Chapter 1
Product Overview

AutoQuant Pro© is a powerful, automated, multi-component, quantitative analysis program for use in analyzing gas, liquid and solid phase samples.

The program provides a comfortable user interface for operating a MIDAC FTIR analyzer, creating analytical methods to compute compound concentrations and automating data collection for multiple sample stream installations.

In continuous monitoring, mobile, and process applications, the program can display and update, in near real-time, the quantitative results, concentration vs. time plots, and generated spectra. The software provides for multi-level alarms, can output results and alarms to analog or digital devices, trigger external devices, and can archive and export spectra and quantitative results to spreadsheet software.

A Crash Course in FTIR

Fourier transform infra-red spectroscopy (FTIR) utilizes the absorption of infra-red radiation at discrete frequencies by analyte molecules. Absorption and emission of infra-red radiation is associated with transitions between vibrational / rotational energy levels in a molecule. A molecule is infra-red active if it possesses modes of vibration that cause a change in dipole moment. This means that monatomic and homonuclear diatomic species (N2, O2, F2, H2, Cl2, etc) are infra-red inactive. This is an advantage because ambient molecular nitrogen and oxygen would quickly "blind" the FTIR. The magnitude of the absorption of radiation is proportional to the number of molecules in the beam path, and hence proportional to the concentration of each absorbing species. The schematic diagram in Figure 1.1 illustrates this principle.

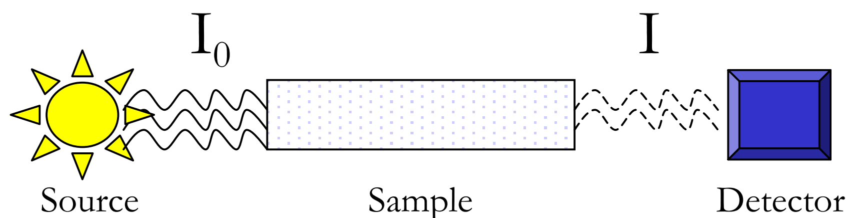

Figure 1.1 Schematic Absorbance Diagram

Where I_0 is the initial intensity of the radiation and I is the radiation attenuated by the amount absorbed by the sample being a solid, liquid, or gas. In order to determine the concentration of absorbing species we must first measure I_0 through an empty sample cell. This measurement creates a *background spectrum*. Once we have a background spectrum we can fill the sample cell and record a *sample spectrum*. The ratio I / I_0 (sample / background) is called the *transmission* spectrum. The transmission spectrum plots the fraction of the emitted radiation reaching the detector on the y-axis with wavenumbers (1/cm) on the x-axis. A transmission spectrum is shown in Figure 7.4 in Chapter 7. The transmission spectrum is related to the concentration of absorbing species logarithmically. An *absorbance* spectrum is generated by taking the $\log_{10}$ of (1/T), where T is the transmission. The absorbance is linearly related to concentration (subject to limitations discussed later in this section), and it is the absorbance that is used to determine the concentration of analytes. The relationship between absorbance and concentration is given by the Beer – Lambert law:

$$A_i = e_i C_i \, l$$

Where A_i is the absorbance of the *ith* component, e_i is the *absorption coefficient* (a constant at each frequency for each molecule) of the *ith* component, C is the concentration of the *ith* component and l is the distance that the radiation travels through the sample, known as the *pathlength*.

The above discussion applies to *monochromatic* radiation (radiation of a single wavelength). However, we need to look at a wide range of wavelengths in order to build up a spectrum. Early infra-red spectrometers used diffraction gratings and apertures to select one wavelength at a time. This method is slow and subject to large uncertainties in the x-axis values. As computing

power increased it became possible to generate infra-red spectra using *interferometry*. A schematic diagram of an interferometer is given in Figure 1.2.

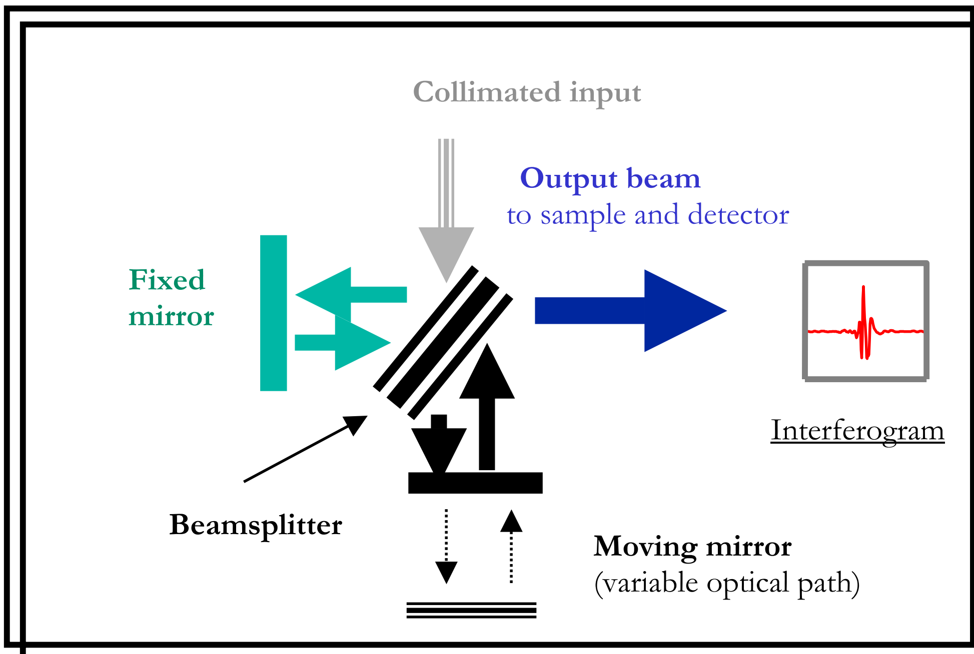

Figure 1.2 Schematic diagram of an interferometer

In an interferometer, radiation from a source is collimated and guided to a beamsplitter. A portion of the beam is reflected onto a fixed mirror, while the rest travels through the beamsplitter to a moving mirror. Both these beams are reflected back to the beamsplitter where they are recombined. At this point the beam may either pass through the beamsplitter and travel back to the source, or be reflected to the detector. Of the two paths to the detector, one is fixed while the other is varied by the distance traveled by the moving mirror as it scans back and forth. As the moving mirror travels through distances which are integer multiples of the radiation wavelength the interference at the recombined beam is completely constructive. The distance the mirror travels determines the resolution of a spectrum. A 0.5 cm-1 resolution accounts for a data point every 0.241 wavenumbers and over 32,000 data points in the interferogram. The opposite is true when the path is a half integer multiple of the wavelength, that is to say the interference is completely destructive. As well as integer and half integer multiples, the distance traveled by the beam will also pass through every fractional multiple of the wavelength. This results in an interference pattern, known as an interferogram. A simplified interferogram is illustrated in Figure 1.3.

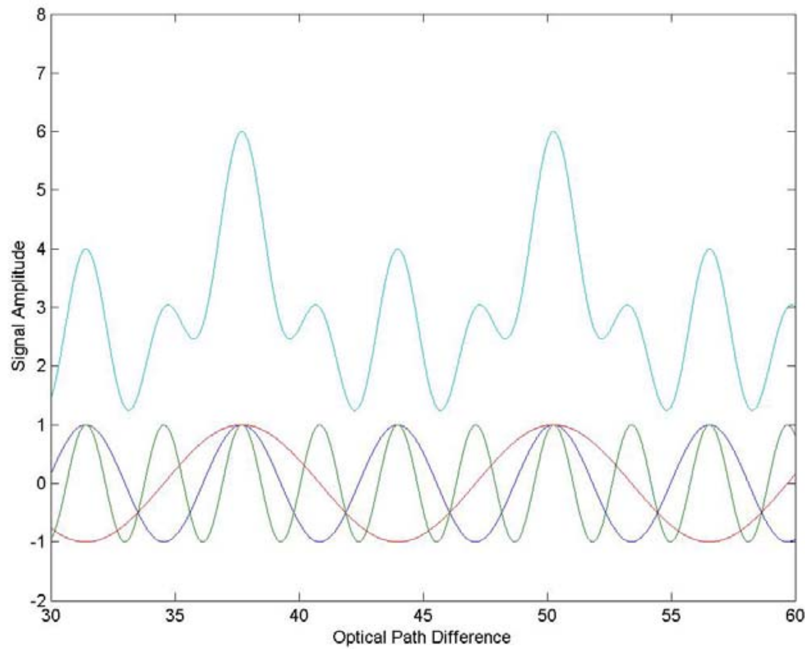

Figure 1.3 Simplified Interferogram

Figure 1.3 shows three cosine waves and their sum, offset by three signal units for clarity. An actual interferogram is more complex, with the amplitude decreasing with distance from the ZPD burst as shown in Figure 1.4.

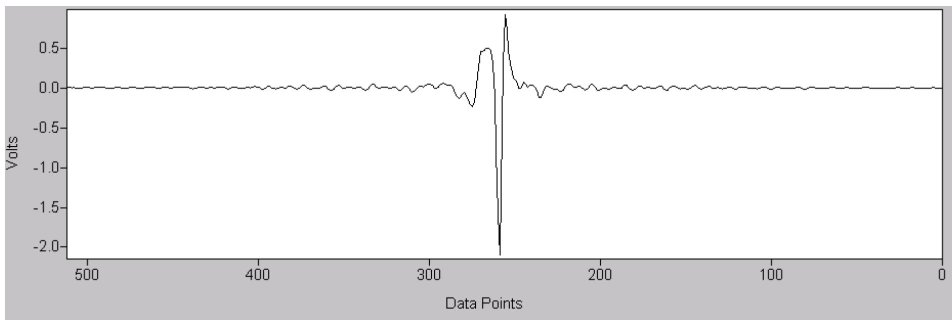

Figure 1.4 Actual Interferogram

The large peak at the center of the interferogram corresponds to the point at which the moving mirror and the fixed mirror are in such positions that all wavelengths of the radiation are in phase and thus constructive. This point is known as zero path difference or ZPD. The radiation reaching the detector contains 'encoded' information about all other wavelengths. This information can be recovered using a Fourier transform. The Fourier transform of an interferogram is called a ***Single Beam*** spectrum. While a

full description of a Fourier transform is beyond the scope of this user manual, the technique may be used to convert data from the time domain (interferogram) to the frequency domain (spectrum). Before a Fourier transform is performed however, it is necessary to take into account a disconnect between theory and practice. In theory the Fourier transform is integrated over the limits $-\infty$ to $+\infty$. In practice of course, the moving mirror can only travel a finite distance. This means that the start and end of the interferogram introduce anomaly effects in the transform. The interferogram may be treated to remove artifacts caused by transforming a data set of finite length. This treatment is known as *apodization* (from the Greek 'no feet') as the aim is to remove side lobes generated on peaks in the spectrum. AutoQuant Pro© uses a function known as *triangular* apodization (default), but also offers *medium Beer-Norton* apodization or boxcar (no apodization). Once the spectrum has been treated in this way, it can be used with the Beer-Lambert law to determine concentrations. There are limitations to consider when selecting absorbance bands to use in a quantitative calculation. Consider the spectrum shown in Figure 1.5.

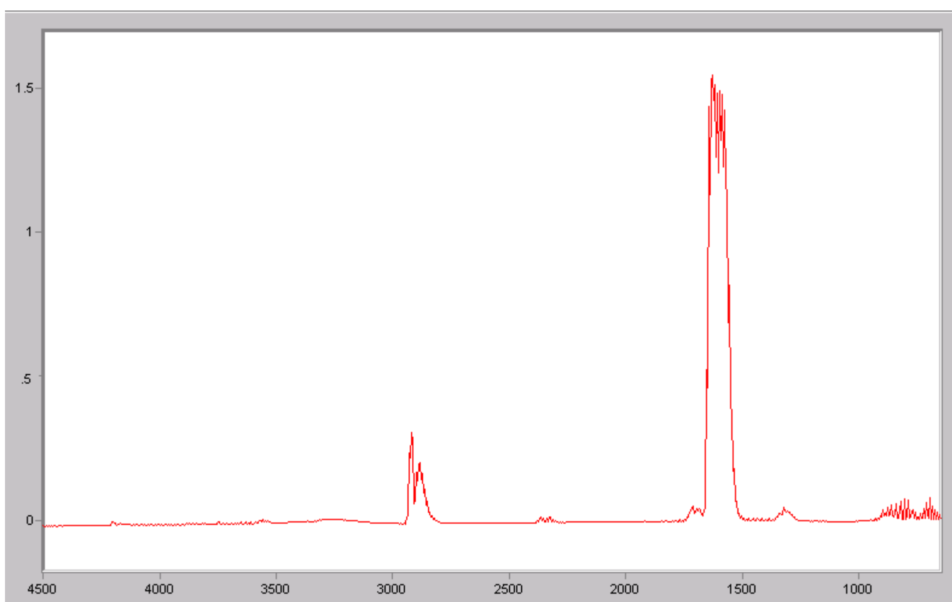

Figure 1.5 NO_2 at 8000ppm-m

The band at approximately 1600cm^{-1} has an absorbance peak of around 1.5 units. Converting this to transmission we find that only 3% of the initial radiation reaches the detector. When transmission drops to approximately 10%, the instrumental resolution begins to cause a loss of information. This translates as an apparent loss of linearity in the Beer-Lambert law. In an analysis, the band at 2900cm^{-1} should be used, as more than 50% of the initial

radiation arrives at the detector. The real problem is the use of certain detectors that can exhibit non-linear tendencies when too many photons are striking the detector. The detector linearity can change with total photon flux. Some detectors are more linear than others. Some non-linear detectors are the MCT and some linear detectors are DTGS and InSb.

The entire process of data acquisition and processing is summarized in Figure 1.6.

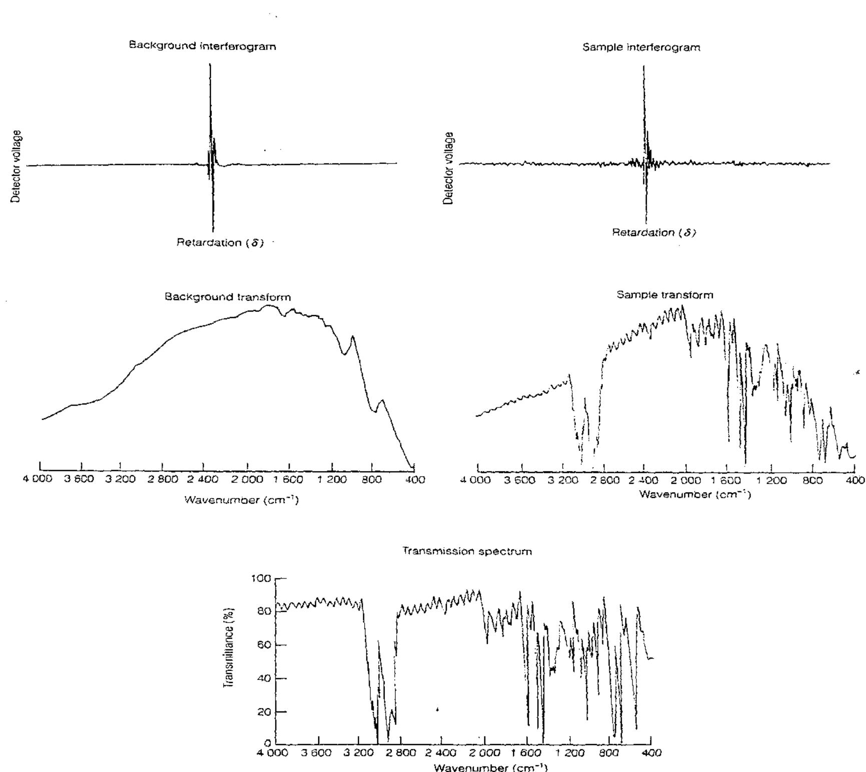

Figure 1.6 Summary of FTIR Data Generation

1) Background and sample interferograms are recorded
2) The interferograms are Fourier transformed from the time domain to the frequency domain
3) The sample single beam spectrum produced has its ratio performed point by point against the background single beam to produce a transmission spectrum
4) The negative logarithm of the transmission spectrum yields the absorbance spectrum. The absorbance is linearly related to concentration.

A note about signal to noise:

There are many factors that impact on signal-to-noise in an FTIR spectrum. Electronic, mechanical and optical sources all produce noise in a spectrum. The two most significant factors under the control of the user are the resolution at which the spectrum is recorded and the time spent collecting data for that spectrum. High resolution spectra are inherently noisier than low resolution. This can be explained in terms of the interferogram. Consider Figure 1.4. In a very low resolution spectrum, the interferogram would consist of the area around the ZPD and little else. The signal in this region is very strong, and so signal to noise is high. In order to record higher resolution spectra however it is necessary to use data further out on the wings of the interferogram. The further out on the "wings" we travel, the higher the resolution but the lower the signal, and noise has larger effects on the quality of the data. The second user controllable parameter affecting signal to noise is the integration time (or number of co-added scans used to create the interferogram). <u>As the time interval over which the interferogram is recorded doubles, the signal to noise improves by a factor of the square root of 2</u>. This is discussed further in Chapter 6. However, bear in mind that S/N is really a function of the time scanning. The longer time scanning, the better the signal to noise ratio. The MIDAC spectrometer is truly integrating and will provide improved signal to noise by increasing the number of scans and thus time scanned. It is not unusual for users to scan one sample for many minutes to provide extremely low noise signatures. The MIDAC spectrometer is truly only detector noise limited.

File Compatibility:

Spectral files collected in AutoQuant Pro© are compatible with Grams file formats (.spc).

Additionally, the MIDAC software package AutoQuant Pro© provides fully automated control for long-term continuous data acquisition over multiple sample streams. Together, the suite of software can control multiple valving and pump configurations and can automatically collect background spectra, calibration spectra, and data from multiple sample lines and/or pumps, switches, and valves up to presently **60**. Data are organized automatically in subfolders with their own respective results file and can be stamped according to date and time (down to the millisecond) of acquisition or sequentially numbered. Sockets technology and command line operations allow interfacing with other software packages or custom programs for remotely starting and stopping collections or sending spectral data.

The AutoQuant Pro© software is based on a C++ platform for stability and high-speed execution of most arithmetic and collect functions.

This approach gives MIDAC users tremendous flexibility in the development of custom routines for process, environmental, or QA/QC-type applications.

Chapter 2
Installation and Setup

AutoQuant Pro© software can be installed on any desktop or notebook PC that runs MS-Windows 2000 or higher operating system software.

System Requirements
The PC must meet the following minimum hardware requirements:

- Pentium III or higher CPU (800 Mhz or higher)
- At least one free PCI or PCMCIA slot that the computer can assign 32 bits of memory allocation
- VGA or display with 1024 x 760 resolution
- At least 128mb RAM (256mb or more recommended)
- At least 20 Gb hard drive, with at least 50mb free space for installation of software
- Significant additional free disk space for method calibration files and for data collection
- R/W CDROM for installing software and archiving data
- Windows 2000 Professional operating system with latest service paks. AutoQuant Pro© will run on other platforms although Windows 2000 is preferred
- Mouse or other pointing device

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Installing the Hardware:

Interface Card
The system requires a proprietary spectrometer interface card (which is shipped from the MIDAC factory with each instrument) to handle communication between the spectrometer and computer.

Two types of interface cards are used: PCI cards for desktop computers and PCMCIA cards for notebook computers. These cards require a proprietary software device driver that's compatible with the interface card and with the type of electronics used in your particular spectrometer (either single ADC or dual ADC).

If you are uncertain which type of ADC your system contains, check the original packing list and/or sales documentation, which should specify Single or Dual ADC in the description. A general rule is that most systems shipped prior to May 2002 are equipped with Single ADC electronics; while most shipped after that date are equipped with Dual ADCs. However, there are some exceptions. If you are unable to determine by any other means, the type of A/DC is printed on the circuit board inside the spectrometer. Refer to your *Operator's Manual* or MIDAC's service department (714) 546-4322 for appropriate cautions and procedures before opening the spectrometer to check.

Installing the Software

1. With MS-Windows running, close all application programs before installing the AutoQuant Pro© software package.

2. Place the AutoQuant Pro© CD in your CD-ROM drive. Click the **Start** button on your Windows taskbar, then select **Run.**

3. Type the drive designator for your CD-ROM drive plus the term *setup_aq4* in the space provided.

   For example:

   d:\setup_aq4 or *e:\setup_aq4*

(Or click on the **Browse** button and find the *setup_aq4.exe* file on the CD).

4. Follow the directions provided on the program screens to progress through the software installation.

When the setup program has finished, the AutoQuant Pro© icon will appear on the screen, and the AutoQuant Pro© software will appear under Programs on your Start menu.

5. If you've installed the software on the computer of an existing FTIR system that is fully functional and able to collect data (i.e., via Grams software), your installation is complete. There's no need to install a new device driver. If you are updating your AutoQuant Pro© software to a newer version, simply install over the previous version. No data or methods will be overwritten.

   To run the software, double click on the desktop icon or select **Start >> Programs >> AutoQuant >> AutoQuant Pro©.**

6. If you are changing computers or installing a new system, you'll need to install your spectrometer/data system interface card and the appropriate device driver, as described below.

Device Driver Software

The simplest way to install the appropriate device driver is to turn off the computer, install the interface card in the appropriate expansion slot, turn the computer back on, and let MS-Windows automatically detect the hardware and install the driver. You'll then be prompted to provide the information described below.

Alternatively, you can open the MS-Windows "**Control Panel**" and select the "Add/Remove Hardware" option to start the installation process. When you select "Add/Remove Hardware" you will activate the **Installation** Wizard.

Following are the steps for use with the **MS-Windows 2000 Installation Wizard:**

1. On the "Choose a Hardware Device" screen, select "Add a new device."

2. On the next screen, "Find New Hardware," select "No, I want to select hardware from a list."

3. On the next screen, "Hardware Type," select "Other devices."

4. On the next screen, "Select a Hardware Driver," click on "Have Disk" button.

5. When the "Install From Disk" dialog box appears, select "Browse" and locate the directory on your hard drive where the appropriate driver is located.

Note All driver names are identical, so you MUST select the driver from the proper directory. By default, AutoQuant Pro© is installed under "Program Files."

The individual driver directories are located under the "drivers" subdirectory under the Autoquant4 program as follows:

C:\Program Files\AutoQuant4\drivers\single_pci (for the single ADC PCI board)

C:\Program Files\AutoQuant4\drivers\single_pcmcia (for the single ADC PCMCIA board)

C:\Program Files\AutoQuant4\drivers\dual_pci (for the dual ADC PCI board)

C:\Program Files\AutoQuant4\drivers\dual_pcmcia (for the dual ADC PCMCIA board)

Once the AutoQuant Pro©© software and the spectrometer device driver have been installed, reboot the computer.

To run the software, double click on the desktop AutoQuant Pro© icon or select **Start >> Programs >> AutoQuant >> AutoQuant Pro©.** You're ready to go.

Chapter 3
Getting Around the Menus

The AutoQuant Pro© display is rich with information and features, providing the familiar feel of many Windows applications.

You can operate the software via menus, graphic toolbars, push buttons, or a combination of all three, depending on how you like to work.

The program and its displays are designed to match the flow of your work, from setting up the instrument to defining an analytical method, activating data collection, and displaying results.

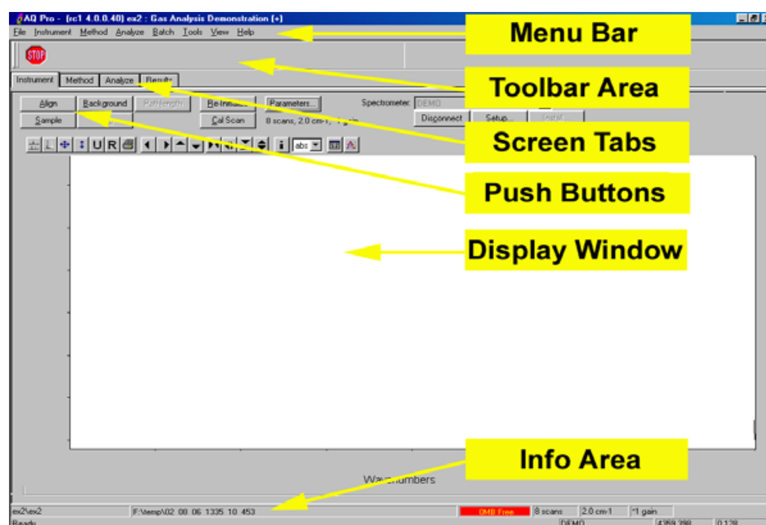


Figure 3.1 Main Sections of Screen

Menu Bar

The menu bar along the top of the display provides access to all the major program functions. Item-by-item descriptions are provided in Chapter 5.

Figure 3.2 Main Menu Bar

The menu items on the main menu bar are as follows:

File	Provides all basic file operations for handling defined methods such as loading, saving, importing, and opening new methods.
Instrument	Provides the means for configuring the instrument prior to data collection as well as basic instrument controls.
Method	Provides a variety of functions useful in building your analytical method as well as method file handling utilities. Automatically opens the "Method Screen" when a menu item is selected.
Analyze	Provides information entry to configure and to initiate single, continuous or high-speed data collection runs. Automatically opens the "Analyze Screen" when a type of data collection is selected.
Batch	Provides the means for reprocessing stored data. Useful for implementing method refinements and adjustments.
Tools	A collection of useful tools including instrument setup parameters, spectral search, library and alarm functions.
View	Provides for selection and de-selection of toolbars to customize the AQ Pro display according to individual preferences.
Help	Access to Help files and software version information.

Toolbars Graphic toolbars can be used as an alternative or supplement to the main menu bar. Use the View menu to select toolbars you wish to display.

Some users prefer the easy "single click" access to functions provided by the toolbars; others prefer the added display area without them.

The four toolbars available with AutoQuant Pro© are as follows.

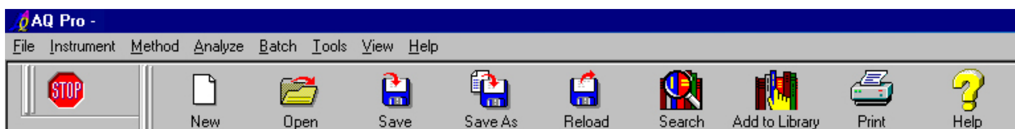


Figure 3.3 File Toolbar

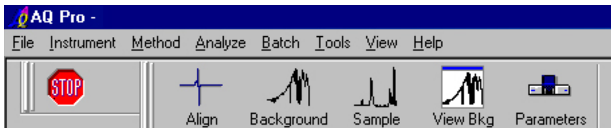


Figure 3.4 Instrument Toolbar

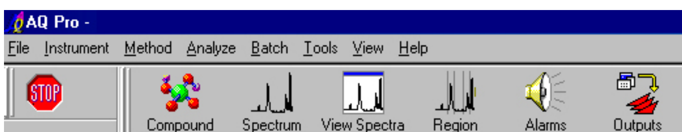


Figure 3.5 Method Toolbar

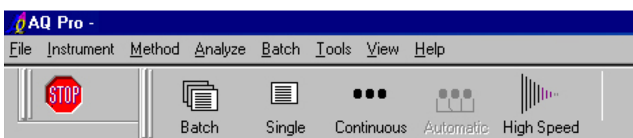


Figure 3.6 Measurement Toolbar

By default, toolbars are displayed along the top and left sides of the screen. However, you can drag and place them anywhere you want. To move a toolbar, click on its handle (or an inactive area around the icons), then hold down the left mouse button while moving the toolbar to the desired location.

To remove a toolbar, position the cursor over any part of the toolbar area and *right click* your mouse. Uncheck the toolbar you want to remove. You can also do this via the ***View*** menu. Similarly, to display a hidden toolbar, click the desired selection on the list. A check will appear next to the item, and the toolbar will be displayed. You can then arrange the toolbars as you please.

One special toolbar icon is the red ***Stop Sign*** that appears near the upper left corner by default. Use the ***Stop Sign*** icon to terminate any data collection activity in progress (the same function is provided by the ***Stop*** button on the ***Instrument*** screen). Although you can move the ***Stop Sign*** icon around, or remove it entirely, we recommend that you keep it displayed where you can access it conveniently.

Screen Tabs and Push Buttons

The four primary display screens (Instrument, Method, Analyze, and Results) are accessed by the four tabs near the upper left corner of the display. They are automatically displayed when certain menu or toolbar items are selected. The screens are presented in the order in which tasks are usually performed – starting with the ***Instrument*** screen.

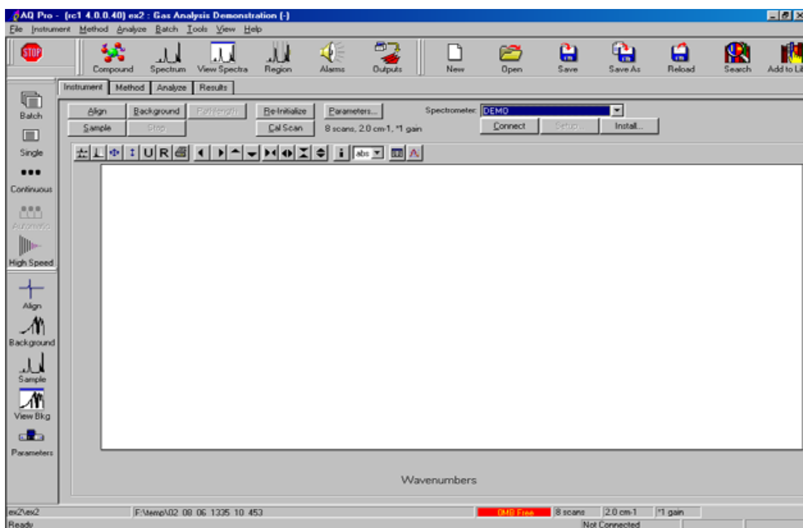


Figure 3.7 Instrument Screen With Toolbars Displayed

Pushbuttons on this screen (and the other three main screens) let you perform essential functions with a single click. They duplicate the functionality of most key toolbar icons, so that you can still have single-click operation — even when you hide toolbars to gain greater display area. Buttons for each screen will be described in detail in the next chapter.

The primary focus of the four main screens is:

a) Spectral display on the Instrument Screen
b) Reference spectra file information on the Method Screen
c) Spectral display/trend chart/concentration table on the Analyze Screen
d) Report table for collected data on the Results Screen

Information and Status Lines

The two lines at the bottom of the AutoQuant Pro© display screen provide a convenient reminder of the currently chosen analytical method, instrument status and data collection parameters.

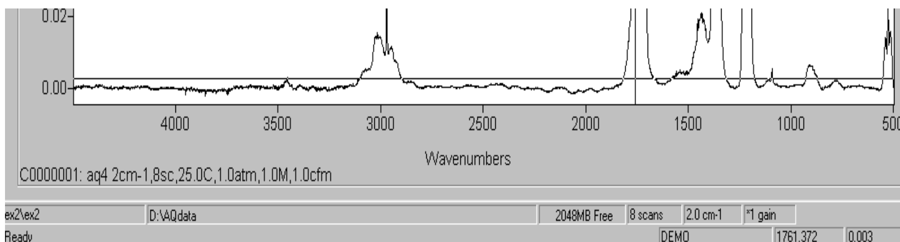


Figure 3.8 Information and Status Lines

For example, Figure 3.8 shows the lower portion of the spectral display window. File information for the displayed spectrum appears just above the Information and Status Lines. At the far left of the upper ***Information Line***, you see "ex2\ex2". This is the directory location and the name of the currently active method. Moving to the right, "D:\AQdata" indicates the directory chosen for storage of collected data. Continuing to the right, "2048MB Free" indicates the amount of available hard disk space remaining. The last three fields indicate current data collect settings for scan sets, resolution and gain.

The lower ***Information Line*** in Figure 3.8 starts with "Ready", indicating that the spectrometer is connected and ready to collect data. Moving to the right, "DEMO" is the type of instrument connected (usually this will include the type of interface card and A/D processor). The final two fields are the X and Y axis values for the current cursor position in the spectral display window.

Right Mouse Click Functions
A primary goal of AutoQuant Pro© is to let you be as efficient as possible. This includes minimizing the amount of time you spend looking for tools within the program and maximizing the time you spend intelligently building and implementing your analytical methods. In keeping with this goal, the right mouse button provides quick access to features directly related to where you are onscreen.

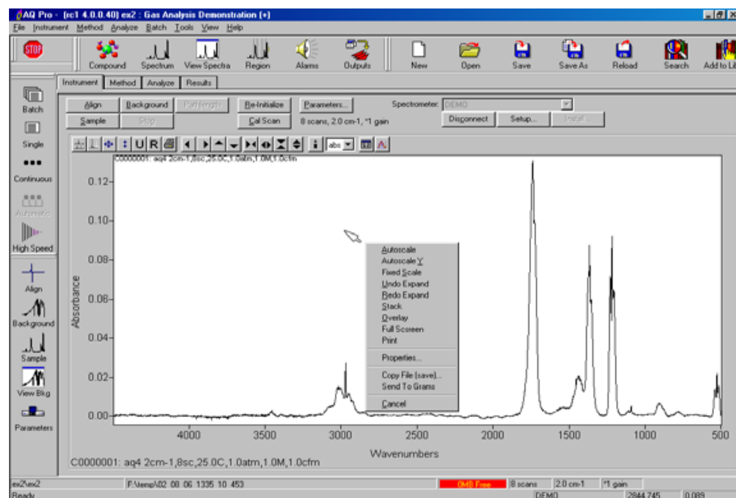


Figure 3.9 "Right-Click" Menu

This "context sensitive" feature means that a right click on the spectral display window brings up display manipulation tools; a right click on the strip chart brings up chart options; and a right click on the spectra area of the

method screen lets you add or view spectra without going to the Main Menu bar. In short, try right clicking on the mouse wherever you are onscreen as the first step to quickly accomplish a task.

Chapter 4
Feature Descriptions

This chapter presents AutoQuant's four major program screens.

Building an accurate and robust analytical method that returns reliable measurements across a range of process conditions and sample concentrations is iterative. AutoQuant Pro© takes you through the process in a logical progression of steps. In fact, the sequence of four screens is designed to match your workflow through the four major tasks in obtaining data:

1. Configuring the instrument to fit your needs.
2. Selecting and collecting references to build your analytical method.
3. Activating data collection to analyze your samples.
4. Recording and displaying results of the analysis.

Chapter 5 provides an item-by-item walkthrough of each menu/toolbar on the four screens. Most AutoQuant Pro© functions can be accessed in any of three ways (via pushbuttons, menus, or toolbar icons) with identical results.

The Instrument Screen

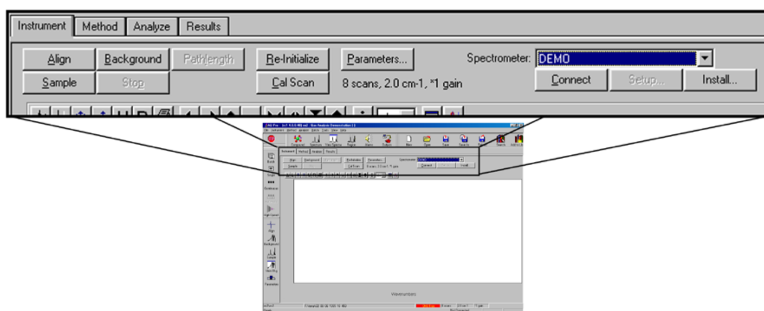


Figure 4.1 Push Buttons on the Instrument Screen

The Instrument screen includes eleven pushbutton controls, as shown in Figure 4.1.

The Align Button

This button allows viewing of the interferogram signal levels as you align the fixed mirror to optimize performance. When pressed, Align will immediately begin continuously collecting and displaying either interferograms, single beam spectra or both, (as shown below), depending on the display format selected.

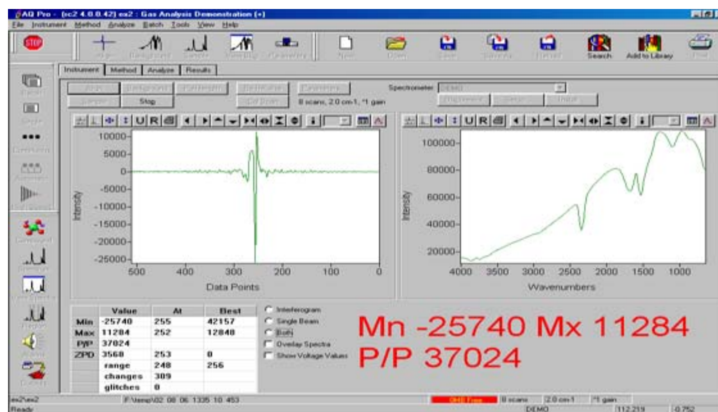


Figure 4.2 Align Screen Display Formats

You may choose whether the interferogram signal is displayed in voltage or data bit format. The purpose of alignment is to maximize signal at the detector without overflowing the ADC capacity. Since the interferogram is rarely symmetrical at the centerburst, alignment should be done by observing both the singlebeam spectrum and the minimum or maximum signal value, whichever is greatest in absolute value. The singlebeam spectrum allows the user to optimize the signal in the more difficult to obtain higher energy areas above 2800 cm-1. Additionally, the absolute value of the Max **OR** Min

should fall between 70% and 90% of the A/DC capacity (this translates to approximately 23,000 – 29,500 data bits, or 1.75 – 2.25 Volts). The Min, Max, and Peak-to-Peak values are displayed in large red characters on the Align screen for easy reference as you adjust the fixed mirror. Please refer to subsequent chapters for alignment procedures.

Note: Newer Dual ADC systems do not need the ADC to be nearly saturated for good signal to noise ratios. A max or min number of above 8000 is adequate but maximizing the signal is better for high moisture streams.

The Align screen also allows you to overlay signals on the display for a visual record of stability and changes over time. Each subsequent scan will be superimposed over previous data in a different color. Data are also displayed in tabular form on the lower left.

The Sample Button

This button initiates collection of a sample spectrum and displays the results. If a method is defined and active, the data will be collected according to parameters specified within the method. If not, the instrument will use default parameters to collect the spectrum. A reminder of the settings currently in use appears just under the Parameters button above the spectral window.

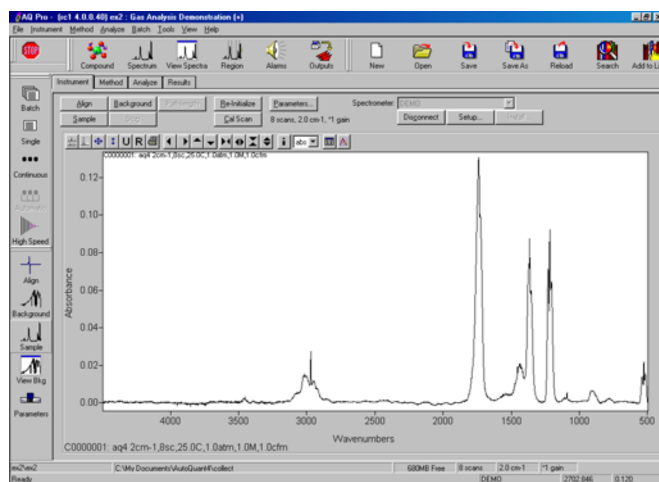


Figure 4.3 Sample Screen Display

Data collection progress is displayed on the upper Information Line, (near the screen bottom), as scans are collected and co-added. Both a scan count and graphic bar are provided. Note that the information contained within the memo field (see parameters discussion) is displayed both within the spectral window and below it.

The Background Button

This button initiates collection of a background reference spectrum and displays the resulting single beam. Operation is the same as described for the ***Sample*** button above.

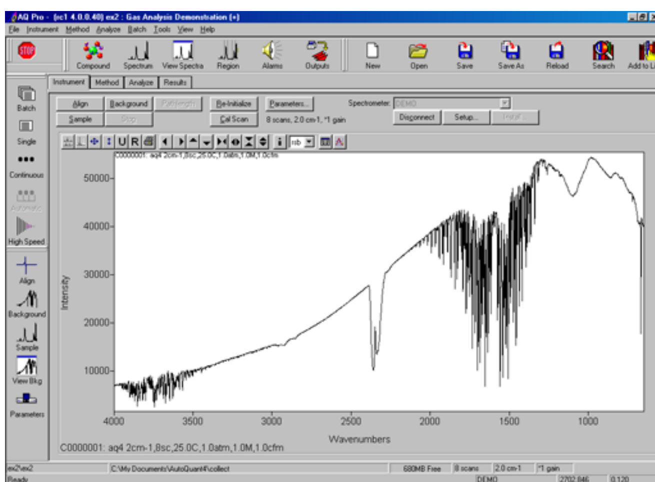


Figure 4.4 Background Screen Display

The Stop Button

This button terminates a data collection in progress (same function as the stop-sign icon).

The Re-Initialize Button

This button is used to re-establish interrupted communication between the computer and spectrometer. It is used if the instrument has lost power, been disconnected or has otherwise been taken off line.

The Cal Scan Button

This button initiates a data collect scan for the purpose of locating the Zero Path Difference (ZPD) of the interferogram. The ZPD occurs when the fixed and moving mirror are at the exact same distance from the beamsplitter, resulting in perfect constructive interference. Accurate identification of the ZPD is essential when co-adding scans. The Cal Scan function is only used if some problem is encountered in collecting data; it is not used during routine operation.

The Parameters Button
This button is used to access settings for virtually all aspects of software operation and instrument configuration.

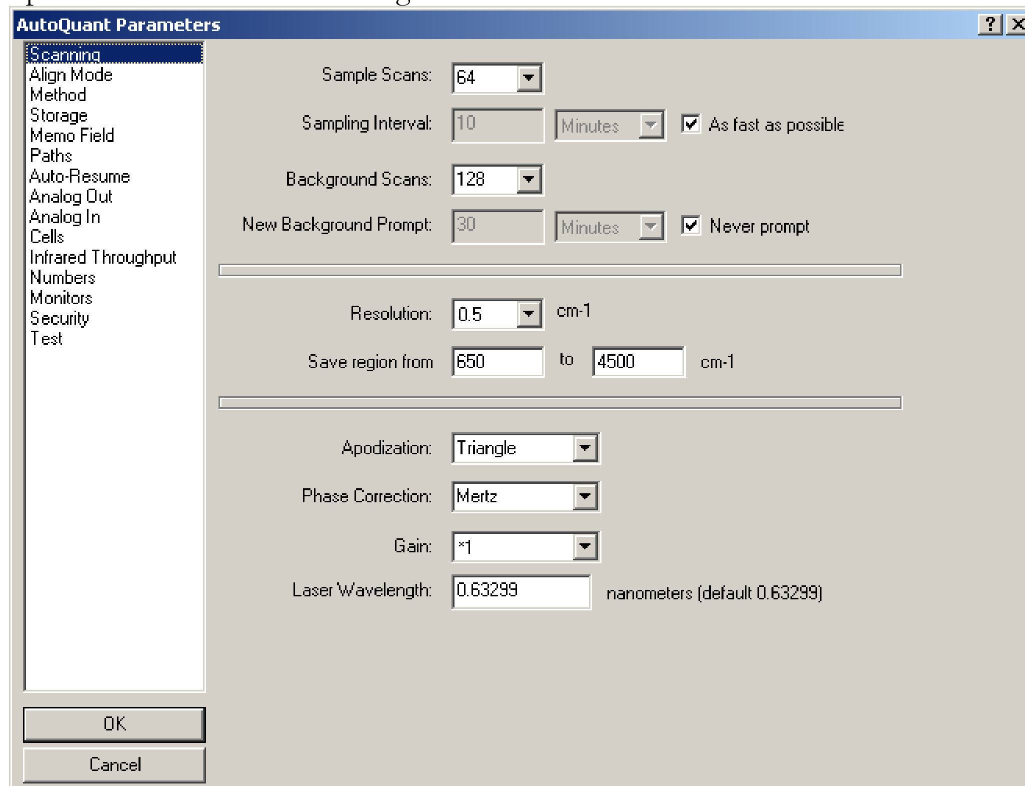


Figure 4.5 Parameters: Scanning Display

Parameters: Scanning

Note: One sample spectrum is usually comprised of a number of scans. One scan represents one completion of the mirror travel. Scans are usually co-added to improve signal to noise.

Sample Scans - Select the number of scans to be co-added for the sample spectrum. The number of scans may be selected from a drop down menu in powers of 2, up to a maximum of 256 scans. Alternatively, any number of scans may be entered manually. (Note: more scans results in better S/N)

Sampling Interval - Applicable only to continuous monitoring mode. If "As fast as possible" is checked, the system initiates a new set of scans immediately after the current set is complete. If the box is not checked, an interval of seconds, minutes or hours can be specified. The system will

collect a scan set, suspend data collection for the specified interval, then collect the next scan set automatically.

Background Scans - Select the number of scans to be co-added for the background reference spectrum (from 1-256), but as with the sample scans any number may be entered manually. (**Note:** hundreds of scans are not unusual but time constraints usually limit the number to 8, 16, 32, or 64 scans)

New Background Prompt - You can specify a prompting interval. If the current background is older than this interval, a prompt will appear informing the operator that a new background is indicated. However, if the system is in continuous mode, data collection will continue unabated unless you respond to the prompt. When the prompt appears, you have the option to ignore it, or to pause the data collection while you collect a new background. The software will use the last background collected in processing samples unless the user specifies otherwise.

Resolution - Select the wave number resolution of any collected data (from 32-0.5). It is important to remember that your sample resolution MUST match the resolution of both the background spectrum and the reference spectrum used for compounds included in your method.

Save Region From/To - These parameters allow you to adjust the range of data saved for each measurement to more closely match the spectral features of interest. This can help conserve disk space and possibly improve data quality by discarding information in unused spectral regions, or in areas outside the detector's usable range. Some examples: a range of 400-4000 is standard for general use with a DTGS detector and KBr optics; a range of 650-4500 is appropriate for general use with an MCT detector and ZnSe optics.

Apodization - Select the method of apodization applied to interferograms during the Fourier processing (see the introduction to FTIR in Chapter 1). Boxcar is essentially the same as no apodization and is only recommended for experienced spectroscopists. Triangle produces the least noise of the options, and is the apodization used for MIDAC spectral libraries. Norton-Beer medium most closely approximates the real shape of gas phase spectra. MIDAC recommends triangular for best performance.

Phase Correction – Interferograms are rarely perfectly symmetrical about the centerburst (ZPD). This is mainly due to frequency dependant phase shifts introduced by the beamsplitter materials and the electronics used to process the signal. Each frequency of the light entering the interferometer

results in a cosinusoidal output. The frequency dependant phase shifts introduce sinusoidal components to the interferogram, causing the asymmetry. It is these sinusoidal components that are removed by the phase correction algorithm. AutoQuant Pro© offers two such algorithms: ***Mertz*** and ***Amplitude***. Mertz phase correction is the preferred setting for computing absorbance spectra in most applications.

Gain (Hardware) – This is set using the jumpers on the detector preamp board, and controls the amount of amplification applied to the interferogram signal before it is processed by the ADC. For best results, the gain should be set so that the interferogram center burst is between one-half scale and full scale at its most extreme point. If the gain is set too high, the signal may overflow the ADC; if set too low you will not take full advantage of the analyzer's sensitivity. It is not recommended for customers to change the gain settings on the detector preamp, as signals from photo-diodes have a large offset, and increasing gain without proper monitoring of the detector preamp may result in signal clipping which would not be apparent on inspection of the data.

Gain (Software) – This is set using the software and amplifies the signal from the ADC to the computer.

