# Software User's Manual

Applied Photonics Limited (APL)

## LIBSoft 2020

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|---|---|
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Contents

# 1 Introduction

This manual describes the installation, configuration and use of the Applied Photonics Limited (APL) *LIBSoft 2020* application. A number of videos are also available which demonstrate many of the procedures described in this manual.

The *LIBSoft* application has been developed to control the acquisition and display of spectra using APL LIBS systems. There are two versions of *LIBSoft 2020*:

- *LIBSoft Lite*: provides configuration and control of all system components, acquisition, display and manipulation of spectra
- *LIBSoft Full*: as per *LIBSoft Lite* but also provides enhanced spectrum analysis functionality including the generation and application of quantitative calibrations, peak identification and element identification. *LIBSoft Full* requires a USB key in order to activate and use these additional functions.

*LIBSoft* can be used to control systems comprised of one of a range of lasers and spectrometers together with APL's automated sample chambers and sample imaging kit. The specific components currently supported are as follows:

Laser systems:

- Quantel Ultra CFR (50 or 100 mJ)
- Quantel Q-Smart (450 or 850)
- Quantel Brilliant/Brilliant B
- Litron Nano (266nm or 1064 nm)
- Litron Bernoulli
- APL lasers (as used, for example in the LIBSCAN 25+ system)
- No laser (allows acquisition of spectra when LIBSoft 2020 is used with one of the supported spectrometers but the acquisition is triggered using a device for which there is no software control, for example, a customer's own laser)

Spectrometers:

- Avantes AvaSpec 2048
- Avantes AvaSpec 2048CL
- Avantes AvaSpec 4096CL
- Catalina Scientific EMU-65 spectrometer with Raptor Photonics Falcon camera[(1)]

[1] Also requires Quantum Composers Sapphire 9200 series delay generator

Sample chambers:

- APL computer-controlled sample chambers including XYZ-750

Sample imaging:

- APL imaging kit

IO device:

- National Instruments USB 600x series

# 2 System computer and interfaces

## 2.1 Introduction

The *LIBSoft 2020* application can be installed and run on virtually any computer running under Microsoft Windows (7, 8 or 10) including laptops, desktop and industrial computers. A monitor resolution of 1920 x 1080 is required to ensure accurate display of all application screens. Other resolutions can be used but some small display inconsistencies may occur. The specification of the PC required is quite basic; an Intel i3, i5 or i7 processor (or equivalent) with at least 4 GB of RAM is recommended. However, the required specification does vary depending on the hardware components of the LIBS system that the application is to be used to control. For example, a system incorporating a Catalina Scientific EMU spectrometer will benefit from increased system memory and a faster processor and systems with multiple components will require a greater number of USB ports. APL can provide advice on the specification of PC required for a particular system.

The other features required of the system computer to be used depend on the specific system components that comprise the LIBS system as they use a variety of interfaces. Many of them interface to the system computer via USB. Most of the USB ports required by system components need only be USB 2.0 however, if the high definition version of the optional imaging kit is used this will require one USB 3.0 port for each camera in the system. The Avantes 4096CL spectrometers also require a USB 3.0 port. Additional USB ports can be provided if required by the use of a suitable hub although care should be taken in doing so. For example, in systems which use the Avantes spectrometers these devices are already connected via a USB hub housed in the spectrometer console and the addition of a further hub between the spectrometers and the system computer can lead to occasional communication issues. Some components interface to the system computer using an RS232 serial port. A suitable USB to serial converter can be used if the system computer does not have a serial port, however care should be taken when selecting such a device as the drivers for some of them can be unreliable and lead to communication issues. APL can provide a recommended USB to serial converter if required (see 3.5).

Other components interface to the system computer using an ethernet connection and therefore the computer should be fitted with a suitable ethernet card with an RJ45 input socket. At least one of the possible system components (EMU-65 spectrometer with Raptor Photonics Falcon Blue camera) interfaces to the system computer via a proprietary interface which requires the installation of a PCI Express frame grabber in a desktop computer or an ExpressCard/34 frame grabber in a laptop (see 3.7). This limits the choice of system computer that can be used if this component is included in the system.

These port requirements are summarised in the table below.

| System component | Port |
|---|---|
| Avantes 2048/2048CL spectrometers | 1 x USB2 port for 6-channels systems<br>2 x USB2 port for 8-channels systems |
| Avantes 4096CL-EVO spectrometers | 1 x USB3 port for 6-channels systems<br>2 x USB3 port for 8-channels systems |
| EMU-65 spectrometer with Raptor Photonics Falcon Blue camera | PCI Express frame grabber in a desktop computer<br>ExpressCard/35 frame grabber in a laptop |
| Quantum Composers Sapphire 9200 delay generator (only for systems incorporating an EMU system) | 1 x USB2 port |
| High-definition imaging kit | 1 x USB3 port for each installed camera |
| Laser | Depending on the laser model one of the following:<br>RS232 serial port (or a suitable USB to serial converter)<br>Ethernet card with an RJ45 input socket |
| APL computer-controlled sample chamber | 1 x USB2 |
| National Instruments USB 600x series | 1 x USB2 |

The following paragraphs describe the specific interface requirements of the various system components in more detail.

### 2.2 Quantel lasers

The Quantel Ultra and Brilliant lasers interface to the system computer via an RS232 serial connection. As stated above, a suitable USB to serial converter can be used if the system computer does not have a serial port.

**NB** If a USB to serial converter provided by APL is used it will require driver software to be installed on the system computer. This can be done immediately following installation of the *LIBSoft* application (see section 3.5).

The Quantel Q-Smart lasers interface to the system computer over ethernet. An alternate IP configuration must be specified prior using *LIBSoft* with one of these lasers (see section 3.6)

### 2.3 Litron lasers

The Litron lasers interface to the system computer via an RS232 serial connection using a non-standard proprietary lead supplied by the manufacturer. A USB to serial converter can also be supplied by APL to enable the laser to be used with computers that don't have a serial port.

**NB** If a USB to serial converter provided by APL is used it will require driver software to be installed on the system computer. This can be done immediately following installation of the *LIBSoft* application (see section 3.5).

### 2.4 Avantes AvaSpec spectrometers

The Avantes AvaSpec 2048 and 2048CL spectrometers interface to the system computer via USB2 whereas the AvaSpec 4096CL spectrometers use USB3. The 2048 spectrometers use a CCD detector whereas the 2048CL and 4096CL spectrometers both incorporate a CMOS detector. The 2048CL spectrometers were introduced to APL systems in 2018 and the 4096CL spectrometers in 2020. The configuration and operation of all Avantes spectrometers is the same but the range of allowable parameter values varies slightly for each type. The details of the Avantes spectrometer types are summarised in the table below.

| Spectrometer | Port | Detector (Size) | Minimum integration delay (µs) | Minimum integration time (µs) |
|---|---|---|---|---|
| Avantes 2048 | USB2 | CCD (2048 pixels) | 1.27 | 1100 |
| Avantes 2048CL | USB2 | CMOS (2048 pixels) | 0.86 | 30 |
| Avantes 4096CL-EVO | USB3 | CMOS (4096 pixels) | 0.86 | 9 |

Usually one or more Avantes spectrometers are contained in an APL SpectroModule-6 or SpectroModule-8 although it is also possible to use these spectrometers as stand-alone devices. Both the SpectroModule-6 and SpectroModule-8 contain a USB hub which allows multiple spectrometers to be connected to the system computer via a single USB connection. As a result, it is inadvisable to connect these modules to the system computer via an additional hub as this could lead to communications issues. It is therefore important to connect a SpectroModule-6 or SpectroModule-8 directly to a USB port on the system computer.

**NB** The Avantes AvaSpec spectrometers also require driver software to be installed on the system computer. This can be done immediately following installation of the *LIBSoft* application (see section 3.4).

### 2.5 Catalina Scientific EMU-65 spectrometer with Raptor Photonics Falcon camera

The EMU-65 spectrometer with Raptor Photonics Falcon camera interfaces to the system computer via a proprietary interface which requires the installation of a PCI Express frame grabber in a desktop computer or an ExpressCard/34 frame grabber in a laptop (see section 3.7).

*LIBSoft* communicates with the EMU-65 spectrometer and Raptor Photonics Falcon camera using dynamic data exchange (DDE) commands to control Catalina Scientific's KestrelSpec 6.02 (or later) software application and as a result this software must also be running in order to acquire spectra using *LIBSoft*. Section 3.8 of this manual describes the installation of KestrelSpec and section 4.1 how to run it.

Using *LIBSoft* to control the spectrometer and camera it is possible to configure the system to acquire background-corrected spectra using a range of exposure times and integration delays. The integration delay is set by the

Quantum Composers delay generator and *LIBSoft* communicates directly with this device via a USB connection (see section 2.6). It is also possible to control the spectrometer and camera directly from KestrelSpec without the need for *LIBSoft* and doing so enables the use of additional functionality, e.g., different background-correction modes, spectrometer calibration and optimisation, which may prove useful under certain circumstances. Full details of the functionality of the spectrometer and camera can be found in the relevant Catalina Scientific and Raptor Photonics manuals. This manual details only the functions controlled via *LIBSoft*.

### 2.6 Quantum Composers Sapphire 9200 delay generator

*LIBSoft* communicates with the Quantum Composers delay generator via USB. The delay generator is used to configure the integration delay, i.e., the delay between the acquisition trigger pulse (usually from the laser Q-switch) and the start of the exposure of the camera detector. An alternative delay generator could be used for this but would need to be controlled manually rather than from within *LIBSoft*.

### 2.7 APL computer-controlled sample chambers

*LIBSoft* communicates with the XYZ-750 and other APL computer-controlled sample chambers via USB. *LIBSoft* provides manual control of each of the three stages in the sample chamber and automates the movement of the stages as required during the acquisition of LIBS spectra.

### 2.8 APL imaging kit

*LIBSoft* acquires images from the optional imaging kit via USB and displays live video on the main operating screen. Single frame images can also be acquired and saved. The imaging kit can incorporate up to two high definition cameras. One USB3 port is required for each camera in the imaging kit.

**NB** The imaging kit requires the proprietary USB3 cable provided to be used for connection to the system computer. Using a standard USB3 cable may result in a reduced frame rate or image freezing. The imaging kit can work with USB2 ports but again the video frame rate is likely to be reduced and the image may freeze so this is inadvisable.

### 2.9 IO device

A National Instruments USB 600x series IO device is used in some system configurations. For example, there is the facility *LIBSoft* to initiate an acquisition (fire the laser and acquire spectra) on receipt of a TTL trigger signal from an external system and to issue a TTL output signal on completion of the acquisition. Some laser systems also require an external shutter the operation of which is controlled by *LIBSoft*. The IO device is used for these functions.

# 3 Software installation

## 3.1 Introduction

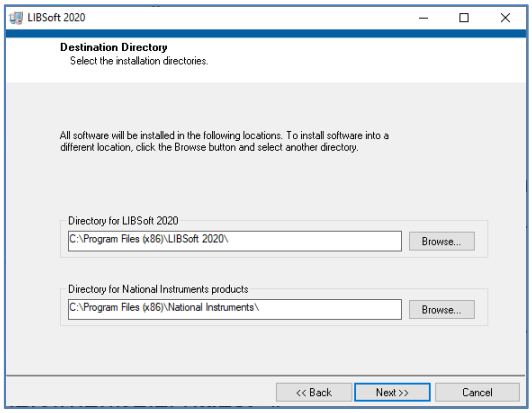
*LIBSoft* is the software application used to control all APL LIBS systems. Subsidiary software and drivers may also need to be installed depending on the hardware configuration of the specific system to be controlled. The installation of the main LIBSoft application is described in the following section and the installation of subsidiary software and drivers in the subsequent sections.

**NB** Do not connect any system component to the target computer until you are instructed to do so in this manual

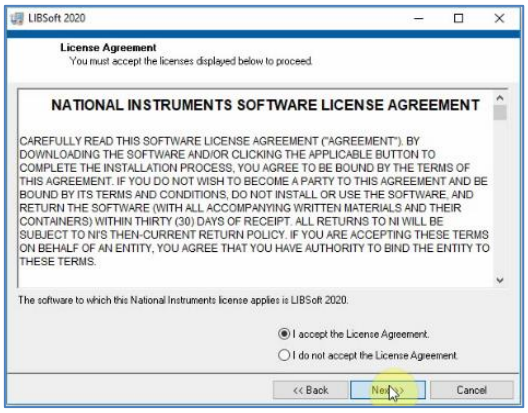
## 3.2 *LIBSoft* installation

The *LIBSoft* installation files will be provided either on a DVD or USB thumb drive with the LIBS system hardware or via an electronic file transfer for download. In the case of LIBSoft Full the installation files are also included on the USB dongle required to activate and use the enhanced analysis functions. The *LIBSoft* application can be installed and run on any PC running under Windows 7, 8 or 10. This description relates to the installation of *LIBSoft* on a standard PC running under Windows 10 however, the basic installation procedure is the same irrespective of the source of the installation files or the operating system. The installation procedure is as follows:

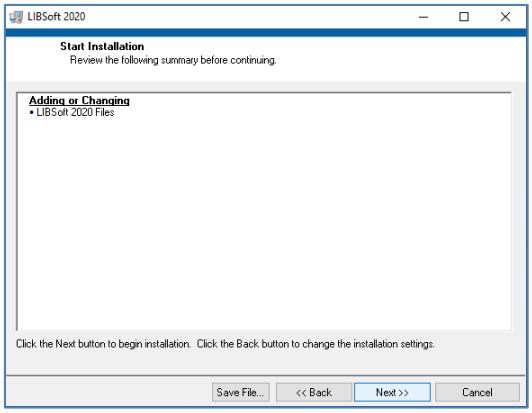
- Locate the installation files in Windows Explorer, navigate to the ***Volume*** sub-folder and run the file ***setup.exe***.
- Follow the Windows prompts for the installation.
- Accept the default installation folders then select ***Next***.



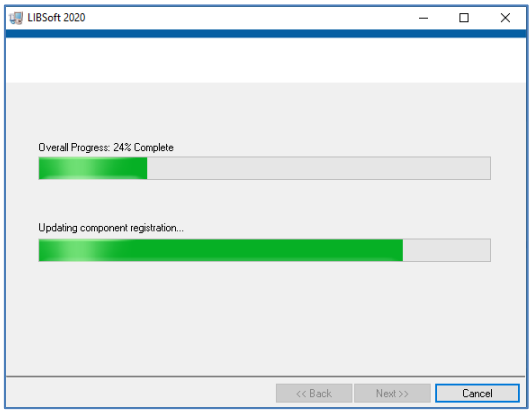

- Accept the displayed licence agreements then select ***Next***.



- Select ***Next*** to start the installation.

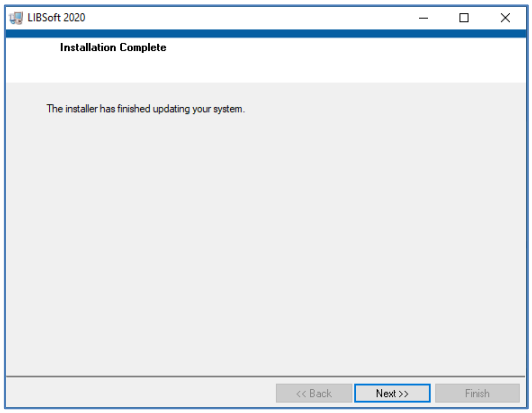



- Wait for the installation to complete.

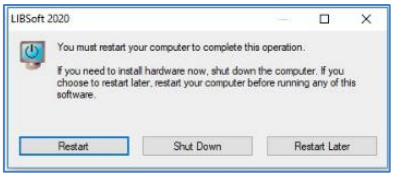



**NB** A new installation could take several minutes to complete depending on the specification of the computer on which the application is installed. An upgrade to an existing installation should take less than a minute.

- When the installation is complete select ***Next*** to close the installer window.




- Restart Windows if requested to do so.




- The *LIBSoft* application is now installed.

Additional software applications and drivers may need to be installed depending on the hardware components in the LIBS system that the *LIBSoft* application is to be used to control. For example:

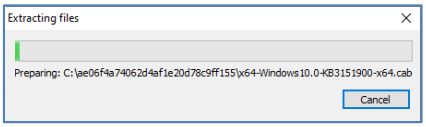
- The *LIBSoft* application requires that the Microsoft .NET Framework used by Windows is version 4.6.2 or higher.

- Systems incorporating a Catalina Scientific EMU spectrometer require the KestrelSpec application and the Raptor Photonics camera drivers to be installed.
- Systems incorporating Avantes spectrometers require the Avantes drivers to be installed.
- Systems using a SeaLevel USB-serial converter provided by APL require the SeaCOM drivers to be installed.

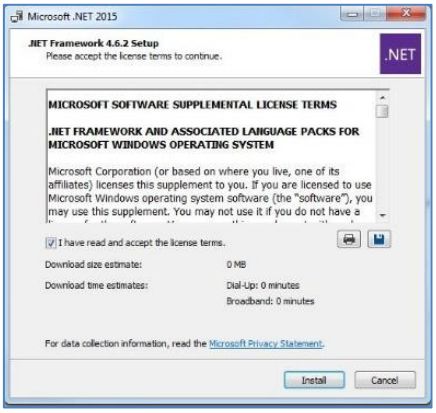
### 3.3 .NET installation

The *LIBSoft* application requires that the Microsoft .NET Framework used by Windows be version 4.6.2 or later. Most recent Windows installations will probably already include a later version of the .NET Framework but if the version currently used by the Windows installation is unknown then running the installer as described below will check and update it if required.

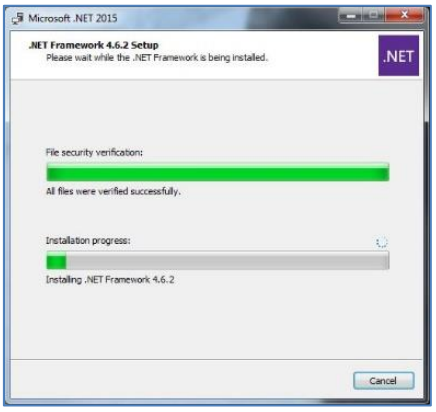
- Locate the *LIBSoft* application in Windows Program files using Windows Explorer and navigate to the ***Drivers*** sub-folder.
- Run the file ***NDP462-KB3151800-x86-x64-AllOS-ENU***.
- This will start the installation of the Microsoft .NET Framework 4.6.2 starting by extracting the relevant files from the installation disk.




- If version 4.6.2 does need to be installed a licence agreement will be displayed.

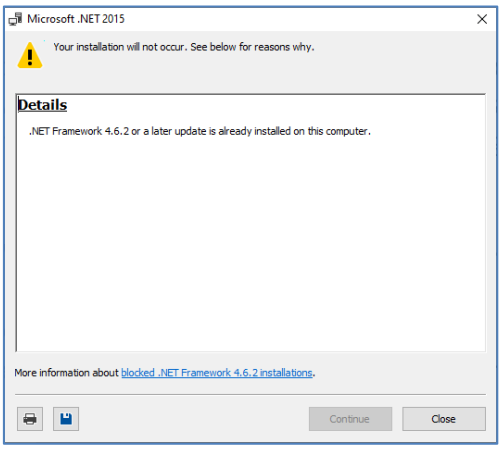



- Check the box to accept the terms of the agreement and select ***Install***.
- Wait for the installation to complete.



- Select ***Finish*** to close the installation window.

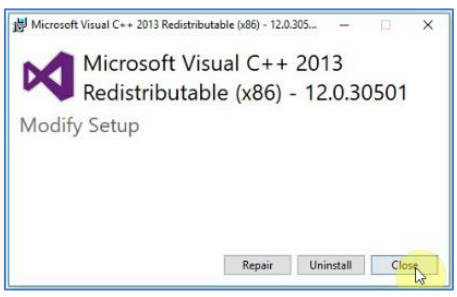

- If the installer finds that version 4.6.2 of the .NET Framework is already installed on the target computer options to either repair the existing version or remove it will be displayed. In this case either the repair option should be selected or the installation cancelled if it is known that the .NET Framework is already correctly installed.
- If the installer finds a later version of the .NET Framework already installed on the system computer a message to this effect will be displayed.
- Select ***Close*** to close the installation window.




### 3.4 Avantes driver installation

APL LIBS systems incorporating one or more Avantes spectrometers require the Avantes software drivers to be installed. This should be done before connecting the spectrometer module to the target computer. The Avantes drivers are included with the main *LIBSoft* installation files. The installation procedure is as follows:

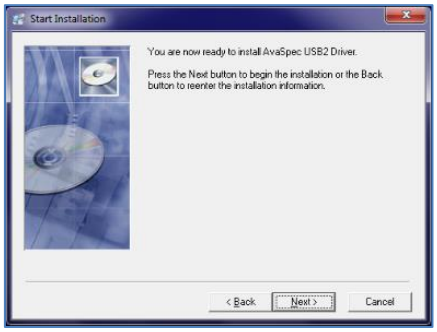
- Locate the *LIBSoft* application in Windows Program files using Windows Explorer and navigate to the ***Drivers*** sub-folder.
- Run the file ***vcredist_x86.exe***.
- Windows will start to install the *Microsoft C++ Redistributable* needed by the Avantes spectrometer DLL.
- Accept the default installation options presented and wait for the installation to complete.
- If Windows indicates that this is already installed the installation can be cancelled by selecting ***Close***.



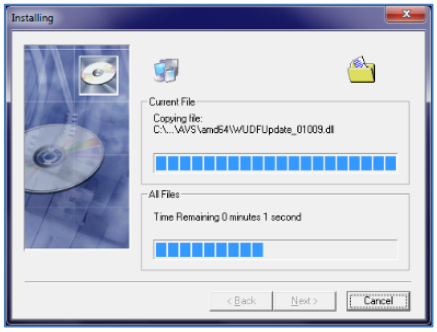

- Return to *LIBSoft* installation files in Windows Explorer and the ***Drivers*** sub-folder.

- Run the file ***dp_avaspec.exe***
- Windows will start to install the Avantes spectrometer DLL.
- Select ***Next*** to accept the default destination folder.

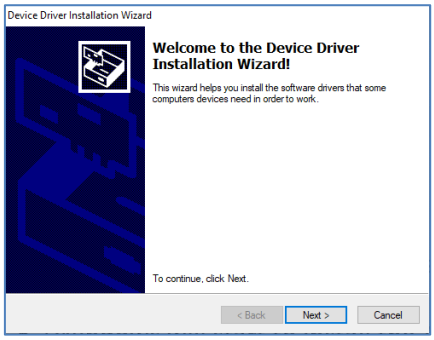

- The start installation window will be displayed.



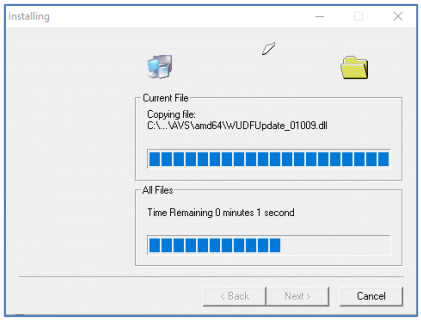

- Select ***Next*** to start the installation.




- A device driver installation wizard will open.

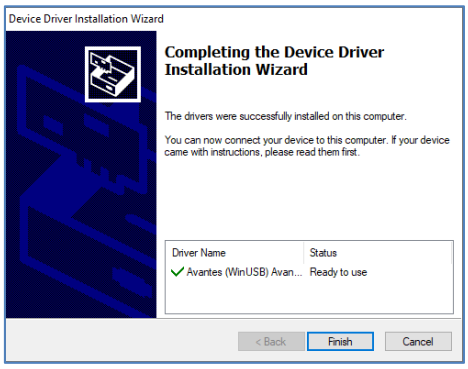


- Select ***Next*** and a window will be displayed indicating that the drivers are being installed.

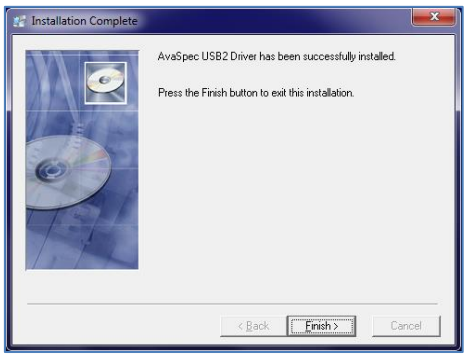



- A Windows security message may be displayed asking for permission to install the spectrometer drivers.

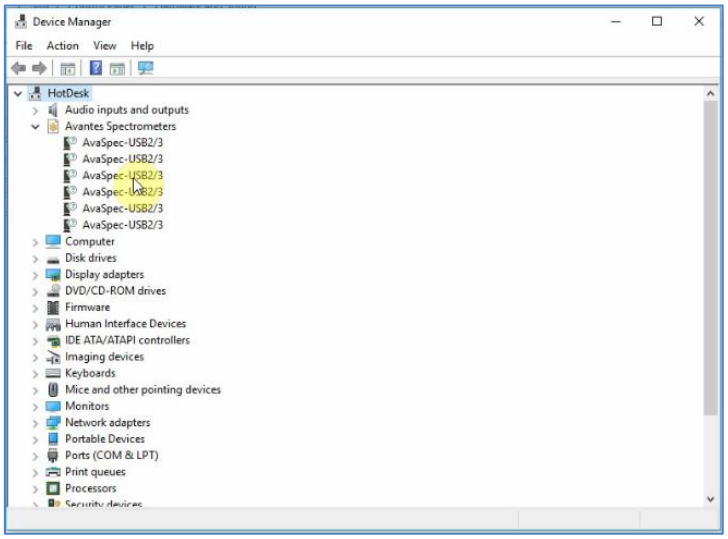

- If such a warning is displayed, select ***Install*** and the driver installation will continue.
- Select ***Finish*** to close the wizard.



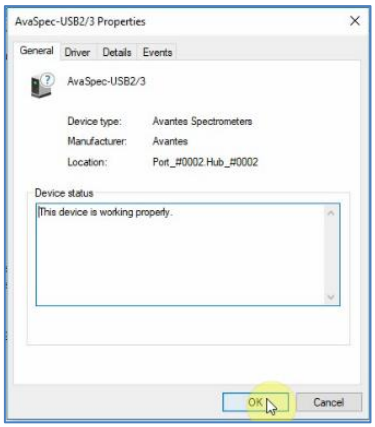

- Select ***Finish*** to close the installation complete window.




- Connect the spectrometer module to the target computer using the USB cable provided and ensure that the spectrometer module is powered.
- The computer will detect the attached spectrometer(s) and automatically load the driver software displaying a message to indicate that the software has been installed correctly.
- Use the Windows Device Manager to check that the spectrometer drivers have been installed correctly.
- There should be an ***Avantes Spectrometers*** heading with an ***AvaSpec-USB2/3*** entry for each of the spectrometers in the system.




- Right-click on these entries to display the device Properties to check that they are working correctly.



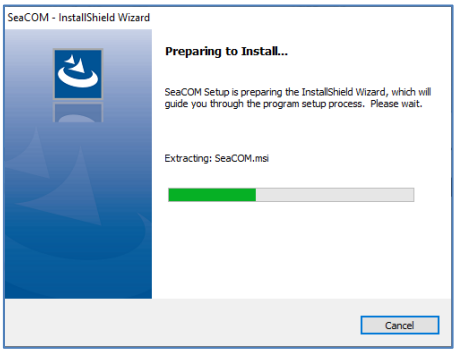

- The Avantes software drivers are now installed.

### 3.5 USB-serial converter driver installation

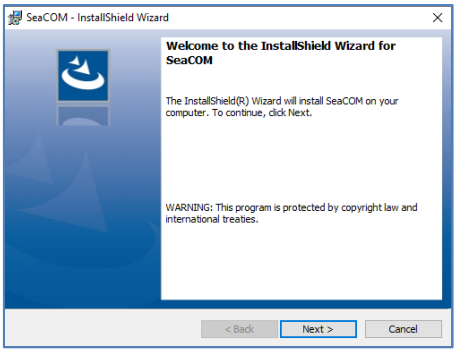
Some of the lasers used in APL LIBS systems use serial communications to implement control from the *LIBSoft* application. If the computer to be used with the LIBS system does not have a serial port, for example, many modern laptops, a USB-serial converter can be used. APL can provide a suitable SeaLevel converter with the system hardware.

This converter requires the installation of the SeaCOM software drivers. These drivers should be installed before connecting the converter to the computer. The installation procedure is as follows:

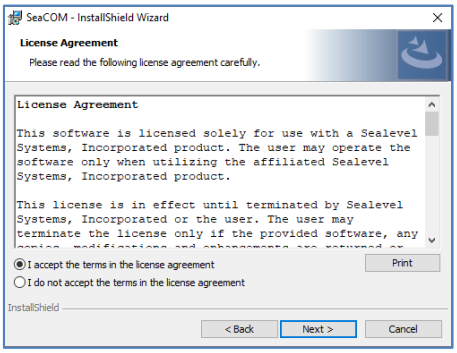
- Locate the *LIBSoft* application in Windows Program files using Windows Explorer and navigate to the ***Drivers*** sub-folder.
- Run the file ***USBConverter.exe***.
- The SeaCOM installation wizard will initialise.



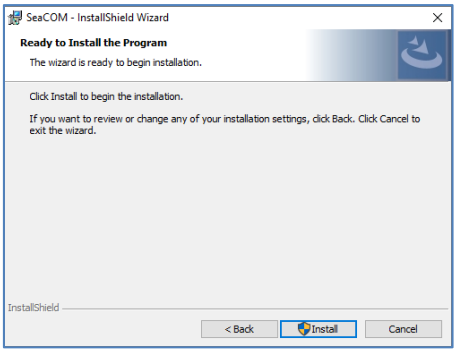

- When the wizard has initialised select ***Next***.



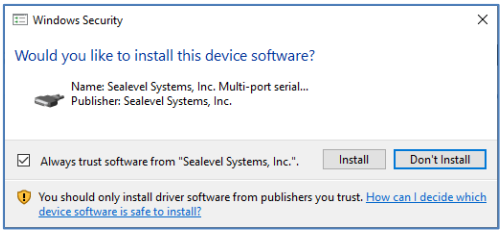

- Accept the licence agreement displayed and select ***Next***.



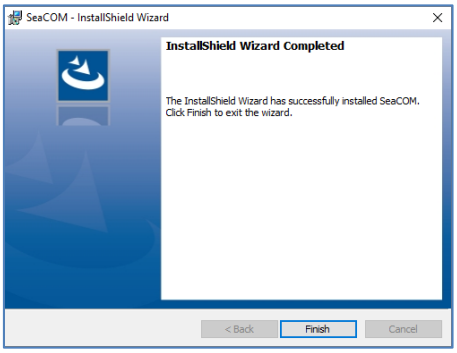

- Select ***Install*** to start the driver installation.



