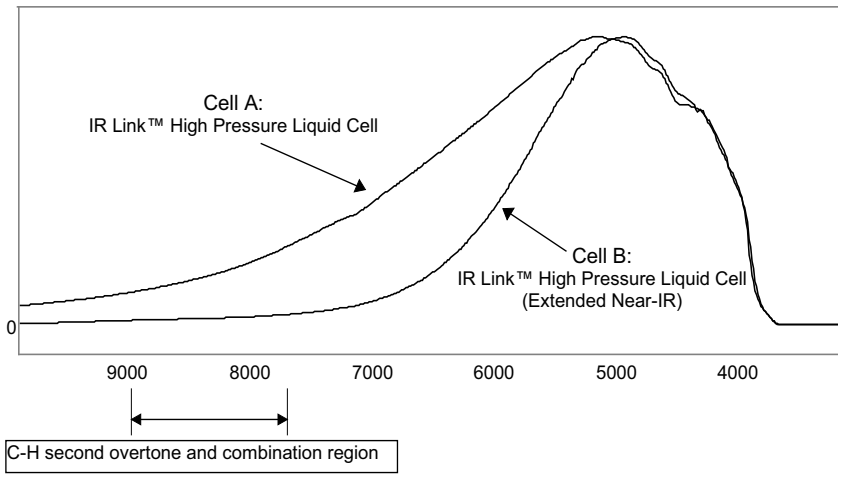


Figure 3-3. Cell optical window

[e]*Normalization is a type of spectral preprocessing algorithm (see Section 4.3.4 (page 4-4).*

One cell in Figure 3-3 (cell A) transmits light in the C-H second overtone and combination region (9200 cm^{-1} to 7850 cm^{-1}) while the other cell (cell B) does not. If we intend to use this region for ***normalization***[e] as is often done in near IR spectroscopy when analyzing hydrocarbons, a cell with low transmission in this region is not acceptable.

3.2.3 Quality of the reference spectrum

The quality of the reference spectra is very important because reference spectra are applied to all spectra used in calibration and measurements. An unwanted *spectral signature* in the reference spectrum indicates that the sampling accessory is not correctly purged, or that the purge gas is contaminated.

Figure 3-4 shows a reference spectrum with an unwanted spectral signature.

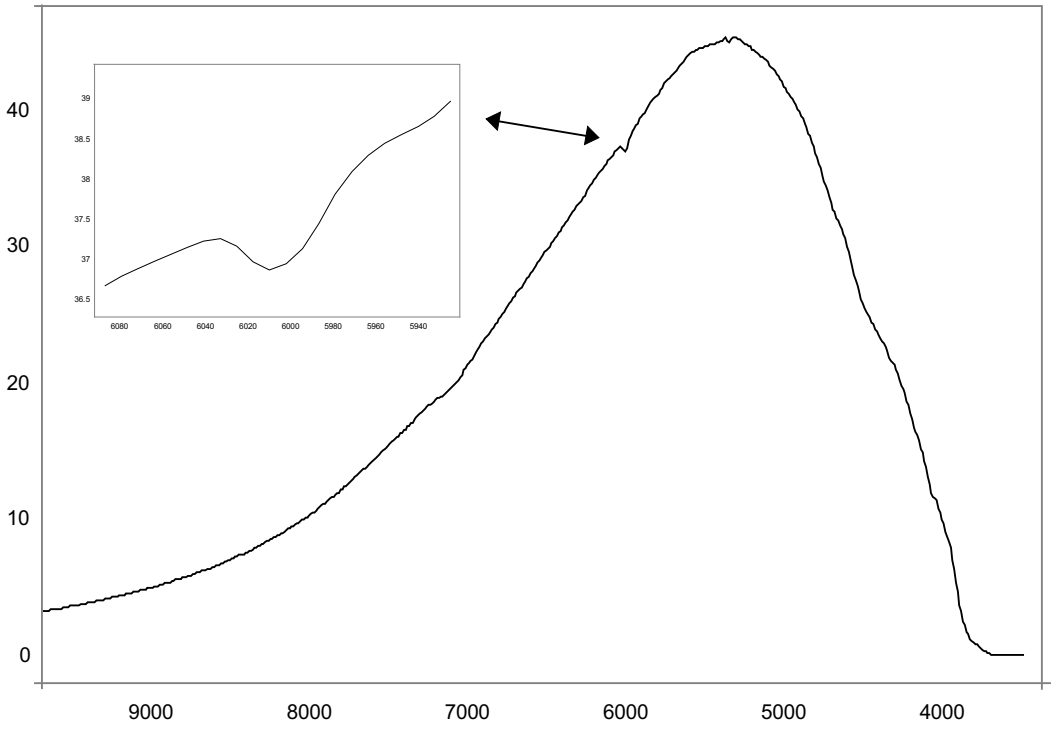


Figure 3-4. Interfering feature in the reference spectrum

3.3 Frequency of referencing

As stated before, a reference spectrum contains information about the instrument including the interferometer, the source, the optical fibers, the sampling accessory, contamination, etc. Once a reference spectrum is acquired and stored, it can be used until any changes occur in the instrument that may affect the spectra. Reasons for needing a new reference spectrum include contamination of the optical components of the sampling accessory, poor sample filtration, large temperature variations, changes in sample homogeneity, maintenance of the instrument, etc.

With clean products such as para-xylene, benzene, toluene, etc., where no deposit or contamination appears in the optical path of the sampling accessory, a reference spectrum can be use for months: typically 4 to 6 months in a fixed process-control industrial application.

In other applications where the sample can deposit contamination on the optical components of the sampling accessory, a new reference spectrum may be required for each measurement.

In many cases, the system is programmed to automatically purge the sampling accessory and acquire a new reference spectrum on a periodic basis. The frequency at which a new reference spectrum is acquired must determined for each specific application.

4. CALIBRATION DEVELOPMENT

4.1 Spectrometer calibration

One of the keys to quantitative analysis using a spectrometer-based analyzer such as the FTPA2000-200 is the relationship between the data (spectra) acquired by the instrument when analyzing samples, and the properties of the constituents of interest in these samples. The goal of calibration is to determine an equation, or a series of equations, which represents this relationship. When applied to the spectrum of an "unknown" sample, these equations should accurately ***predict*** the **properties** of these constituents. The set of equations is known as a ***calibration model***, or simply, a ***model***, and the process of defining a model for a particular application is called ***calibration***.

One step in calibration is the preparation of a ***training set*** or ***calibration set***. A set of standard samples is prepared which cover the ranges of properties expected, as well as any other variations that may affect the spectra, such as temperature or alignment. Each sample is then analyzed using a very precise ***primary method***[f], such as GC (gas chromatography) or wet chemistry, to determine the exact properties of the constituents of interest. This is referred to as **sample calibration** or ***primary value determination***.

[f]Samples which are analyzed by the primary method are sometimes called "calibrated samples", and the corresponding spectra "calibrated spectra".

The primary method is sometimes called the "reference method" or simply the "reference". This is not to be confused with the reference spectrum.

A spectrum of each standard sample is also analyzed using the instrument. The training set consists of the properties measured by the primary method and of the data (spectra) acquired by the instrument.

Once the training set is complete, the equations that make up the model are calculated using a PLS software package. During the calculations, various ***preprocessing*** algorithms are applied to the spectra in order to make any necessary corrections to them (see Section 4.3). The set of all preprocessing algorithms used is called the ***method***.

4.2 Stability

Stability of the entire system is very important during calibration and analysis. All analyzers based on ABB's Michelson-series spectrometers are very stable. However, the stability is also a function of the environment. High precision calibration may require temperature control of the sampling system to within a few degrees. Some environmental variations can be compensated for by preprocessing algorithms in the method, such as baseline correction and normalization.

Figure 4-1 shows the average of 50 ***interferograms*** (upper trace), and the corresponding standard deviation (lower trace). As we can see, the region close to the ***ZPD*** (zero path difference) shows the greatest variation between scans (highest standard deviation). This part of the interferogram corresponds to slowly varying features such as source intensity variations and environmental parameters. Away from the ZPD, the standard deviation drops to a very low value. This means that, except for the ZPD region, there is very little difference

between one interferogram and the next. This gives an indication of the high stability of the instrument.

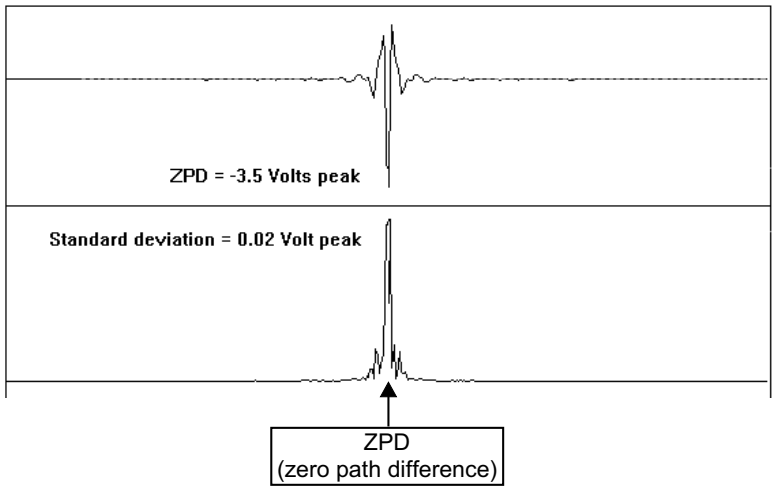


Figure 4-1. Variations in the interferogram (50 scans)

4.3 Preprocessing

A number of different preprocessing algorithms can be included in a method. These include spectral scale correction, spectral region selection, baseline correction, normalization, mean centering, derivative, data reduction, etc. The following sections describe some of the algorithms used.

Note: The same method must be applied to each spectrum in the training set during calibration and to each unknown sample spectrum during analysis.

4.3.1 Baseline correction

Baseline variation in the spectra is not of concern as long as it is possible to correct this variation by a straight line, or a series of straight lines, each defined by a slope and an offset. This is a standard preprocessing algorithm used in calibration.

4.3.2 Spectral scale correction

Spectral scale correction, or frequency correction, is performed to ensure the accuracy of the analyzer's frequency scale calibration.

[g]*SPECTEST is a utility program which measures the frequency scale accuracy of a ABB FT-IR spectrometer.*

Spectral scale correction is based on the results of the SPECTEST[g] test. A sharp water vapor line around 7300 cm^{-1} is used as a standard. The spectral correction calculated with SPECTEST must be applied to all spectra. We recommend applying the correction to the transmission spectra, to prevent introducing

artifacts due to absorbance saturation. Absorbance is calculated, then corrected, using a transmission spectrum.

Figure 4-2 gives an example of such a frequency-corrected calibration spectrum: para-xylene (approximately 85%), toluene (approximately 1%), and a mixture of meta-xylene, ortho-xylene, benzene, and many non-aromatic compounds. The optical path is 6 mm.

Note: With FT-IR and FT-NIR, the frequency shift is defined by the throughput of the accessory or the alignment of a fiber relative to the optical axis. It is set once and for all when the system is assembled. It is necessary to check it only after maintenance as a QA (Quality Analysis) procedure.

The spectrum shown in Figure 4-2 indicates that the absorbance is less than zero where there is no signal. This is because the reference spectrum was acquired with an empty cell. There were two more Fresnel reflections on the window's surface in the empty cell than there were in the cell filled with the liquid. This is because the liquid matches the index of refraction of the window's material, thus removing the two inner Fresnel reflections.

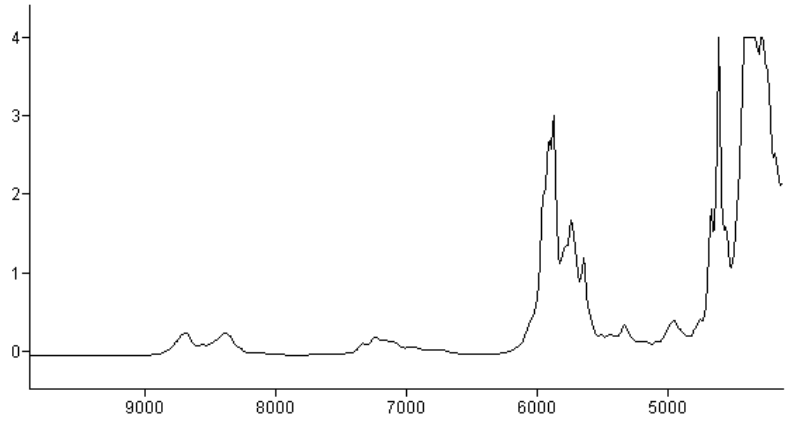


Figure 4-2. Para-xylene process stream

4.3.3 Spectral region selection

[h]Theoretically, the best performance is achieved when the absorbance is at 0.43 (which corres-ponds to a transmittance of 37%).

In many cases, only certain regions of the spectra are selected for use in the analyses. The selection of the spectral regions is very important step in calibration and is done by a spectroscopist. Since noise can induce a considerable error in both high and low absorbances, best results are often obtained by selecting regions where the absorbance is above zero but below one absorbance unit[h], the optimal range being defined by the signal-to-noise ratio in the transmittance domain.

It is also good practice to avoid using regions where the slope is very high, such as those close to a saturation region. These regions are very sensitive to alignment and temperature variations. Refer to Part 2 of this manual for an example involving spectral region selection.

4.3.4 Normalization

Normalization prevents measurement errors due to factors such as variations in cell path length following maintenance, or changes in density due to temperature variations.

Normalization can be achieved in different ways. In the example of Figure 4-2, normalization can be based on the total absorption band of the C-H second overtone and combination region of hydrocarbon (9200 cm^{-1} to 7850 cm^{-1}). The spectrum is normalized by integrating the baseline corrected region and dividing each point in the spectrum by the result of the integration.

The C-H second overtone and combination region is selected because it contains the signature of each product in the mixture and the absorption cross section is equivalent for all hydrocarbons. However, the C-H second overtone and combination bands are relatively weak. This means that, after normalization, some important regions may be saturated and will not be used in the calibration.

Note that noise must be relatively low in the region selected as the basis for normalization. Before integrating the spectral region, a two-point baseline correction (averaged on 50 points) must be performed on the selected region. Each end of the region is selected for the baseline correction. The region is then offset in order to set both limits to zero absorbance.

Figure 4-3 shows the baseline corrected region of Figure 4-2 as well as the result of the integration.

The process of normalization (baseline correction and integration over the selected region, then division of each point in the spectrum by the integration results) is repeated for each spectrum in the calibration and for each sample spectrum.

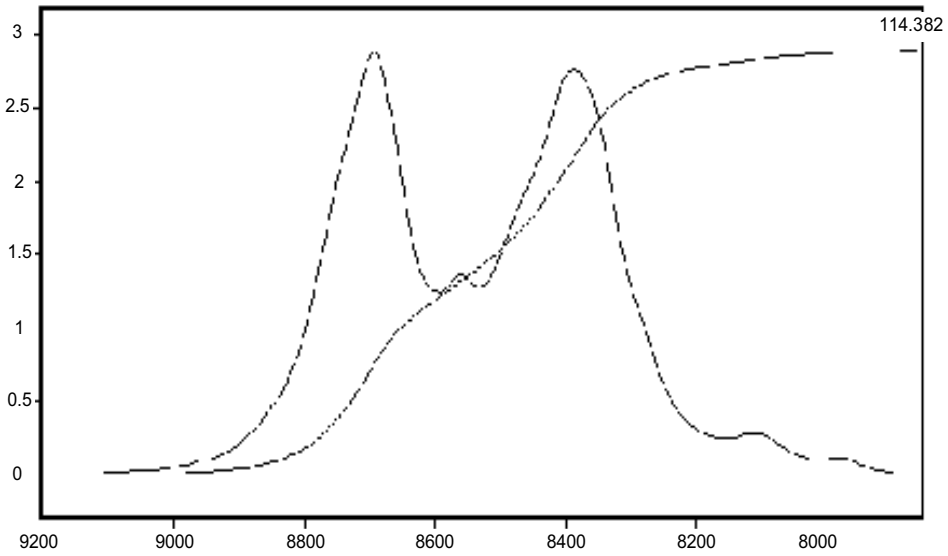


Figure 4-3. Normalization factor by integration

Dividing each point of the spectrum in Figure 4-2 by the results of the integration yields the normalized spectrum shown in Figure 4-4. Note that the shape of the spectrum has not changed, but the absorbance scale values have.

Note: If the method includes normalization, each spectrum used in the calibration, and each sample spectrum, must be normalized using exactly the same procedure. Adding unnormalized spectra to the calibration may cause a dramatic increase in the spectral residual F-ratio[i].

[i]The spectral residual F-ratio is a spectral quality indicator which can help detect whether an abnormal condition has occurred during analysis. Refer to Section 4.7.4 (page 4-15) for more information.

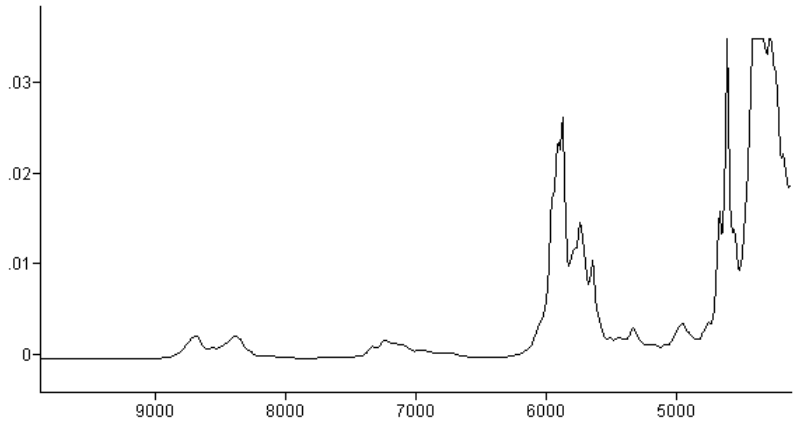


Figure 4-4. Processed spectrum

4.4 Spectral artifacts

***S**pectral artifacts* can have a very detrimental effect on precision and stability. This kind of interference can also have a very important impact on the spectral quality indicator, such as the spectral residual F-ratio.

4.4.1 Channel spectrum

Figure 4-5 shows an artifact often encountered in fiber-optics-based systems. This phenomenon is due to ***Fabry-Perot interference***, also called "***channel spectrum***". It is produced by a gap between two optical surfaces, at a fiber-to-fiber end coupling or a fiber-to-detector interface at the detector end, for example.

Fabry-Perot interference, or channel spectrum, can be detected by performing a spectral derivative on the reference spectrum or on the absorbance spectrum. Since this is a high frequency[j] phenomenon, it will appear amplified in the derivative and will be easier to detect. This is best done on the reference spectrum in a clean region, that is, one without a spectral signature.

[j]Fabry-Perot interference fringes have a high frequency with respect to the horizontal (wavenumber) axis of the spectrum. When present, they appear throughout the entire spectrum and their intensity is proportional to the strength of the signal in the single-beam spectrum.

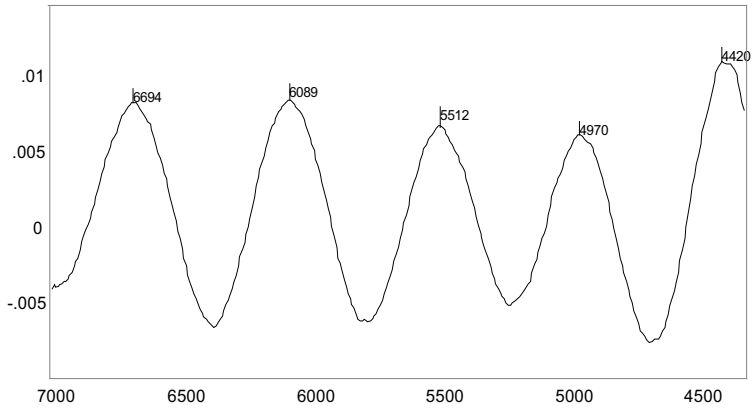


Figure 4-5. Fabry-Perot interference fringes

Although the 10 milli-absorbance level shown in Figure 4-5 is quite small, it can be great enough to generate an F-ratio in the order of 50, as shown in Figure 4-6.

This figure shows how the spectral residual F-ratio varied over time in an application designed to measure the concentration of para-xylene. In spite of channel spectrum, the measurement was relatively accurate because this kind of artifact normally produces only an offset in the concentration reading. In this application, however, the offset varied by more than 0.5% when the ambient temperature varied slightly. This was unacceptable, since the precision required for the measurement was 0.1% at two standard deviations.

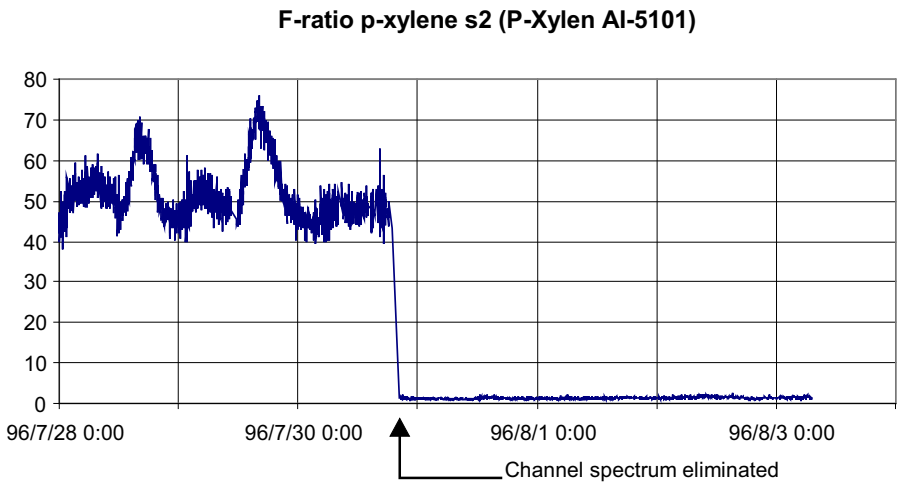


Figure 4-6. Spectral residual F-ratio and channel spectrum

Other spectral artifacts can be induced by non-linearity in the analog section of the detection system, or by a systematic sampling error. Most spectral artifacts produce an offset in the measurement. When an artifact is very stable in time, it can be compensated for by an offset in the prediction algorithm.

Spectral artifacts can be easily detected by looking at indicators such as the spectral residual F-ratio. If the software used for the development of the calibration gives access to the **residual spectra**[k], artifacts will often be easily identifiable in these spectra. In the example above, Fabry-Perot fringes were easily observed in the residual spectra.

[k] *In PLS analysis, the term "residual spectrum" refers to the point-by-point difference between the original absorbance spectrum and the reconstructed (predicted) spectrum. Refer to Section 4.7.3 (page 4-15) for more information.*

It may be necessary to use optical index matching gel on the fiber tips and at the fiber optic launcher to prevent channel spectrum. For more information, refer to *Using fiber-Optic Cables* (Part No. IMZ8416).

4.4.1.1 Estimating the gap size

In the case of Fabry-Perot fringes, the size of the gap is a good indicator of the source of the problem. If the size is only a few microns, the gap is probably in one of the fiber-to-fiber interfaces. The size of the gap generating the fringes can be estimated from the period *p* (distance between two successive maxima). You can also use the distance *d* between *N* maxima in the calculation, as shown in Equation 4-1.

$$g = \frac{1}{2 \times n \times p} = \frac{N}{2 \times n \times d}$$

Equation 4-1. Channel Spectrum Gap

where:
- g is the gap size in centimeters
- n is the index of refraction of the material in the gap
- p is the period of the Fabry-Perot fringes in wavenumbers (cm^{-1})
- N is the number of fringes occurring over a range of wavenumbers
- d is the difference in wavenumbers between the first fringe and the last one.

Using the four fringes in Figure 4-5, for example, if the index of refraction is 1 (air gap), the gap size is:

$$g = \frac{4}{2 \times 1 \times (6694 - 4420)} = 8.8 \times 10^{-4}\,\text{cm} = 8.8 \text{ microns}$$

Figure 4-7 shows a plot of this equation using one fringe and an index of refraction of 1 (air gap). If the material in the gap has a different index of refraction (e.g. 1.54 for glass), divide the gap indicated by the graph in Figure 4-7 by the index. If more than one fringe are used for the calculation, multiply the indicated gap by the number of fringes used.

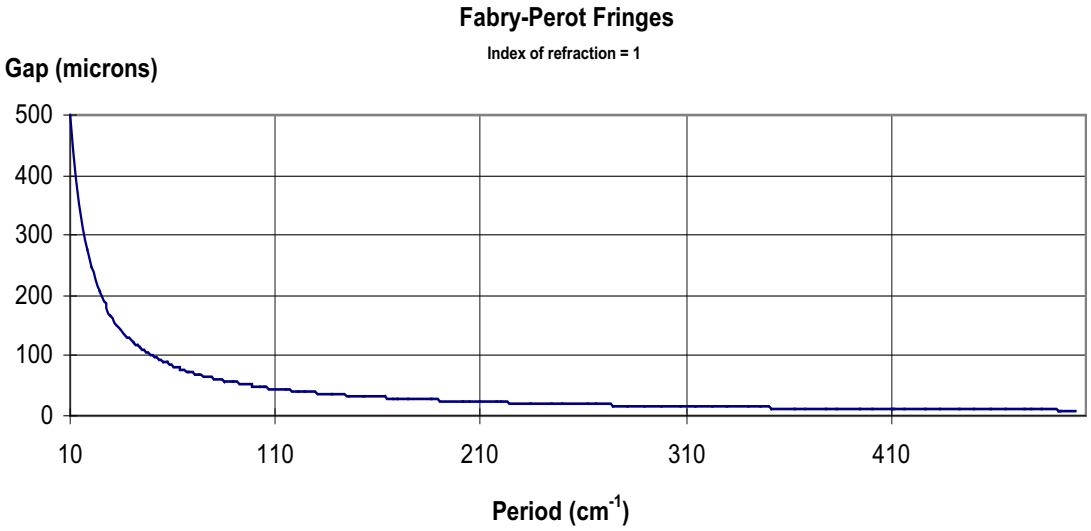


Figure 4-7. Channel spectrum for air gap (n = 1)

4.5 Startup calibration

Calibration requirements are a function of the precision, the range of measurement, and the complexity of the mixture to be analysed. In some applications, the startup calibration may be good enough to give the required precision. Other applications, where the precision requirements are high, will require fine tuning when process, environmental, or sampling conditions change.

The startup calibration can be achieved in two ways:

- in a laboratory with controlled samples representative of the process, or
- on-line (field) calibration directly at the process with the installed system.

In both cases, you must grab samples, analyse them using a primary method, and define a representative training set. You must also set the frequency scale of the spectra, and determine physical parameters such as temperature, pressure, etc.

For laboratory calibration, the spectra can be acquired after the samples have been analysed and the training set has been defined. For on-line calibration, a spectrum must be acquired at the exact time each sample is grabbed.

It is good practice to coadd longer during the acquisition of spectra for the training set. If noise is low, the calibration will be more precise and there will probably be less noise included in your calibration.

4.5.1 Grab sampling

Grab sampling is used to obtain samples for primary method analysis and is a very important step in preparing the training set. It is widely recognized that

3. REFERENCING (ZEROING) THE ANALYZER

3.1 Need for a reference spectrum

A ***raw spectrum*** from the analyzer contain information not only about any sample present in the sampling cell, but also about the whole instrument—the interferometer, the source, the optical fibers, the sampling accessory, and any contamination present. During an analysis, however, only information pertaining to the sample is of interest. To obtain this information, all information concerning the instrument must be removed from the raw spectrum.

This is accomplished by purging the sampling accessory with a gas or liquid which has no (or a known and stable) absorption in the spectral region of interest, then acquiring a spectrum. This spectrum, called the reference, or zero, spectrum, is stored for later use. Normally, since no sample was present in the sampling accessory, the reference spectrum acquired only contains information about the instrument.

[c]*This is described in Part 3 of this manual.*

Once the reference spectrum is acquired, analyses of the sample can begin. Each raw spectrum acquired of the sample is processed[d] to remove the information contained in the reference spectrum. This yields an **absorbance spectrum**[d] which only contains information about the sample.

[d]*In this manual, the word "spectrum" refers to an absorbance spectrum, unless specifically referring to a different type of spectrum.*

Figure 3-1 shows a typical reference spectrum. Here, the system is equipped with a transmission cell and zirconium fluoride fibers. The cell as well as the spectrometer is purged with dry nitrogen. The detector is an Extended InGaAs detector at room temperature.