Parameters: Align Mode

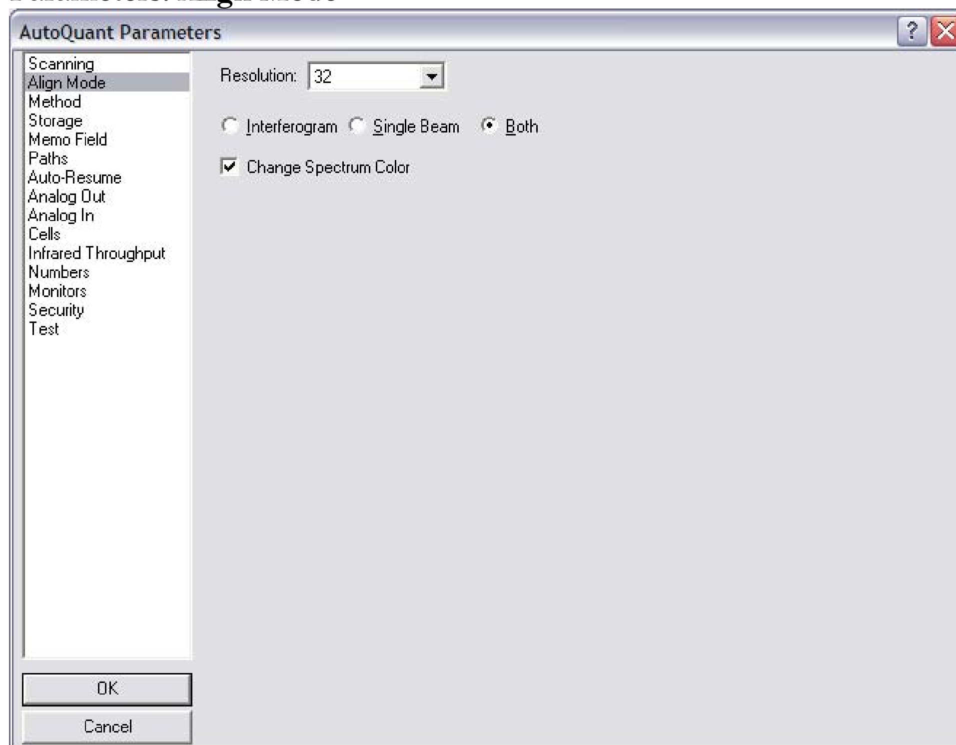


Figure 4.6 Parameters: Align Mode Display

The ***Align Mode*** setting on the ***Parameters*** menu lets you select the resolution for interferogram or single beam spectra that will be displayed during fixed mirror alignment and the format in which the data will be displayed on screen. Alignment should usually be performed at low resolution (i.e., 16 or 32cm^{-1}) for speediest display updates and minimal delay in viewing effects of mirror adjustments. You may choose to display interferograms, single beam spectra or a dual screen with both formats.

Parameters: Method

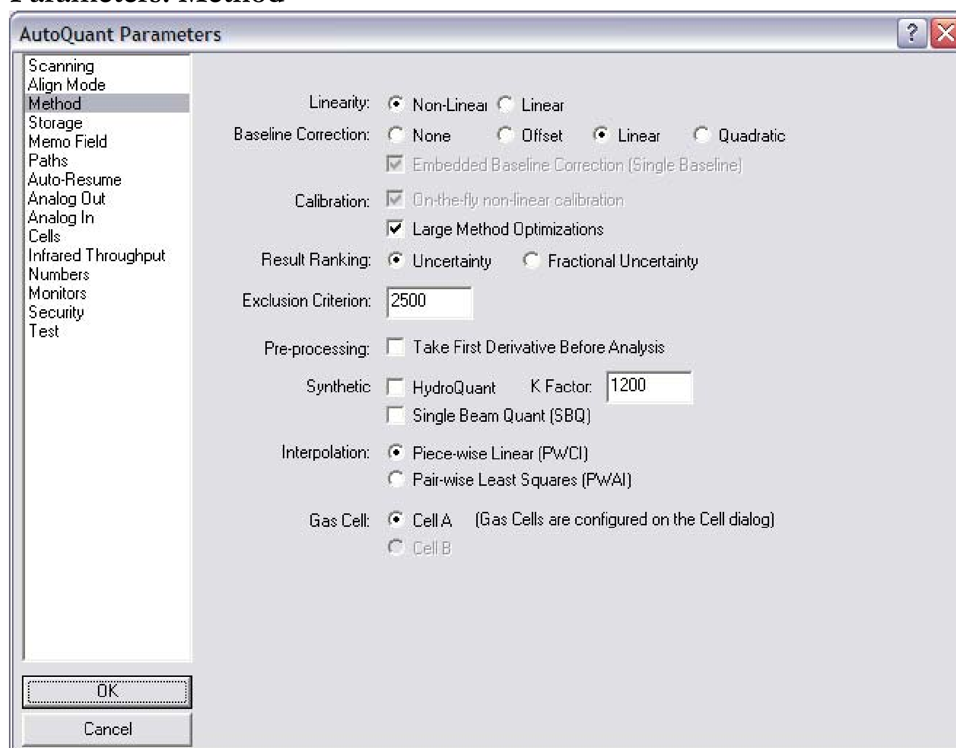


Figure 4.7: Parameters: Method Display

Linearity - Specify whether the method is linear or non-linear. Linear methods use only one reference spectrum for each compound (0,0 and the spectrum chosen as the primary spectrum). Non-linear methods use all of the reference spectra and can use up to 32 reference spectra for each compound. Much greater accuracy is achieved by using non-linear mode as all of the reference spectra are used in the calibration. The spectrum selected as primary is used for the linear method but does not matter in a non-linear calibration. Applications in which a relatively small dynamic range of concentrations (say within a factor of ten, with sample concentrations ranging from 2 to 20%, for example) tend to be linear, and so may be

represented by a single spectrum. Wider dynamic ranges of concentration often encounter non-linearity, so multiple reference spectra spanning the anticipated range of concentrations are required for accurate results.

Note Once all reference spectra in a method have been defined, you can use the View Linearity function on the Method menu to determine the degree of linearity of a calibration curve. An excessively non-linear curve (i.e. one in which the gradient at the high end approaches zero) is an indicator that different regions of analysis should be selected. It is important to note that the 1st and 2nd order polynomials fitted to the data in the View Linearity function are solely for the purposes of outlier detection, and in no way represent the proprietary algorithm that performs the quantitative analysis. In other words, those numbers are not the same as the numbers reported by the true AQPro CLS algorithm.

Baseline Correction –
If **None** is selected in this area, all spectral information down to 0 absorbance units is used. This should only be used for sample and reference spectra that exhibit very clean baselines. Since most FTIR analyzers produce some slope or offset of their baselines, this setting is not recommended.

Offset can be selected for spectra that do not exhibit any slope to the baseline. However, **Linear** is the recommended baseline correction setting for most applications.

Linear is the recommended baseline treatment for virtually all sample and reference spectra (both with and without slopes and offsets). Any baseline slope is automatically corrected in the CLS algorithm for both sample and reference spectra.

The **Embedded Baseline Correction** should always be set to **ON**, (the box should be checked). Although the setting can be turned OFF for backward compatibility with previous AQ3 methods, analytical performance is not guaranteed with this setting. Therefore, we strongly recommend that this setting remain ON, even when working with imported AQ3 methods.

Calibration - On-the-fly non-linear calibration checkbox is used primarily to accelerate the method development adjustment and testing process. If this box is checked, AQ Pro will only calculate sub-methods when they are actually required for analysis. Since some non-linear methods may have thousands of sub-methods, this setting eliminates the delay of calculating all these possible but probably unnecessary sub-methods.

A full calibration, (with the **On-the-fly** setting OFF) calculates every possible sub-method (combinations of every reference spectrum for every compound) regardless of whether they are actually encountered in the measurement. A full calibration is highly recommended once a method is determined to meet the required analytical performance. To cut out unnecessary sub methods when conducting analyses it is recommended that you use the ***Large Methods Optimization*** check box.

The **Quadratic baseline correction** is only available with Embedded Baseline Correction turned ON. It can accommodate spectra with broadly curving baselines.

Exclusion Criterion - This parameter determines the cross interferences within a given region that are included or excluded from concentration calculations. The larger the number entered in this field, the more interferences will be included in the sub-method. The lower the number entered, the more discriminating the program becomes and fewer interferences are included. We recommend that this setting be left at its default value of 2500.

The exclusion criterion is the ratio of the sums of the squares of the data points over the analysis regions for the target compound and any interferences. If this ratio is greater than the criterion, interference is minimal, and the interferences are excluded from that particular sub-method.

NOTE: Occasionally, a sample matrix spectrum will exhibit characteristics that cause the software to "exclude" fine small absorbance bands in the CLS algorithm. When this occurs, an interfering species may not be "subtracted" from the spectrum causing an interference problem and a high reported standard error calculation (SEC) number. This can be determined by observing the generated residual spectrum in AQPro to determine if all interfering absorbance bands are being subtracted. If they are not, such as some water bands, it may be necessary to increase the exclusion criterion number to a point that the inclusion of the interfering species is performed. It may be necessary to raise the exclusion number to over 1 million for these special applications.

Pre-processing - The 1st derivative setting is for use in specialized applications and should usually be unchecked unless very low ppb levels are encountered. This condition is most likely to occur when conducting analysis with specialized hardware such as band pass filters and halogen sources. The new ***HydroQuant*** setting is activated to use a dynamically calculated synthetic background spectrum for analysis. This option is frequently used for moisture analysis and other specialized gas applications.

The K factor is a smoothing function applied to the synthetic ***HydroQuant*** background. Larger K factor values result in more smoothing. A full description of the ***Hydroquant*** software may be found in Appendix 3.

Single Beam Quant (SBQ)- Single beam quant is a powerful tool for performing true transmission spectroscopy or utilizing a synthetically user derived background spectrum for both extractive and open-path use. In SBQ, the software will automatically draw a straight line between the 2 endpoint chosen for quantification in the method editor. For example, if a user wants to measure CO2 and is unable to get a clean background, the user selects the 2 endpoints of the single beam spectrum that closely approximate the amplitude of the baseline on either side of the transmission bands. The software will then draw a line between those 2 endpoints and use the resulting single beam spectrum as the newly generated synthetic background spectrum. It is an automated zapping procedure. By careful use with computed compounds, the user can determine compound ratios, peak-heights, integrations, and true transmission spectroscopy. It is extremely useful in applications where FTIRs are mounted with windows onto reactors to monitor reactor vessel processes, optimizations, and endpoints.

Interpolation - Pair-wise Linear may be used for applications with one or two target compounds and little interference. Piece-wise interpolation has been shown to deliver superior results in more complex methods with more interference. Piece-wise is the default setting. **Piece-wise** should always be used for daily operations and complex matrices.

Gas Cells – The Gas Cells check box allows the user to select which of two gas cells to use in a method, for example, a user may wish to use a short pathlength for high concentrations and a long pathlength for a low concentration.

Parameters: Storage

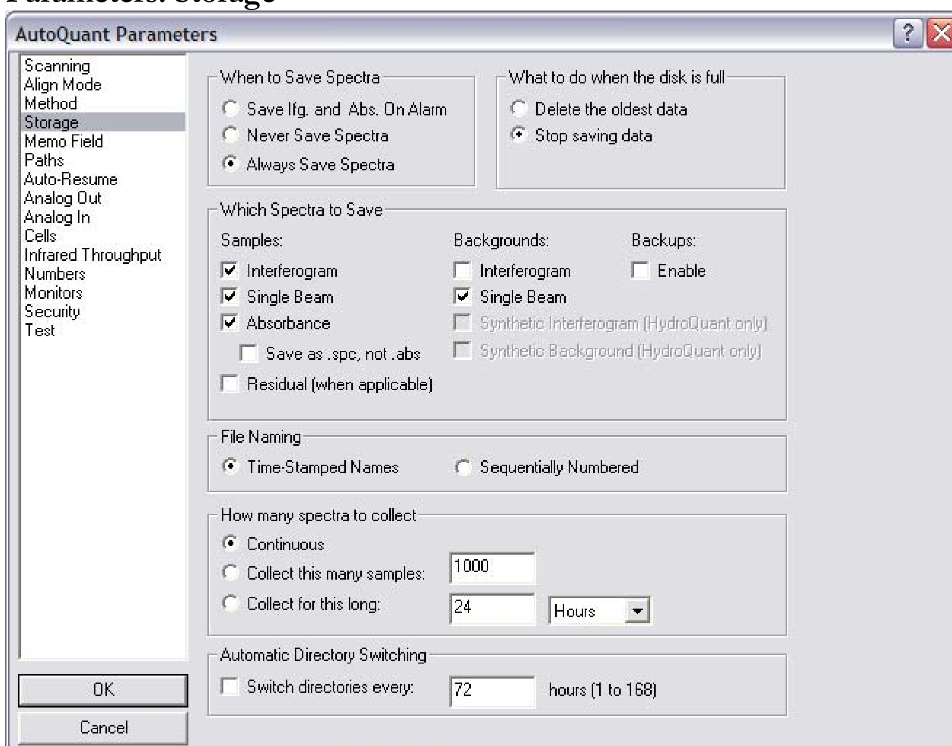


Figure 4.8: Parameters: Storage Display

Settings on this screen let you specify which spectra are stored, no spectra are stored or stored only when preset alarm thresholds are exceeded. The ***Save Abs. On Alarm*** setting is useful for diagnosing concentration excursions. You can also direct the system either to stop storing data or to replace the oldest data to allow analysis to continue if disk space ever becomes critically low.

The ***Storage*** setting on the ***Parameters*** menu is provided for data management when the system is operated in continuous measurement mode. Continuous monitoring can generate very large amounts of data, consuming storage capacity on even large hard drives if left unattended or unmanaged for long periods of time.

The ***Switch directories every*** checkbox allows the user to choose a suitable time interval for generating a new subfolder under the current collection folder. The results file for each time interval is also stored in this subfolder for easy data results viewing without having to re-batch data. This feature

makes for organized data storage and transfer to storage media such as external hard drives, DVDs or cd-ROMs more manageable.

The option exists to store intermediate forms of data as well as, or instead of, the final computed absorbance spectra. Spectral data can be saved in absorbance format or as (.spc) files for automatic recognition by Grams software. It is always a good idea to save the (.ifg) files (interferograms), as all other data types can be generated from this raw data. Please note that the inteferogram is the data in its purest form and the most legally defensible data.

Enabling ***Backups*** automatically stores a duplicate copy of each data file as it is generated. The duplicate can be saved in a different directory, drive, or network location as a measure of insurance against lost or corrupted files. The duplicate data are saved in the location specified on the ***Parameters: Paths*** screen. With backups enabled the results file is also saved to the backup directory. If automatic directory switching is enabled then the backup will switch correspondingly according to the schedule set in the dialog. A separate results file with extension **.aqr** file will be generated each time the directory is switched. The results file can be viewed by clicking on the **File** tab in the uppermost toolbar and choosing "**view previous results**."

The lower area of the ***Parameters: Storage*** display is used for Continuous mode data collection. Select ***Continuous*** to collect data indefinitely until the run is stopped manually. Select ***Collect this many samples*** and enter the desired value to automatically stop data collection after the specified number of spectra have been acquired. The third option is ***Collect for this long***. Select this option to specify how long, (in minutes or hours), the data collection will run before automatically stopping.

Parameters: Memo Field

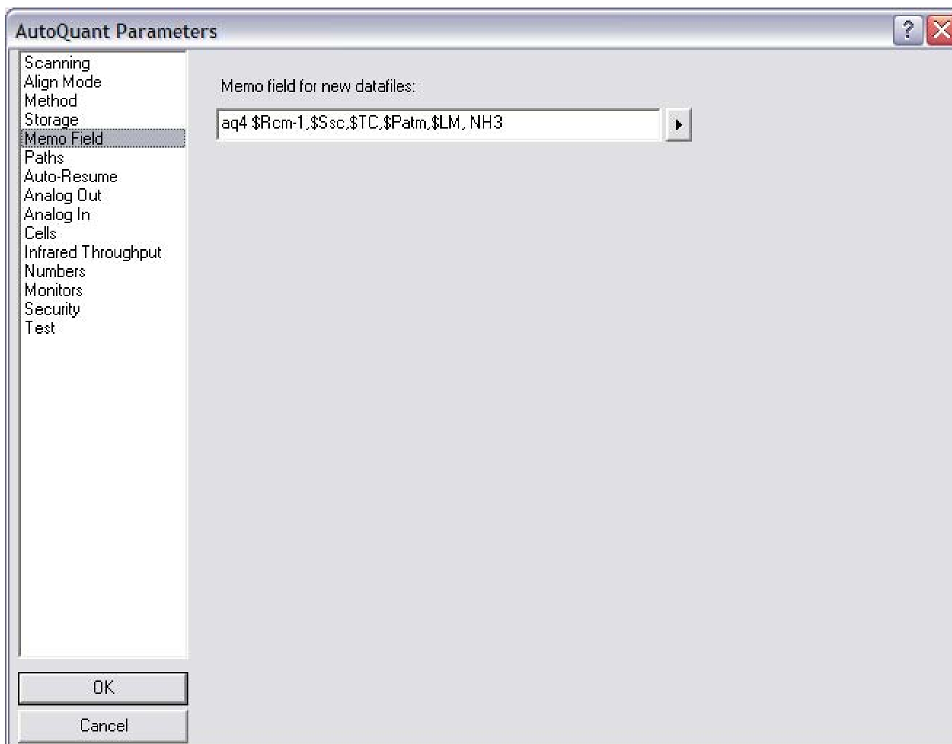


Figure 4.9 Parameters: Memo Field Display

The ***Memo Field*** setting on the ***Parameters*** menu allows the user to specify the annotation that will be stored with each spectrum for identification purposes. Contents of the memo field are automatically tagged to each file saved and are displayed under and in the spectral window along with the spectrum itself. To remove items from the memo field, position the cursor over the item you want to delete, use the left mouse button or *Shift* key to highlight the item, and press the *Delete* key. To add one or more items to the annotation, click on the menu arrow to the right of the memo field, and select the desired items. The code will be automatically inserted into the memo line for you, depending on the parameters set in the software, and the values in effect at the time of data collection for those items will be stored. You can also change the order in which items appear by using standard Windows cut and paste techniques in the memo field. The memo field is important as it allows other users to view a spectrum and have access to the parameters under which that spectrum was recorded. This allows a user to duplicate previous experiments.

Parameters: Paths

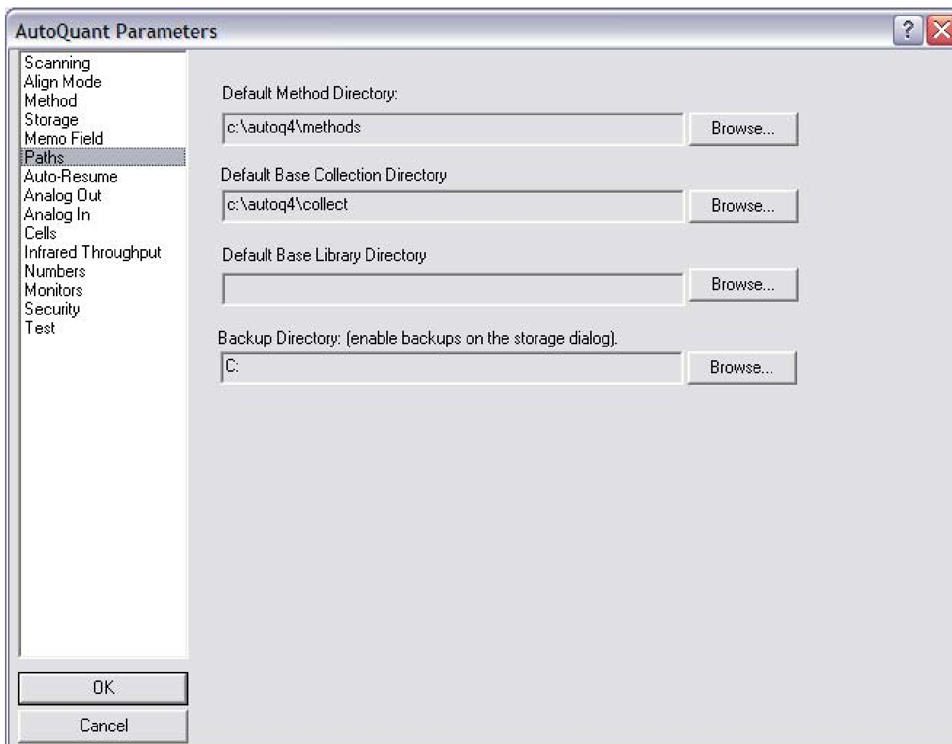


Figure 4.10 Parameters: Paths Display

The ***Paths*** setting on the ***Parameters*** menu lets you specify where the program can find certain files, and where it should store files it creates. These locations can be on the same disk drive as the software, or on an external network-connected drive.

Field 1 specifies where defined methods will be stored, and where the program can find a method to load. Field 2 establishes where collected data will be stored. Field 3 specifies where the program can find spectral reference libraries. Field 4 specifies where backup copies of files will be stored when the ***Backup*** function on the ***Storage*** parameter screen is enabled. (See Parameters: Storage).

Parameters: Auto Resume

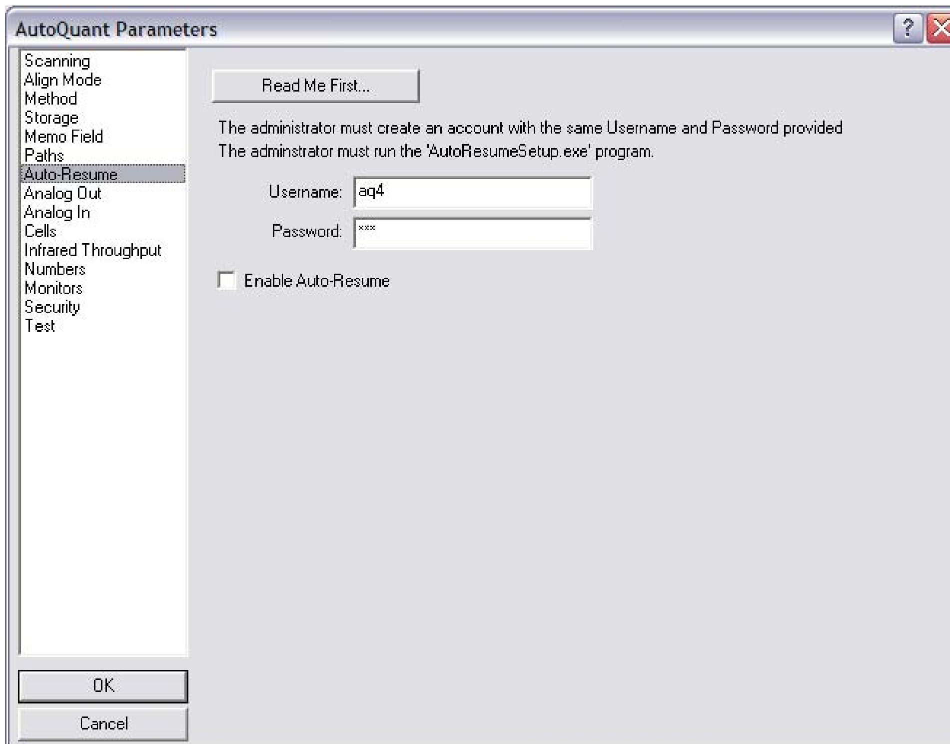


Figure 4.11 Parameters: Auto Resume Display

The ***Auto Resume*** setting on the ***Parameters*** menu allows a data collection that is interrupted by a computer power condition or reboot to resume automatically when the computer is restarted. The software will re-start automatically and continue to collect data to the same directory used before the interruption. If the power interruption occurred in the middle of a scan, that spectrum is discarded. In order to set up the ***AutoResume*** function the administrator is required to create an account for the user. The administrator must then run the 'AutoResumeSetup.exe' program located in the AQPro <u>program directory</u> and provide the same username for the account. This program simply gives the designated user permission to change the registry so that auto-resume can be enabled and disabled by the AQPro.exe program when it is run under the designated user account. On the AQPro Tools/Parameters/Auto-Resume tab, supply the account username and password. Ensure that the 'Enable Auto-Resume' check box is checked. After the setup has been completed ***AutoResume*** should be tested with a deliberate loss of power.

How **auto-resume** works:
When a measurement starts, (AQ4) AQPro modifies the registry:

1. Sets the default user and the default password to those provided.
2. Sets auto-logon so there is no user/password prompt when the system re-starts.
3. Sets up 'aq4 -resume' to run the next time the system starts.
4. Disable disk auto-check so the system will restart without checking the disks for corruption.

If the measurement completes, these modifications are undone.
But if the system power-cycles or is somehow rebooted before the measurement ends, the aq4 user will be logged in automatically, and aq4 will restart with the measurement.

The fact that a resume happened will be logged with the results, and in the 'autoresume.txt' file located in autoq4\bin.
Also "(RESUMED)" will be added to the method name in the program title bar. The "RESUMED" will disappear upon starting a new collection type.

To set up **auto resume**:

1. The administrator is required to create an account for the user.
2. The administrator must run the 'AutoResumeSetup.exe' program located in the AQPro (Autoquant4) program directory and provide the same username used for the account created in step 1. This program simply gives the designated user permission to change the registry so that auto-resume can be enabled and disabled by the aq4.exe program when it is run under the designated user account.
3. On the AQPro Tools/Parameters/Auto-Resume tab, supply the same username and password that were used in steps 1 and 2.
4. Also on the AQPro Tools/Parameters/Auto-Resume tab, make sure the 'Enable Auto-Resume' check box is checked.
5. Be sure to test it on each computer that you set up to do this.

Parameters: Analog Out

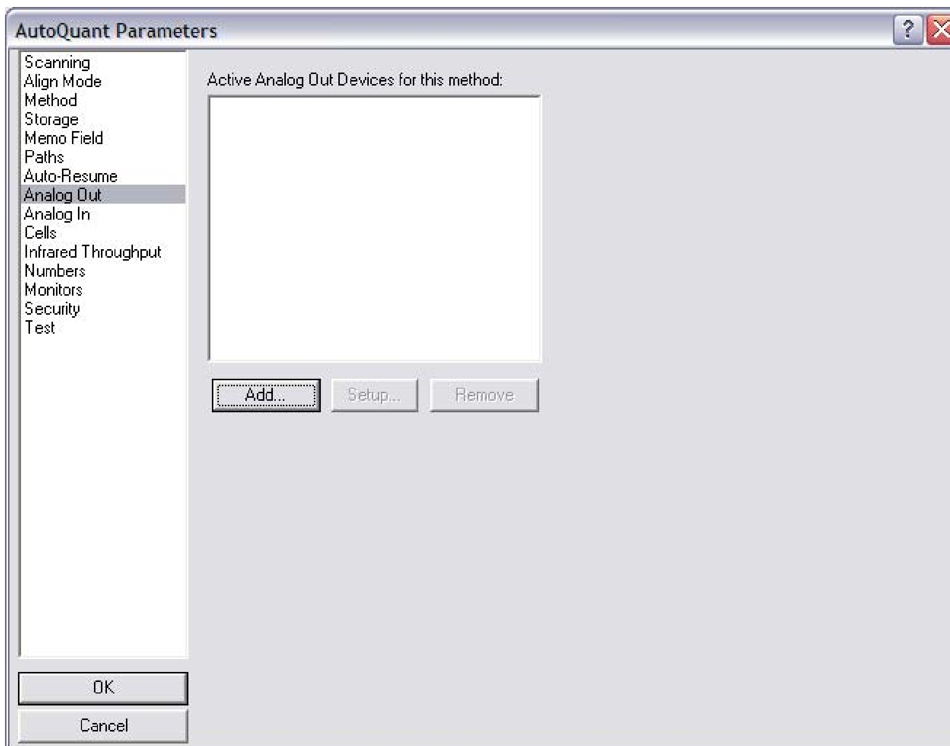


Figure 4.12 Parameters: Analog Out Display

The ***Analog Out*** item on the ***Parameters*** menu is used to configure and test the output of concentration or error "SEC" measurements as analog signals to external devices such as supervisory computers or alarm systems. Click the pull down menu to the right of the ***Analog Out Device*** field to select the type of device you want to configure.

None is the default setting. ***Field Point*** and ***Modbus*** are currently supported interfaces. Custom interfaces can be developed by calling your sales representative.

Note: an ***Analog In*** setup dialog has been added in build 108 and later versions of AutoQuant Pro©. This may be used to configure analog inputs to the method.

Field Point.

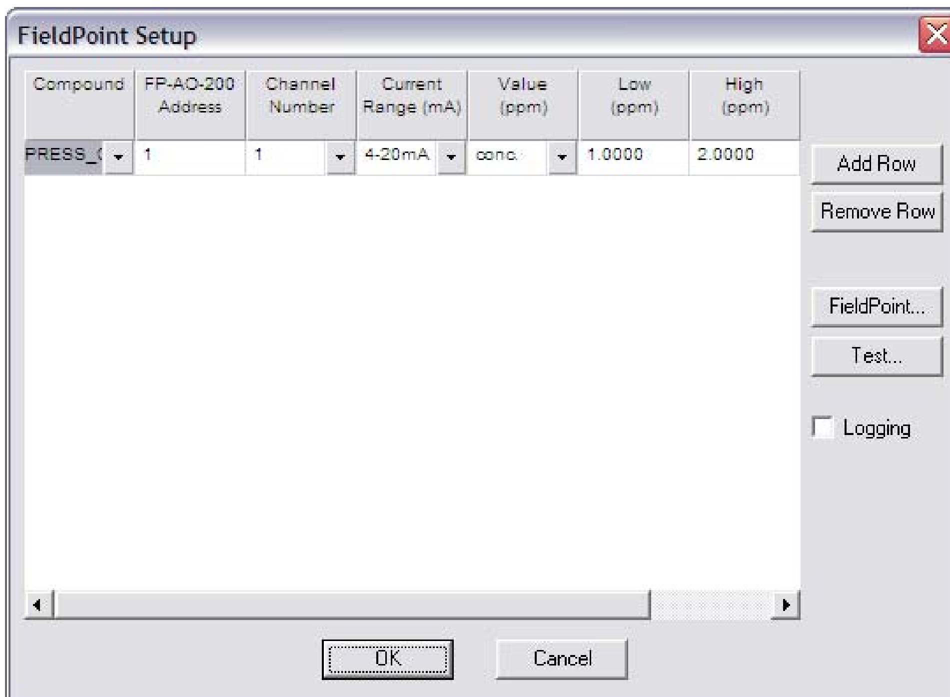


Figure 4.13 Field Point Setup Display

The ***Field Point*** device is an optional interface board available from MIDAC. The manufacturer is National Instruments. You must have the corresponding hardware devices for the software to function properly using Field Point. The two hardware devices used for 4-20 mamp output are the FP-AO-200 and FP-1000 modules. Additional modules are available for other outputs or more channels.

After selecting Field point, click on the ***Setup*** button to access the device configuration features illustrated in Figure 4.13. Select the appropriate serial port to which the analog I/O board is connected from the pull down list in the ***Com Port*** field. Select the appropriate data communication rate from the pull down list in the ***Baud Rate*** field. Now you are ready to define channels. The appropriate dip switches must also be set correspondingly on the Field Point hardware devices.

Click on the ***Add Row*** button to begin definition of a new channel. This will display data entry fields as shown in Figure 4.13. Click on the pull down list in the ***Compound*** column to select from compounds defined in the currently active method.

Type in the appropriate address for the device in the ***FP-AO-200 Address*** field. This may be obtained from the ***Field Point Communications*** dialog delivered by pressing the ***Field point…*** button. This dialog is shown in Figure 4.14.

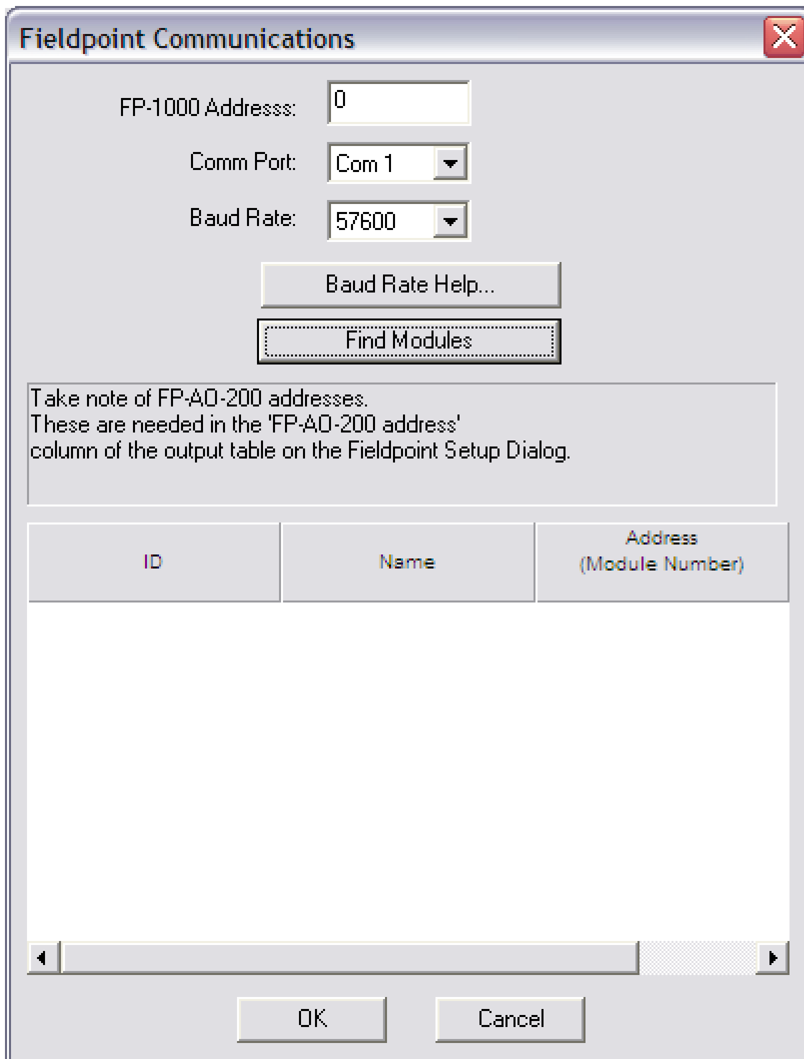


Figure 4.14 Fieldpoint communications dialog

Next, select the ***Channel Number*** on the I/O board that will be assigned to this compound. Up to 16 channels are available with each board. Select the ***Current Range*** from the pull down list. The first 2 are pre-assigned to temperature and pressure of the sample cell leaving 14 additional Inputs.

Specify what type of data is being communicated on this channel (concentration or SEC) in the ***Value*** field. Finally, you will associate the

range of measured values with the range of current output by the analog device. Enter the lowest measured concentration value you want to communicate in the ***Low ppm*** field, and enter the highest measured concentration value you want to communicate in the ***High ppm*** field. These will be associated with the extremes of the output device (ie, 0-20 or 4-20mA) with intermediate values scaled accordingly.

Repeat this procedure for each compound you want to output. The ***Re-Test*** button may be used to check for errors after each channel is configured. Enabling error logging via the ***Logging*** check box creates an error log that can be monitored.

Field Point support exists for the RLY-420 module for alarms. Field point alarms may be linked to sample lines. The setup dialog for this function may be accessed via the valve sequence dialog (see the ***Valves*** section).

All compounds listed in fieldpoint must exist in the method, for example if a compound name is changed then in order for the 4-20 mA output to function correctly the compound name must also be changed in the fieldpoint dialog.

Modbus

Select ***Modbus*** from the drop down menu. Click on the ***Setup*** push button. This returns a dialog box. Pressing the ***Auto Fill*** push button brings up a set of check box options. The user can choose to include error "SEC", create separate sample line entries if multiple sample lines are used and choose to report the sample line number being tested in register 1.

Note: The sample line number is in format *n+1*, for example #1 would be reported as #2, so #n is reported as #n+1. All registers start at 40000 + register number. The system will output all concentrations and external inputs, and computed compounds through modbus TCP-IP through the computer CAT5e interface. Anything the user chooses to output from the AutoQuant Pro© generated numbers will be sent on its own register (over 100 registers available) to a separate data acquisition system. The output is 32 bit floats in the modbus registers, so each value takes up two of the 16 bit modbus registers.

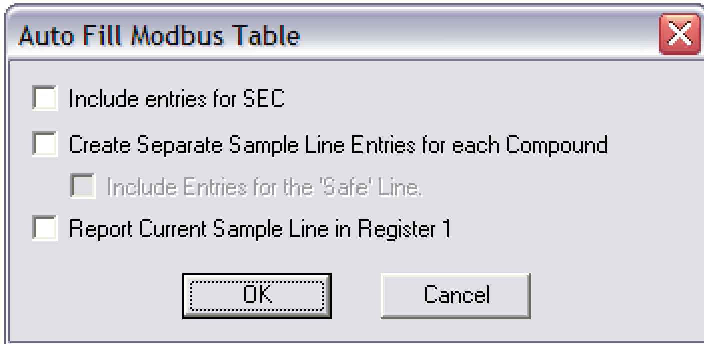


Figure 4.15 Modbus Auto Fill Dialog Box

Check the options as required. If the options selected in Figure 4.15 are checked, AutoQuant will deliver a table based on the compounds in the current method. This table is illustrated in Figure 4.16.

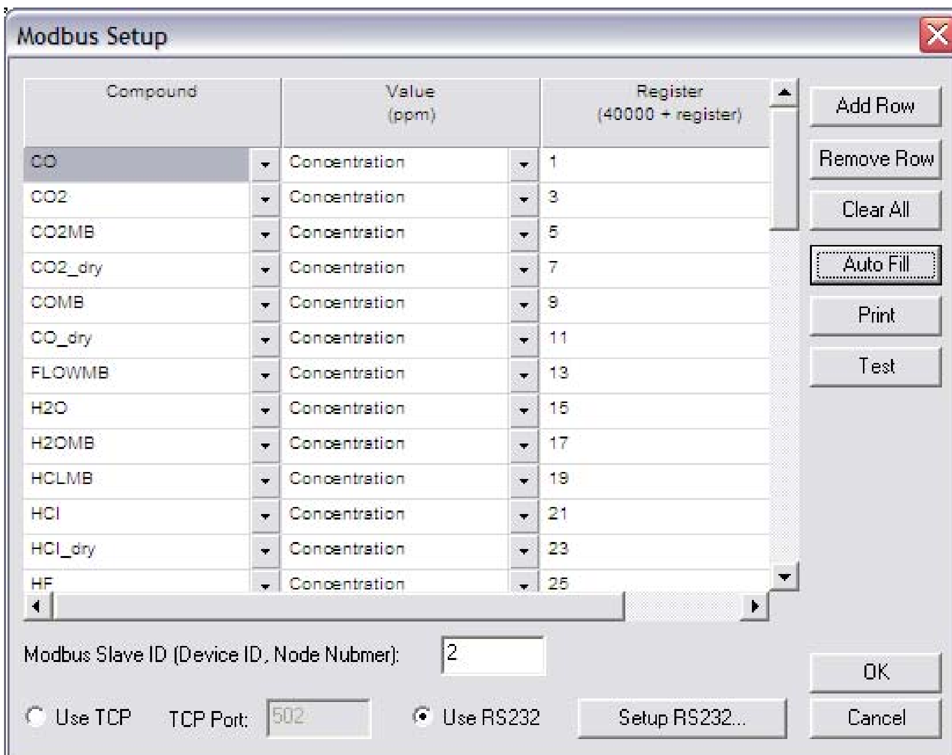


Figure 4.16 Modbus Setup

The ***Add Row*** and ***Remove Row*** buttons may be used to edit the table. Pressing ***Print*** will print a copy of the current table. The ***Test*** button may be used to check the current configuration for errors. The test button holds each registers assigned register number for easy testing. Once the table is complete, check the ***Use RS232*** radio button. Next, press the ***Setup RS232*** button. This displays a setup dialog for the RS232, shown in Figure 4.17.

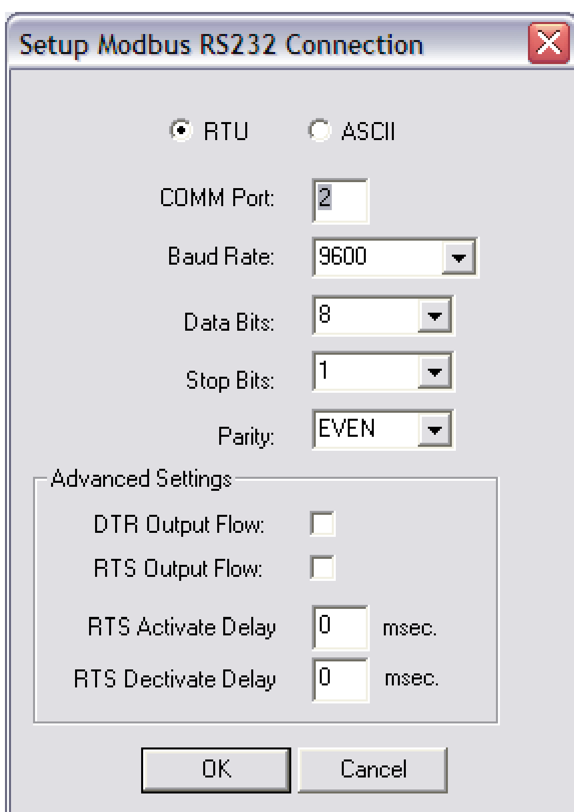


Figure 4.17 RS232 Setup

The appropriate COM port should be selected, together with the Baud rate. The Modus analog out device is now configured for use.

Note: RS-422 or RS-485 may also be used for longer distances. The RS- 232 to RS-422 or RS-485 converter is available through MIDAC.

The capability exists for alarms on temperature of the cell, over pressure of the cell, high concentrations and temperature of any other device that gives input. **<u>However, all inputs must be a 0 to +5V configuration with an isolated ground.</u>** Alarms may be configured to report over the modbus and trigger AQPro to respond in one of the following ways:

1. Continue the analysis sequence and alarm until the condition no longer exists
2. Stay on the current sample line and continuously sample
3. Stop the sequence and switch to the purge manifold parameter

The purge manifold parameter is available through the valve module in the software where a hexadecimal bit set-up is entered to trigger a nitrogen flooding purge or some other assigned condition through the MIDAC control valve manifold.

It should be noted however that only one of these alarm options may be chosen, and will apply to all alarms in the method.

Analog inputs for the fiber optic distribution board may be configured using an interface available from MIDAC. The interface will allow up to 14 inputs from other devices, on the condition that the inputs lie within the range 0 to +5 V (DC). They must be ground isolated or serious problems may occur.

A break-out board connection from the fiber optic distribution board is available from MIDAC that allows easy connection of any inputs.

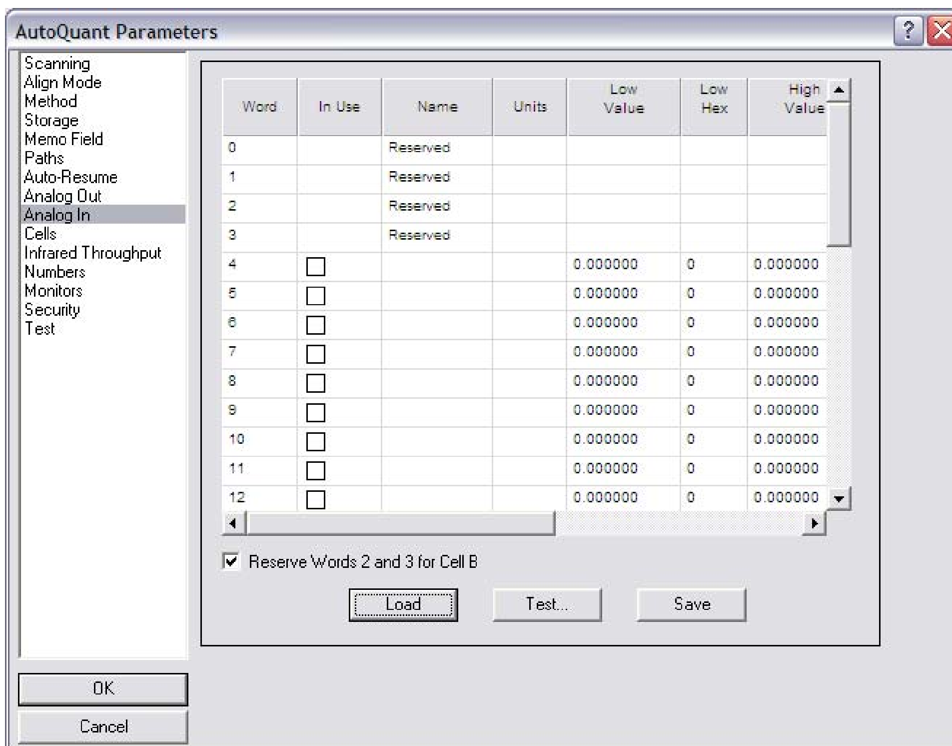


Figure 4.18 Analog In dialog

Parameters: Cells

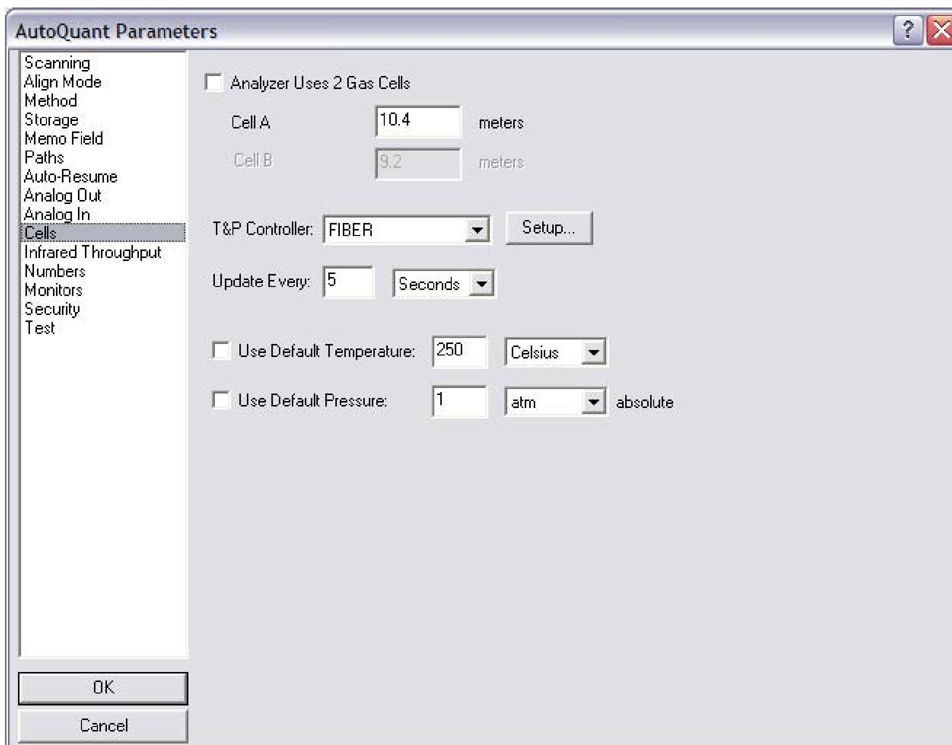


Figure 4.19 Parameters: Cells Display

Enter the factory-supplied cell path length in the ***Pathlength*** field.

Note: Factory cell pathlength is determined based upon ambient temperature and pressure conditions unless specified otherwise in the factory literature. Cell pathlength must be determined at the same temperature and pressure that your samples are to be collected. Please determine your cell pathlength by following the instructions in Chapter 6.

Make the appropriate ***T&P Controller*** selection from the drop down menu if a temperature/pressure sensors and controller are installed. Use the ***Setup*** button to enter configuration information and test the device(s).