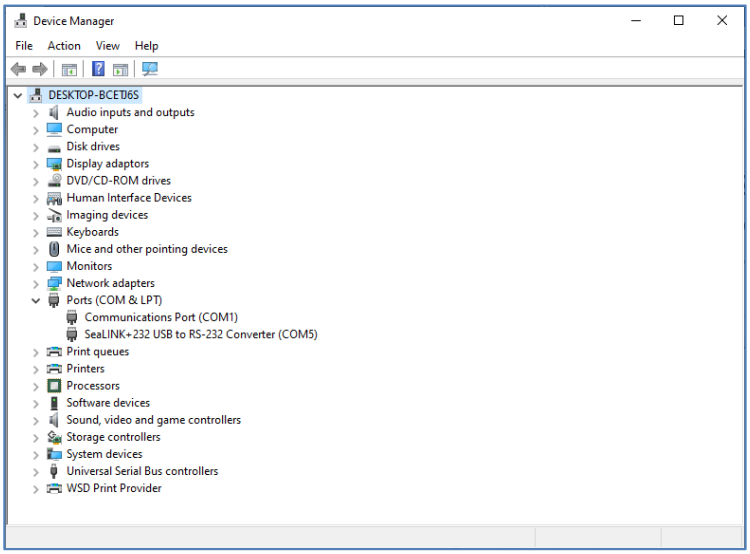
- If a Windows Security warning is displayed, select ***Install*** and wait for the installation to complete.




- Select ***Finish*** to close the installation window.




- Connect the USB-serial converter to a suitable port on the target.
- The computer will detect the attached USB converter and automatically load the driver software displaying a message to indicate that the software has been installed correctly.
- Use the Windows Device Manager to check that the USB-serial converter drivers have been installed correctly.
- There should be a ***SeaLINK+232 USB to RS-232 Converter*** entry under the *Ports (COM & LPT)* heading (the COM port number allocated to the converter is system specific).



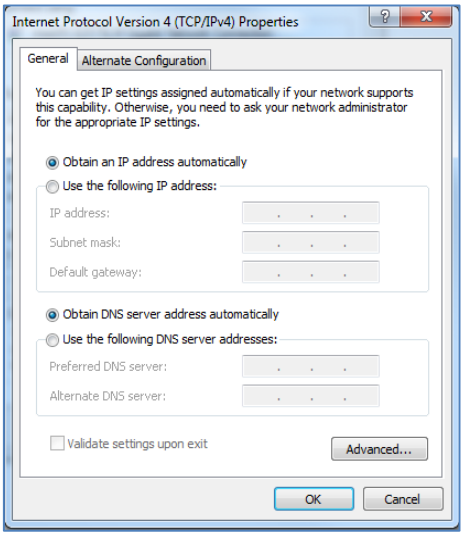

- The software drivers for the USB-serial converter are now installed.

### 3.6 Configuration of communication settings for use with Quantel Q-Smart lasers

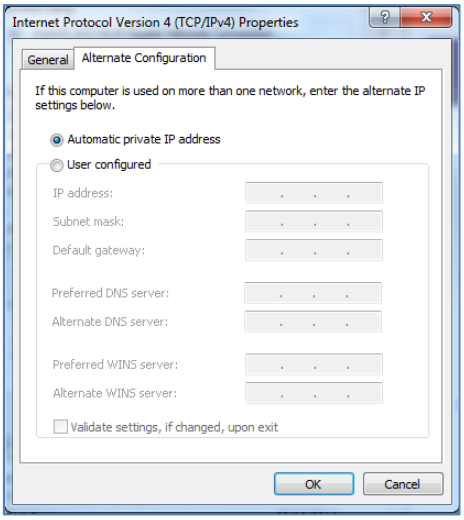
The Quantel Q-Smart 450/850 lasers communicate with the system computer over ethernet. In order to do this the IP settings on the system computer must be configured to match those of the laser. The IP settings required for communication with the laser can be specified as an *Alternate Configuration* in the system computer's network settings. This can be done by following the procedure outlined below (illustrated here using Windows 7).

- Access the *TCP/IPv4 Properties* on the system computer by selecting ***Control Panel > Network and Internet > Network and Sharing Center > Change adapter settings > Local Area Connection > Properties > Internet Protocol Version 4 (TCP/IPv4) > Properties***. The following window will be displayed.

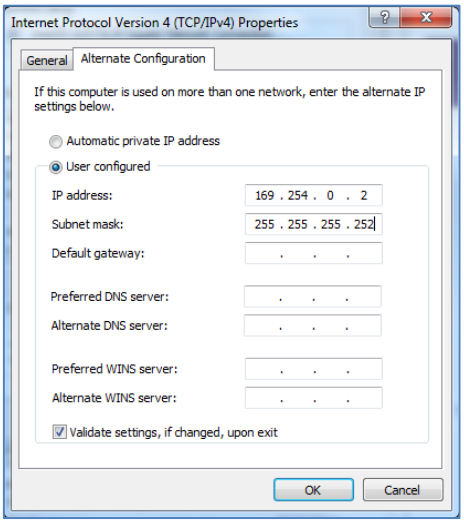
  **NB** The settings displayed may vary depending on the current configuration of the system computer.




- Select the ***Alternate Configuration*** tab




- Select *User configured* and enter ***169.254.0.2*** as the *IP address* and ***255.255.255.252*** as the *Subnet mask*.

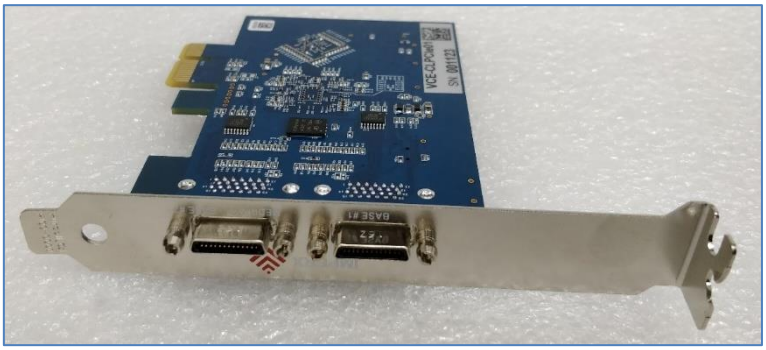



- Select ***OK*** to save these parameters then close all the open Control Panel windows. The system computer will then be configured to control the Q-Smart laser.

### 3.7 Installing the Imperx FrameLink PCIe card

The EMU-65 spectrometer with Raptor Photonics Falcon camera interfaces to the system computer via a proprietary interface which requires the installation an Imperx FrameLink frame grabber card in the system

computer. If using a desktop computer, the FrameLink card should be installed in a suitable PCIe slot in the system computer. If using a laptop, the alternative ExpressCard/34 frame grabber will be required.

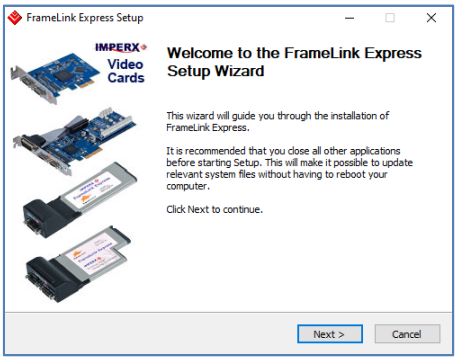


FrameLink card


ExpressCard/34 frame grabber

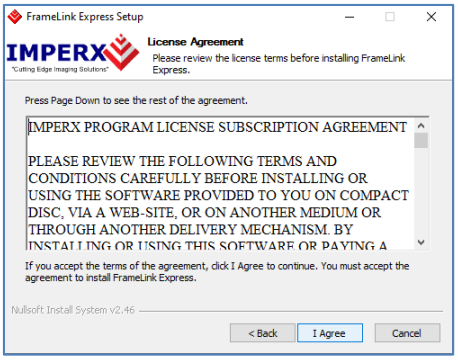
The installation procedure is as follows:

- Install the appropriate card in the system computer.
- Restart the computer.
- In Windows Explorer navigate to the ***Imperx FrameLink*** folder and run the ***Flex Software*** set-up program.
- The FrameLink Express Setup Wizard will open

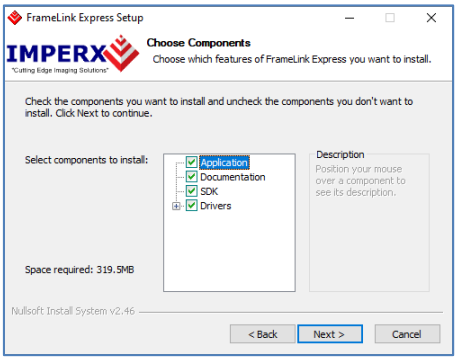



- Select ***Next*** to start the installation.

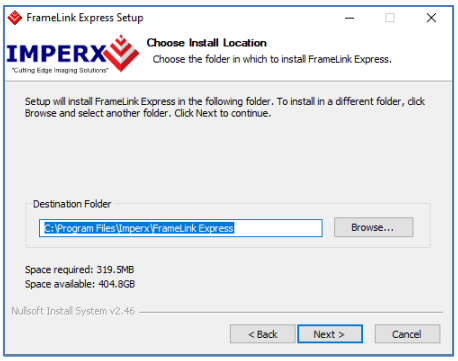
- Accept the licence agreement displayed.



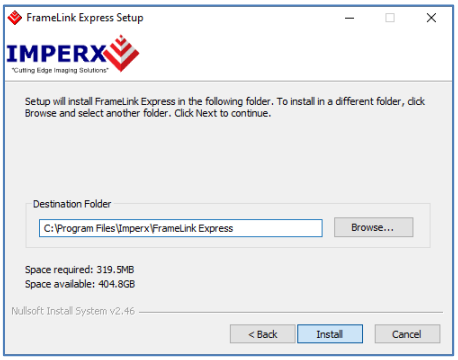

- Accept the default installation components



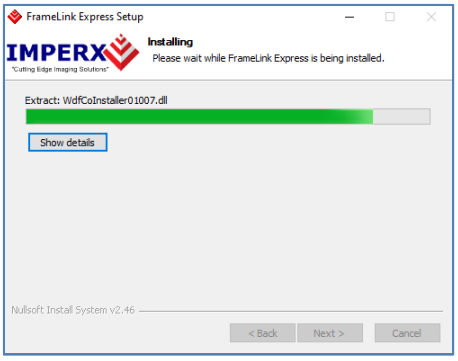

- Accept the default installation folder



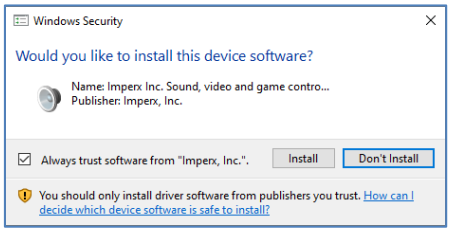

- Select ***Install*** to start the installation.



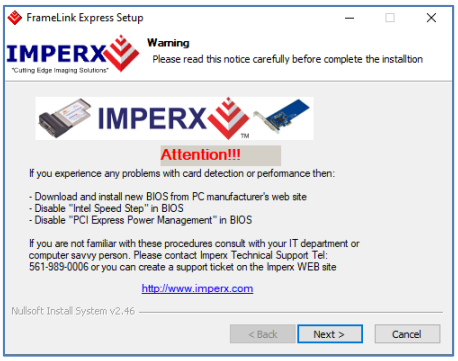
- Wait for the installation to complete.



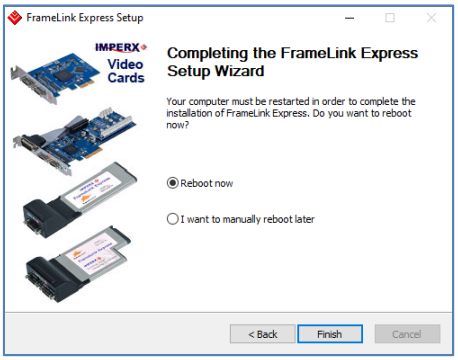

- If a Windows Security warning is displayed, select ***Install***.




- When the installation is complete select Next to close the installation window.




- Reboot the computer if instructed to do so.



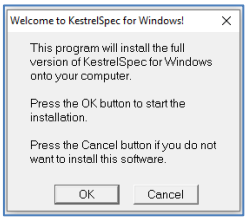

- The Framelink card should now be recognised by Windows.
- Refer to the Catalina Scientific and Imperx documentation shipped with the system for further information.

### 3.8 KestrelSpec installation

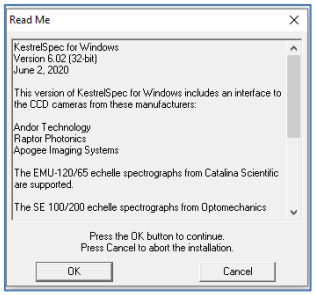
KestrelSpec is a software application written by Catalina Scientific to configure and control their EMU spectrometer. *LIBSoft* communicates with KestrelSpec using Windows Dynamic Data Exchange (DDE) to implement the configuration and control functions required to acquire and display spectra with the EMU spectrometer. KestrelSpec therefore needs to be installed on the target computer and to be running in the background in order for *LIBSoft* to control APL LIBS systems incorporating an EMU spectrometer.

The KestrelSpec installation files will be provided either on a DVD or USB thumb drive with the LIBS system hardware or via an electronic file transfer for download. The installation procedure is as follows:

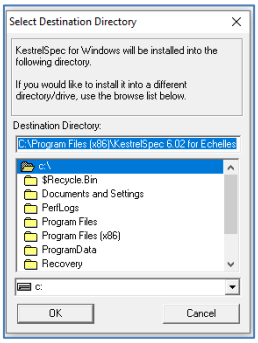
- Load the DVD or insert the USB thumb drive into the target computer or copy the downloaded files to any suitable location on it.
- Locate the installation files in Windows Explorer.
- Run the file ***Setup.exe***.
- The installer will initialise.
- Select ***OK*** to start the installation.



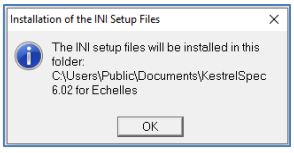

- Select ***OK*** to close the information window displayed.



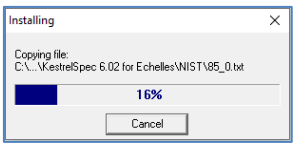

- Select ***OK*** to accept the default installation locations.



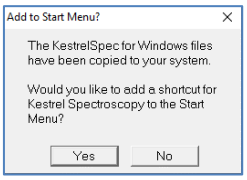

- Select ***OK*** to continue the installation.



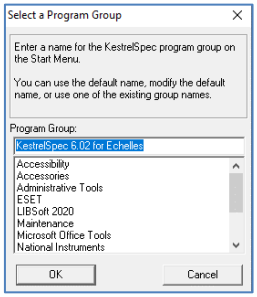
- Wait for the installation to complete.




- Add a shortcut to the Start menu if required.



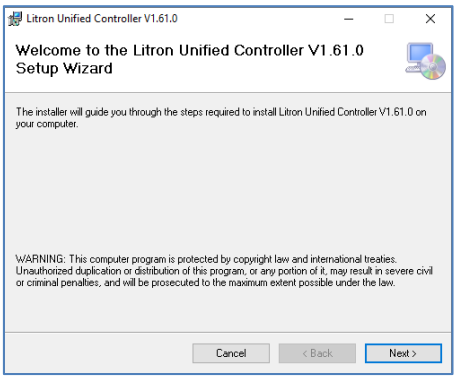

- Accept the default program group.



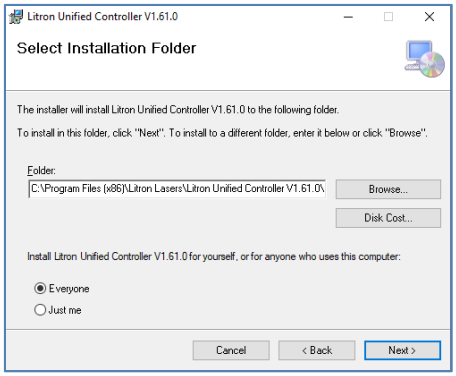

### 3.9 Litron Unified Controller software installation

The Litron Unified Controller software is provided by the manufacturer for the control of their lasers. However, for virtually all Litron lasers all of the required control functionality can be managed by *LIBSoft*. The exception to this is for crystal tuning operations that are required by the Bernoulli laser. Therefore, the Litron Unified Controller software only needs to be installed if the LIBS system in use includes a Litron Bernoulli laser. The installation procedure is as follows:

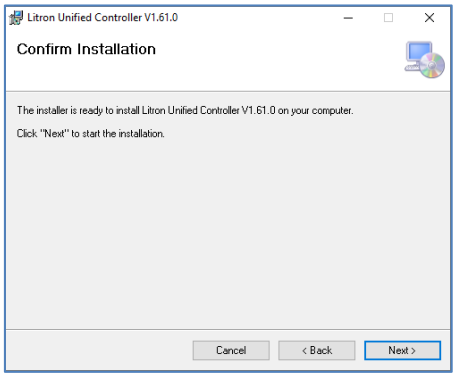
- In windows Explorer navigate to the Folder containing the Litron Unified Controller set-up program.
- Run this program.
- The installation wizard will initialise.
- Select ***Next*** to start the installation.



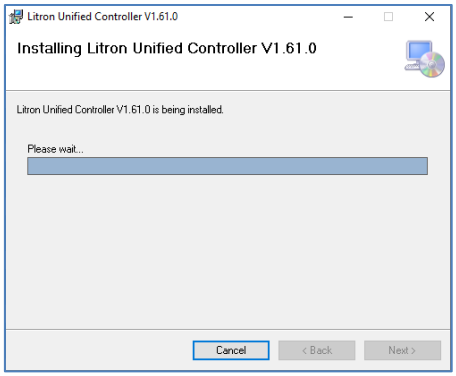
- Select ***Next*** to accept the default installation folder.



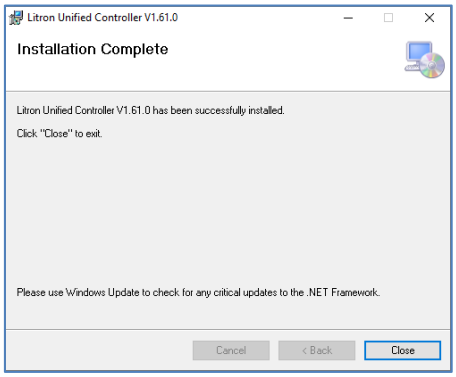

- Select ***Next*** to confirm the installation.




- Wait for the installation to complete.




- Close the installation window.




- The Litron control software should now be installed on the computer.

# 4 Software start-up and initialisation

## 4.1 Starting KestrelSpec (applicable only to systems featuring an EMU spectrometer)

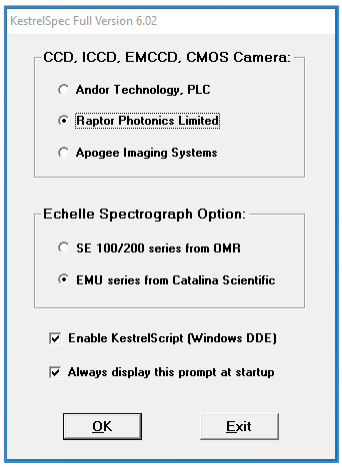
KestrelSpec is a software application written by Catalina Scientific to configure and control their EMU spectrometer. *LIBSoft* communicates with KestrelSpec using Windows Dynamic Data Exchange or DDE to implement the configuration and control functions required to acquire and display spectra with the EMU spectrometer. KestrelSpec therefore needs to be installed on the target computer and to be running in the background in order for *LIBSoft* to control APL LIBS systems incorporating an EMU spectrometer.

Before running the KestrelSpec application, make sure that the Imperx FrameLink PCIe card is correctly installed in the target computer or, if using a laptop, the alternative ExpressCard/34 frame grabber is installed. Also make sure that the Raptor Photonics Falcon camera that is used with the EMU spectrograph is correctly connected to the computer and that the camera is powered using the interface and power supply cables provided.

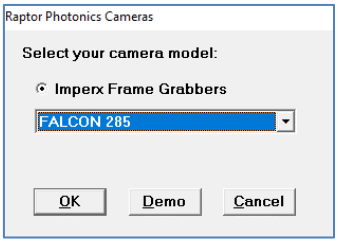
- Start the KestrelSpec application.


- Select the appropriate hardware options from the initial configuration window, in particular ensure that the following options are selected/enabled then select ***OK***:
  - ***Raptor Photonics Limited*** camera
  - ***EMU series from Catalina Scientific*** Echelle spectrograph
  - ***KestrelScript*** (Windows DDE)

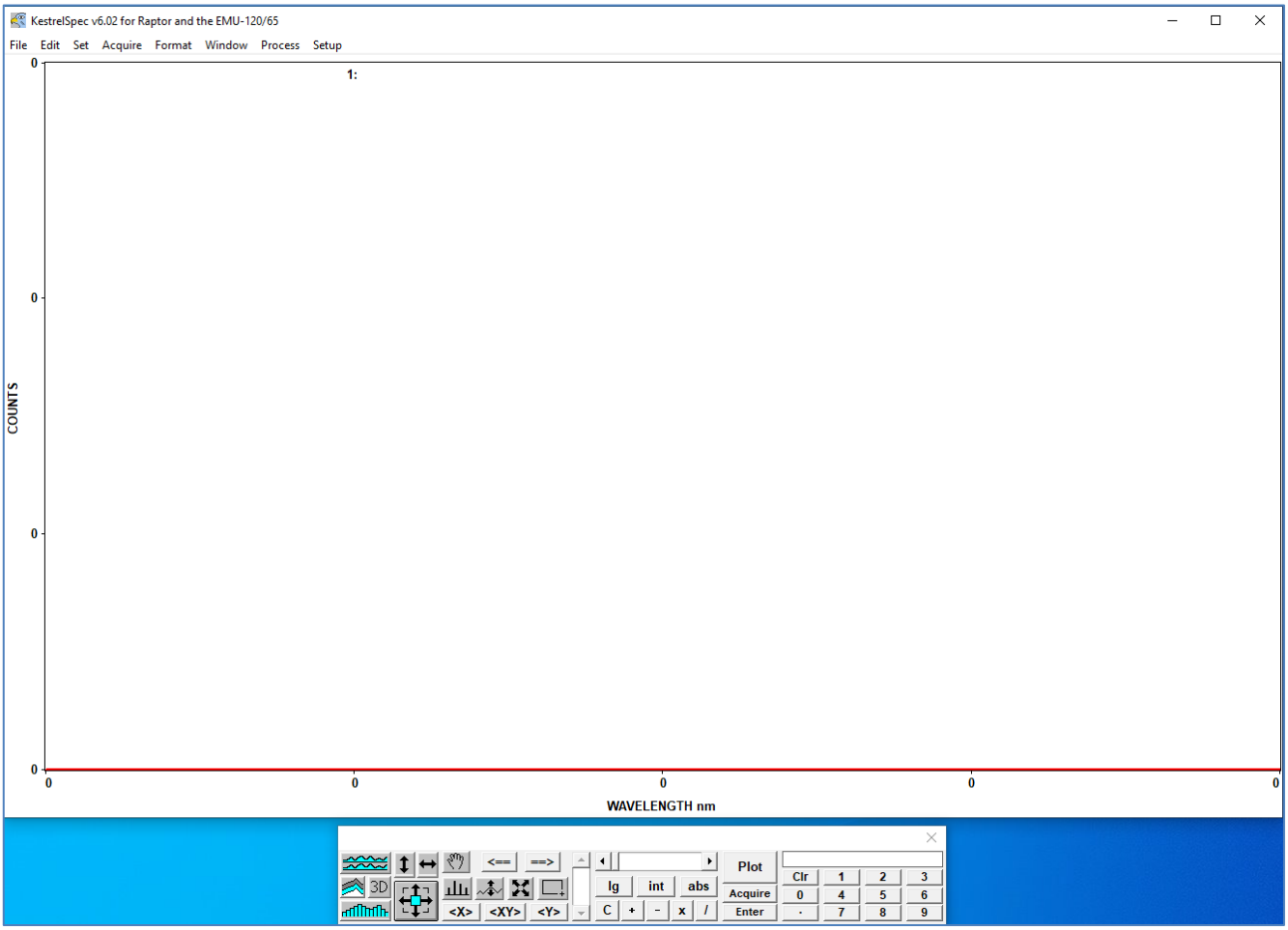
  **NB** It is essential that *KestrelScript* is enabled to allow communication between the *LIBSoft* and KestrelSpec applications.




- Select the ***Falcon 285*** frame grabber on the second configuration window that is displayed then select ***OK***.




- If the camera is connected and powered correctly the KestrelSpec main screen will open.

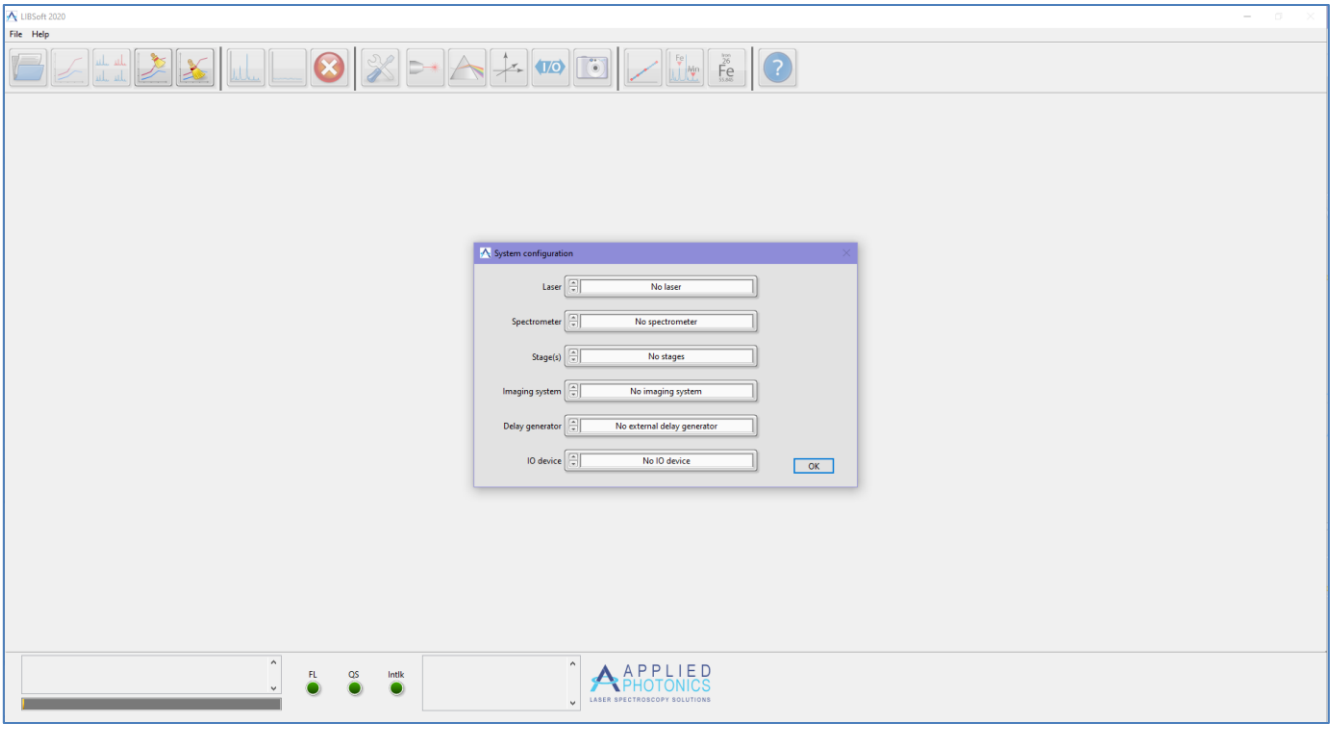



- If a failure to initialise the Imperx frame grabber is displayed check the interface and power connections.
- Once the KestrelSpec main screen has opened it can be minimised and left to run in the background.
  **NB** Avoid using KestrelSpec directly when running *LIBSoft* as this could cause a failure of the DDE and prevent *LIBSoft* from controlling the spectrometer correctly.
- Once the *LIBSoft* application has been shut down, KestrelSpec may also be closed.

Note that the *LIBSoft* user interface provides all the control and functionality necessary to configure the spectrometer to acquire, display and save spectra. Certain specialist functions however, such as calibration of the spectrometer, require use of the KestrelSpec user interface. The EMU spectrometer should be recalibrated periodically, preferably before each daily use to account for possible wavelength drift due temperature variations and to check that the system is operating correctly. This can be done quite simply using a mercury-argon calibration lamp and the KestrelSpec application. Calibration of the spectrometer is described in section Appendix A.

### 4.2 Starting *LIBSoft*

Start the *LIBSoft* application and the main application screen will open together with the *System configuration* window.

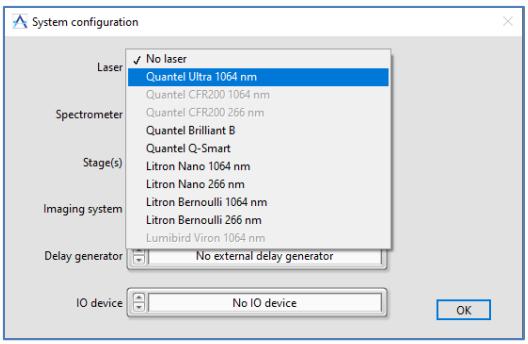



APL LIBS systems are highly modular by design and can therefore incorporate various combinations of hardware components. Each of these hardware components has its own particular interface and configuration requirements. The *System configuration* window allows the hardware components of a particular system to be specified so that the *LIBSoft* application can initialise and control each one correctly. The following components can be specified:

- Laser
- Spectrometer
- Stage(s)
- Imaging system
- Delay generator
- IO device

The first time that the *LIBSoft* application is started no hardware components will be selected. This configuration is the initial default option and can also be used when no hardware is attached to the computer allowing previously saved spectra to be viewed and manipulated. Once a particular configuration has been selected it will be saved to the *LIBSoft* system configuration file when the application is shut down. The saved system configuration will be loaded automatically next time the *LIBSoft* application is started so that there is no need to re-enter the details every time unless the hardware configuration has been changed.

To specify a component, click on the entry to be changed to display a list of the options or click on the up/down arrows to cycle through the options. Note that if a component name is greyed-out, control of that component has not yet been integrated with the version of *LIBSoft* that is currently installed.