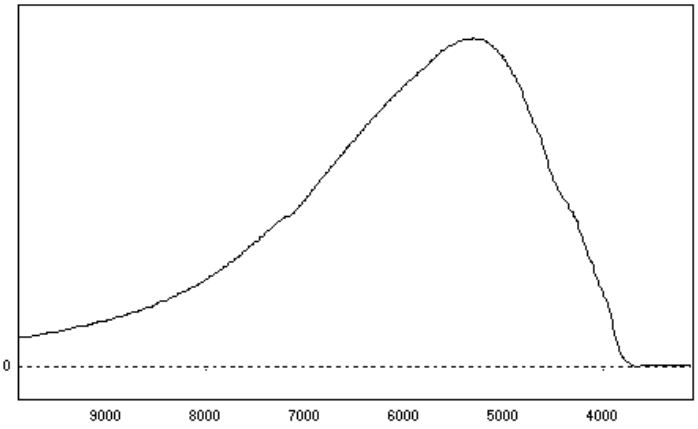


Figure 3-1. Reference spectrum of an FT-NIR spectrometer

Note: The reference and all sample spectra must be acquired with the same resolution, apodization, and spectral line position, etc.

sampling and calibration by a primary method is the main source of error in FT-IR calibration.[a]

It is essential that each sample in the training set be identical to that used to acquire the corresponding spectrum, otherwise some samples may be identified as ***outliers*** in the calibration, or the calibration may be unusable.

Great care must be taken to prevent contamination of the samples. It is also important that the samples be stable both on the chemical level and in their physical phase distribution. For example, emulsions must not evolve between the grab of the sample and the measurement.

If the primary method is not precise enough, the lack of precision may be partly compensated for by increasing the number of samples in the training set. We recommend ten calibrated spectra per ***factor***[1]. Five factors may require fifty calibrated spectra to produce the proper statistics.

[1]The PLS technique analyses all of the spectra in the training set to identify the different variations in these spectra. It then generates a number of spectra, called factors, which represent these variations. Refer to Part 3 for more information.

4.5.2 Defining the training set

The training set must be defined such that the ranges of properties of all products included in the process are correctly represented—even those properties that are not calibrated, including variations in temperature and alignment of the sampling accessory or fiber. You must make sure that no component varies colinearly to an other unless it does the same in the process. Tools such as the correlation function in Microsoft Excel™ can be useful in detecting unwanted colinearity in the training set.

Table 4-1 gives an example of the concentrations used in the definition of a training set. Table 4-2 shows the correlation coefficients between the different products. These show that benzene and toluene are quite collinear, which means that this is not a good training set to discriminate between the two products.

Once you have your training set, you can start to develop the PLS calibration. Refer to the reference manual of the calibration software you have selected.

Benzene	Toluene	Non-aromatic	p-xylene	m-xylene
99.873	0.112	0.012	0.000	0.001
99.875	0.111	0.012	0.000	0.002
99.888	0.094	0.015	0.001	0.002
99.909	0.078	0.011	0.001	0.001
99.913	0.053	0.011	0.001	0.002
99.919	0.068	0.011	0.000	0.002
99.924	0.065	0.011	0.000	0.000
99.935	0.051	0.013	0.000	0.001
99.944	0.048	0.008	0.000	0.000
99.955	0.031	0.011	0.001	0.002
99.964	0.029	0.007	0.000	0.000
99.972	0.016	0.011	0.000	0.001
99.984	0.004	0.012	0.000	0.000

Table 4-1. Table of concentration in training set

	Benzene	Toluene	Non-aromatic	p-xylene	m-xylene
Benzene	1				
Toluene	-0.98	1			
Non-aromatic	-0.45	0.40	1		
p-xylene	-0.21	0.11	0.29	1	
m-xylene	-0.52	0.43	0.53	0.54	1

Table 4-2. Correlation coefficients showing colinearity in training set

4.5.3 Laboratory startup calibration

Startup calibration can be performed on a laboratory unit when representative real samples or synthetic spectra are available. Care must be taken to use optical divergence conditions close to those available on the field system. Spectral water reference lines must be of the same resolution and position. A small shift can be compensated for by software. Sample temperatures must also be within the normal conditions of operation of the field instrument.

A laboratory startup calibration requires validation and fine tuning when installed on the field instrument. The higher the precision required, the greater the amount of fine tuning there will be.

When the mixture is very complex or when the precision requirement is very high, a laboratory startup calibration may not be sufficient or even possible.

When the sample is not stable, it is also more practical to perform a field calibration.

4.5.4 On-line (field) startup calibration

Startup calibration can also be performed with the field instrument. One good approach in the case of the measurement of para-xylene was to grab and calibrate samples every two hours for a week or two, depending on the complexity of the mixture, and to build the calibration with these calibrated spectra.

4.5.5 Controlling the quality of the training set

Various PLS calibration software programs have different tools to control the quality of the training set. First, there is the ***PRESS*** (Prediction Residual Error Sum of Squares). The PRESS is an indicator that helps you select the optimal number of factors to include your calibration. The number of factors will normally be slightly higher than the number of non-colinearly varying properties in the training set. It will also include information about such things as temperature, pressure, or alignment variations.

You must be careful, however, not to include too many factors as this would add information about noise to the calibration. Some PLS packages will suggest a number of factors corresponding to the minimum[m] of the PRESS, while others will suggest setting the calibration to one or two factors before the minimum. The latter case is often better in near-infrared calibration.

[m]As the number of factors included in the calibration is increased, the PRESS will first decrease, then begin to increase. See "How the PRESS is calculated", page 4-12.

Once you have determined the optimal number of factors to include in the calibration, you can look at the prediction report. Here, samples that have a spectral residual F-ratio corresponding to two or three standard deviations[n], depending on the software, will be identified as possible outliers. You may decide or not to keep these samples in the calibration training set.

[n]Refer to the manuals of the PLS calibration development program you are using for the exact criteria used to identify outliers in the training set.

We suggest adding another criterion to the selection of possible outliers, namely, the requirements of the calibration. For example, if a sample shows a spectral residual F-ratio above 3 but less than 15, and the error in concentration is less than or equal to the required precision, it may be better to leave the sample in the calibration.

All samples that you have identified as real outliers must be removed from the training set. You redo the calibration until you get an acceptable result, that is, when no outlier is left in the training set.

Note: Keep all outlier spectra since they may be used later for calibration fine-tuning. They may appear as outliers simply because there are not enough representatives of the same kind to get a good calibration.

How the PRESS is calculated

The PRESS for a given number of factors is calculated by building a calibration model using that number of factors. Then samples of known concentration (usually the training set samples themselves) are predicted using this model. The PRESS is calculated as the sum of the all of the **concentration residuals** (the differences between the predicted and the known concentrations).

$$PRESS = \sum Rc^2$$

Equation 4-2. PRESS

where: Rc are the concentration residuals

Self-prediction versus cross-validation

After building a model using the spectra in the training set, the simplest way to test the model is to predict the spectra in the training set using this same model. This is called self-prediction. It is very easy to perform but not very useful because the predicted samples are the same as the samples used to build the model. As more and more factors are added to the calibration, the PRESS value will continue to decrease and will never increase.

Cross-validation is a much more time-consuming procedure but is much more reliable. With this method, the spectra and concentration values corresponding to the first sample are removed from the training set, and the model is rebuilt with the remaining samples. The factors and PRESS values are recalculated and the removed sample predicted using the new model. Then the sample is returned to the training set, the next sample removed, and the whole process repeated. As each sample is left out and predicted using different numbers of factors, the squared residual values are added to the previously-calculated PRESS values.

The advantage of cross-validation is that is simulates the prediction of unknown samples, and thus better estimates the performance of the model. It also better detects outliers in the training set.

4.6 Fine tuning

After the startup calibration, you can use outlier detection indicators to decide when to grab new samples to complete and fine tune the calibration. This approach normally converges rapidly, and applies to both laboratory and field startup calibration.

The on-line control techniques described in Section 4.7 can also indicate when fine tuning is necessary.

4.7 On-line control

When the system is running, there are different ways of looking at the quality of the analysis performed by the calibration: control and correlation charts, standard deviation estimation, spectral residual, spectral residual F-ratio, prediction, ranges of scores PLS-factors, etc.

4.7.1 Control and correlation charts

Control and correlation charts can be used for controlling the precision and the stability of the calibration even after the initial startup.

Figure 4-8 and Figure 4-9 show these of two tools. Microsoft Excel™ is very well adapted to this kind of control.

[o]The coefficient of determination R^2 is a value used to determine the goodness-of-fit for a linear regression. A value of one (1) indicates a perfect fit.

Figure 4-8 shows a plot of the concentrations predicted by the FT-IR analyzer versus the "known" valued determined by the GC. The fact that the points are all very close to a straight line show that there is good correlation between the two sets of values. The coefficient of determination[o] R^2 is very close to one, which indicates a good fit to a straight line.

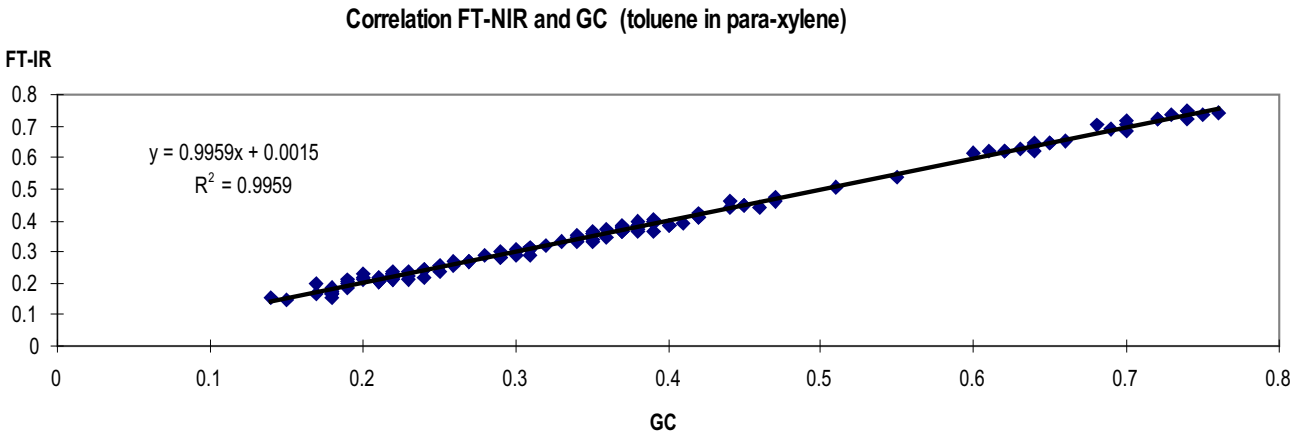


Figure 4-8. Correlation chart

The control chart in Figure 4-9 can be used to detect patterns that reveal systematic errors or time-dependent errors. This is a plot of the difference between the predicted concentration and the known concentration. This difference is known as the **concentration residual**.

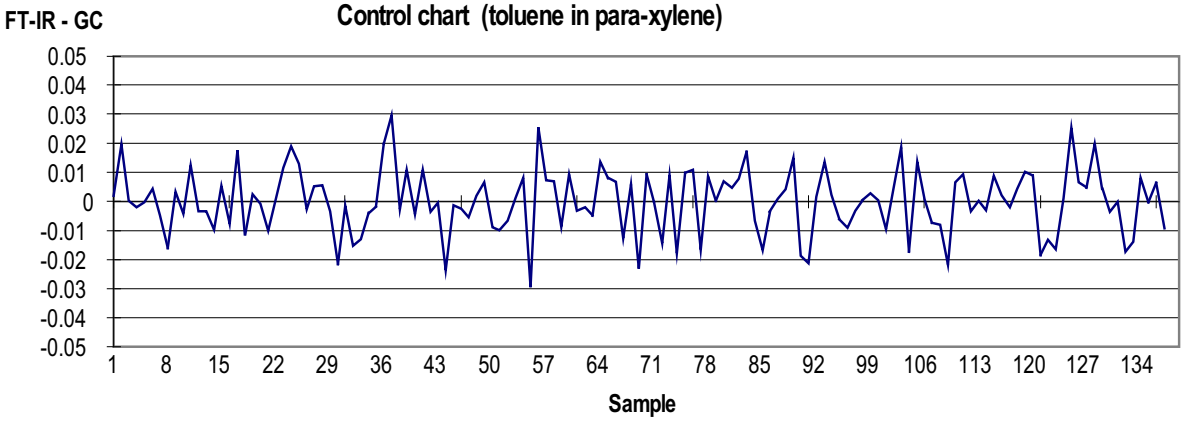


Figure 4-9. Control chart for toluene

4.7.2 Standard deviation estimation

It is very useful to compare the precision of the reading obtained from the FT-NIR system with that of a reference method. The relative precision can be estimated by calculating the standard deviation of the difference between the two readings.

Calculating the standard deviation

The equation used in this case is the one defined for duplicate measurements.[b]

$$s = \sqrt{\frac{\sum Rc^2}{2 \cdot k}}$$

Equation 4-3. Standard deviation (duplicate measurement)

where: s is the estimation of the standard deviation

Rc is the concentration residual (the difference between the FT-NIR reading and the value obtained with the reference method)

k the number of degrees of freedom, that is, the number of samples

Table 4-3 shows an example of measurements taken for standard deviation estimation. In this table, *Rc* is "FT-NIR – GC". All values are in percentage concentration.

Sample	Product	GC	FT-NIR	FT-NIR - GC
Sample File: pxla332	Toluene	0.22	0.2219	0.00192
Sample File: pxla333	Toluene	0.22	0.2396	0.01964
Sample File: pxla334	Toluene	0.21	0.2104	0.0004
Sample File: pxla335	Toluene	0.21	0.208	-0.002
Sample File: pxla336	Toluene	0.21	0.2096	-0.00038
Sample File: pxla337	Toluene	0.21	0.2145	0.00447
Sample File: pxla338	Toluene	0.18	0.1752	-0.00479
Sample File: pxla339	Toluene	0.18	0.164	-0.016
Sample File: pxla340	Toluene	0.18	0.1834	0.0034
Sample File: pxla341	Toluene	0.18	0.1759	-0.00414
Sample File: pxla342	Toluene	0.29	0.3026	0.01262
Sample File: pxla343	Toluene	0.27	0.2666	-0.00336
Sample File: pxla344	Toluene	0.26	0.2567	-0.0033
Sample File: pxla345	Toluene	0.3	0.2903	-0.0097
Sample File: pxla346	Toluene	0.34	0.3453	0.0053
Sample File: pxla347	Toluene	0.34	0.3323	-0.00771
Sample File: pxla348	Toluene	0.35	0.3676	0.01764
Sample File: pxla350	Toluene	0.47	0.4586	-0.01137
Sample File: pxpr31	Toluene	0.31	0.3126	0.00258
Sample File: pxpr32	Toluene	0.3	0.2993	-0.00068

Table 4-3. Calibration control

Performing the calculation yields $s = \sqrt{\frac{0.0015}{2 \times 20}} = 0.0061\,\%$.

4.7.3 Spectral residual

The PLS algorithm analyses an absorbance spectrum by attempting to reconstruct it from the available factors. The original and the reconstructed (or predicted) spectrum, however, are never identical. The spectral residual is a value which gives an indication of how different the two spectra are. The greater the difference, the higher the spectral residual. The spectral residual is therefore a very useful indicator of the quality of the analysis.

Calculation of spectral residual

The spectral residual[p] is calculated as follows. For each data point, the difference between the original and the predicted spectrum is squared, and the squares are summed, as shown in Equation 4-4.

$$Rs = \sum_{k=1}^{p} \left(Aorig_k - Apred_k \right)^2$$

Equation 4-4. Spectral residual

[p] *The term "spectral residual" is sometimes used to refer to the residual spectrum, that is, the point-by-point difference between the original spectrum and the predicted spectrum. In this case, the value Rs calculated by Equation 4-4 is called the "sum squared spectral residual".*

where: Rs is the spectral residual
p is the number of data points
$Aorig_k$ are the absorbances of the original spectrum
$Apred_k$ are the absorbances of the predicted spectrum

4.7.4 Spectral residual F-ratio

The spectral residual F-ratio is a another very useful indicator of the quality of the analysis. The advantage of using the F-ratio is that it automatically contains information about the calibration spectra as well as about the current spectrum. It also provides a more standardized basis for judging the quality.

A high spectral residual F-ratio is an indirect indication of a condition that was not included in the calibration. Table 4-4 shows some of the probable causes of a high F-ratio.

F-Ratio	Probable cause
> 150	• problem with the method or the system • error when adding spectra to the calibration (e.g. adding unnormalized spectra when the method requires normalized spectra)
15 – 150	• spectral artifacts (e.g. channel spectrum)
< 15	• outlier • variation in the process • incorrect frequency scale calibration

Table 4-4. F-ratio values and probable causes

When the F-ratio goes too high, it is good practice to grab additional samples, calibrate them with a reference method (GC, wet chemistry, etc.), and include them in the calibration. Over time, the number of alarms will decrease.

An example of the type of error detected with this indicator is an error in the frequency calibration of the spectrometer. Figure 4-10 shows the error of prediction induced by a line shift due to a spectral frequency calibration error.

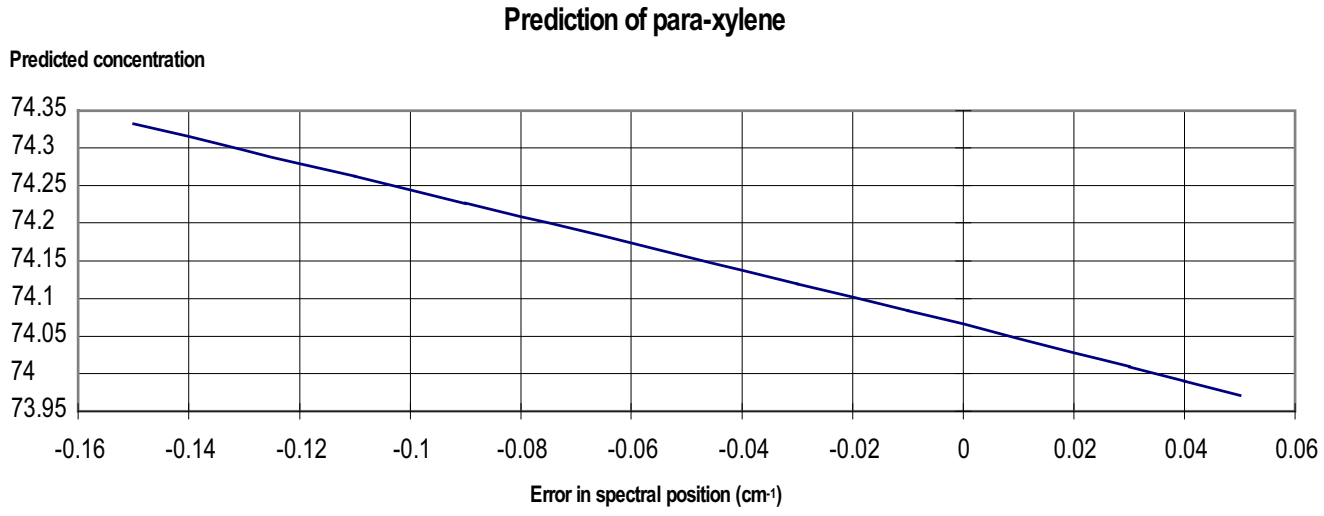


Figure 4-10. Prediction versus frequency scale calibration error

Figure 4-11 shows the corresponding F-ratio. This figure shows that even very small variations in frequency scale calibration are detected with this indicator.

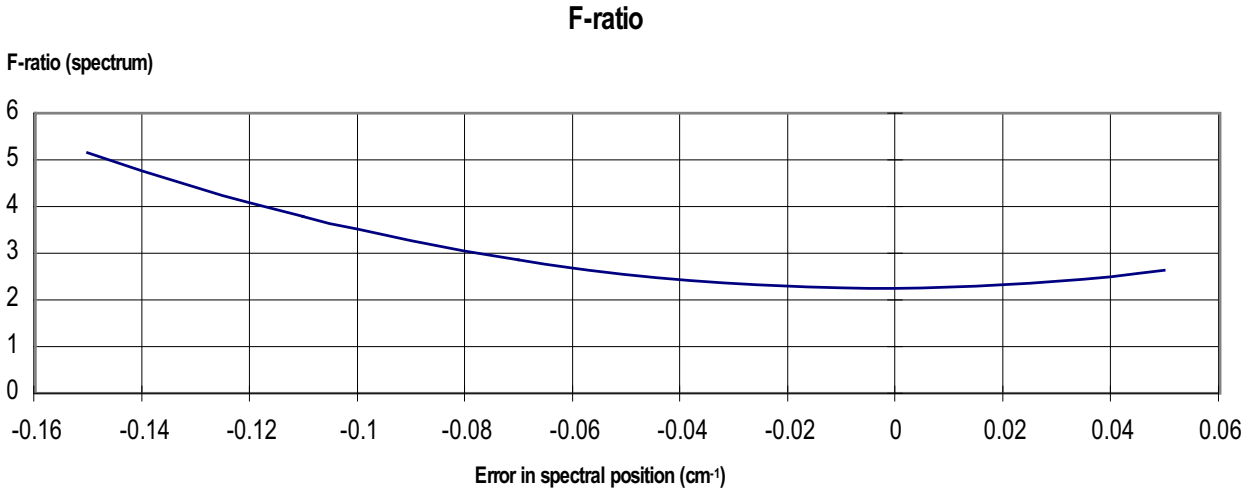


Figure 4-11. Spectral residual F-ratio

Calculation of spectral residual F-ratio

The is F-ratio of a spectrum calculated as follows:

$$F = \frac{Rs}{\overline{Rc}}$$

Equation 4-5. Spectral residual F-ratio

where: F is the spectral residual F-ratio

Rs is the spectral residual, as calculated in Equation 4-4

$\overline{Rc}$ is the mean of the spectral residuals of all spectra used in the calibration

4.7.5 Outlier characterization

Outlier characterization is a very important but difficult task. Many techniques can be used to determine the reason for the outlier.

One technique is to apply a transformation to the spectrum, such as a derivative. This will help identify problems such as channel spectrum.

Another technique is to look at the residual left by the PLS algorithm, if the software used for the prediction gives access to that residual. This will help identify artifacts such as channel spectrum and will also indicate whether the problem is due to artifacts or to an incomplete calibration. This requires the expertise of a spectroscopist, but it is probably the most powerful technique.

If an outlier is identified during a control procedure, it does not necessarily mean that either the calibration or the system is at fault. It may be due to a problem with the primary method (wet chemistry, GC, etc.), an error in manipulation of the sample, an error in sample identification, etc. The indicator implemented in the calibration method may suggest the source of the problem. If the error is in the primary method, then the indicator will not give an alarm.

4.8 Calibration maintenance

Once implemented, the calibration may require maintenance from time to time. Maintenance may be required after the modification of any component in the optical path of the modulated beam, such as the source, the detector, the modulator, or the index matching gel at fiber ends. The need for calibration maintenance can be determined from the alarm indicator used in the method.

Figure 4-12 shows the predicted concentration of para-xylene after a source change. Although the predicted values were still in agreement with the GC reference, the value of the spectral residual F-ratio, as shown in Figure 4-13 was higher than it was before the source was changed.

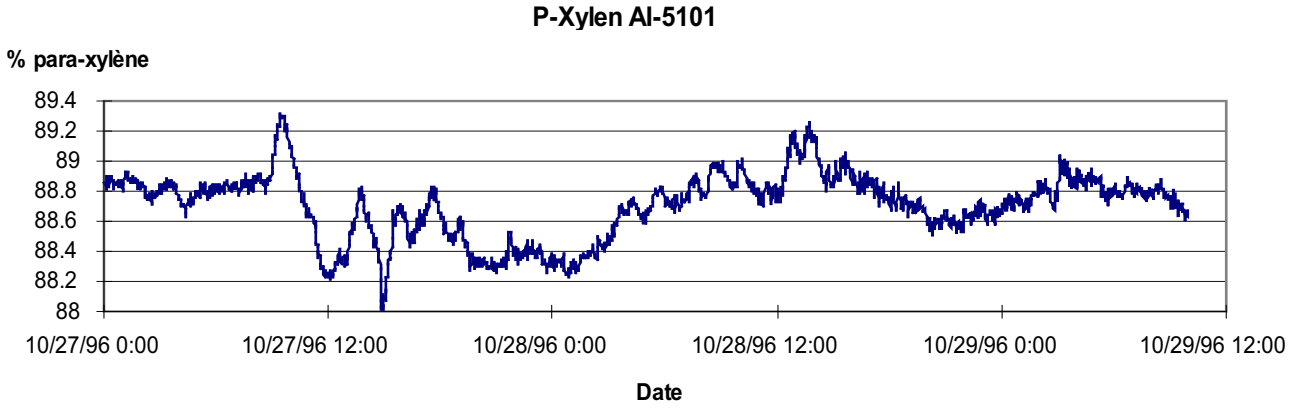


Figure 4-12. Para-xylene concentration after source change

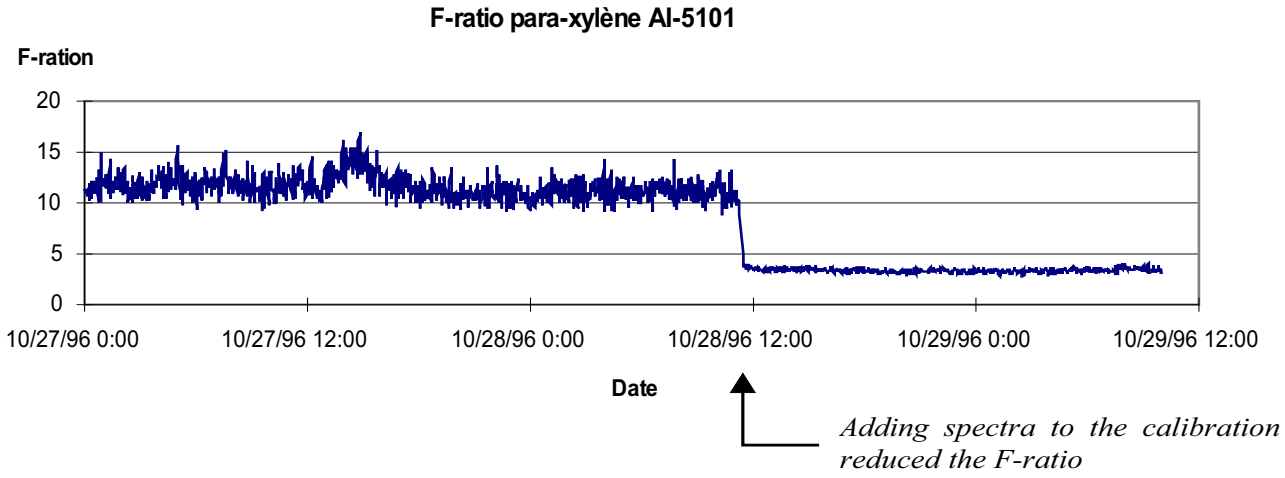


Figure 4-13. F-ratio during maintenance

Calibration maintenance is very simple when the original calibration is correctly done. Figure 4-13 shows how the addition of only 5 calibrated spectra was able correct the system (the original calibration had 130 spectra).

It is not essential to add spectra after a source change, since small differences induced by this maintenance can be corrected by adjusting the offset. However, adding a few calibrated spectra when required by the chosen indicator strengthens the calibration and makes it more robust. This causes new conditions to be included in the model: source temperature, small variations in alignment, new temperature conditions, etc.

4.9 Handling training-set samples

4.9.1 Primary value determination

The primary value determination is probably the most critical part of a calibration. It is recognized in the literature as the main source of error. The primary method should be at least ***ten times*** more precise than the calibration requirement.

The primary method used for this calibration must be checked and calibrated according to the supplier's specifications before starting to calibrate the samples in the training set.

4.9.2 Acquisition of spectra

It is best to acquire spectra under conditions that give very clean results. A signal-to-noise ratio ten times greater than that achievable with the process system should be aimed at for the training set.

4.9.2.1 In the laboratory

IR spectra of calibration samples may be acquired in a laboratory using a bench-top FT-IR. The unit must be adjusted to give a divergence close to that of the on-line process control system. The other characteristics such as linearity, baseline stability, spectral scale, and position, etc. should be identical to those of the process analyzer.

When a calibration is developed using a bench-top FT-IR, it may be necessary to include some calibrated spectra acquired with the on-line system to make sure that the characteristics of the on-line system are correctly included in the calibration.

4.9.2.2 On-line

As for calibration performed with the bench-top lab system, calibration spectra acquired with an on-line system must be characterized in terms of spectral scale and spectral line position. Each channel of a multi-channel analyzer must be considered separately, since they each see a different divergence distribution in the infrared beam.

4.9.2.3 Reference determination channel

A reference determination channel is not required with the ABB FT-IR Spectrometer series of products. The use of such a channel may even be detrimental where high precision is required, since it does not represent the real condition of the sampling loop in either fiber or sampling accessories.