Temperature and Pressure Control: Watlow Setup

There are currently three options for temperature and pressure communication, None, Fiber Optics and Watlow. Please determine which your system uses before continuing. If your system is equipped with a peripheral control device (PCD), then it uses the Fiber option. If the option ***Watlow*** is selected, pressing the setup button delivers the dialog shown in Figure 4.20.

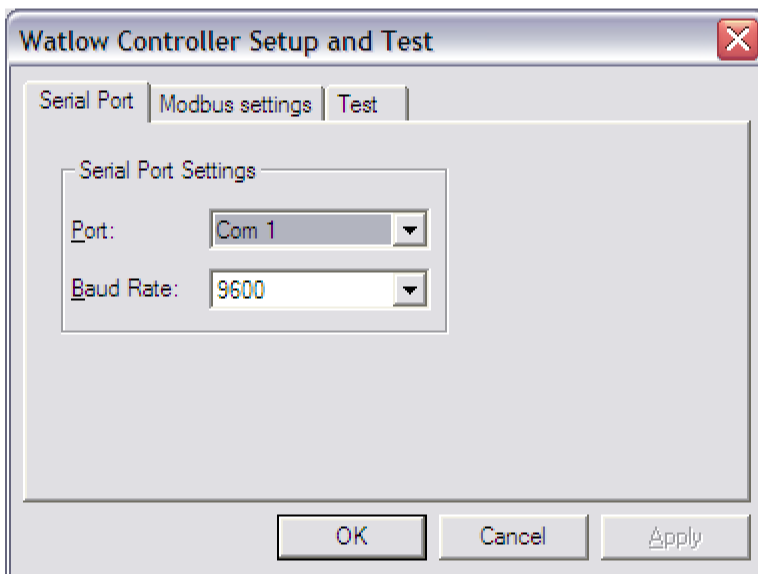


Figure 4.20 Watlow Temperaure / Pressure Setup

The dialog has three tabs, ***Serial Port, Modbus settings*** and ***Test***. On the ***Serial Port*** tab select the appropriate Com port (usually Com 1) and set the baud rate to **19200**. The ***Modbus settings*** tab allows registers to be defined. The default settings will normally be used. The pressure units shown on this tab should be set to ***psi***. The ***Test*** tab is used to check that temperature and pressure are read correctly. If incorrect readings or errors result from pressing the ***Test*** button, refer to the **Troubleshooting** section of this manual.

Temperature and Pressure Control: Fiber Optic Setup

If the user has purchased the peripheral control device (PCD) system from MIDAC, the ***Fiber*** option must be selected, the ***Setup*** button yields the dialog shown in Figure 4.21.

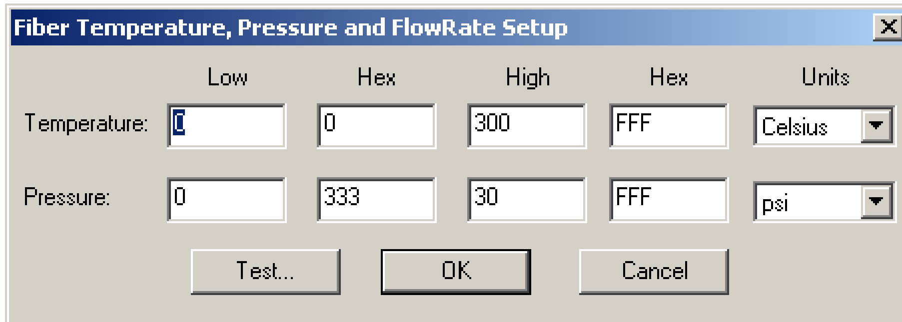


Figure 4.21 Fiber Optic Temperature / Pressure Setup

The dialog box provides drop down menus selection of units, and a ***Test*** button allows readings to be checked. Pressure units should be set to psi. If incorrect readings result from pressing the ***Test*** button, refer to the **Troubleshooting** section of this manual. The fiber optic controller will check for over / under temperature, pressure and flow parameters.

In Figure 4.21, the units should be set accordingly. There are 3 types of pressure transducers used; Voltage 0-30, Amperage 0-30, and Amperage 0-50. You can determine which transducer you have by reading the stamping on the side of the transducer. Adjust the High pressure reading in the window accordingly to your transducer to obtain the correct pressure reading.

The digital readout on the PCD has no bearing on the actual pressure input to the software as they are 2 separate channels. You must determine that the correct pressure is being read into the software by clicking the **Test** button. Small changes to correct for actual barometric pressure under ambient conditions can be made at the setup screen by simply adjusting the High pressure value until the reading is correct under the **Test**… condition. The digital readout on the PCD can then be adjusted to read what is actually being read into the software directly on the face controller by entering the set-up menu of the controller.

The ***Update Every*** field specifies how often you want the system to take temperature and pressure readings. Each time the specified interval elapses, the system will take fresh readings and record them with the other file information for each spectrum it collects. All readings taken over the time interval of the acquisition of a spectrum are averaged and tagged to that spectrum. For this reason more readings per sample are more representative of the actual conditions.

Note: If you are performing a high speed or fast collection where time intervals are critical, the ***Update Every*** field should be set to a longer time period. Every time the software polls the temperature and pressure, some fraction of a second (depending on computer) is expended to write the info to the hard disk resulting in a slight change in time interval. If time intervals must be exact, MIDAC recommends using the default feature or a longer update time.

The ***Use Default Temperature*** and ***Use Default Pressure*** options allow you to enter the appropriate environmental conditions when temperature and pressure instrumentation are not installed or operational.

Parameters: Infrared Throughput

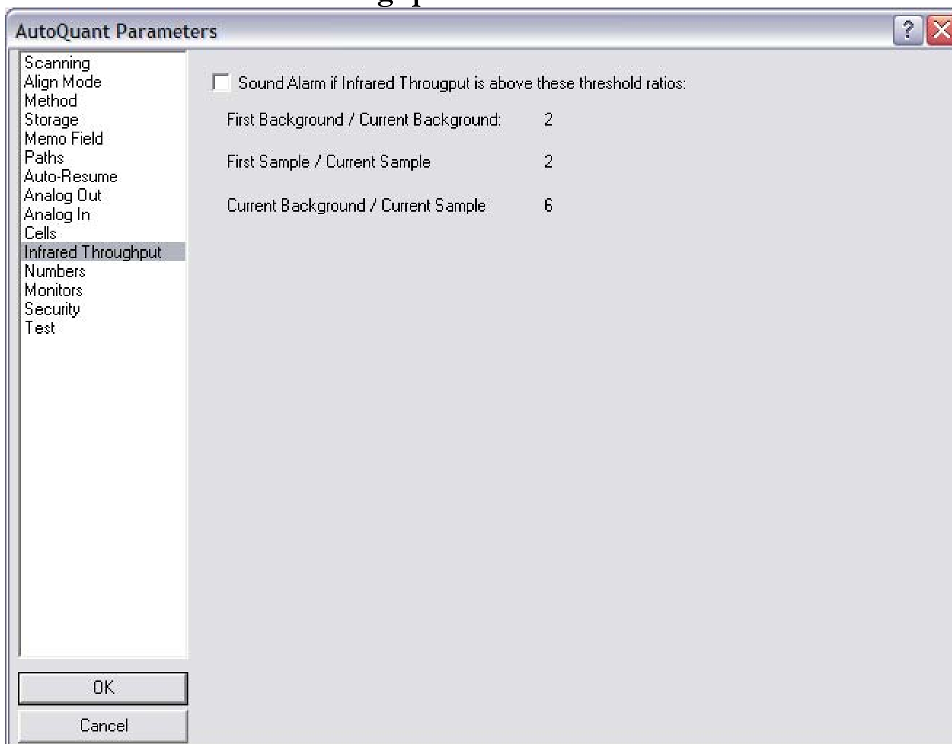


Figure 4.22 Parameters: Infrared Throughput Display

The ***Infrared Throughput*** setting on the ***Parameters*** menu lets you enable an alarm display if the system detects that the IR signal has fallen below the listed threshold values. This can be a useful indicator that corrective action is needed (such as refilling a liquid nitrogen Dewar or cleaning optics) to avoid poor data quality during extended continuous monitoring runs.

However, for a very high moisture matrix or high concentration matrix, the alarm may sound erroneously, since many of the photons are attenuated by the species in the matrix. In this case, the IR throughput alarm should not be used.

Parameters: Numbers

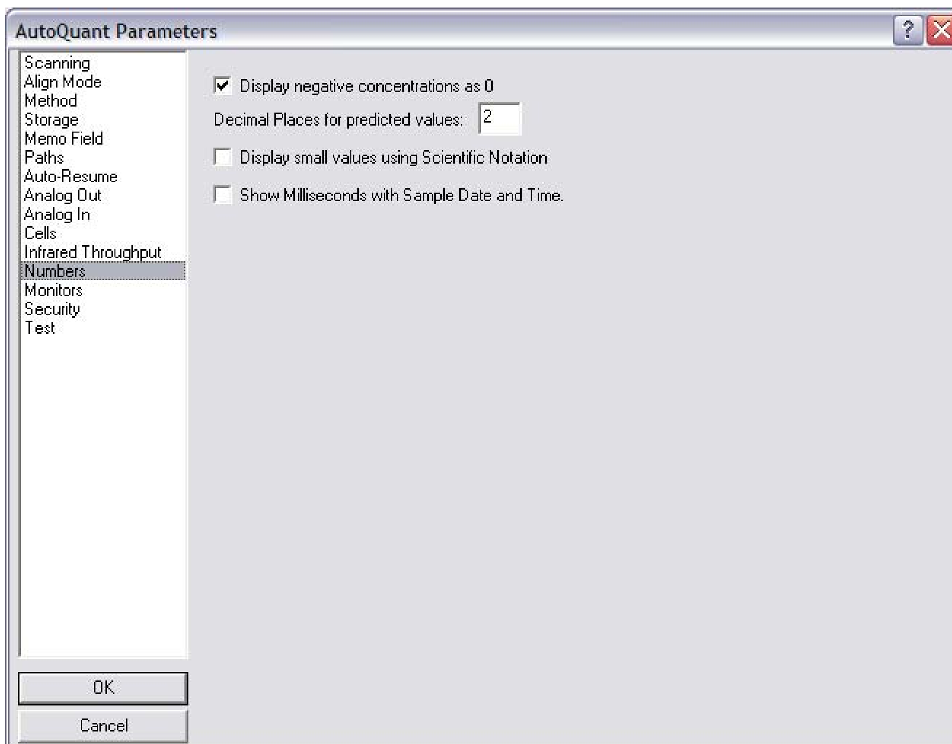
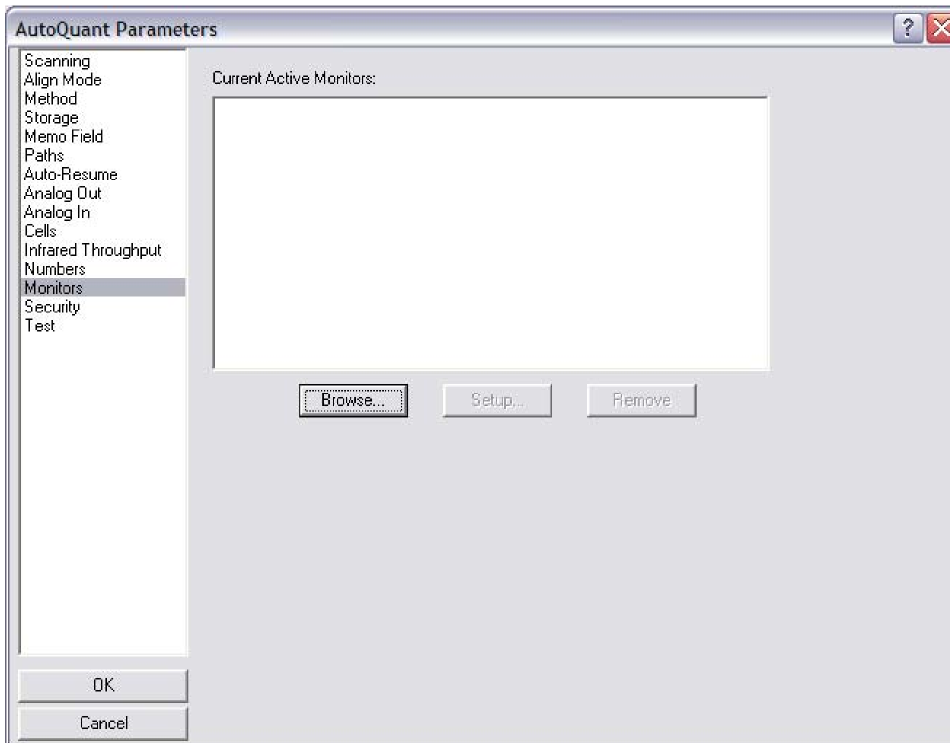


Figure 4.23 Parameters: Numbers Display

The ***Numbers*** setting on the ***Parameters*** menu allows control of the format and precision in which various data are displayed and/or stored according to your preferences. Options exist for displaying negative concentrations as zero and for displaying high resolution time information, which may be useful in reaction kinetics experiments.

Parameters: Monitors

The monitor's dialog allows automated detection of currently configured monitors on the system.



4.24 Monitors Dialog

Parameters: Security

The security tab on the parameters dialog allows the user to set a password, which will then be required to start or stop data acquisition, alter method parameters or to access a locked method. The security dialog is shown in Figure 4.25

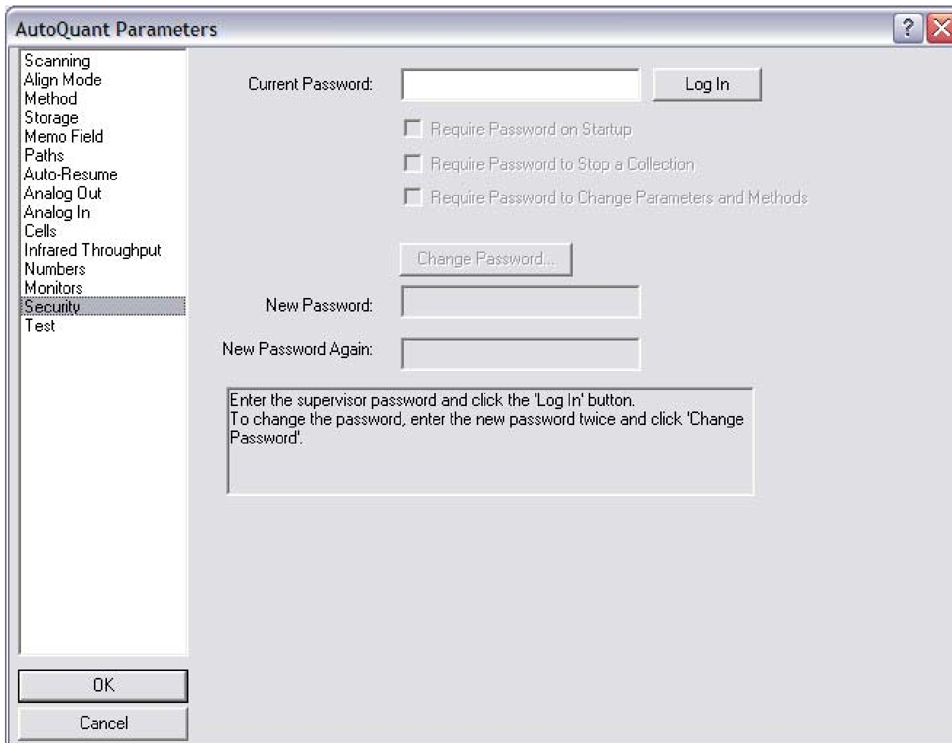


Figure 4.25 Security Dialog

Parameters: Test

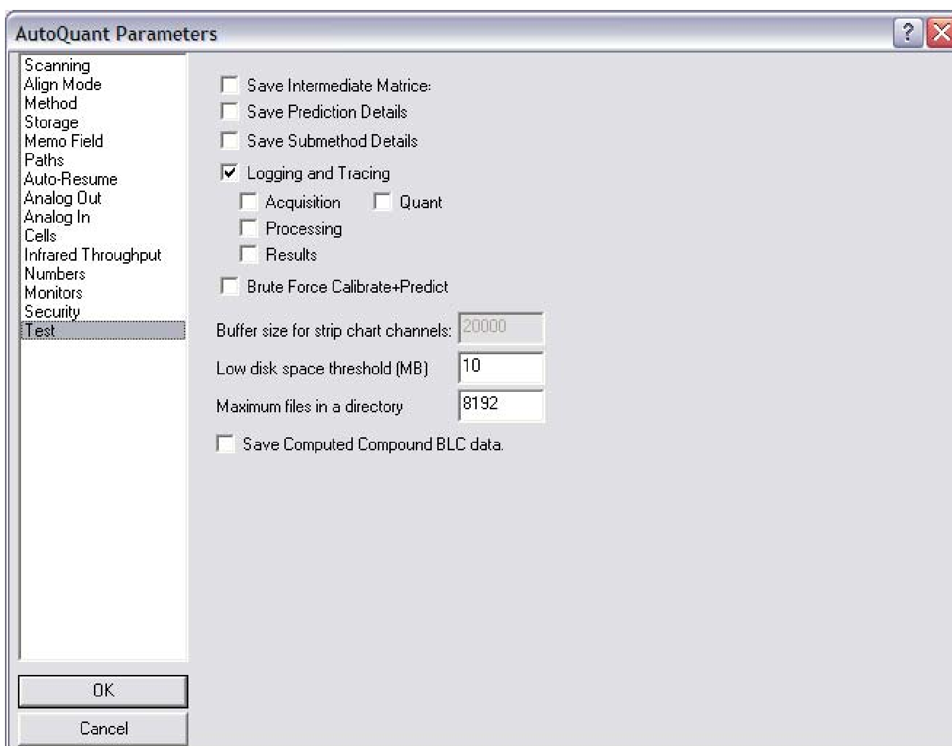


Figure 4.26 Parameters: Test Display

The ***Test*** setting on the ***Parameters*** menu contains a variety of diagnostic settings that can be activated in consultation with MIDAC customer support personnel to help troubleshoot system or software malfunctions. This screen should not be used for normal operation.

The Connect, Setup, and Install Buttons

The last three push buttons on the ***Instrument Screen,*** (Connect, Setup, and Install), are located under the ***Spectrometer*** field. These buttons are used only for initial installation purposes and can be disregarded during routine operation. Select the appropriate combination of computer/spectrometer interface card and ADC electronics for your system from the pull down list. The DEMO instrument selection is provided for educational purposes only. The ***Install*** button provides guidance for proper installation of instrument driver files. The ***Setup*** button is related to the DEMO instrument mode, and can, therefore, be disregarded by most users. The ***Connect/Disconnect*** button is initially used to establish communication between the analyzer and computer. Once connected, there is seldom any reason to use the disconnect button. Its primary purpose is to facilitate switching between different instruments.

The Spectral Display Buttons

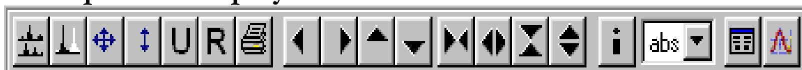
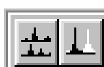
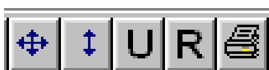


Figure 4.27: Spectral Display Window Buttons

Beneath the large spectral display window on the ***Instrument*** screen is a row of graphic manipulation buttons. These buttons let you select display formats to suit the task at hand and manipulate spectra displayed within the window. If any function is not immediately obvious, position the cursor over a button and let it rest for a moment without clicking. The description of that button's function will appear.



The two left-most spectral display buttons determine the format in which multiple spectra are displayed. These buttons are only active on the ***View Spectra*** screen that is used to simultaneously display the various reference spectra you have selected within a method. Clicking on the ***Stacked*** (left) format button results in each successive spectrum being placed in its own "mini window" within the spectral display area; clicking on the ***Overlay*** (right) format button results in all selected spectra being superimposed. Both are useful in observing the relative positions of key features in your reference spectra.



The left-most button in the next group of five is used to ***Auto-scale*** the display along both X and Y axes. This automatically applies the maximum level of horizontal and vertical expansion allowable while fitting all data in the window. It is a one-step way to return from a highly magnified view to a full spectrum view. You can get the same results by left-clicking the mouse with the cursor in the spectral window.

Moving to the right, the ***Vertical Auto-scale*** button scales the Y axis to accommodate the largest feature within the currently displayed X axis boundaries, (the X axis scale remains unchanged). This gives you the best possible view (maximum expansion while all inclusive) of all data within a selected wavenumber range.

The ***Undo*** (U) and ***Redo*** (R) buttons step you backward and forward through the history of display manipulation. Clicking ***Undo*** once takes you one step back, (undoes the last expansion, scroll etc.). Subsequent clicks take you sequentially further back through recent operations. Clicking ***Redo***

takes you forward one step at a time until you reach the most recently performed display manipulation.

Click on the ***Print*** button to print the current display window contents.

The next four buttons ***Scroll*** the window contents to the left, right, up and down, respectively. Single click on a button to move a small increment. Click and hold the mouse button down to scroll continuously until the desired region is displayed.

To the right of the ***Scroll*** buttons are the ***Horizontal Contraction***, ***Horizontal Expansion***, ***Vertical Contraction*** and ***Vertical Expansion*** buttons. Single click for incremental expansion or contraction with these buttons, click and hold for continuous action.

Another way to quickly zoom in on exactly the spectral features you need to examine is to use the mouse directly in the spectral display window. Position the cursor above and to the left of the area you want to zoom in on, hold down the left mouse button and drag downward and to the right. This will form a temporary box around the area. Click once inside the temporary box and its contents will be scaled to fill spectral display window.

The last four spectral display buttons begin with the ***Information*** (**i**) button. Click this button to display the memo field, collection date and time, and a variety of other file information stored with the spectrum.

To the right of the information button is a small field with a pull down list. As discussed in the ***Parameters: Storage*** section, multiple data formats can be saved during data collection (including absorbance, single beam and interferogram). This field lets you select the format you want displayed from the list. The list will change depending on what formats have been stored.

The next button to the right allows users to ***Set Display Properties***. Click this button to enter maximum and minimum values for the X and Y axes, and to specify automatic or manual scaling in the spectral display window. These settings are made separately for each of the various data formats that can be displayed. The entered X and Y axis values are not used when the ***AutoScale*** boxes are checked. To use the entered values, uncheck the relevant ***AutoScale*** box(es), click the ***OK*** button, *right-click* the mouse on the spectral display window, then select ***Fixed Scale*** from the right-click menu.

The display window will then be scaled to your specified X and/or Y axis values. You can then toggle between Auto Scale and Fixed Scale modes using the right-click menu.

The second tab on the information entry box, ***Colors,*** lets you select different background colors for the spectral display window from a palette.

The last button in the row is used to directly export the displayed data into Grams/32 software. Grams software must be installed on your computer for this ***Export*** function to operate.

The Method Screen

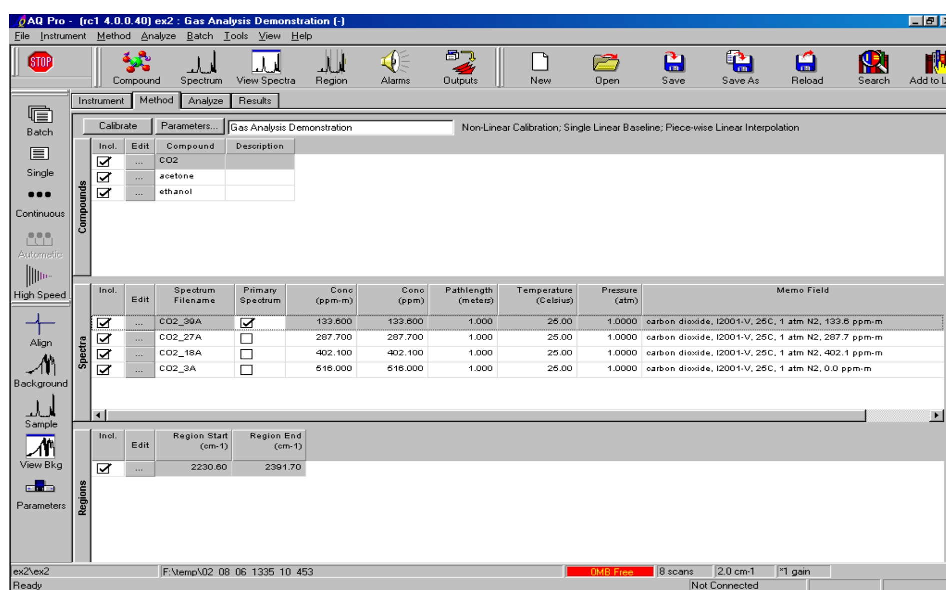


Figure 4.28 The Method Screen Display

The method screen is accessed by clicking on the ***Method*** tab, and comprises three panes. The uppermost of these is the ***Compounds*** pane. This section allows compounds to be defined. The center pane is the ***Spectra*** pane, which facilitates the selection of reference spectra representative of each compound in the method. The final pane is the ***Regions*** pane, which is the interface for the definition of spectral regions for analysis. Regions are specified for each spectrum of each compound. The ***Method*** screen is automatically displayed when you select any of the first group of ***Method Menu*** items or any of the ***Method Toolbar*** icons.

Above the three panes of the Method Screen (namely, the Compounds, Spectra and Regions panes) are two push buttons and an information field.

The ***Calibrate*** button is used after you have defined the compounds, reference spectra, and spectral regions for inclusion in your method. During calibration, AutoQuant Pro© performs two operations:

1. It generates sub-methods
2. It calculates prediction matrices

A sub-method consists of one reference spectrum for each compound used to calculate a prediction matrix. In a full calibration, a sub-method is created for each possible combination of reference spectra for every compound. Therefore, the number of sub-methods generated by a given method is determined by multiplying the number of spectra in each compound, and then multiplying by the total number of compounds in the method. For example, a method in which compound #1 has three reference spectra, compound #2 has two reference spectra, and compound #3 has one reference spectrum will generate a total of 3 x 2 x 1 x 3 = 18 sub-methods.

The number of possible sub-methods increases exponentially with additional reference spectra and/or compounds. However, the more reference spectra used in the method, the better the accuracy and precision of the reported results.

The ***Parameters*** button is identical to the ***Parameters*** button on the Instrument Screen. Please refer to the descriptions provided in the ***Instrument Screen*** section for a full explanation of options for all menu items under the ***Parameters*** button.

The information field to the right of the ***Parameters*** button identifies the currently active method. A brief summary of key settings defined for this method also appears to the right of the Information field.

A right mouse click in any of the three panes will display an appropriate menu for actions appropriate to the area in which the mouse is clicked. These menus are described below. Note, a right mouse click on the pane background provides an abbreviated menu to add a compound, spectrum or region, or to view a spectrum. A right mouse click on an item already defined in the table provides a menu with many more options.

The Compound Pane

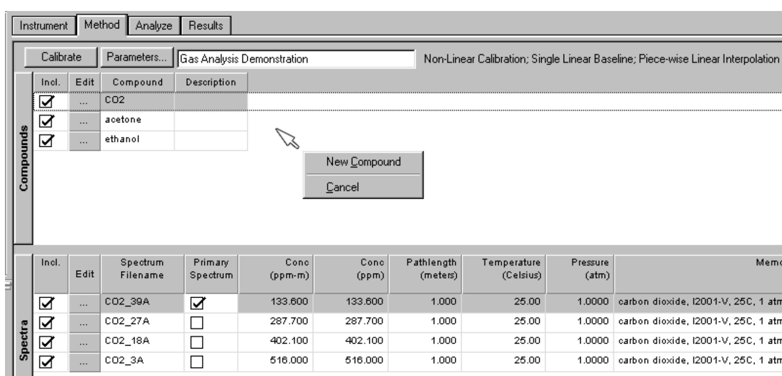


Figure 4.29 *Right-Click* Compound Table Menu (brief)

Figure 4.29 shows the brief menu displayed when you *right click* on the background area of the Compound Table. The only item on this menu is ***New Compound***. Select this item when you want to add to the list of defined compounds. A small box for entry of the name, description, molecular weight is provided. An option to input a ***Computed Compound*** is also provided.

Computed Compounds

A computed compound is sometimes referred to as a 'virtual' compound, as opposed to a 'real' compound. A 'real' compound is one which has spectra associated with it. A computed compound has no spectra associated with it; the results for a computed compound are derived from those of real compounds and/or sensors or inputs and a user-defined equation. This allows the user to combine results from real compounds to produce results for a virtual compound (such as NO_x), or to include calculated results such as mass flow in the output or to correct to dry concentrations, a predesignated O_2 level, or CO_2 concentration, or all three. The results for a computed compound are treated as results for actual compounds by AutoQuant Pro©, so that computed compounds appear in the results table, may be used in alarms and can be reported over modbus or analog out.

When a new computed compound is added to a method, (either using the ***Right Click*** menu for the ***Compound*** pane or using the ***Method*** menu) the dialog shown in Figure 4.30 appears.

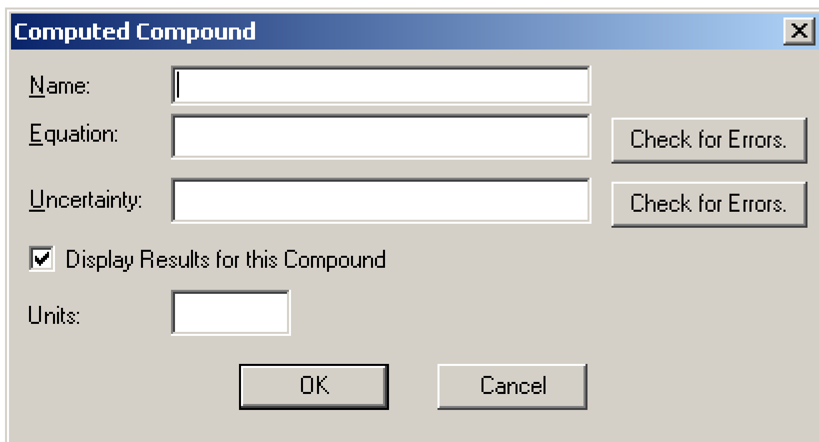


Figure 4.30 The Computed Compound Dialog

It is necessary to assign a name, units, and equations for the computed compound.

The computed compound equation

Consider a method with three 'real' compounds named C1, C2 and C3.

Available 'variables'

C1	The calculated concentration for compound C1.
C2	The calculated concentration for compound C2.
C3	The calculated concentration for compound C3.
C1_SEC	The calculated uncertainty (SEC) for compound C1.
C2_SEC	The calculated uncertainty (SEC) for compound C2.
C3_SEC	The calculated uncertainty (SEC) for compound C3.
C1_MW	The molecular weight of compound C1, as defined in the method setup.
C2_MW	The molecular weight of compound C2, as defined in the method setup.
C3_MW	The molecular weight of compound C3, as defined in the method setup.
C1_integral	The integrated area of C1's analysis region(s) for the current sample.
C2_integral	The integrated area of C2's analysis region(s) for the current sample.
C3_integral	The integrated area of C3's analysis region(s) for the current sample.
C1_integralBLC	Baseline corrected integrated area of C1's analysis region(s) for the current sample
C2_integralBLC	Baseline corrected integrated area of C2's analysis region(s) for the current sample
C3_integralBLC	Baseline corrected integrated area of C3's analysis region(s) for the current sample
Timestamp	The timestamp of the current sample minus the time the timestamp of the start of the current measurement, representing the time elapsed in milliseconds for the current collection.
sampleNumber	The number of the current sample since AQ Pro was started. The first sample is sample 1.
temperature	In degrees C, from the sensor or a default value.
pressure	In atmospheres, from the sensor or a default value.
flowrate	In cubic feet / minute, from the sensor or a default value.
pathlength	In meters, from the defined value for the active cell.
Timestamp	The timestamp of the current sample minus the timestamp of the start of the data measurement. It represents elapsed time in milliseconds for the current collection.

Analog Inputs	Any name from the analog inputs table
throughput	Returns "1" if the throughput test is passed, "0" if failed.
sampleNumber	The sample number of the current sample since AQPro was started. The first sample is sample 1.

Data file timestamps are expressed as milliseconds since midnight (00:00:00) January 1st 1970, coordinated universal time. The timestamp reported here is the data file timestamp minus the timestamp of the start of the measurement at the time the ***Start*** button was pressed in ***AutoQuant Pro©***. It represents elapsed time in milliseconds since the start of the measurement. These can represent time until 19:14:07, January 18th 2038. The sampleNumber is meant to be used in conjunction with an external watchdog program that monitors Modbus output. If for any reason the sample number does not increment, the watchdog program can flag a problem. User-defined inputs (up to 16) can be assigned to any fiber optic input register. These user-defined names will be available for use in the equation. For instance, an oximeter detector may be available, in which case the user may define it is 'percentO2'. Then 'percentO2' will be available as a variable for computed compounds.

Math Operators

*	Multiply
/	Divide
%	Modulo: 10 % 3 = 1 : remainder
^	Power (x^y)
+	Addition
-	Subtraction (or unary negation)
(*and*)	Precedence: define the order of evaluation

Normal arithmetic precedence applies to equation evaluation. When in doubt, use '(' and ')' to make the order of evaluation explicit.

Available Constants

pi	3.14159265358979323846
e	2.71828182845904523536

Available Functions

log	Log base 10
ln	Natural log
sqrt	Square Root

sqr	Square
sin	Sine
cos	Cosine
tan	Tangent
asin	Arc Sine
acos	Arc Cosine
atan	Arc Tangent
abs	Absolute value: abs(-2) = 2
neg	Negate: neg(2) = -2
exp	Exponentiation: exp(2.302585) = 10.0
pow	Power: pow(2,3) = 8
frac	Calculates the fractional part of a number: frac(1.2) =0 .2
mod	Calculates the floating-point remainder f of x /y such that x =i * y + f, where i is an integer, f has the same sign as x, and the absolute value of f is less than the absolute value of y: mod(-10, 3) = -1
PeakAt(wavenumber1, wavenumber2)	Returns the maximum absorbance value found between wavenumber1 and wavenumber2 for the current sample. See notes below.
ValueAt(wavenumber)	Returns the absorbance value at the given wavenumber for the current sample. See notes below.
Integrate(wavenumber1, wavenumber 2)	Returns the integrated area over the region defined by wavenumber1 and wavenumber2 for the current sample. See notes below.
Integrate2(wavenumber1, Wavenumber2)	Like the above, with extra 'method' parameter. If method is 0, the integral is calculated to a baseline of 0. If method is 1, a linear baseline between wavenumber1 and wavenumber2 is subtracted before the integral is taken. Integrate2(wavenumber1, wavenumber2, 0) is equivalent to the above integrate(wavenumber1, wavenumber2) function.
throughput	Returns a value according to the results or a throughput test, 1 for a pass and 0 for a fail. These values in common with other computed compound outputs may be linked to an alarm.

The functions PeakAt, ValueAt and Integrate use a baseline corrected version of the current sample unless it is a single beam spectrum. The baseline correction order is determined by the method's baseline correction order on the method setup dialog. For the computed compound calculator, the baseline order of 3 (quadratic) is not used. For second order (linear) baseline correction it uses a DRIFTS method. The baseline corrected spectra can optionally be written to disk for testing purposes by turning on the checkbox labeled 'Save Computed Compound BLC data' on the Tools/Parameters/Test dialog. The BLC'd data will be written into the same directory as the sample, with the same filename as the sample except that '_blc' is appended to the root filename. If the sample is a single beam, the data is first inverted and then offset back to zero (the data is multiplied by –1, then the minimum value is found and subtracted from each point), but it is not baseline corrected. Integration uses the composite Simpson rule, which needs at least 4 datapoints in the given region.

Example Equations for a Computed Compound

2*C1 + 3*C2 + 4*C3	Weighted sum of individual concentrations.
C1 / C2 * 100	C1 as a percent of C2.
C1_SEC / C1	Ratio of uncertainty to concentration.
C1 * C1_MW * flowrate	Basis of 'mass emissions' calculations.
temperature	Will simply report the temperature in a column of the results table. Associate with an alarm to signal over-temperature conditions.
1	A constant: the number 1. Useful as a placeholder for undefined uncertainty calculations.

Reserved Names

This affects the name that you give a compound. Some words are reserved and cannot be used for the names of real or computed compounds in the method. Compound names cannot end in '_MW' or '_SEC'. Compound names cannot be the same as any of the function names (log, ln, etc). Compounds cannot be named 'temperature', 'pressure', 'flowrate', or 'pathlength'.

Names are evaluated without case sensitivity: 'Flowrate' matches 'flowrate'.

Other Restrictions

In future releases, users will be able to define arbitrary values that are input via the fiber optic registers. The user-assigned names will not be allowed to collide with compound names, built-in function names, etc.

Computed compounds cannot be used in the calculation of other computed compounds because this could create circular references and evaluation order dependencies.

The uncertainty equation

Forming a correct uncertainty equation for a given computed compound involves the evaluation of partial derivatives. It's beyond the scope of a program like AQPro to automatically determine the uncertainty equation for any given computed compound equation. The user has to provide a correct equation for the uncertainty of a computed compound.

For example, assume a computed compound equation that is the simple ratio of two quantities: C1/C2. The uncertainty equation is:

sqrt(sqr(1/C2_SEC)+sqr(-1*C1_SEC/(C2_SEC*C2_SEC))).

That is, it's the square root of the sums of the squares of the partial derivatives of the individual component uncertainties. The individual component uncertainties are the partial derivatives of C1_SEC/C2_SEC, which are (1/C2_SEC) with respect to C1_SEC and (-1 * C1_SEC / C1_SEC * C2_SEC) with respect to C2_SEC.

In many cases the uncertainty associated with a computed compound is of little or no importance. In these cases a constant may be used as the computed compound uncertainty equation. This constant may take the value zero.

Compounds

Three compounds are defined (CO_2, acetone and ethanol) in the method depicted in Figure 4.25. The first column in the table, ***Incl***, indicates which compounds are currently included in the method. You can include or exclude any of the defined compounds to suit your needs during method

development or for actual analysis. Excluding extraneous compounds can greatly reduce computation time and disk space as the system determines the need for and builds calibration matrices to perform an analysis. Excluding extraneous compounds can also improve the accuracy of the concentrations of other compounds because every time a compound is subtracted whether it is present or not, some additional noise is added to the resulting subtraction spectrum

Clicking on the second column, ***Edit***, lets you enter a description and molecular weight for the compound as shown in Figure 4.31.

Compound Properties

Name: NO

Description: Nitric Oxide

Molecular Weight: 0

OK

Cancel

☑ Display Results for this Compound

☐ Report 0 PPM if the ratio of SEC to PPM is greater than: 0

Figure 4.31 Compound Properties Edit Window

In Figure 4.31, the molecular weight can be added to compute mass emissions in mass/time. Additionally, the box labeled report 0 ppm if the ratio of the SEC to PPM is greater than X can be checked to prevent any false positive results for a compound. A false positive is a concentration that is reported for a compound that is not really present in the sample. AQPro will attempt to calculate a concentration based upon the spectral area(s) chosen for quantification. Although the compound absorbance bands may not be present, any noise of interfering compounds may exhibit a reported concentration. However, the standard error calculation (SEC) is also reported with the concentration indicating how well the target compound fit the reference spectra. The SEC represents 1 standard deviation or a 68% CI. Multiplying the SEC by 2 results in a 95% CI and by 3 a 99% CI. If the SEC number is high, it is up to the user to determine if the target compound is truly present. This can be achieved by examining the residual spectrum. If the SEC is high, the reported result may be a false positive. By setting the ratio in this box to a predetermined concentration, false positives can be averted. Typically if the SEC is ½ the reported concentration or higher, then the result is suspect. By typing in 0.5 in the ratio field, any SEC results that are greater than ½ the reported concentration will be automatically reported as zero. The SEC can be reduced by adding in a interfering species to the method that allows the software to subtract out the interference.

The last two columns on the right in Figure 4.26 contain the compound name and description fields. ***MW*** is used only for mass emission reporting where flow rate is recorded through an external device or the default is used. The dialog may also be used to enter a threshold for the ratio of concentration to SEC. This enables the software to distinguish between legitimate low concentrations and baseline noise.

Items in the Compound Table, as well as the Spectra and Regions Tables can be sorted according to the information in several of the columns. To sort by a column, place the cursor on the column heading and click. To reverse the order of the sort, click again. An indicator in the column head points upward or downward for ascending or descending order.

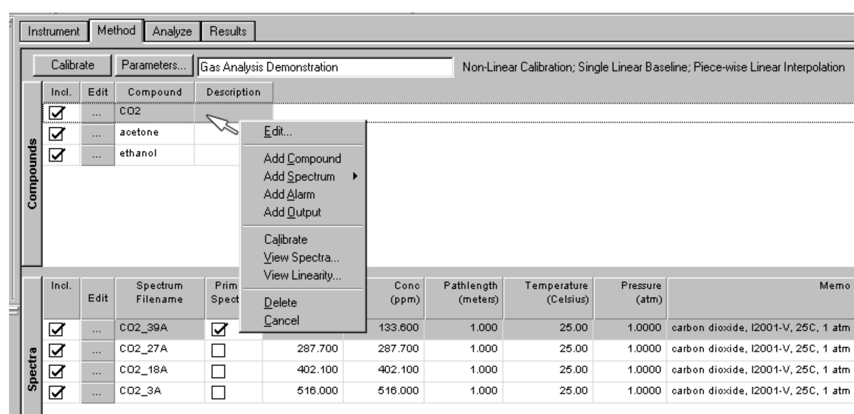


Figure 4.32 ***Right-Click*** **Compound Table Menu (full)**

Figure 4.32 shows the more extensive *right click* menu provided when the cursor is positioned on a defined compound. Note that all three tables on the ***Method Screen*** are linked - when you click on a defined compound the reference spectra defined for that compound will appear in the Spectra pane, and the regions that have been selected for analysis for those spectra will appear in the Regions pane.

The first two items on the menu, ***Edit*** and ***Add Compound***, are explained in preceding paragraphs.

The ***Add Spectrum*** item lets you: select an individual spectrum stored on disk, select a spectrum from a library collection stored on disk, use the last spectrum collected on the instrument or run a new data collection to create the spectrum. When you choose to add a stored spectrum from disk or library, a browser window opens, as shown in Figure 4.33.

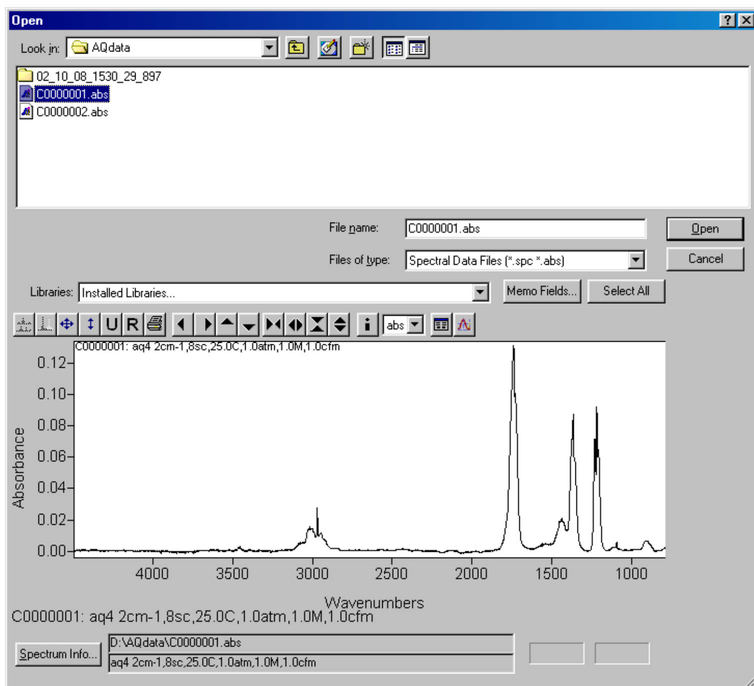


Figure 4.33 Add Spectrum Window

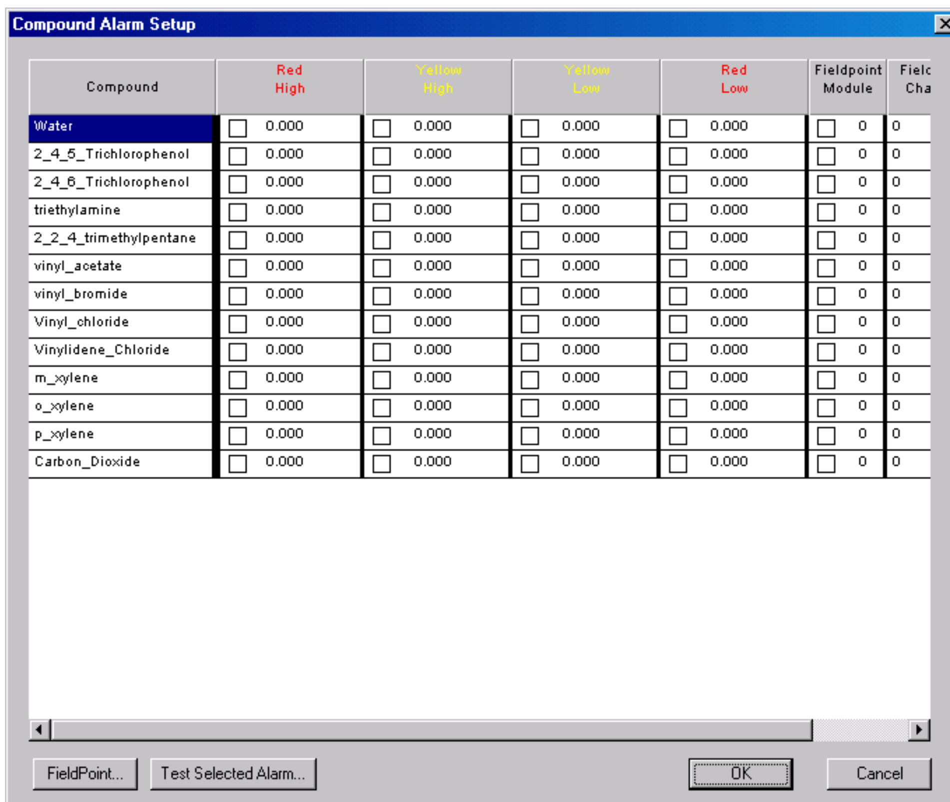
Several features are provided to help you locate exactly the file you are seeking as you browse through spectra stored on disk. When you select a potential candidate, (highlighting with a single mouse click), the spectrum appears in the lower display window with all graphic manipulation buttons available for use. The file's location and memo field information are displayed below the spectrum. Click on the ***Memo Fields*** button to view descriptive information for every spectrum stored in the current directory.

If you select ***From Instrument*** on the ***Add Spectrum*** menu, your choices are to use the last spectrum acquired by the instrument, or to immediately initiate collection of a new spectrum by choosing ***Acquire New***. The spectrum will be acquired using the currently specified instrument parameters. Make sure these settings are compatible with all stored references you are using.

The next item on the full *right click* menu is ***Add Alarms***. Alarms allow you to trap conditions when the concentration of a given compound or input exceeds or falls below threshold levels. For example, continuous monitoring applications may opt not to store spectral data as long as concentrations remain within acceptable ranges. If the ***Save Abs. On Alarm*** option on the ***Parameters: Storage*** menu is activated, the system will immediately begin storing data for archival or post event analysis purposes when an alarm condition occurs. AutoQuant Pro© will notify the user by displaying a

message and sounding an audible alarm. **The software also turns on bit 6 of the spectrometer AUX port when any alarm condition arises.**

You can designate up to four alarm conditions, (red high, yellow high, yellow low and/or red low), for each compound. The ***Add Alarms*** screen allows specification of which alarm conditions you want to activate and the concentration threshold assigned to each alarm.