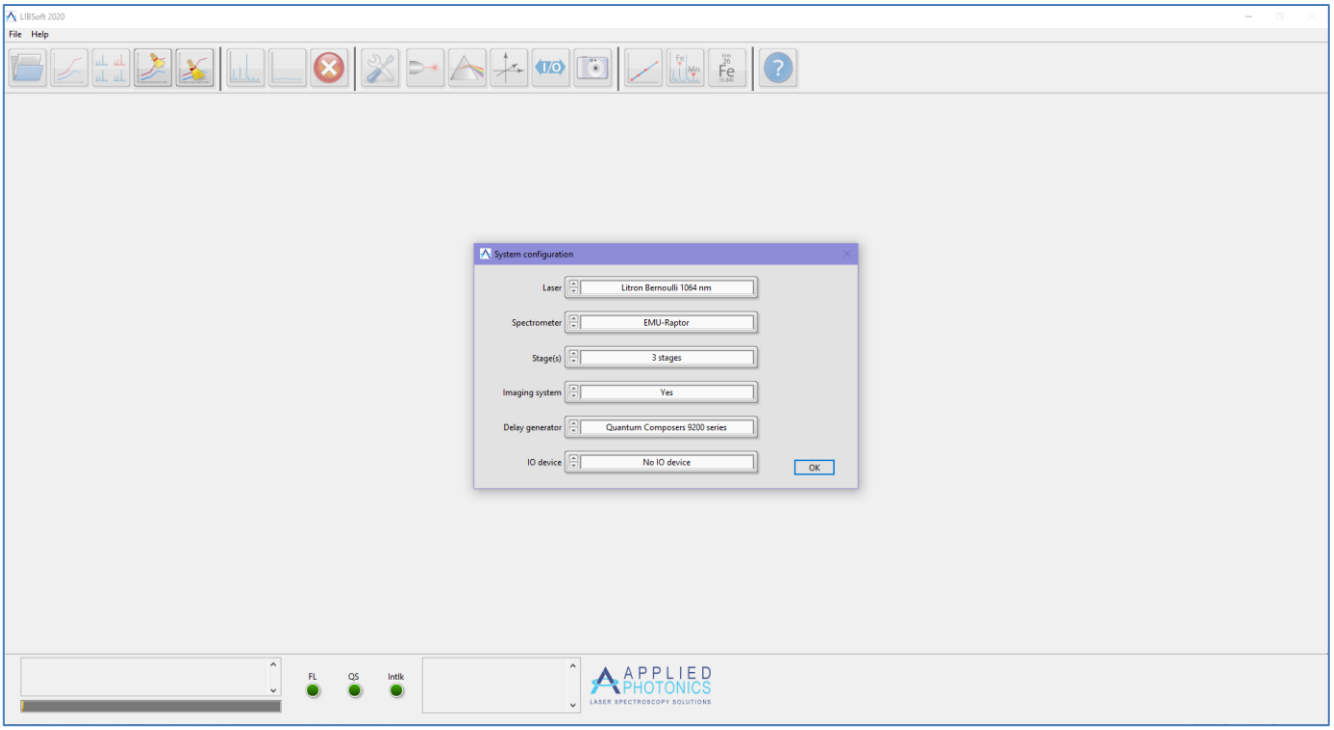
Note also that not all systems require all hardware components. For example:

- Systems incorporating the Avantes spectrometers don't require a delay generator whereas those that use an EMU spectrometer do.
- A computer-controlled sample chamber and an imaging system are optional items and therefore there might be no stages and no imaging system.
- It is also possible to acquire spectra using a laser that is not under the control of *LIBSoft* provided that it is configured to trigger the spectrometer(s) correctly.

However, if a component is not connected it is important that this is specified on the system configuration screen otherwise *LIBSoft* will try and then fail to initialise it.

The following image shows the configuration screen for a system that comprises the following components:

- A Litron Bernoulli laser configured to operate at 1064 nm
- A Catalina Scientific EMU spectrometer with a Raptor Photonics camera
- A computer-controlled sample chamber with 3 translation stages
- An integrated imaging system
- A Quantum Composers 9200 series delay generator




When all of the hardware components have been selected make sure that each of them is connected to the computer and powered correctly and turned on. If an EMU spectrometer has been specified, as it has in this case, it is important to also make sure that the KestrelSpec application has been started and is running in the background. Once this has been done select ***OK***.

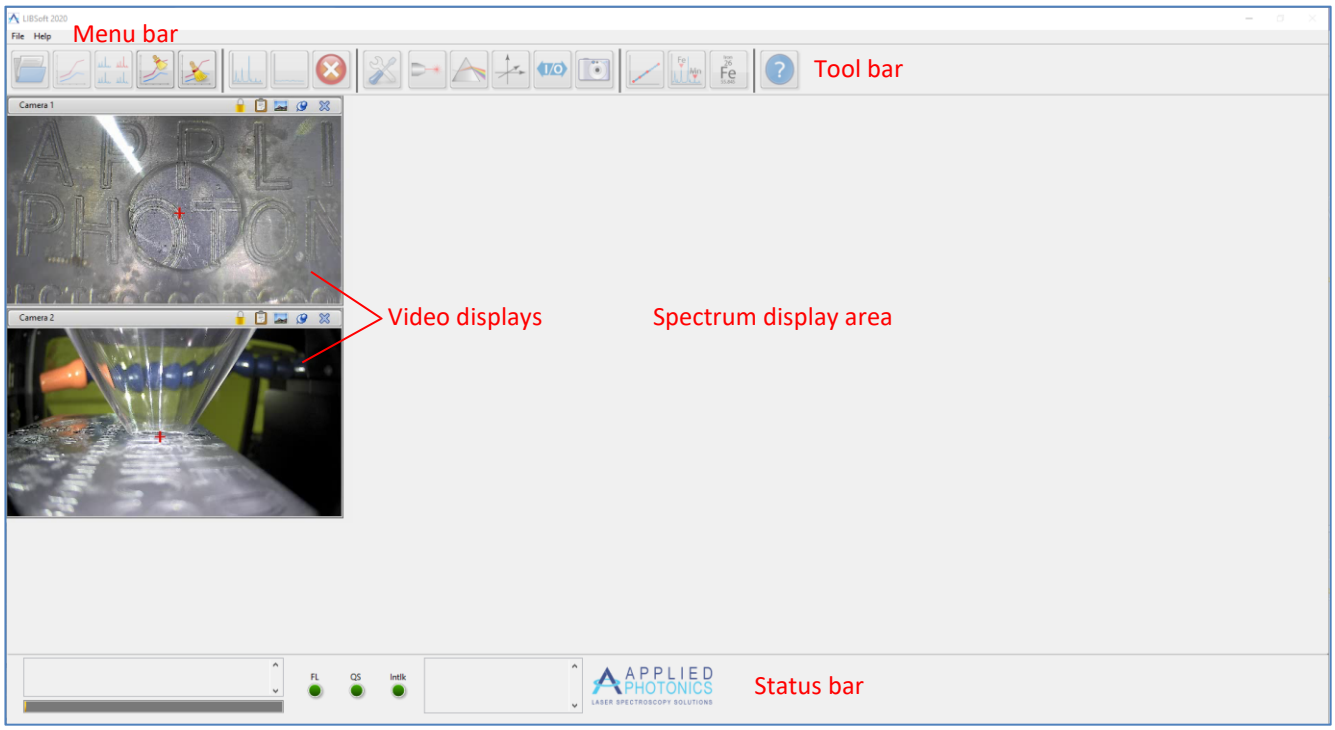
The system configuration window will close and *LIBSoft* will then connect to and initialise each hardware component in turn reporting its progress in the status bar at the bottom of the main screen. Any errors in the initialisation process will be reported in the status bar and/or additional dialogue messages. When the initialisation process is complete the system status will be displayed as ***Ready*** and the shortcut buttons in the main toolbar will be enabled according to the connected hardware components and enabled options. The main *LIBSoft* screen is described in section 4.3. Configuration of the application parameters is described in section 5.

### 4.3 *LIBSoft* main screen

Once the *LIBSoft* application has been configured and initialised correctly the main operating screen will be displayed. This screen is divided into a number of regions:

- At the top there is the *Menu bar*
- Below this there is a *Tool bar* providing shortcut buttons to the most commonly used menu items

- The main region of the screen is the *Spectrum display area* used for the display of acquired spectra
- If an imaging kit is connected the *Video display(s)* are initially positioned at the left-hand side of the screen
- At the bottom of the screen is the *Status bar*




At the far left of the status bar, status messages are displayed describing the current operation of the system. Just below that there is a progress bar that is displayed during certain operations such as when the laser flashlamp is warming up. To the right of the status message window there are three indicators to show the current state of the laser flashlamp (***FL***), Q-switch (***QS***) and interlock (***Intlk***). For these indicators green indicates a "safe" state, for example as shown above, the flashlamp or Q-switch are disabled and there is no laser interlock error. Red indicates a warning, so the flashlamp and/or Q-switch is enabled or that a laser interlock has been activated. Details of any interlock errors are displayed in the window to the right of these indicators.

The shortcut buttons in the tool bar are, from left to right, as follows:

-  : ***Load saved spectra***: select and display spectra previously acquired using *LIBSoft*
-  : ***Compare spectra***: select saved spectra for comparison
-  : ***Select spectrum to view***: select which of the spectra currently in memory to display
-  : ***Close current spectrum***: close the currently displayed spectrum
-  : ***Close all spectra***: close all of the spectra currently in memory
-  : ***Acquire spectra***: initiate the acquisition of spectra using the currently configured parameters
-  : ***Acquire a background spectrum***: manually initiate the acquisition of a background spectrum
-  : ***Abort an acquisition***: stop an ongoing acquisition
-  : ***Open the acquisition configuration window***
-  : ***Open the laser control and configuration window***
-  : ***Open the spectrometer configuration window***
-  : ***Open the stages control and configuration window***

-  : ***Open the I/O device configuration window***
-  : ***Open the camera configuration window***
-  : ***Open the quantitative calibration window***
-  : ***Open the peak identification window***
-  : ***Open the element identification window***
-  : ***Open the application help files***

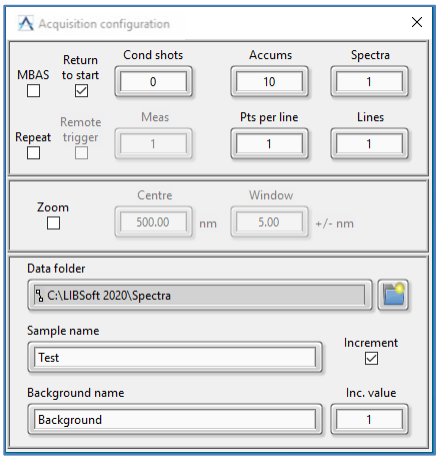
Note that hovering the mouse over any of the toolbar buttons will display a “tip strip” to describe its function. Note also that if a button is greyed-out it means that the hardware component to which it relates is not connected to the system or the option to which it relates is not currently enabled. Details of the functions to which each of these buttons relate are described in later sections of this manual:

- Section 5 describes the configuration screens that are accessed using these tool bar buttons.
- Section 7 describes the acquisition of analysis and background spectra.
- Section 9 describes the display, comparison and manipulation of acquired spectra accessed using these buttons.
- Section 10 describes the quantitative calibration functions (*LIBSoft Full* only)
- Section 11 describes the peak identification functions (*LIBSoft Full* only)
- Section 12 describes the element identification functions (*LIBSoft Full* only)

# 5 Software configuration

## 5.1 Acquisition configuration

The  shortcut button will open the acquisition configuration window. This button will be enabled as long as a spectrometer is connected to the system and has been successfully detected and initialised by *LIBSoft*. Selecting the shortcut button will display the configuration window on top of the main *LIBSoft* screen.



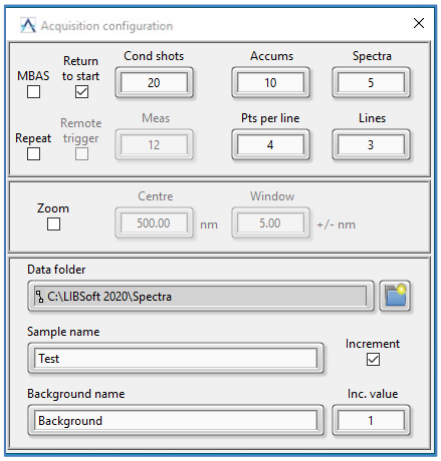

The parameters displayed in this window are virtually the same irrespective of the hardware components used.

At the top of the screen are the parameters that specify the number of laser shots that will be fired to acquire each spectrum and how many spectra will be acquired when an acquisition is initiated.
These parameters are as follows:

- ***Cond shots***: the number of sample conditioning shots
  This is the number of laser shots that will be fired at the start of each measurement before any spectra are acquired. These shots will be fired at the maximum repetition rate of the laser and can be used to clean dirt and debris from the surface of the sample when spectra from the underlying substrate are required.
- ***Accums***: the number of accumulation shots
  This is the number of laser shots during which data are acquired to generate a single spectrum.
- ***Spectra***: the number of spectra
  This is the number of spectra that are acquired at each measurement location
- ***Meas***: the number of measurements
  This is the number of measurement locations from which spectra will be acquired. If the LIBS system includes either a manual sample chamber or no sample chamber at all, the user will be prompted to move the sample between each measurement. If the LIBS system includes a computer-controlled sample chamber with two or more stages, the number of measurements parameter will be greyed-out as shown above. Using such a sample chamber a raster pattern of measurement locations can be specified using the following two parameters.
- ***Pts per line*** and ***Lines***: the number of points per line and the number of lines
  These two parameters specify the dimensions of the raster pattern of measurement locations. The total number of measurements is calculated as the product of these values and the number of measurements parameter is updated accordingly. These two parameters will be hidden if the LIBS system does not include a computer-controlled sample chamber. The distance between the measurement locations can be set in the stages control and configuration window via the X and Y step interval values (see section 5.4 for further details).

As an example, these parameters could be configured as follows:

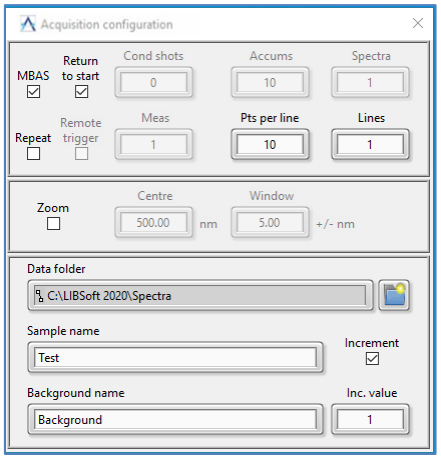
- Number of conditioning shots = 20
- Number of accumulations = 10
- Number of spectra = 5
- Number of points per line = 4
- Number of lines = 3




With this configuration the system will acquire spectra from 12 measurement locations in a raster pattern consisting of 3 lines of 4 locations on each line. At each of the 12 measurement locations the laser will fire 20 conditioning shots to clean the sample surface and then acquire 5 spectra each consisting of an accumulation of data over 10 laser shots.

Also in the top section of the configuration window, is a checkbox labelled ***MBAS***. *MBAS* stands for Move Between Accumulation Shots. The *MBAS* check box allows the analysis location to be moved between each laser shot that makes up the acquisition of a single spectrum. Using the *MBAS* option allows the acquisition of data from the sample surface only and reduces the effect of interferences from the underlying substrate. This can therefore be useful for analysing surface coatings. The surface coating does however need to be uniform over the area analysed.

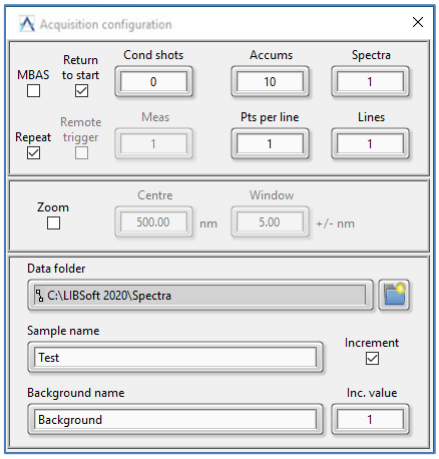
With a manually-controlled sample chamber the user will be prompted to move the sample between each accumulation shot. With a computer-controlled sample chamber the sample will be moved automatically between accumulation shots and they can be specified in a raster pattern using the number of points per line and number of lines parameters. So, in this case if *MBAS* is enabled, the number of accumulations is calculated as the product of the number of points per line and the number of lines and the number of accumulations parameter itself is disabled. If moving the analysis location between each accumulation shot there is no point in firing conditioning shots or acquiring multiple spectra. The number of conditioning shots will therefore also be automatically set to 0 and both the number of spectra and number of measurements to 1 and these controls will be disabled. An example of this for which 10 accumulation shots will be fired in a single line is shown below.




If there is a computer-controlled sample chamber connected to the system a second check box labelled ***Return to start*** will be displayed in this top section of the window. If this is checked the X and Y axis stages will be automatically returned to their starting positions following completion of the specified scan of the sample.

Also in the top section of the configuration window, is a checkbox labelled ***Repeat***. When this is checked the system will continue to repeat the specified acquisition until the ***Abort*** button -  - in the tool bar is selected. This option can be useful, for example, when setting up the system so that repeat acquisitions can be performed while adjusting

the laser focus to observe the effect of doing so on the acquired spectra without needing to initiate each one manually.

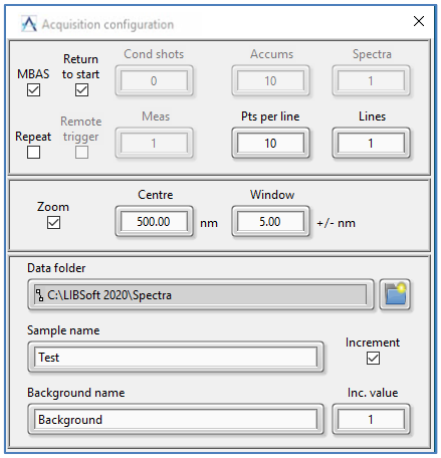



Finally in this top section of the window, there is a ***Remote trigger*** checkbox. This will be disabled and greyed-out unless a suitable IO device is connected to the system and both detected and initialised by *LIBSoft* (see 2.9). If enabled and this option is checked, when an acquisition is initiated from *LIBSoft* using the ***Acquire*** button -  - in the tool bar, the software will wait for a trigger from an external device before performing the specified acquisition and when the acquisition is complete will issue an output signal to the external device to indicate this and that the system is ready to perform another acquisition if required. The ***Abort*** button -  - in the tool bar must be selected to exit this waiting state and return *LIBSoft* to the ready state.

The parameters described above allow the user to configure the acquisition to match the different types of analyses usually performed using LIBS. The table below details typical combinations of parameter values that could be used in several analysis scenarios. However, it should be noted that the combinations suggested are not exhaustive and the values suggested here are intended only as an indicative guide and the user should tailor them to their specific application.

| | |
|---|---|
| Analysis of a solid material at a given sample position | Cond shots = 50<br>Accums = 50<br>Spectra = 1<br>Meas = 1<br>MBAS = Disabled |
| Analysis of a solid material at several sample positions (replicated measurements) | Cond shots = 50<br>Accums = 50<br>Spectra = 1<br>Meas = 5<br>MBAS = Disabled |
| Depth profile analysis at a given sample position | Cond shots = 0<br>Accums = 1<br>Spectra = 100<br>Meas = 1<br>MBAS = Disabled |
| Analysis of a homogeneous thin layer | Cond shots = 0<br>Accums = 10<br>Spectra = 1<br>Meas = 1<br>MBAS = Enabled |
| 3D analysis of a sample (for systems with automatic stages) | Cond shots = 0<br>Accums = 1<br>Spectra = 10<br>Meas = 25 (Pts per line = 5, Lines = 5)<br>MBAS = Disabled |

In the central region of the acquisition configuration window there is a ***Zoom*** check box. If this is enabled the other two parameters in this section, ***Centre*** and ***Window***, will be enabled as shown below.




Enabling the *Zoom* option means that when spectra are subsequently acquired the display will automatically be zoomed to the wavelength range specified by the *Centre* and *Window* parameters. *Centre* specifies the centre wavelength of the displayed wavelength range. *Window* specifies the wavelength range either side of the centre wavelength that will be displayed. The *Zoom* function is useful if a specific peak or region of the spectrum needs to be checked following each acquisition. The full wavelength range of the attached spectrometer is still acquired and saved and the displayed range can easily be expanded to show this full wavelength range of the acquired spectrum.

The lower section of the acquisition configuration window contains the parameters used to specify the file names of the saved spectra.

The ***Data folder*** parameter allows the folder to which both the analysis and background spectra are saved to be specified. This can be done using the folder browser button or by entering a path directly.

The ***Sample name*** parameter specifies the root file name for the acquired spectra. Any spaces in the *Sample name* entered by the user are automatically replaced by underscores. By default, a numeric value is appended to the *Sample name* and is incremented following the acquisition of each spectrum. This avoids the need to update the sample name for each new spectrum and the possibility of spectrum files being overwritten. The ***Inc. value*** parameter specifies the numeric value that will be appended to the sample name of the next spectrum acquired if this option is enabled. This option can be disabled by unchecking the ***Increment*** check box.

When multiple measurements are specified for an acquisition, an indication of the measurement number is also appended to the file name. Similarly, if a measurement consists of multiple spectra these spectra are saved in a single file and the filename is appended with an “S” to indicate this. Details of the file naming principles used by *LIBSoft* are described in section 8.

The ***Background name*** parameter is used to specify the file name of the background spectra acquired by the system. This only really applies when using Avantes spectrometers as background spectra for the EMU spectrometer are held in memory in KestrelSpec and not saved to disk.

The parameter values currently displayed in this configuration window will be saved to the *LIBSoft* configuration file when the application is shut down and automatically reloaded the next time the application is started.

If the system computer has a single monitor the acquisition configuration window will be closed automatically when a different configuration window is opened or one of the other shortcut buttons in the main screen tool bar is selected. If the system computer has dual monitors the acquisition configuration window will remain open. It can then be dragged to the second monitor and left open for faster access. It can however still be closed manually if required.

## 5.2 Laser configuration

### 5.2.1 Introduction

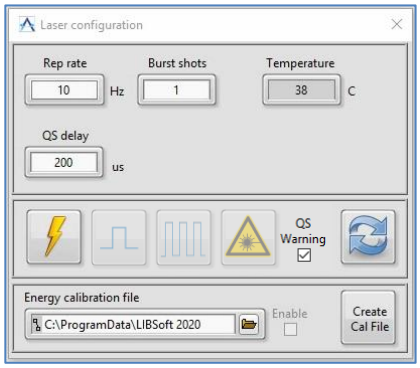
The  shortcut button will open the laser control and configuration window. This button will be enabled as long as a laser is connected to the system and has been successfully detected and initialised by *LIBSoft*. Selecting the shortcut button will display the configuration window on top of the main *LIBSoft* screen. The parameters displayed in this window are the same for most types of laser. The exception to this is the Litron Bernoulli laser the configuration screen for which will be described separately.

The parameter values currently displayed in this configuration window will be saved to the *LIBSoft* configuration file when the application is shut down and automatically reloaded the next time the application is started.

If the system computer has a single monitor the laser control and configuration window will be closed automatically when a different configuration window is opened or one of the other shortcut buttons in the main screen toolbar is selected. If the system computer has dual monitors the laser configuration window will remain open. It can then be dragged to the second monitor and left open for faster access. It can however still be closed manually if required.

### 5.2.2 General laser configuration

The general laser control and configuration window is shown below.




In the central region of the laser configuration window are a set of buttons for controlling the laser manually. These are:

-  : ***Start/stop the flashlamp***
-  : ***Pulse the laser*** (fire a single shot)
-  : ***Fire a burst***
-  : ***Start/stop continuous firing***

During an acquisition the operation of the laser is controlled automatically by the *LIBSoft* application. These manual controls are therefore only used when testing and configuring the laser.

To the right of the *Start/stop continuous firing* button there is a checkbox labelled ***QS warning***. When this is checked and the button is pressed to start the laser firing continuously a warning will be displayed which must be acknowledged by the user before the laser will actually start firing. This is to prevent potential damage to delicate samples if this button is selected by mistake. The default configuration is for this option to be enabled, however it can easily be disabled by unchecking the checkbox. This setting is saved to the system configuration file and is reloaded automatically the next time the application is started.

The  button to the right of these controls can be used to reinitialise the laser. There should be no need to use this button unless for some reason there is a communications failure between the computer and the laser.

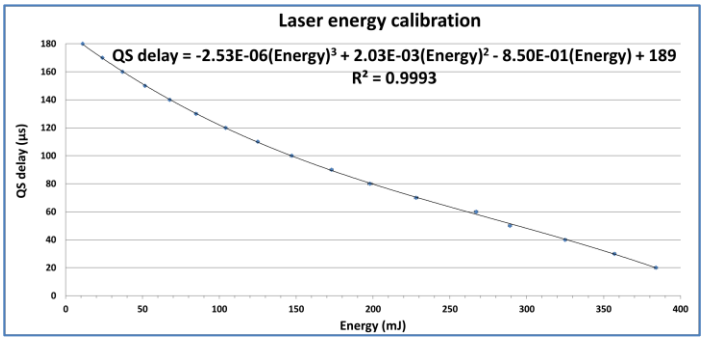
At the top of the laser configuration window there is a continuous display of the laser ***Temperature*** and the parameters that control how the laser operates.

The ***Rep rate*** parameter allows the user to set the repetition rate at which the laser will fire a burst or continuously if the manual laser controls are used and while acquiring spectra. The repetition rate will however be automatically set to the maximum rate for the laser when firing conditioning shots in order to minimise the time it takes to fire these shots. Depending on the performance of the computer and the type of spectrometer used, acquisition timeouts could occur at higher laser repetition rates. If acquisition timeouts are observed the first course of action is to reduce the laser repetition rate.

The ***Burst shots*** parameter sets the number of laser shots that will be fired when a burst is initiated using the manual controls. The number of shots fired during an acquisition is determined by the acquisition configuration parameters.

The ***QS delay*** parameter sets the delay between flashlamp and Q-switch triggers and is used to set the laser energy. Generally, the lower the value the higher the energy. The range of values applicable to each type of laser is different and values entered will be automatically coerced to the allowable range for the specified laser.

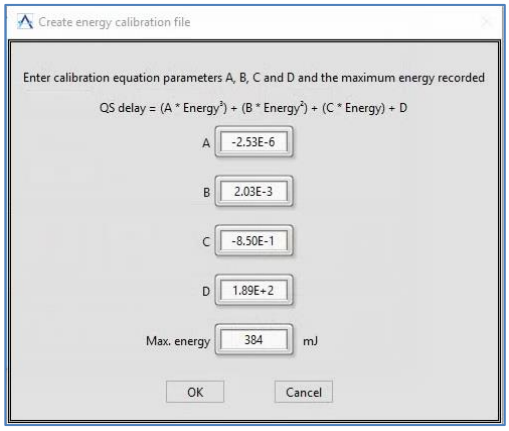
A laser energy calibration is provided by APL as part of the test report shipped with each system. This calibration specifies the relationship between the flashlamp - Q-switch delay and the laser energy. A typical example is shown below.




A calibration file can be created from these calibration data and used by *LIBSoft* to allow an energy value to be entered directly into the software. This value will then be automatically converted to the corresponding value of flashlamp – Q-switch delay and sent to the laser.

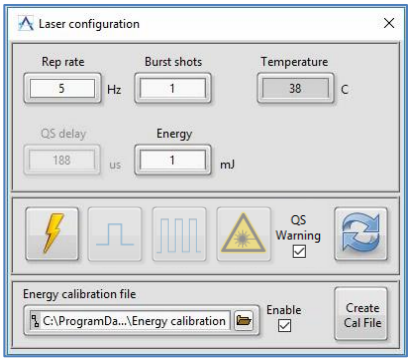
The Create energy calibration file button - 

- can be used to generate a calibration file from within *LIBSoft*. On selecting this button, a new window will be opened into which the calibration parameters detailed in the system test report can be entered.




The energy calibration is in the form of a cubic equation. Enter the calibration equation coefficients and the maximum energy used during the calibration as specified in the test report and select ***OK***. The calibration file

will be generated automatically. Save the file to a suitable location using the file browser. The path to this file will be automatically entered as the ***Energy calibration file*** in the laser configuration window. Enable the calibration by checking the ***Enable*** option.

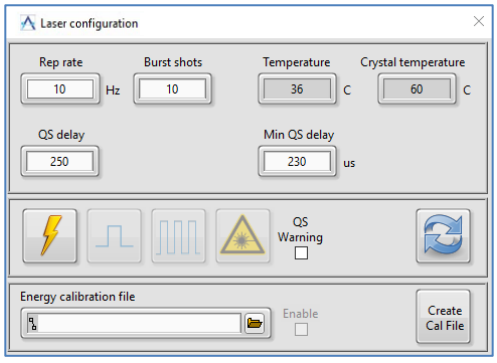



An ***Energy*** parameter will then be displayed and the *QS delay* control will be disabled. Changing the laser energy directly will now automatically update the value of *QS delay*. To check that the coefficients have been entered correctly set a number of different energy values and check that the displayed value of *QS delay* is close to that reported in the system test report. Disabling the laser energy calibration file by unchecking the *Enable* option will cause the *Energy* control to be hidden and the *QS delay* control to be re-enabled.

### 5.2.3 Litron Nano 266 nm configuration

The Litron Nano 266 nm laser control and configuration screen is shown below and includes two additional parameters:

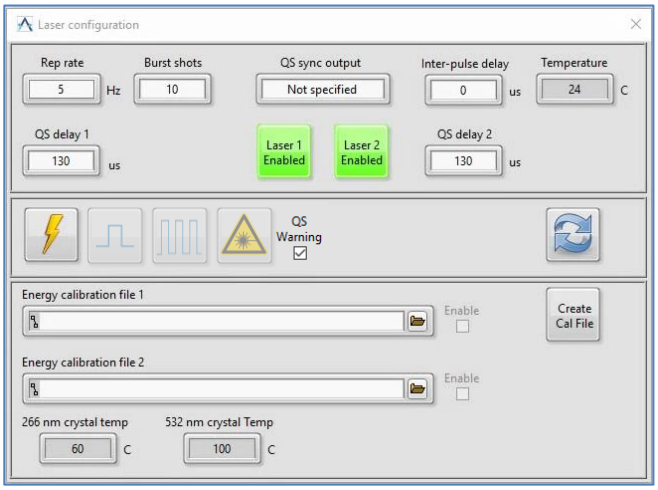
- ***Crystal temperature*** which simply displays the temperature of the crystal which should be ~ 100 °C once stabilised
- ***Min QS delay*** which limits the lowest value of ***QS delay*** that can be entered and hence the maximum ***Energy*** of the laser




**NB** The recommended value of ***Min QS delay*** is laser-specific and indicated in the system test report. It is important that the recommended value is set on the *LIBSoft* laser control and configuration screen before the laser if fired for the first time. Once set the value is saved to the *LIBSoft* configuration file when the system is shut down and automatically reloaded when *LIBSoft* is started subsequently. Reducing the ***QS delay*** below the recommended value and hence increasing the energy could induce damage in delicate samples and/or the laser optics.