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[a] Statistics in Spectroscopy, Howard Mark and Jerry Workman, Academic Press Inc.

[b] Quality Assurance of Chemical Measurements, John Keenan Taylor, Lewis Publishers Inc.

5. CALIBRATION TRANSFER

With ABB's FT-IR spectrometer series, calibrations can be developed on one instrument, then transferred and used on another instrument without modification or software compensation for instrument differences. This is due to the excellent reproducibility between instruments:

- Toluene absorption is reproducible to ± 0.002 A
- H_2O-line wavenumber is reproducible to ± 0.04 cm^{-1}

Certain precautions must be taken, however, before transferring calibrations, to ensure stability and accuracy of the calibrations.

5.1 Calibration stability

Many different parameters may affect on calibration stability. Spectral position or scale is one that can readily be controlled with the validation tools. Others, such as temperature, sampling conditions (e.g. filtering, flow rate in the sampling cell, and contamination of the optical surface) must be controlled and evaluated for each application, and over time during maintenance. All parameters must be kept within the range defined by the training set.

5.2 Spectrum preprocessing

Some preprocessing is required for maximum performance when transferring calibration between instruments. The correction of the spectral scale is one of them. The resolution, the source temperature, the divergence, the alignment of the system, including the accessories and all other instrument parts, must be controlled within the range required by the calibration training set.

If all these parameters are properly controlled but the error in prediction is greater than it was on the first system, you may be required to add a few representative calibrated spectra to the calibration—three to ten depending on the differences between systems. These new spectra will teach the method what the residual differences are between the systems.

It may happen that systems operate with different apodization functions or different scale definitions. ABB has developed tools over the years that allow you to correct many of these problems. If problems occur, please contact our service department and they will help you apply the correct spectrum preprocessing to suit your needs.

PART 2:
ON-LINE CALIBRATION PROCEDURE

6. ON-LINE CALIBRATION

6.1 Description of example

The calibration procedure presented here is an example of a procedure used to develop a toluene calibration for a process control system in a para-xylene process plant. This type of procedure is used when it is not possible or practical to generate representative samples of the process to be analyzed at the factory before shipping. The procedure presented here provides a very precise and stable calibration, but it takes time to develop.

All procedures and data presented here come from this example. These should help the reader understand the importance of the different parameters used in an on-line calibration.

Figure 6-1 shows a flow chart indicating the calibration procedure. This represents the minimum set of activities required to develop a proper calibration.

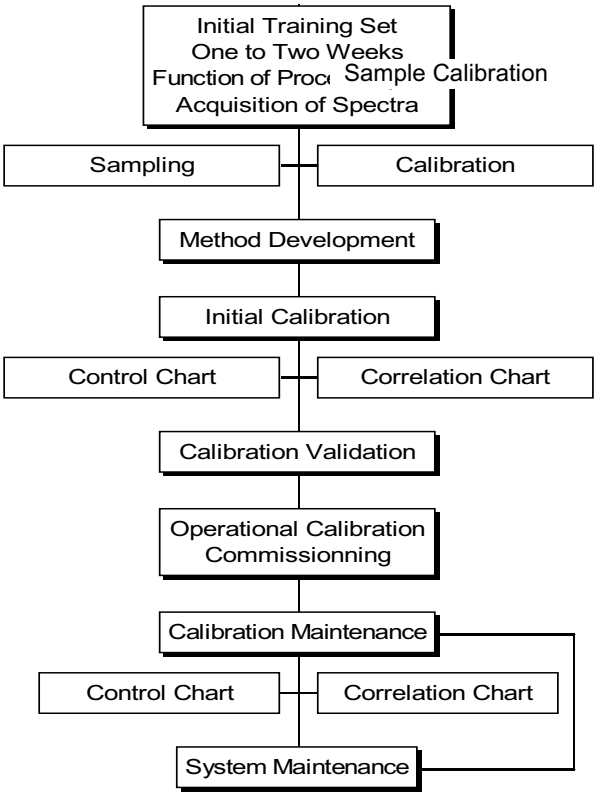


Figure 6-1. Flow chart for on-line calibration

The initial calibration can be developed in one to three weeks depending on how long it takes the process to go through all the variations encountered during normal operation.

Calibration validation can be done within a week or even a few days if enough samples can be calibrated.

It is good practice to gather and keep all calibrated spectra acquired during the validation period to further improve the calibration, even if specifications are already met. Later, some fine tuning may be required as new conditions are encountered in the process or after system maintenance.

Calibration maintenance is easy and will be required less and less frequently over time. The more valid spectra there are in the calibration, the more stable it becomes. Adding spectra allows the PLS algorithm to recognize a larger set of conditions and can correct for variations in the process or in the system.

6.2 Initial calibration

6.2.1 Specifications

Table 6-1 shows the specifications for the analyzer system in this example. The analyzer measures the concentration of toluene in percent.

[q] *This means that the error in the % concentration reading should be less than or equal to 0.1%, 95% of this time. See* ***"****The normal distribution****"*** *page 6-10.*

Concentration range:	0 to 1%
Acceptable error:	Less than or equal to 0.1% at 2 standard deviations[q]
Cycle of measurement:	One minute interval between measurements

Table 6-1. Analyzer specifications

6.2.2 Initial training set

To prepare the initial training set, samples were taken and calibrated (analyzed using a primary method). In this case, gas chromatography (GC) was used as the primary method.

Two GCs were used to measure the concentration of each sample in the training set. The agreement between the two GCs was controlled with an error margin of less than 0.01% thus giving a precision 10 times greater than what was expected from the process system.

A spectrum was also acquired for each sample. Table 6-2 shows the system settings used.

Resolution:	16 cm^{-1}
Corrected position for the 7300 cm^{-1} water vapor line:	7299.98 cm^{-1}
Normalization spectral range:	7850 cm^{-1} to 9200 cm^{-1}
Apodization:	Cosine
Physical absorption path in the sampling cell:	6 mm
Sample temperature:	100ºF
Maximum error in sample temperature:	± 10ºF

Table 6-2. System settings

The acquisition of the calibrated spectra lasted two weeks with one spectrum being recorded every two hours. A sample grabbed from the bypass, leaving the

sampling cell at the same time that the spectrum was acquired by the spectrometer, was carefully identified, sealed in a glass vial and stored in the laboratory. The name of the spectrum was recorded in a table with the date and time.

Each sample was then analyzed with the GC and the results were recorded in the CFL (Calibration File List) of PLSPlus next to the corresponding spectrum. Table 6-3 shows the results.

Spectrum	% toluene	Spectrum	% toluene	Spectrum	% toluene	Spectrum	% toluene	Spectrum	% toluene
U3830148	0.29	U3811633	0.24	U3841328	0.38	U3862107	0.19	U3890104	0.39
U3830339	0.27	U3811925	0.22	U3841529	0.37	U3862234	0.22	U3890253	0.37
U3830528	0.26	U3812117	0.24	U3841915	0.31	U3870043	0.23	U3890440	0.38
U3830715	0.3	U3820008	0.17	U3842104	0.25	U3870249	0.25	U3870701	0.23
U3830924	0.34	U3820124	0.18	U3842306	0.23	U3870435	0.22	U3870911	0.27
U3831131	0.34	U3820421	0.18	U3850124	0.29	U3871513	0.39	U3871317	0.38
U3831330	0.35	U3820655	0.18	U3850353	0.22	U3872115	0.39	U38D0358	0.72
U3831658	0.47	U3820900	0.19	U3850727	0.22	U3872314	0.4	U38D0906	0.7
U3831917	0.31	U3821053	0.19	U3851151	0.28	U3880114	0.37	U38D1520	0.64
U3832140	0.3	U3821255	0.2	U3851500	0.18	U3880353	0.38	U38D1652	0.64
U3810156	0.22	U3821508	0.18	U3851924	0.17	U3880722	0.34	U38E0717	0.6
U3810356	0.22	U3821632	0.14	U3852311	0.21	U3881127	0.35	U38E0830	0.64
U3810556	0.22	U3821928	0.15	U3860354	0.25	U3881428	0.35	U38E0834	0.65
U3810929	0.2	U3822127	0.19	U3860701	0.29	U3881703	0.2	U38E0836	0.66
U3811111	0.22	U3822350	0.51	U3860909	0.3	U3881858	0.22	U38E0840	0.65
U3811307	0.21	U3840424	0.31	U3861148	0.32	U3882055	0.26	U38E1053	0.62
U3811516	0.24	U3841044	0.34	U3861424	0.31	U3882257	0.33	U38E1850	0.47

Table 6-3. Initial calibration training set

The initial calibration covered the range from 0.14% to 0.72% toluene, which represents 58% of the required range shown in Table 6-1.

The original plan was to take a sample every two hours. Operational constraints slightly reduced the number of spectra acquired but the results were still good enough to make the development of the initial calibration possible.

6.2.3 Method development

6.2.3.1 Selection of the spectral region

Note: Selection of the spectral region is normally performed by a spectroscopist.

Figure 6-2 shows a typical spectrum from the calibration training set. The first criterion in selecting the spectral region is to keep absorbance at a low value to avoid errors due to spectral noise. A first limit is set at 0.6 absorbance units; only regions where the absorbance is less than 0.6 should be selected.

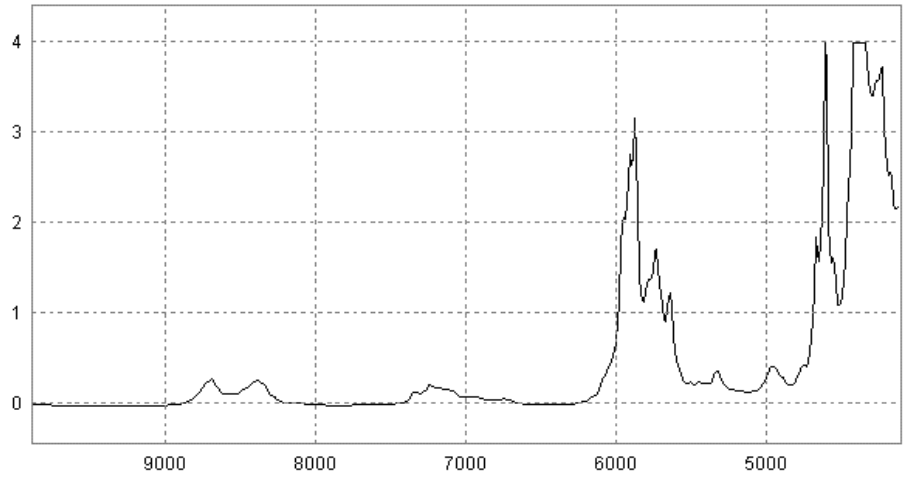


Figure 6-2. Spectrum from the training set

Since spectral regions presenting relatively large slopes are more sensitive to spectral scale errors, another criterion is set based on the derivative of the spectra.

Figure 6-3 shows the derivative of the spectrum presented in Figure 6-2. A threshold of 0.1 is set. Only regions where the derivative is below this threshold should be selected.

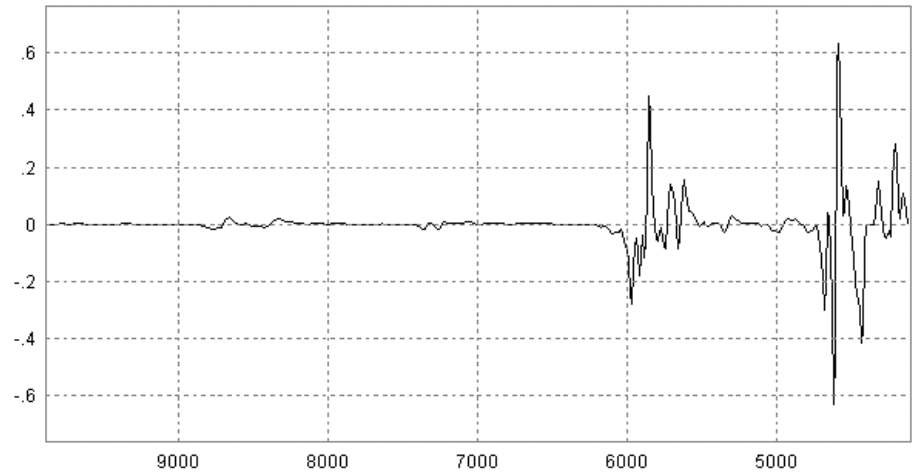


Figure 6-3. First derivative (Savitski-Golay)

The choice of spectral regions can be validated by looking at the correlation spectrum and the determination coefficient spectrum. These can be produced using functions in PLS-Plus™ and PLS-IQ™ from Thermo Galactic Products.

Figure 6-4 shows the correlation spectrum (calculated with PLS-IQ™). This shows the correlation of the absorbance at every wavelength in the training set spectra to the concentrations of the constituents.

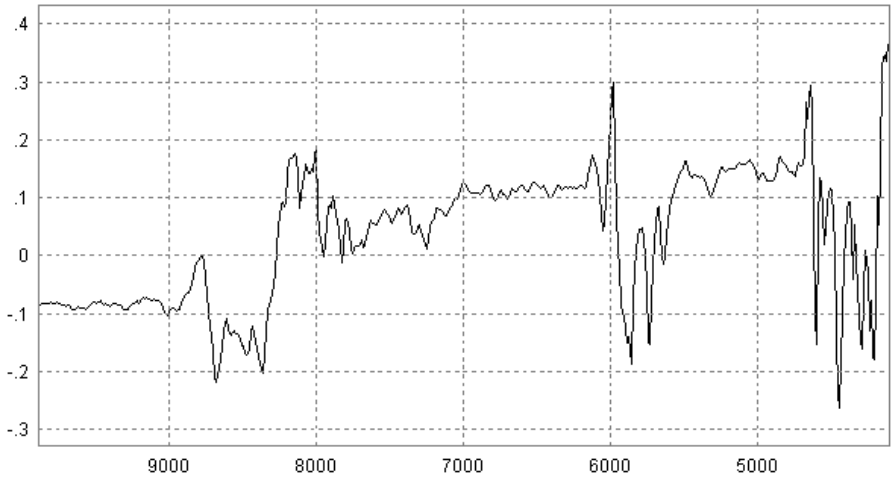


Figure 6-4. Correlation spectrum

[r]The coefficient of determination R^2 is a value used to determine the goodness-of-fit for a linear regression. A value of one (1) indicates a perfect fit.

The determination coefficient spectrum (Figure 6-5) indicates the contribution of each spectral point to the coefficient of determination[r] R^2. In this spectrum, regions with a high value are regions with a high correlation (either positive or negative) between the absorbance and the constituent concentrations. These regions should be selected. Regions with a near zero value are not correlated and can be rejected.

Two regions were finally selected, 9160 cm^{-1} to 6475 cm^{-1}, and 5560 cm^{-1} to 4700 cm^{-1}. Figure 6-6 shows the spectral regions as selected in PLSPlus. These regions are also indicated in Figure 6-7.

The determination coefficient spectrum is produced by squaring each value in the baseline-corrected correlation spectrum.

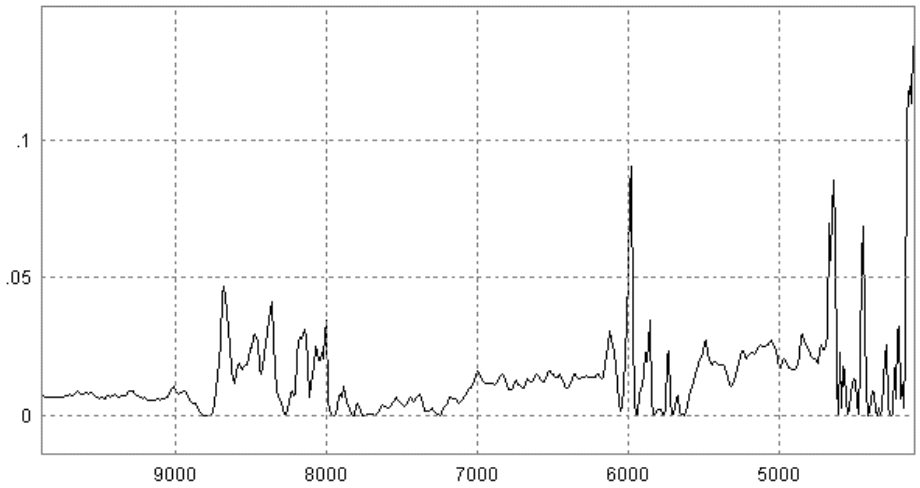


Figure 6-5. Determination coefficient spectrum

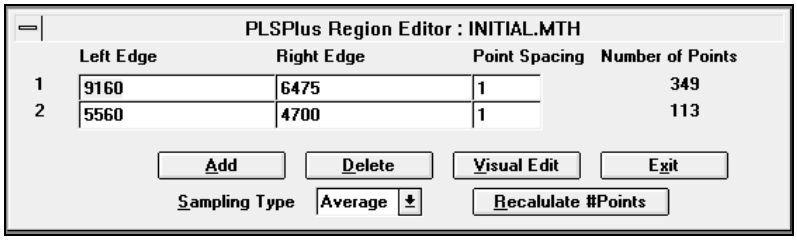


Figure 6-6. Spectral region and weight

Figure 6-7 shows a toluene spectrum along with a spectrum from the training set. It can be seen in the figure that the selected regions contain information about toluene. Since the contribution of toluene to the absorbance will be somewhere between 0 and 1%, the system must be very stable and the method must be very good to reach the required prediction specification.

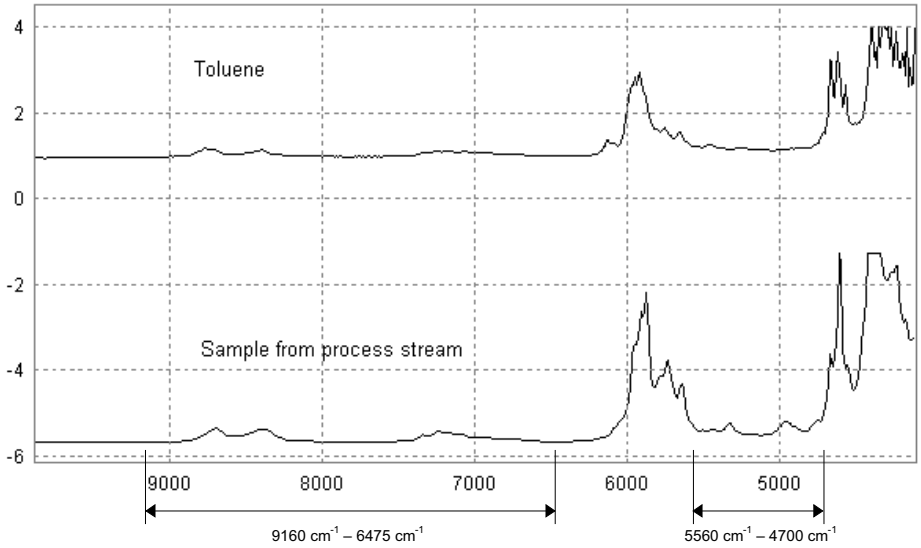


Figure 6-7. Toluene and process spectra, and selected spectral regions

The two spectral regions selected give 349 and 113 points, respectively, that contribute to the determination of the concentration. Since errors add as the square root of the number of measurements, selecting the largest possible number of points, while respecting the above-mentioned criteria, will increase the precision. Tests were performed using other spectral regions for producing a calibration. However, using the regions presented here always gave the best results.

6.2.3.2 Preprocessing

The preprocessing algorithms applied to all spectra in the calibration are as follows:

1. Spectral position correction
2. Spectral normalization

3. Mean centering
4. Base-line correction (linear curve fit without peak)

6.2.3.3 Setting the number of factors

The number of factors will normally be slightly higher than the number of non-colinearly varying constituents in the training set. Additional factors will include information about such things as temperature, pressure, or alignment variations.

After calculating the PRESS value and the PRESS F-ratio for each number of factors, the PLS program suggested using 13 factors for the calibration, as shown in Figure 6-8. The report generated by the GC suggested that this was reasonable considering that the temperature of the sample may be varying over time.

The PLS program suggests using 13 factors. This is indicated by an arrow in the right margin.

F-test on PRESS for Toluene

Factors	PRESS	F Ratio	Probability	
0	1.75747	44.2747	1	
1	1.03668	26.1162	1	
2	.563774	14.2027	1	
3	.425095	10.7091	1	
4	.219276	5.52405	1	
5	.151831	3.82497	.999999	
6	.114917	2.89502	.999988	
7	.0902515	2.27364	.999788	
8	.071235	1.79457	.995804	
9	.0636482	1.60344	.984201	
10	.0557207	1.40373	.93905	
11	.0532021	1.34028	.909135	
12	.0504794	1.27169	.863454	
13	.0429486	1.08197	.640738	<--
14	.0426404	1.07421	.628321	
15	.0396947	1	.5	

Figure 6-8. F-Test on PRESS for Toluene

Determining the optimum number of factors

Figure 6-8 shows the PRESS values for factors 0 to 15 as calculated by a PLS program. The PRESS reaches a minimum at factor 15. The F-ratio for each PRESS value is calculated as follows:

$$F_{ratio_i} = \frac{PRESS_i}{PRESS_{\min}}$$

Equation 6-1. F-ratio for PRESS values

The probability for each PRESS F-ratio is determined using statistical calculations. The program suggests using the number of factors which cause the probability to fall at or below 0.75 (in this case, 13 factors).

6.2.4 Diagnostics

A number of diagnostics techniques can be used to evaluate the initial calibration. The main ones are explained in the following sections.

6.2.4.1 Concentration residual report

[s]*The software program determines the F-ratio of each spectrum in the training set, then calculates the mean and the standard deviation of all the F-ratios. Spectra whose F-ratio is above the mean by more than three times the calculated standard deviation will be identified as possible outliers.*

Figure 6-9 shows the concentration residual report for the prediction of concentrations in the training set. This figure shows the error in the predicted concentration for each numbered training set spectrum. Only one spectrum appears as outlier (on the basis of 3 standard deviations of the F-ratio[s]). This outlier was not removed from the training set since the error (0.07488%) was within the specification of 0.1% at two standard deviations.

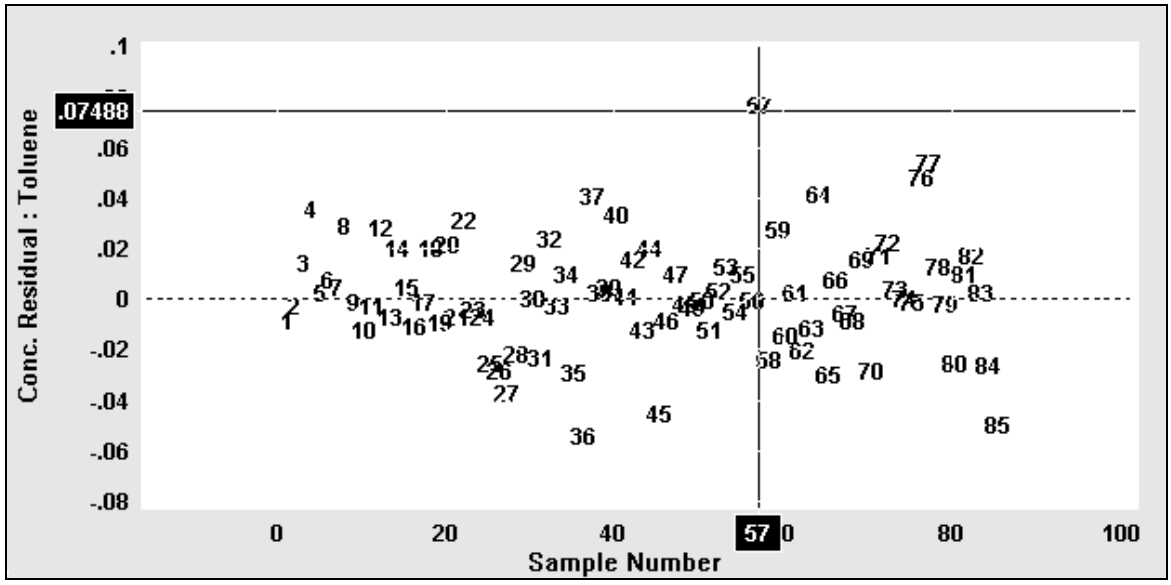


Figure 6-9. Concentration residual for toluene

If outliers are detected outside the specified limits, they should be removed from the training set and the PRESS recalculated to determine the optimum number of factors. This process should be repeated until no outliers are left in the calibration.

6.2.4.2 Correlation chart

[t]*Root-mean-square deviation, another term for standard deviation.*

Figure 6-10 shows the correlation between actual and predicted values (both in % concentration). It also shows the coefficient of determination R^2 which is equal to approximately 0.9756. The RMSD[t] value shown as approximately 0.02% is the **standard deviation** of the concentration residuals.

[u]*See "The normal distribution" page 6-10.*

The error at two standard deviations[u] is therefore 0.04%. Note that this is better than the acceptable error level of 0.1% at two standard deviations given in the analyzer specifications (Table 6-1).

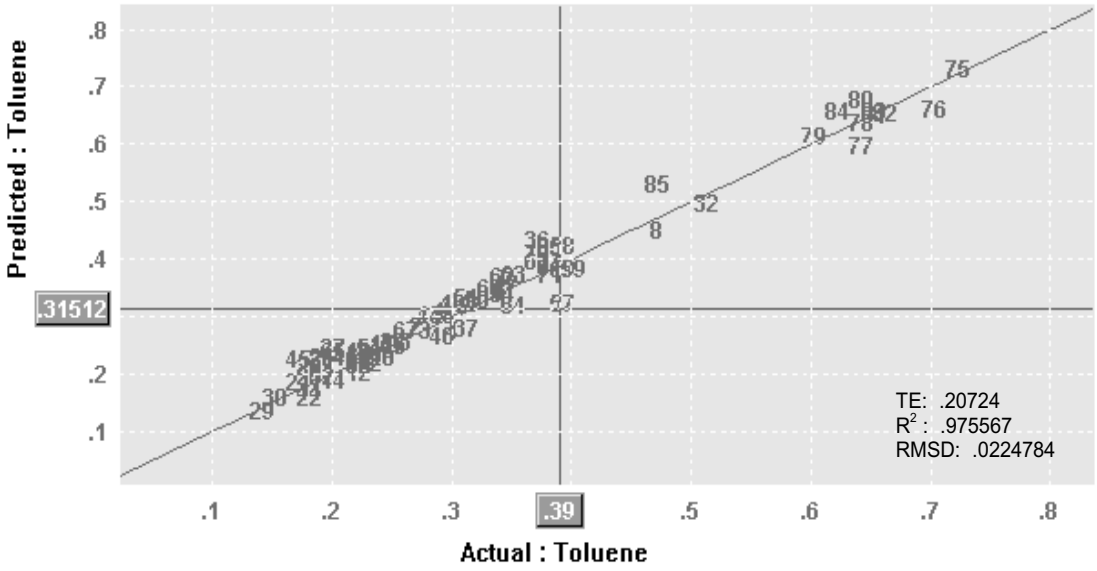


Figure 6-10. Correlation between predicted and actual concentrations

6.2.4.3 Bias histogram

[v]*Because the concentration residual is a random variable, we expect its distribution to be symmetrical and roughly bell-shaped. Since positive and negative errors are be equally probable, it should be centered near zero. (See "The normal distribution" page 6-10.)*

If the distribution is not as expected, a systematic error may be responsible. For example, the primary method may be poorly calibrated, or the samples may be changing chemically between the moment they are grabbed and the time they are analysed by the primary method.

The analysis of the quality of the calibration is completed by looking at the bias histogram shown in Figure 6-11. This histogram shows the distribution of the prediction errors, or concentration residuals. The distribution can be considered close enough to a **normal distribution** to conclude that no detectable systematic errors[v] are included in our calibration. This is important because such errors may indicate a problem with the procedure or the system.

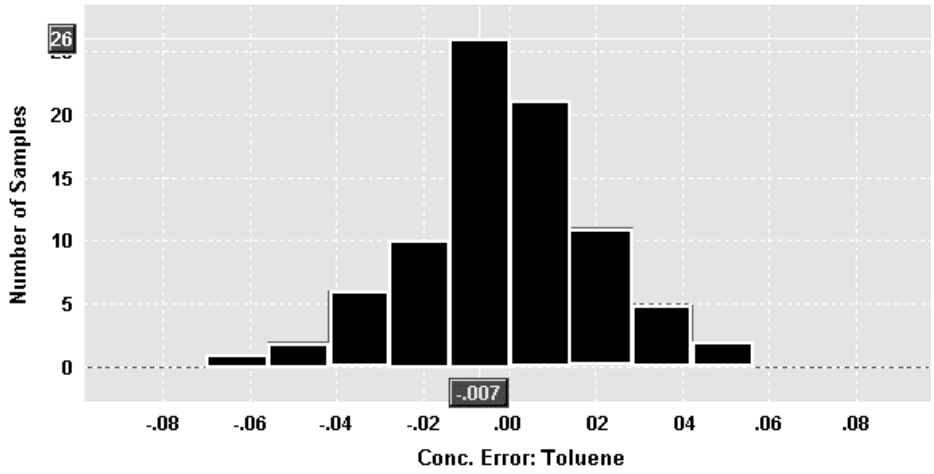


Figure 6-11. Predicted concentration error histogram

The normal distribution

If a large number of samples of a random variable are taken, their distribution tends to be normal. A normal distribution is represented by a symmetrical bell-shaped curve, as shown in Figure 6-12.