Compound Alarm Setup

Compound	Red High	Yellow High	Yellow Low	Red Low	Fieldpoint Module	Fielc Cha
Water	0.000	0.000	0.000	0.000	0	0
2_4_5_Trichlorophenol	0.000	0.000	0.000	0.000	0	0
2_4_6_Trichlorophenol	0.000	0.000	0.000	0.000	0	0
triethylamine	0.000	0.000	0.000	0.000	0	0
2_2_4_trimethylpentane	0.000	0.000	0.000	0.000	0	0
vinyl_acetate	0.000	0.000	0.000	0.000	0	0
vinyl_bromide	0.000	0.000	0.000	0.000	0	0
Vinyl_chloride	0.000	0.000	0.000	0.000	0	0
Vinylidene_Chloride	0.000	0.000	0.000	0.000	0	0
m_xylene	0.000	0.000	0.000	0.000	0	0
o_xylene	0.000	0.000	0.000	0.000	0	0
p_xylene	0.000	0.000	0.000	0.000	0	0
Carbon_Dioxide	0.000	0.000	0.000	0.000	0	0

FieldPoint... Test Selected Alarm... OK Cancel

Figure 4.34 Alarm Setup Window

The ***Field Point*** button may be used to set up the alarms over a field point output. This option is discussed in the section on field point setup.

The next item on the full *right click* menu is ***Add Output***. This feature allows communication of concentration levels for a given compound to an external input device. It is fully described in the ***Parameters: Analog Out*** section of this manual. Note: the analog output device must be selected in the Parameters menu before the ***Add Output*** menu item can be used.

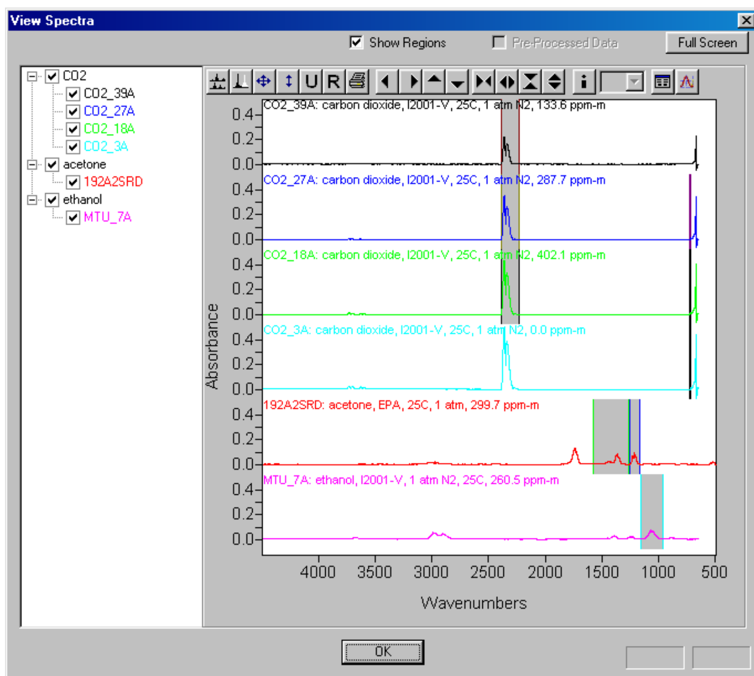
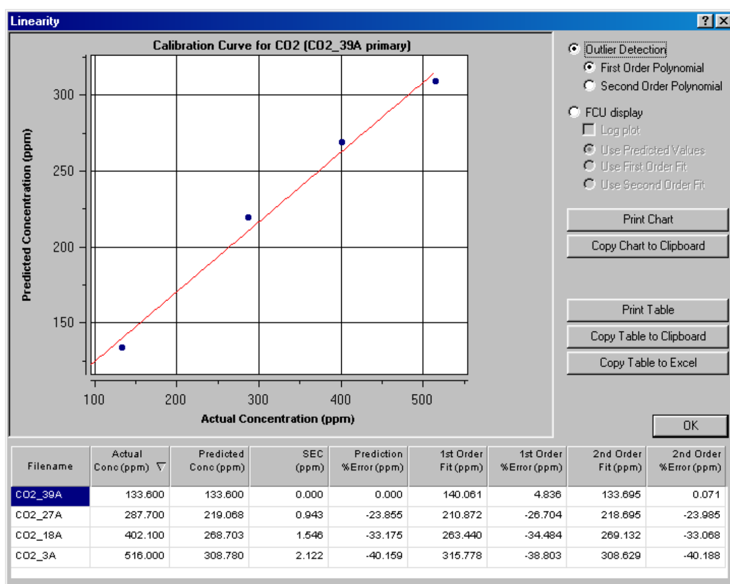


Figure 4.35: View Spectra Window

The next item on the full *right click* menu is ***View Spectra.*** This feature allows you to display any or all of the reference spectra already assigned to compounds defined in your method. You can choose to overlay the various spectra, or view them in "stacked" format as shown in Figure 4.35. The grayed sections of the display indicate which regions of each spectrum have been selected for inclusion in concentration calculations. This "selected region" feature can be toggled on and off with the ***Show Regions*** check box at the top of the window. A ***Full Screen*** push button in the upper right-hand corner of the window lets you toggle between the large, full screen view and smaller window format. Clicking on individual file names on the list to the left alternately includes and excludes spectra from the display (as indicated by the check boxes beside the file names).



Filename	Actual Conc (ppm)	Predicted Conc (ppm)	SEC (ppm)	Prediction %Error (ppm)	1st Order Fit (ppm)	1st Order %Error (ppm)	2nd Order Fit (ppm)	2nd Order %Error (ppm)
CO2_39A	133.600	133.600	0.000	0.000	140.061	4.836	133.695	0.071
CO2_27A	287.700	219.068	0.943	-23.855	210.872	-26.704	218.695	-23.985
CO2_18A	402.100	268.703	1.546	-33.175	263.440	-34.484	269.132	-33.068
CO2_3A	516.000	308.780	2.122	-40.159	315.778	-38.803	308.629	-40.188

Figure 4.36 View Linearity Window

The last items on the full *right click* menu are ***View Linearity, Delete and Cancel***. Use ***Delete*** to remove the highlighted compound and its associated reference spectra from the method. Use ***Cancel*** to exit the menu.

The ***View Linearity*** window presents a graphic display of the predicted concentrations, (based on the model produced by the currently defined method), versus actual concentrations of reference spectra. This display is useful in determining the degree to which reference spectra for a given compound exhibit linearity over the range of concentrations you have chosen. If, in fact, the compound is highly linear, you may be able to save the extra computation time and disk space required by a non-linear method, or you may be able to reduce the number of reference spectra used in concentration calculations. A highly non-linear curve (i.e. one in which the gradient at the high end is close to zero) is a good indicator that the regions chosen for analysis are too highly absorbing to conform to Beer's law, and different regions should be selected.

Outlier Detection and ***FCU Display***

There are two choices for displaying how closely your prediction model matches up to actual concentrations. ***Outlier Detection*** can be displayed as either First or Second Order Polynomials. These polynomials are for illustrative purposes only, and in no way reflect the actual quantification algorithm. The ***FCU Display*** is the Fractional Calibration Uncertainty and represents data as the % error of each data point from the linear model. This feature allows the user to determine two things:

1) Is the compound linear for the regions and concentrations chosen for quantification?
2) Are there any data points that do not fall along a predictive curve, and so can be considered outliers?

The pushbuttons on this display are fairly self-explanatory – allowing you to print or export the chart or table for use outside AutoQuant Pro©.

The table at the bottom of the window displays the calculated values for data points in the plots above.

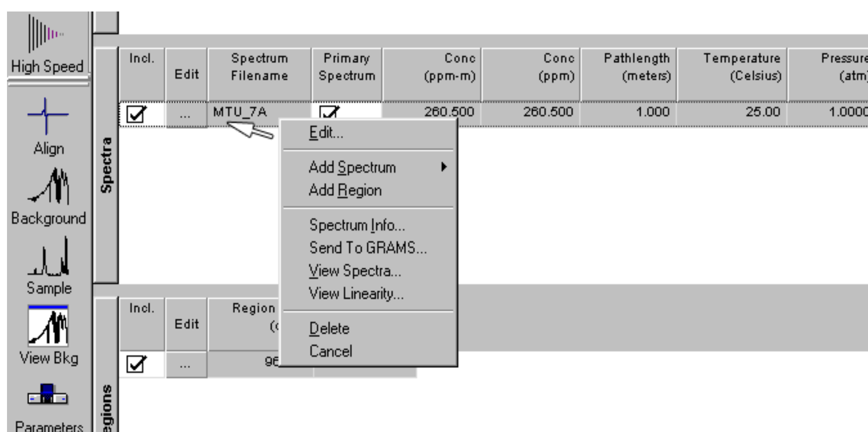


Figure 4.37 ***Right-Click*** **Spectra Table Menu (full)**

A right mouse click on the Spectra Table background brings up the brief menu version with three choices: ***Add Spectrum***, ***View Spectra***, and ***Cancel***. A right mouse click on a reference spectrum within the Table displays the full menu shown in Figure 4.37.

The ***Add Spectrum***, ***View Spectra***, and ***View Linearity*** items are described in the preceding Compound Table menu discussion.

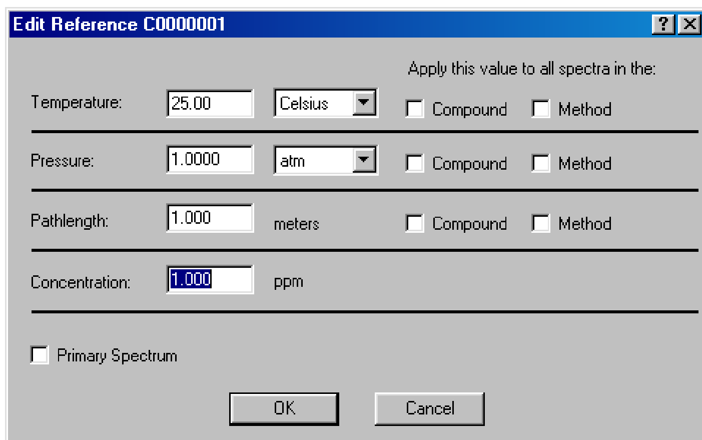


Figure 4.38 The Edit Reference Window

The first menu item, ***Edit***, opens the window shown in Fig. 4.38. You may enter or revise Temperature, Pressure, Pathlength, or Concentration information in this window. The first three of these values can be applied either to the highlighted spectrum alone or across all reference spectra for one or more compounds in the method. Of course, global editing of reference information should be used with care. The ***Primary Spectrum*** check box near the bottom of the window can only be used for one reference spectrum per compound. A linear method uses **only** the primary spectrum from each compound to build the matrices used for concentration calculations, even when multiple references have been defined for one or more compounds. Therefore, you should designate the reference spectrum of highest concentration that represents the most commonly encountered sample conditions as your ***Primary Spectrum.***

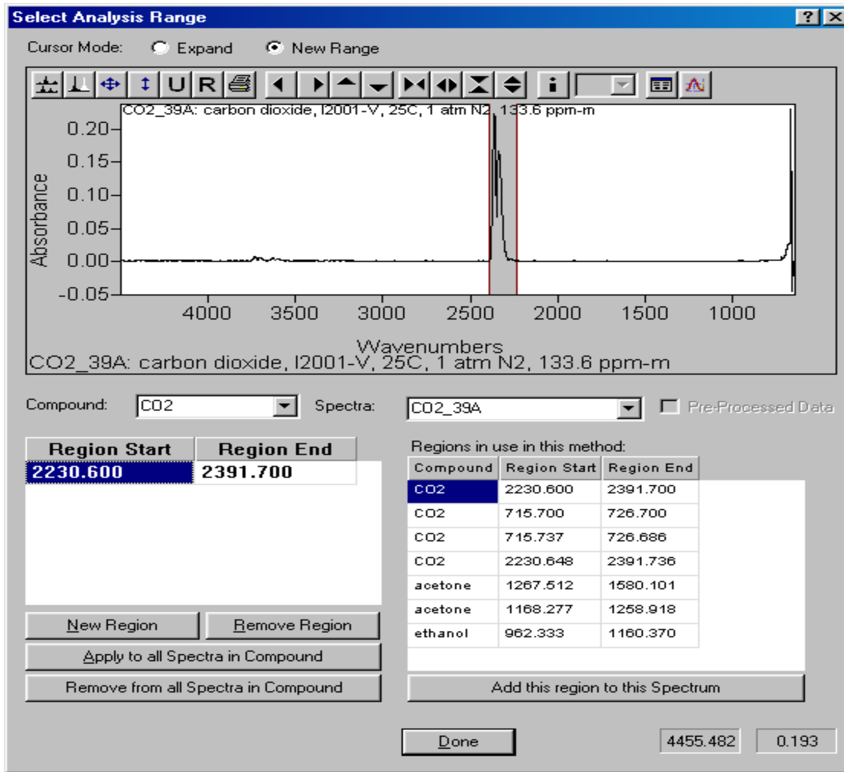


Figure 4.39 The Add Region Window

The ***Add Region*** window provides several features for selecting the exact spectral regions for use in concentration calculations.

The Analyze Screen

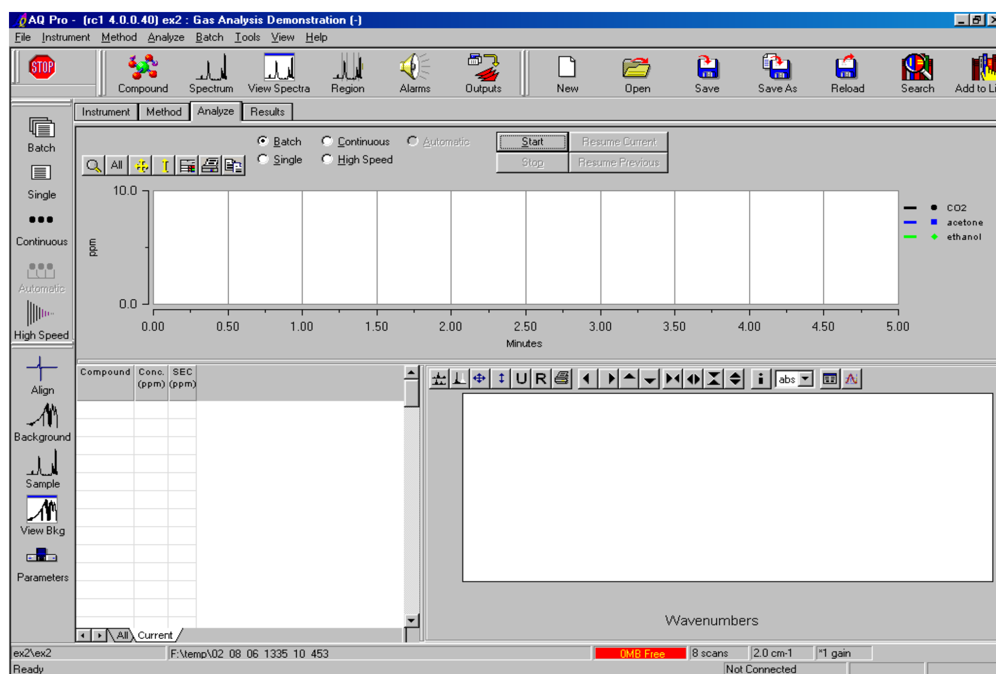


Figure 4.40 The Analyze Screen Display

The ***Analyze*** screen is accessed by clicking on the analyze tab. The screen comprises three main sections. The uppermost of these is a strip chart. This chart graphs the concentration of compounds in the method against time. This chart is generated either as part of a real time analysis or whenever data is re-batched. The bottom left of the ***Analyze*** screen houses a results table. This table has two tabs, ***All*** and ***Current***. The ***All*** tab displays results and standard error calculations (SEC) for each time point of the analysis. The ***Current*** tab displays results for the current time point only. At the bottom right of the ***Analyze*** screen is a spectral display window. This display shows the most recently acquired spectrum of the current analysis. The spectral display is actively linked to the results table and the concentration strip chart. Clicking on either a concentration from the results table or a data point on the strip chart results in the associated spectrum being displayed in the spectral display section. Functions present on the side toolbar are also duplicated on the ***Analyze*** screen via radio buttons. This provides a number of ways of accessing the data acquisition modes ***Batch***, ***Single***, ***Continuous***, ***High Speed*** and ***Automatic***. Also present are four pushbuttons. These are ***Start***, ***Stop***, ***Resume Current*** and ***Resume Previous***. The ***Start*** button initiates analysis in the selected mode. ***Stop*** ends the analysis. ***Resume Current*** picks up the analysis that was most recently stopped, without changing data subdirectories, while ***Resume Previous*** resets the analysis to

the previous mode and preferences. We will now treat each of the three sections of the ***Analyze*** screen in detail.

The Concentration Strip Chart

The strip chart is illustrated in Figure 4.41.

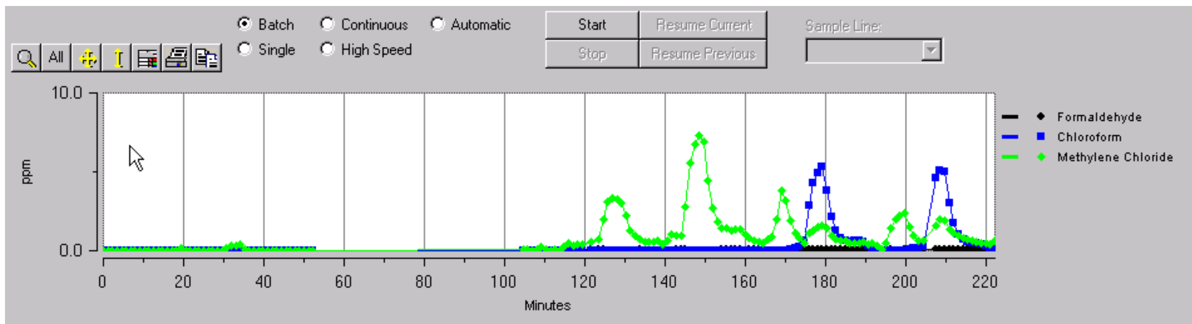


Figure 4.41 The Concentration Strip Chart

The chart plots the output of the analysis against time. The view can be manipulated using the graphic control buttons located on the top left of the chart area. Also included on this toolbar are options to set the chart properties, print the chart and to copy the chart to the clipboard as a Windows Metafile. Metafiles may be pasted directly into word processing, powerpoint, or spreadsheet document. Pressing the strip chart properties button delivers the dialog shown in Figure 4.42.

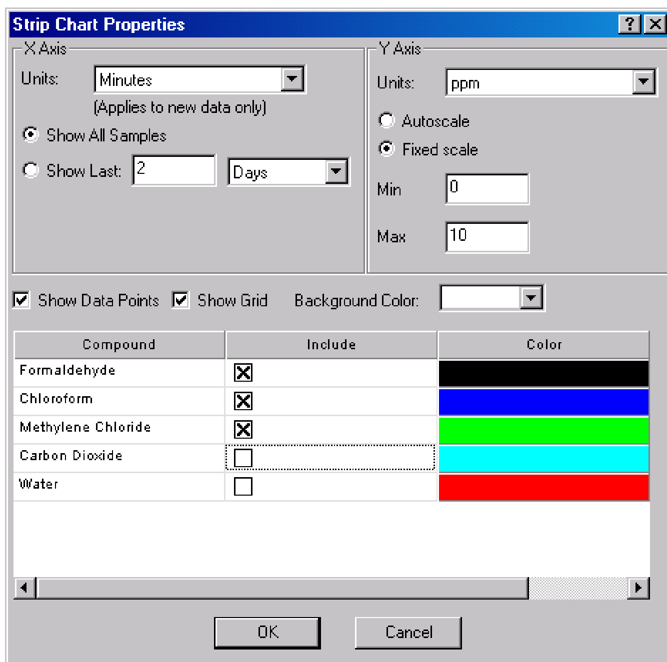
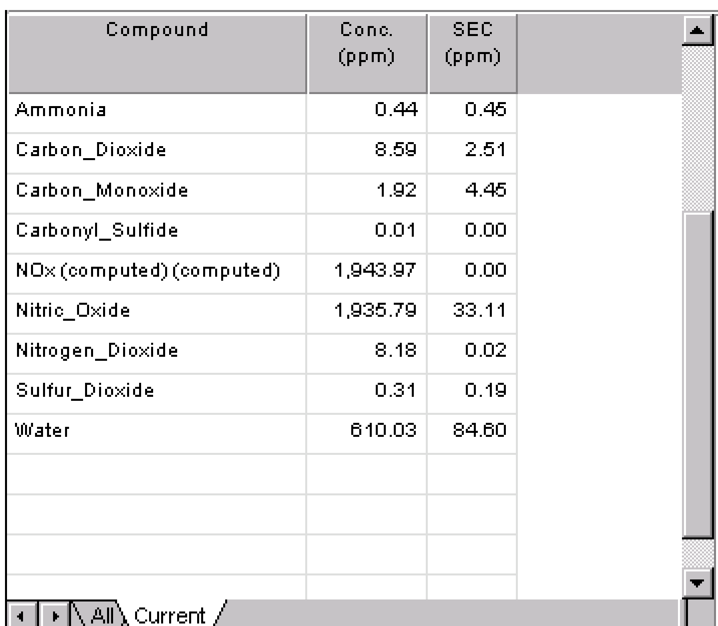


Figure 4.42 The Strip Chart Properties Dialog

The dialog may also be accessed by right clicking in the strip chart area. A drop down menu allows selection of time units for the x-axis. A similar menu for the y-axis allows selection of either ppm or ppb as concentration units. The radio buttons ***Show all Samples*** and ***Show Last:*** specify whether the whole of the analysis is plotted or, in the case of extremely long analyses, a portion of the results may be displayed. The time points to be displayed in the latter option are defined using the text box and the drop down menu beside the radio button. Similarly, the scale of the y-axis may be defined by selecting either ***Autoscale*** or ***Fixed Scale.*** The scale is specified by entering the appropriate minimum and maximum y-values into the text boxes provided. The data points may be included or excluded from the output using the ***Show Data Points*** check box. A grid may be displayed on the chart or removed using the ***Show Grid*** check box. A drop down menu allows selection of the chart background color. The compounds used in the analytical method are displayed on the left of the lower window of the dialog. In the center of this window are a series of check boxes that allow selection or de-selection of each compound to be displayed. The color assigned to each compound in the display may be specified by clicking on the color associated with the compound. This action returns a palette, from which an appropriate color may be chosen.

The Analysis Results Monitor

While the analysis is in progress, results may be monitored using the results table section of the ***Analyze*** screen. This table is shown in Figure 4.43.



Compound	Conc. (ppm)	SEC (ppm)
Ammonia	0.44	0.45
Carbon_Dioxide	8.59	2.51
Carbon_Monoxide	1.92	4.45
Carbonyl_Sulfide	0.01	0.00
NOx (computed) (computed)	1,943.97	0.00
Nitric_Oxide	1,935.79	33.11
Nitrogen_Dioxide	8.18	0.02
Sulfur_Dioxide	0.31	0.19
Water	610.03	84.60

Figure 4.43 The Results Monitoring Table

The table has two tabs. ***Current*** shows the results from the most recent spectrum, while ***All*** displays results from the whole analysis. These results are for monitoring purposes only, and do not have the output functions of the ***Results*** screen. If "display negative numbers as 0" is checked under Parameters – Numbers, then any zero in red is really a negative number. Negative numbers are statistical numbers.

The Spectral Display Area

The third area of the ***Results*** screen is the spectral display area. As an analysis progresses, the most recently acquired spectrum is displayed in the window. An example is shown in Figure 4.44.

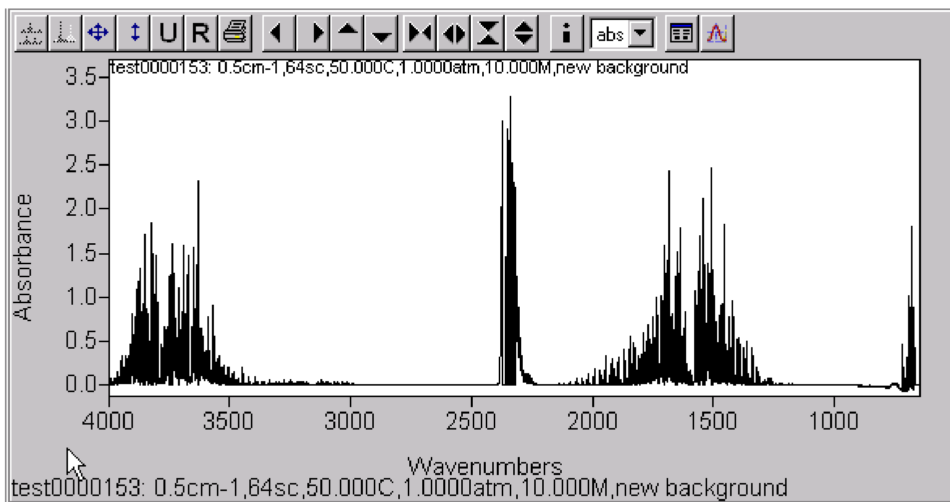


Figure 4.44 The Spectral Display Area

Parameters associated with the acquisition of the spectrum currently displayed are listed in the window. The display may be manipulated as normal, using either the graphic control buttons above the spectrum or using a mouse to select and expand areas. The display is dynamically linked to the results and strip chart areas of the ***Analyze*** screen, making it possible to view a particular spectrum simply by selecting a result or time point. A spectrum displayed in this window is available to Grams via the ***Send To Grams*** button, on the extreme right of the toolbar.

The Results Screen

The ***Results*** screen is the section of AutoQuant Pro© that summarizes the results of a complete analysis. The screen is shown in Figure 4.45.

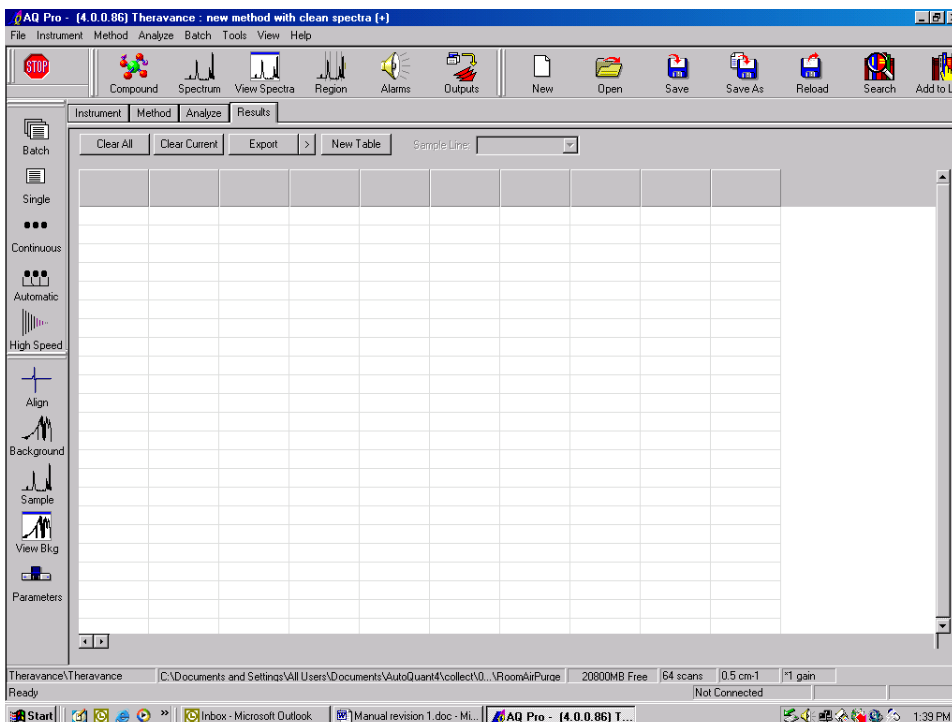


Figure 4.45 The Results Screen

The ***Results*** screen is accessed by clicking the ***Results*** tab. The major feature of this screen is a results table, which resembles a spreadsheet. Four push buttons are located on the top left of the screen. These are ***Clear All***, ***Clear Current***, ***Export*** and ***New Table***. A drop down menu labeled ***Sample Lines*** completes the list of functions applicable to this screen An example of results output is illustrated in Figure 4.46.

Clear All | Clear Current | Export > | New Table | Sample Line:

Date	Method	Filename	Sample Line	Chloroform (ppm)	SEC (ppm)	Formaldehyde (ppm)	SEC (ppm)	Methylene Chloride (ppm)	SEC (ppm)
2/9/2004 4:24:39 PM	Theravance	test0000196	N/A	0.00	0.03	0.03	0.03	1.95	0.22
2/9/2004 4:25:47 PM	Theravance	test0000197	N/A	0.00	0.03	0.03	0.03	2.21	0.22
2/9/2004 4:26:58 PM	Theravance	test0000198	N/A	0.00	0.03	0.06	0.03	2.39	0.22
2/9/2004 4:28:06 PM	Theravance	test0000199	N/A	0.04	0.03	0.04	0.03	1.47	0.21
2/9/2004 4:29:14 PM	Theravance	test0000200	N/A	0.13	0.03	0.05	0.03	0.93	0.21
2/9/2004 4:30:22 PM	Theravance	test0000201	N/A	0.18	0.03	0.05	0.03	0.62	0.20
2/9/2004 4:31:30 PM	Theravance	test0000202	N/A	0.22	0.03	0.08	0.03	0.67	0.20
2/9/2004 4:34:40 PM	Theravance	test0000203	N/A	4.63	0.03	0.08	0.03	1.62	0.21
2/9/2004 4:35:48 PM	Theravance	test0000204	N/A	5.12	0.03	0.08	0.03	2.00	0.21
2/9/2004 4:36:57 PM	Theravance	test0000205	N/A	5.02	0.03	0.06	0.03	1.89	0.21
2/9/2004 4:38:05 PM	Theravance	test0000206	N/A	3.04	0.03	0.07	0.03	1.38	0.20
2/9/2004 4:39:13 PM	Theravance	test0000207	N/A	1.72	0.03	0.07	0.03	1.10	0.20
2/9/2004 4:40:21 PM	Theravance	test0000208	N/A	1.04	0.03	0.05	0.03	0.92	0.20
2/9/2004 4:41:30 PM	Theravance	test0000209	N/A	0.69	0.03	0.06	0.03	0.77	0.19
2/9/2004 4:42:38 PM	Theravance	test0000210	N/A	0.53	0.03	0.07	0.03	0.70	0.20
2/9/2004 4:43:46 PM	Theravance	test0000211	N/A	0.50	0.03	0.06	0.03	0.60	0.20
2/9/2004 4:44:54 PM	Theravance	test0000212	N/A	0.46	0.03	0.07	0.03	0.54	0.20
2/9/2004 4:46:02 PM	Theravance	test0000213	N/A	0.43	0.03	0.07	0.03	0.47	0.19
2/9/2004 4:47:11 PM	Theravance	test0000214	N/A	0.34	0.03	0.08	0.03	0.51	0.20
2/9/2004 4:48:19 PM	Theravance	test0000215	N/A	0.19	0.03	0.08	0.03	0.40	0.20
2/9/2004 4:49:27 PM	Theravance	test0000216	N/A	0.07	0.03	0.07	0.03	0.65	0.20

Table 1 | Batch 1

Figure 4.46 Results Table

The results for a specific time point may be read across a row. The first entry in a row is a time and date stamp, which is attached to a spectrum upon acquisition. The second entry is the method name. The third entry is the filename of the spectrum. The forth entry details the sample line from which the sample was introduced (if only one sample line is used N/A is displayed). Entries subsequent to this alternate between concentrations for each compound in the method and their associated standard error calculation (SEC). This SEC represents a 1σ standard uncertainty, and so $2 \times$ SEC is approximately equal to a 95% confidence interval. The Columns may be expanded or collapsed in the same way as spreadsheet columns. Copy and printing options may be accessed via the ***Right Click*** menu. If a new analysis is started a new table will be inserted into the ***Results*** screen. It is possible to switch between the results tables using the tabs at the bottom of the table. Each table may be renamed by right-clicking on the tab and typing the new name. Clicking the ***Clear All*** button deletes all tables in the ***Results*** screen. Clicking the ***Clear Current*** button clears only the table currently on display. The ***Export*** button has two options. These are displayed by clicking on the chevron just to the right of the button. This displays a check toggle, from which either ***To Clipboard*** or ***To Excel*** may be selected. The ***To Clipboard*** option copies the current table to the clipboard, making the data available to any program that accepts pasted data. The ***To Excel*** option allows direct transfer to Microsoft Excel, assuming the program is installed. Once the desired option has been chosen, clicking ***Export*** will complete the operation. It is also possible to send the results to a CSV (comma-separated value) disk file.

Clicking the ***New Table*** button inserts a new table into the screen. The table will be titled ***Run x*** where ***x*** is the number of the run. If multiple sample lines are in use, data from specified lines may be accessed by selecting the desired line from the drop down menu ***Sample Lines***.

Chapter 5
Menus and Toolbars

The File Menu

In this chapter we will treat in depth the menu items and toolbars first encountered in Chapter 3. Menu items often have associated 'Hot Keys'. These short cuts are listed to the right of the menu items when available. The first menu to be detailed is the ***File*** menu, illustrated in Figure 5.1.

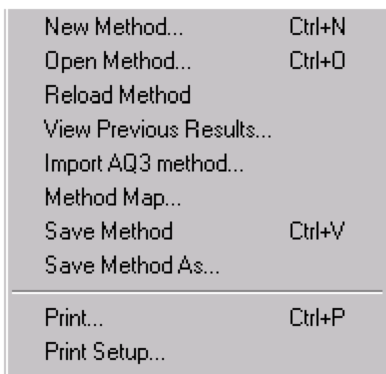


Figure 5.1 The File Menu

The menu items will be treated sequentially.

New Method

The New Method item generates a blank method, and displays a dialog box which is used to input information on the new method. The ***New Method*** dialog is shown in Figure 5.2.

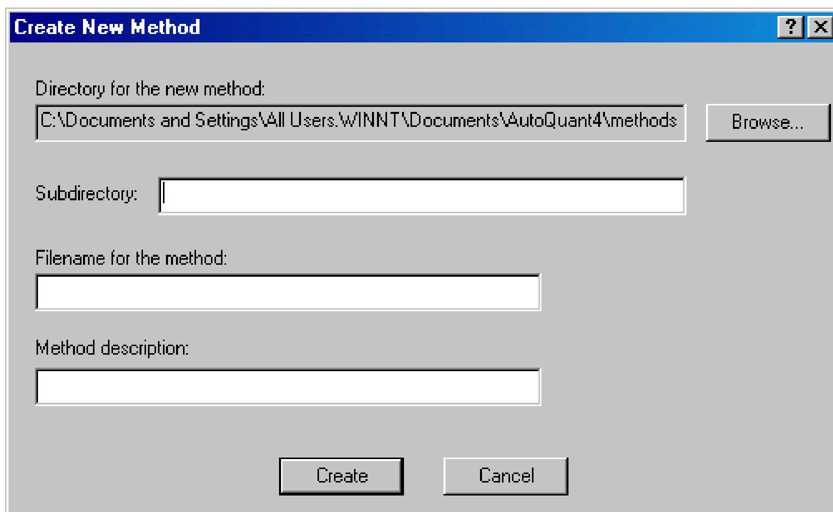


Figure 5.2 New Method Dialog Box

The directory in which the new method will be filed is displayed in the grayed out text box. This directory may be changed using the ***Browse*** button. The default when using Windows 2000 professional is **C:\Documents and Settings\All Users.WINNT\Documents\AutoQuant4\Methods**. The default directory for methods can be changed using the ***Tools/Parameters/Paths*** dialog

Three other text boxes are displayed. Two of these are used to enter names for the method subdirectory and the file name for spectra acquired under the method. The final text box in the dialog is used to enter a description of the method, which may be useful for future reference.

Open Method

The Open Method menu item is used to select and open a previously generated method. A dialog box opens to display a list of methods previously assembled by the user in the default directory. This dialog is shown in Figure 5.3 Other directories may be accessed using a drop down menu.

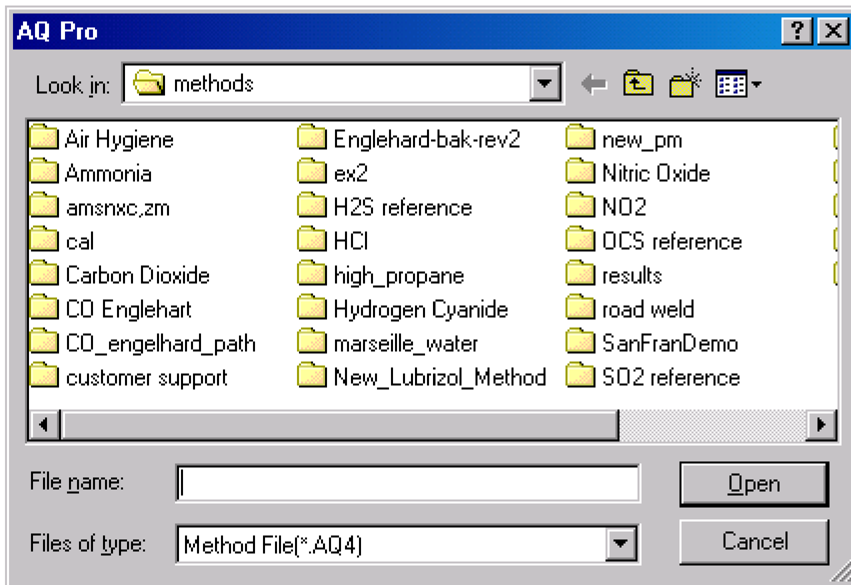


Figure 5.3 Open Method Dialog Box

Only methods with the file extension .AQ4 may be opened in this way. The subdirectories listed in the dialog may be double clicked to display the AQ4 method file.

Reload Method

This menu item reloads a copy of the current method. This is useful if you have made changes to the method that you want to discard and return to the last saved version of the method.

View Previous Results

This menu item allows loading of a set of previous results into the current method. The results are loaded as a file with the extension .aqr from the dialog box shown in Figure 5.4.

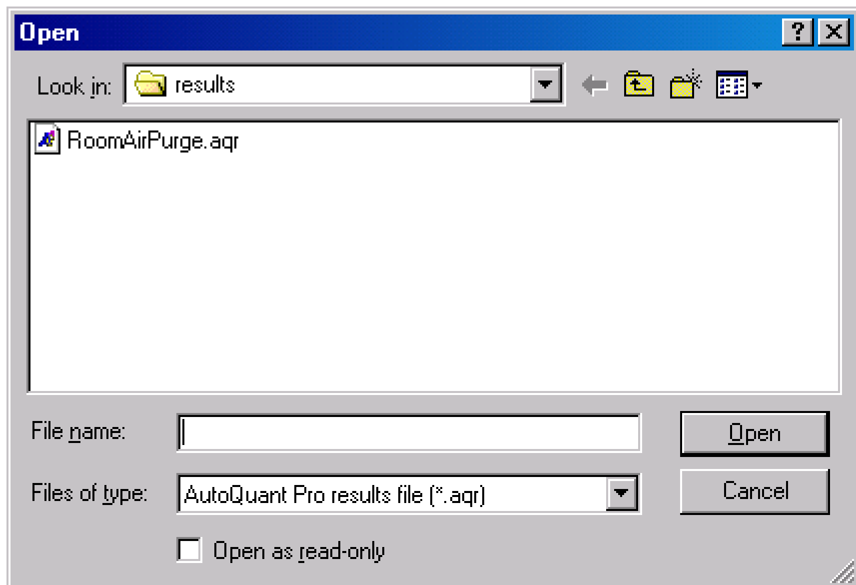


Figure 5.4 Previous Results Dialog Box

As with the ***Open Method*** dialog a set of results may be located using a drop down menu.

Import AQ3 Method

For reasons of back compatibility AutoQuant Pro© includes a utility for importing AutoQuant 3 method files. This menu item works in an analogous manner to the ***Open Method*** function, the difference being that only files with the extension .me can be loaded in this way. Please check all parameters after importing an AutoQuant 3 method for errors.

Method Map

This menu item is used to provide detailed information on the currently loaded method. The ***Method Map*** window is illustrated in Figure 5.5.

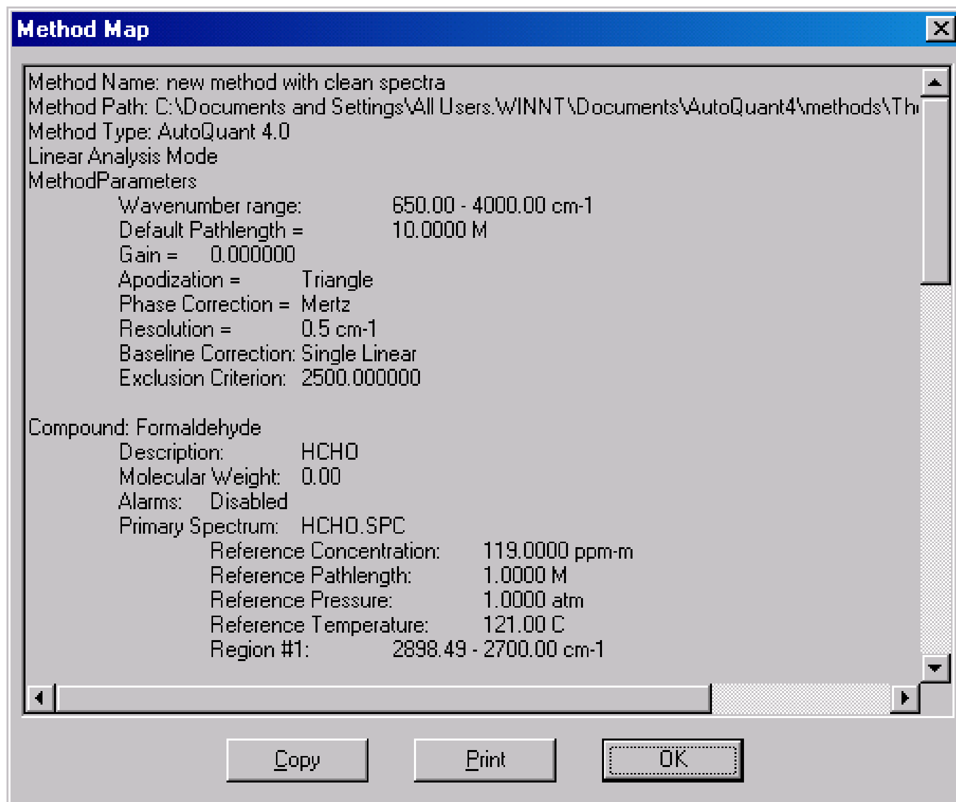


Figure 5.5 Method Map

All information associated with a method is detailed in the map. This information represents everything needed to reproduce a method should the original be lost for any reason. The map may be copied to a clipboard or printed directly using the push buttons at the bottom of the map window.

Save Method

This menu item saves the currently loaded method to its directory with a single click. A method must be saved before closing after modification or all changes will be lost. The save as button may be used if you would like to save the changes under a different name, avoiding overwriting a previous method.

Save Method As

The ***Save Method As*** menu item allows the user to save the current method to a different directory with a new subdirectory and filename. The Save Method As dialog is shown in Figure 5.6.

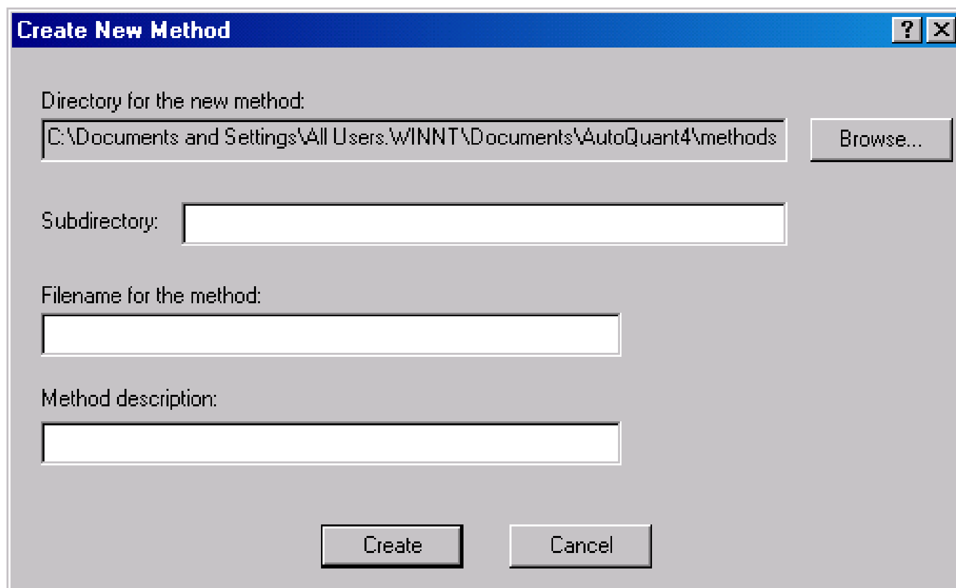


Figure 5.6 The Save Method As Dialog Box

The directory must be changed to prevent the method file being overwritten. This is achieved using the ***browse*** button. If the create button is pressed without changing the destination directory a warning notice will be displayed, and the method will not be saved. If the method is 'saved as', the 'saved as' method is now the current method

Print and Print Setup

The AutoQuant Pro© screen may be printed using the ***Print*** and ***Print Setup*** menu items. This item is context sensitive. For example, when in ***Instrument*** view a spectral plot will be printed, when in ***Results*** view a results table will be printed.

At the bottom of the ***File*** menu a list of recently loaded method files appears. This list allows convenient loading of these files by left clicking on the desired method.

The Instrument Menu

The ***Instrument*** menu is shown in Figure 5.7.

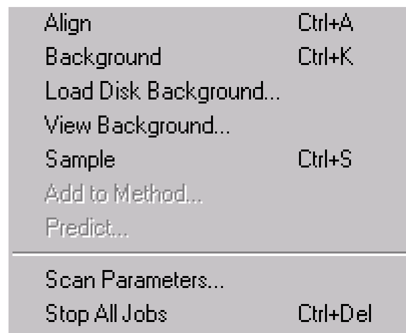


Figure 5.7 The Instrument Menu

The menu items ***Align***, ***Sample, Background*** and ***Stop*** duplicate the functions of the buttons with the same name. These functions are described in detail in Chapter 4. The remaining menu items are:

Load Disk Background

The menu item ***Load Disk Background*** allows a previously acquired background spectrum to be used in the creation of absorbance spectra in the current method. The ***Load Disk Background*** dialog is shown in Figure 5.8.