### 5.2.4 Litron Bernoulli laser configuration

The Litron Bernoulli laser control and configuration window is shown below.



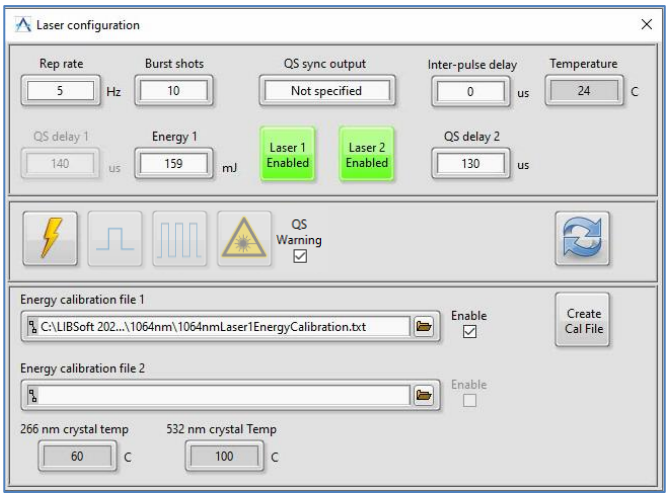

The parameters displayed in this window for the Litron Bernoulli laser are slightly different to those displayed for other lasers. This is because the Litron Bernoulli actually comprises two lasers some of the parameters for which need to be configured separately. This means that the configuration parameters are essentially duplicated. There are also a number of additional controls.

It should be noted that the Litron Bernoulli laser can be configured to operate either at 266 nm or 1064 nm. The configuration required to set the operating wavelength is done in hardware and can then be optimised using Litron's own software (see section 3.9) outside of the *LIBSoft* application. The only software configuration changes are made during the initialisation of *LIBSoft* and as long as the correct operating wavelength for the Bernoulli laser is selected in the *LIBSoft System configuration* window, no further changes are required. This laser configuration window is the same irrespective of the operating wavelength of the Bernoulli laser.

The manual laser controls are just the same as for all other lasers and are displayed in the central region of the laser configuration window. As will be described shortly, the Bernoulli laser can be configured to use either of the two lasers of which it is comprised or both of them together. The manual controls will therefore operate whichever of the lasers is enabled or both together if both lasers are enabled.

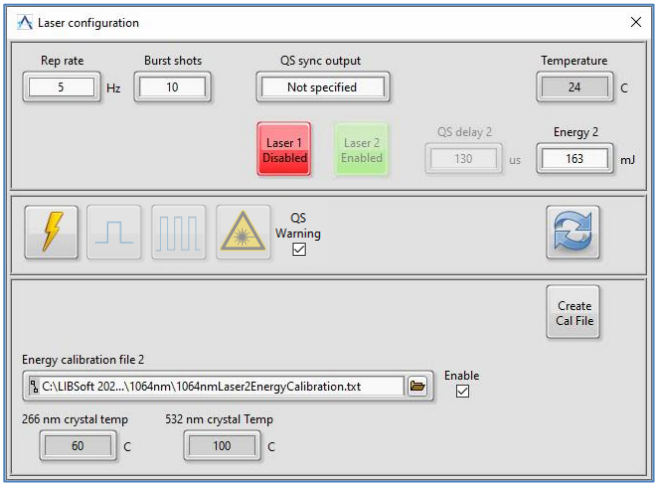
The ***Rep rate*** and ***Burst shots*** controls displayed in the upper part of the configuration window are just the same as used for other lasers. These parameters apply to whichever of the two lasers is enabled or both of them if both lasers are enabled.

Two ***QS delay*** controls are displayed, one for each laser. This allows a different output energy to be configured for each laser. In addition, a second laser ***Energy calibration file*** can be specified in the lower section of the screen. In this way a separate energy calibration can be applied for each laser. The calibration file can be enabled in the same way as for other lasers. When a calibration is enabled, an ***Energy*** control is displayed for the laser to which it relates and the *QS delay* control for that laser is disabled (as shown below).



When using both lasers it is possible to add a delay between the shots generated by the two lasers. This delay is configured using the ***Inter-pulse delay*** control at the top of the configuration window. A positive value of delay will cause laser 1 to fire before laser 2. A negative value of delay will cause laser 2 to fire before laser 1. If only one of the lasers is enabled this value has no meaning and the control is therefore hidden.
When using both lasers the Q-switch synchronisation output from either of the lasers can be used to trigger the spectrometer. This choice is a hardware configuration depending solely on which socket on the laser power supply is connected to the trigger input on the spectrometer. However, a ***QS sync output*** selector is provided at the top of the configuration window to be used as an aide memoir. This selector does not affect the laser operation in any way but its setting is added to the parameter configuration file saved with each acquired spectrum as a reminder of the Q-switch sync output used for the acquisition. It is the responsibility of the user to select the option that matches the actual hardware configuration.

The Laser 1 Enabled and Laser 2 Enabled buttons in the middle of the upper section of the configuration window can be used to enable/disable an individual laser. When a laser is disabled in this way the controls for that laser are hidden as shown in the configuration window below where Laser 1 has been disabled.




Note that if either laser is active then these buttons will be disabled, i.e., if the flashlamp and/or Q-switch on either laser is enabled, then the laser selection cannot be changed.

The only other difference between the laser configuration window for the Bernoulli laser and other lasers is the display of the crystal temperatures at the bottom of the window. The ***266 nm crystal temp*** should be approximately 60 °C and the ***532 nm crystal temp*** should be approximately 100 °C for stable operation. These temperatures should stabilise at or near these values a short time after the laser is powered on and initialised by *LIBSoft*.

## 5.3 Spectrometer configuration

### 5.3.1 Introduction

The  shortcut button will open the spectrometer configuration window. This button will be enabled as long as a spectrometer is connected to the system and has been successfully detected and initialised by *LIBSoft*. Selecting the shortcut button will display the configuration window on top of the main *LIBSoft* screen.

*LIBSoft* can control either one or more Avantes AvaSpec spectrometers or a single Catalina Scientific EMU spectrometer. The Avantes AvaSpec spectrometers can be one of three types: 2048, 2048CL or 4096CL and are usually housed in an APL SpectroModule-6 or SpectroModule-8 although it is also possible to use these spectrometers as stand-alone devices.

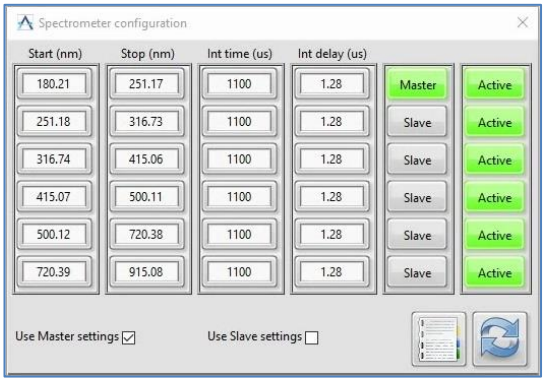
The parameters that need to be configured for the AvaSpec and EMU spectrometers are slightly different and therefore the configuration window displayed for each type of spectrometer is also different. These configuration windows are described in the following two sections.

The parameter values currently displayed in this configuration window will be saved to the *LIBSoft* configuration file when the application is shut down and automatically reloaded the next time the application is started.

If the system computer has a single monitor the spectrometer configuration window will be closed automatically when a different configuration window is opened or one of the other shortcut buttons in the main screen toolbar is selected. If the system computer has dual monitors, the spectrometer configuration window will remain open. It can then be dragged to the second monitor and left open for faster access. It can however still be closed manually if required.

### 5.3.2 Avantes spectrometer configuration

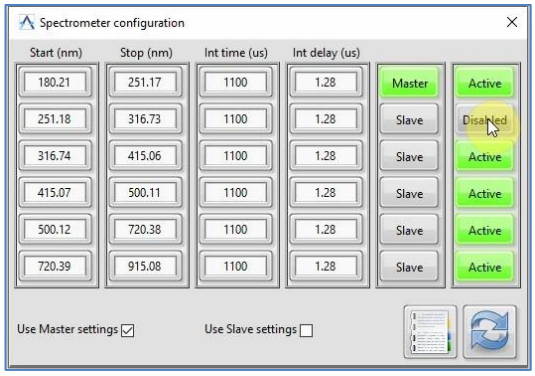
An APL spectrometer module can contain from 1 to 8 Avantes spectrometer channels depending on the overall bandwidth of the module. The spectrometer configuration window shows the parameters for each channel separately. The configuration window for a 6-channel spectrometer module is shown below.



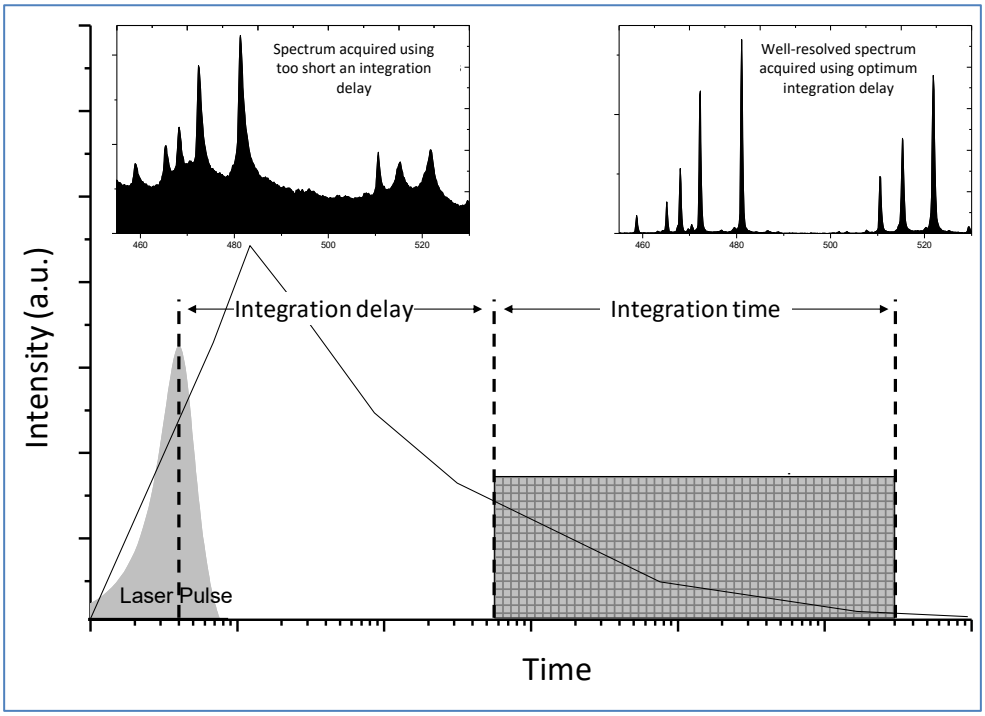

One of the channels is designated as the ***Master*** channel and the remaining channels as ***Slave*** channels. The trigger signal from the laser Q-switch is connected to the *Master* channel and the *Slave* channels are synchronised to the *Master*. The *Master* channel is factory-set as the channel with the lowest wavelength range. It is therefore important that this channel is configured as the *Master* in the spectrometer configuration window. This should be set by default and there is no reason to change this setting unless the hardware in the spectrometer module is reconfigured. If the incorrect channel is set as the *Master* in the spectrometer configuration window, spectrum acquisitions will time-out as the spectrometers will not receive a trigger signal from the laser Q-switch.

The wavelength range of each channel is also factory-set so that the overall wavelength range of the spectrometer module is continuous without any wavelength gaps or overlaps between channels. The wavelength range of a channel can be adjusted, within the set limits for that channel, but there should be no need to do so.

Individual spectrometer channels can also be disabled if required as shown below. No data will then be acquired from the disabled channel. This is however generally unnecessary and potentially even undesirable. The *Master* channel however, cannot be disabled.




The primary spectrometer parameters that are adjusted therefore are the integration time (***Int time***) and the integration delay (***Int delay***). The integration time is the length of time for which the spectrometer sensors are exposed to the plasma light generated by the interaction of the laser output with the sample. The integration delay is the delay between the laser shot and the time at which the sensors are first exposed to the plasma light.




The three different types of Avantes AvaSpec spectrometers that can be used in the APL spectrometer modules each have slightly different performance features and limits on the parameters that can be set so it is important that the right one is selected in the *System configuration* window when the *LIBSoft* application is started. Once initialised correctly the integration time and delay values will be automatically coerced to the allowable range for the spectrometer type in use.

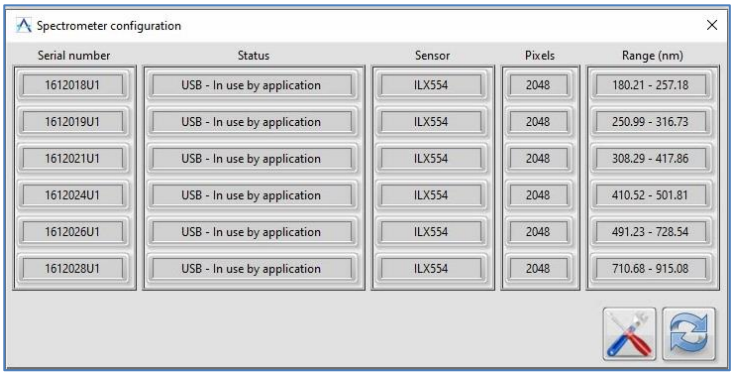
At the bottom of the spectrometer configuration window are two check boxes to select between either ***Use Master settings*** or ***Use Slave settings***. If *Use Master settings* is selected the integration time and delay for all channels will be set to those of the *Master* channel. If *Use Slave settings* is selected it is possible to select different values of integration time and delay for each channel. This latter option is potentially advantageous if there is a significant difference in the peak intensities or spectrometer sensitivity in different regions of the overall wavelength range.

At the bottom right of the configuration window there are two buttons.

The  button can be used to reinitialise the spectrometers. This is generally only necessary if there is an unexpected communications failure between the computer and the spectrometer module.

The  button can be used to open an additional window to display further information about the different spectrometer channels. The data displayed includes:

- The serial number of each channel
- The channel status
- The sensor type
- The number of pixels in the sensor
- The nominal maximum wavelength range of each channel



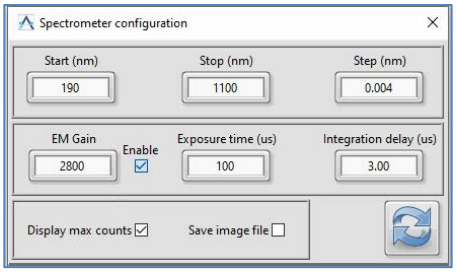

These data are for information only and cannot be changed by the user.

The spectrometer re-initialisation button is duplicated at the bottom of this screen.

The  button next to it returns the screen to the display of user-configurable parameters.

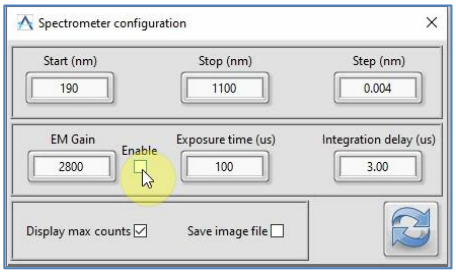
### 5.3.3 EMU spectrometer configuration

When using an EMU spectrometer, the Catalina Scientific KestrelSpec application must be running in the background before *LIBSoft* can successfully complete the initialisation of the system. The spectrometer configuration window for the EMU spectrometer is shown below.




The parameters in the top section of the spectrometer configuration window specify the wavelength range and the interval between points in the spectrum. The ***Start*** and ***Stop*** parameters specify the range. The maximum wavelength range of the spectrometer is typically 190 – 1100 nm but a narrower range can be selected if required. The ***Step*** parameter specifies the interval between points and affects the full width half maximum (FWHM) of the peaks and therefore the resolution of the instrument. Typical values of these parameters are shown. Refer to the KestrelSpec manual for further details. APL can also provide advice on the parameters that should be used. Once set, these parameters can generally be left unchanged.

The parameters in the central region of the configuration window directly affect the acquired spectra. A typical ***EM gain*** value is 2800 but this can be adjusted, within certain limits, depending on the intensity of the acquired spectra. If the ***Enable*** check box is unchecked the gain will be effectively set to zero.




The ***Exposure time*** is the time for which the detector is exposed to the plasma light generated by the interaction of the laser output with the sample. A minimum *Exposure time* value of approximately 100 µs is recommended to prevent frame transfer smearing (see the KestrelSpec manual for further details). The ***Integration delay*** is the delay between the laser pulse and the time at which the detector is first exposed to the plasma light. For the EMU spectrometer this delay is introduced by a separate delay generator. This is usually a Quantum Composer 9200 series device that is shipped with APL systems that use the EMU spectrometer. *LIBSoft* communicates directly with this device to set the delay and therefore this delay generator must be specified in the initial *LIBSoft System configuratio*n window and then successfully initialised by the application.

There are two check boxes in the lower section of the configuration window.

If the ***Display max counts*** box is checked then the maximum number of counts detected in the acquired spectrum is displayed in the title bar of the spectrum display (see section 9.1). This value can be useful in gauging the overall intensity of the spectrum and whether the spectrometer parameters, for example, the *EM gain*, should be adjusted to improve the acquired data.

If the ***Save image file*** box is checked then the image data acquired by the spectrometer is saved alongside the spectrum file. KestrelSpec can be used separately to reprocess the data in the image file if required. This is however, not usually necessary. Refer to the KestrelSpec manual for details.

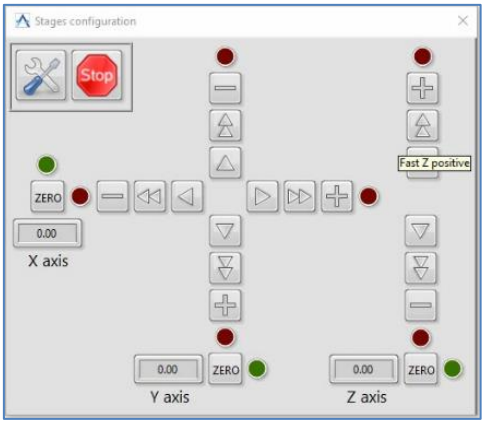
In the bottom right-hand corner of the configuration window there is a button to reinitialise the spectrometer. This is generally only necessary if there is an unexpected communications failure between the computer and the spectrometer module.

### 5.3.4 EMU spectrometer calibration

The EMU spectrometer should be recalibrated periodically, preferably before each daily use to account for possible wavelength drift due temperature variations and to check that the system is operating correctly. This can be done quite simply using a mercury-argon calibration lamp and the KestrelSpec application. This procedure is detailed in Appendix A.

## 5.4 Control and configuration of sample chamber stages

The  shortcut button will open the stages control and configuration window. This button will be enabled as long as a computer-controlled sample chamber is connected to the system and has been successfully detected and initialised by *LIBSoft*. The window will be displayed on top of the main *LIBSoft* screen.



Initially the stages control screen is displayed allowing each of the stages to be controlled manually. During an acquisition the stages are moved automatically by *LIBSoft* as specified by the acquisition configuration. There is a set of controls for each axis.

- The X axis moves the sample left and right.
- The Y axis moves the sample forward and back.
- The Z axis moves the sample up and down.

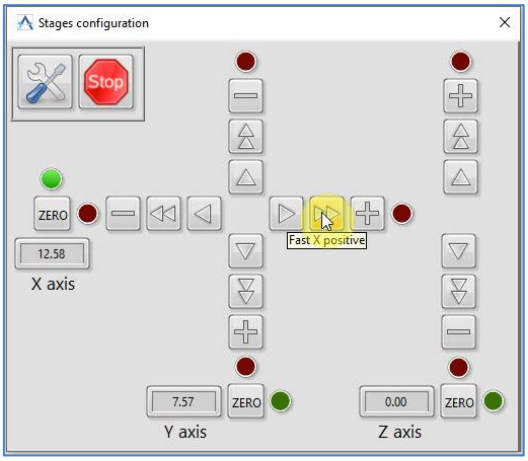
The Z axis is therefore used primarily to set the focus position of the laser output on the sample surface.

Controls are available for each axis to:

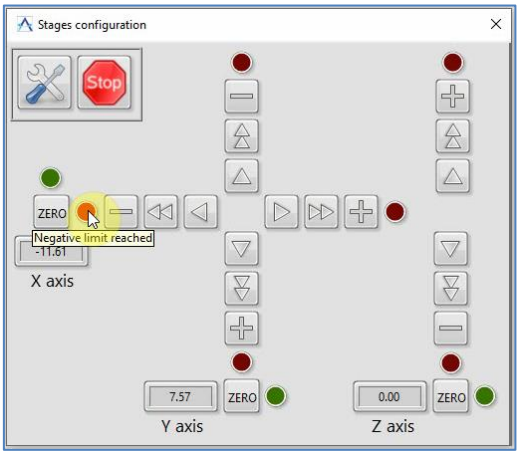
- and : ***Jog the stage*** forwards or backwards by a fixed distance
- and : ***Move the stage continuously*** for as long as a button is depressed in either direction at a slow or a fast speed
- ZERO : ***Zero the displayed stage position***

It is important to note that the controls for the X and Y axis are laid out in such a way as to indicate the direction in which the analysis position on the sample will move when viewed from above. It is easiest to imagine the top left-hand corner of the sample when viewed from above as the origin of movement, so the zero position.
Moving the X axis stage in the positive direction will move the sample to the left and therefore the analysis position to the right. Similarly, moving the Y axis stage in the positive direction will move the sample towards the back of the sample chamber and therefore the analysis position towards the bottom of the sample when viewed from above. Automated sample movements during an acquisition will always be in this positive direction on both the X and Y axes.

In addition to the movement controls there is a green indicator for each axis that is illuminated when that axis is moving.




There are also 2 red indicators for each axis. These correspond to the limit switches that are at either end of the range of travel for each axis. If a limit switch is activated the stage movement is automatically stopped and the corresponding indicator is illuminated. If a limit switch is activated during an acquisition the acquisition will be stopped. It is therefore important to ensure that the specified scan area for the acquisition is within the available range of movement for the stages.



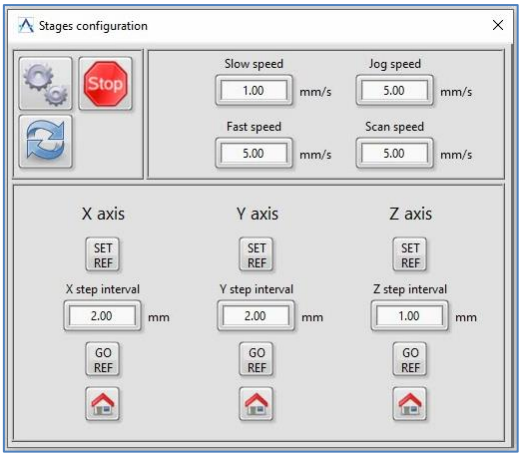

There is also a display of the stage position for each axis. It should be noted that this is not an absolute position, unless the stage has been homed, and can be zeroed at any time by pressing the zero button.

In the top left-hand corner for the screen are two further buttons.

The 

button will halt the movement of all of the stages.

The  button will display the stages configuration screen as shown below which allows configuration of the movement parameters for the stages.




In the top section of this screen are the speed settings for the stages. These include:

- ***Slow speed***: The speed at which the stages move when the slow, continuous movement buttons are pressed on the stage control screen.
- ***Fast speed***: The speed at which the stages move when the fast, continuous movement buttons are pressed on the stage control screen.
- ***Jog speed***: The speed at which the stages move when the jog buttons are pressed on the stage control screen.
- ***Scan speed***: The speed at which the stages move during an acquisition scan.

In the lower section of this screen there are controls that allow the distance each axis stage moves when jogged to be specified. The ***X***, ***Y*** or ***Z step interval*** is the distance a stage moves when the jog buttons on the stages control screen are pressed. It is also the distance a stage moves between each measurement location in an acquisition scan.

The 

button displayed for each axis, also in the lower section of this screen, will set the current stage position as a reference position.

The 

button for that stage will then return the stage to this saved reference position at a later time.

The  button displayed for each stage in this lower section of the screen, will home the corresponding stage. Selecting this button will cause the stage to move in the negative direction until it reaches the limit switch, move away from the limit switch by 1 mm in the positive direction and then stop and zero the stage position indicator.

In the top left-hand corner of the window there is a duplicate of the stop button which when pressed will halt all movement on all stages.

There is also a  button to reinitialise the communications with the stages if required.

Finally, there is a  button to return to the stages control window.

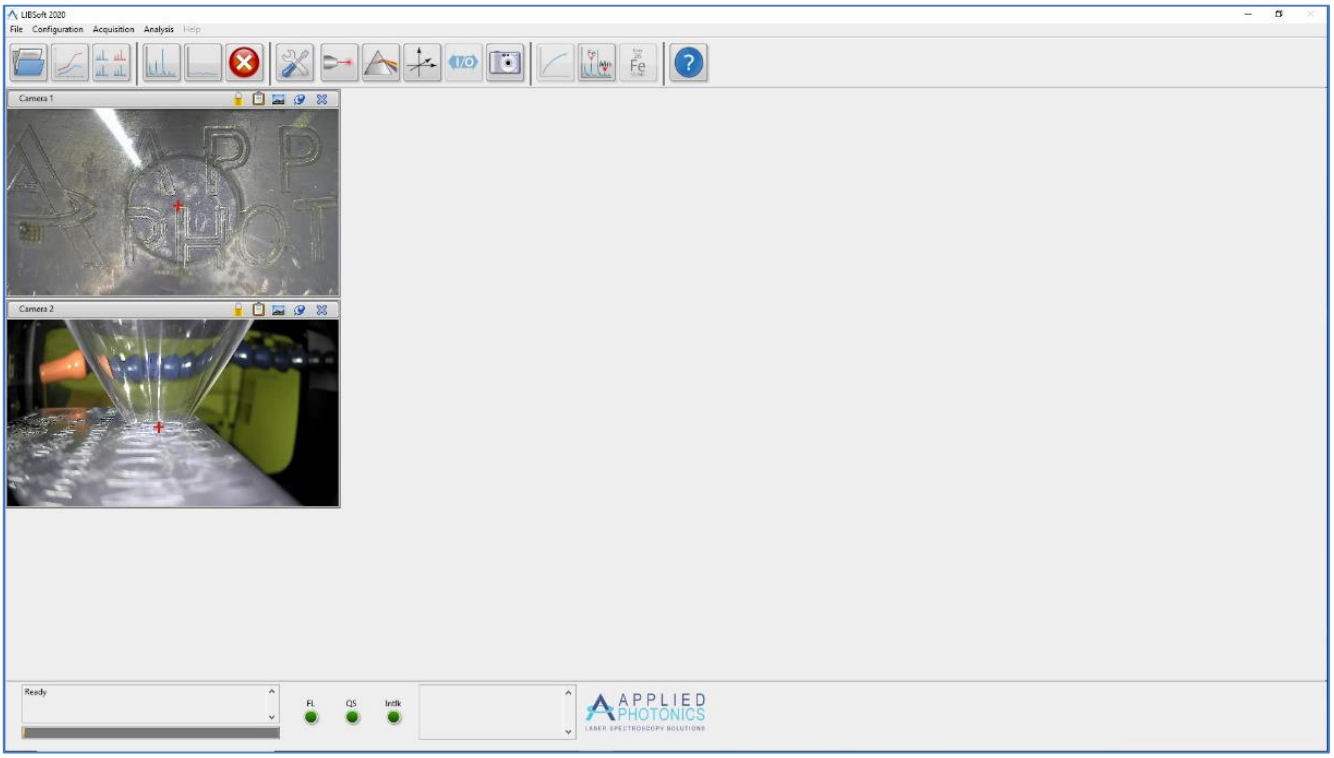
The parameter values currently displayed in the stages configuration window will be saved to the *LIBSoft* configuration file when the application is shut down and automatically reloaded the next time the application is started.

If the system computer has a single monitor the stages control and configuration window will be closed automatically when a different configuration window is opened or one of the other shortcut buttons in the main screen toolbar is selected. If the system computer has dual monitors, the stages configuration window will remain open. It can then be dragged to the second monitor and left open for faster access. It can however still be closed manually if required.

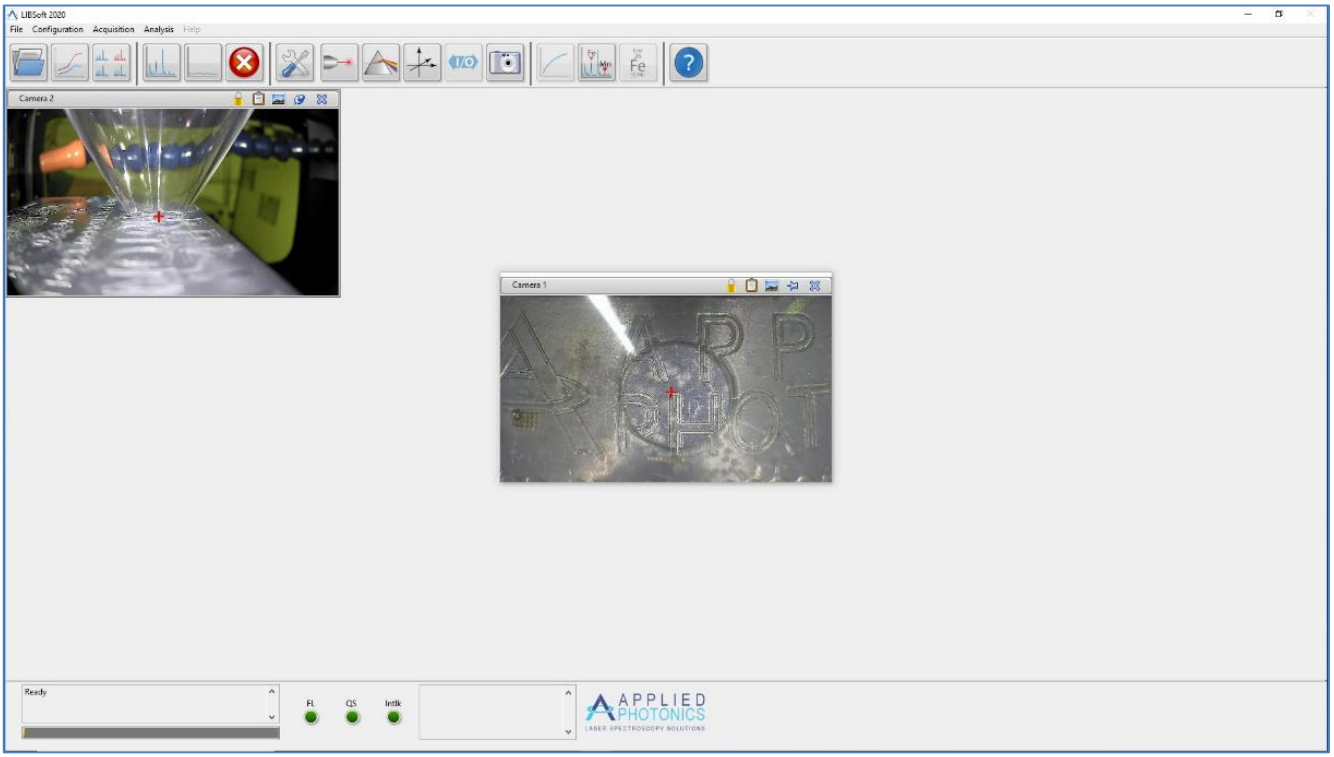
## 6 Camera image display and manipulation

An optional imaging kit is available for use with APL LIBS systems. The standard imaging kit comprises a single high-definition camera installed in the LIBS module and providing a view of the sample surface. It is however possible to add a second, high-definition camera, in a sample chamber usually to provide a side view of the sample. Each camera in the imaging kit is connected to a video grabber device connected to the computer.