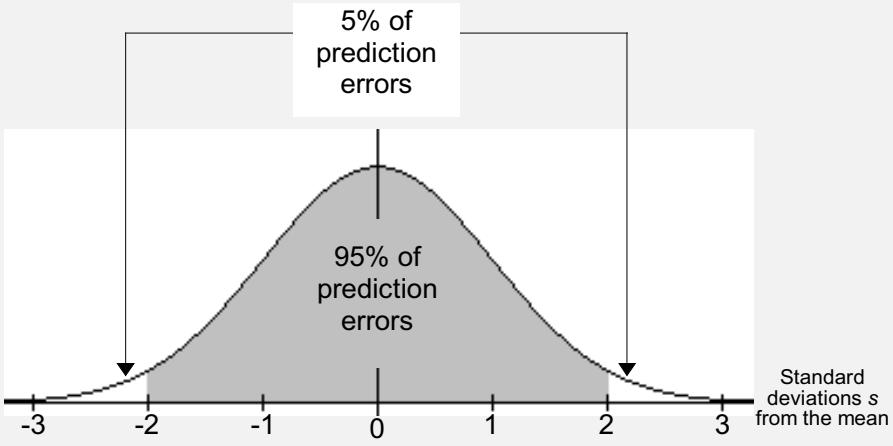


Figure 6-12. Normal distribution of prediction errors

The horizontal axis represents the number of standard deviations *s* of the variable from the mean. Areas below the curve represent probabilities.

In any normal distribution, the area between -2 and +2 standard deviations from the mean (the grey area in Figure 6-12) is approximately 95% of the total area under the curve. This means that the probability that any one value of the random variable will lie within this range is approximately 95%.

The probability that the value will be less than -2 standard deviations or greater than +2 standard deviations from the mean is represented by the white areas and is approximately 5%.

Figure 6-10 indicates that the standard deviation of the concentration residuals (the standard error) for the initial calibration is approximately 0.02%. The "error at two standard deviations" is twice this, or 0.04%. This means that 95% of the prediction errors are within ±0.04%.

6.2.4.4 F-ratio plot

Since we have decided to use the spectral residual F-ratio as an outlier indicator, we can apply the calibration to all spectra in the training set and plot the F-ratio as a function of the sample number (see Figure 6-13).

The *x* scale of the plot gives the sample number; all samples are in chronological order. This plot gives an indication of how well process variations are modeled.

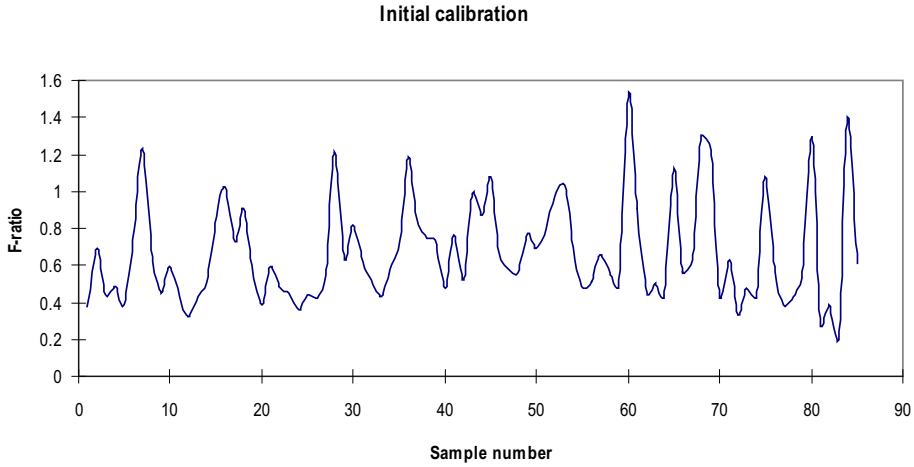


Figure 6-13. F-ratio indicator applied on training set

6.3 Calibration Validation

To validate the calibration, new samples are grabbed and analysed, and their spectra acquired, at the rate of one every two hours for one week. Then this new data, called a **validation set**, is used to produce correlation, control, and indicator value charts. The evolution of the concentration over the period of the validation can also be examined.

[w]*This chart shows the prediction errors for 14 samples. In practice, all of the samples in the validation set will be included control chart.*

The control chart in Figure 6-14 shows the prediction error of some[w] of the samples. This chart indicates that the calibration is working according to specification, since none of these measurements have an error above the specified level (0.1% at two standard deviations).

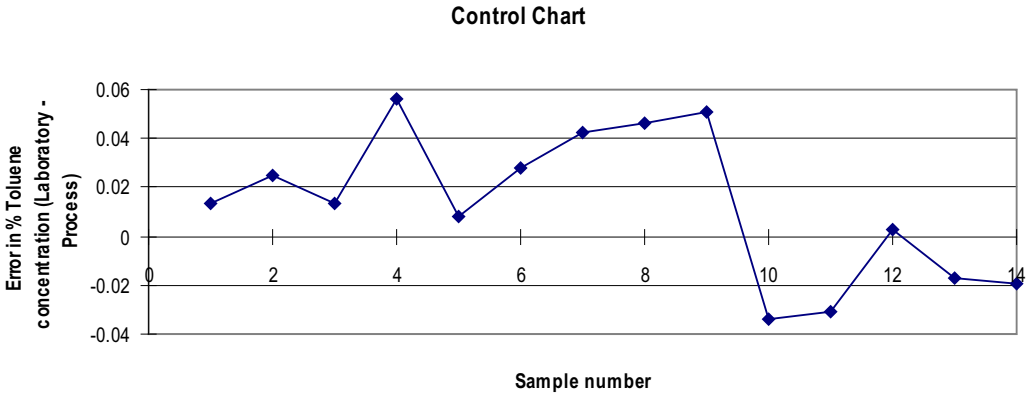


Figure 6-14. Error of prediction (validation)

Table 6-4 gives the values predicted by the calibration and the calculated error in prediction. All values are in percentage concentration. Using Equation 6-2, the standard deviation is then found to be 0.02%. Therefore at two standard deviations the error is 0.04%.

Sample	Actual concentration	Predicted Concentration	Error in Prediction
U38F0312	0.55	0.53661	0.01339
U38N0946	0.39	0.36474	0.02526
U38N1103	0.38	0.36623	0.01377
U38N1107	0.4	0.3439	0.0561
U38N1114	0.39	0.38169	0.00831
U38O1151	0.42	0.39218	0.02782
U38O1157	0.42	0.37768	0.04232
U38O1205	0.42	0.37364	0.04636
U38O1216	0.41	0.35924	0.05076
U38O1626	0.38	0.41394	-0.03394
U38O1628	0.37	0.40063	-0.03063
U38O1630	0.37	0.36729	0.00271
U38O1634	0.37	0.38735	-0.01735
U38O1636	0.37	0.3895	-0.0195

Table 6-4. Actual and predicted concentrations, and error (concentration residual)

$$s = \sqrt{\frac{\sum Rc^2}{2 \cdot k}}$$

Equation 6-2. Standard deviation (duplicate measurement)

where: s is the estimation of the standard deviation

Rc is the concentration residual (the error in prediction)

k the number of degrees of freedom, that is, the number of samples

Although the results are within the specifications, the calibration can be improved by adding the data from the validation set to the training set used to build the calibration.

Table 6-5 shows the new PRESS values and F-ratios. These indicate that the number of factors should be increased to 14 to take into account the additional information supplied by the validation set. A model is built using 14 factors, then the diagnostics tests described in Section 6.2.4 (page 6-8) are repeated.

F-test on PRESS for Toluene

Factors	PRESS	F Ratio	Probability	
0	1.86711	43.8286	1	
1	1.1444	26.8636	1	
2	.726678	17.0581	1	
3	.580018	13.6154	1	
4	.301314	7.07305	1	
5	.240214	5.63879	1	
6	.15367	3.60726	1	
7	.118316	2.77736	.999993	
8	.0941702	2.21056	.999868	
9	.0730922	1.71577	.995764	
10	.063377	1.48771	.974895	
11	.0588368	1.38114	.944329	
12	.0557394	1.30843	.90739	
13	.0508065	1.19263	.807546	
14	.0476113	1.11763	.708733	<--
15	.0441495	1.03637	.569846	
16	.0430097	1.00961	.518665	
17	.0426002	1	.5	

Table 6-5. F-Test after adding validation spectra

The correlation graph, Figure 6-15, indicates that the coefficient of determination R^2 and the error of prediction (RMSD) are stable. (Compare with Figure 6-10, page 6-9.)

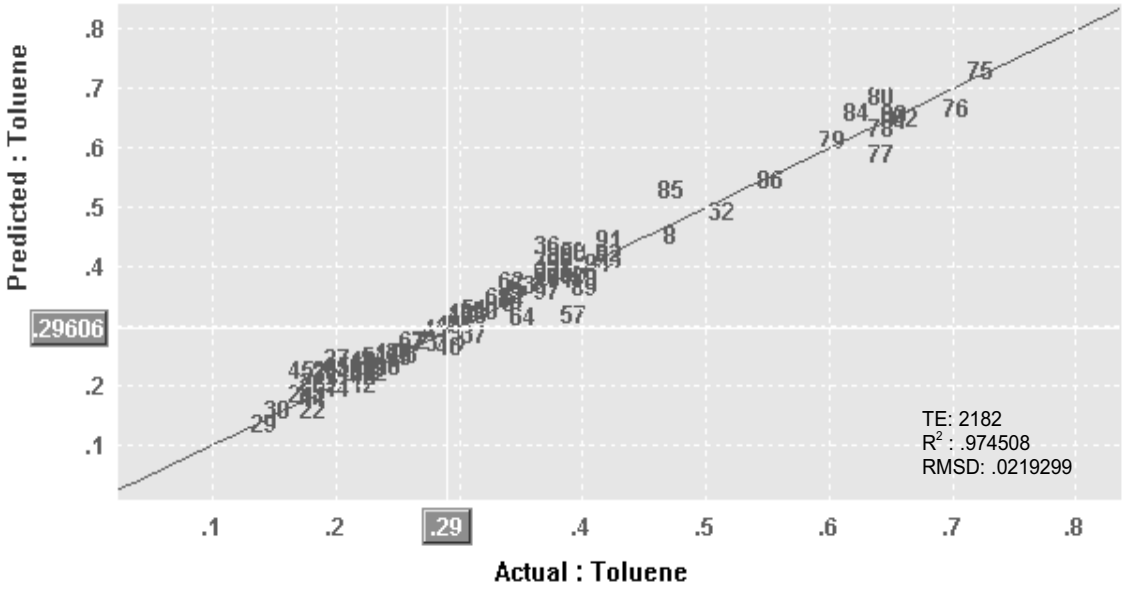


Figure 6-15. New correlation

It was observed that the error of prediction was within the specification when the spectral residual F-ratio was less than or equal to 10. Therefore, the F-ratio alarm for outlier detection was set at 10.

This means that each time the spectral residual F-ratio is above 10, new samples must be grabbed and calibrated with the GC. When enough spectra are available, they will be included in the calibration training set, providing they are not identified as outliers during calibration process.

Over time, as more and more samples are added to the calibration training set, the number of outliers will diminish to a point where the process is correctly modeled in the calibration. When this point is reached, the process of modifying the calibration is stopped. From then on, periodic control and maintenance is performed on the calibration, as illustrated in Section 6.4.

After three weeks, the performance of the system described in this example was accepted. The system was put on-line controlling the process via a 4-20 mA loop feed back, commissioned, and integrated into the feedback loop controlling the process.

6.4 Calibration Control and maintenance

In many cases, a training set acquired over three weeks cannot contain all information about the process. Some conditions may not be covered during such a short period. In this example, grab sampling was continued for a time on a daily basis. Instead of 12 sample analyses a day, however, only one was performed. The data from these samples is called the control set.

In Figure 6-16, the sharp increase in spectral residual F-ratio around sample 100 indicates the point where the NIR source was changed.

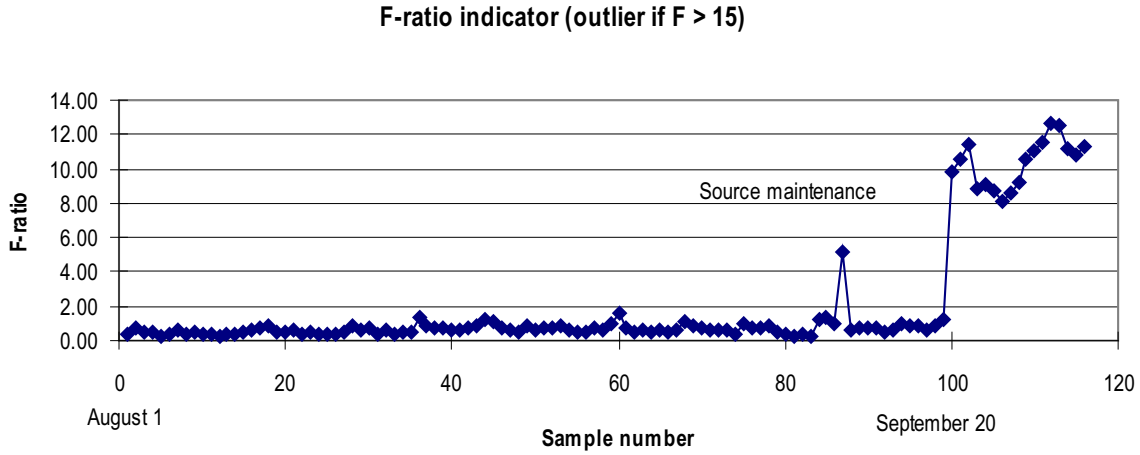


Figure 6-16. F-ratio indicator (4 months of data)

Figure 6-17 shows the error of prediction for the same period. Again, there is a sharp increase in error, beyond the specification of 0.1%, due to source maintenance.

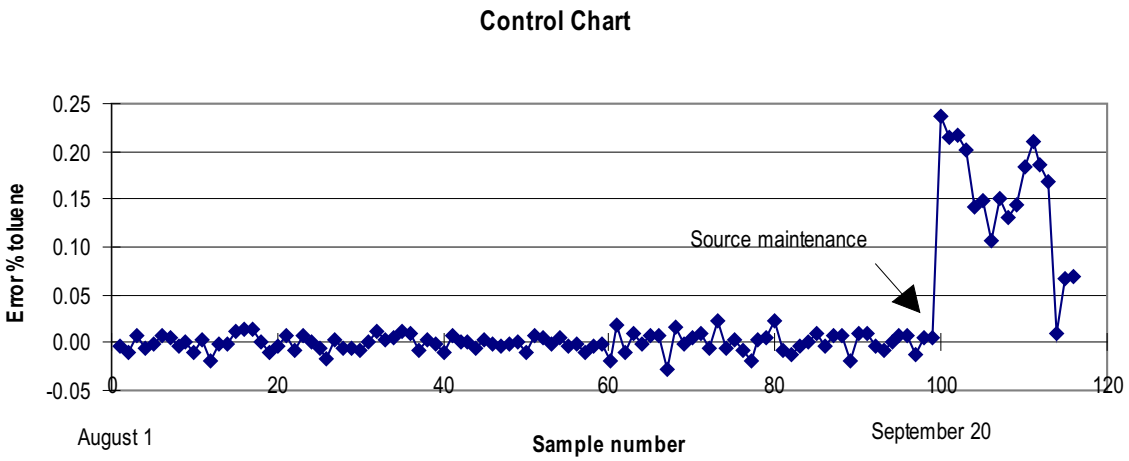


Figure 6-17. Control chart for error of prediction

This control chart indicates that the value of 10 set for outlier detection is too high. We have to reset the value to 10 in order to keep the precision of prediction at or under 0.1% at two standard deviations.

The calibration was improved by adding 5 calibrated spectra from the control set. Figure 6-18 shows how these additional spectra stabilized the calibration outlier indicator. This indicates that the error was due to features already included in the calibration but not correctly represented.

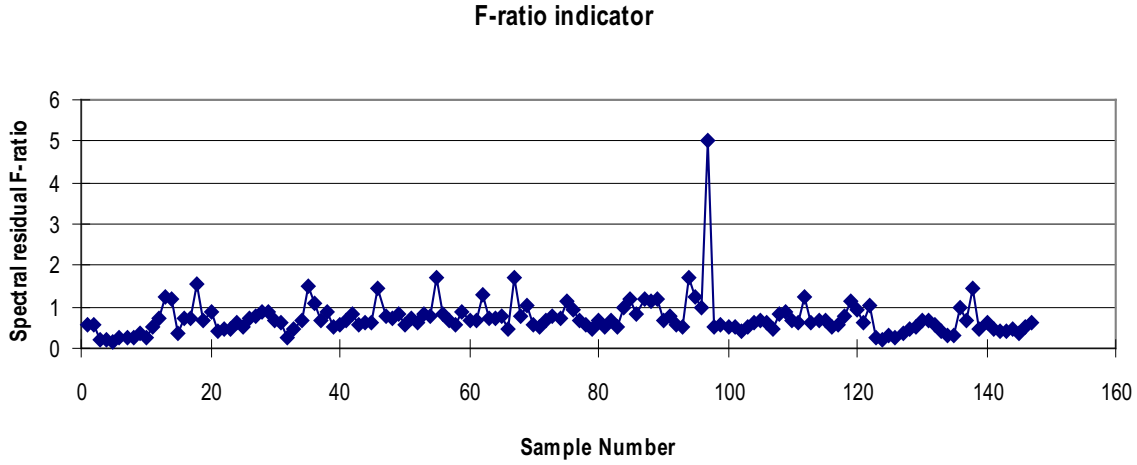


Figure 6-18. F-ratio indicator after adding 5 calibrated spectra

The control chart presented in Figure 6-19 indicates that the precision of the prediction was also greatly improved by adding the five new spectra. (Compare with Figure 6-14, page 6-11.)

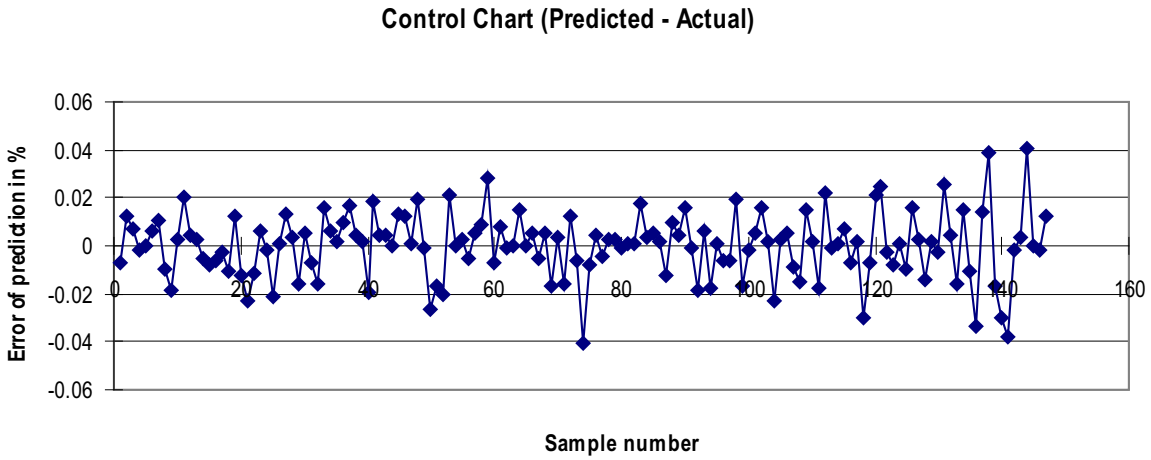


Figure 6-19. Control chart for error of prediction

After adding the new spectra, estimates of the standard deviation of the error of prediction give 0.01%. This is well within the specification of 0.1% at two standard deviations.

The range now covered by the calibration extends from 0.14% up to 0.98%. This is getting closer to the specified range. More spectra can be added to complete the calibration as the process spreads over the remaining range.

Maintenance of the calibration can be scheduled to occur at the same time as the system maintenance, or as required by the F-ratio indicator. In this example, the first system maintenance was scheduled for 6 months after commissioning.

PART 3: SPECTROMETER CALIBRATION

7. BASIC SPECTROSCOPY CONCEPTS

7.1 How light interacts with matter

Light can be considered as photons or as electromagnetic waves. Since light behaves as an electromagnetic wave, we can look at the electric component of its field to understand its interaction with matter.

Matter will be considered at the atomic and molecular level. In spectroscopy, molecules are what interest us. These are made of combinations of atoms.[x] As an example, consider the water molecule shown in Figure 7-1.

[x] *Atoms are the smallest division of basic elements. If an atom is divided into smaller particles (electrons, protons, neutrons), it loses its identity.*

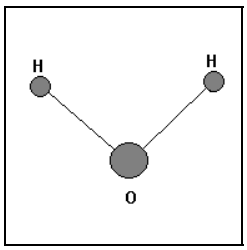


Figure 7-1. Water molecule

One can imagine an elastic link between the hydrogen and oxygen atoms. The link makes the distance and the angle between each atom the same for all water molecules. Since the link is elastic, it can be stretched or bent, but it will oscillate around its normal position. The molecule can also rotate around its center of mass.[i]

The force that ties the atoms together in the molecule comes from the exchange of electrons between the three atoms. The final result is an odd distribution of electrical charges within the molecule. This imbalance of charge is what light needs to interact with the molecule; the electric field of the light wave interacts with the field caused by the odd distribution of charges in the molecule.

This helps explain why symmetric molecules such as nitrogen cannot interact with light. When the distribution of charges is symmetrical, the molecules are transparent to infrared radiation. Only non-symmetric molecules such as water, carbon monoxide, and sulfur dioxide, absorb infrared radiation and can be analysed using infrared spectroscopy.

7.2 Beer-Lambert's absorption law

When infrared radiation passes through a gas, some photons pass through without interacting with the molecules, while others collide with non-symmetric molecules and are absorbed. The proportion of absorbed photons over the total number of photons that enter the gas is in direct relation to the number of absorbing molecules.

---

[i] Infrared Spectroscopy, by Bill George and Peter McIntyre, Analytical Chemistry by Open Learning, John Wiley & Son, 1987.

Figure 7-2 (a) shows infrared radiation coming from the left and passing through a transparent reservoir. The reservoir contains a certain number of absorbing molecules shown as small circles. Some of the photons are absorbed by the molecules, whereas others pass through the reservoir.

If the number of molecules per liter doubles in the reservoir, as shown in Figure 7-2 (b), the number of infrared photons that are absorbed also doubles.

Similarly, if the length of the reservoir (the pathlength) doubles while the same number of particles per liter is maintained, as shown in Figure 7-2 (c), the number of infrared photons that are absorbed also doubles .

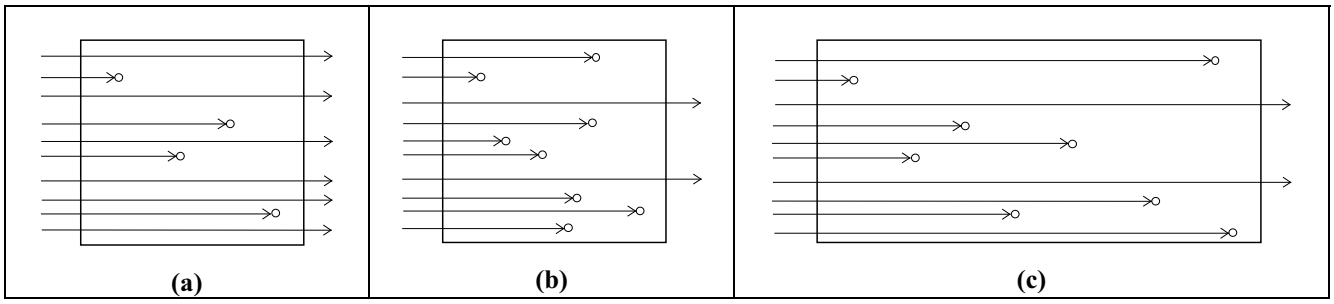


Figure 7-2. Light absorbed by molecules

This is the principle of Beer-Lambert's law.[ii] It describes the absorption of light by molecules by a very simple equation:

$$A_\lambda = \varepsilon_\lambda \times b \times C$$

Equation 7-1

For industrial applications, the concentration C is often given in percentage volume.

The pathlength b can be only a few millimeters long for highly absorbent materials, or up to many meters long for gasses.

where A_λ is the sample's absorbance value at a specific wavelength (λ)

ε_λ is the absorption coefficient of the material at that wavelength

b is the pathlength through the sample

C is the concentration of the absorbing gas

Because the pathlength through the sample doesn't change in a particular application, and because the value of the absorption coefficient of a given material at a particular wavelength is a constant, the pathlength b and the absorption coefficient ε_λ can be combined into a single constant K_λ. Beer-Lambert's law can then be rewritten as:

$$A_\lambda = K_\lambda \times C$$

Equation 7-2

[ii] Fourier Transform Infrared Spectroscopy, by Peter R. Griffiths and James A. de Haseth, a Wiley-Interscience publication, John Wiley and Sons, 1986.

Figure 7-3 shows a graphic representation of Beer-Lambert's law.

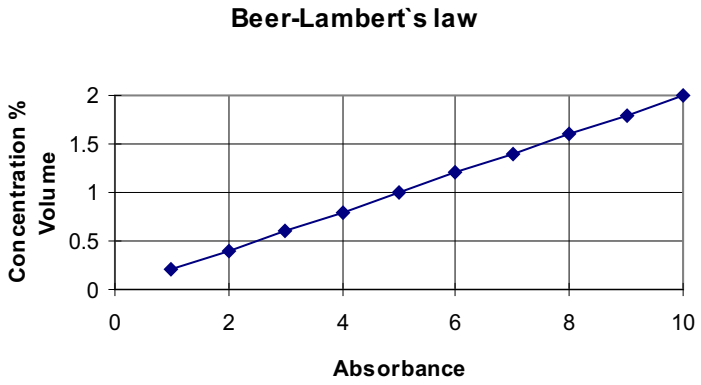


Figure 7-3. Beer-Lambert's law of absorption

By measuring the absorbance of an unknown sample at the appropriate wavelength, one can **predict** the concentration of the sample using Equation 7-3.

$$C = \frac{A_\lambda}{K_\lambda}$$

Equation 7-3

7.3 Spectra

In Section 7.2, the absorbance at a single wavelength is used in Beer-Lambert's law to predict the concentration of an unknown sample. However, the absorbances at many different wavelengths are often used. Since the absorption coefficient has a different value at each wavelength, the absorbance also varies with the wavelength. In other words, the absorbance A and the absorption coefficient ε of a molecule are both functions of the wavelength, and therefore of the frequency, or wavenumber.

Wavenumbers

In spectrometry, the spectroscopic wavenumber (σ) is usually used as a measure of frequency.

The wavenumber is the number of cycles of a wave in unit length.

The wavenumber is the reciprocal of the wavelength (λ): $\sigma = \frac{1}{\lambda}$

If the unit of wavelength is cm, the unit of the wavenumber is $\frac{1}{\text{cm}}$ or cm^{-1}.

[y]*In absorbance spectra:*

- *the Y-axis (ordinate) is the absorbance (in absorbance units)*
- *the X-axis (abscissa) is the wavenumber (in cm^{-1}).*

An absorbance spectrum is a graph of the absorbance as a function of the wavenumber. Figure 7-4 and Figure 7-5 show two different absorbance spectra.[y]

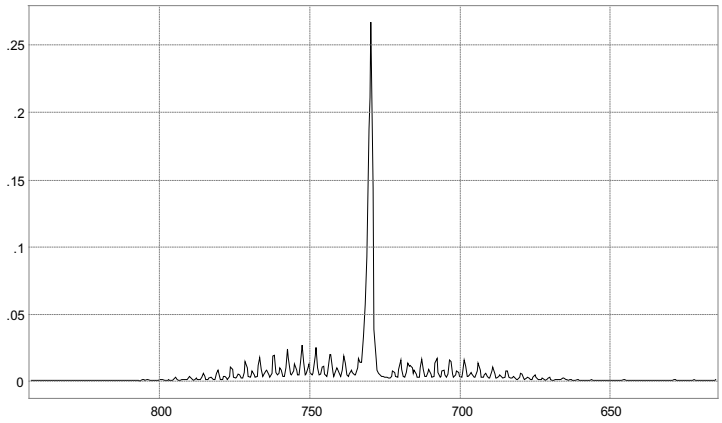


Figure 7-4. Acetylene absorbance spectrum (40 ppm in N_2 at 1 atm.)