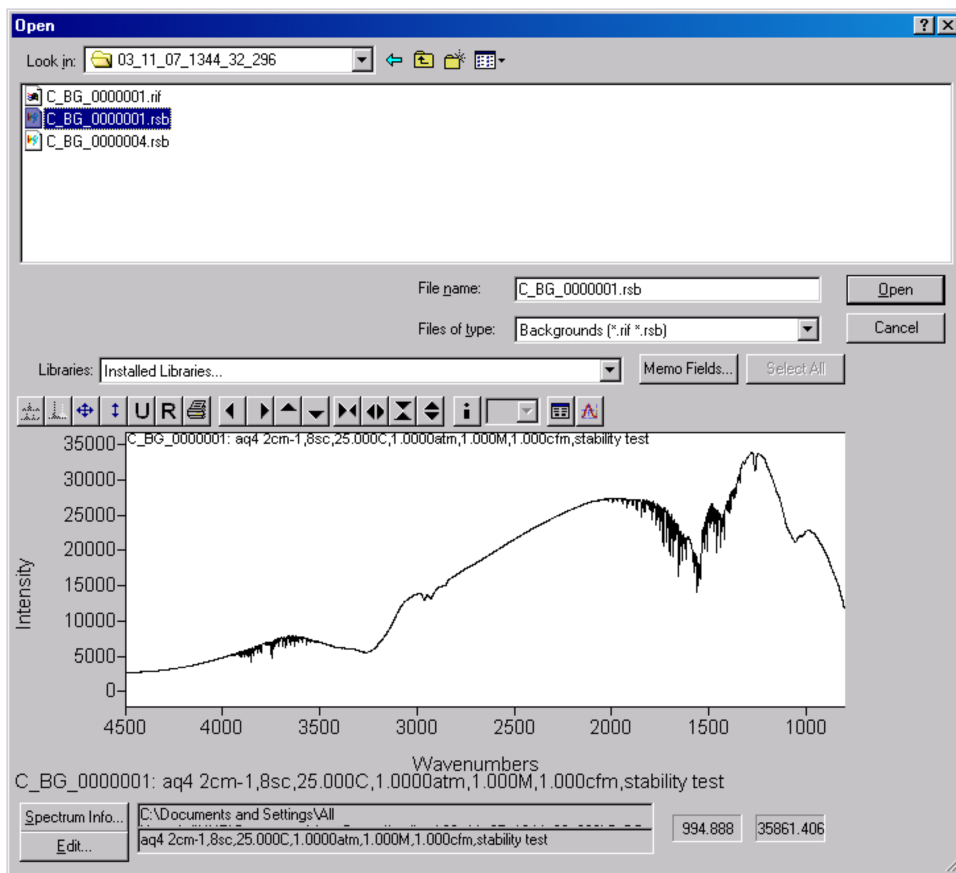


Figure 5.8 Load Disk Background Dialog Box

Background spectra are stored with the file extension .rsb, as opposed to the extension .abs applied to sample spectra. The extension .rif designates a background interferogram. A browser window occupies the upper portion of the dialog. From this window it is possible to navigate through all available drives in order to locate a desired background spectrum. A drop down menu below the browser labeled ***Libraries*** may be used to browse folders specified to AutoQuant Pro© as libraries. The topic of creating and managing libraries will be covered in detail later in this section. The lower portion of the dialog is taken up with a spectral display, with options for displaying and editing associated information.

View Background

The ***View Background*** menu item is used to display, save and collect background spectra. Memo information associated with the background is also available for editing. The View Background dialog is shown in Figure 5.9.

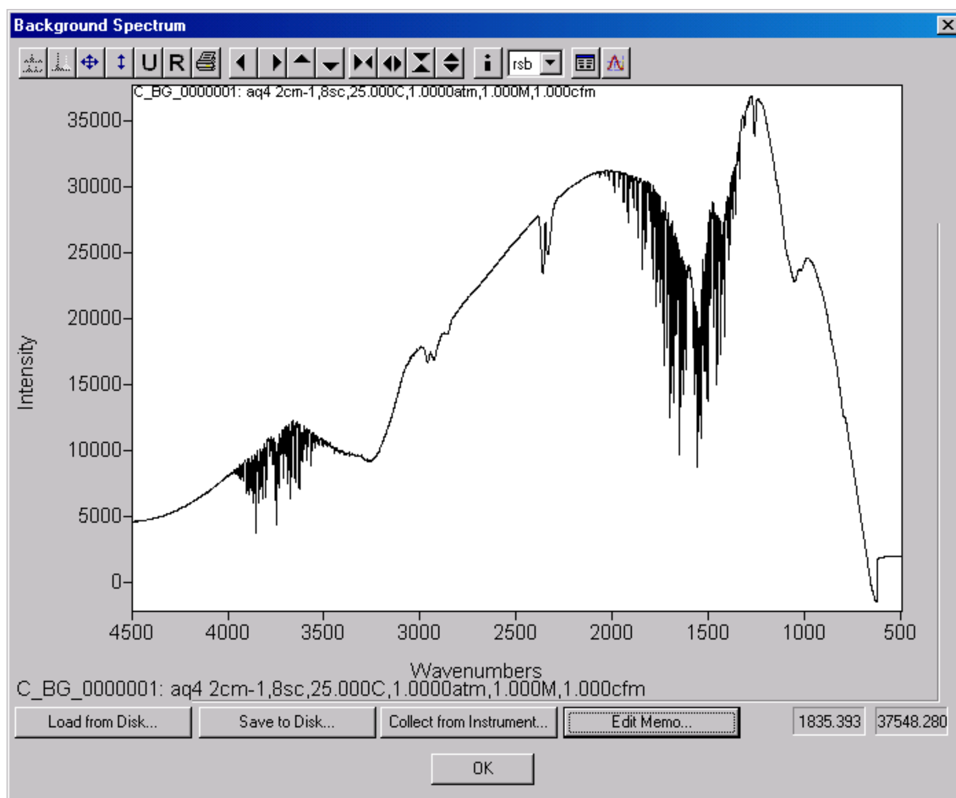


Figure 5.9 View Background Dialog Box

The ***Load from Disk*** button displays the Load Disk Background dialog box illustrated earlier in Figure 5.8. The ***Save to Disk*** button allows the background spectrum currently displayed to be saved to an available drive. The ***Collect from Instrument*** button begins acquisition of a new background spectrum, using the parameters defined in the method for background collection. Once acquisition is complete, the new background is displayed in the window. Information associated with the background spectrum may be edited using the ***Edit Memo*** button.

Sample

The ***Sample*** menu item may be used to initiate collection of a sample spectrum. This item duplicates the function of the ***Sample*** button, discussed in Chapter 4.

Scan Parameters

The ***Scan Parameters*** menu item displays the ***Parameters*** dialog box, shown in Figure 4.5. From this dialog all parameters related to acquisition of data may be set, as discussed in chapter 4.

Stop All Jobs

The ***Stop All Jobs*** menu item is one of a number of options that may be used to terminate data collection. This function is identical to the ***Stop*** button on the ***align*** and ***method*** screen, as well as the red ***Stop*** sign displayed in the upper left corner of the AutoQuant Pro© desktop.

Add to Method

The ***Add to Method*** menu item is used to include a new sample spectrum in a method.

Predict

The ***Predict*** menu item is not implemented at this time.

The Method Menu

The ***Method*** menu is illustrated in Figure 5.10.

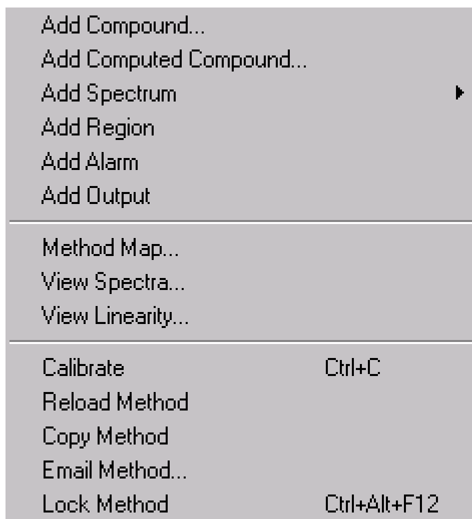


Figure 5.10 The Method Menu

Add Compound

The ***Add Compound*** menu item is used to specify analyte compounds for inclusion in the method. The Add Compound Dialog is shown in Figure 5.11.

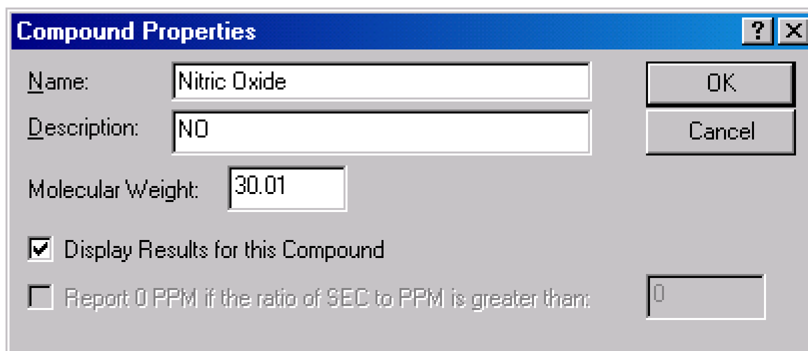


Figure 5.11 Add Compound Dialog Box

The name of the compound is entered in the top text box. If the user intends to add a ***computed compound*** to the method (see Chapter 4 for definition) the compound name must be treated as one word, for example Nitric Oxide becomes Nitric_Oxide. This is necessary in order for the ***computed compound*** function to evaluate the compound name as a variable. The molecular formula for the compound is usually entered as a description. The molecular weight is entered only so that mass flow calculations may be performed when reading in flow rates or velocities from an external device. There are two check boxes. The first of these allows the user to specify whether to display results for this compound. The second check box allows spurious concentrations to be eliminated. If a target compound is not present in a matrix, AutoQuant Pro© may try to interpret noise as a signal. Setting an appropriate threshold ratio between concentration and SEC distinguishes between real and false results.

Add Computed Compound

The Add ***Computed Compound*** menu item allows the user to combine results from real compounds in order to produce a required result for output. The Term ***Computed Compound*** is more fully defined in Chapter 4, together with a list of operators and functions that may be used. The Computed Compound dialog is shown in Figure 4.27.

Add Spectrum

The ***Add Spectrum*** menu item is used to specify reference spectra for quantification of a compound. This function is discussed in Chapter 4, and the Add Spectrum dialog is illustrated in Figure 4.29.

Add Region

The ***Add Region*** menu item is used to specify regions for analysis for each compound. The ***Add Region*** dialog box is shown in Figure 4.35, and the feature is fully detailed in Chapter 4.

Add Alarm

The ***Add Alarm*** menu item allows the user to set alarms for compounds with concentrations which exceed or fall below specified tolerances. The ***Add Alarm*** feature is discussed in Chapter 4, and the ***Add Alarm*** dialog is shown in Figure 4.30.

Add Output

The ***Add Output*** menu item is used to configure analog output of results from AutoQuant Pro©. Currently supported outputs are field point and modbus. Instructions for configuring these outputs are detailed in Chapter 4.

Method Map

The ***Method Map*** menu item displays a printable record of all parameters associated with a method. The ***Method Map*** is discussed in the File menu section of this chapter, and an example is shown in Figure 5.5.

View Spectra

The ***View Spectra*** menu item allows the user to view all spectra used in a method. The ***View Spectra*** window is shown in Figure 4.31, and the feature is discussed in Chapter 4.

View Linearity

The ***View Linearity*** menu item may be used to check the linearity of a calibration curve. The curve is fitted to either a linear equation or a 2nd order polynomial. It should be noted that the ***View Linearity*** screen is primarily a tool for diagnosing outliers in the calibration, and that the polynomial equations do not represent the actual AutoQuant Pro© quantification algorithm. The View Linearity window is shown in Figure 4.32, and the feature is given a more detailed review in Chapter 4.

Calibrate

The ***Calibrate*** menu item initiates the calibration step that generates the sub-methods necessary to the AutoQuant Pro© quantification algorithms. The method is calibrated before use in an analysis, and must be re-calibrated after any changes are made to the method. The calibration function is discussed in more detail in Chapter 4.

.

Reload Method

The ***Reload Method*** menu item loads the copy of the current method into AutoQuant Pro©. This function is also available from the ***File*** menu.

Copy Method

The ***Copy Method*** menu item enables the user to save a copy of the current method. The ***Copy Method*** function delivers the dialog box shown in Figure 5.6. The method may be renamed and / or saved to another directory. The method copied will be retained as the current method.

Email Method

The ***Email Method*** menu item interfaces with the users preset-up email program in order to send a compressed copy of the method. This function provides both users and MIDAC Corporation applications scientists with a convenient way of troubleshooting applications. Should the ***Email Method*** function fail for any reason, the method zip file will still be created in the method directory.

Lock Method

The ***Lock Method*** menu item is used to protect a method from unauthorized changes. The ***Lock Method*** dialog box is shown in Figure 5.12. The function should be used as a simple protected / not protected toggle switch for a method. Additional security is located in the Security section of the Parameters dialog.

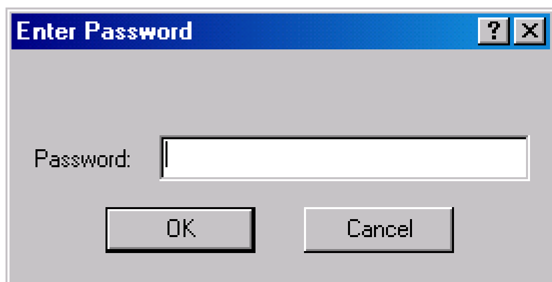


Figure 5.12 Lock Method Dialog Box

The Analyze Menu

The ***Analyze*** menu is shown in Figure 5.13.

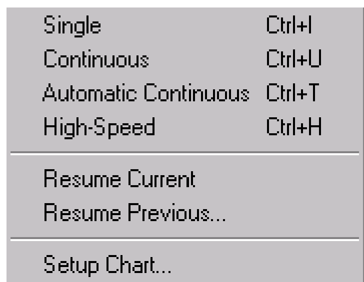


Figure 5.13 The Analyze Menu

The first four items on the ***Analyze*** menu are modes of data collection. We will discuss these sequentially. The method requires a valid background to be collected before any sample spectra are acquired.

Single

The ***Single*** mode of data collection initiates acquisition of one sample spectrum, under the parameters set using the ***Scan Parameters*** option from the ***Instrument*** menu. The collection dialog is shown in Figure 5.14. This dialog is identical for all collection modes.

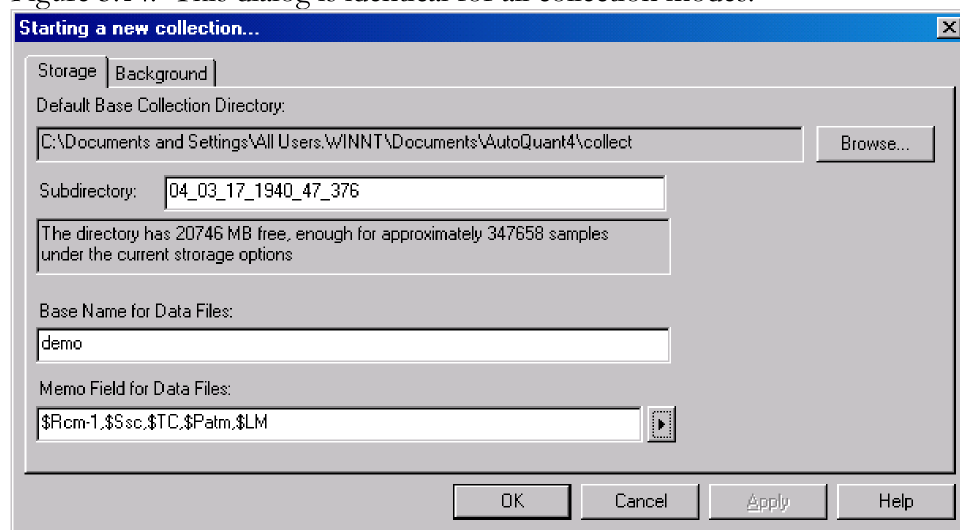


Figure 5.14 Data Collection Dialog

The ***Background*** tab on the dialog allows the user to select a desired background for the analysis. Upon conclusion of data collection the spectrum will be analyzed according to the current method, and the results for each compound in the method will be displayed in the ***Analyze*** screen, and reported in the ***Results*** screen.

Continuous

The ***Continuous*** menu item initiates collection of a series of spectra. Upon acquisition each spectrum is analyzed and the results reported. The ***Storage*** page of the ***Parameters*** dialog allows the user to choose between true continuous acquisitions, or to specify a number of spectra to collect. Alternatively, a time limit for the analysis may be set in this way.

Automatic Continuous

The ***Automatic Continuous*** menu item initiates a program of data collection controlled by the ***Valves*** module of AutoQuant Pro©. The ***Valves*** module is discussed in the ***Tools*** menu section of this manual. The valve/switch/pump operations are set-up through the valve editor sequence under the tools-valves pull-down menu on the top toolbar.

High Speed

The ***High Speed*** menu item initiates data collection with the fastest possible data acquisition parameters. Under the ***High Speed*** collection program only interferograms are stored, with no processing step to slow the analysis. Once data collection is complete, the interferograms may be converted to absorbance spectra and analyzed as normal. The ***High Speed*** function is usually applied when high time resolution is crucial to the success of an experiment. Millisecond timestamps are added to the interferograms during acquisition, these refined timestamps may be displayed using the ***Parameters – Numbers*** dialog.

Resume Current

The ***Resume Current*** menu item allows the user to recommence an analysis that has been terminated without changing data directories or other storage parameters.

Resume Previous

The ***Resume Previous*** menu item allows the user to restart the analysis using a user specified (.aqr) file, which holds the analysis parameters. The ***Resume Previous*** dialog is shown in Figure 5.15.

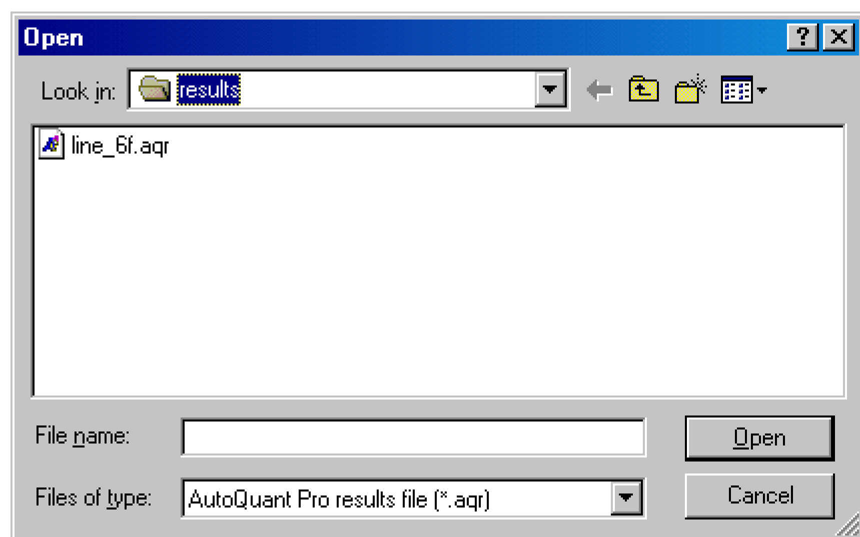


Figure 5.15 Resume Previous Dialog Box

Setup Chart

The ***Setup Chart*** menu item may be used to access the strip chart properties dialog box, shown in Figure 4.38. This dialog box is used to configure preferences for the plot of compound concentration against time discussed in Chapter 4.

The Batch Menu

The Batch menu has two items.

Batch

The ***Batch*** menu item allows the user to reprocess data acquired in earlier analyses, or to reprocess files to other file types, for example interferograms (.ifg) to single beam (.sb) to absorbance (.abs). The Batch dialog box is shown in Figure 5.16.

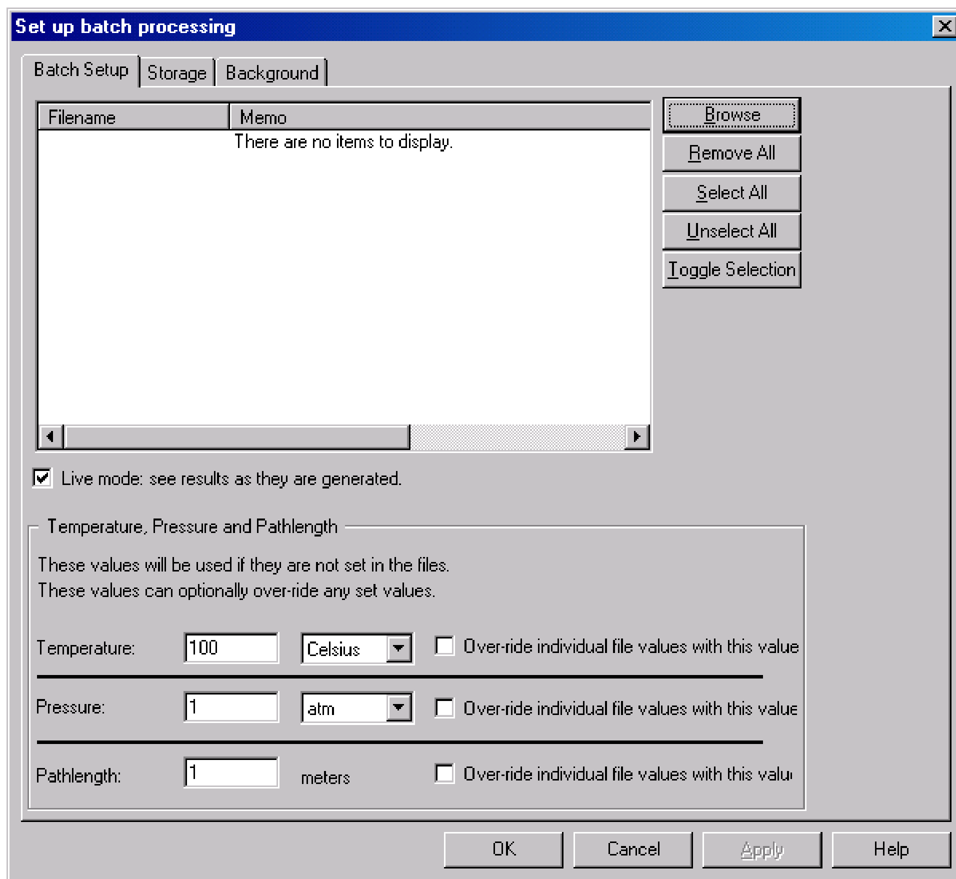


Figure 5.16 The Batch Dialog Box

On the ***Batch Setup*** tab of the dialog there are five push buttons to the right of the file viewer. The ***Browse*** button allows the user to navigate to the location where the desired files are stored. The ***Remove All*** button removes any selected spectra from the file viewer. The ***Select All*** button loads all spectra files in a folder into the batch processor. The ***Unselect All*** button reverses this action. The ***Toggle Select*** button toggles between deselecting files and reselecting those files. Directly beneath the file viewer is a check box labeled ***Live mode: see results as they are generated***. This may be unchecked for increased analysis speed. The three parameters listed below the check box may be entered and set as defaults using the text boxes and check boxes. These options should only be used on spectra which have no associated information stored in the (.abs) or (.spc) file. The ***Storage*** tab of the dialog box allows the user to define subdirectories for data storage. Also present are options to

save single beam spectra, absorbance spectra or to process interferograms without performing an analysis. The ***Background*** tab allows the user to apply a specific background spectrum to the files undergoing ***Batch*** processing.

Rebatch

The ***Rebatch*** menu item enables the user to batch process the last set of files analyzed. This may be useful when results from an analysis are unsatisfactory and changes are made to a method. The data may then be re-batched in this manner.

The Tools Menu

The ***Tools*** menu contains a number of complex and useful functions that have not yet been discussed in detail. The Tools menu is shown in Figure 5.17.

Figure 5.17 The Tools Menu

The menu items will be discussed sequentially.

Parameters

The ***Parameters*** menu item allows the user to access the ***Parameters*** dialog box discussed in Chapter 4 and illustrated in Figure 4.5. This dialog box enables the user to set all parameters associated with data acquisition, storage and analysis.

Valves

The ***Valves*** menu item allows the user to configure the ***Valves*** module of AutoQuant Pro©. The ***Valves*** module makes it possible to automate sampling from multiple sample lines, using options from the ***Valves Sequence Editor*** dialog box shown in Figure 5.18.

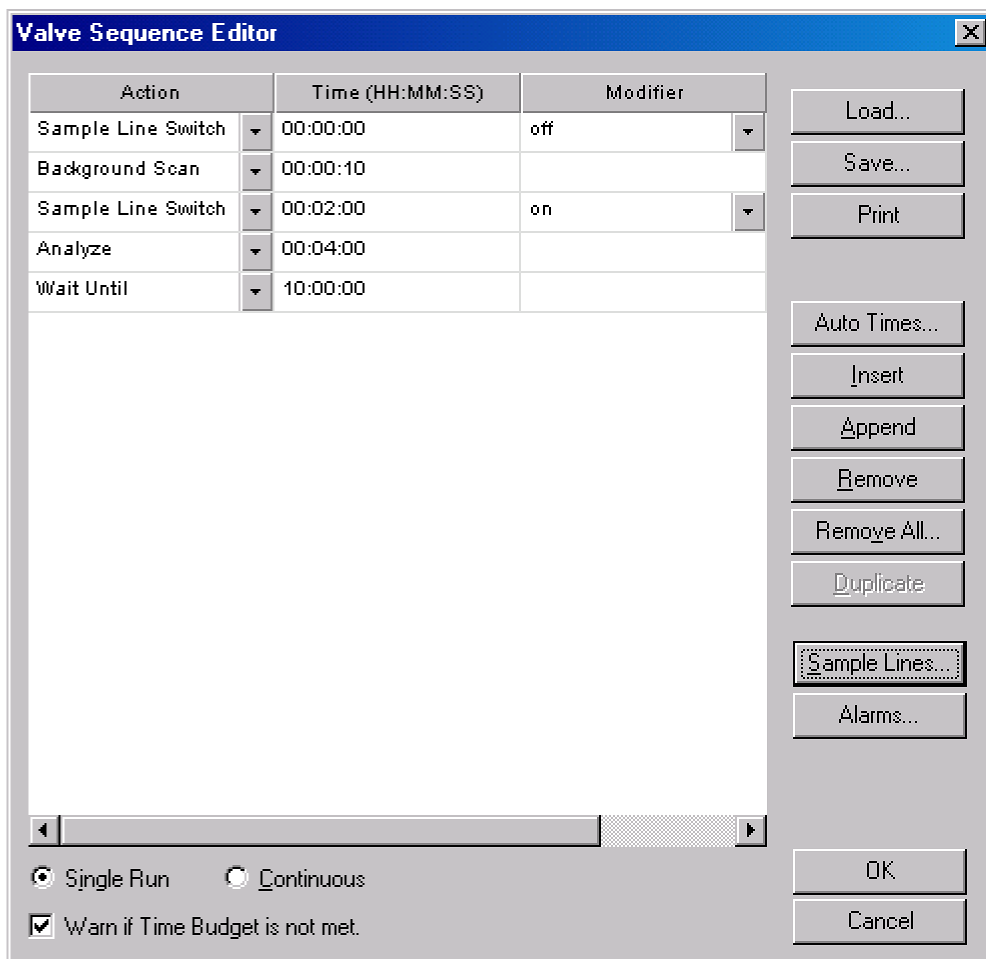


Figure 5.18 Valves Sequence Editor

The ***Valve Sequence Editor*** consists of a sequence viewing window and a series of push and radio buttons on the right side of the dialog box. The ***Auto Times*** button summons a dialog requesting default timings for the various steps in the sequence. The timings are then filled automatically. Otherwise the timings must be calculated and entered manually. The ***Load*** button may be used to load a pre-existing sequence file. Sequence files have the file extension (.seq). The ***Save*** button is used to save a sequence file to disk. The sequence file (.seq) is saved in the AutoQuant Pro© program directory and not the method folder so that different methods can be loaded automatically for different sample lines. The most recent edit of the sequence and sample lines is automatically saved as "default.seq" or "default.sl" file in the program directory although a different name was assigned. The user must assign a new name to any changes to a sequence or a sample line so that the changes are not lost upon closing the program. The last used sequence or sample line file (default.x) will automatically be loaded upon opening the program. The ***Insert*** button may be used to place a new row into the sequence at the selected time point, while the ***Append*** button places a new row at the end of the sequence. The ***Remove*** button is used to delete a selected row. The ***Remove All*** button deletes all rows from the sequence. The ***Duplicate*** function is not implemented at this time. The radio buttons labeled ***Single Run*** and ***Continuous*** allow the user to specify whether the sequence should run only once or continue until manually interrupted. The ***OK*** button saves the sequence and quits the editor

while the ***Cancel*** Button quits without saving. Before discussing the ***Sample Lines*** button, we will examine the process of sequence building more closely.

When beginning a new sequence we start with a blank viewing window, either by default or by pressing the ***Remove All*** button, and pressing ***OK*** on the confirmation dialog box. We are now ready to insert the first row into the sequence, using the ***Insert Row*** button. Note that the row is split into 3 columns, labeled ***Action***, ***Time*** and ***Modifier***. The new row may be configured using the drop down menu in the ***Action*** column. The options on the menu are ***Sample Line Switch***, ***Analyze***, ***Background Scan***, ***Repeat Analyze*** and ***Wait Until***. An actual sequence would be application specific and dependant on the number of sample lines in the system, but for our purposes we will construct an example sequence starting with the ***Sample Line Switch*** option. This actuates a specified sample line, usually of purge gas. A sufficient time interval must be allowed for the switch (or any other operation) to reach completion. This time interval is set by double clicking in the ***Time*** Column and entering the desired time point. For example, we would wish to allow the ***Sample Line Switch*** sufficient time to actuate and flow a reasonable amount of purge gas through the gas cell, and so the time point of the following step should reflect this. The time point must be entered in the format hh:mm:ss. The operation ***Sample Line Switch*** is also subject to a modifier, which is set using the drop down menu in the ***Modifier*** column. The switch may set the line to ***On***, ***Off*** or ***Safe***. The next line should be a ***Background Scan***, in order to have a valid background in place for the analysis. The time for this step is set at 00:00:10 to allow time for the Sample Line Switch discussed earlier. Using these guidelines the example sequence shown in Figure 5.18 may be built. Any errors in the sequence will be flagged upon saving the file.

In order to run an ***Automatic*** sequence it is necessary to have a sample line file in the method. The sample line file works with the sequence file, and has the extension .sl. ***Sample Line*** files use hexadecimal instructions to control sets of valves. An example of a (.sl) file pertaining to a sampling system with 13 lines and one gas cell is given in Figure 5.19. The sample line file (.sl), in common with the sequence file is saved under the AutoQuant Pro© program folder and not the method folder. Both the sample line and sequence files are automatically saved as the defaults. Beginning an automatic analysis the defaults .seq and .sl files are loaded. The software will continue to use these files until new defaults are set up.

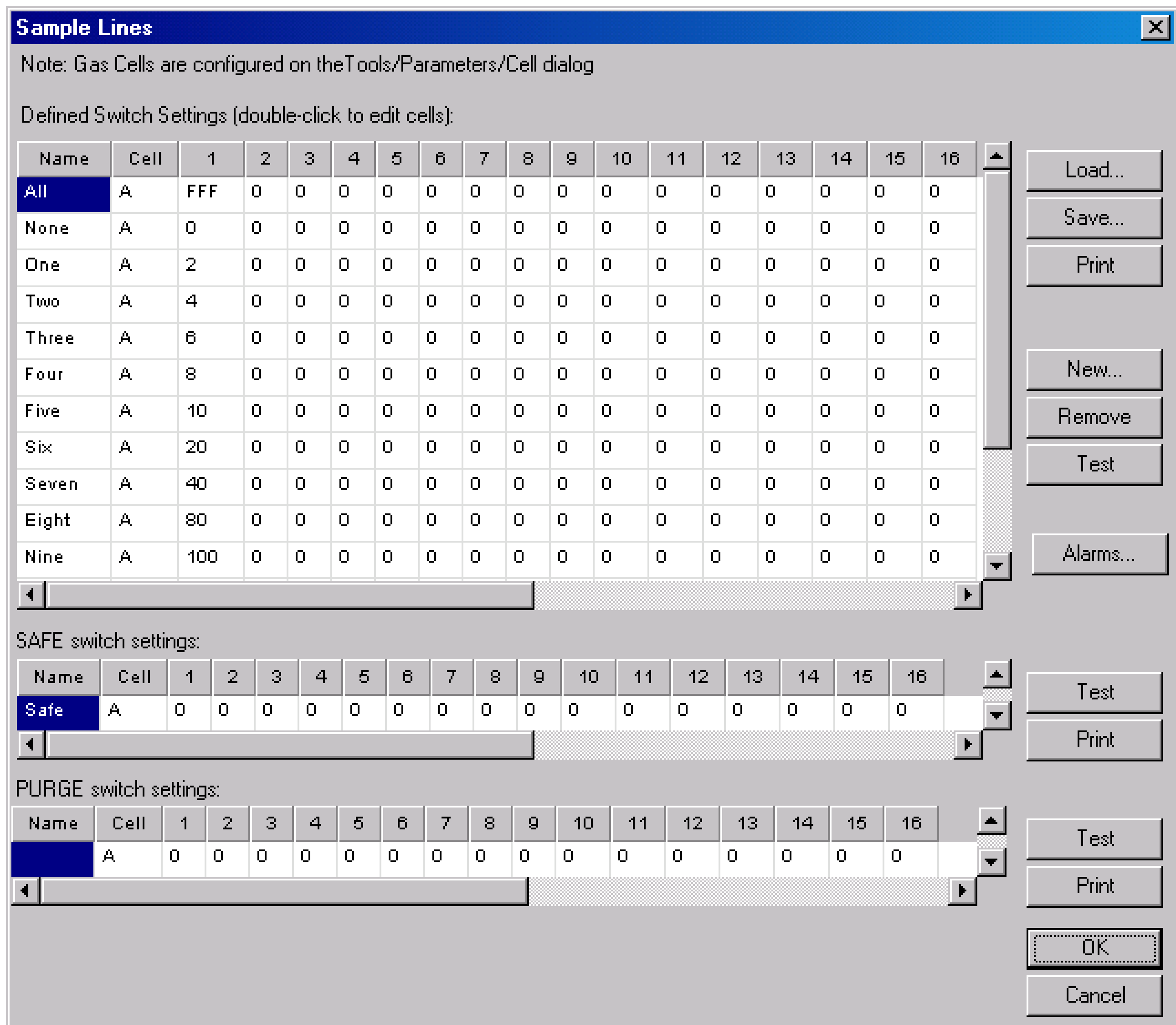


Figure 5.19 Sample Lines Dialog Box

The dialog box shown in Figure 5.19 is accessed using the ***Sample Lines*** push button on the ***Valves*** dialog. ***The Sample Lines*** dialog is similar in layout to the ***Valves*** dialog. The Load and Save buttons allow the user to open and save (.sl) files. The ***New*** button places a new line into the viewing window. The ***Remove*** button is used to delete lines. The two ***Test*** buttons are used to debug the configuration, and will generate error warnings if mistakes are present. The ***Alarms*** button delivers the dialog shown in Figure 5.20. This dialog allows the configuration of alarms linked to sample lines and may be configured according to one of the three conditions discussed in the section on ***Modbus*** setup.

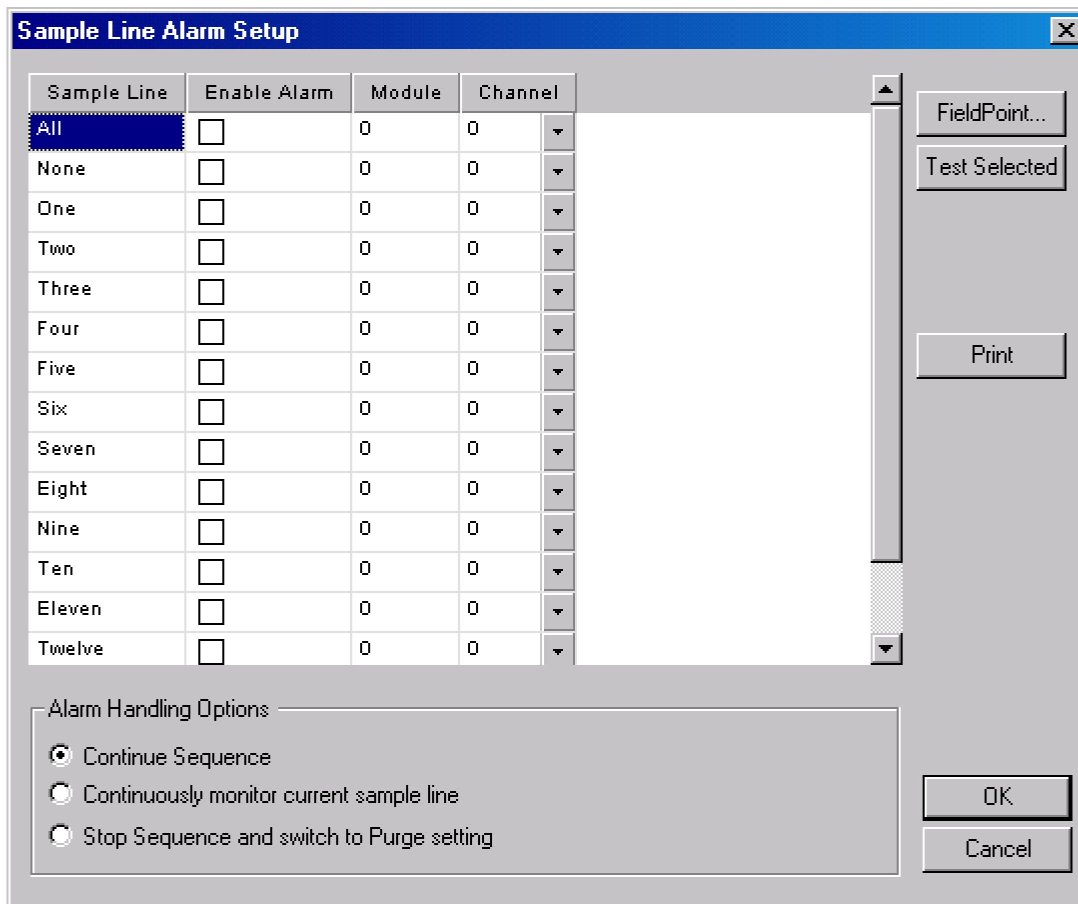


Figure 5.20 Sample Line Alarm Setup

Field Point alarms are available for configuring via the ***Field Point button***. The OK button saves the (.sl) file and quits the ***Sample Lines*** editor, while the ***Cancel*** button quits without saving. The ***Setup*** button is used to access the ***Setup*** dialog box. The ***Setup*** dialog allows the user to configure temperature, pressure and flow rate monitoring. An example of a fiber optic setup table is shown in Figure 5.21. Depending on the pressure transducer used, the High and Hex codes may need to be changed. Typical high values are 30 or 50 psi.

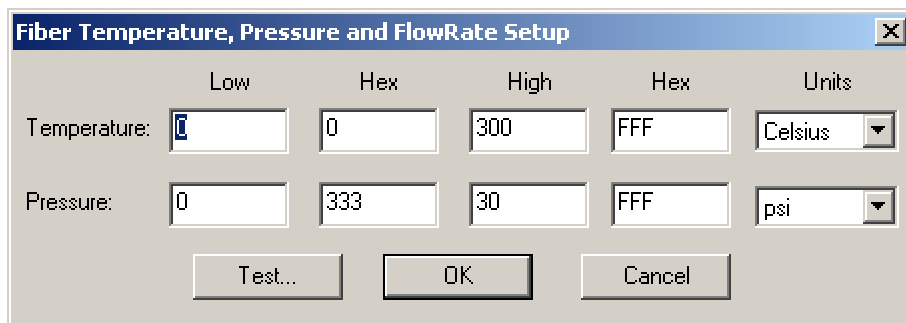


Figure 5.21 Fiber Optic Setup Table

The switches are operated by the software and computers as hexadecimal entries in column one of Figure 5.19. Each toggling of the switch is operated by a specific hexadecimal code. Codes may be multiplied together using a hexadecimal calculator to derive new codes that toggle multiple switches or turns all switches on or off. The user must determine which hexadecimal code toggles that switch. Typical codes are shown in Figure 5.19. Safe mode corresponds to the toggle settings determined by the application and the user to be the 'safe' configuration.

Once both the (.seq) file and the (.sl) file have been configured correctly, the ***Automatic Continuous*** item on the ***Analyze*** menu may be used to initiate the collection sequence.

Alarm Log

The ***Alarm Log*** menu item displays a table containing information on all alarms triggered during an analysis. The ***Alarm Log*** table is shown in Figure 5.22.

Figure 5.22 The Alarm Log Table

If an alarm has been triggered the ***Alarm Log*** table enables the user to view the date and time of the alarm, the method used, the data file that triggered the alarm, the type of alarm, the compound responsible, the concentration of the compound and the alarm thresholds. When running an automatic collection the alarm window will stay active until the alarm condition is satisfied, for example until a sample is analyzed with concentrations that fall between the alarm thresholds. The alarm log however will retain information on any alarms triggered during the analysis. The checkbox ***Sound alarm for information alerts*** makes the distinction between alerts and alarms. An alert may be a warning of low disk space, for example. If the alert sound is turned off the dialog will still display the alert with no sound. The siren may not be turned off for alarms. The method must be saved in order for this preference to be maintained in the next AutoQuant Pro© session.

Libraries

In AutoQuant Pro© ***Libraries*** are folders containing spectra that may be interrogated using the ***Search*** item on the ***tools*** menu. An existing folder containing spectra may be designated as a library, or a library may be built from an empty folder, with collected spectra being saved to the new library. The ***Library*** menu item allows the user to manage these libraries. The ***Libraries*** dialog box is shown in Figure 5.23.

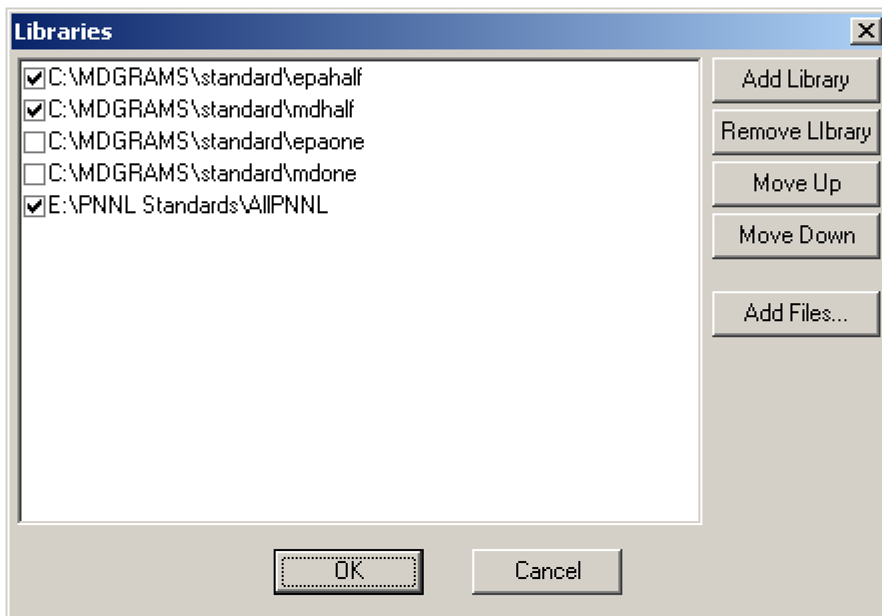


Figure 5.23 The Libraries Dialog Box

The display portion of the ***Libraries*** dialog shows folders that have been designated as libraries. The ***Add Library*** button allows the user to navigate to a specific folder and include it in the list of libraries. The ***Remove Library*** button removes a folder from this list. The buttons ***Move Up*** and ***Move Down*** may be used to change the order in which libraries are searched. The ***Add Files…*** button is used to navigate to a set of spectra and add the files to the selected library.

Add To Library

The ***Add To Library*** menu item may be used to acquire data and include the collected absorbance spectrum in a library. The Add To Library dialog box is shown in Figure 5.24.

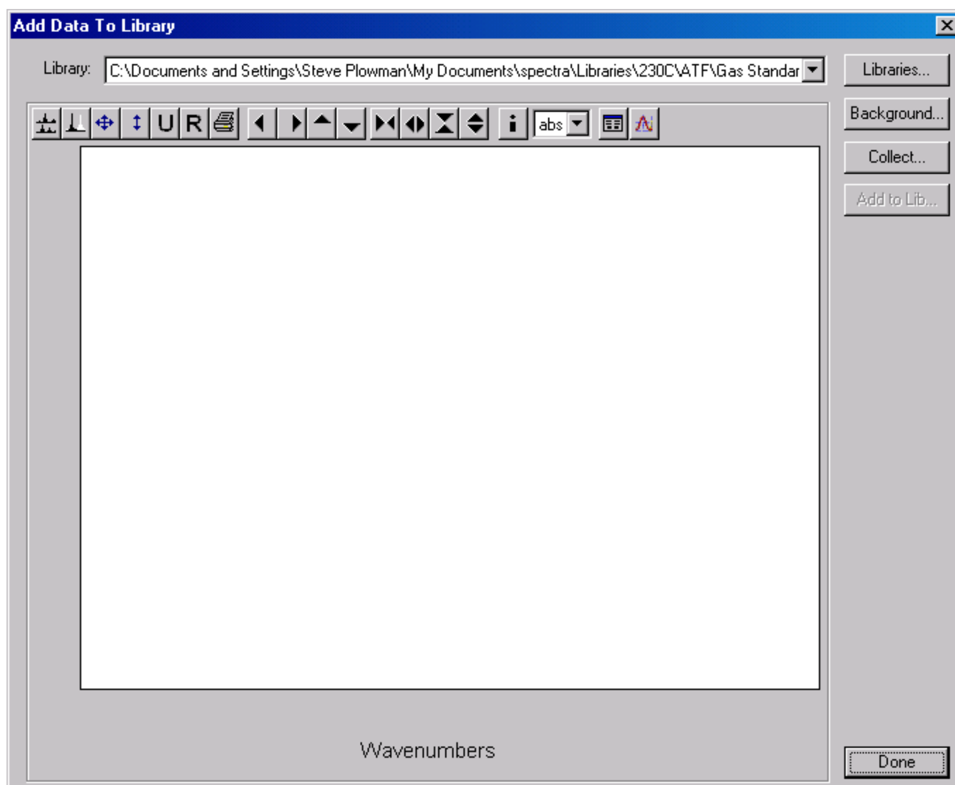


Figure 5.24 The Add To Library Dialog Box

The dialog consists of a spectrum viewer that displays the collected spectrum, a drop down library selection menu, and a series of buttons. The drop down menu labeled ***Library*** allows the user to specify a parent library for the collection. The acquired spectrum will be placed in the library displayed in the text box. In order for a library to be available for use in this way it must first be included in the Libraries list shown in Figure 5.23.

Note: If the ***Add to Library*** button is used the options in the ***Storage*** section of the ***Parameters*** dialog will default back to the ***Never Save Spectra*** option. The user must re-select the desired saving options before continuing analysis.

The ***Background*** button allows collection of a background spectrum or gives the option to specify a disk background. The ***Collect*** button begins acquisition of a spectrum using the scan parameters for the current method. Once the collected spectrum has been inspected for suitability the ***Add To Library*** button is used to include the collected spectrum in the selected library. The ***Done*** button dismisses the dialog box. The ***Libraries…*** button is not implemented at this time.

Search

The ***Search*** menu item is a module of AutoQuant Pro© that allows automatic comparison of spectra or selected regions of spectra with library standards. This search function enables the user to identify unknown sample components from their absorbance bands. The ***Search*** dialog box is shown in Figure 5.25.