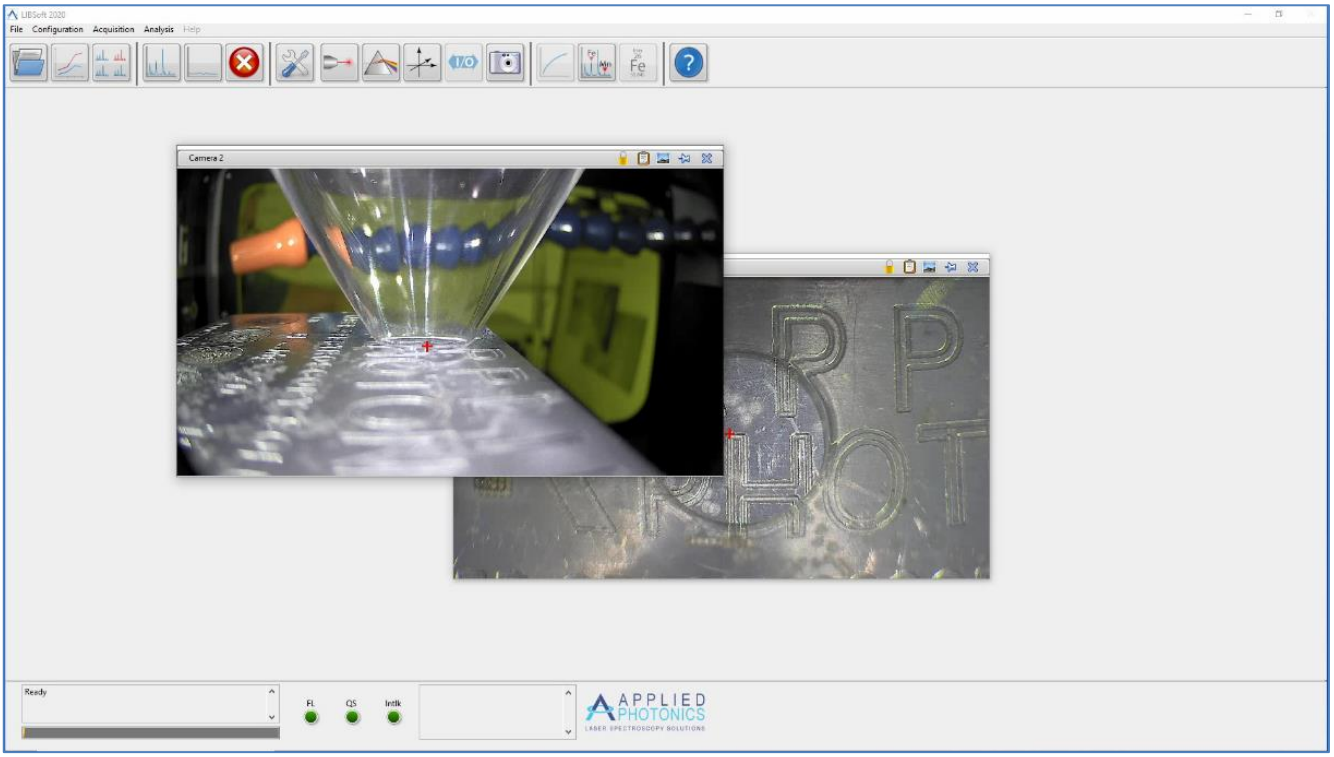

*LIBSoft* will automatically detect the number of cameras connected during the initialisation process. The main screen of the application will then be configured to display live video from each of the cameras detected. The video output from the cameras will be displayed in one or two windows as appropriate. The video display windows are initially pinned to the left-hand side of the screen. This means that if a single monitor system is used both the live video and the acquired spectra are visible simultaneously. The *LIBSoft* main screen for a system with an imaging kit comprising two cameras is shown below.




It is however possible to unpin the video display windows so that they can be repositioned and enlarged as required. This can be useful if a dual-monitor system is in use so that the video displays can be moved to the second monitor and enlarged while displaying the acquired spectra on the primary monitor. To unpin a video display simply click on the pin icon in the title bar of the video display. If the camera 1 window is unpinned the camera 2 window will be moved up to replace it as shown below.




Once a window is unpinned it is then possible to left-click and drag it to the required position. It can also then be resized either horizontally or vertically. The aspect ratio of the window will however be maintained when it is resized. The camera 2 window, if present, can also be unpinned and then repositioned and/or resized.




To return a display window to its pinned position simply click the pin icon again. The window will be resized and repositioned automatically. If there are two cameras and both display windows are pinned then the camera 1 window will be positioned above the camera 2 display window.

Holding down the shift key and left-clicking on a camera display window will zoom in on the image by a factor of 2 centred on the cursor. Holding down the control key and left-clicking on a camera display window will zoom out of the image by a factor of 2 centred on the cursor.

A red crosshair marker is displayed on each image. This can be used to mark the position on the image at which the laser output is incident on the sample. Right-clicking on the display window will toggle the visibility of the crosshair. When *LIBSoft* is run for the first time this crosshair is positioned at an arbitrary position. However, when *LIBSoft* is run subsequently the crosshair will be placed at the last used position. When *LIBSoft* is started the crosshair position is initially locked so that it can't be moved accidentally. To unlock it click on the padlock icon in the title bar of the display window.

To reposition the crosshair, first unlock it by clicking on the padlock icon then hold down the shift key and right-click on the image at the required position. Small adjustments to the position of the crosshair can also be made using the arrow keys on the keyboard provided that the image display is selected. To do this, first left-click on the image display to select it and then press the required arrow key. The crosshair will be moved by 1 pixel in the direction of the arrow for each key press. The crosshair can also be moved in 5 pixel increments by holding down the shift key while pressing an arrow key. To return the crosshair to the saved position hold down the control key and right-click on the image. To relock the crosshair once it has been repositioned to prevent accidental movement of it click on the padlock icon in the title bar of the window again. Once the crosshair position has been locked the saved position will be updated with the current position and saved to the *LIBSoft* configuration file when the application is shut down.

It is possible to copy the currently displayed image to the Windows clipboard by clicking on the clipboard icon in the title bar. The currently displayed image can also be saved to a PNG file by clicking on the photo icon in the title bar. These options are useful for including images of the sample in reports and other documents.

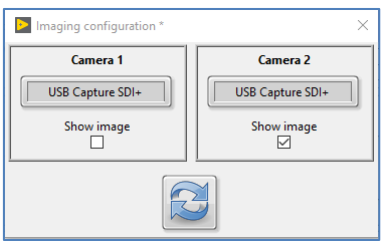
To hide a video display window completely click on the cross in the title bar of the window.

The video display manipulation functions can be summarised as follows:

- *Shift + left-click*: ***Zoom in by a factor of 2*** centred on the cursor
- *Cntrl + left-click*: ***Zoom out by a factor of 2*** centred on the cursor
- *Right-click*: ***Toggle crosshair visibility***
- *Shift + right-click*: ***Position crosshair at cursor position****
- *Cntrl + right-click*: ***Position crosshair at saved position****
- *Arrow key*: move the crosshair 1 pixel in the direction of the arrow*
- *Shift + arrow key*: move the crosshair 5 pixels in the direction of the arrow*
-  : ***Unpin video display*** from main screen
-  : ***Pin video display*** to main screen
-  : ***Unlock crosshair*** position
-  : ***Lock crosshair*** position
-  : ***Copy currently displayed image to Windows clipboard***
-  : ***Save currently displayed image as PNG file***
-  : ***Hide video display***

* Only if the crosshair position is unlocked.

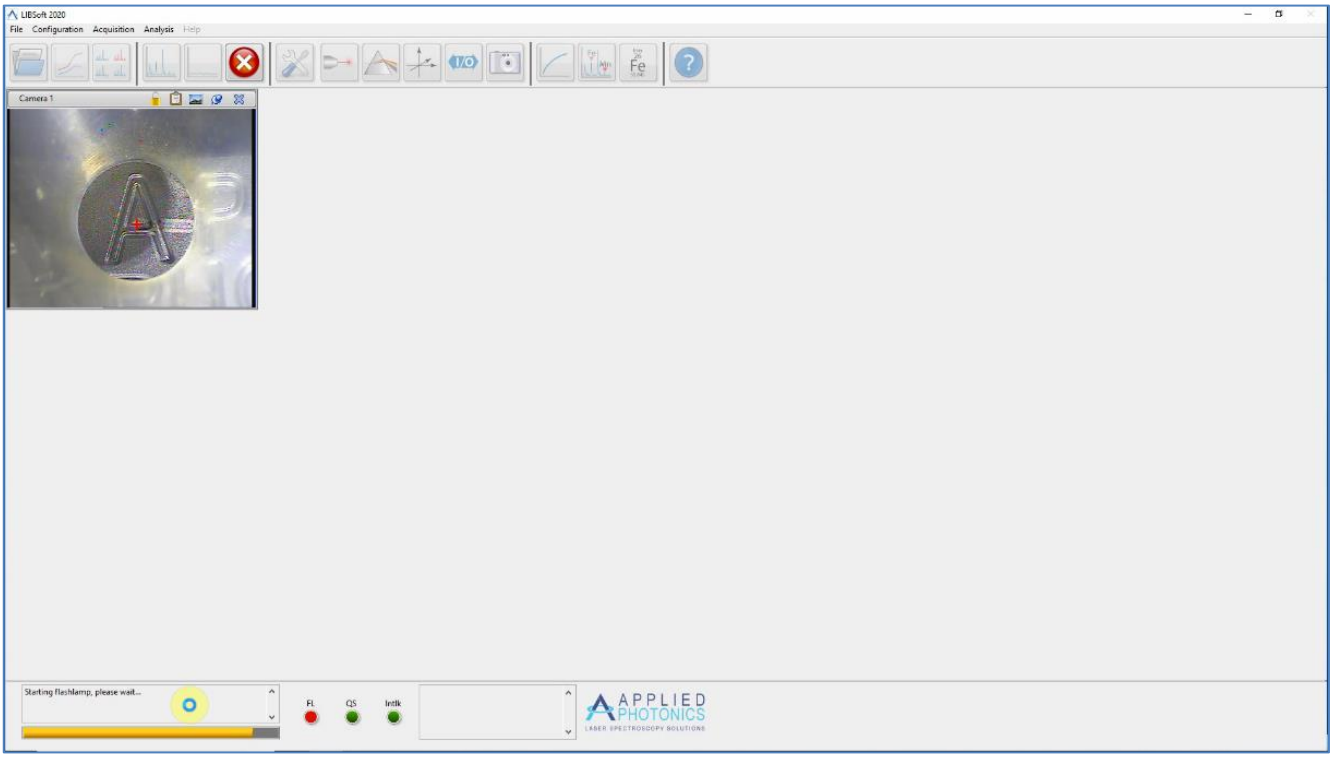
The  button will display the camera configuration window. A hidden video display window can then be redisplayed by ticking the corresponding ***Show image*** check box.



# 7 Acquisition of spectra

## 7.1 Analysis spectra

The  shortcut button in the main screen tool bar can be selected once all the necessary parameters have been configured to initiate the acquisition of a spectrum or spectra. If the laser flashlamp is currently disabled the application will enable it. The progress bar will display an 8 second delay to allow the flashlamp to warm-up and stabilise.

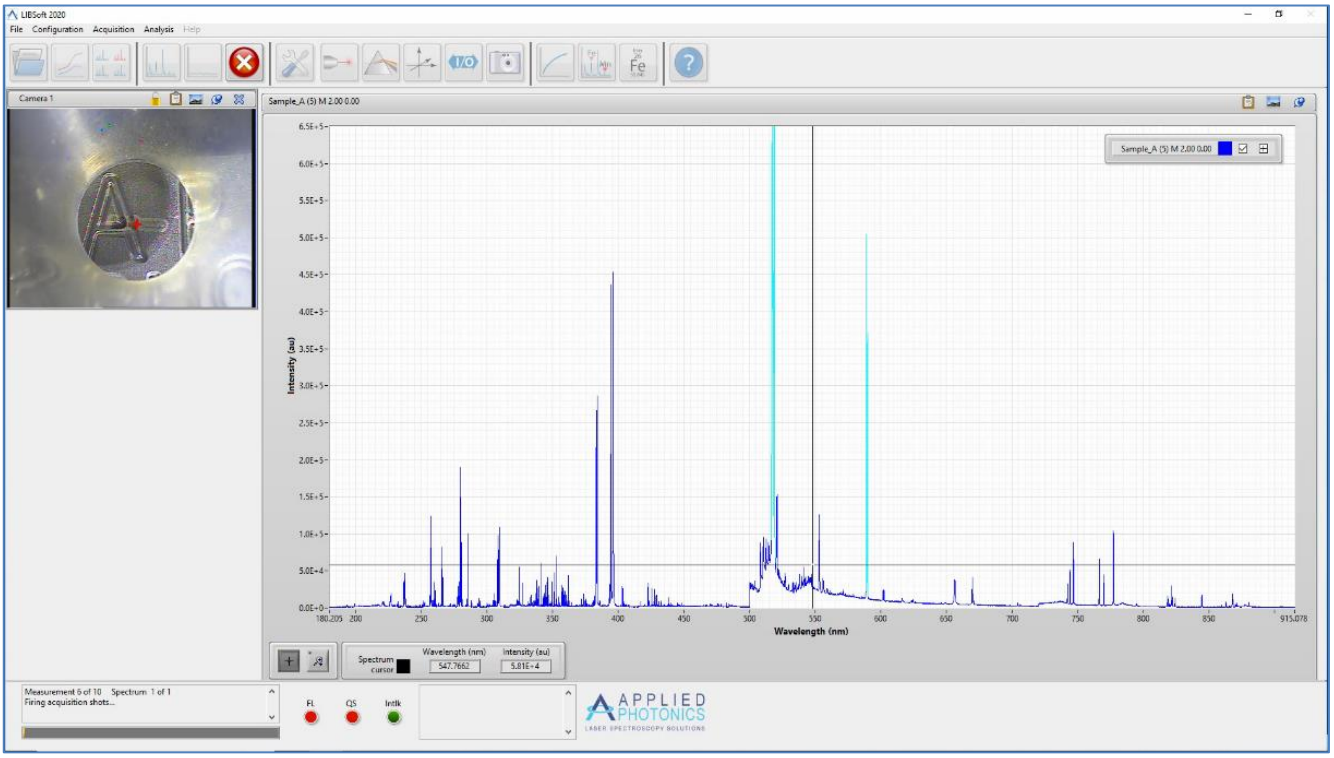



The application will then fire the laser according to the parameters set in the acquisition configuration window.

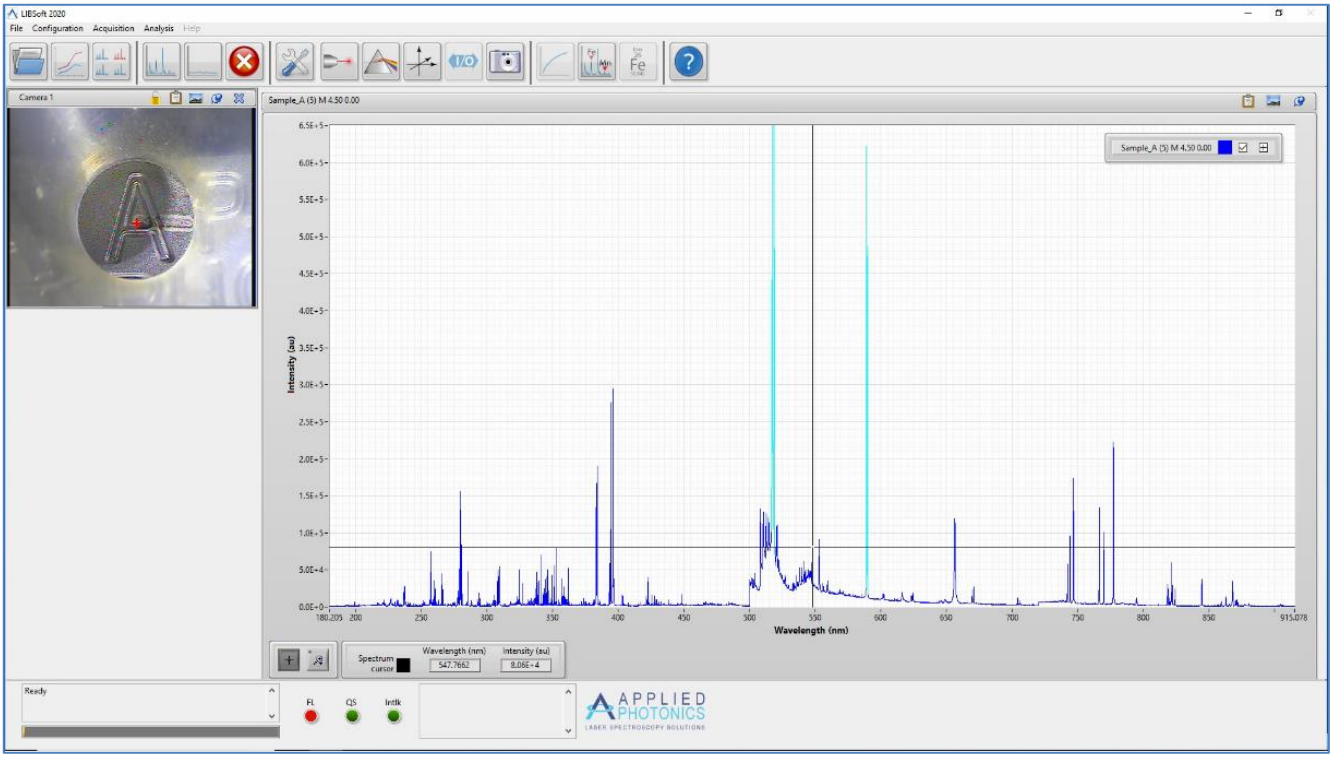
If the *Remote trigger* option is enabled (section 5.1) then *LIBSoft* will wait until a trigger is received from an external system before firing the laser.

If the laser is specified as either *No laser* or *APL laser* then instructions to the user will be displayed in the *Status bar* indicating when to fire the laser manually.

The current operation of the application will be displayed in the status message window as the specified acquisition is performed.




On completion of each measurement specified in the acquisition configuration the acquired spectrum will be saved to disk using the specified file name and displayed on the main screen. On completion of all measurements specified in the acquisition configuration the application status will be returned to *Ready*. The laser flashlamp is not disabled automatically leaving it ready for further acquisitions. However, it can be disabled manually from the laser configuration window if required.




In addition to the spectrum data files that are saved, a parameter configuration file is also saved for each set of measurements. This records the parameters used for the acquisition of those spectra. This file is a simple text file that can be opened in most text editors. The data in it can also be displayed using the *LIBSoft* spectrum display and manipulation tools (see section 9).

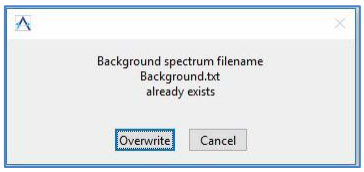
## 7.2 Background spectra

The spectra acquired using *LIBSoft* are background-corrected. If a spectrometer is connected to the system and has been successfully detected and initialised by *LIBSoft*, the application will automatically acquire a new background spectrum once all the hardware components have been initialised. Thereafter, if any parameters that affect the background spectrum, for example the integration time, are changed then a new background spectrum is acquired automatically before subsequent analysis spectra are acquired.

The  shortcut button in the main screen tool bar can however be selected to initiate the acquisition of a new background spectrum manually.

For the EMU spectrometer, the background spectrum is held in memory in KestrelSpec and is therefore neither displayed nor saved to file. For the Avantes spectrometers, the background spectrum is saved to file. The file name used for this spectrum is specified by the *Data folder* and *Background name* parameters set in the acquisition configuration window (section 5.1).

If a background spectrum is acquired manually the user is warned if a background spectrum of the same name already exists and given the choice as to whether to overwrite it.




If the acquisition parameters have been changed and the acquisition of a new analysis spectrum is initiated, a new background spectrum is acquired automatically and the existing file is overwritten.

## 8 File naming

Spectrum files are generally named using the *Data folder* and *Sample name* specified on the acquisition configuration screen (section 5.1) to form the file path. Any spaces in the *Sample name* entered by the user are automatically replaced by underscores. By default, a numeric value that is automatically incremented following each measurement, is appended in parentheses to the file name. This avoids the need to change the sample name after each set of acquisitions and the risk of over-writing spectra acquired previously. Example file names would be:

- Sample_A (1)
- Sample_A (2)
- Sample_A (3)

In certain circumstances however, additional suffices are added to the file name.

If the number of measurements specified is greater than 1 then the letter “M” followed by the measurement number is appended to the file name. Example file names would be:

- Sample_B (4) M 1
- Sample_B (4) M 2
- Sample_B (4) M 3

If the number of measurements specified is greater than 1 and a raster pattern of measurements has been configured using a computer-controlled sample chamber, then the letter “M” followed by the measurement co-ordinates is appended to the file name. In this instance the start position of the scan is designated as 0, 0 and the co-ordinates of each measurement are specified relative to this position. Example file names for a raster pattern of 2 lines with 3 points per line and a step interval of 1 mm would be:

- Sample_C (5) M 0.00 0.00
- Sample_C (5) M 1.00 0.00
- Sample_C (5) M 2.00 0.00
- Sample_C (5) M 0.00 1.00
- Sample_C (5) M 1.00 1.00
- Sample_C (5) M 2.00 1.00

If multiple spectra are acquired at a single measurement location the data for these spectra are saved in a single file. To indicate that a file contains multiple spectra the file name is appended with the letter S. An example file name would therefore be:

- Sample_D (6) S

Finally, if multiple measurements are acquired with multiple spectra for each measurement, these suffices can be used in combination. For example, for a series of 5 measurements each comprising multiple spectra the file names would be:

- Sample_E (7) M 1 S
- Sample_E (7) M 2 S
- Sample_E (7) M 3 S
- Sample_E (7) M 4 S
- Sample_E (7) M 5 S

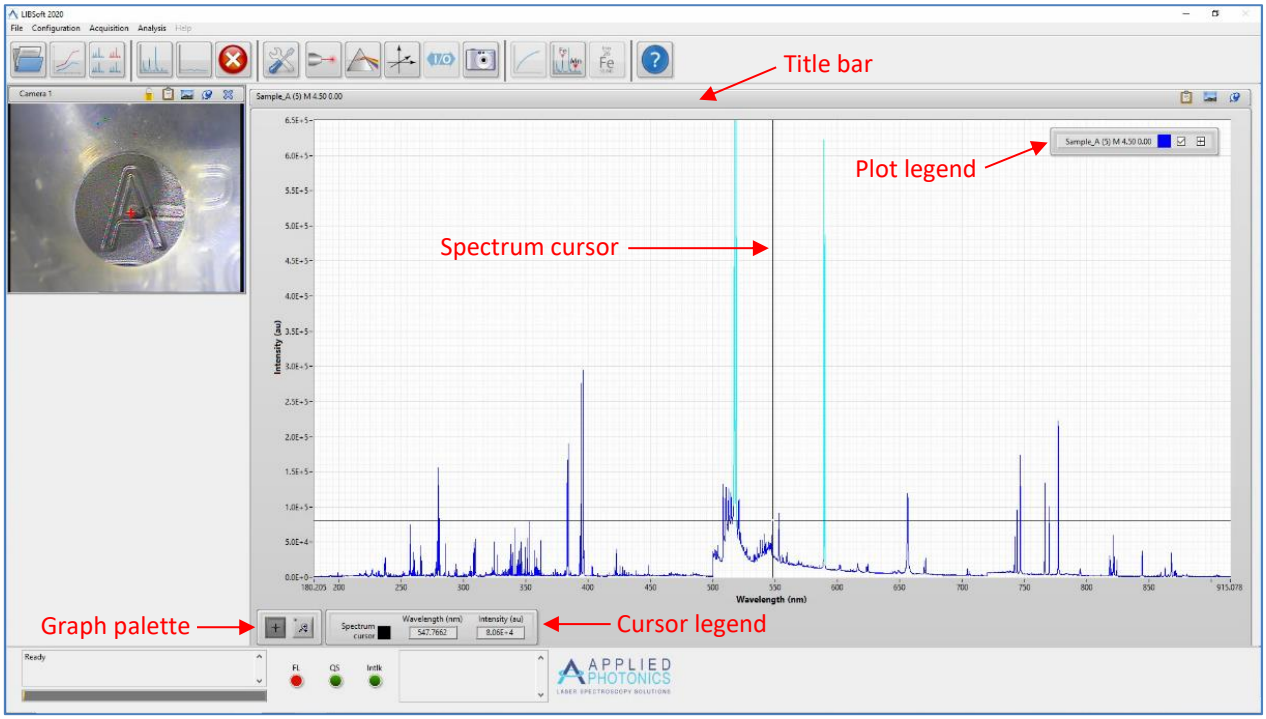
# 9 Spectrum display, manipulation and comparison

## 9.1 Display of acquired spectra

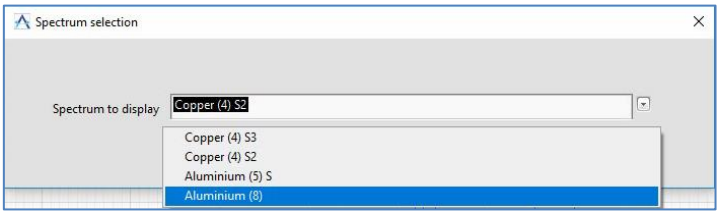
Each spectrum acquired as a result of a measurement is automatically displayed on the main *LIBSoft* screen following completion of the acquisition, replacing any spectrum that was already displayed. It is also added to the list of currently open spectra.

The spectrum display window has a number of features that are worth noting.

- The title bar
- The spectrum cursor
- The cursor legend
- The graph palette
- The plot legend




The  button in the main tool bar can be used to choose which of the currently open spectra to display. Selecting this button opens a window that lists all of the currently open spectra so that the spectrum required to be displayed can be chosen.

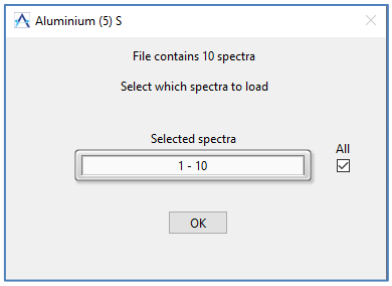



Spectra that have been acquired and saved previously but that are not currently open can also be displayed (see section 9.2). Saved spectra can also be loaded either for comparison with the currently displayed spectrum or with each other (see section 9.4).

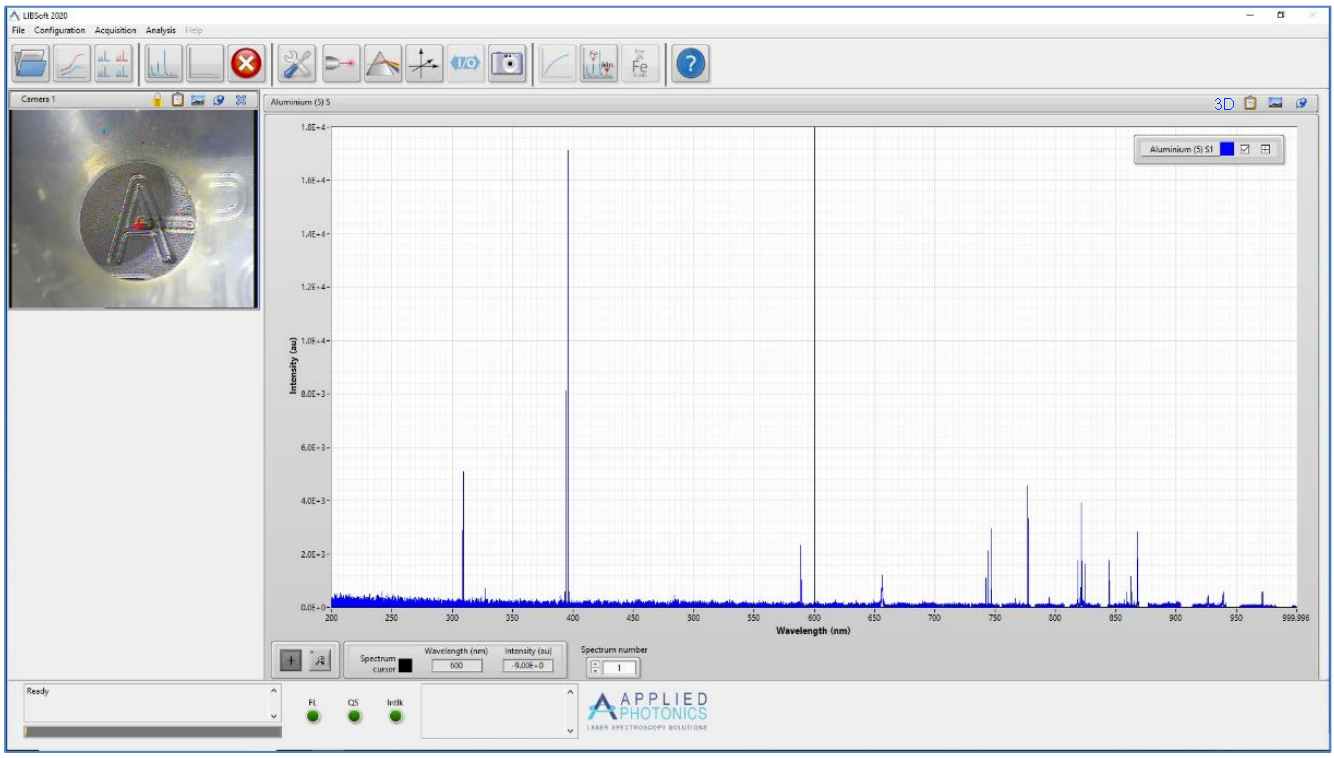
## 9.2 Display of saved spectra

Select the  shortcut button in the main tool bar to open a saved spectrum for display. Select the required spectrum file(s) using the file browser. The selected spectrum will be displayed in the main screen, replacing any spectrum that was already displayed. It is also added to the list of currently open spectra.