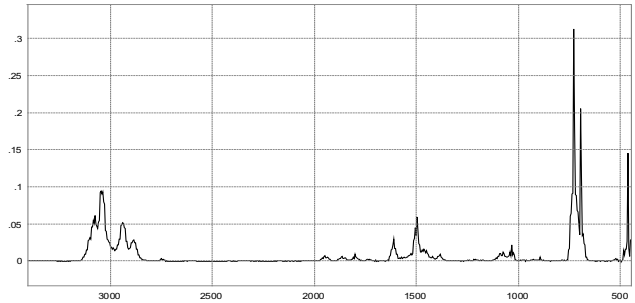


Figure 7-5. Toluene vapor MIR-absorbance spectrum (500 ppm in N_2 at 1 atm.)

[z]*Rotation will normally generate absorption at a low frequency, 10 cm^{-1} to 200 cm^{-1}, while vibration will be seen between 400 cm^{-1} and 2000 cm^{-1}. The stretch of a strong bound like C-H is observed between 2000 cm^{-1} and 4000 cm^{-1}.*

The spectral position of the sharp peaks (absorption lines) or the broad bands are determined by the type of motion[z] or vibration the infrared photon will produce when it is absorbed by the molecules.

The links between the atoms in a molecule are not perfectly elastic. This means there will be bands, called overtone absorption bands, at multiples of the frequency of the fundamental absorption band. Other bands, called combination bands, are also observed.

It is common practice to select certain regions of the spectra to be used for analysis. The choice of the spectral regions is normally determined by physical limitations. For example, if the material is highly absorbing and the pathlength through the sample is relatively long, regions containing overtones or combination bands that are weaker than the fundamental will be used. To detect a very small concentration of a weakly absorbing material, the region containing the fundamental band will be used, because this band absorbs the most.

7.3.1 Finger print

Each molecule has its characteristic spectrum. The region between 400 cm^{-1} and 2000 cm^{-1} is often called the finger print region. This is a spectral region where it is relatively easy to find a unique spectral feature of a given material. It is also a strongly-absorbent region that can be used when the concentration is low, as for gas measurement.

7.3.2 Overtone and combination

For liquids, the near infrared (NIR) part of the overtone and combination region, from 4000 cm^{-1} to 10 000 cm^{-1}, is often used.[iii] Also, this region is often used for the analysis of hydrocarbon-based products.

Figure 7-6 shows a liquid toluene spectrum in this region. The pathlength through the sample was a few millimeters.

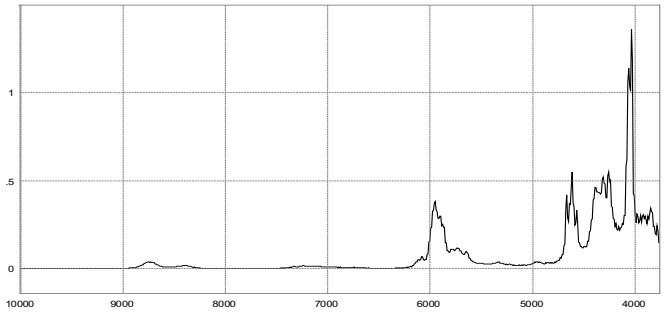


Figure 7-6. Liquid toluene NIR-absorbance spectrum

The spectral structure of this region is, however, very complex and it is often difficult if not impossible to get a specific spectral signature of a chemical compound without interference from other chemical signatures.

[iii] Handbook of Near-Infrared Analysis, edited by Donald A. Burns and Emil W. Ciurczak, Practical Spectroscopy, Published by Marcel Dekker, Inc., 1992.

8. FOURIER-TRANSFORM INFRARED SPECTROMETERS

An FT-IR spectrometer usually consists of a source, a source collimator, a Michelson interferometer, a sample compartment with focusing optics, a detector, and a computer running analytical software, as shown in Figure 8-1.

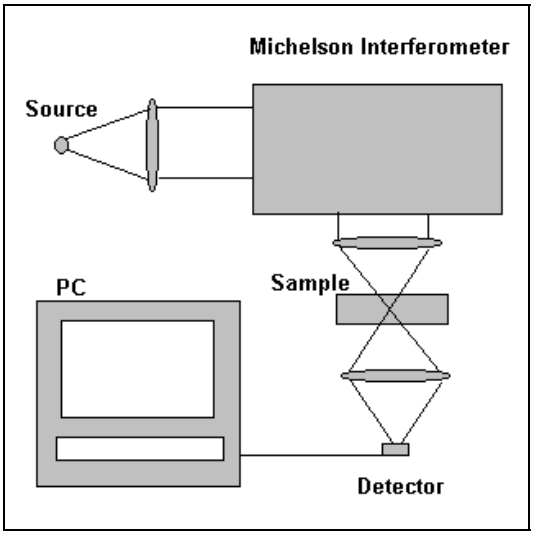


Figure 8-1. FT-IR spectrometers

Some models have no sample compartment located on the spectrometer. Instead, samples are analysed remotely using fiber-optic cables.

Due to their basic principle of operation, Fourier-transform infrared (FT-IR) spectrometers are very precise and stable analytical instruments. Depending on the application, they can work for hours, days, or even months with the same reference spectrum (see Section 8.3).

8.1 FT-MIR and FT-NIR spectrometers

FT-MIR (mid infrared) and FT-NIR (near-infrared) spectrometers are two types of FT-IR spectrometers.

The difference between FT-MIR and FT-NIR spectrometers is mainly in their optical requirements. FT-MIR spectrometers require sources at about 1000K (727ºC) and optics transmitting from approximately 400 cm^{-1} to 4000 cm^{-1}. FT-NIR requires sources at about 2300K (2027ºC) and optics transmitting from approximately 4000 cm^{-1} to 12 000 cm^{-1}. The precision requirement on optical components is more stringent in NIR than in MIR, since the wavelength of the light is smaller.

Note: ABB offers analyzers that cover both optical regions (MIR and NIR) without any modification or adjustment other than selecting the spectral range for the acquisition.

8.2 Michelson interferometer

The heart of FT-MIR and FT-NIR spectrometers is the Michelson **interferometer**. An interferometer modulates light in such a way that the spectral information the light contains can be retrieved.[iv] In its simplest form, the interferometer consists of a fixed mirror, a moving mirror, and a beam splitter (see Figure 8-2).

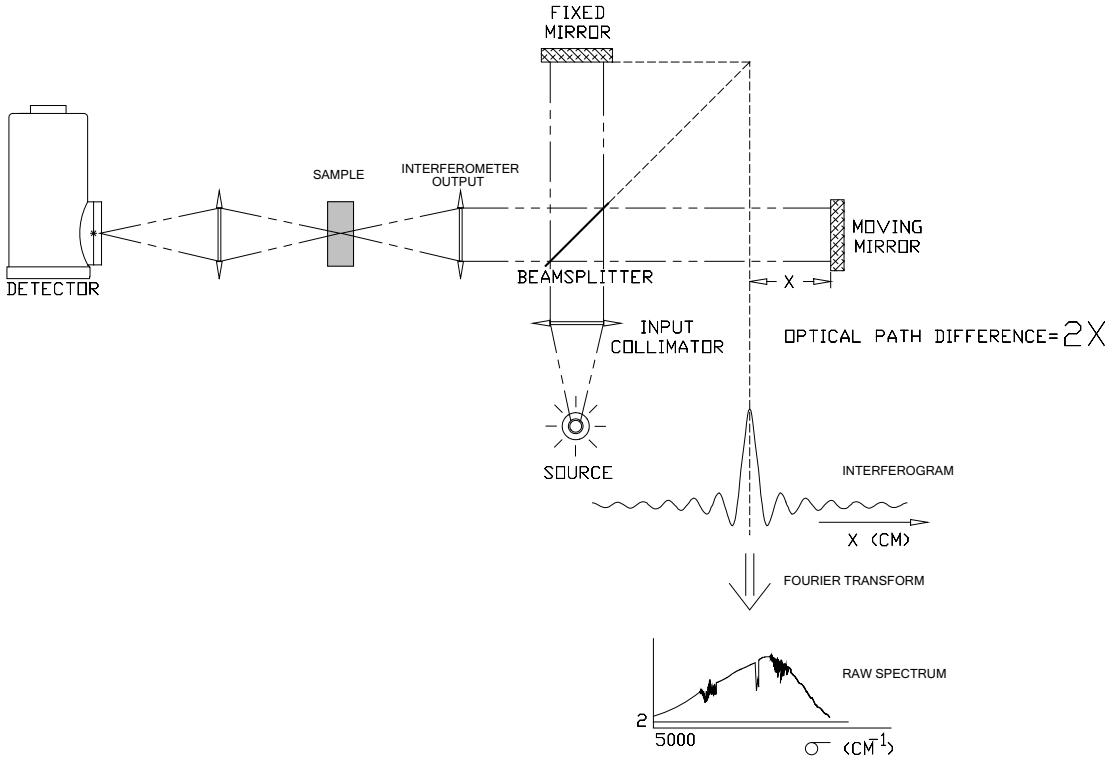


Figure 8-2. Michelson interferometer in a spectrometer

The light from the infrared source enters the interferometer and is divided into two equal beams by a beam splitter. One beam is reflected towards the fixed mirror, which reflects it back towards the beam splitter. The other beam is reflected towards the moving mirror, which reflects it back towards the beam splitter. At the beam splitter, the two reflected beams recombine. The interference between the two beams modulates the light.

After leaving the interferometer, the modulated light passes through the sample which absorbs some of the light. The remaining light then reaches the **detector** which converts it into an electrical signal.

Note: In ABB's FT-IR Spectrometer, the fixed and moving mirrors are cube-corner, high-precision retro-reflectors that make permanent alignment of the interferometer possible.

[iv] Fourier Transform Infrared Spectroscopy, by Peter R. Griffiths and James A. de Haseth, a Wiley-Interscience publication, John Wiley and Sons, 1986.

Figure 8-3 shows a representation of the electrical signal from the detector. This representation is call an **interferogram**, since it is the result of the interference of all the wavelengths contained in the optical beam which reaches the detector.

An interferogram is a graph of the voltage at the output of the detector as a function of the position of the moving mirror.

The Y-axis is the voltage (in V) and the X-axis is the number of data points from the beginning of the scan.

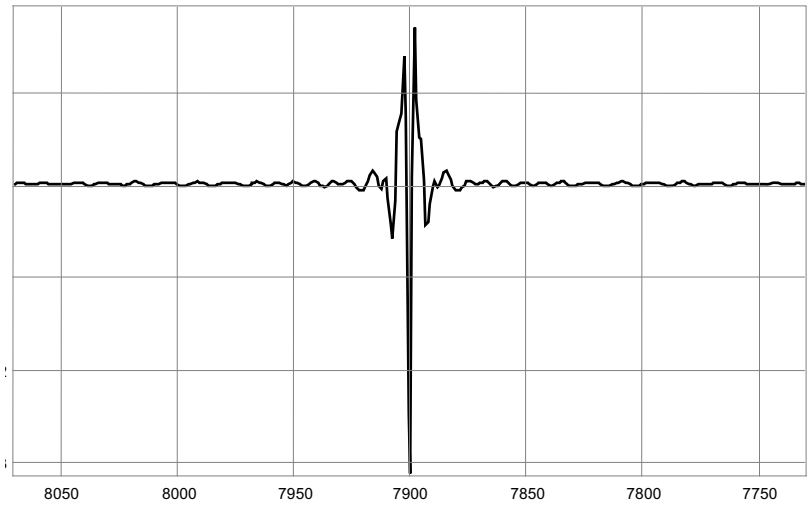


Figure 8-3. Interferogram

8.2.1 Fourier Transform

The spectral information contained in the interferogram is retrieved using a Fourier transform. A Fourier transform is a mathematical process which can be used to convert an interferogram into a spectrum.

Performing a Fourier transform on an interferogram yields a **raw** (or **single beam**) **spectrum**. This type of spectrum contains information not only about any sample present in the sample compartment or sampling accessory, but also about the whole instrument, including the source, all the optical components, the ambient air, as well as any contamination there may be in the optical path.

8.3 Reference and absorbance spectra

[aa]A reference spectrum is often simply called a "reference" or "zero". It is also called a "background spectrum".

When analysing a sample, only the information about the sample is of interest—all information not related to the sample has to be removed from the raw spectrum. To do this, before analysing samples, a **reference** (or **zero**) **spectrum**[aa] is acquired and stored for later use. The stored reference spectrum will be used to remove unwanted information from the raw spectra.

To acquire a reference spectrum, the sampling cell is filled with a zero gas, such as dry nitrogen, or a zero liquid, that is, a liquid that has no spectral signature in the region of interest. Then a spectrum is acquired. Since the zero gas or liquid does not absorb light in the region of interest, this reference spectrum only contains information about the instrument.

Figure 8-4 shows an example of a typical reference spectrum. Although all reference spectra for FT-IR spectrometers have the same general shape, the exact

shape depends on many different factors (source, type of transmission cell, type of optical fibers, type of detector, contamination, etc.). In this case, the cell as well as the spectrometer was purged with dry nitrogen. The detector was an extended InGaAs detector at room temperature.

In reference and raw sample spectra:

- *the Y-axis is the intensity of light measured by the detector (in arbitrary units*
- *the X-axis is the frequency in wavenumbers (cm^{-1})*

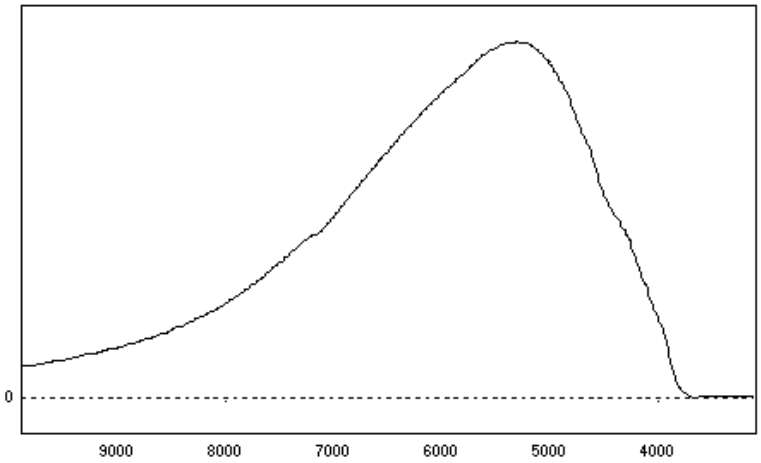


Figure 8-4. Reference spectrum

Once the reference spectrum is acquired and stored, analyses of the sample can begin. The system acquires raw spectra of the sample, then processes each raw sample spectrum.

Figure 8-5 shows a reference spectrum and a raw sample spectrum. By comparing the two spectra, it can be seen that the sample absorbs light at different wavelengths.

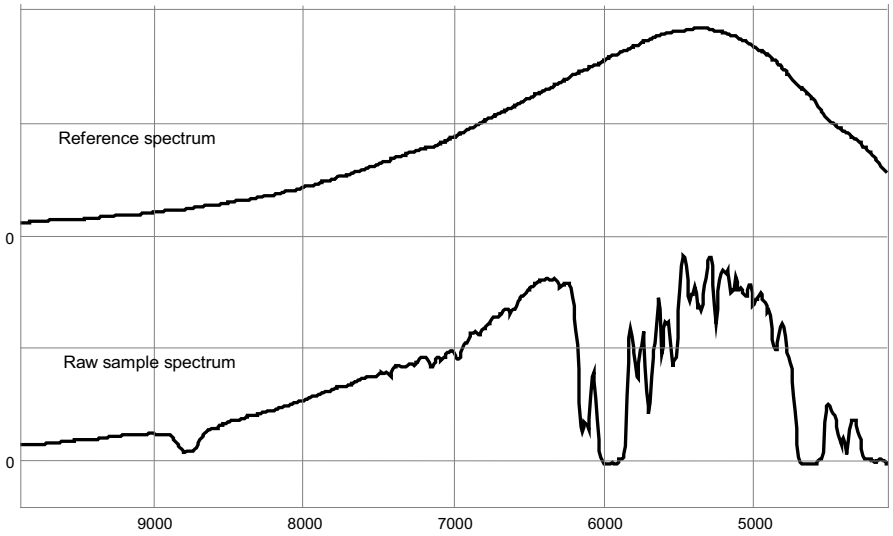


Figure 8-5. Reference and raw sample spectra

Equation 8-1 shows how the information in these two spectra is processed to produce an absorbance spectrum. The value at each wavelength in the sample spectrum is divided by the value at the corresponding wavelength in the reference spectrum, and the negative logarithm taken of the result. This give the absorbance value at that wavelength.

$$A = -\log_{10}\left(\frac{sample}{reference}\right)$$

Equation 8-1

Plotting the calculated absorbance values yields the absorbance spectrum shown in Figure 8-6. This spectrum shows the absorbance of the sample, as described by Beer-Lambert's law (Equation 7-2), for all wavelengths from 4000 cm^{-1} to 10 000 cm^{-1}.

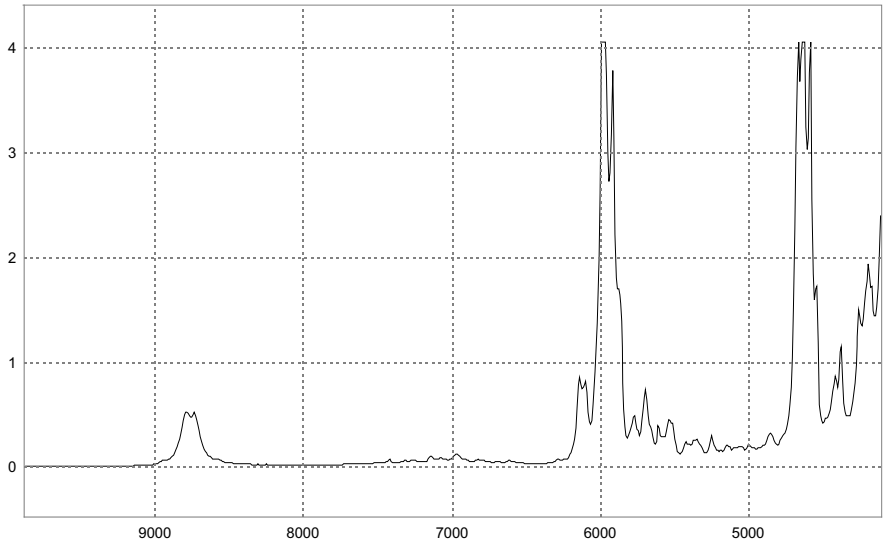


Figure 8-6. Absorbance spectra from a process sample

The advantage of using absorbance spectra is that the concentration of the sample is proportional to the absorbance (as shown in Equation 7-3). It is with such spectra that calibrations for spectrometers are developed.

9. CALIBRATION

We saw that the absorbance spectrum of a sample depends on the concentration[bb] of the constituents in the sample. If we know the relationship between the absorbance spectrum and the concentrations, we should be able to use the absorbance spectrum to determine (predict) these concentrations.

[bb] *Concentration is just one type of sample **property** that can be measured by infrared spectroscopy. Refer to Part 1 for examples of other measurable properties.*

The process of defining an equation, or a series of equations, which represents the relationship between the absorbance spectrum and the concentrations, is called **calibration**. The resulting equation, or series of equations, is called a **calibration model**.[cc] Calibration can be very simple, as when measuring a single chemical having a simple spectral signature, or very elaborate, as when analysing a complex mixture.

[cc] *The terms "**calibration**" or "**model**" are often used instead of "**calibration model**".*

To help explain high-performance, multivariate calibration, such as PLS (partial least squares), we will start with basic calibration algorithms, such as peak height, and then progress towards more sophisticated concepts.

9.1 Peak height

In peak-height calibration, the concentration (or other sample property) is related to the height of a peak in the spectrum by a simple linear equation. Peak-height calibration can be used when the constituent of interest has well-resolved bands and no interference with other constituents in the mixture.

The principle behind peak-height calibration will be illustrated using two examples for acetylene calibration. Peak-height calibration is an appropriate calibration algorithm for measuring the partial pressure of acetylene in nitrogen. Acetylene presents a well-resolved band between 700 cm^{-1} and 750 cm^{-1} and nitrogen does not absorb infrared radiation.

9.1.1 Example 1: Calibration based on a single spectrum

In this example, the calibration is based on the acquisition of a single spectrum of acetylene at a known[dd] concentration (40 ppm). Figure 9-1 shows the acetylene absorbance spectrum.

[dd] *The sample concentration is measured using a precise primary calibration method, such as gas chromatography (GC) or titration.*

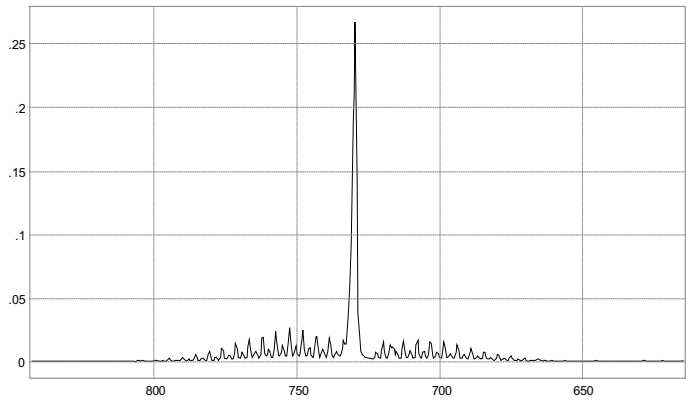


Figure 9-1. Acetylene absorbance spectrum (40 ppm in N_2 at 1 atm.)

Figure 9-2 shows a closer look at the highest peak. Since this peak is narrow, great care must be taken in instrument and sampling system adjustment to prevent any shift of spectral scale due to variations in divergence of the optical beam.

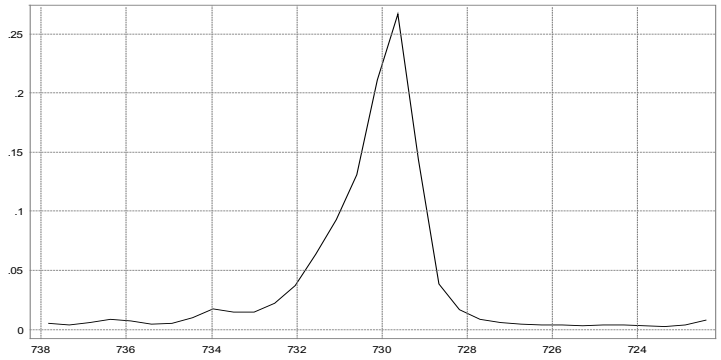


Figure 9-2. Peak absorbance for acetylene (40 ppm in N_2 at 1 atm.)

Table 9–6 shows the measured absorbances and wavenumbers of the main peaks of the spectrum. As shown in this table, at the wavenumber corresponding to the highest peak (729.75 cm^{-1}), the absorbance is 0.267 absorbance units for a concentration of 40 ppm. The calibration is developed using the absorbance at this wavenumber.

Peak center (X) (Wavenumber)	**Peak height (Y)** (Absorbance)
698.62915	.01576771
703.35478	.01598990
708.06820	.01724872
712.77409	.01674165
719.95797	.01568105
729.75008	**.26730788**
738.65265	.01873724
743.36883	.02066066
748.08314	.02531269
752.77861	.02665214
757.45214	.02433438
762.15293	.01956648
766.83768	.01839582
771.48785	.01488409

Table 9–6. Acetylene (40 ppm in N_2 at 1 atm.)

The calibration constant K_λ in Equation 7-2 (Beer-Lambert's law) gives the relationship between the absorbance and the concentration at the selected wavenumber. The constant K_λ is calculated by rearranging Equation 7-2 to give Equation 9-1.

$$K_\lambda = \frac{A_\lambda}{C}$$

Equation 9-1

where C is the known concentration of acetylene

A_λ is the measured absorbance at a wavelength λ

Once the constant K_λ has been determined, the concentration of unknown samples, measured under the same conditions, can be predicted by measuring the absorbance at the same wavelength and then using Equation 9-2.

$$C_x = \frac{A_{\lambda x}}{K_\lambda}$$

Equation 9-2

where C_x is the predicted concentration of acetylene in sample x

$A_{\lambda x}$ is the absorbance value at wavelength λ for sample x

For this example, the calibration constant at 729.75 cm^{-1} can be calculated using the absorbance from Table 9–6:

$$K_{729.75\ cm^{-1}} = \frac{A_{729.75\ cm^{-1}}}{C} = \frac{0.267\ absorbance_units}{40\,ppm} \cong \frac{1}{150}\frac{absorbance_units}{ppm}$$

Equation 9-3

Now that the calibration constant has been calculated, the concentration C_x for any unknown sample x can be determined from the absorbance of that sample at 729.75 cm^{-1}:

$$C_x = \frac{A_{729.75cm^{-1}\cdot x}}{K_{729.75cm^{-1}}} = A_{729.75cm^{-1}\cdot x} \times 150\ \frac{ppm}{absorbance_units}$$

Equation 9-4

This is a simple linear relationship, as shown in Figure 9-3. The slope is $1/K_\lambda$ and the zero is at the origin.

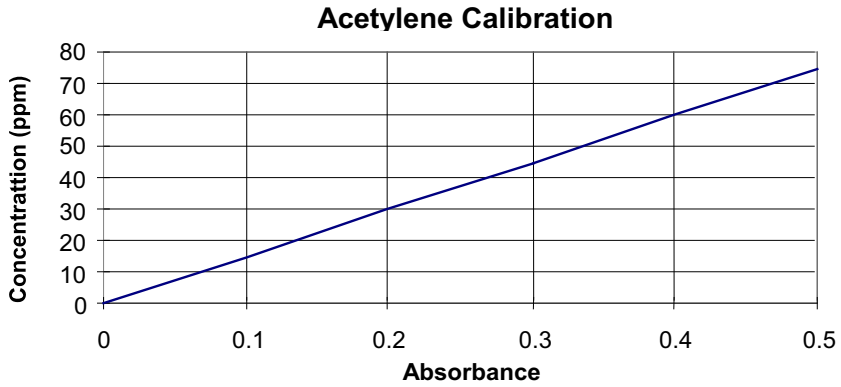


Figure 9-3. Peak-height calibration plot

The concentration of unknown samples can now be predicted by acquiring a spectrum of each sample and using the calibration constant K_λ in Equation 9-4. For example, if the absorbance at 729.75 cm^{-1} for a particular sample is 0.2, the acetylene concentration is:

$$C_x = 0.2\ absorbance_units \times 150\ \frac{ppm}{absorbance_units}$$
$$= 30\,ppm$$

When a peak-height calibration is based on a single spectrum, it requires a very precise primary calibration method and very little noise in the absorbance spectra, since any error in measurement when developing the calibration will affect the accuracy of all predictions of unknown samples. Note that in this example, there is no indication of how accurate the predictions will be.

9.1.2 Least-squares regression

[ee]Most hand-held calculators as well as many types of software, such as Microsoft Excel™, support least-squares regression algorithms for linear regression.

When developing a calibration, it is possible to improve the accuracy of the calibration constant by acquiring several spectra of the same known sample, under the same conditions, to get an averaging effect. The calibration constant is then found using a statistical technique called **least-squares regression**.[ee] This is a method of determining the relationship that best describes the observed data.

This algorithm is referred to as "least squares" because it minimizes the sum of the squares of the differences between the known concentrations and the concentrations predicted by the linear relationship. The differences are squared in order to prevent positive differences from canceling out negative ones when they are summed.

This algorithm is illustrated in the following example.

9.1.3 Example 2: Calibration based on a number of spectra

Peak-height calibration using least-squares regression requires a number of sample spectra acquired on the same instrument under the same conditions.

Table 9–7 shows the absorbances of the main peaks (at 729.75 cm^{-1}) of the acquired spectra. Due to the many possible variations (such as noise, instrumental variations, sample handling errors, etc.) each result is slightly different.

Concentration (ppm)	**Absorbance** (Absorbance units)
40.5	0.261
39.8	0.292
40.4	0.258
39.8	0.289
38.7	0.255
40.5	0.254
40.8	0.290
40.6	0.305
40.6	0.298
39.9	0.299
40.0	0.263
40.5	0.267
40.7	0.291
40.5	0.300
40.6	0.291
39.6	0.297
39.9	0.249

Table 9–7. Acetylene data

The fact that each measurement is slightly different shows that a calibration based on only one measurement would not be very reliable. Figure 9-4 shows a graphical representation of the information in Table 9–7.