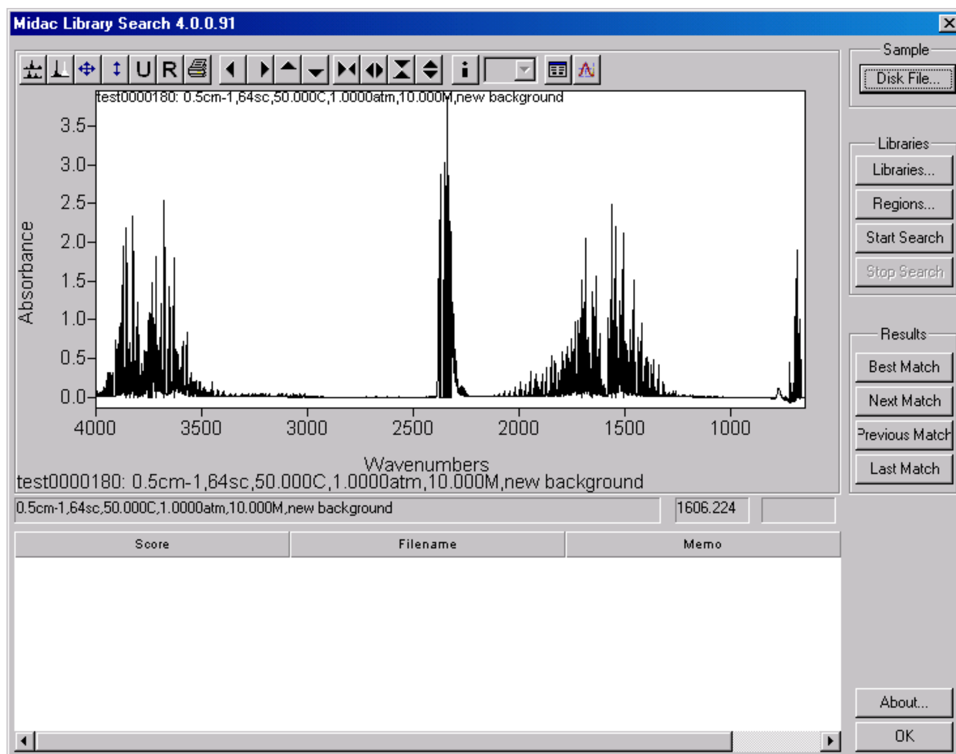


Figure 5.25 The MIDAC Library Search Dialog Box

The dialog consists of a viewing window for spectral display, a table of results and a series of buttons on the right hand side of the dialog. The display window shows the sample spectrum to be examined. This spectrum may be specified using the ***Disk File*** button in the ***Sample*** section of the dialog. The ***Libaries*** section of the dialog contains four buttons. The ***Libraries…*** button allows the user to choose which standard libraries are to be searched. The ***Regions*** button displays the dialog box shown in Figure 5.26.

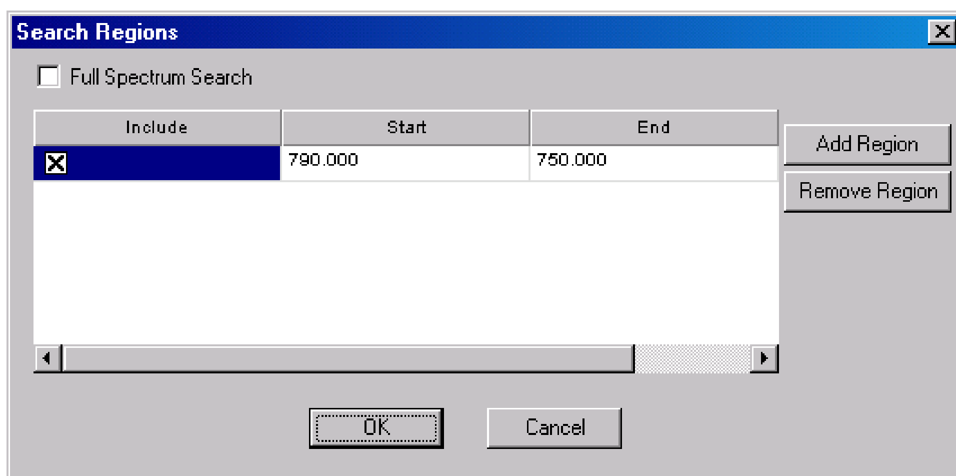


Figure 5.26 Search Regions Dialog Box

The regions selected are compared against the corresponding regions of the library spectra. The check box labeled ***Full Spectrum Search*** sets the search to compare whole spectra. This option should only be used when comparing spectra of a single component. Multiple regions may be selected. The ***Add Regions*** and ***Remove Regions*** buttons are used to manage the search regions.

The ***Start Search*** button on the ***Library Search*** Dialog initiates a search. The ***Stop Search*** button terminates the current search. The results table lists the possible matches according to a correlation ranking system, with a ranking of 1 being a perfect match. The table is illustrated in Figure 5.27.

Score	Filename	
0.984665	C:\Documents and Settings\Steve Plowman\My Documents\My Methods\Theravance\CHCl3.SPC	chloroform, EPA,
0.907528	C:\standard\standard\mdhalf\HFPEZ1A.SPC	hexafluoropropen
0.877684	C:\standard\standard\mdhalf\HFPEH6A.SPC	perfluoropropene,
0.770388	C:\standard\standard\mdhalf\HFPEH1A.SPC	hexafluoropropen
0.740779	C:\standard\standard\mdhalf\MXYL33A.SPC	m-xylene, I2001-
0.740078	C:\standard\standard\mdhalf\MXYL29A.SPC	m-xylene, I2001-
0.739918	C:\standard\standard\mdhalf\MXYL24A.SPC	m-xylene, I2001-

Figure 5.27 Search Results Table

The results in this example indicate that the compound responsible for the absorbance band between 790cm^{-1} and 750cm^{-1} is chloroform. The buttons ***Best Match***, ***Next Match***, ***Previous match*** and ***Last match*** enable the user to navigate easily through a list of possible matches. The act of selecting a match in the results table displays that spectrum in the display window. Comparing matches with the sample spectrum in this way allows confirmation that the predicted match is actually the compound giving rise to the absorbance. An example is provided in Figure 5.28, using the chloroform model outlined previously.

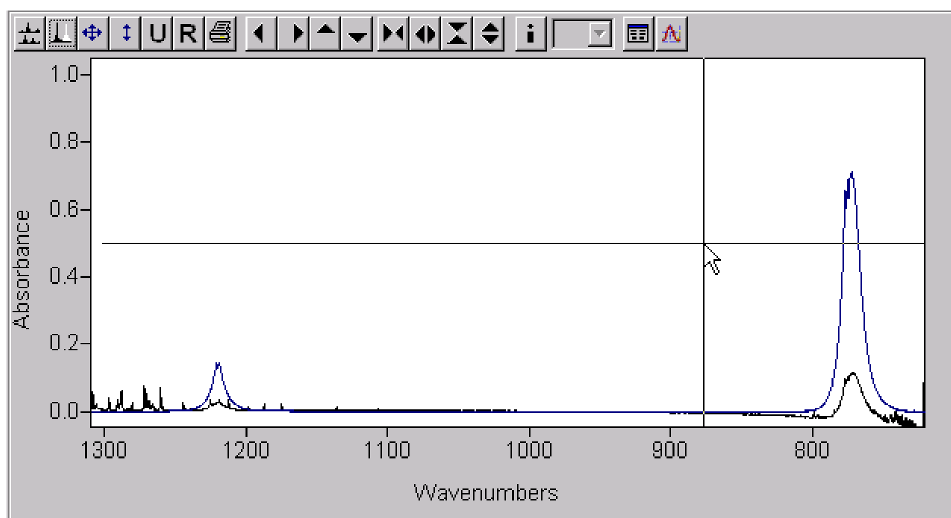


Figure 5.28 Confirmation of Unknown Identification

The library standard and the sample spectra were overlaid using the graphic control buttons along the top of the viewing window. In this case the compound is clearly chloroform, as both bands displayed match.

The View Menu

The ***View*** menu is used to access the ***Toolbars*** options. These are shown in Figure 5.29.

Figure 5.29 Toolbar Options

The four toolbars listed are File, Measurement, Instrument and Method. These toolbars are illustrated in Chapter 3 in Figures 3.3 – 3.6. The ***Reset Toolbars*** option restores the default toolbar settings. The ***Toggle Text Labels*** option toggles button descriptions on and off.

The Help Menu

The Help Menu is shown in Figure 5.30

Figure 5.30 The Help Menu

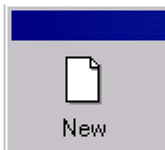
The ***Help Topics*** menu item is not implemented at this time. Please refer to your electronic copy of the manual for searches on topics. The ***About AutoQuant Pro©…*** menu item displays information on the version of AutoQuant Pro©, together with copyright and license details.

Toolbars

Many of the AutoQuant Pro© functions accessed using the menu system are also available via graphic toolbars, as discussed in Chapter 3. The toolbar buttons may be classified into four sets. These are the ***File Toolbar***, The ***Instrument Toolbar***, the ***Method Toolbar*** and the ***Measurement Toolbar***.

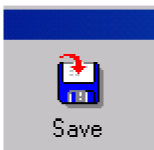
The File Toolbar

The ***File*** toolbar provides access to file handling functions such as creating, opening and saving methods. In addition to this the ***File*** toolbar contains shortcuts to the Search and Library functions, as well as printing and help options. The ***File*** toolbar is shown in Figure 3.3. The functions associated with each button are:

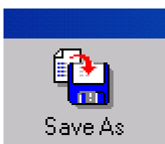


Shortcut to the ***New Method*** dialog

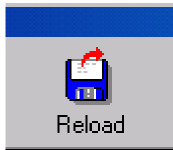
Shortcut to the ***Open Method*** dialog



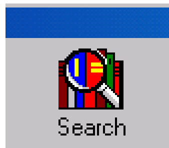
Saves the current method to disk



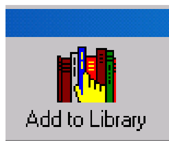
Shortcut to the ***Save Method As*** dialog



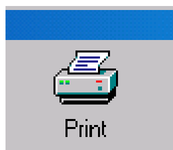
Reloads the current method from disk



Shortcut to the ***Search*** dialog



Shortcut to the ***Add To Library*** dialog



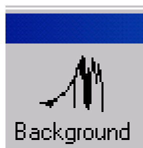
Shortcut to ***Print*** dialog

Shortcut to ***Help*** dialog

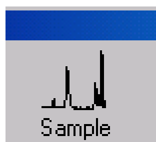
The Instrument Toolbar

Shortcuts to many of the ***Instrument*** menu items may be found on the ***Instrument*** toolbar, pictured in Figure 3.4. The functions associated with each button are:

Shortcut to ***Align*** function, described in Chapter 4

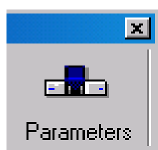


Initiates collection of a new background, using the scan parameters from the current method



Initiates collection of a sample spectrum, using scan parameters from the current method

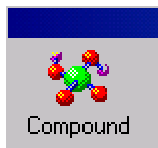
Shortcut to the ***View Background*** dialog



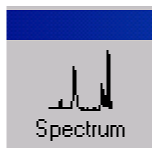
Shortcut to the ***Parameters*** dialog

The Method Toolbar

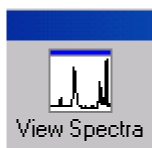
Many of the items from the ***Method*** menu may be accessed using the ***Method*** toolbar, shown in Figure 3.5. These functions are used to build methods and configure alarms. The items on the ***Method*** toolbar are:



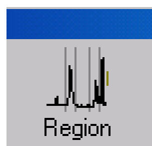
Shortcut to the ***Add Compound*** dialog



Shortcut to the ***Add Spectrum*** dialog

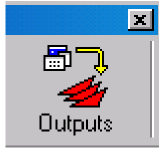


Shortcut to the ***View Spectra*** dialog



Shortcut to the ***Add Region*** dialog

Shortcut to the ***Add Alarms*** dialog

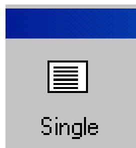


Shortcut to the ***Add Outputs*** dialog

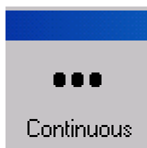
The Measurement Toolbar

The ***Measurement*** toolbar contains functions necessary to collect data from the instrument. The functions on the ***Measurement*** toolbar may also be found in the ***Analyze*** and ***Batch*** menus. The Items are:

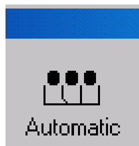
Shortcut to the ***Batch*** dialog



Begins collection of a single sample spectrum



Begins ***Continuous*** data collection



Begins ***Automatic Continuous*** measurement (see ***Valves***)

Begins ***High Speed*** collection of interferograms

Chapter 6

Configuring AutoQuant Pro© for Use

Introduction

The step-by-step instructions in this chapter lead you through the production of high-resolution reference spectra for the analysis of target compounds

These instructions will demonstrate how to set up methods and create spectra. You may have your own preferences or procedures for completing tasks using FTIR spectroscopy to obtain different results.

MIDAC cannot take responsibility for numbers generated from following these procedures, because different sample matrices and methods can produce varying results. It is the user's responsibility to document how spectra were created, why specific method routines were chosen and to provide documentation for data Quality Control and Quality Assurance, so that the user can present a defense of their analytical methodology to meet data quality objectives.

Application of Reference Spectra

If carefully prepared and documented, reference spectra can be successfully applied to an ***AutoQuant Pro©*** method to obtain accurate analytical results. However, the best analytical results are usually obtained when reference spectra are measured using the same instrument, temperature, pressure, pathlength, and resolution used to measure the sample spectra. Errors can be introduced when measuring sample spectra under differing instrumental conditions than those used to measure the reference spectra.

Errors can be introduced into the analysis when using spectra obtained from outside sources. Examples from these sources of error include the following:

- Erroneous pathlength used when calculating library compound optical densities (ppm-m)
- Non-linearity issues from hardware, software, or non-linear compound reference bands
- Different apodization functions used to collect reference spectra and sample spectra
- Different instrumental resolutions used to correct reference spectra and sample spectra
- Erroneous concentrations determined or manufactured when preparing reference spectra
- Peak broadening occurring from increased temperatures and pressures than those used for analysis

- Peak shifting (x-shifting) produced from different instruments used to obtain reference spectra or analyze samples

- Appearance of "hot" bands that occur at higher temperatures for some compounds and not found in a reference spectrum obtained under lower temperatures

- Baseline anomalies between instruments

- Differing window, beamsplitter, or mirror features that occur from different materials

- Contaminants in or incomplete instrument purge when producing background

- Double modulation

- Use of reference spectra apodized differently than the sample spectra

If you are going to make reference spectra that will ONLY be used on your instrument (no transfer of spectra between instruments), you may skip the procedure for "determining cell pathlength using ethylene" (See "Instrument Set-up" below, Step 8). and assume that the cell pathlength is arbitrarily "1" or a specified value (0.1, 0.15, 4 or, 10 meters), and proceed directly to "Making Reference Spectra," below.

The pathlength is used to determine pathlength concentration products (ppm-m), otherwise known as optical densities, which are used to "adjust" the reference spectrum when used on another instrument with a different pathlength. For example: Making a 5 ppm CO_2 reference spectrum, calling the cell 4 meters, assigning the reference spectrum a 20 ppm-m value and entering into the software under the Method "4" meters. The reported concentration will be the same if the user arbitrarily assigns a "1" to the cell, assigns the reference spectrum 5 ppm-m, and entering "1" in the method parameters. However, if you use this reference spectrum on another instrument without assigning it its proper optical density (20 ppm-m), you will receive erroneous results.

Eliminating the pathlength calculation reduces cumulative error in the overall analysis. Small errors in pathlength determination are carried directly through to the final reported number.

Note that cell pathlengths may change under different cell temperatures. Differences as much as 20 percent may occur between room temperature and elevated temperature pathlength determinations. Always determine your pathlength at the same temperature used for sample analysis.

Instrument Set-up

The first step in producing high quality, accurate, high-resolution spectra is to prepare the instrument properly. You must connect the FTIR and computer, heat the cell to the appropriate temperature, turn on instrument power, and allow the instrument to stabilize for a period of one to two hours.

1. IF APPLICABLE, fill the MCT detector with liquid nitrogen (LN2). If your instrument is equipped with a DTGS, no further detector preparation is needed. If an InAs (indium arsenide) or InSb (indium antinomide) detector is used, please fill with LN2, or allow Thermo-Electrical (TE) cooling to stabilize for one to two hours.

2. Purge the instrument with dry nitrogen by removing two of the ¼-inch caps located on three sides of the instrument (three caps on I-series only). Connect a ¼-inch line (Teflon or stainless steel is preferred although others are acceptable) to one of the fittings and connect the other to the sample cell inlet. This procedure allows the FTIR system to be completely purged under nitrogen so that a baseline background reference spectrum can be obtained. Allow nitrogen to flow into the FTIR box at approximately 0.5-2.0 lpm. Initially, much higher flow rates may be used to quickly purge the box and cell, but the flow must be turned down once analysis is started due to turbulence issues in the box.

Note The system must be free of any target compounds before a background reference spectrum is obtained. Otherwise, any contaminant bands will be subtracted out of each sample spectrum and bias your results. Carbon dioxide will purge out of the system quickly while water will take approximately 12-36 hours before the FTIR electronics box is considered dry. The electronics box contains a relatively small optical pathlength that will produce spectral bands of compounds in the gaseous phase within the box unless the box is purged well.

Note Many users will use liquid nitrogen Dewar boil-off or headspace for nitrogen purge. It must be noted that 2-3 ppm of water and trace amounts of carbon dioxide can be present in this boil-off. If water or carbon dioxide are target compounds, it is advisable to send the nitrogen through a molecular sieve scrubber or drying tube. Additionally, FTIR purge gas generators are available from MIDAC.

The light pipes (tubes) connecting the cell and FTIR electronics box on the I-2000 model also have connectors for purging. You may purge with nitrogen in-line with the FTIR box according to the diagrams below.

Note A vacuum on the box may be used to generate reference spectra, but unless a near-perfect vacuum is achieved, the reference spectrum will contain very low concentrations of CO_2 that will be subtracted from your sample analysis. This procedure is not recommended for CO_2 generation of reference spectra at low ppm levels. Also, unless the vacuum option is selected for your instrument when ordered, excessive heat may build up in the FTIR box. The heat build-up in the FTIR electronics box will reduce the life of the components and void warranty.

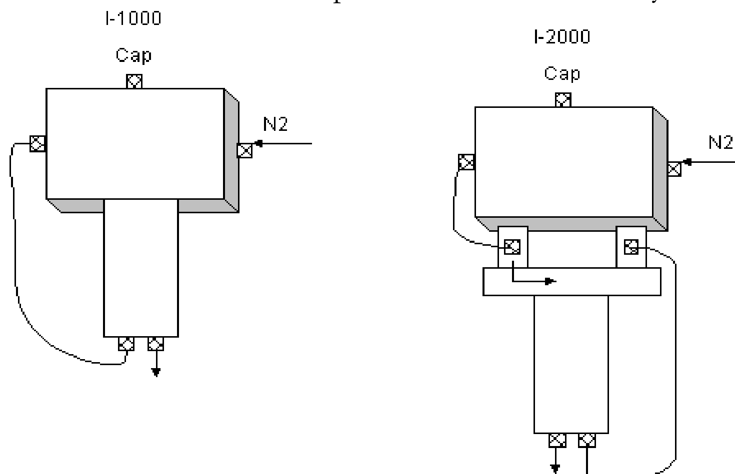


Figure 6.1 Nitrogen Purge Flow Diagram

3. After the instrument has had sufficient time to purge and stabilize, you must perform instrument checkout. Open AutoQuant Pro© and ensure that the instrument is connected by selecting the **Connect** button in the upper left corner of the page.

4. Click on the **Parameters** button located in the top middle of the page or lower left side of the page and select "**Align Mode**." Ensure that "**32**"cm-1 resolution is selected and that "**both**" is selected for single beam and interferogram. Click **OK**.

5. Select the **Align** button at the top left corner of the page.

6. The interferogram and single beam will appear on the screen. To see finer detail in the single beam, go back to the **Parameters** button and select up to 0.5 cm-1 resolution. This will slow down the update screen.

7. Click off on the "**Show Voltage Values.**" The voltage values represent laser signal voltage and are used for diagnostic purposes.

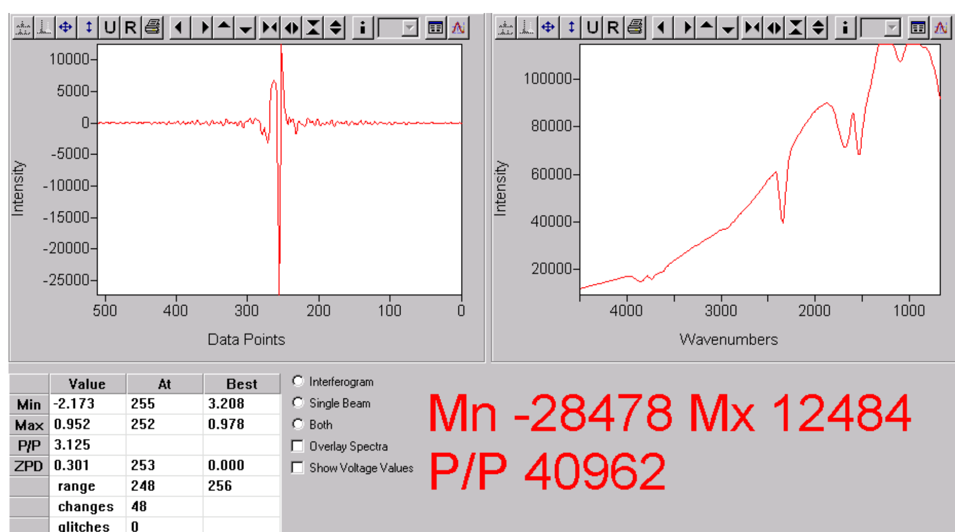


Figure 6.2 Align Display

The display shows an interferogram (ifg) and single beam (sb) spectrum as it is collected. The single beam is the overall black body energy curve for the system over all wavenumbers scanned. The interferogram is a time domain representation of the moving mirror. Use it to view the zero phase differential (ZPD) that indicates the point at which the moving and fixed mirrors are at a distance such that all wavelengths of radiation are in phase, and perfect optical constructive interference. The important numbers to review are the Max (Mx) and Min (Mn) values. The max number should be between 14,000 and 30,000 with a nitrogen-purged system. If the max number is between these limits, then click **Stop** and proceed to method development.

If the "**Max**" number exceeds 32,768 (clipping) or is below 14,000 (low throughput), adjust the detector Gain Setting. Note that the "**Min**" number may not be below –32,768. The fixed mirror alignment may also need adjustment, but doing this is not recommended unless you are familiar with the procedure (see below, "Fixed Mirror Alignment.")

The next important number is the "**ZPD Changes**" number and "**ZPD Glitch Count**." A few changes are OK, especially when the instrument is warming up or MCT detector has just been cooled off with liquid nitrogen. If either number starts to count up rapidly, then the system is in need of repair or adjustment. Please call **MIDAC customer support (949-660-8558** in the USA)

Gain Setting Adjustment
To adjust the gain setting, perform the following:

Open the top of the instrument with the 10 hex-key bolts. If you have an MCT detector, then also remove the 5/8-inch nut on the detector fill tube and slowly pull the fill tube up and out of the detector. The internal gain adjust board is located on the detector preamp and adjacent to the cylindrical detector (MCT) or card (DTGS).

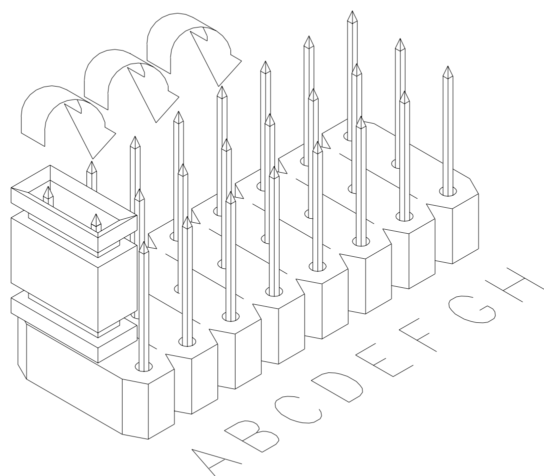


Figure 6.3 Adjust the Jumper Settings

Adjust the jumper setting to change the max level. Set around 25,000. You can have multiple jumpers in ON position. By adding more resistors in parallel you will attenuate the detector signal. Jumper A has most attenuation, Jumper H has lowest (highest GAIN). It is recommended that only up to a series of three jumpers be used to obtain a 14,000 to 30,000 Max number.

For more experienced users, a collected interferogram can be transposed to a single beam spectra down to 0 cm-1 to observe if the MCT detector is being operated "Too hot." If an MCT detector is operated in this configuration, it can result in non-linearity problems when target species are being measured, as well as negative absorbance peaks, or anomalies in the absorbance spectrum. Set the **Parameters** and then **Scanning** to "**save region from**" 0 to 4500 cm-1. The single beam spectrum will be displayed in the open window. Examine the single beam arbitrary y-value around 400 cm-1. The energy with KBr or MCT optics should eliminate all energy (close to zero y value) below this region. If it does not indicate very low energy, or if it slopes upward, too many photons may be hitting the detector. In this

situation, we recommend that a screen be used in front of the detector to cut down on the photons striking the detector. This is not necessary if you are producing your own reference spectra (for more details on this, contact MIDAC applications department **(919-522-2032 or 919-608-0954)**

Fixed Mirror Alignment
(**Note:** Perform only if familiar with procedure)

The fixed mirror alignment adjusts the rotation of the fixed mirror to optimize throughput. This alignment need not be performed routinely. This procedure should only be performed after rough shipping or damage to the FTIR, or as part of an annual service.

The "**Max**" number is an arbitrary relative measure of infrared throughput and is related to the number of bits in the ADC. The value can be changed electronically or by physical attenuation. Adjust the hex keys and watch peak height. *Note that very small movements result in very dramatic changes in the interferogram. Do not exceed 32,768 or –32,768* .

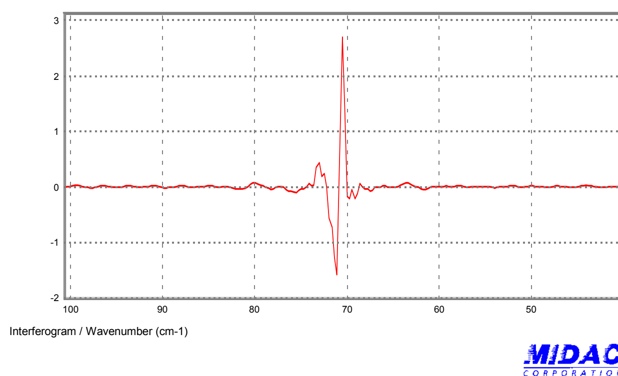


Figure 6-4 Interferogram Peak Height

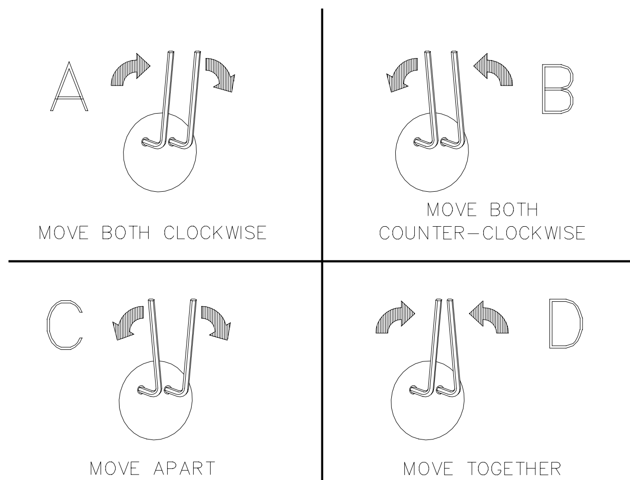


Figure 6.5 Fixed Mirror Alignment

Note You should allow for a minimum of one half-hour for the instrument to stabilize after making a fixed mirror adjustment.

Once you are satisfied that the FTIR is functioning properly, click on "**Stop"** in Align Mode. We are now ready to determine the optical pathlength of the cell, if desired.

Parameter Set-up and Pathlength Determination

1. Click on "**Method"** tab at top left corner of screen.

2. Click on "**Parameters**."

3. Click on "**Scanning**." Set up number of sample scans.

Note: Increasing the number of scans will result in a better signal-to-noise ratio. Signal to noise does not improve linearly however with increasing number of scans. Signal to noise is directly proportional to the square root of the time spent scanning, so that increasing the scans from 32 to 64 does not result in doubling the signal to noise ratio, but increases it by a factor of 1.414. This is a general principle, so that doubling the time spent scanning always results in improvement of signal to noise by a factor of the square root of 2. It is apparent from this consideration that this approach to maximizing the signal to noise ratio is subject to the law of diminishing returns, and that it quickly becomes impractical to seek further improvements after around 1028 scans. It should also be noted that though the signal to noise ratio is proportional to the square root of the time spent scanning, after 1/f noise (characteristic of the electronics used) is at a sufficiently low level the time spent scanning may be substituted for the number of scans. The scan speed of the MIDAC is sufficient to overcome the 1/f noise. The effects of resolution on the signal to noise ratio are discussed in Chapter 1.

4. Choose scanning **interval** for continuous ("as fast as possible"), or add a delay between scans.

5. Choose **number of background scans**. The number of background scans should be equal to or greater than the number of sample scans. It is preferable to subtract out a background single beam with less noise than the sample single beam.

6. Choose when to have "new background prompt" appear.

Note It is up to the user to determine the appropriate interval at which to collect a new background scan. You should flush the system with nitrogen before collecting a new background, unless it is desirable to have the background contain compounds at appropriate levels that you want subtracted out of the sample spectrum. New backgrounds should be collected when you can see: 1. a sloping baseline, 2. a rise or fall in some portion of the baseline, or 3. humps in the baseline that may be present from ice bands associated with some liquid nitrogen-cooled detectors that have lost some of their Dewar vacuum over time.

7. Choose resolution and "save region from."

Note Typical MCT regions with zinc selenide (ZnSe) windows will produce good data from 650 to 4500 cm-1. KBr windows and beamsplitter can go down to 400 cm-1. InSb and InAs detectors with CaF2 windows can typically measure from 2000 to 7000 cm-1.

8. Choose **apodization function**. Default is Triangle.

Note Apodization default is triangle, although many people use medium Beers Norton. Boxcar is essentially no apodization. The MIDAC library has been apodized to triangle.

9. Choose **phase correction**. Default is Mertz.

10. Choose **gain setting**. Default is 1.

Note The gain setting will electronically increase the signal obtained from the detector. It does not improve signal-to-noise ratio because it amplifies both signal and noise. However, it can be used for very small signals down in the baseline so that the software is able to quantify better. Linearity issues can occur with an auto gain. It is still important to not exceed +-32,768 in the align mode. This is called "clipping."

11. Click "**Method**" under **Parameters**.

12. Choose **Linearity**: Default is non-linear.

Note Linear mode will only calibrate the method with a straight line from (0,0) to the reference spectrum ppm-m concentration labeled as "primary." To select the primary spectrum, double click on the column marked "primary" at the same row as the spectrum wanted as the primary. Many compounds measured over large concentration intervals or orders of magnitude will be non-linear in nature. MIDAC recommends using multiple reference spectra that bracket the expected concentrations of your target compounds with a non-linear method. The software will then accurately fit the unknown to the calibration curve. Having only one reference spectrum in a non-linear method produces the same result as using a linear method. The software will then only fit a curve from (0,0) to the reference spectrum optical density.

13. Choose **baseline**. Default is Linear, Embedded Baseline Correction (Single Baseline).

Note The baseline that has been tested and is easily defensible is a "single baseline embedded." The software will then automatically baseline-correct the reference spectra appropriately prior to performing CLS analysis. The other baseline options do have benefits for special applications. It is up to the user to determine if any other baseline correction is warranted. Baseline correction of reference spectra manually may be needed if other options are chosen.

14. Choose if you want "on the fly" linear calibration. Default is "unchecked."

15. Choose **Exclusion Criterion**. Default is 2500.

Note Exclusion Criterion is used for peak detection. It can be made more sensitive by increasing the number. It is not recommended to change from 2500.

16. Choose any **Pre-Processing,** if needed. Default is none.

Note Pre-processing is used for special applications. Taking a first derivative is used to "straighten" out curving baselines for very small absorbance peaks or using synthetic backgrounds. The Hydroquant method is used specifically for measuring extremely small (ppbv) concentrations of

moisture in a sample matrix. This is only used specifically for this application. See Hydroquant section of manual.

17. Choose **Interpolation algorithm**. Default is Piecewise (PWCI).

Note The interpolation algorithm uses two accepted procedures for fitting unknown spectra to a calibration curve that falls between two reference spectra. The PWCI is best for complex multiple compound matrices. The PWAI can be used for single component matrix evaluation.

18. Click on **Storage,** and choose options.

Note Under Storage, it is important to note that if the data is to be legally defensible, the sample and background interferograms must be saved. This is the raw data and is not easily manipulated. All other spectral types can be generated from the interferograms.

SPC or ABS extensions are interchangeable in AutoQuant Pro©. If using other spectral manipulation packages, .SPC is recommended.

19. Click on "**Memo Fields**."

Note Clicking on the arrow pointing to the right at the end of the Memo field will prompt the user to enter abbreviations. AutoQuant Pro© must be able to recognize these abbreviations in order to report the data accurately. Enter them in place of the "$X." These abbreviations will attach to each sample spectrum collected.

20. Click on "**Paths**." Enter appropriate directories for fields. Choose any back-up directory or storage device.

21. Click on **Auto-Resume**. You must run the set-up procedure before you can use this feature. If the computer looses power, the software will automatically start-up and continue to collect spectra if chosen.

22. Click on **Analog Out,** and choose appropriate device if sending signal out to a control room or DAS.

23. Click on "**Cells**." Add in the appropriate pathlength. If you do not know yet, then fill this in after you've determined pathlength. Filling this in is important in order to produce accurate concentrations.

Note If your instrument is set up to read in Temp and Pressure readings through the RS-232 port or the fiber optic card readout, you do not have to use the default Temperature and Pressure option. The software will automatically correct the sample spectrum concentrations for temperature and pressure according to P2/P1 and T1/T2 from the default or directly from the temp and press controller. (See T&P setup section in Chapter 4)

24. Click on "**Gas Flow**," and enter in a flow rate other than "1" if you are going to report numbers as a mass per time (lb/hr).

25. Click on "**Infrared Throughput,**" and check the box if you want the software to alarm visually and audibly when the energy throughput falls below these predetermined levels. Low energy can be caused by a drop in the liquid nitrogen in a cooled detector, dirty optics, fogged beamsplitter, misalignment, or very high concentrations of compounds in the sample cell. Default for this box is unchecked.

26. Click on"**Number**s," and then enter user preferences.

27. Click on "**Test**," and enter user preferences.

28. Click on "**OK**"

29. Click on the "**New**" tab on the top right toolbar to open a new method. Enter the appropriate fields and click on **Create.**

Note The default directory for new methods is under the AQPro\Methods\ directory. Most users will enter the same subdirectory and filename for the new method to avoid confusion. The method description enables the user to distinguish this method from others. Anything can be placed into the description field but no DOS characters should be placed into the subdirectory and filename. DOS characters include .,:;/ %\

30. Click the "**Compound**" tab on the top left toolbar. Enter the appropriate compound. For this exercise, type in "ethylene." Add the molecular weight if reporting mass emissions instead of concentrations.

Note You should already have an ethylene reference spectrum for your pathlength determination. If you do not, use the MIDAC Reference Spectrum "Ety_H19A ethylene, I2001-V, 121C, 1 atm N2, 207.6 ppm-m Gain=001" available from MIDAC or the Standards Library. If you prefer the EPA spectra, then the 5CS0124B, 225 ppm-m spectrum is good for a 20 ppm standard with a 10M cell.

Note For ethylene (or any other target compound), it is best to use a reference spectrum that was produced at the same temperature as the sample cell temperature you will be using to analyze samples. AutoQuant Pro© will adjust for Temperature according to the factor T2/T1 absolute, but will not take into account subtle effects from "peak broadening" or "hot bands" that are variably dependent on the compound, but can add error into your analytical confidence. The MIDAC Library does contain other spectra at other temperatures for ethylene.

Note The EPA library spectra and MIDAC's library spectra are apodized with "Triangle." They should not be used with any other apodization parameter in a method. All sample spectra should be collected with the same apodization as the reference spectra.

31. Click on the "**Spectrum**" tab on the top left toolbar and choose the appropriate directory that your reference spectra have been placed. For this exercise, choose the Ety_5A ethylene, I2001-V, 25C, 1 atm N2, 206.6 ppm-m Gain=001 available from the MIDAC Standards Library. Ensure that the spectrum parameters are pulled into the software correctly and then choose "**OK**."

32. Click on the "**Region**" button, then click on "**<u>N</u>ew Region.**"

33. Input **870 to 1040** in the appropriate space. Then click on "**Done**."

34. Click on the "**Calibrate**" button.

Note The calibration time will depend on the number of compounds and number of reference spectra per compound. The following are timing comparisons with AutoQuant Pro©. The timings were taken on a 1.2Ghz system with 1GB of memory and using a fast NTFS-formatted 75GB disk. The method has 7 compounds with 7, 3, 4, 2, 4, 2, 4 standards in those compounds for 37,632 sub-methods 7*(7*3*4*2*4*2*4):

Prediction times are total times for all 56 absorbance samples done in batch mode:
AQPro calibration prediction on-demand calibration: 30sec2min5sec
full cal: 58sec 1min 48sec

35. Click on the "**Analyze**" tab at the top left toolbar.

36. Click on "**Continuous**" on the top left toolbar. You can now change the base directory, subdirectory, base name, and memo field as you see fit. We recommend that you use the "collect" folder as the base directory.

Note For this exercise, enter "ethylenePL" into the subdirectory position, leave the base filename as "C" (this is the prefix for all generated files-for example, C0001,C0002,etc.). In the memo field, enter $R, $S, $T, $P, $L. The software will then automatically record resolution, number of scans, temperature, pressure, and pathlength. This information will be tagged to the spectrum and interferogram files. Do not click on "OK" yet.

37. You must now ensure that the system (FTIR box and Cell) have been properly purged with nitrogen for the proper period of time. When you've provided enough time for proper purging of the system, ensure that the purge flow has been cut back to between 0.5 to 2.0 lpm and click on the "**Collect**" button

Note If the purge flow rate through the FTIR Electronics box and/or sample cell is too great, then you will have greater noise in the spectra from turbulence effects. Maximum flow rate through the box is 2.0 lpm. The sample cell flow rate depends upon cell type. It is recommended that less than 6.0 lpm be used as a sample cell flow rate for a 10 m cell and 1 lpm for a 3 m cell.

38. You must now collect a new background or select an existing one. Under the "**Continuous**" tab, click on the "**background**" tab and choose "collect from instrument."

39. The FTIR will then start to count up the number of scans you selected and then show a "reference single beam spectrum" .rsb.

40. You must inspect the single beam spectrum visually to determine if the quality is good. The spectrum should look somewhat like below:

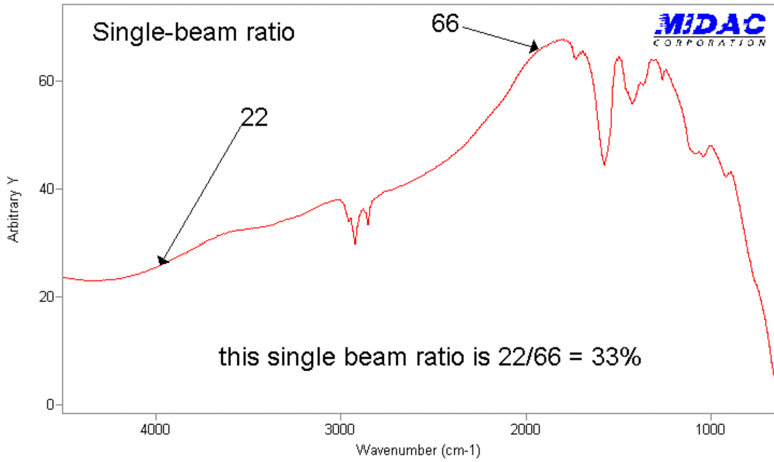


Figure 6.6 Single-beam Spectrum Sample 1

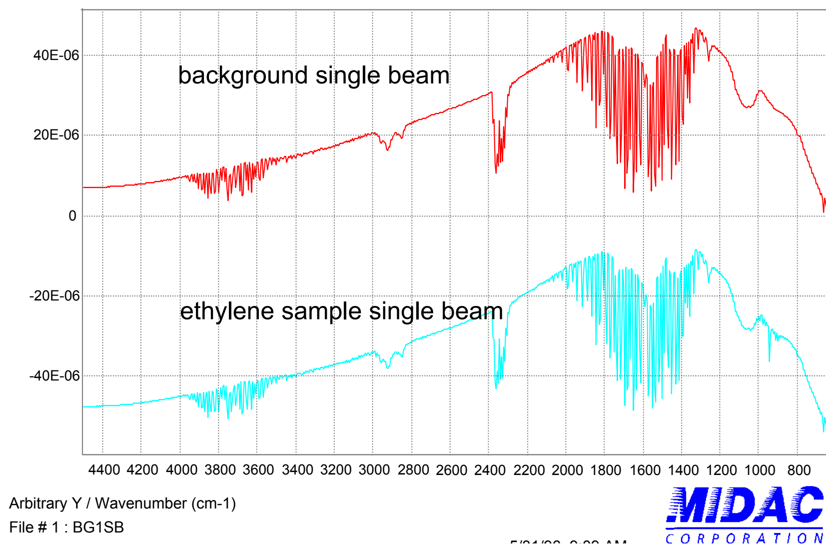


Figure 6.7 Single-beam Spectrum Sample 2

Note The single beam spectrum in **Figure 6.1** shows a proper energy ratio between the high and low wave numbers and is indicative of a properly functioning instrument. The single beam in **Figure 6.2** shows a properly functioning instrument but also shows a not completely purged system. The wave numbers at approximately 1400-2000 and 3500-4000 are indicative of moisture (H_2O) molecules in the system. It is very difficult to remove all the water, and some water is okay. The wave numbers at 2300 to 2400 are CO_2 and can be purged out of the system. A very small amount of CO_2 is okay if you are not measuring CO_2. When measuring CO_2 it is imperative that it be completely removed from the background or the software will subtract that CO_2 amount from your sample and bias the CO_2 concentration in your sample low. This is true of anything in the single beam background spectrum.

41. If you are not satisfied with the single beam, click on the "**Collect from Instrument**" button again.

42. When you are satisfied, click on "**OK**" and the software will use the last collected reference single beam to collect the data, unless another background is recorded or selected by the user.

43. You are now ready to determine the Pathlength using ethylene.

44. Disconnect the nitrogen line to the cell only.

45. Flow a known concentration of ethylene through the cell at 1-2 lpm at the cell temperature that will be used for sampling. Do not exceed 30 PSI on cell. 10 PSI is adequate on the regulator. Flow ethylene through the cell for an appropriate amount of time to get at least 5 cell turnovers (approximately 0.2 L volume in 3M cell; 2 L Volume in 10M cell) (It is important to not flow sample through your cell too quickly as turbulence effects will create added noise in the spectrum. Two lpm is maximum for a 3, 4 meter cell, 15 lpm for a 10 meter cell, and less than 4 lpm for a 20 meter cell.)

46. (Optional) To determine pathlength, go back to **Parameters** and choose "**Cells**." Enter the concentration of the gas cylinder in ppm in the box for cell pathlength. The reported concentration generated by AutoQuant Pro© will be the optical pathlength of the cell. After you get the correct pathlength, change the cell's pathlength number to the newly acquired optical pathlength before making measurements.

47. Check entry fields and click on OK under the "**Continuous" tab**. The analyzer will start up and begin counting to the specified scan numbers.

Note: To collect a single spectrum, click on the **"Single Measurement"** tab; or if you want only to collect interferograms without any software conversion to single beams or absorbance spectra, click on the "**High Speed"** tab. The "**Automatic**" collection tab is used only for valve control (See section on Valve Control in chapter 5).

20 ppm in N2 balance is recommended for a 10m cell.
40-50 ppm in N2 balance is recommended for a 3m cell.
2000 ppm in N2 balance is recommended for a 10cm cell.
20,000 ppm in N2 balance is recommended for a 1 cm cell.

Note: The bottom right side of the screen will show the absorbance spectrum while the bottom left side will show the pathlength being reported as the concentration. Allow the pathlength number to stabilize and when the graph shows the ethylene pathlength as stable, record the cell pathlength. The ethylene spectrum should look something like the spectrum in **Figure 6.7.**

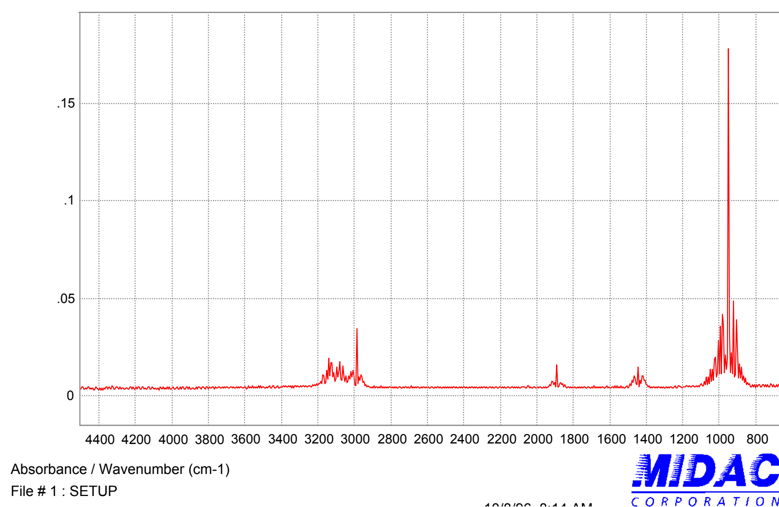


Figure 6- 7

48. When the pathlength has reached a steady-state condition, as evidenced by the graph, absorbance spectrum, and reported concentration, click on the **Stop** button on the toolbar. Enter the new pathlength value only under the Parameters "**Cells**" section under "**Pathlength**."

49. To change the graph options and/or background colors, select the buttons in the upper right corner of the "Analyze" page. Spectral window options can be selected by right-mouse clicking on the spectrum view window on the lower right corner of the "Analyze" page.

50. To view results, click on the "**Results**" tab.

51. You are now ready to make your own reference spectrum or use library spectra for your Method. If using library spectra, repeat the procedure used for making the ethylene pathlength method.

Making Reference Spectra

1. Reconnect the nitrogen gas stream to the gas cell. Also keep the FTIR box purging (approximately 0.5-2.0 lpm).

2. Set your parameters under the "**Parameter**" field. Reference spectra should be collected with a large number of scans for quality spectra (i.e., 64 or 128). As discussed previously, the number of scans will determine the signal-to-noise (s/n) and quality of the spectrum. It is up to the user to determine the data quality objectives of the analysis. Some users will use 32 for DTGS and 64 for MCT. Others will use 128 or 256.

3. Click on the "**Single**" button on the left side toolbar.

4. Enter "library" under the "**Subdirectory**" field.

5. Enter appropriate data in the fields. Do not use DOS characters in the subdirectory name. Enter a distinguishable name for the file in the "Base Name For Data Files" field, for example, "Ethylene20ppm."

6. Click on the "**background"** tab in the same window. Click on "**collect from instrument**." When satisfied with the background, click on OK.

7. The software will collect a spectrum of the compound and save it under the "library" folder you created or under any folder you choose.

8. You can add any collected spectrum to any folder including the library simply by clicking on the "**Add to Library**" button on the upper right toolbar and selecting a folder to place the spectrum into.

Note It is recommended that you collect more than one spectrum of the target library spectrum to determine if steady-state conditions exist. You can collect multiple spectra and then review them for stability. Multiple spectra can be averaged later into an averaged spectra through another spectral manipulation package.