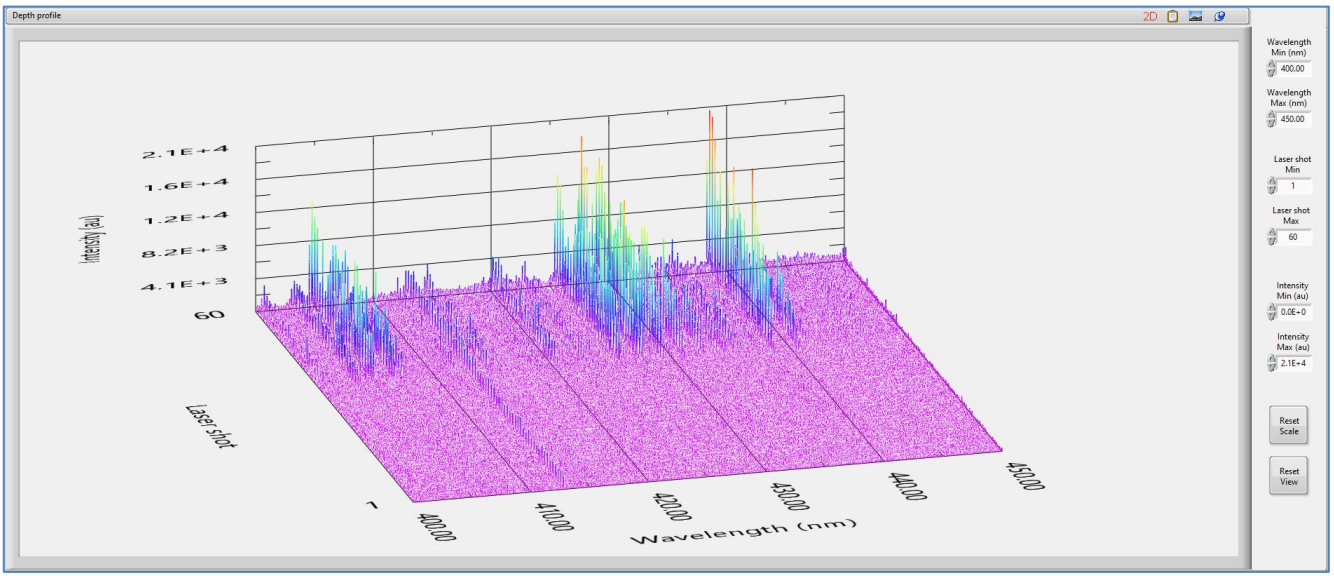
Note that if the selected file is appended with the letter “S” this indicates that the file contains more than 1 spectrum from an individual measurement (see section 8). In this case an additional window is displayed allowing the user to select which of these spectra to open.




The default option is to open all the spectra contained in the file. In this case all of the spectra are displayed in the same window and a control is displayed at the bottom of the window allowing the user to cycle through the spectra.



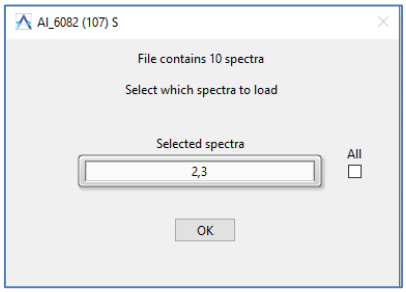

When all spectra in a file are selected in this way an additional 3D icon is also displayed in the spectrum title bar. Left clicking on this icon changes the display to a “waterfall” plot of all of the spectra allowing the evolution of the spectra to be viewed as shown below.



To the right of this plot are several additional controls allowing the axis scales to be modified. Left clicking on the plot and dragging allows it to be rotated thereby adjusting the view. Below the axis scale controls are two further buttons that when clicked will reset the axis scales and the view respectively to their original settings.

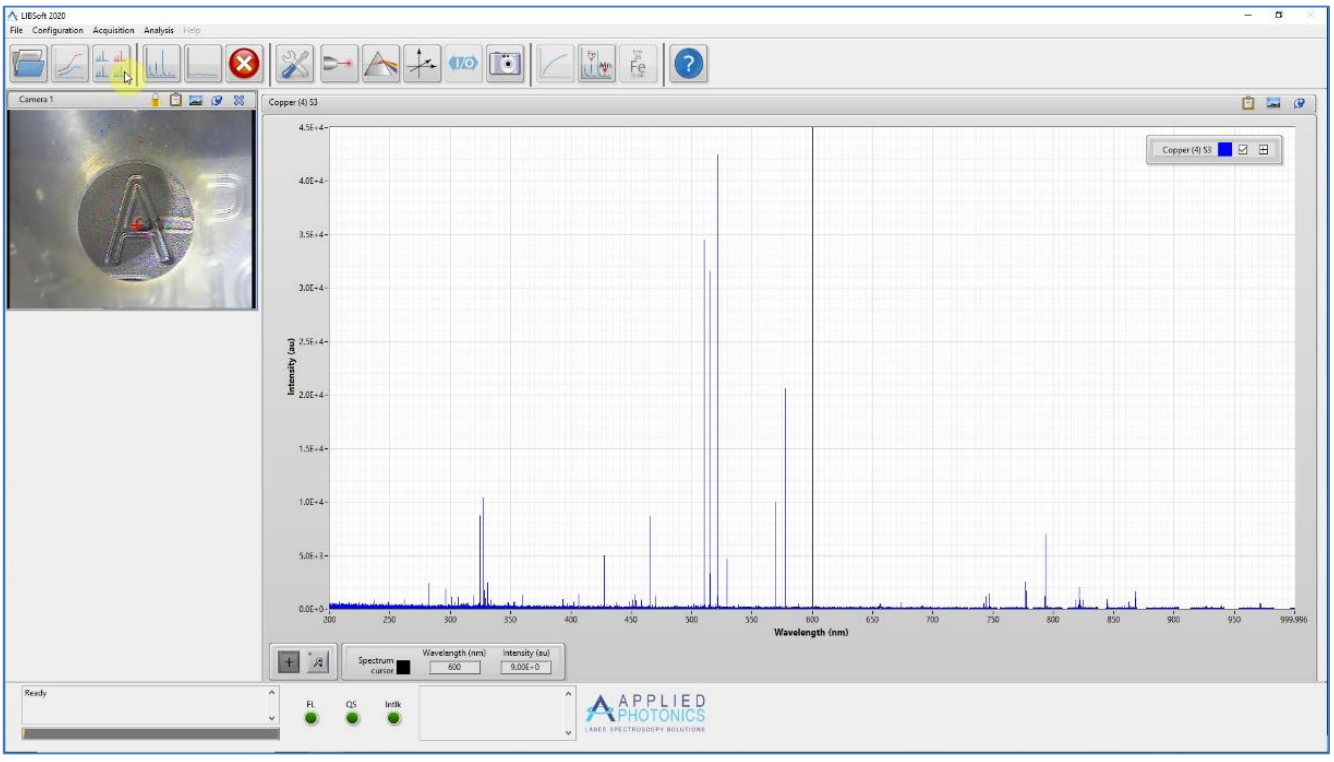
Left clicking on the 2D icon in the title bar will return the spectrum display to the original plot of individual spectra.

It is also possible to choose to display just one or a selection of the spectra in the file. Simply enter the required spectrum numbers separated by commas or specify a hyphenated range of spectra to display.




Note that when spectra are selected in this way each one is opened separately and therefore both the name in the title bar of the spectrum display window and the plot legend indicate the specific spectrum from the file that is displayed.

If more than one spectrum from the file is selected, the button in the main tool bar can be used to select which of the spectra to display.

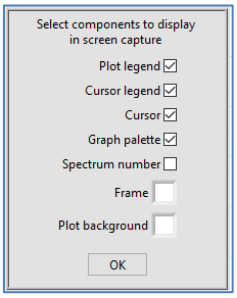



### 9.3 Manipulating spectra

The title bar of the spectrum display window shows the name of the displayed spectrum file. It also contains three icons on the right-hand side:

- : ***Copy an image of currently displayed spectrum to the Windows clipboard***
- : ***Save an image of the currently displayed spectrum as a PNG file***
- : ***Unpin the spectrum display*** from the main *LIBSoft* screen and maximise it.

When the clipboard icon is selected a window is displayed allowing the user to choose which of the display features to include in the image copied to the clipboard. These features can be checked or unchecked as required. Selecting ***OK*** then copies the image of the spectrum to the clipboard.

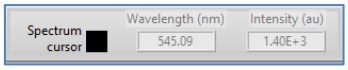



Similarly, when the photo icon is selected, a window is displayed allowing the user to choose which of the display features to include in the image to be saved. Selecting ***OK*** displays a file dialogue to allow the user to choose where to save the image of the spectrum and the file name to be used.

Selecting the pin icon to maximise the spectrum display window can be useful if an imaging kit is connected to the system and the video display(s) is occupying a significant portion of the screen area. The spectrum display window can be re-pinned in the main application screen by selecting the pin icon again.

The spectrum cursor is initially positioned in the centre of the displayed wavelength range. It can be left-clicked and dragged to the required position. Alternatively, the left and right keyboard arrow keys can be used to move it in 1-pixel increments in either direction for each press of the arrow key. A coarser movement is also possible by holding down the shift key and pressing the left or right keyboard arrow keys. This moves the cursor in 10-pixel increments for each press of the arrow key. These discrete movements using the arrow keys are difficult to see when the full wavelength range of a high-resolution spectrum is displayed. However, they are useful when positioning the cursor on a particular peak when the spectrum is zoomed to a narrower wavelength range.

The position of the cursor is displayed in the cursor legend at the bottom of the spectrum display window. The cursor legend displays both the wavelength and intensity in the spectrum at the current cursor position. Right-clicking on the spectrum cursor colour icon in the cursor legend (see below) toggles the visibility of the cursor. The wavelength and intensity indicators are greyed-out when the cursor is hidden.



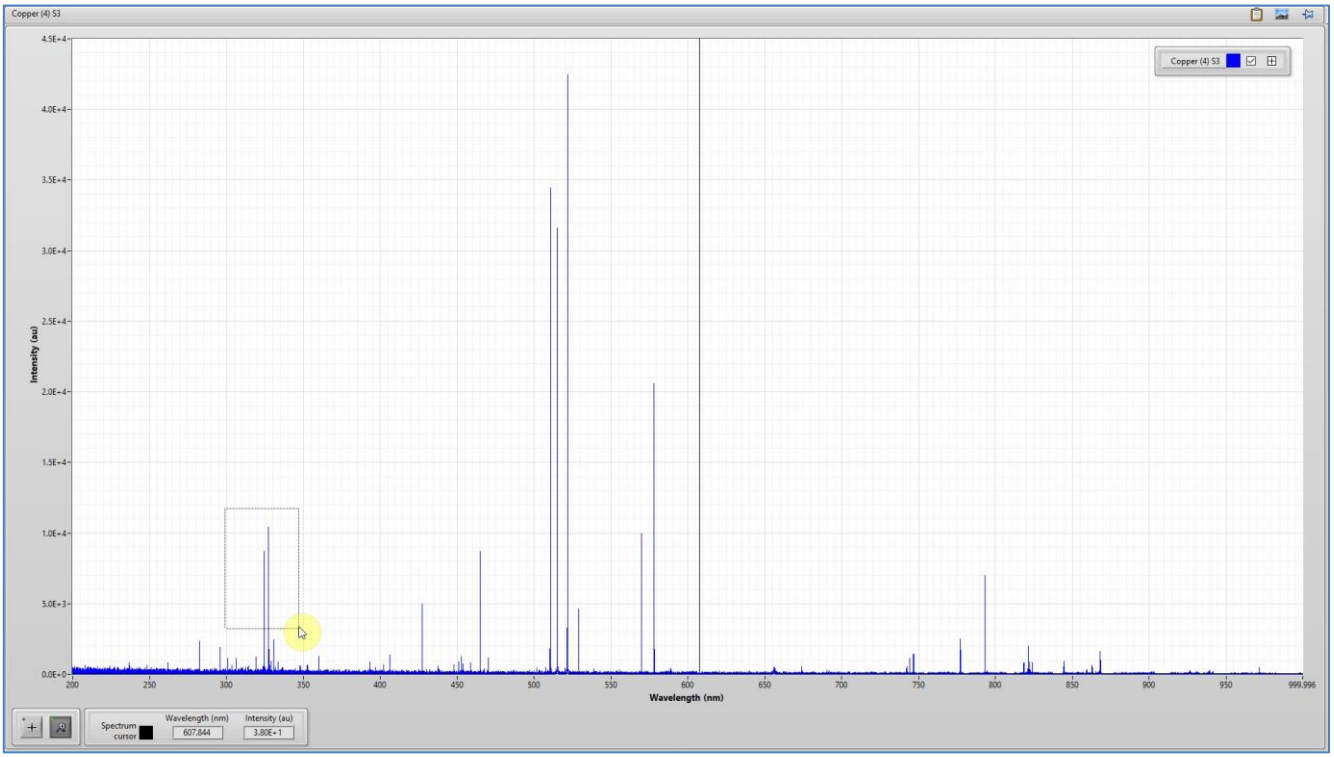

The graph palette is at the bottom of the screen next to the cursor legend. It allows control to be toggled between movement of the cursor and the spectrum zoom functions.

By default, when a spectrum is first displayed, the  cursor control option is selected. This allows the spectrum cursor to be left-clicked dragged as described above.

Clicking on the  zoom option disables the cursor dragging option and displays a palette of five zoom options:

1.  : ***Zoom to a defined region in wavelength and intensity***
2.  : ***Zoom to a defined wavelength region only***
3.  : ***Zoom to a defined intensity region only***
4.  : ***Reset the zoom*** to display the full wavelength and intensity range of the spectrum
5.  : ***Maximise intensity scale*** for the displayed spectra in the current wavelength range

For options 1 -3, once the required option has been selected the user can left-click and drag in the main spectrum display area to define the zoom region as required.




Zoom operations can be repeated as required to further refine the region of the spectrum displayed.

Note that if the current position of the spectrum cursor is within the zoomed region its position will be unchanged following the zoom operation. However, if its current position is outside the zoomed region, it will be automatically repositioned in the centre of the wavelength range displayed following the zoom operation. Note also that after the zoom has been reset the option to zoom to a defined region in wavelength and intensity is selected by default.

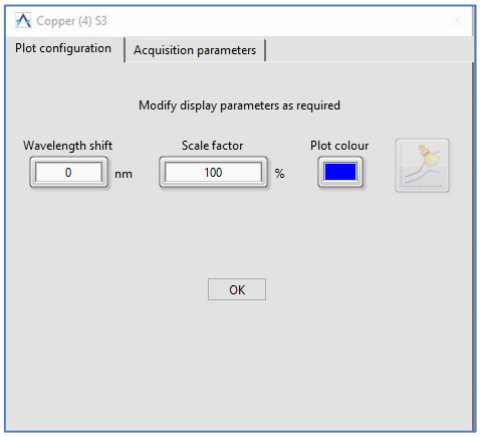
It is also possible to zoom to a specific region of the spectrum, in wavelength and/or intensity, by editing the maximum and minimum scale values on the relevant axes. This can be done by double-clicking on the scale value to highlight it and then entering a new value as required. This allows scale ranges to be specified more precisely.

The plot legend is initially displayed in the top right-hand corner of the main spectrum display area. However, it is possible to left-click on the edge of the legend and drag it to a different position if required, for example if it obscures part of the displayed spectrum. It is also possible to remove it altogether from images of the spectrum for use in reports using the display feature selection options which are displayed when a spectrum image is copied to the clipboard or saved to file as described previously.

The plot legend displays the file name and plot colour of the displayed spectrum. There are also two checkboxes. The left-hand checkbox toggles the visibility of the plot. The one on the right selects the plot to which the spectrum cursor is locked. These options are only really relevant when more than one plot is displayed (see section 9.4).

Right-clicking on the plot legend displays a new window. This window has two tabs:

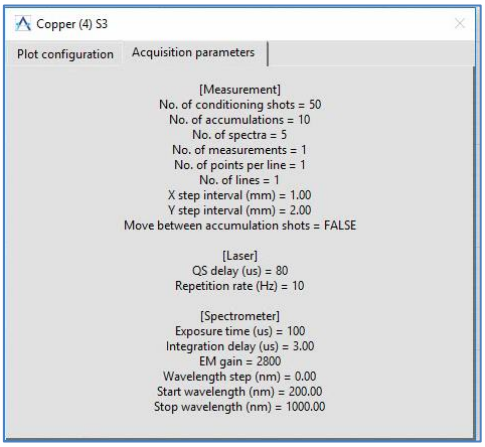
- ***Plot configuration***
- ***Acquisition parameters***




The *Plot configuration* tab provides options to:

- Apply a wavelength shift to the spectrum
- Apply a scale factor to the spectrum intensity
- Change the plot colour
- Clear comparison spectrum (disabled, as shown above, if the spectrum is the current analysis spectrum)

The *Acquisition parameters* tab displays the parameters used in the acquisition of the spectrum. These parameters are read from the parameter configuration file that is saved with each set of measurements acquired using *LIBSoft*.

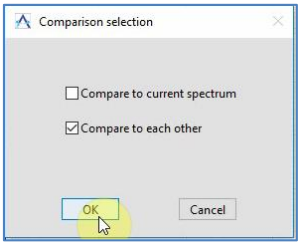



Note that if the parameter configuration file has been moved or deleted and is no longer in the same folder as the spectrum file then a file not found message will be displayed. Similarly, if the parameter configuration file or spectrum file has been renamed and therefore don't match then a file not found error message will be displayed.

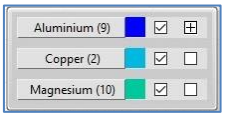
Select ***OK*** on the *Plot configuration* tab to close this window.

### 9.4 Comparing spectra

The  shortcut button in the main tool bar can be used to open saved spectra for comparison, the spectra required to be opened for comparison being selected using the file browser that is displayed. If a spectrum is currently displayed in the spectrum display window, a dialogue will be opened providing the choice to compare the selected spectra to the currently-displayed spectrum or to each other. Tick the required check box then select ***OK***.




The selected spectra will be displayed. The format of the display is the same as for a single spectrum except that the plot legend will be expanded to display entries for each of the spectra in the comparison.




The checkboxes on the left in the plot legend can be used to toggle the visibility of individual spectra. The check boxes on the right can be used to specify the spectrum to which the spectrum cursor is locked. The spectrum cursor will then snap to the selected plot and the cursor legend will display wavelength and intensity values for that plot. By default, the spectrum cursor is locked to the first spectrum listed in the plot legend.


Right-clicking on an item in the plot legend will display the plot configuration window in the same way as for a single spectrum (see section 9.3). This allows for a plot to be wavelength-shifted, scaled and the plot colour to be changed. The acquisition parameters for the selected spectrum can also be displayed if the corresponding parameter configuration file can be found. The zoom and cursor functions are the same as for the display of a single spectrum.

# 10 Quantitative Calibration

## 10.1 Introduction

*LIBSoft 2020* includes a module to generate quantitative calibrations using spectra acquired from suitable calibration standards and apply these calibrations to acquired spectra. This module is only available in *LIBSoft Full* and the corresponding USB key is required to activate and utilise its functions.

The quantitative calibration module can be opened from the main *LIBSoft* application screen by selecting the  shortcut button. This causes the quantitative calibration module main screen to be opened and maximised in front of the main *LIBSoft* application screen which remains open in the background. The quantitative calibration module can be closed at any time to return to the main *LIBSoft* application by left-clicking on the ***X*** in the top right-hand corner of the screen. Any data currently loaded in the quantitative calibration module will however be retained in this instance and will be redisplayed if the module is reopened, provided that the main *LIBSoft* application has not been closed in the meantime.

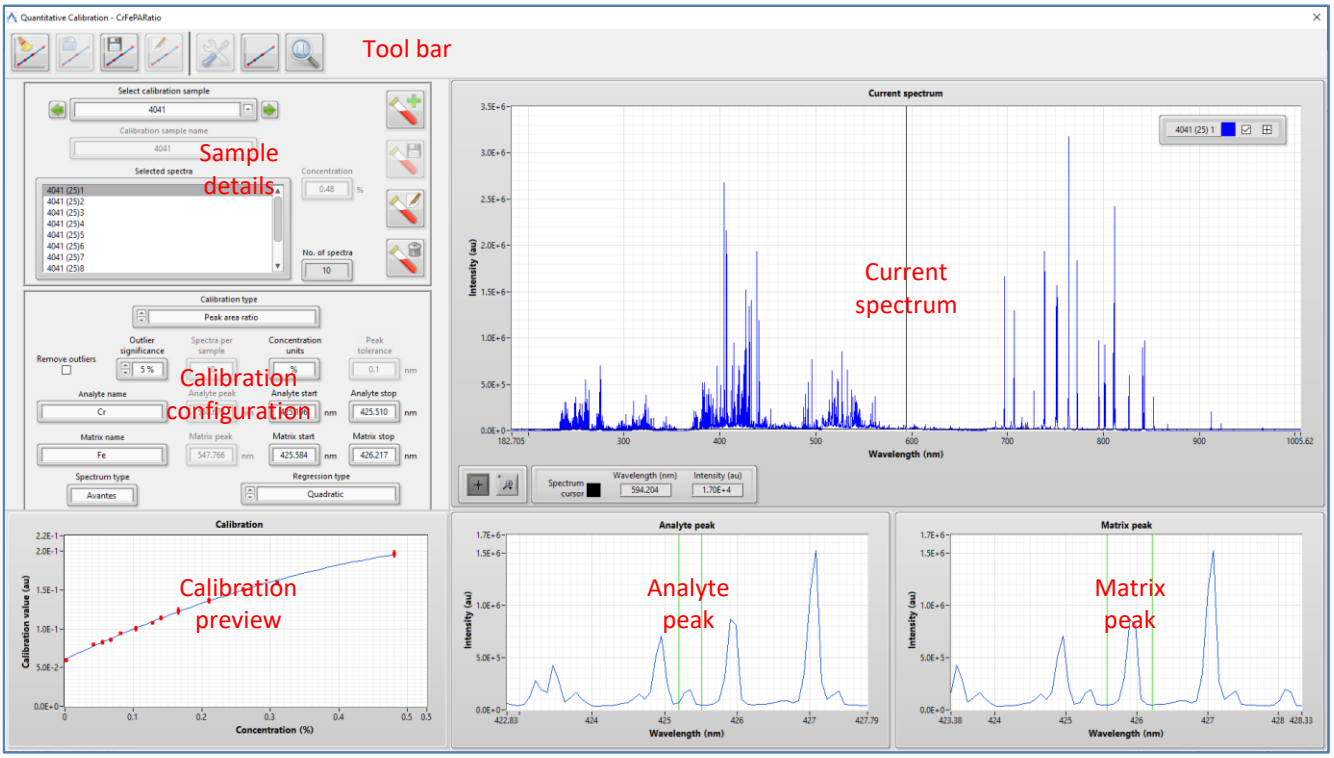
At the top of the calibration module there is a tool bar containing the following shortcut buttons:

-  : ***New calibration***: enable parameters in preparation for generating a new calibration.
  **NB** When the *New calibration* button is selected it changes to:
-  **: *Discard calibration***: discard the current calibration data.
  **NB** If the current calibration data are unsaved the user is warned and given the opportunity to save them.
-  : ***Load calibration***: load a saved calibration from file.
-  : ***Save calibration***: save the current calibration data.
-  : ***Edit calibration***: edit the loaded calibration data.
-  : ***Calibration generation screen***: show the quantitative calibration generation screen (see 10.2).
-  : ***Calibration results summary***: show the quantitative calibration results summary (see 10.4).
-  : ***Analyse spectra***: show the quantitative calibration analysis screen (see 10.5).
-  : ***Conditioning shots analysis***: show the cleaning shots analysis screen (see 10.6)

## 10.2 Quantitative calibration generation screen

Selecting the  button in the tool bar will display to the calibration generation screen.

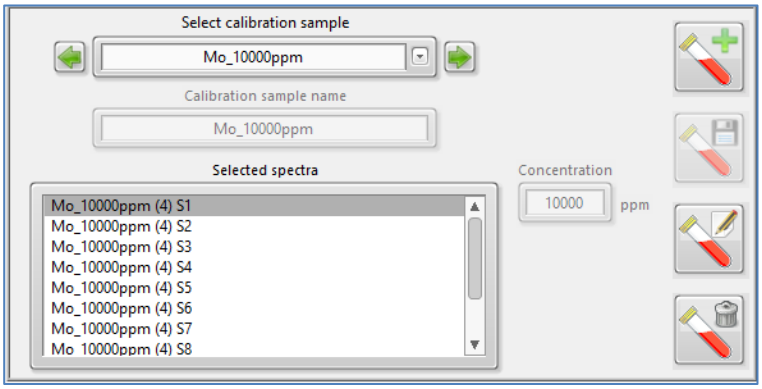
This screen is shown below.




Underneath the tool bar the calibration generation screen is divided into six panels. These are:

- *Sample details*: used for entry and display of data used to generate the calibration
- *Calibration configuration*: used to specify the type of calibration to be generated and the associated parameters
- *Calibration preview*: Preview of the calibration plot generated as sample data are entered
- *Current spectrum*: Display of the sample spectrum currently selected in the sample details panel
- *Analyte peak*: Display of the currently selected sample spectrum in the region of the analyte peak as specified in the calibration configuration panel
- *Matrix peak*: Display of the currently selected sample spectrum in the region of the matrix peak as specified in the calibration configuration panel
  **NB** The matrix peak is only displayed if the selected *Calibration type* is one for which the analyte peak metric is ratioed with that of a matrix peak.

### 10.2.1 **Sample details panel**



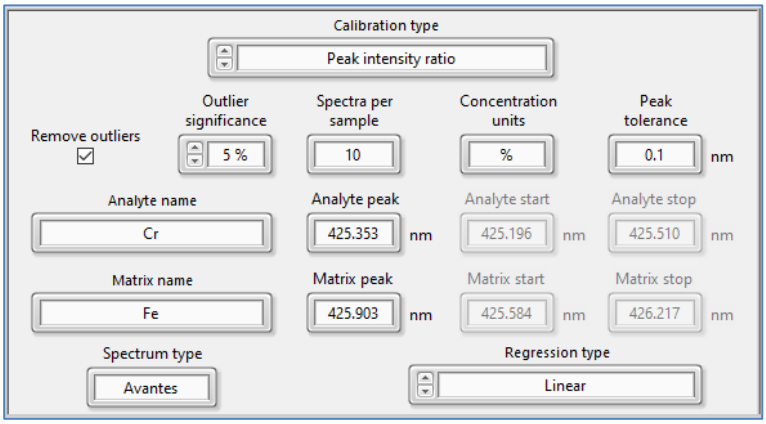

The sample details panel allows for the entry of data for the samples used to generate a calibration. This panel contains five further buttons and a number of parameters as described below.

-  : ***New sample***: enable parameters in preparation for adding details of a new calibration sample.
  **NB** When the *New sample* button is selected it changes to:

-  : ***Discard sample***: discard the current sample data.
-  : ***Save sample***: save the current sample data and add it to the calibration.
-  : ***Edit sample***: edit the selected calibration sample.
-  : ***Delete sample***: delete the current sample data and remove it from the calibration.
- 

: ***Select spectra***: open a file browser to allow selection of the spectra for the current sample to be used in the generation of the calibration.
**NB** This button is only made visible when the *New sample* button has been selected.
- ***Select calibration sample***: a control that displays a list of the samples added to the calibration and allows selection of which sample's details are currently displayed. It is also possible to move forwards or backwards through the list by clicking on the green arrows either side of the control.
- ***Calibration sample name***: the name assigned to the current sample.
- ***Selected spectra***: a list of the spectra selected for the current sample to be used in the generation of the calibration.
- ***Concentration***: the concentration of the analyte in the current sample.
**NB** The units of concentration are set according to the *Concentration units* parameter in the Calibration configuration panel (section 10.2.2).

### 10.2.2 **Calibration configuration panel**

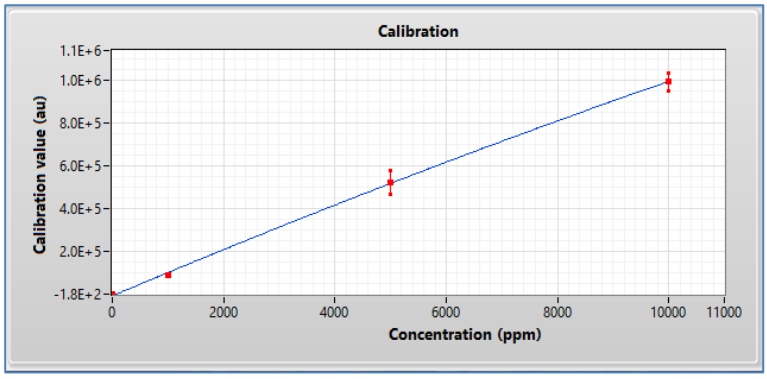



The calibration configuration panel allows the user to set all of the parameters to be used in the generation of a calibration. These parameters are as follows:

- ***Calibration type***: this parameter sets the metric to be used to generate the calibration. The options are as shown below. When a calibration type is selected other parameters in the calibration configuration panel are enabled/disabled as appropriate. See Appendix B for details of the calibration types and the corresponding parameters.
  - *Peak intensity*
  - *Peak intensity ratio*
  - *Peak area*
  - *Peak area ratio*
  - *Baseline-corrected peak intensity*
  - *Baseline-corrected peak intensity ratio*
  - *Baseline-corrected peak area*
  - *Baseline-corrected peak area ratio*
- ***Remove outliers***: checkbox to select whether to apply the Grubbs test to the data for each sample to remove outlier data points from the data used to generate the calibration (see 10.4.2 and 10.4.4 for information on the application of outlier removal in *LIBSoft* and Appendix  for details of the of the Grubbs test used for outlier removal).