There are two distinct groups of data values in this plot. This is due to the fact that the data was acquired by two different operators who had slightly different ways of carrying out the procedure, thus introducing a small systematic error in the data.

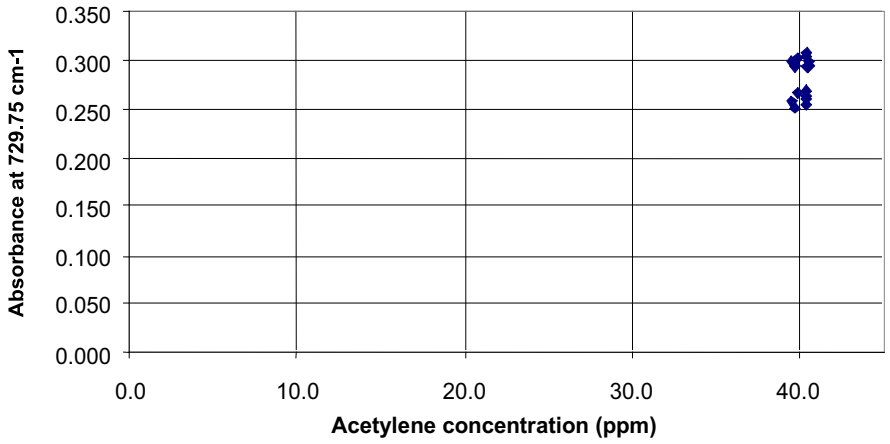


Figure 9-4. Plot of acetylene data

Instead of using the data from only one measurement, as in Example 1, the mean of all measurements, both for concentration and absorbance, are used for the calibration. This is the principle behind the least-square regression algorithm.[v]

[v] Mathematics of Physics and Modern Engineering, by I.S. Sokolnikoff and R. M. Redheffer, Edited by McGraw Hill Book Company, 1966.

The mean concentration is 40.3 ppm with a standard deviation of 0.4 ppm. The mean absorbance is 0.28 absorbance units with a standard deviation of 0.02.

These values are used in Equation 9-1 to calculate the calibration constant.

$$K_\lambda = \frac{A_{729.75\text{cm}^{-1}}}{C}$$
$$= \frac{0.28 \pm 0.02\ absorbance_units}{40.3 \pm 0.4\ ppm}$$
$$\cong \frac{1}{144 \pm 12}\frac{absorbance_units}{ppm}$$

This calibration constant is used Equation 9-4 to predict sample concentrations. Since this constant was calculated using several measurements, it should be more reliable than that calculated in Example 1.

Another advantage of this method is that it gives an estimate of the precision of the prediction (±12 ppm), whereas in Example 1, the precision was unknown.

Note: The precision of the calibration will increase as the square root of the number of measurements.

It is important to mention that this mathematical approach (increasing the number of measurements) reduces statistical error but cannot counteract bias due to systematic error in calibration.

When there is more than one constituent in the samples, a separate band must be used for each constituent of interest, and it is necessary to calculate a calibration constant for each constituent.

Peak-height calibration will not produce accurate results if there are interfering constituents that have spectral bands that overlap those of the constituents of interest. In such cases, it is necessary to use more sophisticated mathematical techniques.

9.2 Matrices

Matrix mathematics allows calibration of complex mixtures, or calibration of simple mixtures of very similar materials. It makes it possible to develop calibrations even in the presence of interfering constituents.

In matrix mathematics, instead of using scalar values, vectors and matrices are used. It is not necessary to understand the elaborate mathematics behind this, since most calibration software used in quantitative analysis performs this type of calibration. In this document, bold-face type is used in equations to represent vectors and matrices.[ff]

[ff] *Experts in vector and matrix mathematics may see a lack of rigor in these equations, however, the principle as presented is more accessible to most people.*

9.2.1 K-matrix

To predict the concentrations of constituents that have overlapping bands, it is necessary to perform calculations using many wavelengths.

It is also necessary to take advantage of part of Beer-Lambert's law which states that the absorbances of multiple constituents at the same wavelength are additive. The total absorbance at a particular wavelength can be calculated from the sum of all the constituent concentrations multiplied by their calibration constants at that wavelength.

It is necessary to have as many equations as there are unknowns. If more than two constituents are present or more than two wavelengths are used, matrix mathematics (linear algebra) can be used to solve simultaneous equations. The algorithm is known as K-matrix, or classical least squares (CLS). It is based on the following matrix equation, similar to Equation 7-2:

$$\mathbf{A} = \mathbf{KC}$$

Equation 9-5[vi]

where **K** is a matrix of calibration constants
C is a matrix of the known concentrations of the constituents
A is a matrix of absorbances at the selected wavelengths

The K-matrix calibration can only be applied to system where the concentration of every constituents in the sample is known.

K-matrix calibration has the advantage of being able to use large regions of the spectrum for calibration, or even the entire spectrum, to gain an averaging effect for the prediction accuracy of the final model.

Equation 9-6 is used to calculate the calibration constants from sampling with known concentrations. In K-matrix calibration, many points from each spectrum are used, each point having its own constant, and many measurements are taken. Equation 9-6 is similar to Equation 9-1. The matrix of calibrated spectra is used for the numerator, and the concentration matrix for the denominator.

$$\mathbf{K} = \frac{\mathbf{A}}{\mathbf{C}}$$

Equation 9-6

[vi] It is important to note that the mathematical representation of vectors and matrix equations used in this document does not follow the normal conventions for this kind of mathematics. This is done on purpose since the objective of this document is to explain the principles of calibration rather than to develop a computer program that will perform the computation. For this reason, we present equations in a form that we believe to be the most accessible to non-mathematicians.

The concentration of unknown samples, measured under the same conditions, can be predicted using Equation 9-7.

$$\mathbf{C_x} = \frac{\mathbf{A}}{\mathbf{K}} \text{ or } \mathbf{C_x} = \mathbf{A}\mathbf{K}^{-1}$$

Equation 9-7

where $\mathbf{C_x}$ is a matrix of the predicted concentrations of the constituents in sample **x**

K-matrix equations

In the case where two constituents are present at two different wavelengths, two equations are needed:

$$A_{\lambda 1} = K_{\lambda 1 \cdot a} \times C_a + K_{\lambda 1 \cdot b} \times C_b$$
$$A_{\lambda 2} = K_{\lambda 2 \cdot a} \times C_a + K_{\lambda 2 \cdot b} \times C_b$$

In matrix terms, these equations are formulated as:

$$\begin{vmatrix} \mathrm{A}_{\lambda 1} \\ \mathrm{A}_{\lambda 2} \end{vmatrix} = \begin{vmatrix} \mathrm{K}_{\lambda 1 \cdot a} & \mathrm{K}_{\lambda 1 \cdot b} \\ \mathrm{K}_{\lambda 2 \cdot a} & \mathrm{K}_{\lambda 2 \cdot b} \end{vmatrix} \begin{vmatrix} \mathrm{C}_\mathrm{a} \\ \mathrm{C}_\mathrm{b} \end{vmatrix}$$

Note: This is a simple example using the spectrum of one sample. When many samples are included in the training set, the matrices are more complex.

This matrix equation can be reformulated as:

$$\mathbf{A} = \mathbf{KC}$$

The K-matrix calibration applies the principles described in Section 9.1.2 “Least-squares regression” to each spectral point involved in the calibration, and uses the average of all the predictions as the output. Selecting spectral regions that are an accumulation of one hundred spectral points leads to an improvement of the order of 10 (the square root of one hundred) in the prediction. This adds to the gain in precision achieved by using many calibration spectra.

Because it uses spectral information from different regions, the K-matrix algorithm can be used to develop a calibration even when there is band overlap, provided the concentrations of all the constituents having a spectral signature in the regions selected are known. This is an important improvement over peak-height calibration.

9.2.2 P-matrix

Knowing the complete composition (the concentration of every constituent) of the calibration mixture is not always possible. Moreover, sometimes only the concentrations of a few constituents in a complex mixtures are of interest. In this case, P-matrix calibration, also known as multiple-linear-regression or inverse least squares (ILS), can be used.

With P-matrix calibration, Beer-Lambert's law is rearranged so that the concentration of each constituent is expressed as a function of the absorbance at a series of given wavelengths:

$$C_a = \frac{A_{\lambda 1}}{\varepsilon_{\lambda 1 \cdot a}} + \frac{A_{\lambda 2}}{\varepsilon_{\lambda 2 \cdot a}} + \cdots$$

By combining each absorption coefficient ε_λ and the pathlength b into a single constant P_λ, this equation can be expressed as:

$$C_a = A_{\lambda 1} P_{\lambda 1 \cdot a} + A_{\lambda 2} P_{\lambda 2 \cdot a} + \cdots$$

This can be expressed as the matrix equation:

$$\mathbf{C} = \mathbf{P}\ \mathbf{A}$$

Equation 9-8

where **P** is a matrix of calibration constants
C is a matrix of the concentrations of the constituents
A is a matrix of absorbances at the selected wavelengths

The P-matrix calibration can be applied to systems where only the concentration of the constituents of interest is known, no knowledge of the complete sample composition is needed.

The calibration constant matrix **P** is calculated using Equation 9-9.

$$\mathbf{P} = \frac{\mathbf{C}}{\mathbf{A}}$$

Equation 9-9

Once **P** has been calculated, the concentration of unknown samples, measured under the same conditions, can be predicted using Equation 9-8.

P-matrix equations

To predict the concentration of two specific constituents in a complex mixture, two equations are needed:

$$C_a = A_{\lambda 1} P_{\lambda 1 \cdot a} + A_{\lambda 2} P_{\lambda 2 \cdot a}$$
$$C_b = A_{\lambda 1} P_{\lambda 1 \cdot b} + A_{\lambda 2} P_{\lambda 2 \cdot b}$$

In matrix terms, these equations are formulated as:

$$\begin{vmatrix} \mathbf{C_a} \\ \mathbf{C_b} \end{vmatrix} = \begin{vmatrix} \mathbf{P}_{\lambda 1 \cdot a} & \mathbf{P}_{\lambda 1 \cdot b} \\ \mathbf{P}_{\lambda 2 \cdot a} & \mathbf{P}_{\lambda 2 \cdot b} \end{vmatrix} \begin{vmatrix} \mathbf{A}_{\lambda 1} \\ \mathbf{A}_{\lambda 2} \end{vmatrix}$$

Note: This is a simple example using the spectrum of one sample. When many samples are included in the training set, the matrices are more complex.

This matrix equation can be reformulated as:

$$\mathbf{C} = \mathbf{PA}$$

The calibration constants matrix **P** can be seen as a weighted average of all spectra included in the training set used for the calibration, the weighting being given by the concentration matrix. It is this weighting that makes the calibration suitable for cases where unknown products are in the sample. However, these unknown constituents must be correctly represented in the training set, otherwise, the calibration will not be precise.

The selected wavelengths must be in a region where there is a contribution of the constituents of interest to the overall spectrum. A measurement of the absorbance at at least one different wavelength is needed for each constituent of interest.

Due to the dimensions of the matrix equations, the number of selected wavelengths cannot exceed the number of training samples. Otherwise, the calibration would be sensitive to colinearities, and therefore less reliable.

The gain in precision with P-matrix calibration comes at the cost of more work—more calibrated spectra are required, and several trials have to be performed before deciding what spectral regions will be selected and what concentration mixture will be used.

9.3 PLS (partial least squares)

There are many different variations in a system that influence the shape of the sample spectra, such as the constituent concentrations in the sample mixture, inter-constituent interactions, instrument variations, changing environmental conditions, and differences in sample handling. When developing a calibration, however, the largest variations in the training set spectra would normally be due to varying concentrations of the constituents of the mixture.

Each of these variations has a specific effect on the spectra. For example, a change in the concentration of one constituent will affect the height of all bands where that constituent has a spectral signature. A change in environmental conditions may affect the baseline of all spectra.

The PLS algorithm decomposes the training set spectra into a relatively small number of variation spectra which are called **factors**. These factors represent the most common variations in the spectra. The number of factors used depends on the number of varying parameters in the training set.

PLS weights the factors according to the known sample properties (such as sample concentrations), taking advantage of the correlation that exists between the spectral data and the property values, to produce factors which are directly related to the properties of interest.

Once the factors have been computed, the spectrum of a sample can be reconstructed[gg] by multiplying each factor by a different scaling constant and adding the results together. The scaling constants are called scores.

[gg] *The reconstructed spectrum only approximates the sample spectrum. The difference between the two is called the* ***spectral residual****. The spectral residual gives an indication of how closely the reconstructed spectrum matches the sample spectrum.*

Different algorithms have been developed to compute a PLS calibration. They each result in a series of calibration vectors that completely model the relationship between the absorbance spectra and the properties to be measured.

9.3.1 Example 3: Calibration using PLS

If three spectroscopically active chemical constituents are present in a mixture, it should be possible to describe all of them with two calibration vectors. In this case, because the total concentration is 100%, only two chemical constituents can vary independently, the third one will always depends on the two others.

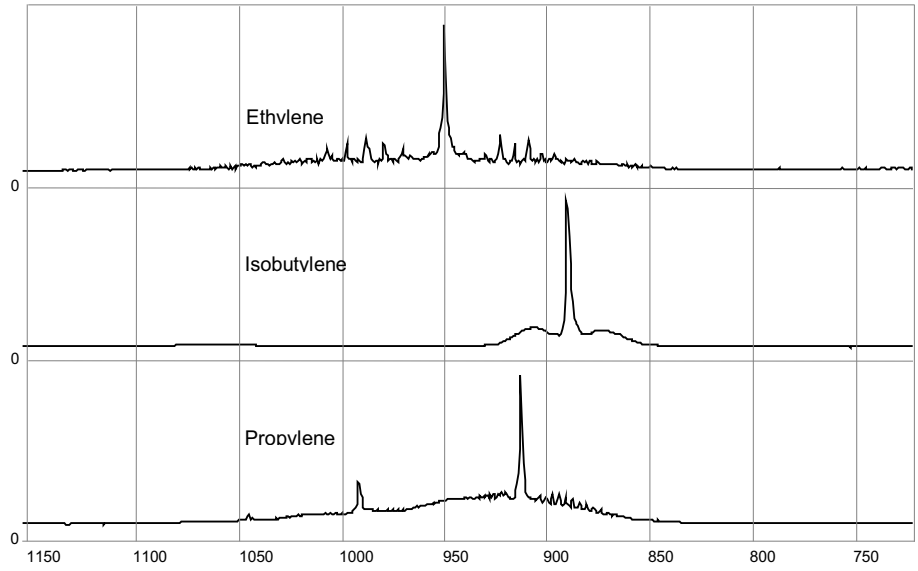
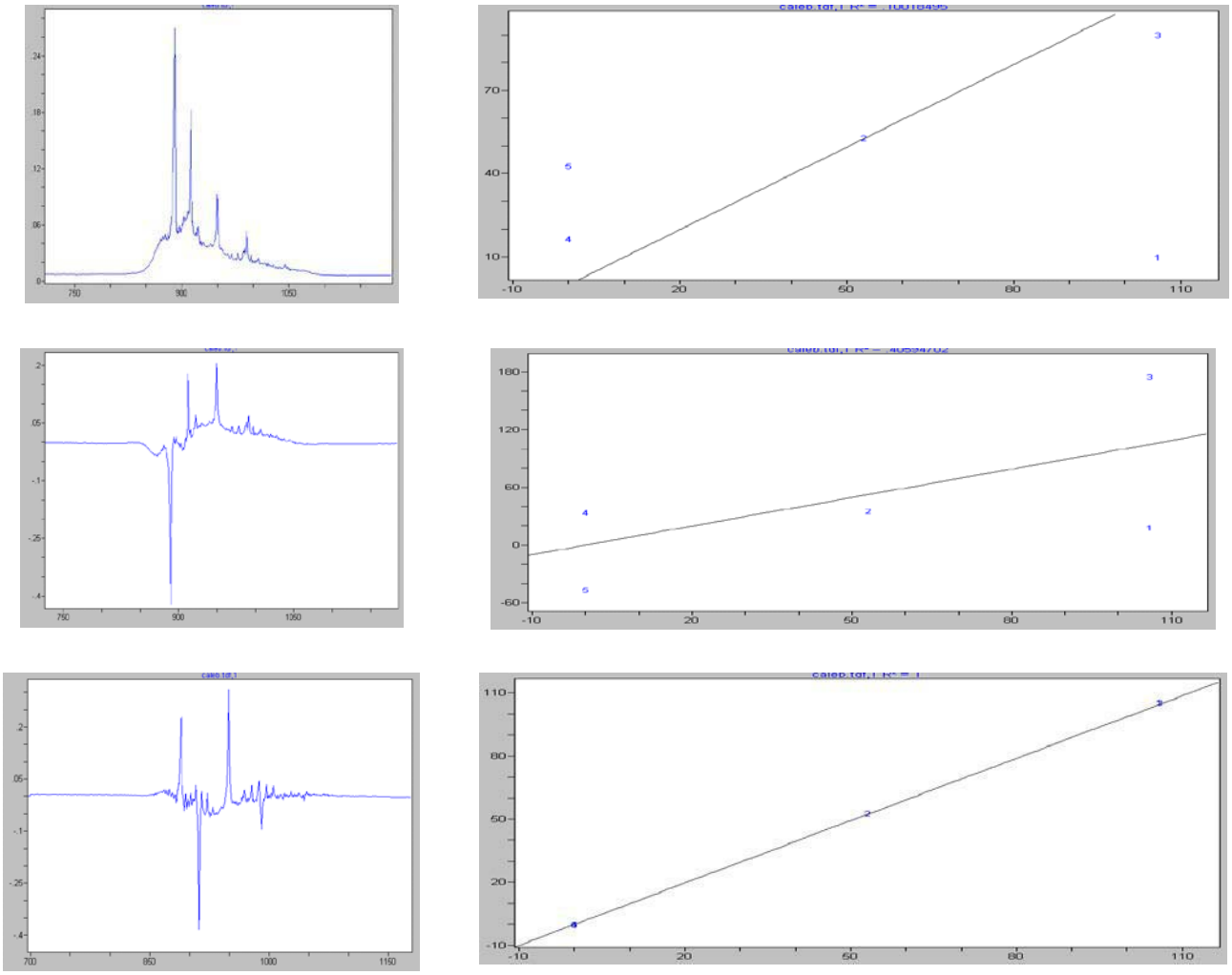


Figure 9-5. Chemical and spectral signature

Figure 9-5 shows the spectral signatures of the three chemical constituents included in the mixture. They are mixed in different concentrations in nitrogen, a gas without a spectral signature in the region of interest. Only the concentration of ethylene is known and two values are used in the mixture: 106 ppm and 53 ppm. In this example, no data preprocessing is used.

The calibration is developed using PLS-IQ from Thermo Galactic Products PLS-IQ suggests using three factors. Figure 9-6 shows the three factors computed by PLS-IQ, as well as the correlations between the measured concentration values and the PLS-predicted values.



PLS factors **Actual vs. predicted correlations for each factor**

Figure 9-6. PLS factors and predicted correlations for each factors

When an unknown sample is analysed, a spectrum of the sample is acquired, then the analysis software attempts to reconstruct the sample spectrum from the

factors. The three factors are each multiplied by a specific score and then added together to rebuild the sample spectrum. The software determines the three scores which best reconstruct the spectrum. These scores are then used by the software to compute the concentration using the correlation table constructed during the calibration process.

In this example, although there are spectral colinearities and although the concentrations of two chemical constituents are not known, PLS-IQ is able to give a precise calibration. This is possible, because the generated factors are directly related to the constituent of interest.

10. SELECTING THE APPROPRIATE CALIBRATION ALGORITHM

When developing a calibration, it is important to select the appropriate calibration algorithm. Using the most elaborate one may result in wasting time acquiring too many spectra. Among the parameters to be considered is the real need for precision. High-precision calibration algorithms require many spectra and the use of complex statistical algorithms.

Table 10–1 gives an overview of parameters that should be considered in the choice of the appropriate calibration algorithm.

Calibration algorithm	Number of spectra required	Supports interference from unknown elements in calibration	Able to model non-linearity	Requires specialized software
Peak Height	One	No	Never	No (can be done manually)
Least Square	A few (2 to 30)	No	Never	No (can be done manually)
K-matrix	At least one per spectroscopically active chemical in the compound.	No	Never	Yes (such as Array Basic, Microsoft Excel)
P-matrix	At least one per spectroscopically active chemical in the compound.	Yes	Sometimes	Yes (such as Array Basic, Microsoft Excel)
PLS	As many as there are variables in the spectra: spectroscopically active chemicals, instrument spectral variations, etc. (We suggest at least 10 per factor for high precision calibration)	Yes	Often	Yes (Many commercial packages are available: PLS-plus, PLS-IQ, Unscrambler, Pirouette)

Table 10–1. Selecting the appropriate calibration algorithm

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B GLOSSARY

Note: The following terms are defined as they are used in this manual.

Absorbance spectrum:

A graph of the absorbance of a sample as a function of the wavenumber. The absorbance spectrum is obtained from the raw sample spectrum and the reference spectrum, using Equation 8-1 (page 8-5).

Absorbance unit:

An arbitrary unit for absorbance. Since absorbance is the logarithm of a ratio (see Equation 8-1), it is dimensionless.

Calibration:

1 The process of developing a calibration model for a particular application. **2** The calibration model so developed.

Calibration model (or calibration or model):

The set of equations which represents the relationship between the absorbance spectra of a set of samples and the properties of the samples.

Note: PLSPlus and Pirouette both allow multiple properties to be estimated from a single multivariate calibration model. Some programs, however, require a separate model for each property.

Calibration set (see training set)

Channel spectrum (see Fabry-Perot interference)

Concentration residual:

In analysis using the PLS algorithm, the difference between the actual and predicted concentration for a sample constituent.

Detector:

A device in a spectrometer which extracts information from the modulated infrared radiation, after it has passed through the sample, and converts it into an electrical signal.

Fabry-Perot interference (or channel spectrum):

Interference produced by a small gap between two optical surfaces, for example, at a fiber-to-fiber joint or at the fiber-to-detector interface.

Factor:

In analysis using the PLS algorithm, one of a series of special spectra which represent the most common variations in a given set of spectra (also known as latent vectors, characteristic vectors, spectral loadings, loading vectors, principal components, or variation spectra.).

Interferogram:

A representation of the electrical signal from the detector of a spectrometer. The interferogram is a graph of the voltage at the output of the detector as a function of the position of the moving mirror. The spectral information contained in the interferogram is retrieved using a Fourier transform.

Interferometer:

An instrument designed to produce optical interference which modulates light in such a way that the spectral information the light contains can be retrieved. The interferometer splits the infrared beam into two beams using a beamsplitter, introduces a difference in path length between the two beams, and recombines the beams to produce a signal of constructive and destructive interference.

Least-squares regression:

The analysis or measure of the association between a predicted variable (dependent variable), such as concentration, and one or more predictors (independent variables), such as absorbance values. The association is usually formulated as an equation in which the predictors have parametric coefficients. The equation enables future values of the predicted variable to be predicted.

The algorithm is referred to as "least squares" because, when determining the coefficients, it minimizes the sum of the squares of the differences between the predictors and the predicted variables. The differences are squared in order to prevent positive differences from canceling out negative ones when they are summed.

Method:

1 In spectrometer calibration, the training set spectra, and the preprocessing algorithms, spectral region selections, diagnostics, etc. applied to these spectra, used to preparing a calibration model. **2** In sample analysis, a set of preprocessing algorithms and discrimination criteria applied to sample spectra, as well as the model or models, required to obtain a prediction.

Model (see calibration model):

Nonlinearity:

A deviation from the normally linear relation between the output and the input of a device. Nonlinearity occurs when the output of a device does not vary in direct proportion to the input. For example, saturation of the detector in a spectrometer induces nonlinearity which causes stray light.

Normal distribution:

In statistics, a distribution that is continuous and is symmetrical with mean, median and mode coincident. It is also known as the Gaussian distribution, or the familiar "bell curve".

Normalization:

In spectrometry, the transforming of spectra to a common basis. For example, the adjustment of spectra to compensate for differences in path length, temperature, alignment, etc.

Outlier (outlier sample):

A sample in a set of samples for which a predicted property value lies significantly outside the main cluster of the corresponding property values for that set. Outliers can be caused by many different factors including inconsistent sample handling, changes in the performance of the instrument, or anything that contributes to a significant change in the spectrum of a given sample.

Predict:

In spectroscopy, obtain the value for a specific property of a sample from its absorbance spectrum by using a calibration model.

PRESS (Prediction Residual Error Sum of Squares):

In analysis using the PLS algorithm, an indicator used to determine the optimal number of factors to be included in a calibration.

Primary method:

A very precise laboratory technique for measuring the properties of samples. When developing a calibration, the "known" property values of the training set samples are determined by measurement using the primary method.

Primary value determination (see sample calibration):

Process bypass loop:

In an industrial process, a loop which provides a parallel flow for sampling that can be completely isolated from the process for maintenance or repair.

Property:

A single, measurable characteristic of a sample, whether it be a physical property or a chemical concentration.

Raw spectrum (or single beam spectrum):

The spectrum which results from performing a Fourier transform on an interferogram. The raw spectrum contains information not only about any sample present in the sample compartment or sampling accessory, but also about the instrument (including the source, all the optical components, the ambient air, as well as any contamination there may be in the optical path).

Reference spectrum (or zero spectrum):

A raw spectrum that only contains information about the instrument. It is obtained by filling the sampling cell with a zero gas or liquid (a gas or liquid that has no spectral signature in the optical region of interest) and acquiring a spectrum.

Residual spectrum:

In analysis using the PLS algorithm, a spectrum obtained by taking the point-by-point difference between the original sample spectrum and the predicted spectrum.

Sample calibration (or primary value determination):

In spectrometer calibration, the process of measuring the exact properties of the constituents of interest in a training-set sample by using a primary method.

Sampling system:

In an industrial process, the interface between the spectrometer sampling accessory and the process. It includes valves, filters, flow restriction systems, pumps, etc.

Single beam spectrum (see raw spectrum):

Standard deviation:

An estimation of the square root of the variance based on a limited sample set.

Stray light:

1 Apparent optical energy, caused by nonlinearity, in a spectral region where no energy is expected. **2** Modulated light reaching the detector without having passed through the sample.

Training set (or calibration set):

In spectrometer calibration, a set of standard samples which cover the ranges of properties expected, as well as any other variations that may affect the spectra, such as temperature or alignment.

Validation set:

In spectrometer calibration, a set of samples used to confirm the accuracy of the calibration. A new set of spectra is measured under the same conditions as the training set and then calibrated by the primary method. This new data set is then predicted against the calibration models built from the training set.

Zero spectrum (see reference spectrum):

ZPD (zero path difference):

The point where the scanning mirrors of an Michelson interferometer are positioned so that the two beams from the beamsplitter travel exactly the same distance before being recombined.