9. When you have completed your library spectra, you are ready to generate a Method.

Adding Spectra to a Method

1. Either "**Open**" an existing Method or click on the "**New**" button on the top right toolbar. AutoQuant3 methods can be imported by clicking on the "**File**" menu on the top toolbar and selecting "**Import AQ3 method**."

2. Check your "**Parameters**" menu to make sure you've chosen the correct parameters for your method.

3. Enter a subdirectory, filename, and Method description in the appropriate fields.

4. Click on "**Create**."

5. Click on "**Compound"** and add Name and Description (optional). Add Molecular Weight only if you want numbers reported in Mass Emissions (lb/hr). A flow rate will then be needed.

6. Click on "**Spectrum**" and browse to the appropriate folder by clicking on one of the buttons associated with the "look in" field.

7. Double click on the absorbance file. The file must have an .abs or .spc extension.

8. Click on "**Region**" on the top left toolbar.

9. Click on '**New region**" and either enter the region numerically or click on the radial "**New Range**" button and drag the mouse by holding down the left-mouse key and then releasing to select your region for quantification. You may zoom in or expand any part of the spectrum for finer detail by using the appropriate keys.

10. Click OK and the spectrum selected will be used as the new reference spectrum for that compound.

11. Continue this procedure until you've placed all your target compounds and any interferences into the method.

12. Click on "**Calibrate**." The method is completed. You will want to collect new backgrounds as needed throughout your analysis of samples.

It is important to collect backgrounds periodically as this will affect the quality of you data and hence accuracy and precision. The software can handle gently sloping baselines and offset baselines very well. However, when the baseline curves up or down in both directions, some error may be introduced. By collecting backgrounds periodically, you eliminate the baseline anomalies caused by temperature differences, changes in LN2 levels, deposits on optics, ice formation, etc.

Chapter 7
Developing a Method

In the preceding chapter we covered the basic details and mechanics of creating an AutoQuant Pro© method. In this chapter we will discuss the general philosophy of method development. FTIR is a uniquely powerful analysis technique, using fundamental physical properties of the analyte molecules to form a complete picture of the components in a matrix in a single measurement. The absorbance spectra gained from the mid infra-red region of the electromagnetic spectrum contain information of both a qualitative and quantitative nature, allowing identification of components and quantification in a single step. Getting the most from such a large volume of information of course involves very careful interpretation, and it is the purpose of this chapter to provide general guidelines for successful analysis of infrared spectra using AutoQuant Pro©. Remember that unless the method is optimized erroneous results may be reported. However, two different methods can easily achieve the same results for each target compound. This chapter focuses on achieving accuracy in the method in a logical and defensible manner.

Consider a matrix composed of a mixture of components. The spectrum from the matrix will contain absorbance bands from all infrared active components (those whose modes of vibration cause a change in dipole moment). Such a spectrum is shown in Figure 7.1.

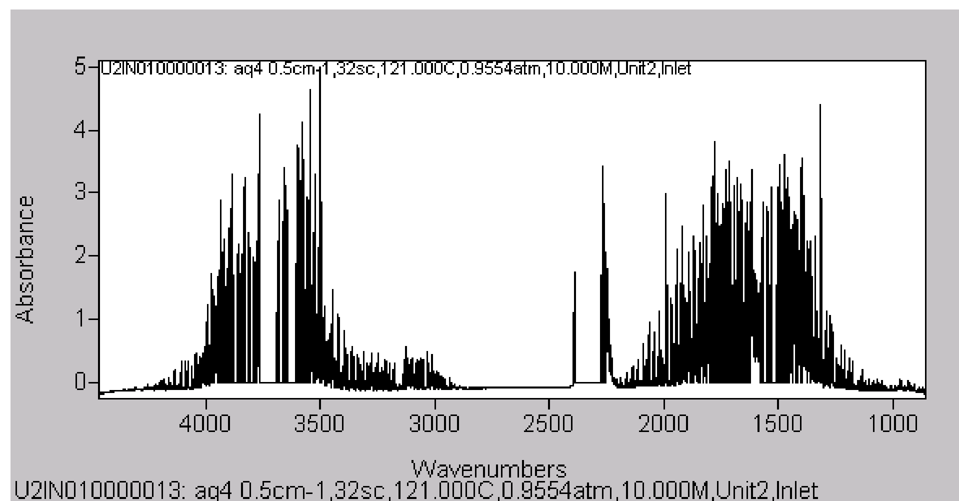


Figure 7.1 Saturated Spectrum of a Gas Mixture

Immediately obvious on inspection of the spectrum in Figure 7.1 are the two large absorbance bands between 4300cm^{-1} - 2900cm^{-1} and 2200cm^{-1} – 1000cm^{-1}. These bands are due to water, and unless dealt with water is the principle obstacle to successful data interpretation as it interferes over such a wide region. In fact, this spectrum is an extreme case, with water and carbon dioxide present at high levels. Levels high enough to completely attenuate the photons in these regions making none available for the detector. Looking at these water bands in detail, we notice that some regions of the bands appear perfectly flat, as shown in Figure 7.2.

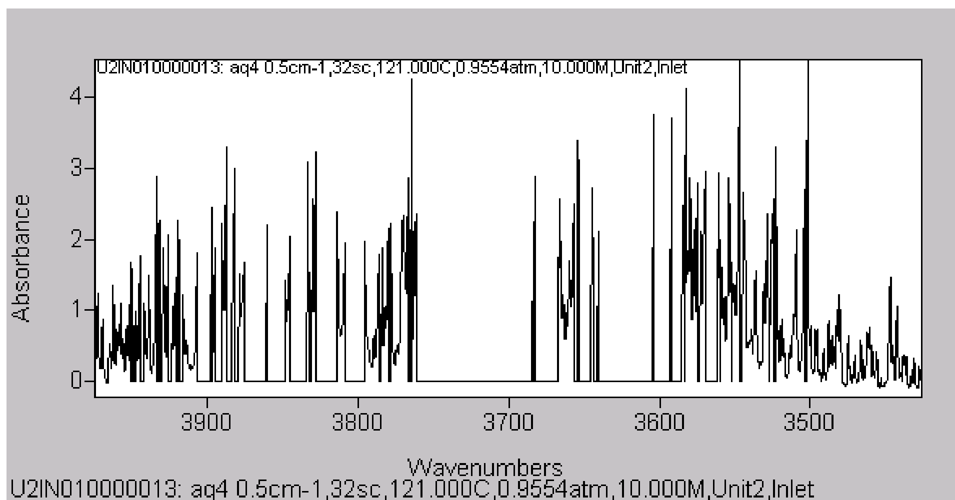


Figure 7.2 Saturated Water Bands

At first glance it may seem that this is good news, the absorbance recorded is zero, therefore the water does not absorb at this frequency. Unfortunately the opposite is true, these flat regions are said to be **Saturated**. Note that the flat regions may be at zero or at the highest peak heights in the region. This is due to detector non-linearity. You may see the saturation either way. Comparing the water band in Figure 7.2 to the band in Figure 7.3 we find that the flat regions in the first figure correspond to regions of highest absorbance.

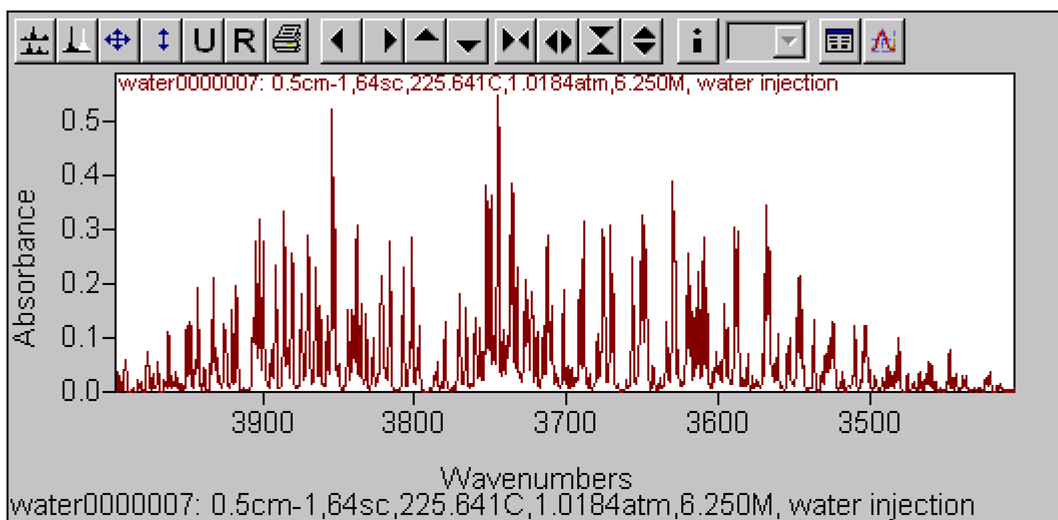


Figure 7.3 Unsaturated Water Spectrum

To understand why the saturated regions are displayed as zero we must review some FTIR theory. A Fourier transform infrared (FTIR) spectrometer records **Interferograms** as raw data. These interferograms consist of a plot of detector response against time and thus in the time domain. Although a full discussion of interferometry is beyond the scope of this document, an example of an interferogram is shown in Figure 7.4.

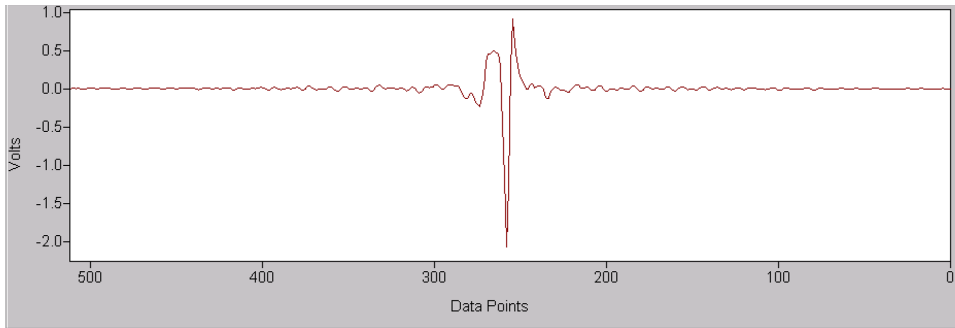


Figure 7.4 Interferogram

The largest peak (ZPD) corresponds to the point at which interference in the interferometer is completely constructive. A fast Fourier transform (FFT) is applied to the interferogram, the output of which is a single beam spectrum (see **A Crash Course in FTIR** in Chapter 1), examples of which are shown in Figures 6.6 and 6.7. The next step is to transform a single beam spectrum into a transmission spectrum. This is achieved by ratioing a single beam sample spectrum with a single beam background spectrum. An example of a transmission spectrum is shown in Figure 7.5.

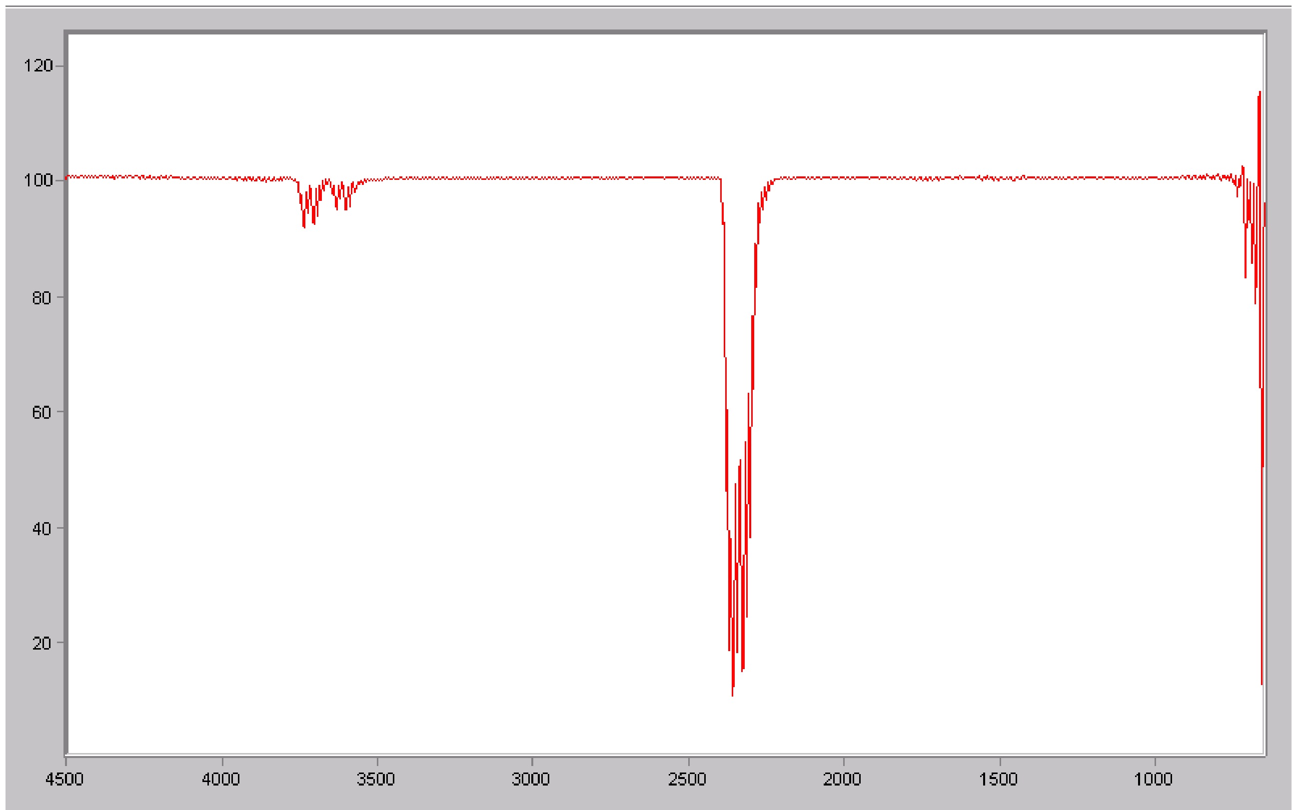


Figure 7.5 Unsaturated Transmission Spectrum

The transmission spectrum shown represents carbon dioxide at 2500 ppm-m. The y-axis shows the percentage of radiation from the source reaching the detector, with wavenumbers on the x-axis. A transmission spectrum is related to component concentration logarithmically and not linearly. For this reason, transmission spectra do not feature heavily in AutoQuant Pro© (except for single beam quant (SBQ) see associated Chapter), although the software may be configured to examine these spectra. In

order to generate a spectrum with a linear relationship between band intensity and component concentration, the negative logarithm (base 10) of the transmission spectrum is taken to produce the absorbance spectrum. In a saturated region, the transmission will be zero and any logarithmic relationship fails. When this failure occurs, the software will set the absorbance values to zero (if the single beam values in those regions are negative due to some non-linearity of the detector as common in MCT detectors). It is now clear that the parts of the water and CO_2 bands that show zero intensity are saturated, and cannot be used in any analysis. Even in such unfavorable circumstances as these, there are still many regions in the spectrum that we can use for analysis.

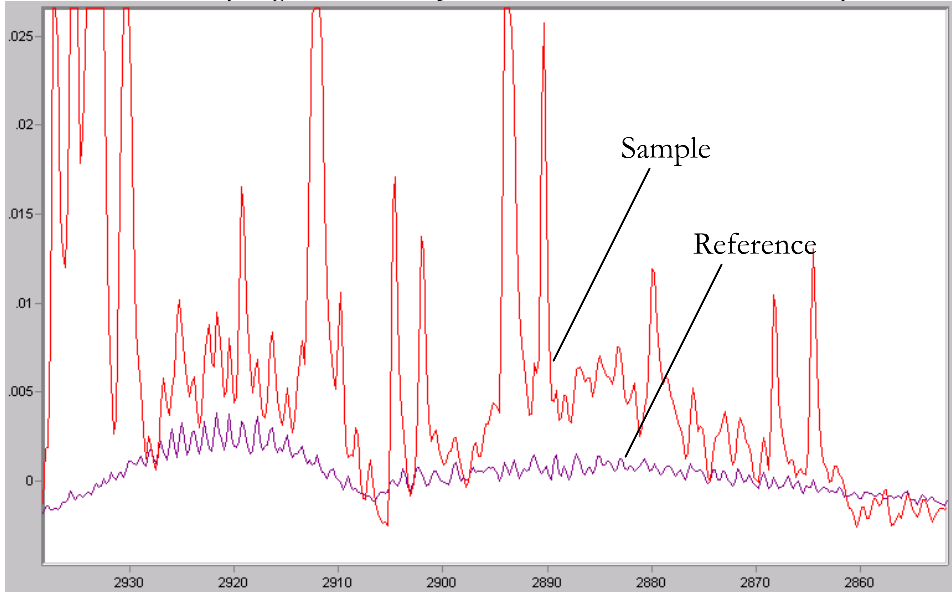


Figure 7.6 Nitrogen Dioxide and Water

In Figure 7.1 it is not immediately apparent that a significant amount of nitrogen dioxide (NO2) is present. Consider the region depicted in Figure 7.6. AutoQuant Pro© determined this region to represent a NO_2 concentration of 39 ppmv. This is consistent with the reference spectrum concentration of 30ppm. Figure 7.7 shows the contaminated spectrum in the previous figure after subtraction of water.

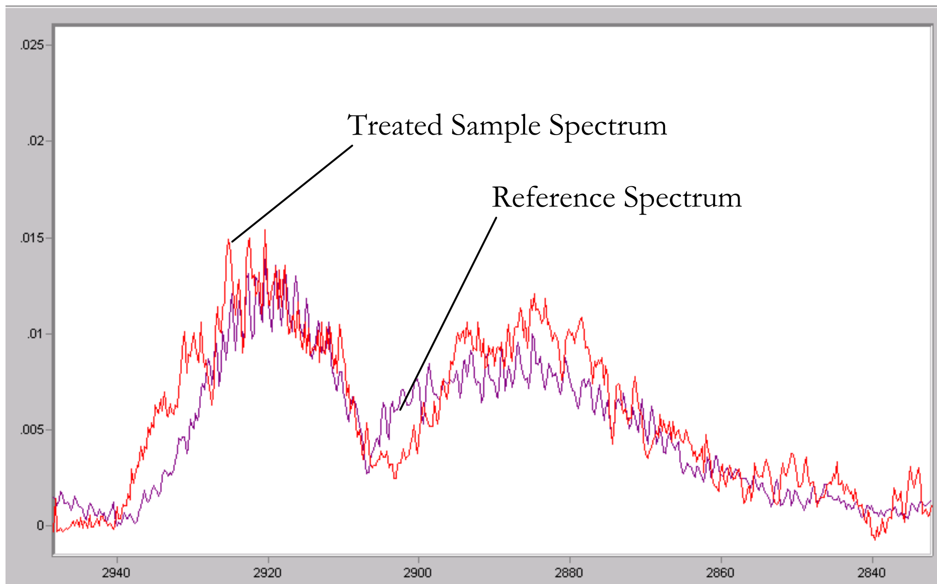


Figure 7.7 Sample Spectrum After Water Subtraction

While water interferes in this region, AutoQuant Pro© is able to correct for this interference so long as

a) The absorbance due to water is not saturated
b) Moisture spectra (or other interfering compound) are used in the method, with analysis regions overlapping those of the target compound. These water spectra should have absorbance bands of similar intensity to the sample water absorbance, and be recorded at the same temperature and pressure as the sample spectra.

This general principle is true of all interferences. While some iterations may be necessary to find the best combinations of reference spectra and analysis regions, analysis of even very complex spectra is possible. In order for the interfering band to be taken into account in the analysis, it is necessary to analyze for the interferent over the same region as the analyte. As has already been stated, this is not possible if the interfering band is saturated as the subtraction fails. A better solution in some cases would be to find bands in the spectrum which are unaffected by interference. Consider the ammonia bands in the same sample spectrum shown in Figure 7.8.

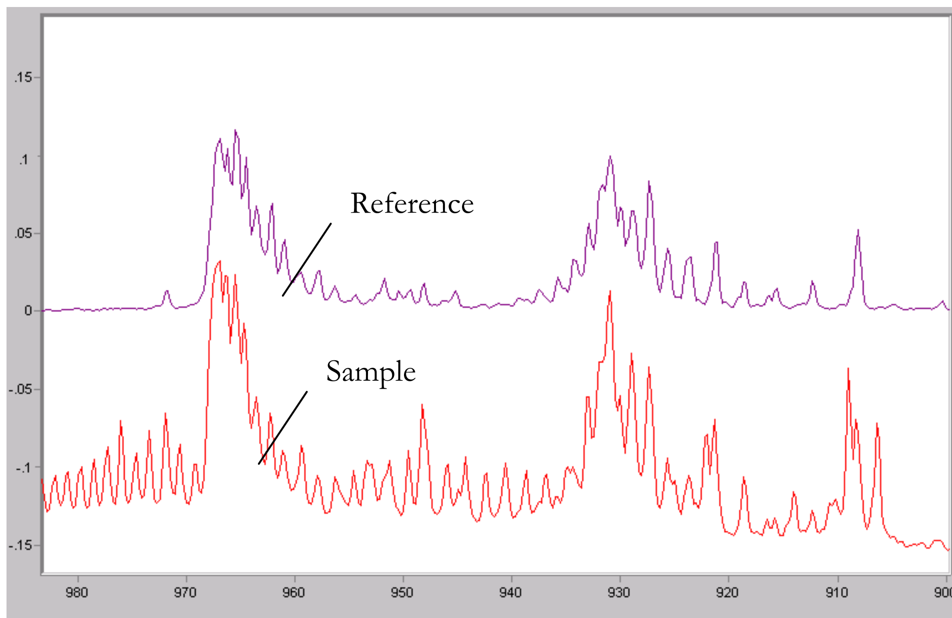


Figure 7.8 Ammonia Absorbance Bands

The ammonia bands illustrated are subject to minimal interference from water. AutoQuant Pro© determined this region to represent 27.4 ppmv, which appears accurate as the reference spectrum in Figure 7.8 represents 25 ppmv of ammonia.

Analysis for nitric oxide (NO) can prove especially challenging, as NO exhibits only one absorbance band in the mid infrared region, which is almost completely obscured by the water band at 2900cm^{-1} to 2200cm^{-1}. Even within this water band however there are very narrow windows through which we can measure NO. One of these regions is situated from 1901cm^{-1} to 1899cm^{-1}. Though narrow, this region

may be used to give good quantification of NO at single digit ppm levels and above as long as the same region is used for moisture for subtractive purposes.

The following is an exercise in the analysis of a complex matrix containing ammonia, nitric oxide, nitrous oxide, nitrogen dioxide, sulfur dioxide, hydrogen cyanide, carbonyl sulfide, carbon monoxide, carbon dioxide and water. This matrix is represented by the spectrum shown in Figure 7.9.

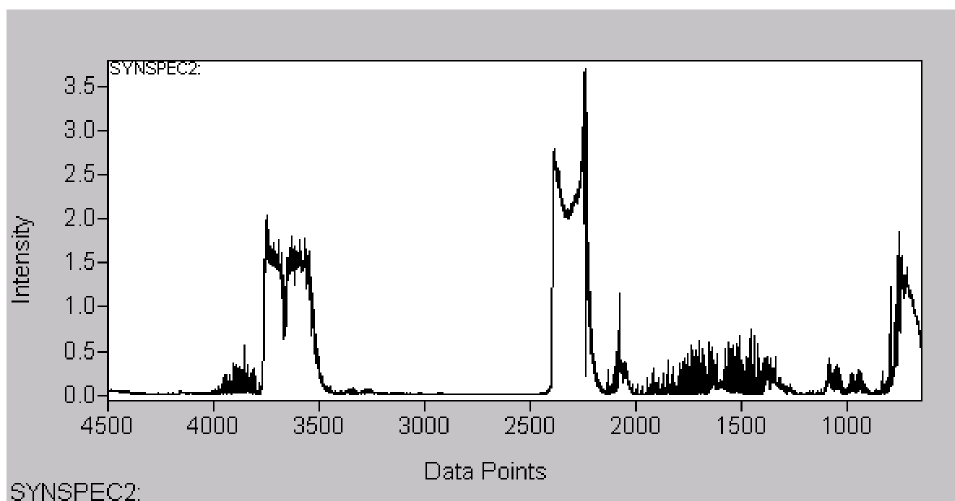


Figure 7.9 Sample Spectrum

The spectrum in Figure 7.9 contains saturated CO_2 bands together with high levels of water (see the positive saturated bands as compared to the zero saturated bands). This presents a challenge, particularly with respect to quantification of NO. How do we set about developing a method to analyze this spectrum? The first step is the recording of reference spectra (including the main interfering species carbon dioxide and water) according to the procedure set out in Chapter 6. These reference spectra should be recorded at the same temperature and pressure regime as samples are to be acquired under. In addition to this, reference spectra should be collected at concentrations that encompass the expected concentrations in the samples, so as to enable 'bracketing' of the unknown sample components concentrations. ****In order to maximize the accuracy of these reference spectra, it is necessary to remove absorbance bands of contamination, and to correct any baseline defects. Unless contaminating absorbance bands are removed in your reference spectra, your results will be biased low for those target compounds that are contaminants in the reference spectra of other target compounds.** ** This may be achieved using GRAMS. For example, take the NO spectrum, shown in Figure 7.10.

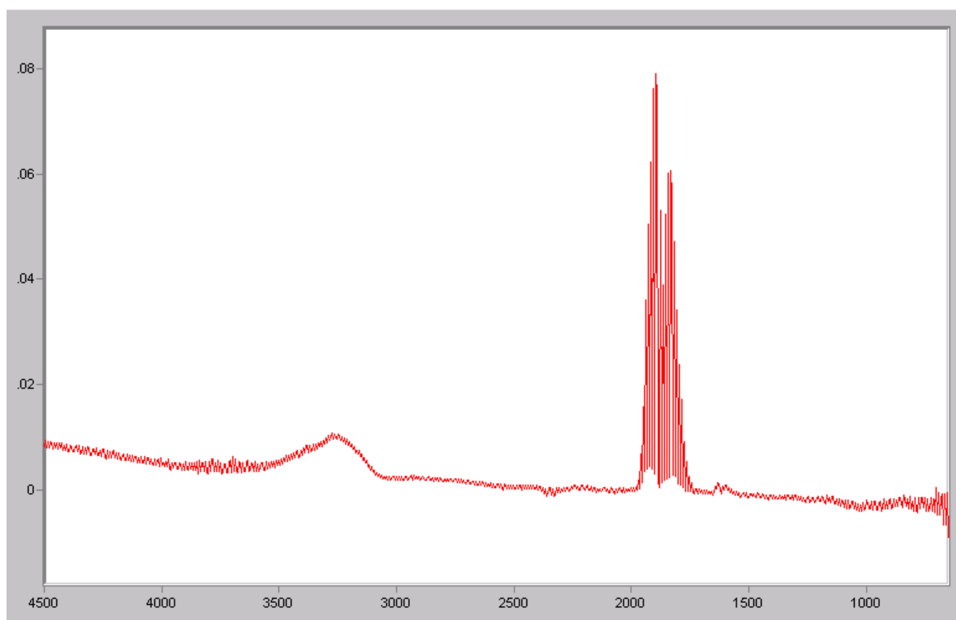


Figure 7.10 Nitric Oxide at 100ppm

The spectrum shown in Figure 7.10 represents nitric oxide at 100ppm. Also present in the spectrum is a large band at approximately 3300cm^{-1}. This band is due to ice forming on the liquid nitrogen cooled detector window after a long period of operation. This anomaly can be ratio'd out by taking a new background spectrum periodically. This is characteristic of a detector Dewar that has slowly lost vacuum over time and needs to be re-evacuated. Another less obvious impurity is the small nitrogen dioxide band centered at 1610cm^{-1}. While smaller, this band is potentially more damaging to an analysis as it could bias quantification of NO_2 to the low end. These impurities are removed in the following way:

1) On the GRAMS menu select ***Applications* – *Utilities*** - **Zap**
2) Right click in the lower pane to select zap regions. These regions may be clicked and dragged until the desired area(s) are covered, as illustrated in Figure 7.11.

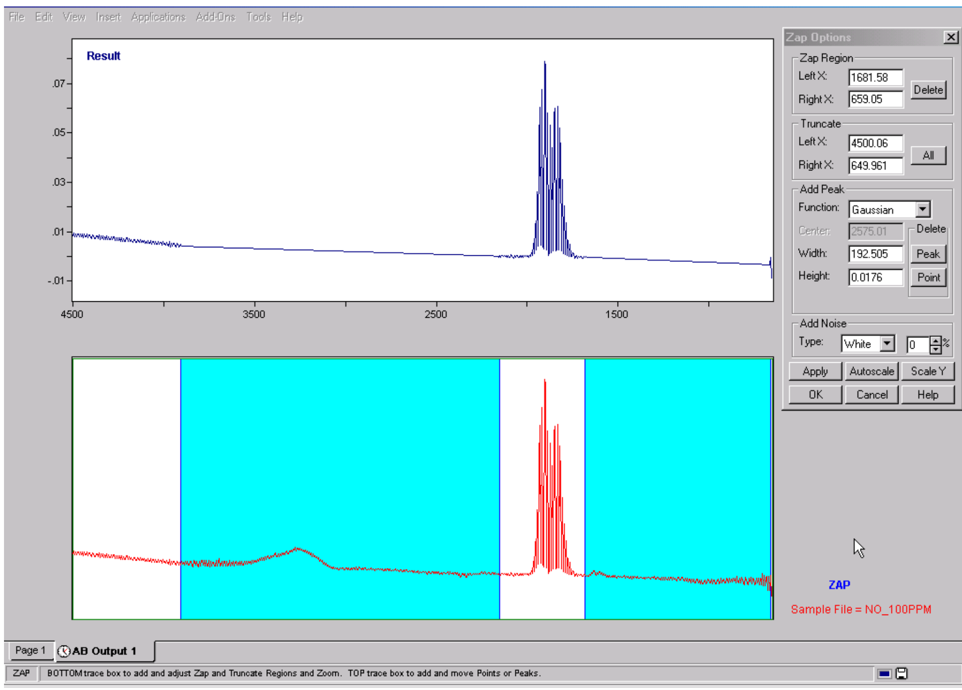


Figure 7.11 Zap Regions

3) Once the regions are selected click ***OK – Add new*** (it is vital to retain the original spectrum for future reference).
4) The regions selected are now smoothed. However, the baseline still requires correction.
5) From the menu select ***Applications – Baseline Correction***
6) Select the options ***Multi Point***, ***Force Points Onto Data*** and ***Level And Zero*** as shown in Figure 7.12.

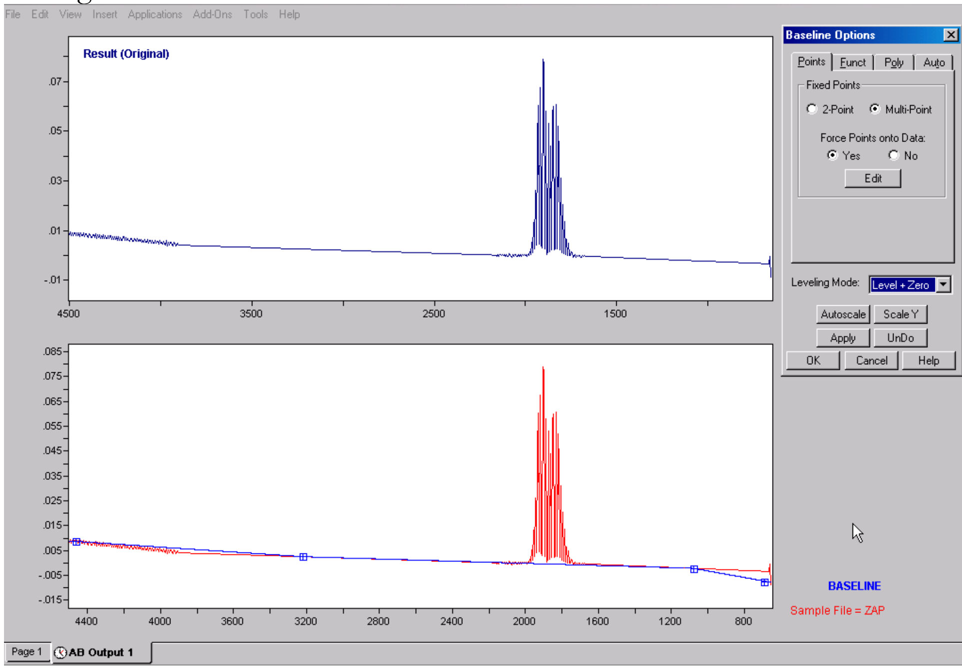


Figure 7.12 Baseline Correction

7) Click ***OK***, then ***Replace***
8) Save the corrected spectrum before closing GRAMS

Once all reference spectra are corrected they may be loaded into the method. We can now examine the reference spectra for analysis regions, using the ***View Spectra*** button. The spectra are shown in Figure 7.13.

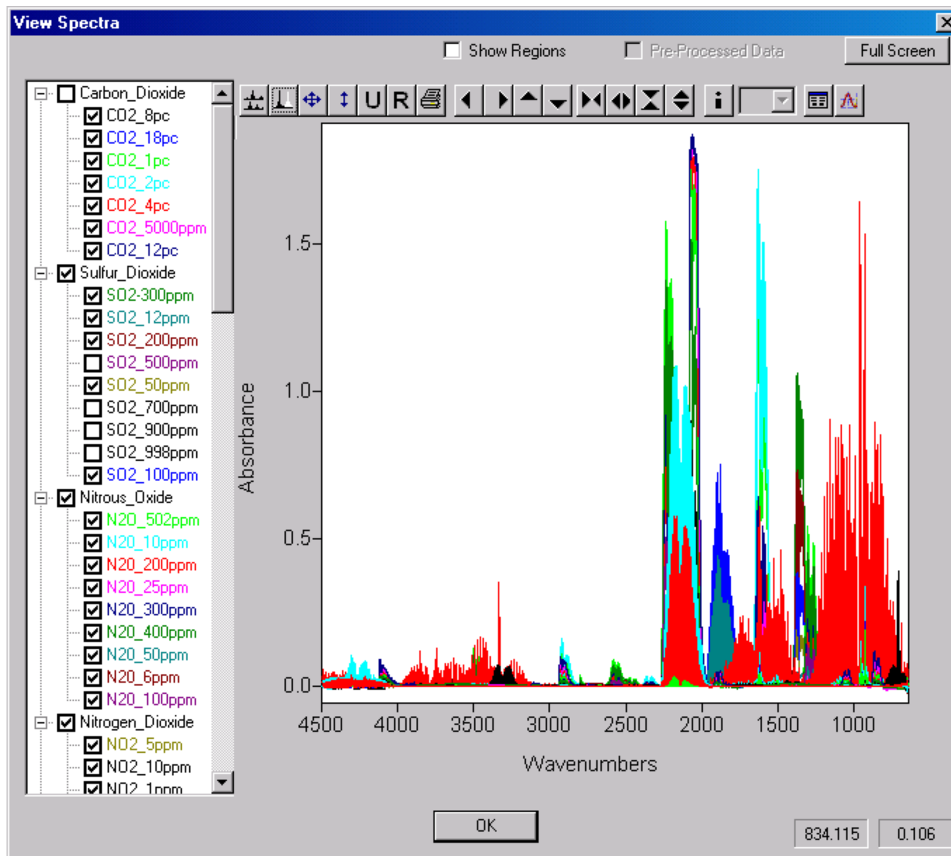


Figure 7.13 View Spectra Window

Using this tool we can zoom in on analyte absorbance bands and check for interfering species. Zooming in on the NO band at 1900cm^{-1} we see interferences from both water and COS, as shown in Figure 7.14.

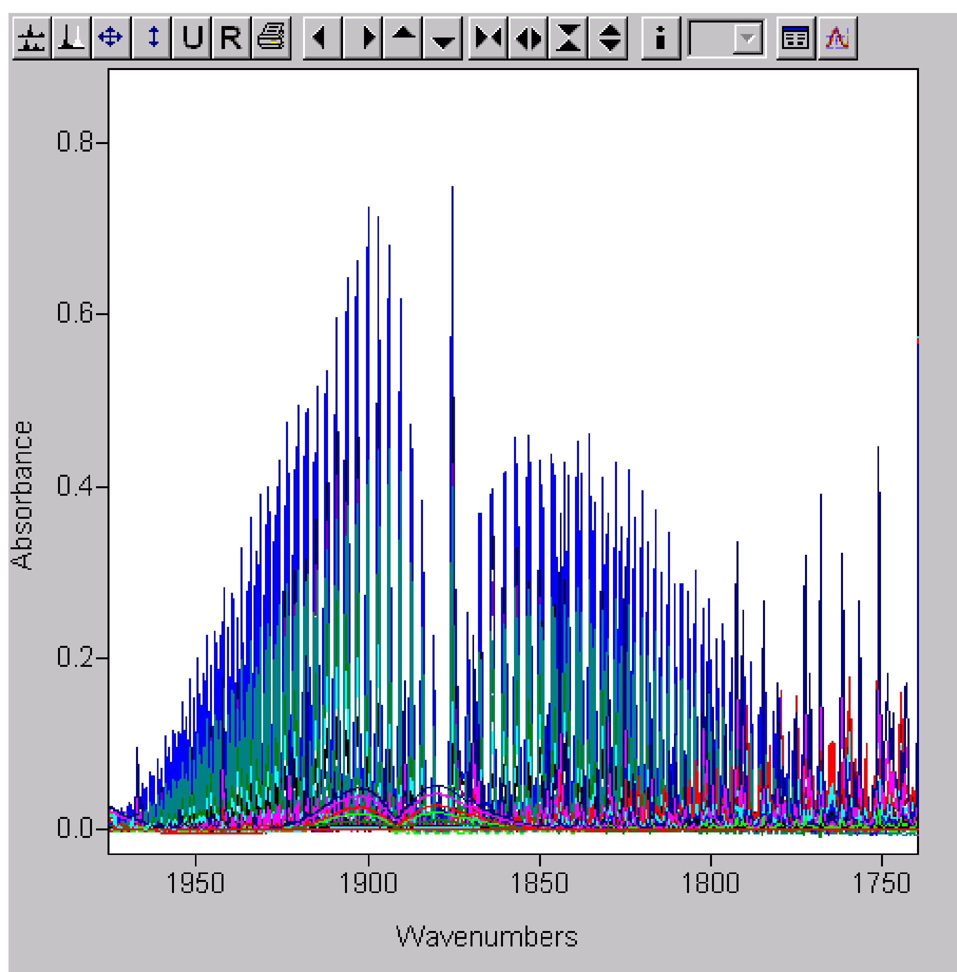


Figure 7.14 Nitric Oxide From Water And Carbonyl Sulfide

From the information in this view we can decide how to proceed. The absorbance bands of the interfering species are not saturated. In fact they are low enough (below 0.8 absorbance units) to behave linearly, in accordance with Beer's law. This means that we do not have to choose regions that avoid the water and COS, AutoQuant Pro© will be able to subtract the interferences as part of the analysis. The most difficult interferent to treat in this way is usually water, as it is a highly non linear compound due to its strong inter molecular forces causing deviations from Beer's law and does not transfer well from instrument to instrument. Only water spectra recorded on the spectrometer used in the analysis should be considered for inclusion in the method.

Important Note On Water Interference

As mentioned above, water interference is particularly challenging to subtract accurately from sample spectra. Water has broad absorbance features in the mid infrared, and has an apparent non-linear response to concentrations changes, even at low levels. For this reason it is important that water spectra included in the method are acquired on the spectrometer used in the analysis, and that the spectra are recorded under the same temperature and pressure regime used in the analysis of sample data. In addition to this, the concentration intervals between water spectra should be as small as possible, i.e. the larger the range of water spectra in the method the better the subtraction. If these precautions are taken excellent spectral subtraction are achievable.

It is possible to select regions for the other analyte compounds that are subject to little or no interference. The regions chosen for this method are shown in Figure 7.15.

Regions in use in this method:

Compound	Region Start	Region En
Ammonia	1007.000	1008.000
Carbon_Dioxide	1930.000	1940.000
Carbon_Monoxide	2130.000	2132.000
Carbonyl_Sulfide	2015.244	2094.684
Hydrogen_Cyanide	3267.000	3269.000
Nitric_Oxide	1790.000	1937.000
Nitrogen_Dioxide	1648.500	1651.500
Nitrous_Oxide	1274.000	1278.000
Sulfur_Dioxide	1380.000	1400.000

Add this region to this Spectrum

Figure 7.15 Analysis Regions

To illustrate the importance of including interferences in the method, consider the results table shown in Figure 7.16

Species	Actual Conc. /ppm	Analyzed Conc. / ppm	Without H_2O / CO_2
NH_3	10	9.99	18.16
CO	25	25.45	41.63
COS	12	12.31	17.36
HCN	30	29.55	26.93
NO	100	100.76	33.54
NO_2	25	25.23	25.60
N_2O	50	49.54	43.20
SO_2	50	50.64	83.51

Figure 7.16 Results

Once all interfering species as well as target species are included in the method, accurate results will be generated. As the results demonstrate, interferences that are unaccounted for can result in erroneous results.

The final topic in this section is calibration curves. The calibration curves for a particular compound may be viewed by right clicking on a compound and selecting ***View Linearity*** from the context menu. The ***View Linearity*** function is discussed fully in Chapter 4. While the curve fitted to the data points is not representative of the quantification algorithm, it is an important diagnostic tool. Consider the curve for ammonia shown in Figure 7.17.

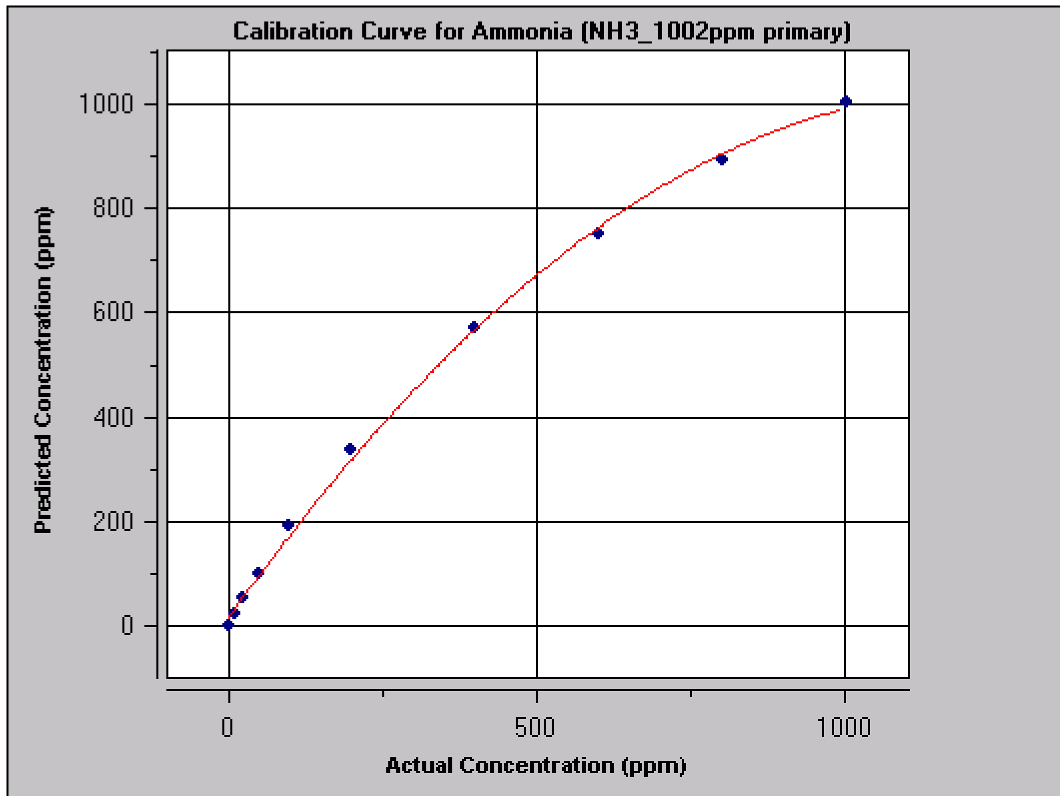


Figure 7.17 Non-Linear Ammonia Calibration Curve

Curves may exhibit apparent non-linearity due to one or any combination of the following regions:

1) The physical properties of the target molecule
2) The regions selected for analysis
3) The wide range of concentrations in the calibration

This non-linearity does not necessarily present a problem, as long as it is recognized and the curve possesses sufficient data points for accurate interpolation. With the curve in figure 7.19, accurate measurements of ammonia samples of concentrations in the 200ppm – 400ppm region may be problematic, as the calibration between the points at 200ppm and 400ppm may exhibit excessive curvature. If it is not possible to fill in the gap with reference spectra at 250ppm, 300ppm and 350ppm,

then it may be necessary to make the calibration curve more linear by choosing an analysis region of lower (and hence more linear) absorbance.

In conclusion, AutoQuant Pro© is capable of analysis of complex gas mixtures. The development of a suitable method is however crucial to the success of such an analysis. It must be stated that each method should be **Matrix Specific**, and that what works in one case may not be the best method for a different set of measurements. The building of methods becomes easier with practice, and as long as the principles outlined here are adhered to accurate results can be generated for most matrices. An important tool is the software is the SEC number and the residual spectrum. These are important tools for optimizing methods. The SEC tells you how well a predictive model works (CLS) and the residual spectrum is a visual representation of the SEC. By using an iterative process and examining the SEC and residual to obtain the lowest SEC achievable, you can easily obtain highly accurate results.

MIDAC's applications department is available to answer any questions you have on method optimizations or source sampling. There may be a charge for in depth method development and optimization. In addition, target compound spectrum generation at user specified concentrations, temperatures, pressures and optical densities are available through MIDAC's laboratories for a fee. Our fully outfitted laboratory is also available for training courses and client use for hardware and software training and reference spectrum and method development.