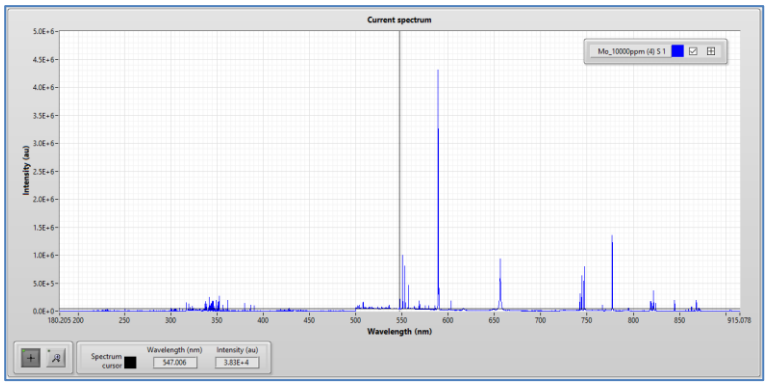
- ***Outlier significance***: the significance level to be used in the application of the Grubbs test (see Appendix ).
- ***Spectra per sample***: the number of spectra to be used for each sample in the generation of the calibration.
- ***Concentration units***: the units of concentration to be used for the calibration samples.
  **NB** Concentration units are for display purposes only and do not have any effect on determination of the calibration.
- ***Peak tolerance***: the wavelength tolerance to be used when identifying the maximum intensity of the analyte and matrix peaks (see Appendix B).
- ***Analyte name***: name of the analyte for which the calibration is to be generated.
- ***Analyte peak***: the wavelength of the analyte peak to be used in the generation of the calibration.
- ***Analyte start***: wavelength used to define the start of the analyte peak.
- ***Analyte stop***: wavelength used to define the end of the analyte peak.
- ***Matrix name***: name of the matrix element used in ratio-based calibration types.
- ***Matrix peak***: the wavelength of the matrix peak used in ratio-based calibration types.
- ***Matrix start***: wavelength used to define the start of the matrix peak.
- ***Matrix stop***: wavelength used to define the end of the matrix peak.
- ***Spectrum type***: the type of spectrum to be used to generate the calibration.
  **NB** The higher resolution EMU spectra need to be processed slightly differently to the spectra acquired using Avantes spectrometers therefore it is important that this parameter is set appropriately for the sample spectra.
- ***Regression type***: the type of regression analysis used to fit the calibration curve generated to the sample data (linear or quadratic).

### 10.2.3 Calibration preview panel




This panel displays a preview of the calibration plot. As the data for each sample is added to the calibration and saved a new data point is added to the plot. Error bars are marked on each data point corresponding to plus/minus one standard deviation of the calibration value. When sufficient samples have been added as determined by the specified *Regression type*, the calculated calibration curve is added to the plot: linear – two samples, quadratic – three samples.

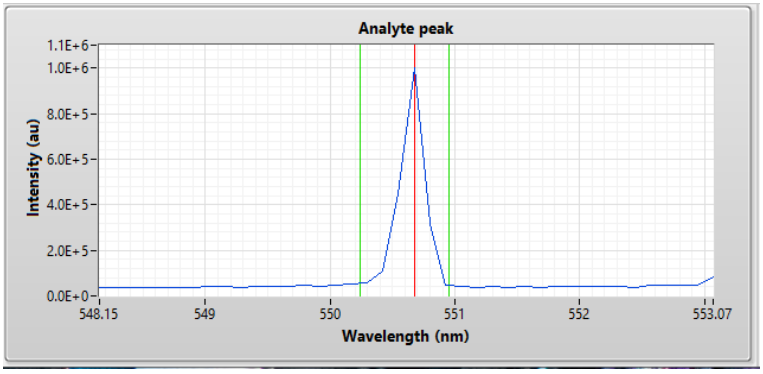
### 10.2.4 Current spectrum panel



This panel shows the currently selected spectrum in the list of *Selected spectra* (see 10.2.1).

### 10.2.5 **Analyte peak panel**

This panel displays the specified analyte peak for the currently selected spectrum in the list of *Selected spectra* (see 10.2.1). The peak is marked with up to three vertical lines depending on the *Calibration type* selected. A red line indicates the *Analyte peak* wavelength and two green lines mark the *Analyte start* and *Analyte* stop wavelengths (see below). If any of these specified wavelengths are updated then the corresponding marked line will be repositioned accordingly. Lines for those wavelengths not used for the current *Calibration type* are not displayed.



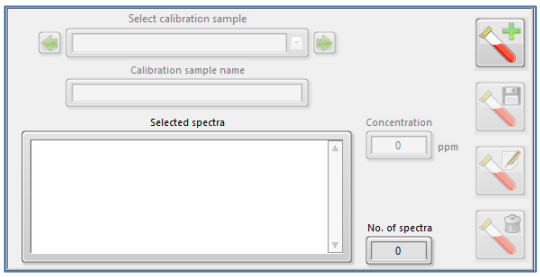

### 10.2.6 **Matrix peak panel**

This panel displays the specified matrix peak for the currently selected spectrum in the list of *Selected spectra* (see 10.2.1). The specified matrix peak is only displayed if a ratio-based *Calibration type* is selected. As for the analyte peak, the matrix peak is marked with up to three vertical lines depending on the *Calibration type* selected. A red line indicates the *Matrix peak* wavelength and two green lines mark the *Matrix start* and *Matrix stop* wavelengths. If any of these specified wavelengths are updated then the corresponding marked line will be repositioned accordingly. Lines for those wavelengths not used for the current *Calibration type* are not displayed.

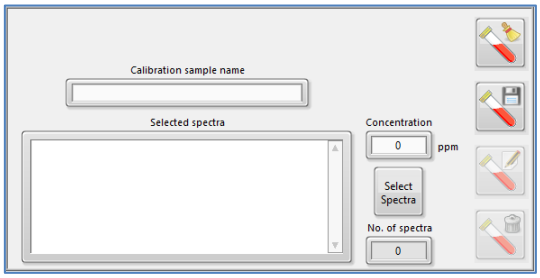
## 10.3 Generating a calibration

The calibration configuration screen is used to generate a new calibration. The procedure for doing so is as follows:

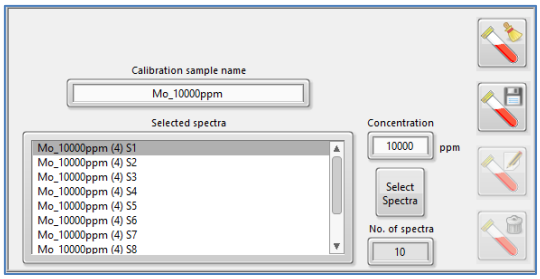
- Select the *New calibration* button.
  **NB** If any calibration data is already displayed this will need to be cleared using the *Discard calibration* button in order for the *New calibration* button to be visible.



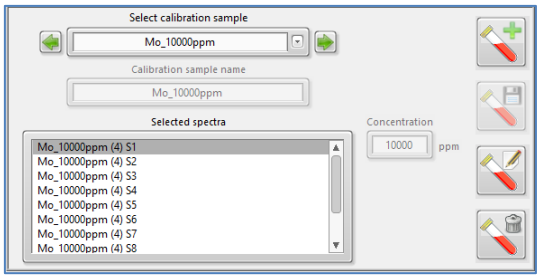

- Select the *New sample* button. This will enable the parameters required for entry of data for the new sample including making the *Select spectra* button visible and hiding the *Select calibration sample* control.




- Select the *Select spectra* button and use the file browser displayed to select the spectra to be used in the calibration for the new sample.
  **NB** The spectra used could be in the form of individual files or a single file containing multiple spectra.
- When the spectra have been selected their names are displayed in the list of *Selected spectra*. The first spectrum in the list will be highlighted and displayed in the current spectrum panel. The analyte peak and (matrix peak if appropriate) will be displayed in the corresponding panels.
- The *Calibration sample name* is automatically populated with the root file name of the selected spectra but can be edited at this point if required.
- Enter the *Concentration* of the sample in the specified units.




- When all of the required data has been entered select the *Save sample* button.
  **NB** If any of the required data has not been entered a warning to this effect will be displayed.
- The sample data will be added to the calibration, the calculated calibration value will be added to the preview plot displayed in the calibration panel and the *Select calibration sample* control will be redisplayed and will updated to include the name of the new sample.




- Add further samples to the calibration as required by repeating the above procedure.
- Once all samples have been added select the *Save calibration* button and choose a file name and location for the saved calibration. Once saved the file name of the calibration will be displayed in the title bar of the quantitative calibration window.

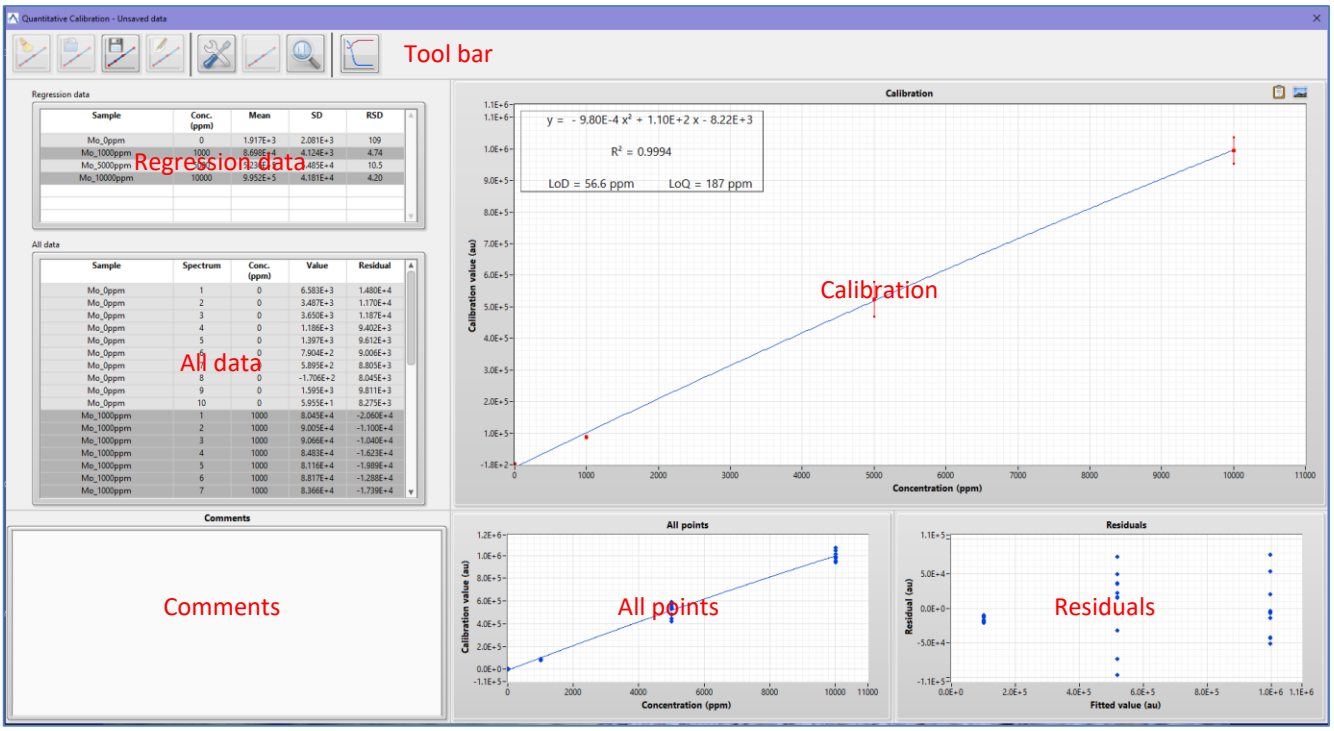
Saved calibrations can be loaded for viewing/editing and/or application to acquired spectra as required by selecting the *Load calibration* button. The saved calibration file includes details of the file paths for the spectra used to generate the calibration and if the *Edit calibration* button is selected, *LIBSoft* will try to identify those files and, if successful, will enable the calibration parameters so that they can then be edited. If the spectrum files have been moved and/or deleted since the calibration was created and thus can't be found, a warning will be displayed and it will not be possible to edit the calibration.

If the calibration is editable then any of the calibration parameters can be changed as required and the calibration will be updated accordingly. Data for specific samples can also be edited by selecting the sample to be updated in the *Select calibration sample* control and then selecting the *Edit sample* button. The parameters for that sample will then be displayed and enabled such that they can be updated as required. To save the changed sample data select the *Save sample* button. New samples can also be added to the calibration and/or existing samples deleted by selecting the *New sample* or *Delete sample* buttons respectively.

### 10.4 Quantitative calibration results summary

The Quantitative calibration results summary can be accessed by selecting the  button in the tool bar. It displays details of all the data used to generate the calibration and can be accessed at any point while adding sample data to a calibration.

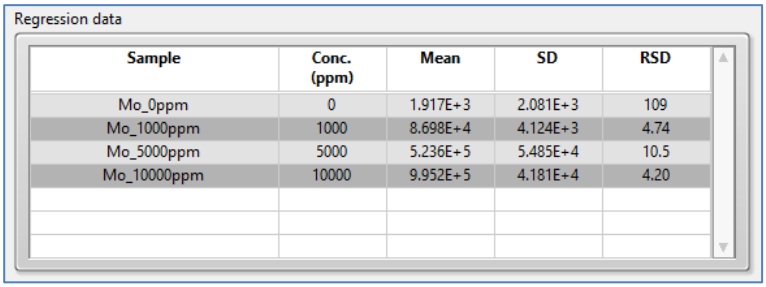
This screen is shown below.




Underneath the tool bar the calibration display screen is divided into six panels. These are:

- *Regression data*: details of the calculated calibration values for each sample, including the mean, standard deviation (SD) and relative standard deviation (RSD).
- *All data*: the calibration values calculated for each individual spectrum.
- *Calibration*: The calibration plot generated as sample data are entered.
- *All points*: A plot of the calibration displaying each individual point. This graph can be useful in identifying outliers.
- *Residuals*: A plot of the residual calculated for each individual spectrum
- *Comments*: Space for the user to add text comments regarding the calibration to be saved with the calibration file.

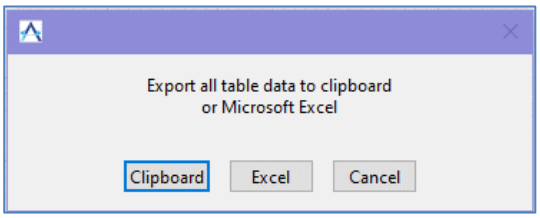
### 10.4.1 **Regression data panel**




This panel displays the calibration data calculated for each sample using the specified *Calibration type* metric together with the sample name and the known analyte concentration. The mean value of the calibration metric, standard deviation (SD) and residual standard deviation (RSD) are displayed. The RSD is calculated as:

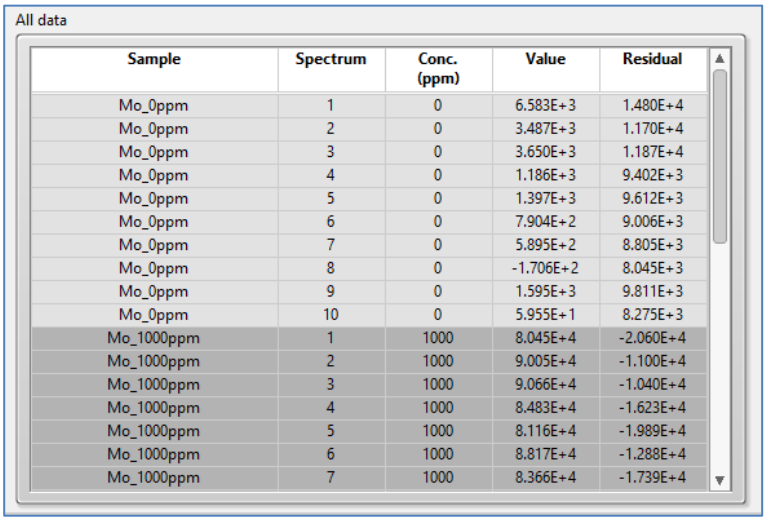
$$RSD = (100 \times SD) / Mean$$

Right-clicking on the table of regression data will cause a dialogue to be displayed giving the option to export all of the data in the table either to the Windows clipboard or to Microsoft Excel.




**NB** If the Excel option is selected then Excel will be opened automatically (if installed on the computer running *LIBSoft*) and the data from the table copied into a new worksheet and the file given a temporary name. The worksheet can then be saved with a name of the user's choice.

### 10.4.2 **All data panel**



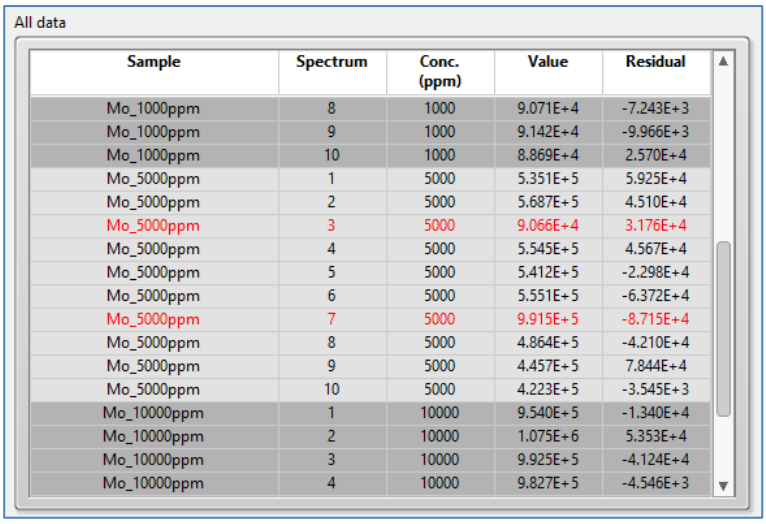

This panel displays the value of the specified *Calibration type* metric for each spectrum used to generate the calibration and its residual together with the sample name, spectrum number and the known analyte concentration. The residual value is calculated as:

$$Residual = Value - Value_{Calc}$$

where $Value_{Calc}$ is the value calculated using the regression equation.

Right-clicking on the table of all data will cause a dialogue to be displayed giving the option to export all of the data in the table either to the Windows clipboard or to Microsoft Excel (see 10.4.1).

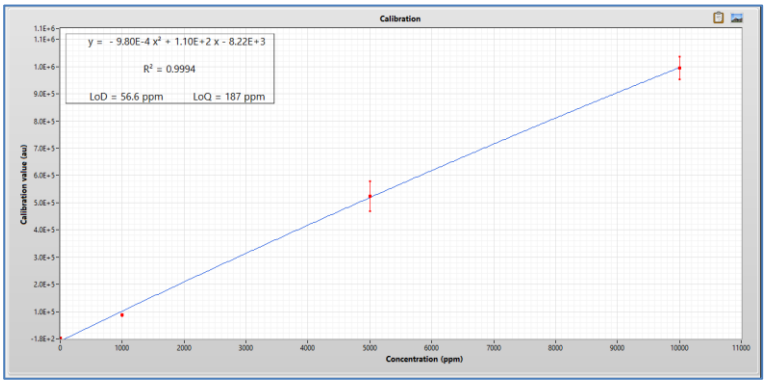
When the *Remove outliers* option is enabled (see 10.2.2), outliers are identified using the specified significance level and they are automatically removed from the data used to generate the calibration equation. The outlier points identified are highlighted in red. This is shown below.


All data

| Sample | Spectrum | Conc. (ppm) | Value | Residual |
|---|---|---|---|---|
| Mo_1000ppm | 8 | 1000 | 9.071E+4 | -7.243E+3 |
| Mo_1000ppm | 9 | 1000 | 9.142E+4 | -9.966E+3 |
| Mo_1000ppm | 10 | 1000 | 8.869E+4 | 2.570E+4 |
| Mo_5000ppm | 1 | 5000 | 5.351E+5 | 5.925E+4 |
| Mo_5000ppm | 2 | 5000 | 5.687E+5 | 4.510E+4 |
| Mo_5000ppm | 3 | 5000 | 9.066E+4 | 3.176E+4 |
| Mo_5000ppm | 4 | 5000 | 5.545E+5 | 4.567E+4 |
| Mo_5000ppm | 5 | 5000 | 5.412E+5 | -2.298E+4 |
| Mo_5000ppm | 6 | 5000 | 5.551E+5 | -6.372E+4 |
| Mo_5000ppm | 7 | 5000 | 9.915E+5 | -8.715E+4 |
| Mo_5000ppm | 8 | 5000 | 4.864E+5 | -4.210E+4 |
| Mo_5000ppm | 9 | 5000 | 4.457E+5 | 7.844E+4 |
| Mo_5000ppm | 10 | 5000 | 4.223E+5 | -3.545E+3 |
| Mo_10000ppm | 1 | 10000 | 9.540E+5 | -1.340E+4 |
| Mo_10000ppm | 2 | 10000 | 1.075E+6 | 5.353E+4 |
| Mo_10000ppm | 3 | 10000 | 9.925E+5 | -4.124E+4 |
| Mo_10000ppm | 4 | 10000 | 9.827E+5 | -4.546E+3 |

If the significance level is modified the calibration is recalculated and the results are updated accordingly. If the *Remove outliers* option is disabled all of the data are used to generate the calibration.

### 10.4.3 **Calibration panel**



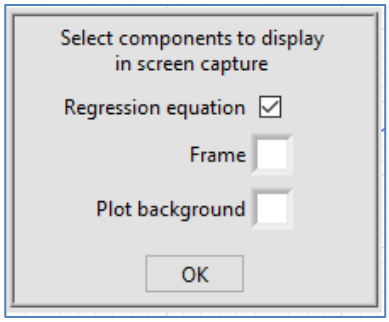

This panel displays a plot of the calibration. It is very similar to the plot displayed in the calibration preview panel on the quantitative calibration configuration screen (see 10.2.3) but also includes the equation of the calibration regression line, the $R^2$ value and estimates for the limit of detection (LOD) and limit of quantification (LOQ) for the calibration equation (see Appendix D). As for the calibration preview, the plot is updated as the data for each sample is added to the calibration and error bars are marked on each data point corresponding to plus/minus one standard deviation of the mean calibration value. The regression line plot, equation and associated values are only displayed when sufficient samples have been added as determined by the specified *Regression type*: linear – two samples, quadratic – three samples.

The calibration panel includes two icons in the top right-hand corner. These are:

- : ***Copy an image of the calibration to the Windows clipboard***
- : ***Save an image of the calibration as a PNG file***

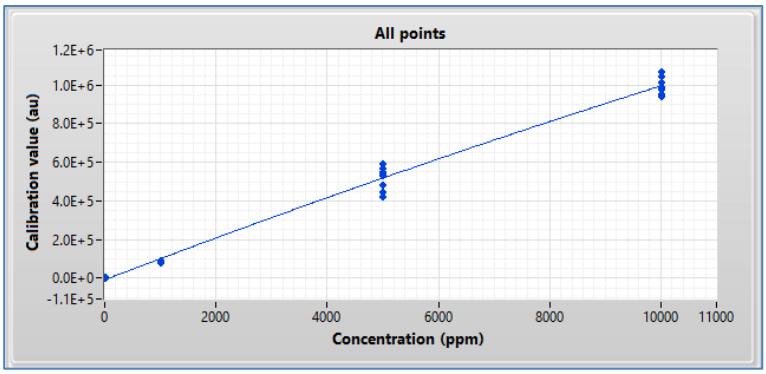
When the clipboard icon is selected, a window is displayed allowing the user to choose whether to include the regression equation in the image copied to the clipboard and the colour of the plot frame and background.

These selections can be updated as required. Selecting ***OK*** then copies the image of the spectrum to the clipboard.



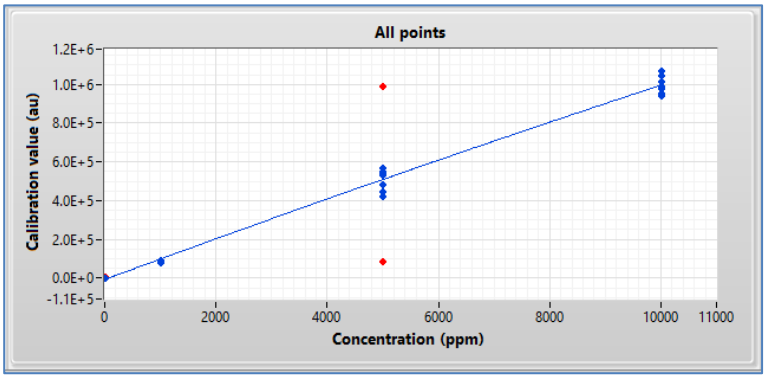

Similarly, when the photo icon is selected, a window is displayed allowing the user to choose whether to include the regression equation in the image to be saved. These selections can be updated as required. Selecting ***OK*** displays a file dialogue to allow the user to choose where to save the image of the spectrum and the file name to be used.

### 10.4.4 **All points panel**



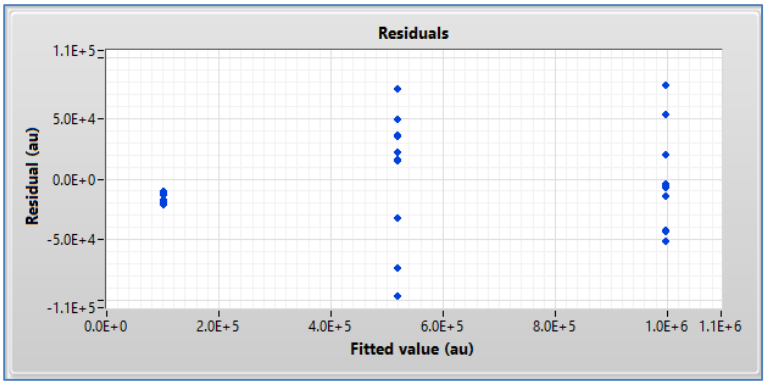

This panel displays a plot of the values of the specified *Calibration type* metric determined for each individual spectrum used to generate the calibration against the known concentration of the sample. When sufficient samples have been added as determined by the specified *Regression type* the regression line is also overlaid on the plot. The plot in this panel can help in the identification of any outlier points in the calibration.

When the *Remove outliers* option is enabled (see 10.2.2), outliers are identified using the specified significance level and they are automatically removed from the data used to generate the calibration equation. The outlier points identified are highlighted in red. This is shown below.



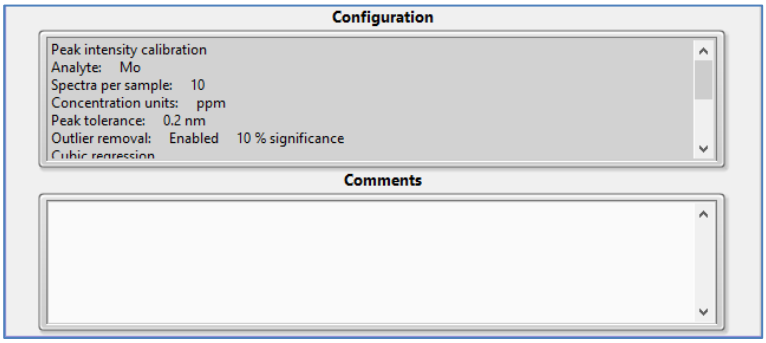

If the significance level is modified the calibration is recalculated and the results are updated accordingly. If the *Remove outliers* option is disabled all of the data are used to generate the calibration.

### 10.4.5 **Residuals panel**




This panel displays a plot of the residual value calculated for each individual spectrum used to generate the calibration against the calibration value for that spectrum derived from the regression equation.

### 10.4.6 **Comments panel**

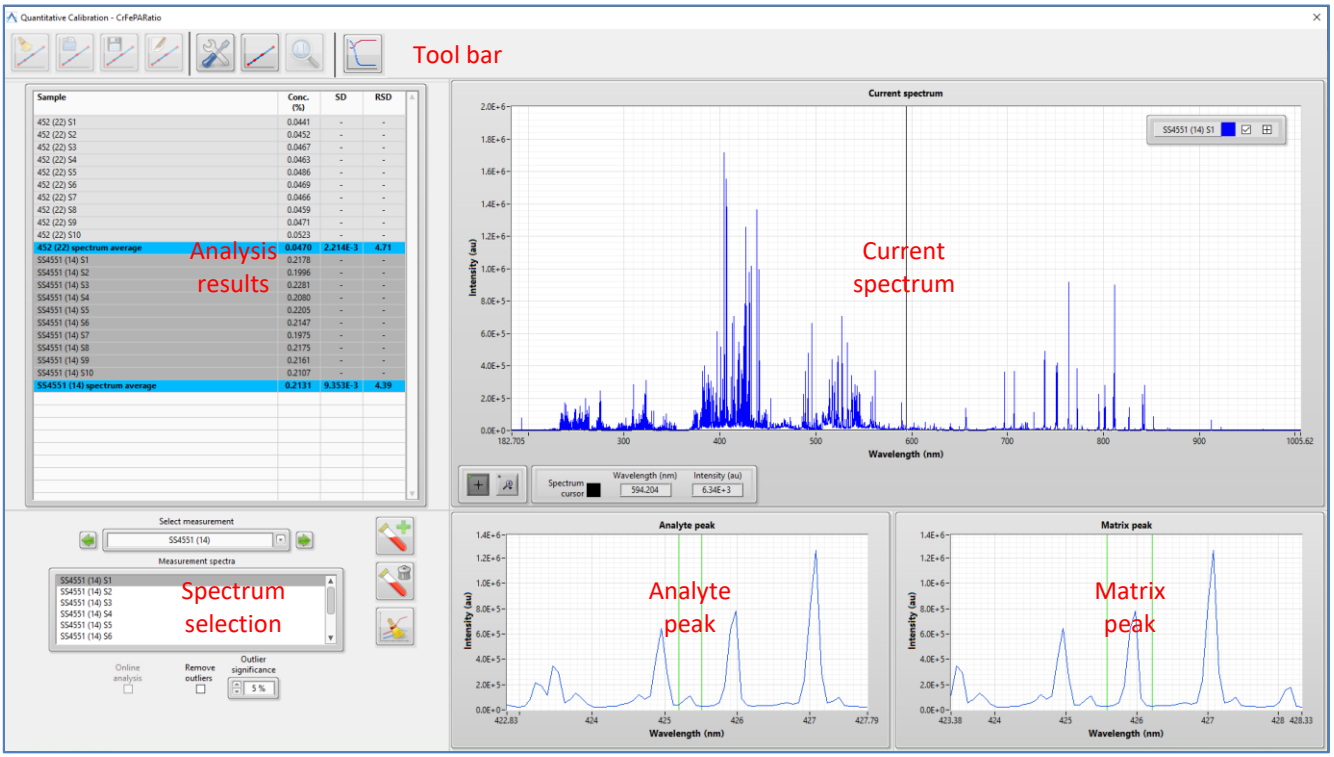



This panel provide displays a summary of the current calibration configuration and space for the user to add text comments, if required, regarding the calibration. Any comments entered will be saved to the calibration file and redisplayed if the calibration is loaded at a later time. Right-clicking on either the *Configuration* or *Comments* window will copy the text from both windows to the clipboard so that it can be inserted into a document.

## 10.5 Quantitative calibration analysis screen

The Quantitative calibration analysis screen can be accessed by selecting the  button in the tool bar. This button is, however, only enabled when a valid calibration has been created or loaded, i.e., there is a calibration equation with which to analyse spectra.

This screen is shown below.




Underneath the tool bar the calibration analysis screen is divided into five panels. These are:

- *Spectrum selection*: Controls used to load the spectra to be analysed.
- *Analysis results*: The results of the analysis of the loaded spectra using the current calibration
- *Current spectrum*: Display of the currently selected spectrum for the currently selected measurement.
- *Analyte peak*: Display of the currently selected spectrum in the region of the analyte peak.
- *Matrix peak*: Display of the currently selected spectrum in the region of the matrix peak.
  **NB** The matrix peak is only displayed if the selected *Calibration type* is one for which the analyte peak metric is ratioed with that of a matrix peak.