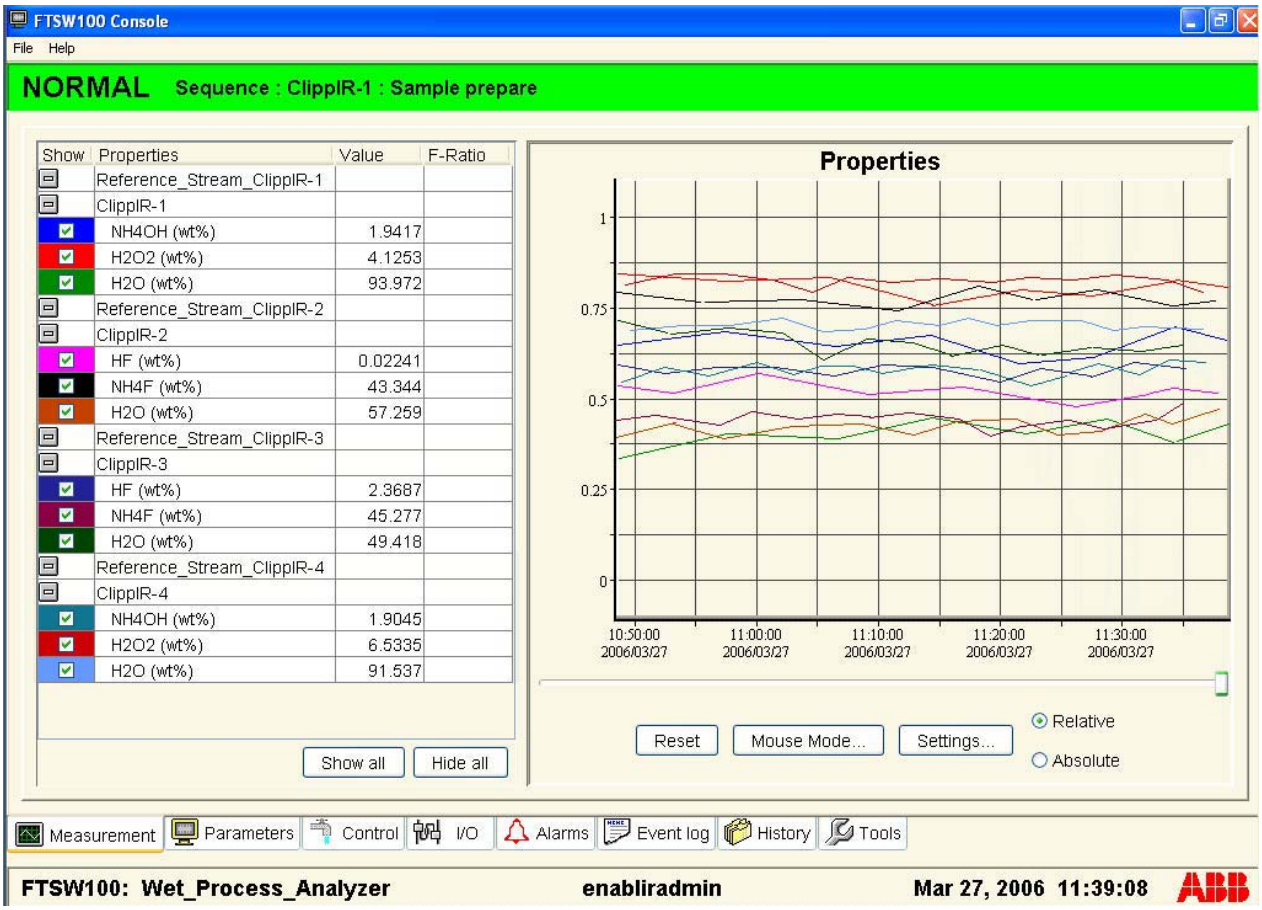
Measurement & Analytics
3400, Rue Pierre-Ardouin
Québec (Québec) G1P 0B2
CANADA

Phone: 418- 877 2944
North America: 800-858–3847
France: 0810 020 000
Fax.: 418- 877-2834
E-mail: ftir@ca.abb.com
www.abb.com/analytical
http://www.abb.com/analytical

Printed in Canada

FTSW100 Configuration Manual

This manual contains: *Specific Information for Wet Process Analyzer FTSW100 configuration.*



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France: 0810 020 000
Fax: 418-877-2834
E-mail: ftirsupport@ca.abb.com
Web: www.abb.com/analytical

Important: *Please be prepared to provide the serial numbers of all units.*
Refer to the section ***troubleshooting*** *of the FTSW100 user's guide (ABB part #AA001386-01) for details.*

You can also consult ABB's web site at **www.abb.com/analytical**

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1 Introduction

1.1 Purpose

This document is intended to describe the main functionalities and specifications of the Wet Process Analyzer (WPA) FTSW100 application configuration. The document contains an overview of the configuration (sequencing, I/O mapping, stream and properties). It also contains information on how to customize the configuration (load new model file, adjust the I/O ranges, trending and alarms ranges).

If the need to perform modification is not described in this manual arise, refer to a qualified ABB technician, for instructions on how to perform those modifications.



For further information regarding FTSW100 software specifications please refer to the FTSW100 User's Guide (ABB part # AA001386-01).

2 Hardware and software information

2.1 System Overview

The WPA configuration is defined for a system that can analyze up to eight streams using multiple ClippIR sampling accessories (multi-channel). These streams analyze different chemistries and predict components properties by using PLS models. All results and analyzer status (alarms, warnings, etc.) can be sent to an external control system (PLC/DCS) through the preferred input or output link. The I/O communications supported within the configuration is limited to CanOpen, ModBus and/or OPC DA 2.0. For further information on Basic I/O device configuration e.g. Baud rate, parity, server name, address, etc. please refer to your configuration specific inputs and outputs table as an appendix to this manual.

Note: *The configuration is designed and configured to offer the capability to communicate with an external or receiving device or to a control system (DCS or PLC) through ModBus RTU and OPC data access 2.0 communication protocols. If those communication capabilities are not used this will not affect the system operation or cause any alarms or faults.*

2.2 Instrument

The instrument is an FTPA2000-200 series (SYM3300G) equipped typically with eight detectors and possessing remote control (gain and resolution) capability via software.



For further information, refer to the FTPA2000-200 User's Guide (ABB part # IMZ9782).

2.3 Controller

Each Controller (or PC) for WPA, is pre-configured with FTSW100. The controller for WPA is intended to be dedicated for FTSW100 operation and no other software or process (e.g. anti-virus software) must interfere with FTSW100 to ensure stability of the system.

However, it is acceptable to install anti-virus software as long as it is not in continuous scan mode. Before scanning your computer for viruses, make sure you stop any running FTSW100 application.

2.4 Installation (when required)

Important: *The system is typically shipped pre-installed with FTSW100 software and WPA configuration included. Typically, there is no software installation to be done unless obtained separately when ordered from ABB.*

In case the system has to be re-installed completely, follow the instructions contained in the "Computer set-up procedure" and the "FTSW100 software set-up procedure" documents provided with the system. Those documents are contained on the DVD labeled "**Documentation For FTSW100 FT-IR Process Software**". After FTSW100 installation, it is then necessary to install the application configuration files as follows:

1) Locate the last version of the FTSW100 configuration file (.ftsw100), the report generator configuration file, the console parameters file (Console.config), the appserver initialization file (appserver.ini) and the electronic version of the manual. On the CD-ROM labeled "**Wet Process Analyser FTSW100 Configuration**" supplied with the system there are two directories that contains the original versions of those files.
    - FTSW100 Configuration that contains the application configuration file, the Report generator configuration file, the console parameters file and the Appserver initialization file.
    - FTSW100 Documentation, which contains a PDF version of the application manual.

    Copy these two directories (or folders) to the root of the C drive on the FTSW100 computer.
2) Copy the Database Report Tool configuration file ReportGeneratorConfig.xml to C:\BOMEM\ENABLIR. If a warning message is displayed, select to replace the existing file.
3) Copy the console parameter file (Console.config) to C:\Bomem\Enablir\jars and replace the existing file.
4) Copy the appserver initialization file (appserver.ini) to C:\Bomem\Enablir\ini replacing the existing file.
5) There are four other folders on the CD (FTSW100 Reports, FTSW100 Models, FTSW100 Exported Spectra and FTSW100 Event Logs), which are empty but must also be copied to the root of the C drive.
    - FTSW100 Reports, FTSW100 Exported Spectra and FTSW100 Event Logs will be the default saving directory for the different FTSW100 tools.
        - FTSW100 Reports for the report generator in the Tools panel.
        - FTSW100 Event Logs for the export function in the Event log panel.
        - FTSW100 Exported Spectra for the export function in the History panel.
    - FTSW100 Models is used to backup the calibration files of the application. In some cases, this folder can contain the models used for the initial version of the configuration.

Note: *If there are calibration files in that folder, the read only attribute should be removed in order to be able to load the models in the configuration.*

6) Start the Configuration Tool, import the XML configuration file, save it as current version and commit it to the database. For details on how to load and commit the configuration, see chapter 5 in the FTSW100 User's Guide (ABB part #AA001386-01).

Note: *You must control the configuration file version by generating a new one for each modification made to the configuration file after installation.*

3 Application overview and operation

3.1 Sequence description

This section describes the basic sample and reference sequencing for WPA. On FTSW100 software start-up, the system is Offline and can be started from the Control panel of the FTSW100 console using the Start / Stop buttons, see section 6.3.3 of the FTSW100 User's Guide (ABB part # AA001386-01) for details. When the system is set Online, if applicable, a short delay (30 seconds) is required for CanOpen I/O modules initialization before any reference or sample acquisition is performed. After the system is Online, it will remain idle until ClippIR are enabled from the control system (or from the console if no communication to a control system is used), or a new reference is trigger from the Console's Parameter panel.

Note: *When stopping the sequence (Stop button), the current analysis (sample or reference) will be immediately stopped. However, the spectrum will be computed and saved with the number of scans acquired at that point.*

3.1.1 Sample cycle

After starting the sequence, the software will remain idle (no analysis) until at least on of the defined streams is enabled from the control system through CanOpen, ModBus or OPC communication or from the Console within the Parameters panel.

Stream	Stream Status	Operations currently performed
For all the streams (ClippIRs) in the sequence.	Sample prepare	- Check if the stream is enabled, if not skip the analysis. (this signal can come from the control system or external device over CanOpen, ModBus or OPC or it can also come from an input within the Console's Parameters panel.)
	Sample acquire	- Perform data acquisition
	Sample compute	- Compute and Display analysis results. - Send the results and status to the control system or external device (if present) via CanOpen, ModBus and/or OPC link.

3.1.2 Reference cycle

For each channel, a reference (background) is required for the stream linked to those channels. For the current application there are two ways that a reference is taken.

3.1.2.1 Automatic Reference

- **At FTSW100 first start up.**

The initial and current reference spectra for the streams are saved in the **C:\Bomem\Persistence** directory. If that folder is empty when the application is started, a reference is automatically taken for each stream in the sequence.

If necessary, a new initial reference can be acquired for any of the ClippIRs. To do so, shutdown the AppServer, then delete all spectrum files associated to the ClippIR in the C:\Bomem\persistence directory and restart FTSW100 software (AppServer).

Note: ***All the files with the name containing "ClippIR-x", where x is the ClippIR number for which the new reference is needed, must be deleted. It is really important to make sure the system is ready to acquire a new reference (empty and clean tube) before restarting the AppServer***

Important: *Since the reference is acquired on a dedicated stream, do not use the "Initial Reference" button in the console control panel, to acquire a new initial reference.*

3.1.2.2 Manual Reference

- **Manually triggered from the Console (Parameters tab).**

A new reference can be acquired from the console by committing 1 to the Reference_Trigger_ClippIR-x digital input.

3.1.3 Detailed Reference Operations

The following table outlines the reference cycle execution and associated software operations. The current stream state is displayed in the console header and in the control panel: see section 6.1.3 of the FTSW100 User's Guide (ABB part # AA001386-01) for details.

The reference is acquired on a dedicated stream that acquires the reference spectrum and performs diagnostics to validate the system reliability and base performance criteria. For purpose of automatic diagnostics, a transmittance Noise test is performed to validate the analyzer performance that consists of a second sequential acquisition to measure the spectral noise level.

Stream	Stream Status	Operations currently performed
Reference Stream for all ClippIRs	Reference prepare	- Reset the trigger.
	Reference acquire	- Perform data acquisition
	Reference compute	- All diagnostics results associated to the reference spectrum are computed and outputted in the Parameters panel (Output tab). - If the reference is valid, copy the spectrum file for the sample analysis stream. - Trigger the transmittance noise test acquisition.

Stream	Stream Status	Operations currently performed
Transmittance Noise test	Reference prepare	- No action.
	Reference acquire	- Perform data acquisition
	Reference compute	- The transmittance noise test result is computed and outputted in the Parameters panel (Output tab).

3.2 Alarm(s) handling

The following section provides a description of the alarms and their causes. The alarms may be reported to the Control system through ModBus RTU Master Input Status registers and/or through OPC data access 2.0 tags.

Note: *The fault signal on the sample (LossOfIntensity_No_Light_To_The_Detector) indicates that there is a problem in the light path between the source and the detector.*

If all the streams are in fault condition, this indicates that the light source could be burned. If the fault appears only on some streams, it could indicate a broken optic fiber or a problem in the sampling device for that specific stream.

The fault messages are outputted in the console's alarm panel

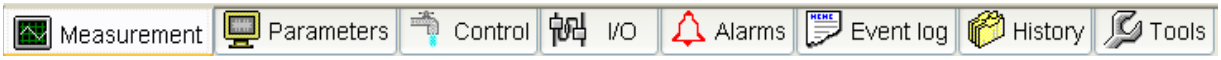
3.2.1 Alarm matrix

Note: *The matrix below is based on a system with one ClippIR; refer to the I/O table specific for your application. This table can be found in appendix at the end of the manual.*

Alarm	**Online / Offline**	**Fault**	**Alarm**	**Warning**	**Bad_Reference _ClippIR_X**	**Data_Invalid _ClippIR_X**	**Remark**
ModBus registers addresses	1	2	3	4	5	6	**Refer to the I/O table for details on ModBus registers addresses**
At FTSW100 start up it is OffLine and can be set OnLine from the console Control panel using the Start button							
The reference failed the Vibration test, Spectral noise > 0.01							
The reference failed the linearity test, peak height > 0.001							
The reference failed the loss of intensity test, Intensity loss > 40 %							
The reference failed the Tube Contamination test, peak height > 0.005							
The system failed the Transmittance Noise test, Spectral Noise > 0.008							
The reference almost failed the Vibration test, 0.005 < Spectral Noise ≤ 0.01							
The reference almost failed the loss of intensity test, 30 % < Intensity loss ≤ 40 %							
The system almost failed the Transmittance Noise test, 0.007 < Spectral Noise ≤ 0.008							
The F-Ratio is almost out of the range for any of the properties on the ClippIR. 75 < F-Ratio ≤ 100							
The F-Ratio is out of range for any of the properties on the corresponding ClippIR. F-Ratio > 100							
Major software error							Difference between the resolution of the model and the resolution set on the instrument.
Major hardware problem (Prevent the system from running)							The analyzer (FTPA2000-200) is not powered up or the Ethernet cable is not plugged. The light source on the instrument is down and needs to be replaced. Any cause that prevent the light signal to go to the detector. (Optic fibre broken)

3.3 Console defined for the application

In the console, the operator can access 8 different screens (also called panels) from which it is possible to monitor the analyzing process, get information on the properties value, access alarm and warning messages, etc.



The operator has also access to Inputs/Outputs and Parameters that provide the capability to enable/disable streams, monitor streams or system status (Fault, Alarms, etc.), consult components and reference diagnostics value.

The console functionalities and particulars for each are described in the FTSW100 User's Guide (ABB part # AA001386-01).

3.4 Database Report Tool configuration file

This file defines the report configurations. A Database Report Tool configuration file is typically provided form ABB when configured from the factory and provided on the Configuration CD. There is one report configuration for each sample analysis stream (associated with each ClippIR) and one for the reference diagnostics of each stream. Refer to the Database Report Tool manual (ABB part #AA003614-01) for detailed use.

Report configuration type	Report configuration name	Reported values
Sample stream (one for each stream in the sequence)	*Stream Name* – Sample	All components concentration of the corresponding stream.
Reference stream (one for each ClippIR hooked to the system)	*ClippIR X* - Reference Diagnostics Values	All reference diagnostics, which are: Vibration test (Spectral noise), Non linearity (Peak Height), loss of intensity, tube contamination (Peak Height), ZPD amplitude value and a transmittance noise test.
Sample stream (one for each stream in the sequence)	ABB "ClippIR X" Results – Sample **Note:** *This configuration will report the data on which the application specialist will base the slope and bias adjustment calculation for the system.*	- Components PLS Concentration - Components PLS F-Ratio - Components concentration Those values are reported for each components of the corresponding stream.

To modify those configurations or to create new ones, refer to the Database Report Tool manua (ABB part #AA003614-01) for details.

4 How to customize your application

Important: *The following modifications can be performed through the configuration tool. You should be cautious when performing those modifications.* ***Improper modifications to the FTSW100 configuration can cause the function and operation of analyzer to be in fault or provide undesired results.*** *Any needed modifications, other than the one described here after, should be performed with the assistance of an ABB trained representative.*

Note: *Every modification done to the configuration file requires being committed in the configuration database in order to take effect in the FTSW100 run-time application at the next restart of the AppServer.* ***An XML file (export of configuration) must be saved every time a modified configuration is committed in order to maintain a copy of configuration in case of major complication (e.g. PC failure).***

Refer to section 5.2.3 Exporting an application in the FTSW100 User's Guide (ABB part # AA001386-01) for details.

On the left hand side of the FTSW100 configuration tool window, is the configuration tree always containing the same six folders or nodes. Like in Windows Explorer, you can expand each node using the plus on its left.

4.1 How to load new model file

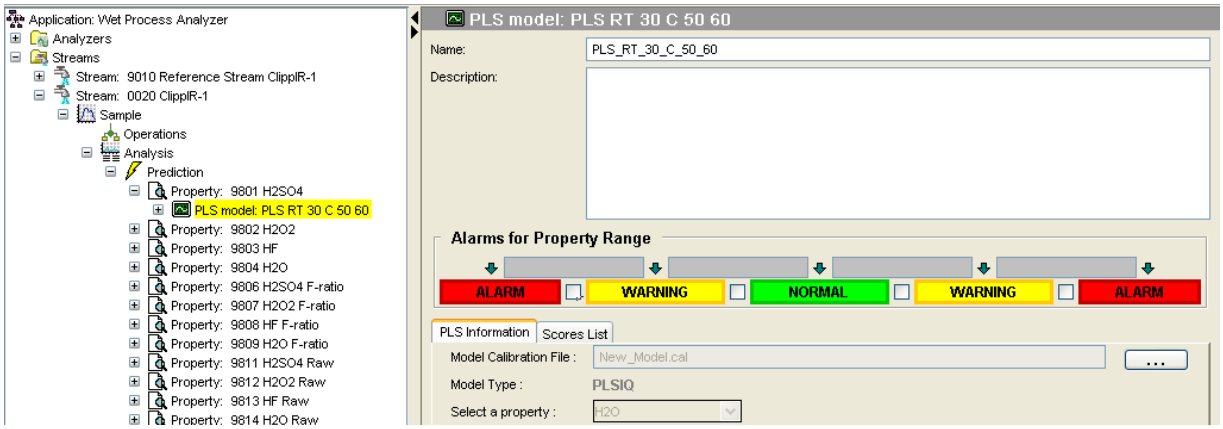
Note: *The application specialist should give the instruction if a new reference is needed when loading new models. By convention, the model files are saved on the FTSW100 computer's hard drive in the* ***C:\FTSW100 Models*** *directory.*

Models are files containing information to predict a property for a given sample. During the life of the system, you may have to update these models.

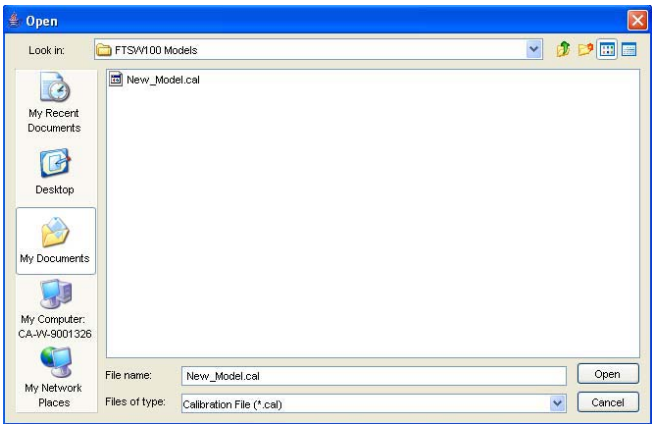
Important: *Since the model files are imbedded in the configuration file (.XML), be sure to have a copy of the .CAL files or keep a backup copy of the .XML file for the current running configuration before loading new model file. After loading the new model file, there is no way to retrieve the previous model files except by re-loading the .CAL file or committing the previous .XML file in the configuration Tool.*

For example: to load a new model for first property of the first stream.

Expand the configuration tree like the figure below to reach the PLS model node. In the settings window, you will find information regarding the current model file. To load the new model file, use the browse button ... at the right hand side of the Model Calibration Files field.



Then, in the open dialog box as below, select the new model file to be loaded and click open



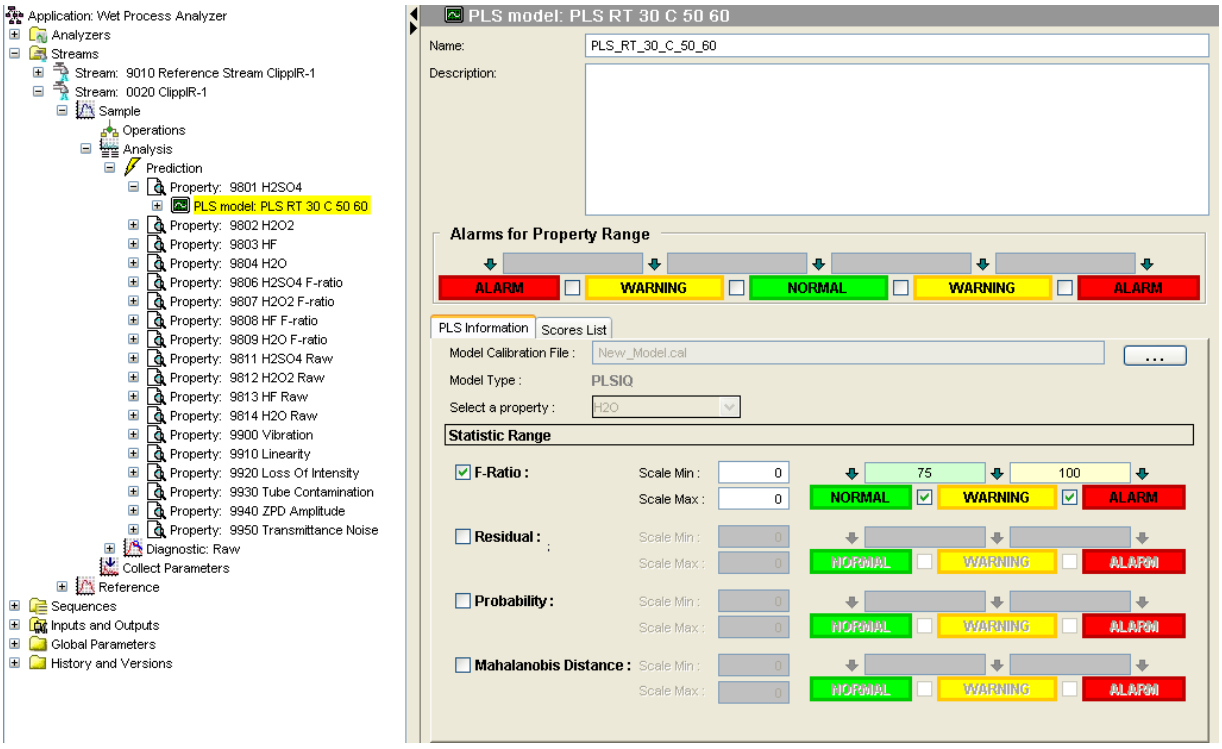
Note: *Note that the name of the .CAL file is for the example needs and can differ. Refer to the application specialist for the new model file name.*

4.2 How to change model alarm criteria (outlier limits)

For each model, a range can be defined for the statistic values (F-Ratio, Residual, etc.). These ranges will be used to define the alarm criteria (warning or alarm) for each model. The application specialist should define these ranges.

For example: To modify alarm criteria for the first property model of the first stream.

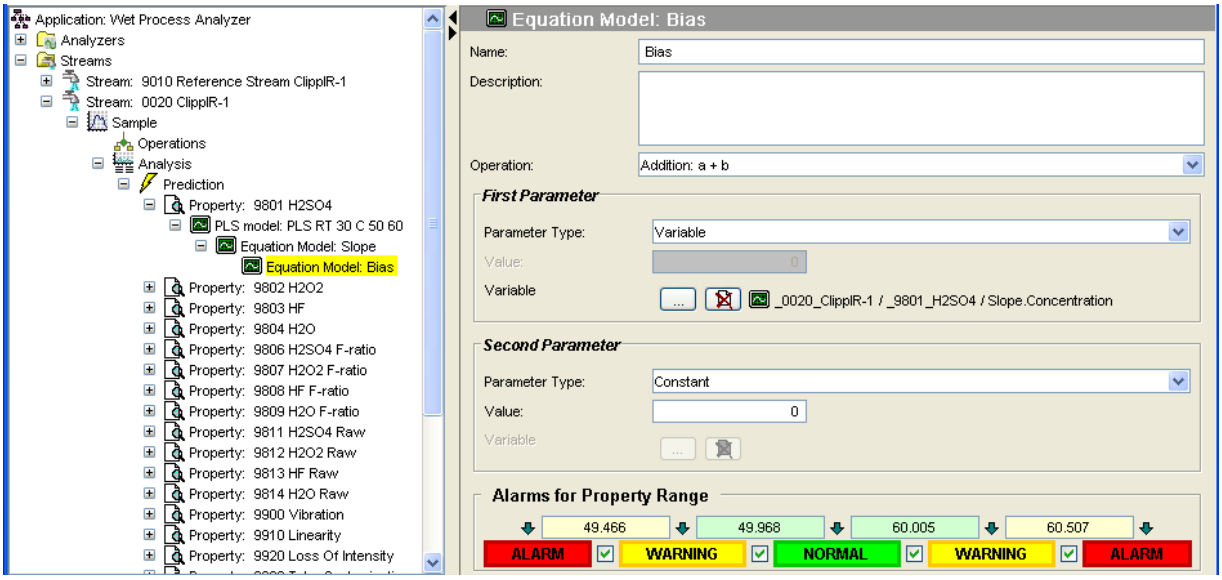
Expand the configuration tree like the figure below to reach the PLS model node. Enable the alarm criteria you want to use and specify the limit values.



Note: ***The F-Ratio value is not reported in the Console's Measurement screen, the column will not contain any value. The F-Ratio value will be validated against the range for alarms or warning. It will only be available as a separate but hidden property to be reported using the Database Report Tool. Refer to section 3.4 Database Report Tool configuration file for details.***

4.3 How to change the prediction alarm and warning ranges

For each property, an alarm and warning range is defined. Those ranges are pre configured and are dependant of the PLS model.



4.4 How to change the Slope and Bias adjustment applied to a model

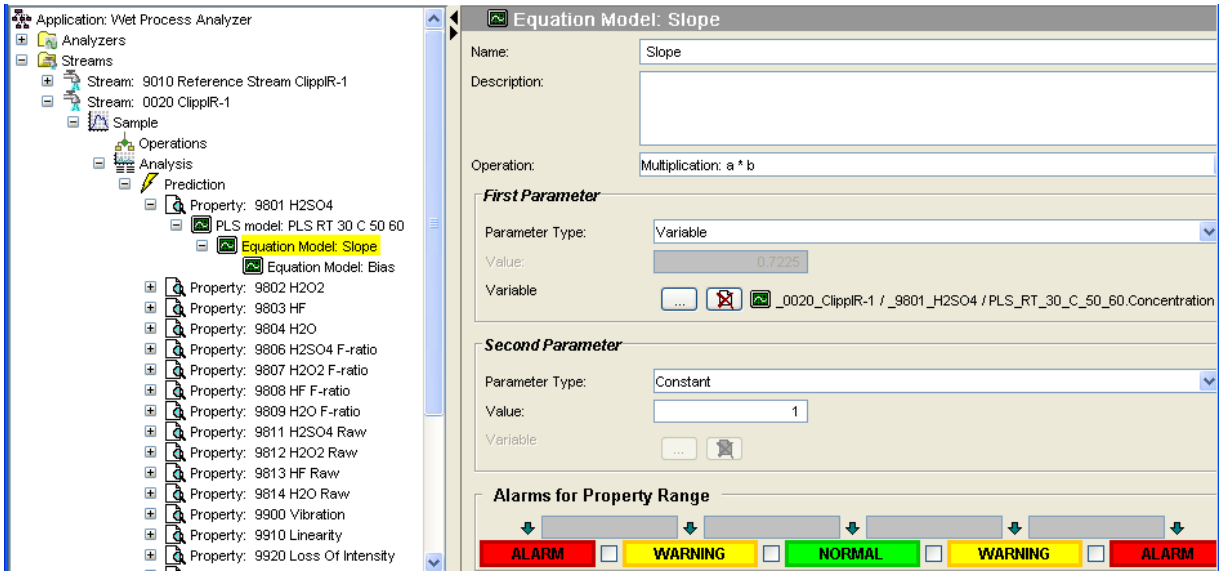
Note: ***You should consult an ABB qualified representative before modifying the slope and bias values. These values have a direct impact on the WPA prediction results and should be defined carefully.***

4.4.1 How to change the Slope adjustment value

The Slope value represent the factor applied to the PLS value.

For example: to change the Slope value for the first property on the first stream.