Chapter 8
Open-Path Systems (Supplement)

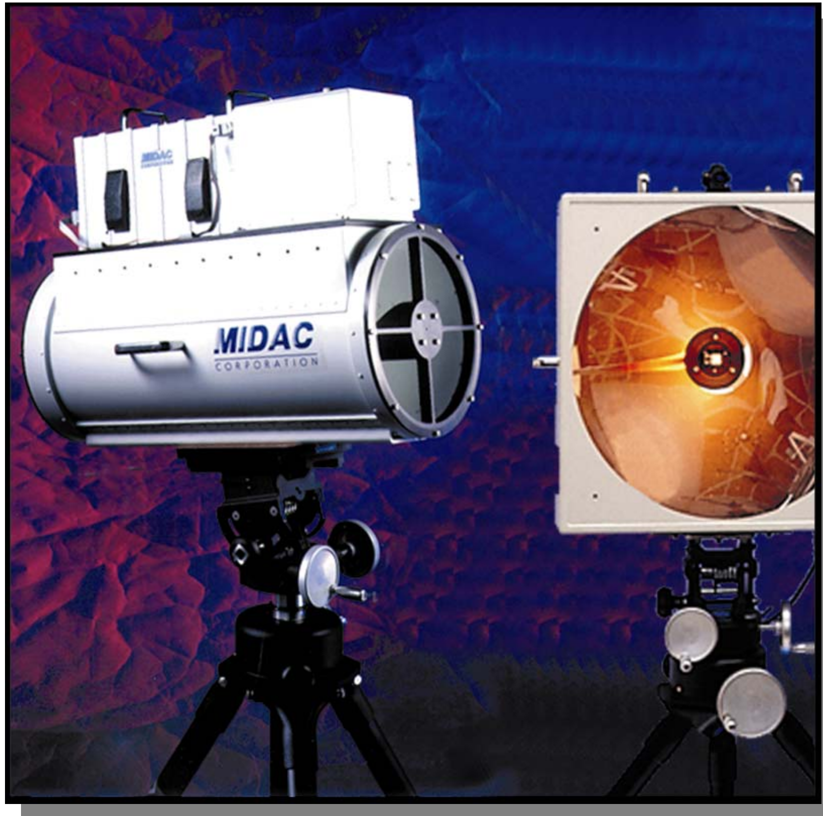


Figure 8.1 Bistatic Telescope and Source

Figure 8.2 Illuminator without Telescope

MIDAC
CORPORATION
17911 FITCH AVENUE, IRVINE, CA 92614
PH (949) 660-8558, FAX (949) 660-9334

Figure 8.3 Aries Open-Path Monitoring System

MIDAC Corp. manufactures three types of Open-Path, ambient monitors (AM-FTIR) systems, mono-static, bi-static, and Aries. The difference between the monostatic and bistatic is that the bistatic uses an external source that sends photons to the instrument and then to the interferometer and then detector. The monostatic uses an internal source to send photons to the interferometer and then to an external retro-reflector and back to the detector. The disadvantage of the monostatic unit is that only half of the photons are sent to the retro reflector so that the maximum distance that you can use the system is at least cut in half. Since the IR beam is modulated prior to being sent to a retroreflected unit (Monostatic), the IR beam must first pass through the beamsplitter where half of those photons are attenuated. The advantage of a monostatic unit is that it is easier to align the retro reflector because the infrared beam is reflected back to its source although it may be slightly off axis. Retro reflectors are typically three mutually perpendicular surfaces available in different types of reflective materials, typically being gold or silver. Retro reflectors are typically referred to as a corner cube or a prismatic retro reflector.

The bistatic sources are 12VDC external sources with a silicon carbide glower (400-7000 cm-1) or quartz halogen source (1800-7000 cm-1) mounted in the center of a parabolic mirror.

The systems can also be set-up to measure actively (with an external source or corner cube) or passively (using external stray light, solar energy, or an object that is at an elevated temperature of at least 10C than ambient temperatures. Typically, it is more difficult although not impossible to quantify without and external source if the pathlength is not known.

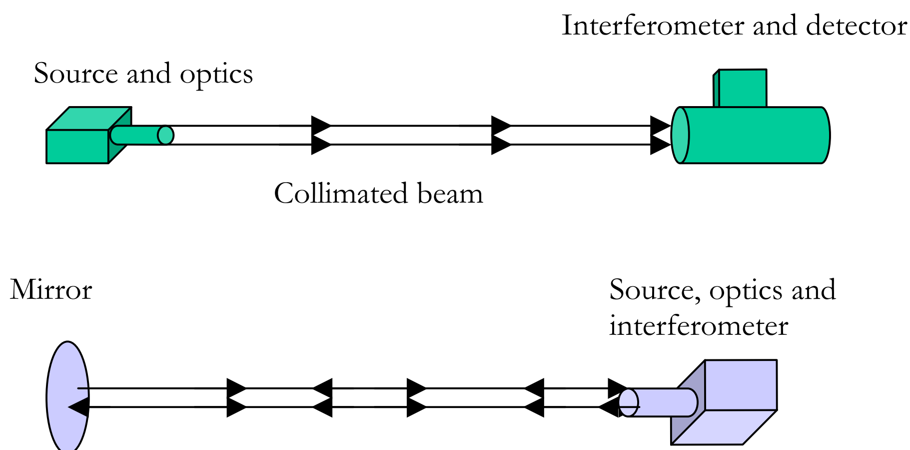


Figure 8.4 Bistatic and Monostatic Open Path Configurations

The advantage of open-path systems is that they can be set-up to measure over very long optical pathlengths typically 1000 meters. The longer the pathlength, the lower the detection limit of the target compound being measured. The disadvantage is that interferences, typically ambient moisture and carbon dioxide can quickly saturate in their regions making it impossible to measure detector response in those regions (see Figure 8.6). It is important to understand that the FTIR will measure molecules with the pathlength between the detector and source but the software will report the same number for a small plume of higher concentration (e.g. 100 ppm over a 1 meter pathlength) as a low concentration plume over a longer pathlength (10 ppm over 10 meters) and is illustrated schematically in Figure 8.5.

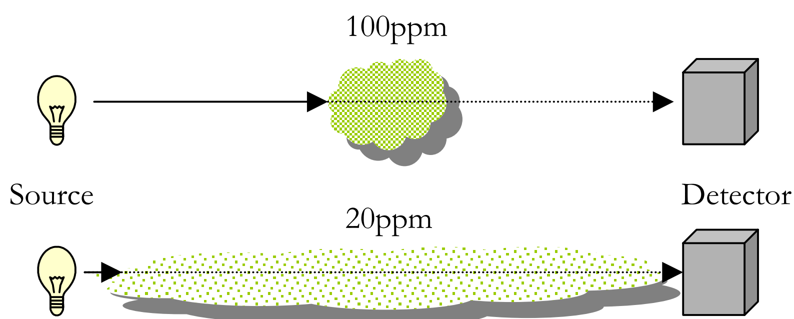


Figure 8.5 Different Gas Concentrations May Give Similar Results

In more formal terms, the reported concentration of a matrix component is the average concentration value in the space between the source and detector. No account is taken of the distribution of analyte molecules over the beam path.

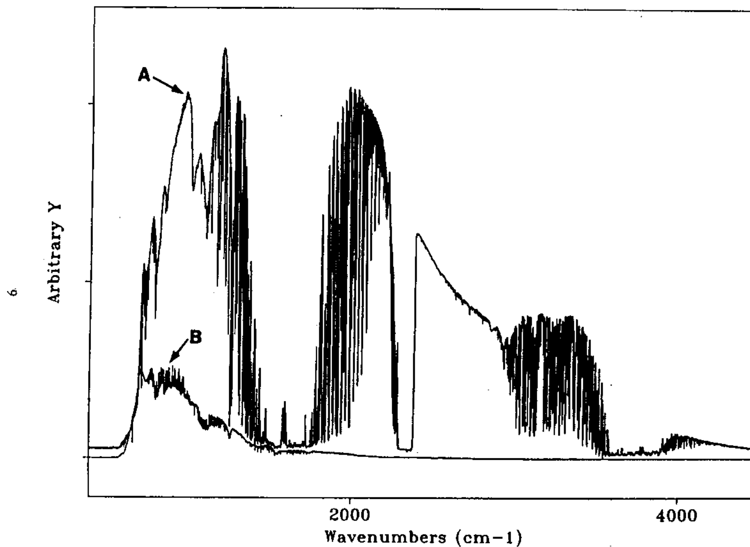


Figure 2. Open-path FT-IR spectra collected over a 207-m path with (A) the active source on and (B) the active source off.

95-WA73A.05

Figure 8.6 Open Path FTIR Spectra: A) with active source, B) active source off

From Figure 8.6, it is easy to see that the total energy available for measurement is drastically different with the source on versus the source off. It is important to ensure proper alignment of the system to the source when performing open-path measurements.

The openpath systems typically use an Illuminator M-series spectrometer mounted to a 10 or 12" Newtonian telescope with a Field of View (FOV) of 3 mrads. The Illuminator is detachable and can be used separately. The telescope is only used to collect photons over longer distances.

The Aires Open-Path monitoring system is a combination of an extractive fixed pathlength and open-path system. The pathlength is fixed at 80 meters or 105 meters and the shroud or hardcover can be pulled up over the optics so that the pathlength can be filled with nitrogen or air to collect a background. It is then run exactly as an extractive system.

Aligning the Source:

The longer the distances used in openpath measurements, the more difficult it is to focus the telescope onto the "hot" source. Typically, alignment is performed using a "rifle-scope" mounted on the telescope and source. These need to be periodically aligned to aid in finding the source over long distances. The procedure to do this is to place the telescope and source or corner cube at a shorter distance than that used in the field (e.g. 100 meters). Adjust the legs of each tripod until the leveling bubble is directly in the center of the reference circles on each tripod. Put the instrument in the "Align" mode (see Chapters 4 and 6) and set the align resolution to 32 cm-1 to update the system faster. View the inteferogram and singlebeam spectrum and adjust the telescope tripod gears up and

down and side to side until the maximum inteferogram is achieved and the energy at the higher regions (2000-4500 cm-1) of the single beam come up in energy (y-axis direction). Once the maximum is achieved, dial in the rifle scopes on both components so that the cross-hairs are focused directly onto a reference point on each component. When the components are moved to farther distances, the system will be easier to align. Other devices such as laser pointers or GPS may be used. Distances may be calculated to determine pathlength at the discretion of the user.

Figure 8.7

Figure 8.8

Collecting a Background:

It is generally more difficult to collect a background with an open-path system versus an extractive unit because you cannot effectively fill the entire pathlength with an infrared invisible gas such as nitrogen. There are several techniques to perform backgrounds that are beyond the scope of this manual. Please contact MIDAC's applications department for more specific questions on techniques and methodologies.

Typical background techniques involve:

1. Collecting a background upwind of the sample area that does not contain the target compounds of interest but at the same pathlength.
2. Using a synthetic or spectral manipulation package to remove target compound bands of interest from a single beam spectrum collected at the sampling site and using that as the background.
3. Using the "Single Beam Quant" option in the AutoQuant Pro© Software. Using this function under Parameters-Methods-Synthetic Single Beam Quant (SBQ) essentially uses the endpoints selected for quantification for each target compound in the method. The software will then use the collected single beam spectrum and draw a straight line between these points and use the new single beam as the background spectrum. This is essentially doing the same thing as manually "zapping" out the target compound bands using Grams software. It is important to

select the endpoints carefully and the same for each reference spectrum so that the energy represented by the single beam spectrum matches the sample spectrum.

Quantification:

Reference spectra collected with an extractive fixed pathlength system can be used as reference spectra for open-path calibrations. Library spectra may also be used. Field generated spectra may also be used with a 1 meter sample cell placed in the open-path beam. Please refer to EPA/625/R-96/010B Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - TO-16 for more information on Open-Path measurements.

Chapter 9
Troubleshooting

In this chapter we will address the most common problems encountered by users. In most cases, these problems are caused by incorrect instrument setup, and are readily solved using the procedures outlined here.

Problem: My temperature and pressure readings are incorrect or temperature and pressure are not read by the software.

Fix: If the temperature and pressure readings are incorrect, the first thing to check is that the units are correctly specified in the peripheral setup. Readings of 14.7 atmospheres or 1.007 psi can result if the units are incorrectly entered. If this does not fix the problem then the user should identify whether the system uses fiber optic communication or Watlow via RS-232 and follow the appropriate steps given below.

Watlow: First check that the settings on ***Parameters – Cells – Setup*** are correct. The port should usually be COM1 and the baud rate is 19200. If these are correct and the problem still persists then we need to configure the controller itself by taking the following steps:

Temperature:

1) Access the setup page on the controller. This is achieved by holding the up and down buttons simultaneously for 6 seconds. After 3 seconds a menu will appear, continue to hold and the setup page will become active.
2) Using the up and down keys select input 1 (InP1)
3) Using the advance key select sensor type (SEn1)
4) Using the up and down keys select the thermocouple input (tc)
5) Using the advance key select sensor type (in 1)
6) Using the up and down keys select thermocouple (J)
7) Using the advance key select range low (rL 1) and enter minimum temperature 0C
8) Using the advance key select range high (rh 1) and enter maximum temperature 240C
9) Use the advance key to return to input 1 (InP2)
10) Using the up and down keys select output 4 (out 4)
11) Using the advance key select baud rate (baud)
12) Using the up and down keys select 19.2k
13) Using the advance key select address (addr)
14) Using the up and down keys enter 1
15) Use the advance key to return to output 4 (out 4)
16) Use the up and down keys to select the global menu (glbl)
17) Use the advance key to select (C/F)
18) Use the up and down keys to select C for units
19) Press the home key to take you back to the beginning
20) Use the advance key to select auto tune (Aut)
21) Use the up and down keys to select tune (tunE)
22) Press the advance key 3 times to select the temperature parameters

23) Use the up and down keys to select the desired auto tune temperature
24) The red display will start to blink. The tuning process takes approx. 10 minutes.
25) The temperature setting procedure is complete.

Pressure:

1) Access the setup page as described earlier
2) Using the up and down keys select input 1 (InP1)
3) Using the advance key select sensor type (SEn1)
4) Using the up and down keys select process input (Proc)
5) Using the advance key select input 1 type (In 1)
6) Using the up and down keys select the 4-20 mA input (4-20)
7) Using the advance key select decimal (dEC 1)
8) Use the up and down keys to select 0.00
9) Use the advance key to return to range low (rL 1)
10) Use the up and down keys to select 0.00
11) Use the advance key to get to range high (rh 1)
12) Use the up and down keys to select 30.00
13) Use the advance key to return to input 1 (InP1)
14) Using the up and down keys select output 4 (Out 4)
15) Using the advance key select baud rate (baud)
16) Use the up and down keys to select 19.2k
17) Using the advance key select address (addr)
18) Using the up and down keys enter 2
19) Use the home key to exit setup. The controller should be reading approx. 14.7 psi.
20) The pressure setting procedure is complete

Fiber Optic: First check that the fiber optic cables are correctly connected to the fiber card in the computer by reversing the cables. If this does not correct the problem the following steps should be taken:

Access the fiber optic setup using ***Parameters – Cells***. Enter the set of parameters shown in Figure 8.1. You may need 50 instead of 30 for the pressure high value depending on transducer equipped.

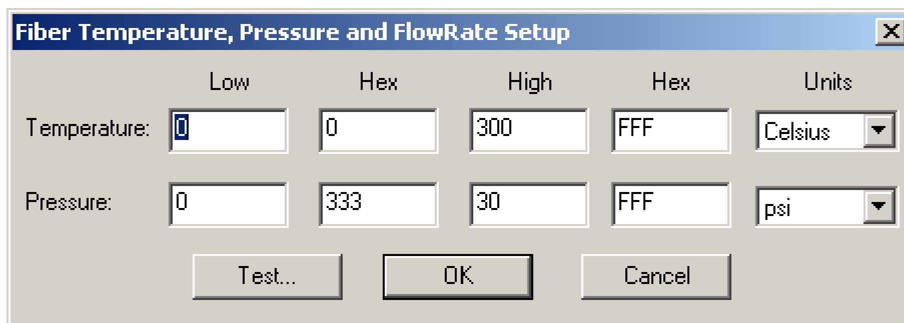


Figure 8.1 Fiber Optic Setup

Ensure that the default temperature, pressure and flow boxes are unchecked. If the problem persists after the apparatus is tested, please contact MIDAC applications support.

Problem: The throughput in align mode has dropped to unacceptable levels.

Fix: If applicable check the liquid nitrogen levels in the detector Dewar. If the detector is topped up and the throughput is still low the cell optics should be checked for deposits on the mirrors. Deposits are often formed when cell temperature is too low to prevent condensation on the mirrors. In order to check the mirrors it is necessary to remove the end plate from the cell. This should be done carefully as the mirrors are directly attached to the end plate on most cells. Access the second set of mirrors by removing the cell from the instrument casing. If deposits are found the mirrors should be washed by squirting the surface with polar (methanol) and non-polar (methylene chloride) solvents in an effort to dissolve the contaminants. Acetone also works well to dissolve non-polar deposits. Do not directly touch the mirror surface. **ON NO ACCOUNT SHOULD ACIDS BE USED ON THE MIRRORS**. This will result in severe damage to the gold coating. After washing, the mirrors should be blow dried with dry nitrogen or acetone and inspected. If the deposits have been mostly cleared by washing, the cell should be reassembled and the instrument throughput checked. If insoluble deposits still remain, it may be necessary to take further cleaning steps. The mirror coating is extremely delicate, and may be scratched even by a light touch, and so rigorous care must be taken to avoid directly touching the gold surface. There is however a procedure that has been found to give good results, although MIDAC can accept no responsibility for any damage caused while following this procedure. The mirrors should be immersed in clean de-ionized water. While fingers should never touch the coating directly, if a layer of **Ivory** soap is applied to the fingertip it is possible to gently wipe the surface without damage. Ivory soap is used due to its lack of additives. The mirrors should then be rinsed and dried. The cell should then be reassembled and the throughput checked. If the instrument throughput is still unsatisfactory, it may be necessary to re-align the fixed mirror, as described in Chapter 6. It should be noted that this procedure is unsuitable for inexperienced operators. If in doubt, call MIDAC applications support.

Appendix 1

CLS Summary

In many cases, a linear model of infrared absorbance known as Beer's Law provides useful estimates of gaseous concentrations in mixtures of gases. A classical least squares (CLS) technique, described below, is useful for generating these estimates from a measured sample spectrum and a number of reference spectra representing the sample gas constituents.

The measured absorbances of certain compounds do not follow Beer's Law over large ranges of concentration. Two mathematical methods that can be used in such cases to obtain approximate concentrations are described below. The first method, referred to here as piece-wise concentration interpolation (PWCI), is based on 1) the concentrations of two reference spectra, 2) the results of *two independent* CLS analyses, each of which uses a *single* reference spectrum for the compound, 3) a *concentration*-based interpolation involving an empirically determined parameter. The second method, referred to here as a pair-wise absorbance interpolation (PWAI), is based on 1) the concentrations of the two reference spectra, 2) the results of a *single* CLS analysis using the two reference spectra, and 3) a linear model describing the sample *absorbance* of in terms of the absorbance of a pair of the compound's reference spectra at each infrared frequency.

The determination of accurate residual spectra and concentration uncertainties is problematic within the PWCI approximation, since it requires the performance of two independent CLS analyses; it is not clear how these independent results should be combined to provide the residual spectra and uncertainties. In contrast, the PWAI approximation, which is based on a single CLS analysis, provides clearly defined residual spectra and concentration uncertainties.

In several other aspects regarding the determinations of concentration in single-component spectra of CO_2, the PWAI method is shown below to yield concentration estimates superior in most regards to those of the PWCI method. The accuracy advantage of the PWAI approximation over the PWCI approximation is particularly marked when the number of reference spectra is limited.

CLASSICAL LEAST SQUARES (CLS) ANALYSIS

Definitions of Beer's Law and the CLS Parameters

Fourier transform infrared (FTIR) spectrometers provide data suitable for the determination of unknown concentrations of individual compounds in multi-component samples. For gas samples, FTIR-based quantitative analyses are usually based on a linear model of the sample absorbance known as Beer's Law, which can be written as

$$A_i = \sum_{j=1}^{M} a_{ij} L C_j \quad , \; i = 1, 2, ...N \qquad \text{Eq. (1)}$$

where

- M = The number of compounds assumed to absorb in the spectral region analyzed (with index j);
- A_i = The number of infrared frequencies used in the analysis (with index i);
- N = The observed sample absorbance at the ith infrared frequency;
- C_j = The (unknown) volumetric concentration of the jth component of the mixture;
- L = The absorption path length used in recording the sample spectrum;
- a_{ij} = The absorptivity of the jth compound at the ith infrared frequency.

The absorptivities a_{ij} are characterized, though not necessarily directly calculated, in spectroscopic studies of the compounds of interest under well-known conditions. Information regarding the absorbance of each compound is usually embodied in a library of "reference" or "standard" spectra.

The "classical least squares" (CLS) approach to determining the desired concentrations C_j, as defined in this work, involves minimizing the squared errors associated with Equation 1. The basic approach is thoroughly described in a series of papers written by David Haaland and co-workers.[1, 2, 3]
This work employs the following expression of Beer's Law:

$$A_i^S = \alpha + \beta \nu_i + \varepsilon_i + \sum_{j=1}^{M} \gamma_{ij} S_j \quad , \; i = 1, 2, ...N \qquad \text{Eq. (2)}$$

where

A_i^S = measurements of the sample absorbance at the frequencies ν_i;

ν_i = infrared frequency of the ith absorbance point within the "analytical region" selected for the analysis;

$\alpha + \beta\nu_i$ = linear baseline correction to Beer's Law for the selected absorbance points (see below);

ε_i = Deviations from Beer's law (or the model "errors") including those related to the baseline corrections, at the frequencies ν_i;

S_j = "scaling factor" for the jth reference spectrum included in the analysis;

γ_{ij} = "reduced absorptivity" of the jth reference spectrum at the ith absorbance point within the "analytical region" (see below).

Two quantities found in Equation 2 require further description.

First, the quantity γ_{ij} is defined as the "reduced absorptivity" of the jth reference spectrum at the ith frequency (ν_i). In terms of experimentally available parameters, this quantity is

$$\gamma_{ij} = A_{ij}^{R} \frac{T_j}{L_j p_j C_j^R} \qquad \text{Eq. (3)}$$

where

A_{ij}^R = absorbance of a single reference spectrum of the (pure) j[th] compound at the frequencies ν_i;

T_j = absolute temperature (Kelvin) at which A_{ij}^R was recorded;

L_j = absorption path length (meters) at which A_{ij}^R was recorded;

p_j = absolute pressure (atm) at which A_{ij}^R was recorded;

C_j^R = volumetric concentration (ppm) at which A_{ij}^R was recorded.

The reduced absorptivity γ_{ij} of Equation 3 is a representation of the absorptivity a_{ij} after normalization for the effects of the reference gas density, reference gas pressure, reference absorption pathlength, and reference gas volumetric concentration. In the following arguments, it is assumed that the values γ_{ij} require no additional corrections for baseline effects.

Second, the terms $\alpha + \beta\nu_i$ in Equation 2 represent a linear baseline correction to Beer's Law in the sample spectrum over the frequencies ν_i. An extension to higher (n[th]) order baseline corrections is

possible with the inclusion of similar terms proportional to ν_i^n. Such terms are excluded from the mathematical arguments presented below.

CLS Estimates of the Concentrations, Baseline Parameters, and Uncertainties

Equation 2 provides accurate CLS estimates of the parameters α, β, and the scaling factors S_j. These estimates are denoted below by $\bar{\alpha}$, $\bar{\beta}$, and $\bar{S}_j$, and are calculated as follows.[4]

The "design matrix" **D** with M+2 columns and N rows is defined as

$$\mathbf{D} = \begin{pmatrix} \gamma_{11} & \gamma_{12} & .. & \gamma_{1M} & 1 & \nu_1 \\ \gamma_{21} & \gamma_{22} & .. & \gamma_{2M} & 1 & \nu_2 \\ .. & .. & .. & .. & .. & .. \\ \gamma_{N1} & \gamma_{N2} & .. & \gamma_{NM} & 1 & \nu_N \end{pmatrix} \qquad \text{Eq. (4)}$$

Each the first M columns of **D** corresponds to the jth compound, and consists of the N values γ_{ij}. The (M+1)th column consists of N entries of any non-zero constant, representing the constant baseline offset term α, the (M+2)th column consists of the N values ν_i. If the row vector $\mathbf{A_S}$ represents the N measured ("sample") values, the column vector **X** represents the M+2 unknown quantities {S_1, S_2,...S_M, α, β}, and the row vector **E** represent the N errors ε_i, the linear model in Equation 2 takes the form

$$\mathbf{A_S} = \mathbf{DX} + \mathbf{E} \qquad \text{Eq. (5)}$$

The matrix Equation 4 is over-determined, that is, there are more absorbance values (N) available than there are parameters (M+2) to be estimated. To proceed, it is necessary to assume that the errors ε_i posses a joint distribution with zero means and a variance-covariance matrix of the form

$$\mathbf{M}_f = \begin{pmatrix} \sigma_1^2 & \sigma_1\sigma_2\rho_{12} & . & \sigma_1\sigma_N\rho_{1N} \\ \sigma_1\sigma_2\rho_{12} & \sigma_2^2 & . & . \\ . & . & . & . \\ \sigma_1\sigma_N\rho_{1N} & . & . & \sigma_N^2 \end{pmatrix}. \qquad \text{Eq. (6)}$$

It is worth noting that generating valid least-squares parameter estimates is possible without assuming a normal distribution of the errors ε_i. However, it is necessary to assume further that $\mathbf{M}_f$ is known only to within a scaling factor σ^2, that is,

$$\mathbf{M}_f = \sigma^2 \mathbf{N} \quad . \qquad \text{Eq. (7)}$$

Under these conditions, where the matrix transpose is denoted by the superscript **t** and the matrix inverse by the superscript **–1**, the desired least squares estimates of the quantities **X** are given by

$$\overline{\mathbf{X}} = \left(\mathbf{D}^t \mathbf{N}^{-1} \mathbf{D}\right)^{-1} \mathbf{D}^t \mathbf{N}^{-1} \mathbf{A}^S \quad . \qquad \text{Eq. (8)}$$

The matrix $\mathbf{N}^{-1}$ is the "weight matrix." In the simplest case (when all the observed quantities A_i have equal variance σ^2), $\mathbf{N}^{-1}$ is accurately approximated by the identity matrix **I**. In this case $\mathbf{M}_f = \sigma^2 \mathbf{I}$, and Equation 8 simplifies to the form used below:

$$\overline{\mathbf{X}} = \left(\mathbf{D}^t \mathbf{D}\right)^{-1} \mathbf{D}^t \mathbf{A}_S \quad . \qquad \text{Eq. (9)}$$

Measures of the "uncertainties" in the least squares estimates $\overline{\mathbf{X}}$ are also available. The residual vector (or "spectrum") is

$$\mathbf{V} = \mathbf{A}_S - \mathbf{D}\overline{\mathbf{X}} \quad . \qquad \text{Eq. (10)}$$

V is (at each frequency) the difference between the measured absorbance $\mathbf{A}_S$ and the least squares estimate $\mathbf{D}\overline{\mathbf{X}}$. From **V**, a least-squares estimate of the moment matrix $\mathbf{M}_f$ is available:

$$\overline{\mathbf{M}}_f = \left(\frac{\mathbf{V}^t \mathbf{V}}{N - M - 3}\right)\left(\mathbf{D}^t \mathbf{D}\right)^{-1} \qquad \text{Eq. (11)}$$

and the marginal standard deviations Δ_j (often referred to as the "1σ uncertainties") in the parameter estimates $\overline{X}_j$ are given by

$$\Delta_j = \sqrt{(\overline{\mathbf{M}}_f)_{jj}} \quad . \qquad \text{Eq. (12)}$$

Please note that the denominator (N-M-3) of Equation 11 reflects the use of a linear baseline correction. In general the denominator is (P-Q-1), where P is the number of data (absorbance) points and Q is the total number of parameters determined in the CLS analysis.

The least squares estimates of the concentrations C_j are given in terms of the first M values of $\overline{\mathbf{X}}_j$ by

$$\overline{C}_j = \frac{T_S}{L_S p_S} \overline{S}_j \qquad \text{Eq. (13)}$$

where

L_S	=	absorption path length (meters) at which A_i^S was recorded;
T_S	=	absolute temperature (Kelvin) at which A_i^S was recorded;
p_S	=	absolute pressure (atm) at which A_i^S was recorded;
$\overline{S}_j$	=	the least squares estimates of the scaling factors, contained in the first M elements of the vector $\overline{\mathbf{X}}$.

Similarly, an unbiased 1σ estimate of the uncertainty U_j in each of the concentration estimates is given in terms of the marginal standard deviations by

$$U_j = \frac{T_S}{L_S p_S} \Delta_j \quad . \qquad \text{Eq. (14)}$$

Appendix 2

AQPro Socket Interface

AQPro exposes an interface to allow it to be controlled by remote clients via standard network TCP/IP sockets. It uses port number 5000. This allows AQPro to be controlled by other programs, or interactively by remote users over the network. If, for security reasons, you don't want AQPro to enable this interface, add the '/noserver' flag to the command line of the shortcut that starts AQPro.

Interactive Usage.
Telnet can be used to control AQPro via the socket interface. First start AQPro, then run 'telnet localhost 5000' if AQPro is running on the same machine, or 'telnet IPADDRESS 5000' if AQPro is running on a different machine. The IP Address can be determined by running the windows 'ipconfig.exe' program on the machine where AQPro is running. The IP address has a format like '192.168.0.5'. Telnet will then connect to AQPro, which will respond by sending back the string 'AQPro A.B.C.D', where A.B.C.D. is the build number of the version of AQPro. Then, type 'echo' followed by Enter and AQPro will be friendlier to use interactively, and you will then see the prompt 'AQPro>'. . (AQPro does not automatically echo back commands because programs, not people, usually drive the socket interface).

Programmatic Usage
An example Visual Basic client project is available. This project presents a simplified user interface with just Background, Scan, and Analyze buttons. It illustrates how to build a remote control socket client for AQPro.

Command Set

If you type '?' at the AQPro> telnet prompt, you will see:
Supported Commands:

loadMethod <name> load AQPro method specified by 'name'
path <directory> set the collection directory to 'directory'

calibrate calibrate the current method

break attempt to break out if the server appears hung

background collect a new background

loadBackground <name> load a background datafile from disk.

scan collect a new sample

getLastFilename returns the filename of the last collected data
analyze analyze the last sample

batch analyze all the samples since the last background

echo [0,1] turn echo on (1) or off (0). Defaults to 'on'

exportImage copy the instrument view's data window to the clipboard

format <csv,xml> set the format of analysis results

beginCollect <single, continuous, highspeed, automatic> begins data collection and analysis in the given mode.

endCollect stops a collection begun with beginCollect (if one is in progress).

getTemperature returns the last-read temperature value, in Celsius

getPressure returns the last-read pressure value, in ATM.

getFlowrate returns the last-read flowrate value, in CFM.

stop terminates the socket connection

Commands are not case sensitive. Commands must be terminated with carriage return / line feed codes.

The 'loadMethod', 'path', 'loadBackground', and 'format' commands require arguments, which is specified in the list above with the '<>' notation. Do not include the '<' and '>' in the command.

In the case of loadMethod, the argument is the filename of the method. This can be the full path of the method:

C:\Documents and Settings\All Users\Documents\AutoQuant4\methods\ex2\ex2.aq4
Fortunately, this can be shortened.

You can always leave off the .aq4 extension, the software will add it if needed.
If the method is in the default method directory, which is set on the Tools/Parameters/Paths dialog in AQPro, then the argument can be shortened to:
ex2\ex2 This can be shortened even more. If the method is in the default method directory, and the base method filename (the filename without the .aq4 extension) is same as the name of the subdirectory it is in, just specify the name of the subdirectory:
ex2 Data collected through the socket interface is always saved to disk, regardless of the method's storage settings. The path command tells AQPro where to put data that is collected. The directory is created automatically if it does not exist. Data is saved in the GRAMS file format as floating-point numbers.

The format command has two options: csv or xml. The default is xml. Csv (Comma

separated Values) format is very terse. Each compound's results are given by a comma separated triple: compoundName, concentration, uncertainty. All the compound triples
for a sample are returned on one line. The csv format is a standard way of importing data into programs such as excel and is easily parsed by software. The XML (Extensible Markup Language) format is the internal representation of results that AQPro uses and is very verbose, containing a lot of additional information. XML is an industry-standard format for data interchange; much information about it is freely available on the Internet. The results generated by 'analyze' or 'batch' will be returned in the specified format. The echo command takes optional arguments (specified with the '[' and ']' enclosures). Do not include the '[' or ']' in the command. With no argument, it turns echo on.

Note that the 'exportImage' command exports the spectral data plot from AQPro's instrument view to the clipboard of the host computer (the one that AQPro is running on). This is of no benefit if you are controlling AQPro from a remote computer. GetTemperature, getPressure and getFlowrate return the last-read values for these parameters. These values are read at times defined in the method. The handlers for these commands do not go to the sensors and request new values. Rather, they return the values that were latched the last time they were read in the course of a measurement.

In versions of AutoQuant Pro© build 99 and higher a new socket monitor called xmlSocket.mon is available. On the Tools/Parameters/Monitors dialog, click 'Browse' and select 'xmlSocket.mon'. This monitor streams all reported concentrations, uncertainties and alarms out of the TCP port in xml format. Xml is a standard format for data interchange, and this output may be parsed by custom software built to read the xml data. After selecting the xml monitor into an aqpro method and starting a measurement, it is possible to connect to the socket by typing 'telnet localhost 20000' from a command line on the same computer. An example of a Telnet session is given below:

```
AQPro 4.0.0.107
> AQPro> getTemperature
> 90.000000
> AQPro> getPressure
> 1.000000
> AQPro> beginCollect continuous
> OK, collect message sent
> AQPro>
```

Localhost is a stand-in for the local computer's IP address. 20000 is the default TCP port for the xml socket monitor. The xml socket may then be accessed from any computer on the network, as long as the IP address for that computer is substituted for 'localhost'.

Appendix 3
Hydroquant

The HydroQuant method of FTIR gas analysis was developed at MIDAC for the specific application of measuring moisture in corrosive gases. The hardware typically used is includes an I-series spectrometer that is evacuated to lower than 10^{-3} torr to remove all background moisture and gases. Because of the corrosive and dangerous nature of most sample gases, a technique had to be developed that allowed data to be taken without collecting a background spectrum. Also since very low levels of moisture are to be measured, even small amounts of water in the background could adversely affect results.

The HydroQuant algorithm creates a synthetic background from each sample interferogram. The sample interferogram is multiplied by a Gaussian function that can be described as:

$$e^{-\left(\frac{x^2}{k^2}\right)}$$

After multiplying the interferogram by this function, the resulting interferogram has been smoothed out. The function approaches zero as you travel down the wing of the interferogram. The resulting single beam is a smooth instrument response profile without the sharp lines from the water. It is very similar to a fully purged system background.

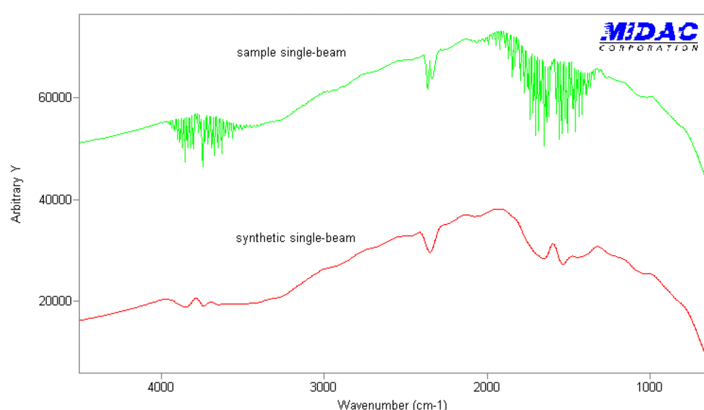


FIGURE: A sample single-beam (top) and its corresponding synthetic background (bottom) are shown. The sample is air and was collected at 2cm^{-1}, 256 scans with a K-value of 1200.

The k value is a user selectable parameter to modify the behavior of the Gaussian function. The higher the K-value, the faster the Gaussian decays and the more deresolved the interferogram appears. Researchers at a national lab as well as customers in the gas supply industry typically use a k-value of 1200 with samples collected at 2.0 cm^{-1} with 256 or more co-added scans.

In doing analysis with this type of method, it is very important to keep the k-value consistent. The method should have spectra processed with the same k-value as the sample spectra because the k-value will ultimately affect the shape and intensity of the absorbance peaks.

Using a synthetic background saves an enormous amount of time that would be required to generate a background spectrum. Typical moisture analysis consists of low ppb measurements, and it would take many hours to dry a gas cell to below that level. This approach works great with compounds with narrow features. Although it is referred to as "HydroQuant", it has been used to monitor other sharp-band compounds like HF and other acid gases. However, this method does not work well with broad band compounds.

Appendix 4

Jumper Settings

Below is a table for the 102818 mirror drive board jumper configuration for the various scan speeds. The corresponding dual 102713 ADC filter settings for J1 or J2 are listed in actual layout form as found on the board.

102818 Mirror Drive Board **JMP4 Mirror Speed Adjust Headers** *(shaded values not currently available)*			**102713 Dual ADC Board Filter (kHz)**
(X=jumper, O=open)	MIRROR SPEED (kHz)		**J1**
OOO	469		156
OOX	234		88
OXO	117		48
OXX	59		27
XOO	29		16
XOX	15		8.8
XXO	7		4.8
XXX	4		2.7
			J2

ZPD adjustment is similar to previous boards.

102818 ZPD DELAY ADJUSTMENT (JMP1) *(Adding jumpers decreases zpd by the indicated # of points)*						
MSB						LSB
	4096	2048	1024	512	256	

● New grounding scheme: **The interferometer is no longer isolated** from chassis. The gray silpad found between interferometer and base plate has been removed.

● **Detector modules are now isolated** from the chassis. Nylon dowel pins and nylon mounting screws are used with an isolation pad to prevent electrical contact with the chassis.

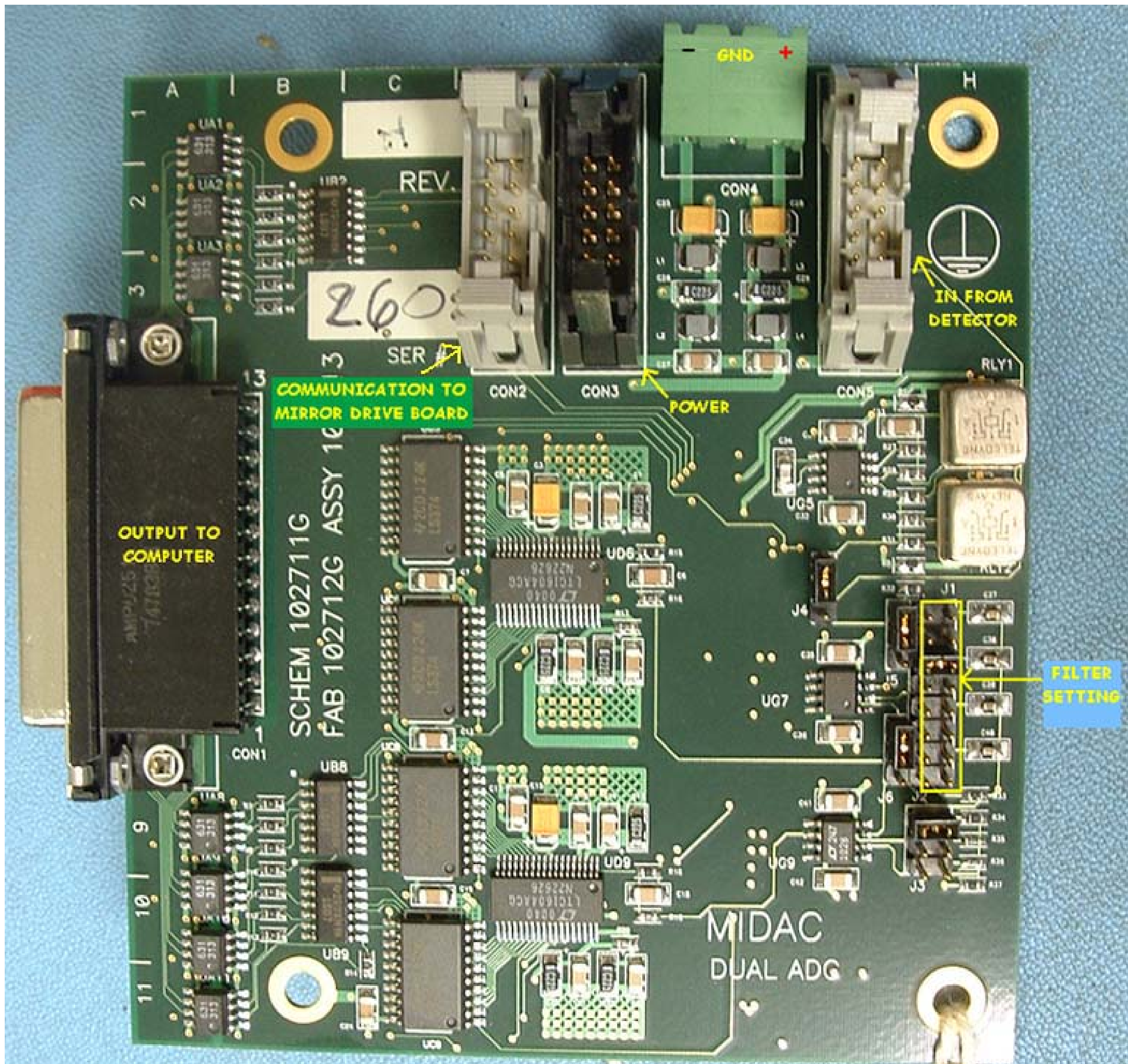
● Laser gain/test points: Laser gain jumpers are still adjusted in pairs, now with two separate groups of headers: JMP2 and JPM3. There are now three jumper settings for each channel. As before, removing jumpers increases

gain. For ground you can use the indicated test points or any metal contact (mounting screws, chassis, etc.)
Note: Peak-to-peak laser signal can reach a maximum of approximately 11 volts before clipping occurs.

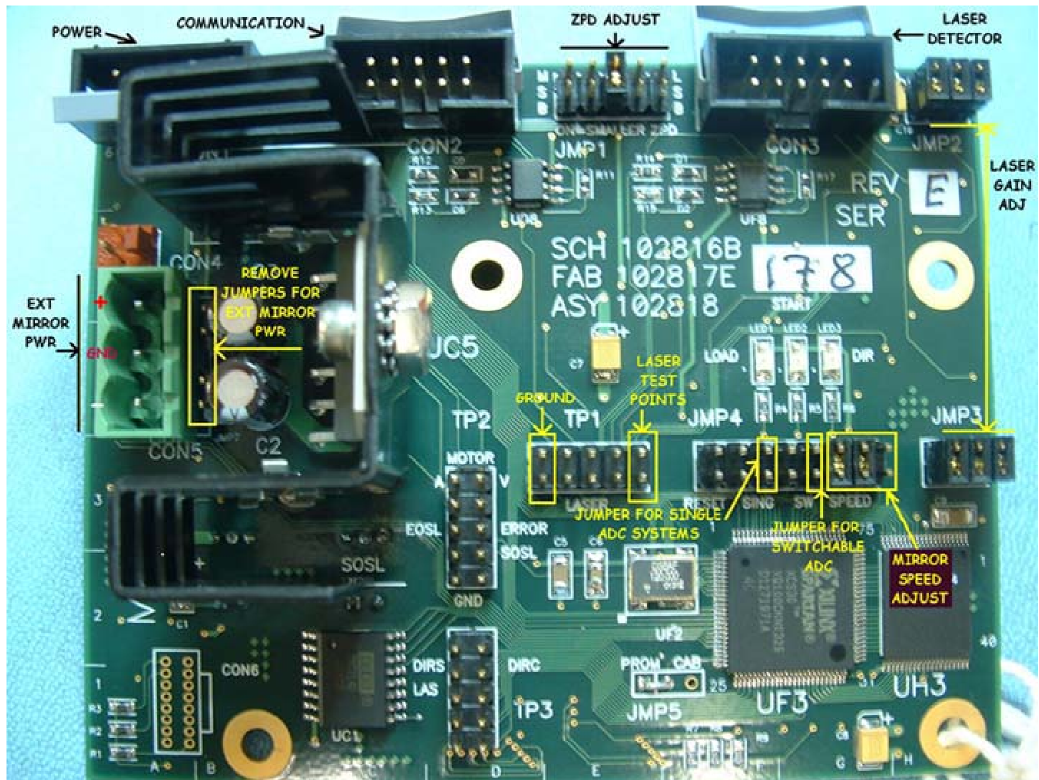
● The new mirror drive board can function with power supplied through the ribbon cable when used with old/single ADC systems. Removing the indicated jumpers and using the auxiliary 3-terminal phoenix connector with the new power distribution board will provide improved mirror scanning stability.

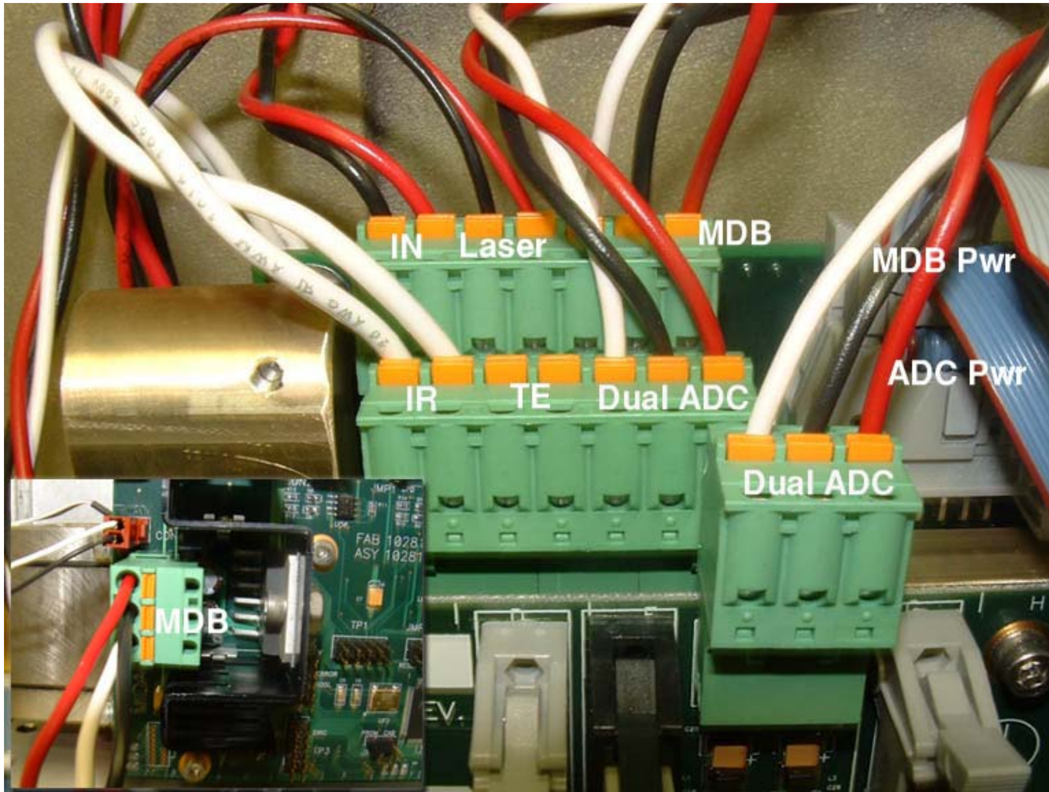
Interferometers with the new 102818 (Rev E and up) mirror drive boards **will** stroke without computer communication.

● Interferometers with the old combo mirror drive boards can still be used with Dual ADC systems. The J2 jumpers must be in the upper position (old fiber optic setting) and the isolation silpad should be removed.



GND
COMMUNICATION TO MIRROR DRIVE BOARD
POWER
IN FROM DETECTOR
OUTPUT TO COMPUTER
FILTER SETTING
SCHEM 102711G
FAB 102712G
MIDAC
DUAL ADC


POWER
COMMUNICATION
ZPD ADJUST
LASER DETECTOR
LASER GAIN ADJ
EXT MIRROR PWR
+
GND
-
REMOVE JUMPERS FOR EXT MIRROR PWR
GROUND
LASER TEST POINTS
JUMPER FOR SINGLE ADC SYSTEMS
JUMPER FOR SWITCHABLE ADC
MIRROR SPEED ADJUST
CON2
CON3
CON4
CON5
JMP1
JMP2
JMP3
JMP4
JMP5
TP1
TP2
TP3
UC5
C2
REV E
SER 178
SCH 102816B
FAB 102817E
ASY 102818
LOAD
START
DIR
MOTOR
EOSL
ERROR
SOSL
GND
DIRS
DIRC
LAS
RESET
SING
SW
SPEED
LASER
PROM
CAB
UF3
UH3
UC1
CON6


IN
Laser
MDB
MDB Pwr
IR
TE
Dual ADC
ADC Pwr
Dual ADC
MDB