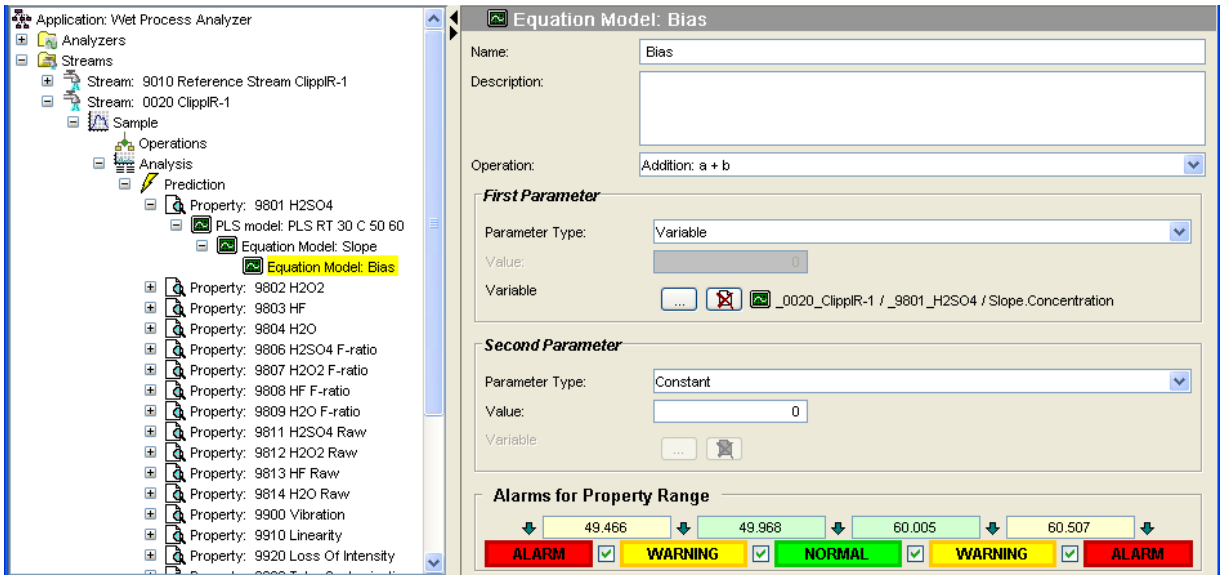
Expand the configuration tree like the figure below to reach the Equation Model: Slope node and change the value for the "Second Parameter" as needed. The other parameters must remain as predefined.



4.4.2 How to change the Bias adjustment value

For example: to change the Bias value for the first property on the first stream.

Expand the configuration tree like the figure below to reach the Equation Model: Bias node and change the value for the "Second Parameter" as needed. The other parameters must remain as predefined.

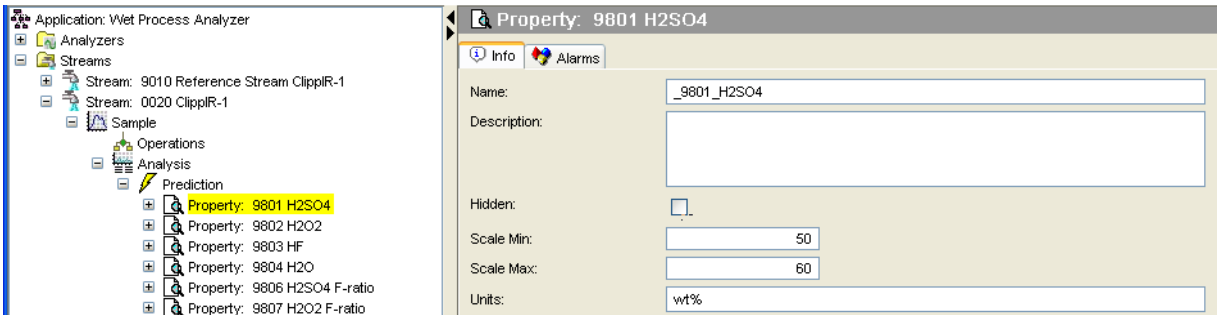


4.5 How to change property range (for trending)

For each property, a range has been defined for the trending of the values in the FTSW100 operator console's Measurement screen Trend chart. These ranges can be modified to suit the needs of the process.

For example: To modify the trending range for the first property on first stream:

Expand the configuration tree like the figure below to reach the first property node on ClippIR 1 and select it. Set the trend line minimum and maximum values in the "Scale Min" and "Scale Max" fields.



Note: *When ModBus RTU or CanOpen hard wired communication is defined, the Analog output range should be modified accordingly. Refer to section* ***4.7 How to change Analog output ranges***

4.6 How to change ModBus device configuration

When changing the device configuration settings, all keywords are case insensitive, however, no white spaces should be added before or following the equal (=) sign.

4.6.1 How to change ModBus address (slave ID)

Expand the "**Inputs and Outputs**" node and select the "**Modbus: Mod BUS**" node. In the "**Device Config Data**" field, enter the desired address by using the keyword "**NODE=**" (1). The default address is 1 (i.e. when the keyword is not used).

4.6.2 How to change ModBus baud rate

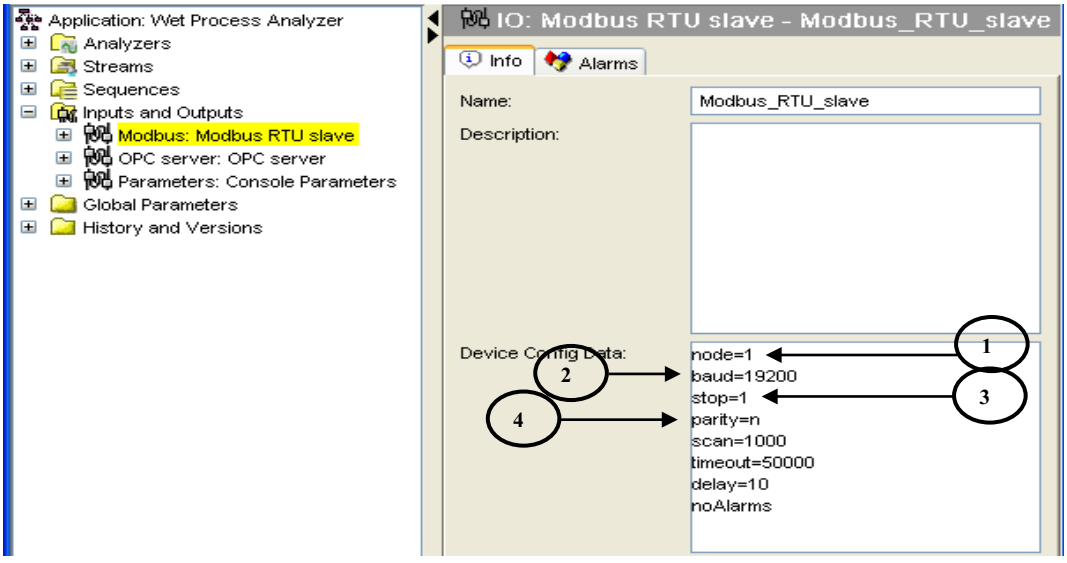
Expand the "**Inputs and Outputs**" node and select the "**Modbus: Mod BUS**" node. In the "**Device Config Data**" field, enter the desired baud rate by using the keyword "**BAUD=**" (2). The default value is 19200 (i.e. when the keyword is not used). Valid Modbus rates are 75, 110, 150, 300, 600, 1200, 1800, 2400, 4800, 7200, 9600, 14400, 19200, 38400, 56000, 57600, 115200, and 128000 but not all systems will support all of these bit rates.

4.6.3 How to change the number of ModBus stop bit(s)

Expand the "**Inputs and Outputs**" node and select the "**Modbus: Mod BUS**" node. In the "**Device Config Data**" field, enter the desired number of stop bit(s) by using the keyword "**STOP=**" (3). The default value is 1 (i.e. when the keyword is not used). Only 1 or 2 stop bits can be defined for data characters.

4.6.4 How to change ModBus parity

Expand the "**Inputs and Outputs**" node and select the "**Modbus: Mod BUS**" node. In the "**Device Config Data**" field, enter the desired parity by using the keyword "**PARITY=**" (4). The default is no parity (i.e. when the keyword is not used). The types supported are: "N" (none), "E" (even), "O" (odd), "M" (mark), or "S" (space).



The three other keywords are necessary and define the following parameters:

scan: *is how often (in ms) FTSW100 will polls the external device for new data or checks for received message.*

timeout*: is the maximum period in milliseconds to wait for request or response from external device, before identifying the connection as having failed (bad quality for all I/O points in device).*

Delay: *default 10ms (configurable)is a delay before FTSW100 (RTU Slave) sends an answer to a request received from the ModBus master*

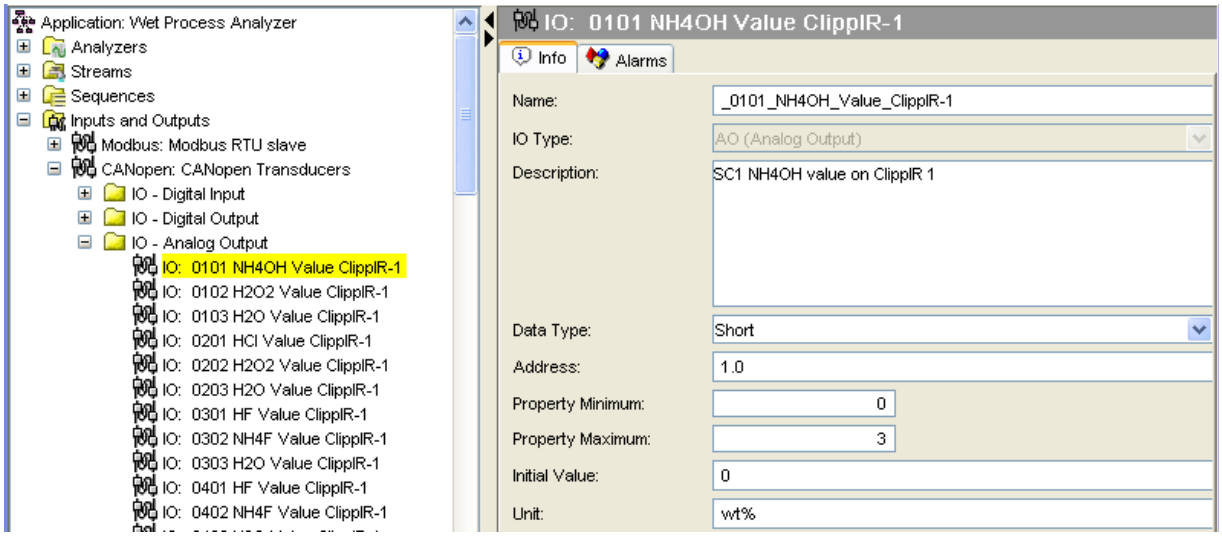
Important: *The noAlarms keyword is used to disable the ModBus communication validation from FTSW100 when that communication type is not used. That way, if the communication fails or if the ModBus RTU Master is not responding, there will be no fault reported in the FTSW100 console. To enable the validation, just remove the keyword and commit the new version of the configuration.*

4.7 How to change Analog output ranges

4.7.1 Hard wired modules

When present, hard wired Analog Outputs can be used to send the property values via CANopen protocol to an external location. The ranges of these outputs can be customized.

Expand the configuration tree, as shown in the figure below, and select the appropriate AO module entry. Change the Property Minimum field, corresponding to the lower output value of the CanOpen module (4mA) and Property Maximum field, corresponding to the higher output value of the module (20mA). This would be valid for range setting of a 4-20mA analog output. A synchronization of range limits is required within configuration and external or receiving device to ensure the information is properly relayed.

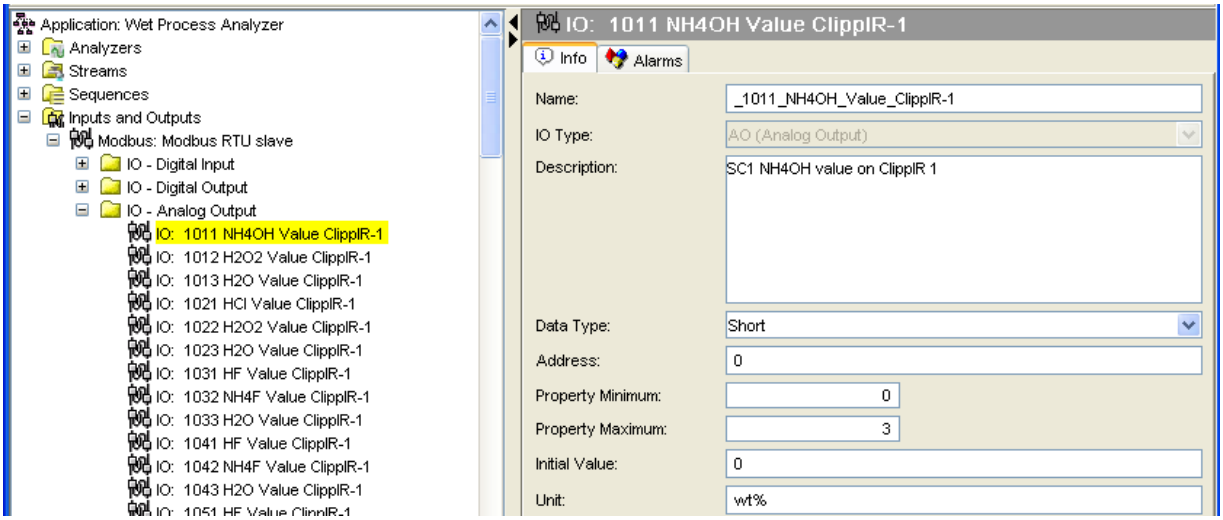


Note: *The CanOpen AO range should be the same as its component range.*

ModBus registers

ModBus Analog Output can also be used to send the property values to an external location. The ranges of these outputs may also need customization.

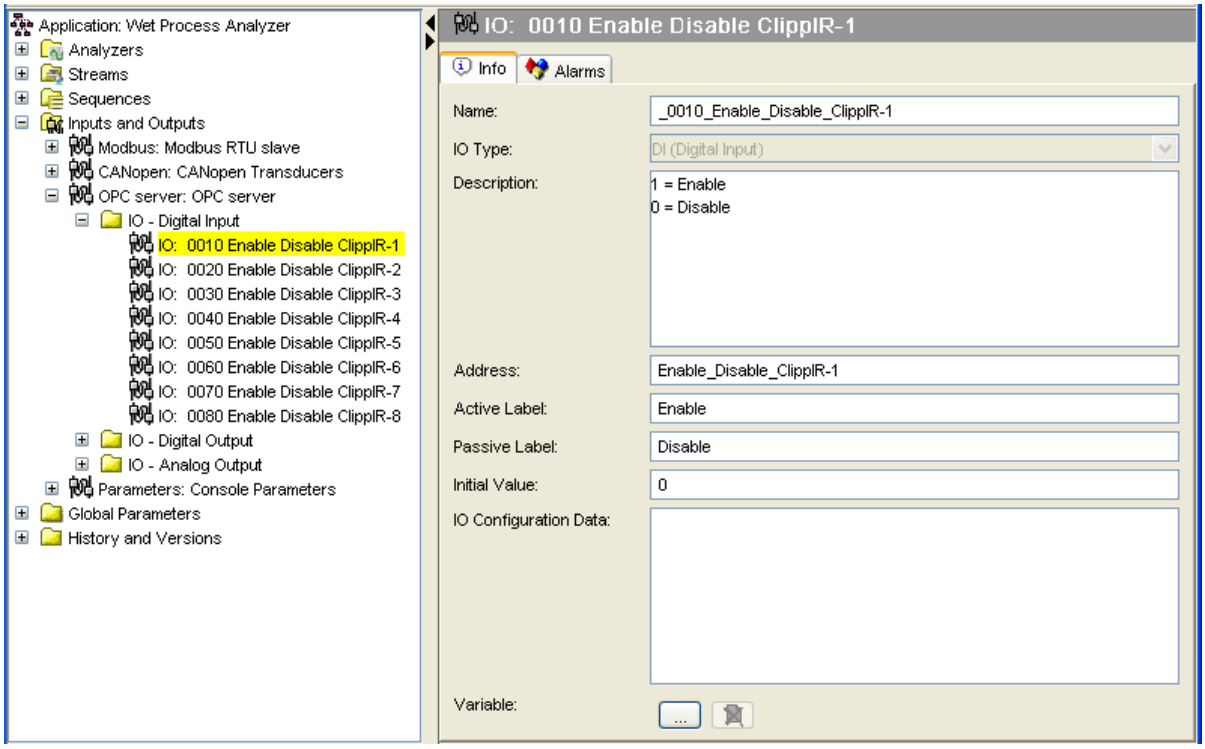
Expand the configuration tree, as shown in the figure below, and select the appropriate AO register entry. Change the Property Minimum field, corresponding to the Low Scale value and Property Maximum field, corresponding to the High Scale value. A synchronization of range limits is required within configuration and external or receiving device to ensure the information is properly relayed.



4.8 How to change OPC Tag names

When using the OPC communication to a control system, it is possible to customize the tag names. It is strongly suggested, however, that the default tags be used to limit modifications and possible errors within configuration.

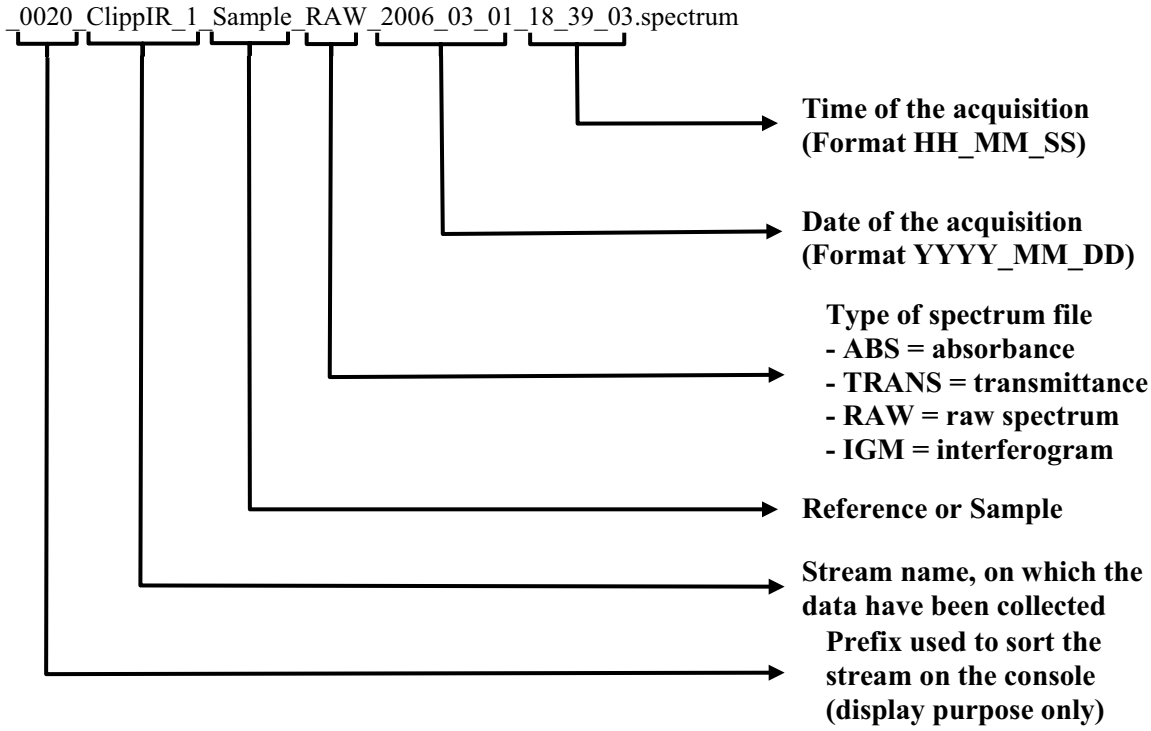
Expand the configuration tree like the figure below and select the appropriate OPC entry. Change the name entered in the Address field to change the tag name. A synchronization of OPC tag names is required within configuration and external or receiving device to ensure the information is properly relayed.



5 Spectrum file naming

Here is an example of Spectrum files and its naming description.

For a complete description of the "saveFile" directory and spectrum file format, refer to the FTSW100 User's Guide (ABB part# AA001386-01).



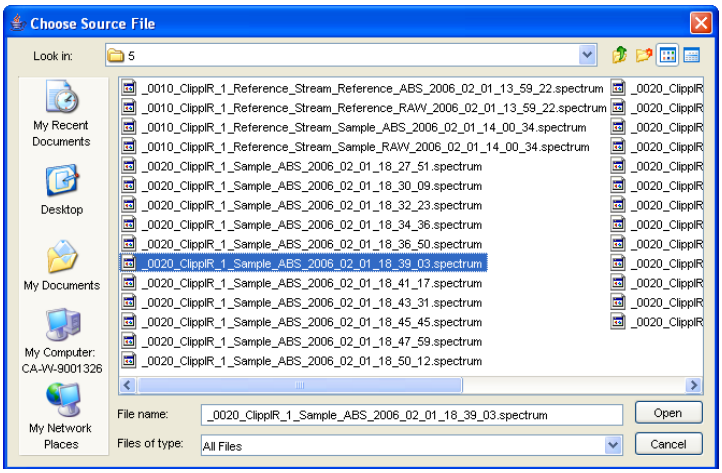
Note: *Only the RAW and Absorbance spectrum are saved.*

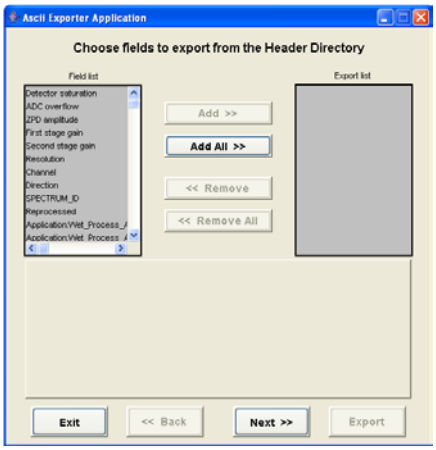
6 ASCII Exporter Application

The ASCII Exporter Application converts files from the internal FTSW100 file format (.spectrum) to FTSW100 ASCII format.

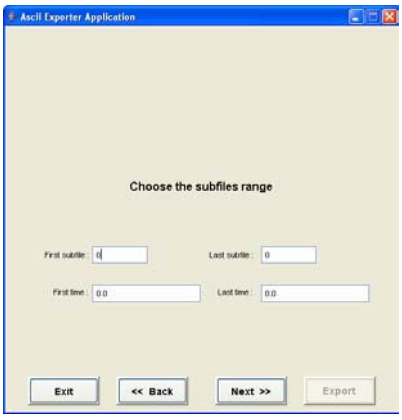
To open the ASCII Exporter Application select "**Programs**" from the "**Start**" menu then point "**FTSW100**", "**Utilities**" and select "**Bomem File Explorer**".

The ASCII Exporter Application interface will appear after a few seconds prompting you to select a file to extract data from. Select the spectrum file and click on "Open". On the next screen, click on "Add All" to have all the variables exported and click on "Next".





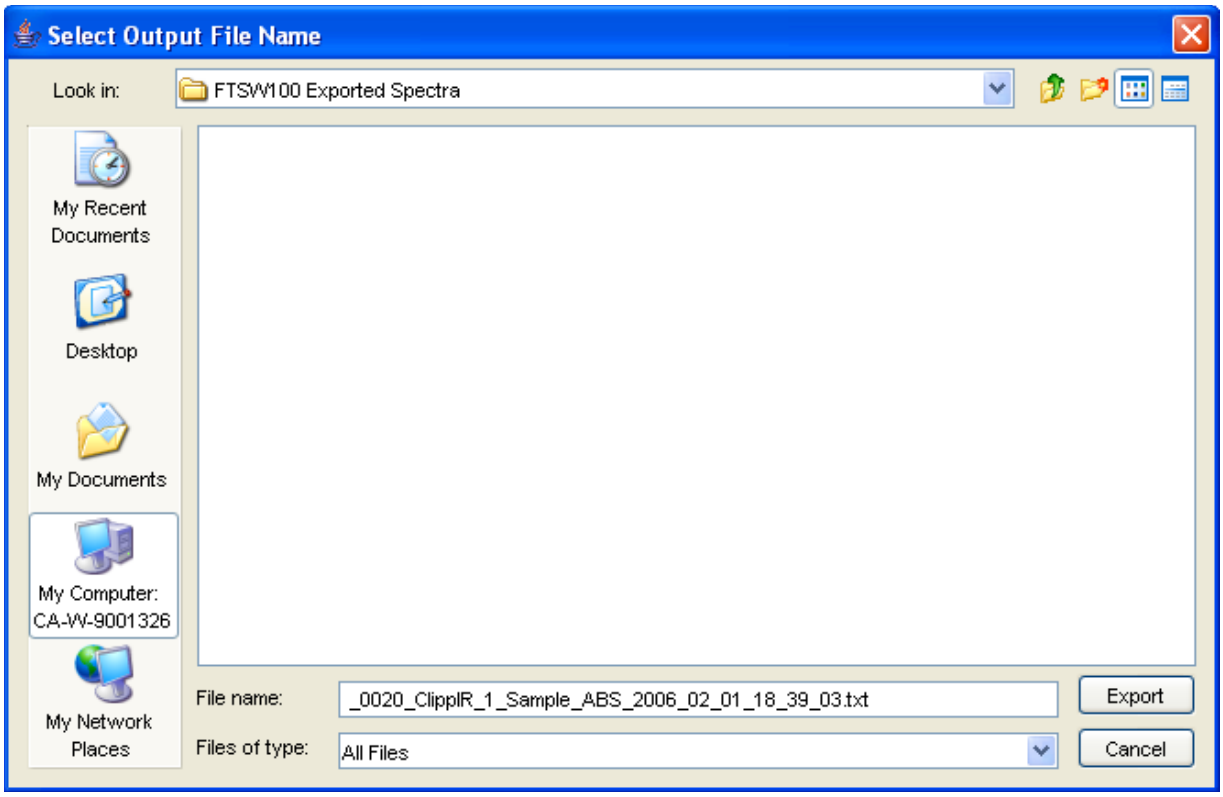
Since FTSW100 generates single files you don't have to enter any information in the "subfiles range" window (below on the left side). On the next screen (below on the right side), click on “Add All” to export all variables and click on “Export”.





You now have to enter a name and folder where to save the exported file. The easiest way to name it is to use the same name as the original file with the TXT extension.

Important: *The default export path is C:\FTSW100 Exported Spectra.*



Enter a path and name to save the file

The application will be closed after you click the export button and no message will be displayed to validate the results.

You can now go to the directory you exported the file to and open it with Windows Word pad application. If available, you can also view the results in Microsoft Excel.

Note: *With FTSW100, there are some other tools that can be utilized to manipulate and manage the data acquired by the run-time application. The operation of those utilities is described in the FTSW100 User's Guide (ABB part # AA001386-01).*

7 CHEMOD properties description

This section shows all the CHEMOD components and their prediction range. It also state the success criteria for each.

CHEMOD-SC1				
Property	**Model Type**	**Range**	**Repeatability**	**Temperature range**
NH4OH	PLS Model	0 – 3 w/w %	0.1 w/w %	20 °C to 70 °C
H2O2	PLS Model	0 – 7 w/w %	0.1 w/w %	
H2O	PLS Model	90 – 100 w/w %	0.2 w/w %	
CHEMOD-SC2				
Property	**Model Type**	**Range**	**Repeatability**	**Temperature range**
HCl	PLS Model	0 – 7 w/w %	0.1 w/w %	22 °C to 70 °C
H2O2	PLS Model	0 – 6 w/w %	0.1 w/w %	
H2O	PLS Model	88 – 100 w/w %	0.2 w/w %	
CHEMOD-BOE				
Property	**Model Type**	**Range**	**Repeatability**	**Temperature range**
HF	PLS Model	0 – 10 w/w %	0.15 w/w %	21 °C to 35 °C
NH4F	PLS Model	22 – 41 w/w %	0.10 w/w %	
H2O	PLS Model	55 – 77 w/w %	0.25 w/w %	
CHEMOD-BHF				
Property	**Model Type**	**Range**	**Repeatability**	**Temperature range**
HF	PLS Model	0 – 10 w/w %	0.15 w/w %	21 °C to 35 °C
NH4F	PLS Model	0 – 22 w/w %	0.10 w/w %	
H2O	PLS Model	65 – 100 w/w %	0.25 w/w %	
CHEMOD-DHF				
Property	**Model Type**	**Range**	**Repeatability**	**Temperature range**
HF	PLS Model	0 – 2 w/w %	0.08 w/w %	21 °C to 35 °C
H2O	PLS Model	98 – 100 w/w %	0.2 w/w %	

Note: *The repeatability is referred to a 3/4 " line. Repeatability for 1/2 " lines must be multiplied by a factor 1.15.*

A specific listing of the CHEMOD configured for each ClippIR is included in appendix

Note: ***Specifications are subject to change without notification***

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