### 10.5.1 **Spectrum selection panel**

This panel provides the facility to load spectra for analysis. It contains three buttons and a number of parameters as described below.

-  : ***New measurement(s)***: opens a file browser allowing the user to load spectrum files for analysis.
-  : ***Delete measurement***: deletes the currently selected measurement and removes the corresponding data from the analysis results panel.
-  : ***Clear all measurements***: deletes all measurements and clears all data from the analysis results panel.
- ***Select measurement***: a control that displays a list of the measurements selected for analysis and allows selection of which measurement's details are currently displayed. It is also possible to move forwards or backwards through the list by clicking on the green arrows either side of the control.
- ***Measurement spectra***: a list of all of the spectra included in the currently selected measurement
- ***Online analysis***: checkbox which when checked enables the analysis using a loaded calibration as spectra are acquired (see 10.5.6).
  **NB** This checkbox is only enabled if the system in use is capable of acquiring spectra, i.e., there a spectrometer is connected and has been successfully detected and initialised by *LIBSoft*.
- ***Remove outliers***: checkbox to select whether to apply the Grubbs test to the data for measurement which include multiple spectra to remove outlier data points from the calculation of the spectrum average (see 10.5.2 for information on the application of outlier removal from multi-spectra measurements and Appendix  for details of the of the Grubbs test for outlier removal).

- ***Outlier significance***: the significance level to be used in the application of the Grubbs test (see Appendix C).

When the New measurement button is selected a file browser is displayed allowing the selection of one or more files for analysis.

When a file is loaded then all of the spectra in this file will be loaded and automatically analysed using the current calibration and the results of the analysis will be displayed in the analysis results panel (see 10.5.2). The name of the file will be added to the list in the *Select measurement* control and the spectra included in the loaded file will be added to the list of *Measurement spectra.*

If a file is selected but *LIBSoft* identifies that there are actually multiple files in the current folder with the same root file name, then the user will be given the option to either select all of the files identified or the single file selected. For example, if the file selected is:

*Mo1000ppm (2) M1*

But the current folder includes spectra from multiple measurements on that sample, i.e.,

*Mo1000ppm (2) M1*
*Mo1000ppm (2) M2*
*Mo1000ppm (2) M3*
*:*
*Mo1000ppm (2) Mn*

then the user will be given the option to load just *Mo1000ppm (2) M1* or all the files with the *Mo1000ppm (2)* root file name. If the user elects to load all of the files identified each of the spectra will be analysed automatically using the current calibration and the results of the analyses will be displayed in the analysis results panel (see 10.5.2). Multiple files can also be selected directly.

Additional spectra can be selected for analysis as required by selecting the *New measurement(s)* button. The results of the analysis of any new spectra will be added to those already displayed in the analysis results panel. To clear the results for a specific measurement from the analysis results panel, select the chosen measurement from the list in the *Select measurement* control and then select the *Delete measurement* button. To clear the results for all measurements from the analysis results panel select the Clear all measurements button.

### 10.5.2 **Analysis results panel**

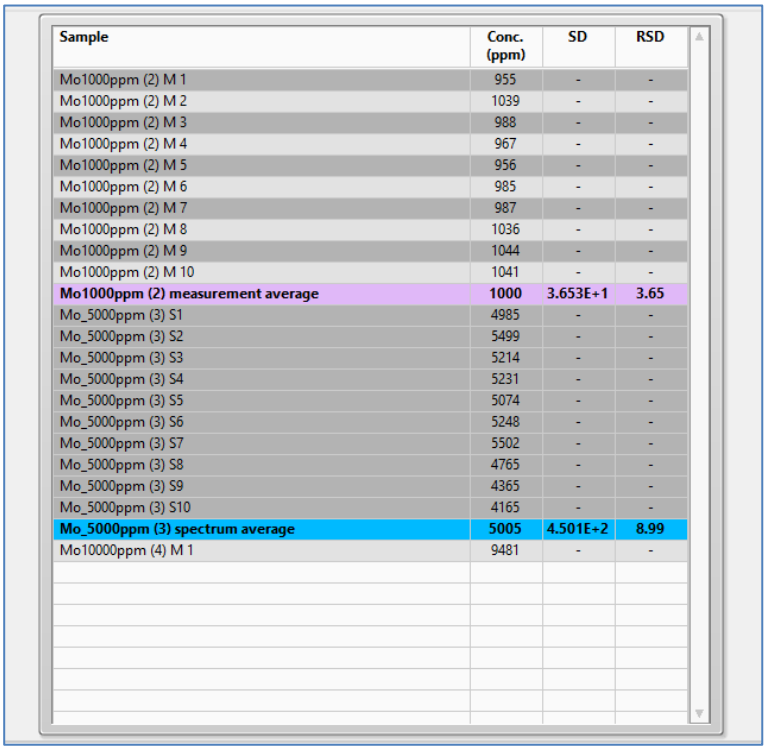
This panel displays a table of the results of the analysis of the selected spectra. The name of each spectrum analysed together with the concentration calculated from it using the current calibration are displayed.

If multiple measurements on the same sample are analysed then an average value of concentration, together with the standard deviation (SD) and residual standard deviation (RSD) are also displayed below the results for the multiple measurements. These are named using the root file name and a *measurement average* suffix and the cell background is coloured lilac for clarity.

If a measurement containing multiple spectra is analysed then an average value of concentration, together with the standard deviation (SD) and residual standard deviation (RSD) are also displayed below the results for the individual spectra. These are named using the root file name and a *spectrum average* suffix and the cell background is coloured blue for clarity.

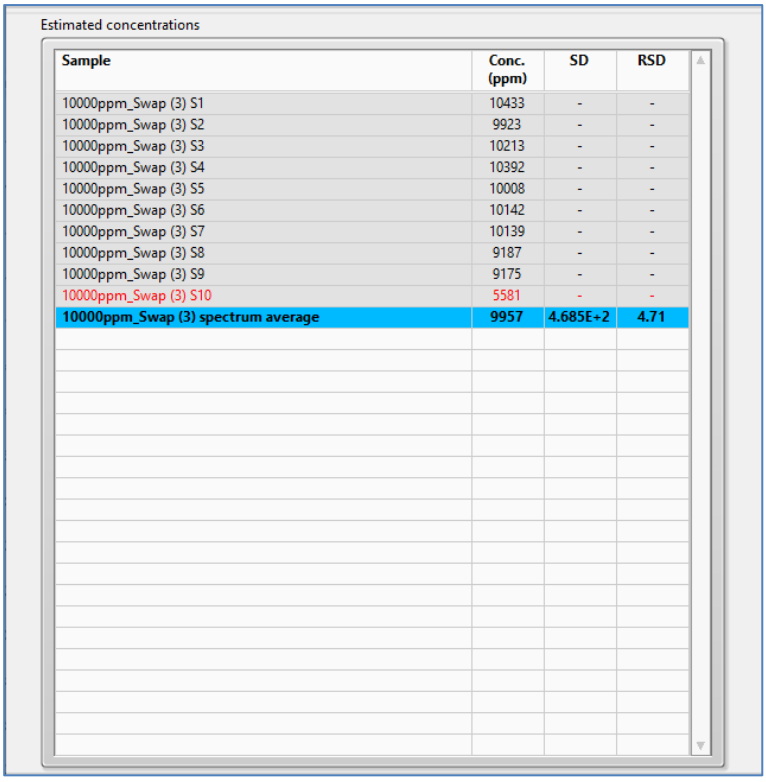
If multiple measurements each comprising multiple spectra are analysed then multiple spectrum averages and a single measurement average equal to the mean of the analysis results for all of the spectra will be calculated.

An example of the analysis results panel is shown below to highlight these features.



| Sample | Conc. (ppm) | SD | RSD |
|---|---|---|---|
| Mo1000ppm (2) M 1 | 955 | - | - |
| Mo1000ppm (2) M 2 | 1039 | - | - |
| Mo1000ppm (2) M 3 | 988 | - | - |
| Mo1000ppm (2) M 4 | 967 | - | - |
| Mo1000ppm (2) M 5 | 956 | - | - |
| Mo1000ppm (2) M 6 | 985 | - | - |
| Mo1000ppm (2) M 7 | 987 | - | - |
| Mo1000ppm (2) M 8 | 1036 | - | - |
| Mo1000ppm (2) M 9 | 1044 | - | - |
| Mo1000ppm (2) M 10 | 1041 | - | - |
| **Mo1000ppm (2) measurement average** | **1000** | **3.653E+1** | **3.65** |
| Mo_5000ppm (3) S1 | 4985 | - | - |
| Mo_5000ppm (3) S2 | 5499 | - | - |
| Mo_5000ppm (3) S3 | 5214 | - | - |
| Mo_5000ppm (3) S4 | 5231 | - | - |
| Mo_5000ppm (3) S5 | 5074 | - | - |
| Mo_5000ppm (3) S6 | 5248 | - | - |
| Mo_5000ppm (3) S7 | 5502 | - | - |
| Mo_5000ppm (3) S8 | 4765 | - | - |
| Mo_5000ppm (3) S9 | 4365 | - | - |
| Mo_5000ppm (3) S10 | 4165 | - | - |
| **Mo_5000ppm (3) spectrum average** | **5005** | **4.501E+2** | **8.99** |
| Mo10000ppm (4) M 1 | 9481 | - | - |

If outlier removal is enabled (see 10.5.1) any spectra identified as being outliers will be removed from the calculation of any averages. The outliers will also be highlighted in red in the table of results. See below.



Estimated concentrations

| Sample | Conc. (ppm) | SD | RSD |
|---|---|---|---|
| 10000ppm_Swap (3) S1 | 10433 | - | - |
| 10000ppm_Swap (3) S2 | 9923 | - | - |
| 10000ppm_Swap (3) S3 | 10213 | - | - |
| 10000ppm_Swap (3) S4 | 10392 | - | - |
| 10000ppm_Swap (3) S5 | 10008 | - | - |
| 10000ppm_Swap (3) S6 | 10142 | - | - |
| 10000ppm_Swap (3) S7 | 10139 | - | - |
| 10000ppm_Swap (3) S8 | 9187 | - | - |
| 10000ppm_Swap (3) S9 | 9175 | - | - |
| 10000ppm_Swap (3) S10 | 5581 | - | - |
| **10000ppm_Swap (3) spectrum average** | **9957** | **4.685E+2** | **4.71** |

Right-clicking on the table of analysis results will cause a dialogue to be displayed giving the option to export all of the data in the table either to the Windows clipboard or to Microsoft Excel (see 10.4.1).

### 10.5.3 **Current spectrum panel**

This panel shows the currently selected spectrum. The measurement for which spectra are displayed can be selected using the *Select measurement* control and the specific spectrum for that measurement can be selected by clicking on the appropriate item in the list of *Measurement spectra* (see 10.5.1).

### 10.5.4 **Analyte peak panel**

As for the corresponding panel on the calibration configuration screen (see 10.2.5), this panel displays the specified analyte peak for the currently selected spectrum. The peak is marked with up to three vertical lines depending on the *Calibration type* selected. A red line indicates the *Analyte peak* wavelength and two green lines mark the *Analyte start* and *Analyte* stop wavelengths (see below). If any of these specified wavelengths are updated then the corresponding marked line will be repositioned accordingly. Lines for those wavelengths not used for the current *Calibration type* are not displayed.

### 10.5.5 **Matrix peak panel**

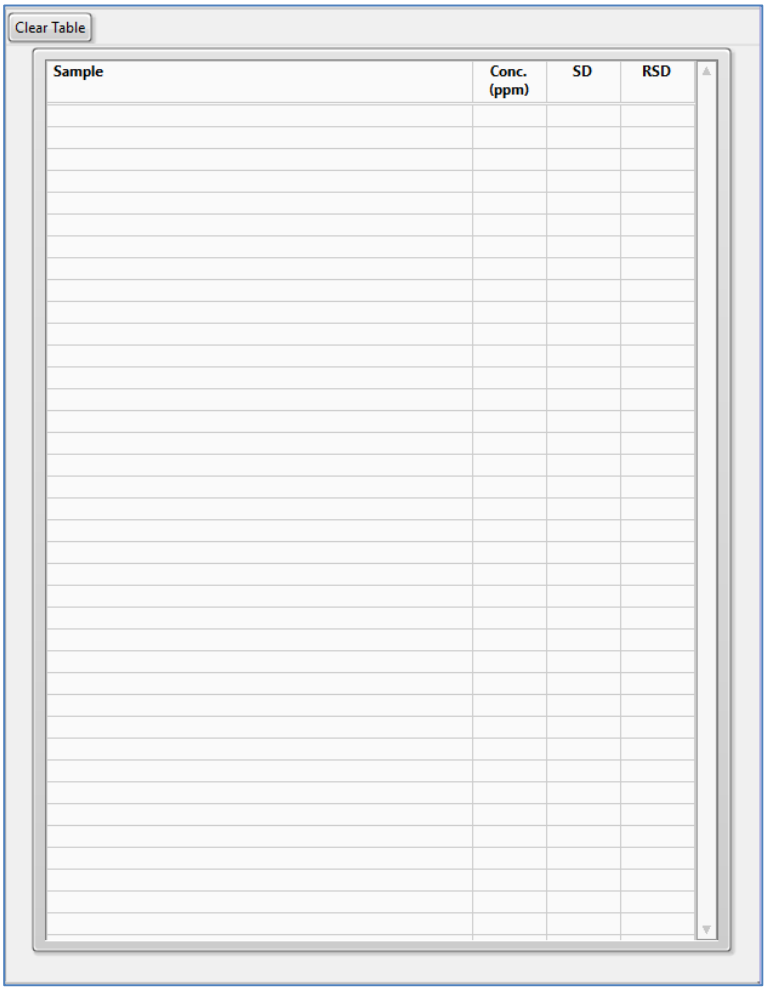
As for the corresponding panel on the calibration configuration screen (see 10.2.6), this panel displays the specified matrix peak for the currently selected spectrum. The specified matrix peak is only displayed if a ratio-based *Calibration type* is selected. As for the analyte peak, the matrix peak is marked with up to three vertical lines depending on the *Calibration type* selected. A red line indicates the *Matrix peak* wavelength and two green lines mark the *Matrix start* and *Matrix stop* wavelengths. If any of these specified wavelengths are updated then the corresponding marked line will be repositioned accordingly. Lines for those wavelengths not used for the current *Calibration type* are not displayed.

### 10.5.6 **Online analysis**

If the *Online analysis* option is checked (see 10.5.1) the currently loaded calibration will be used to analyse spectra as they are acquired.

**TIP:** This option is only enabled for selection if a spectrometer is connected to the system and has been detected and correctly initialised by *LIBSoft*, i.e., the system is capable of acquiring spectra.

Once this option has been enabled, close the quantitative calibration module to return to the *LIBSoft* main screen. The table of analysis results will be displayed on the main screen to the right of the acquired spectrum display. The format of the table will be the same as used in the quantitative calibration module except that an additional *Clear table* button will be displayed just above it.




Acquire spectra as normal. The acquired spectra will be analysed automatically using the calibration and the results displayed in the table. As further spectra are acquired the results of the analysis of these spectra will be added to the table of results. However, the *Clear table* button can be used to delete any existing results prior to an acquisition if necessary.

If the quantitative calibration module is opened when data are displayed in the analysis results table on the main *LIBSoft* screen, these results will also be displayed in the quantitative calibration module.

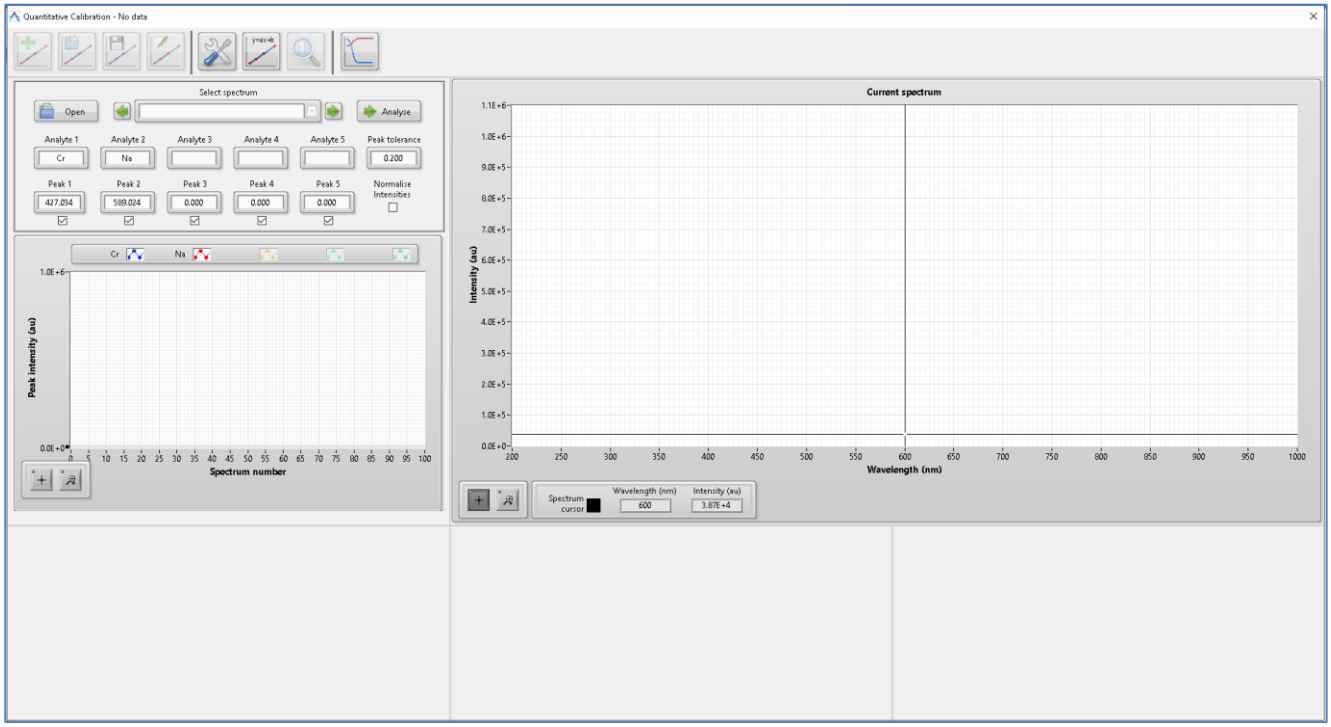
The results export options (see 10.5.2) can also be used from the *LIBSoft* main screen.

If the online element identification is also enabled (see 12.11), additional buttons will be displayed alongside the *Clear table* button at the top of the table allowing the user to toggle between the display of the online quantitative calibration results and the online element identification results.

## 10.6 Conditioning shots analysis

### 10.6.1 Introduction

The Quantitative calibration conditioning shots analysis screen can be accessed by selecting the  button in the tool bar.




The surface of a calibration sample may be contaminated even if it has been cleaned with a solvent. The easiest way to remove such contamination is by firing a number of laser shots to clean or condition the surface before acquiring a spectrum. There is not a fixed number of conditioning shots that can be used as this can vary from sample to sample, but 10 - 100 shots are typically used. It is important to ensure that the peaks corresponding to emission lines of contaminant elements such as Na, Ca or Mg decay before acquiring calibration spectra but also that the intensity of peaks corresponding to the emission lines of interest is stable. The conditioning shots analysis screen can be used to plot the intensity evolution of contaminant element lines as well as those of the elements of interest as a function of the number of laser shots in the same sample position.

### 10.6.2 Acquisition of conditioning shot data

To use the conditioning shots analysis screen, first acquire a series of spectra from the same position on the calibration sample to be assessed. A series of single-shot spectra could be used for this purpose or a series of spectra comprising a number of accumulations, particularly if it is considered that the contamination may be more difficult to remove and therefore require a significant number of conditioning shots.

**NB** A series of spectra can be acquired by configuring the *Spectra* parameter on the acquisition configuration screen appropriately (see section 5.1). The spectra will then be saved in a single file with the filename appended with an *S* suffix to indicate that it is a multi-spectrum file (see section 8).

### 10.6.3 Analysis of conditioning shot data

Once the spectra have been acquired and saved they can be loaded for analysis by selecting the *Open* button on the conditioning shot analysis screen and selecting the saved multi-spectrum file using the file browser that is displayed. Each spectrum in the file will be loaded individually and listed in the *Select spectrum* display to the right of the *Open* button. Each spectrum will be named using the the root filename appended with an *Sn* suffix where *n* is the spectrum number in the file. The first spectrum in the file will be displayed by default in the window on the right hand side of the screen. The displayed spectrum can be changed by left-clicking on the small down arrow at the right of the *Select spectrum* display and then selecting the required spectrum

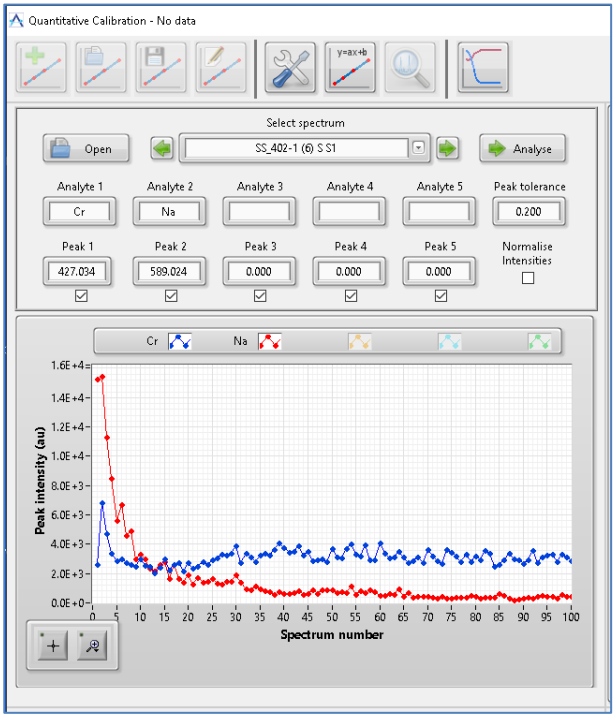
from the list. Alternatively the green arrows to the left and right of the *Select spectrum* display can be used to move up an down the list of loaded spectra and display the selected spectrum.

Once the spectra have been loaded the peaks to be analysed can be specified. Up to five peaks can be selected for analysis at any one time. In each case the symbol of the element to which the peak relates can be entered in the *Analyte n* window and the corresponding wavelength of the peak entered in the *Peak n* window.

**NB** The analyte name has no effect on the analysis itself. It is simply used to identify the different analytes in the resulting plot of conditioning shot analysis data. The peak wavelengths can be identified by using the cursor and zoom functions on the displayed spectra. These functions are the same as for other spectra displayed LIBSoft (see 9.3). If there is any doubt about which peak corresponds to which element emission line the Peak Identification module (see section 11) can be used to assist in selecting the best peaks for the analysis.

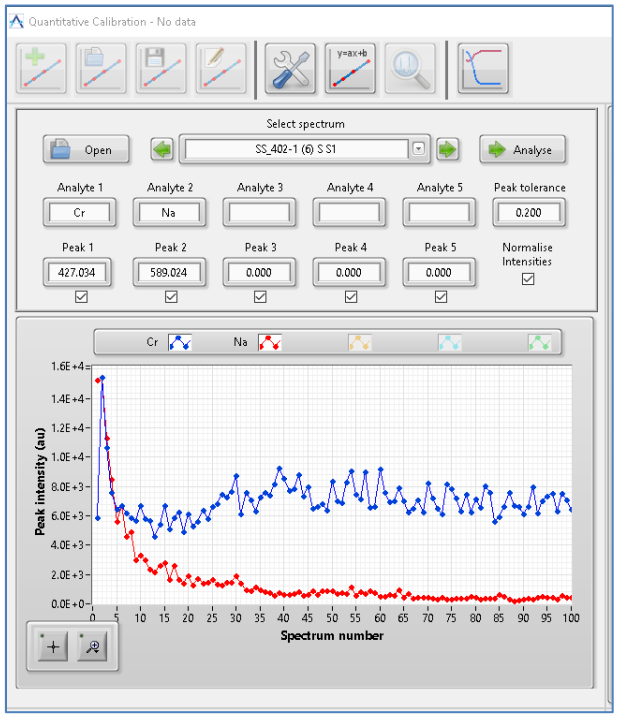
The *Peak tolerance* parameter specifies the wavelength tolerance to be used when identifying the maximum intensity of the analyte peak. Typical values for Avantes spectrometers are 0.1 - 0.2 nm and typical values for EMU spectrometer are 0.01 - 0.02 nm.

Once the peaks for analysis have been specified the spectra can be processed by selecting the *Analyse* button. The intensity of each of the specified peaks in each of the loaded spectra will be determined and plotted as a function of spectrum number on the graph below. The image below shows the intensity evolution of Cr and Na peaks in a series of 100 single-shot spectra acquired from a stainless steel sample.




The effect of surface contamination can be seen as the intensity of the specified Na peak is initially high but falls to a low and relatively stable level. The intensity of the Cr peak is initially variable before gradually rising to a more stable level. These spectra were acquired to assess the number of cleaning shots that should be used when determining a calibration for Cr in stainless steel. From the above plot it would be sensible to use ~40 sample conditioning shots to remove the Na surface contamination and allow the Cr peak intensity to stabilise.

Also on this conditioning shot analysis screen is a checkbox option to *Normalise Intensities*. When this option is selected any currently loaded data are reanalysed and the intensities of all peaks are normalised to the maximum of all the peak intensity data. This can sometimes make the intensity evolution trends clearer especially when there is a large difference between the intensities of different peaks. The following image shows the same Cr and Na peak intensity data but this time normalised to the maximum intensity.




Deselecting this checkbox will reanalyse the data and plot the raw intensities.

Only intensity data for analyte peaks that have both an analyte name and a non-zero wavelength specified will be plotted. Below each peak wavelength specification there is a checkbox which allows the visibility of individual intensity plots to be toggled. The default is for the intensities of all peaks for which both an analyte name and a non-zero wavelength are specified to be plotted, however temporarily hiding one or more of the intensity plots can sometimes make the intensity evolution trends clearer.

# 11 Peak Identification

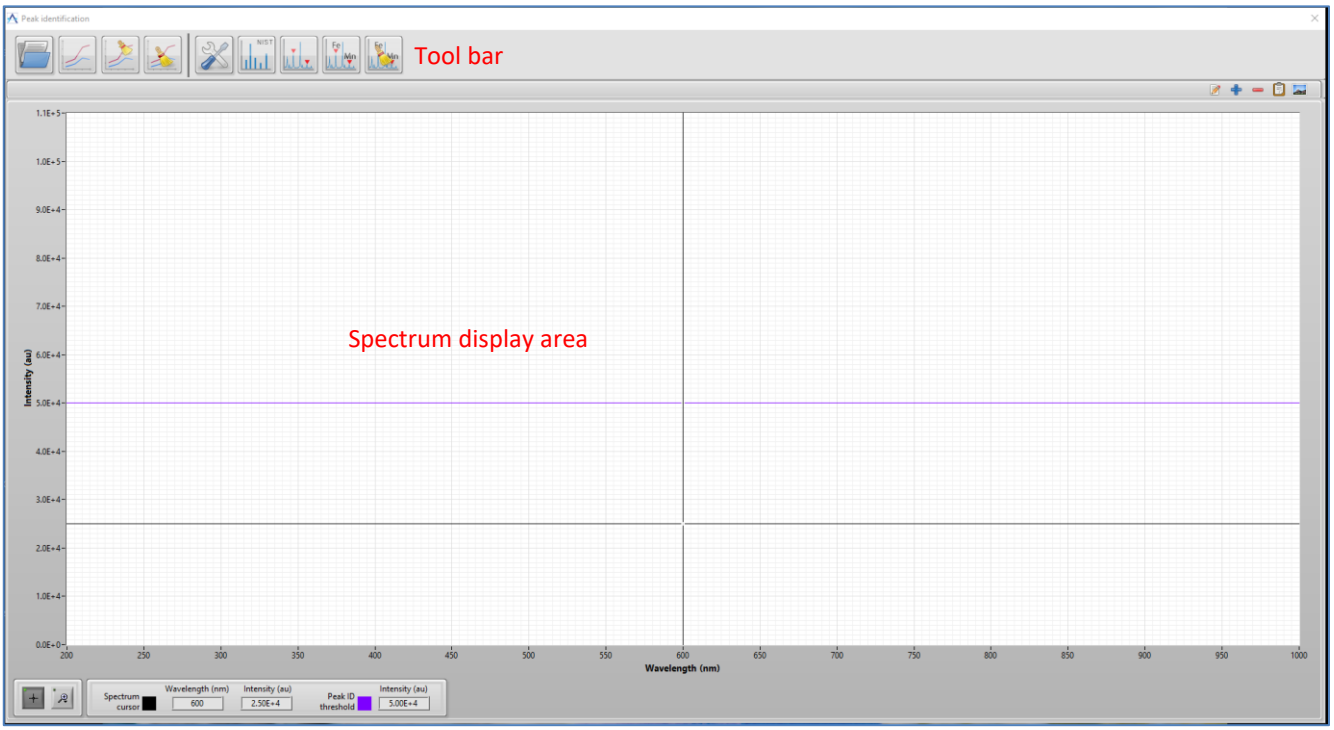
## 11.1 Introduction

*LIBSoft 2020* includes a module to assist with the identification of peaks in acquired spectra. This module is only available in *LIBSoft Full* and the corresponding USB key is required to activate and utilise its functions.

The peak identification module includes several useful tools to help the user during the identification of the peaks in the spectrum. From this module the user can access a spectral database (which includes for example spectra acquired from high purity samples) and compare those spectra with the spectrum under analysis. In addition the emission lines from the NIST atomic emission database can be overlayed over the spectrum to help in the identification of the spectrum peaks. Finally, it provides the ability to automatically detect, mark and label peaks in the spectrum. The results of the identification process can be exported/saved easily using the provided options.

The peak identification module can be opened from the main *LIBSoft* application screen by selecting the  shortcut button. This causes the peak identification module main screen to be opened and maximised in front of the main *LIBSoft* application screen which remains open in the background. The peak identification module can be closed at any time to return to the main *LIBSoft* application by left-clicking on the ***X*** in the top right-hand corner of the screen. Any data currently loaded in the peak identification module will however be retained in this instance and will be redisplayed if the module is reopened, provided that the main *LIBSoft* application has not been closed in the meantime.

At the top of the peak identification main screen there is a *Tool bar* providing shortcut buttons to access various functions and the peak identification configuration screen. The main region of the screen is the *Spectrum display area*.




The shortcut buttons in the tool bar are, from left to right, as follows:

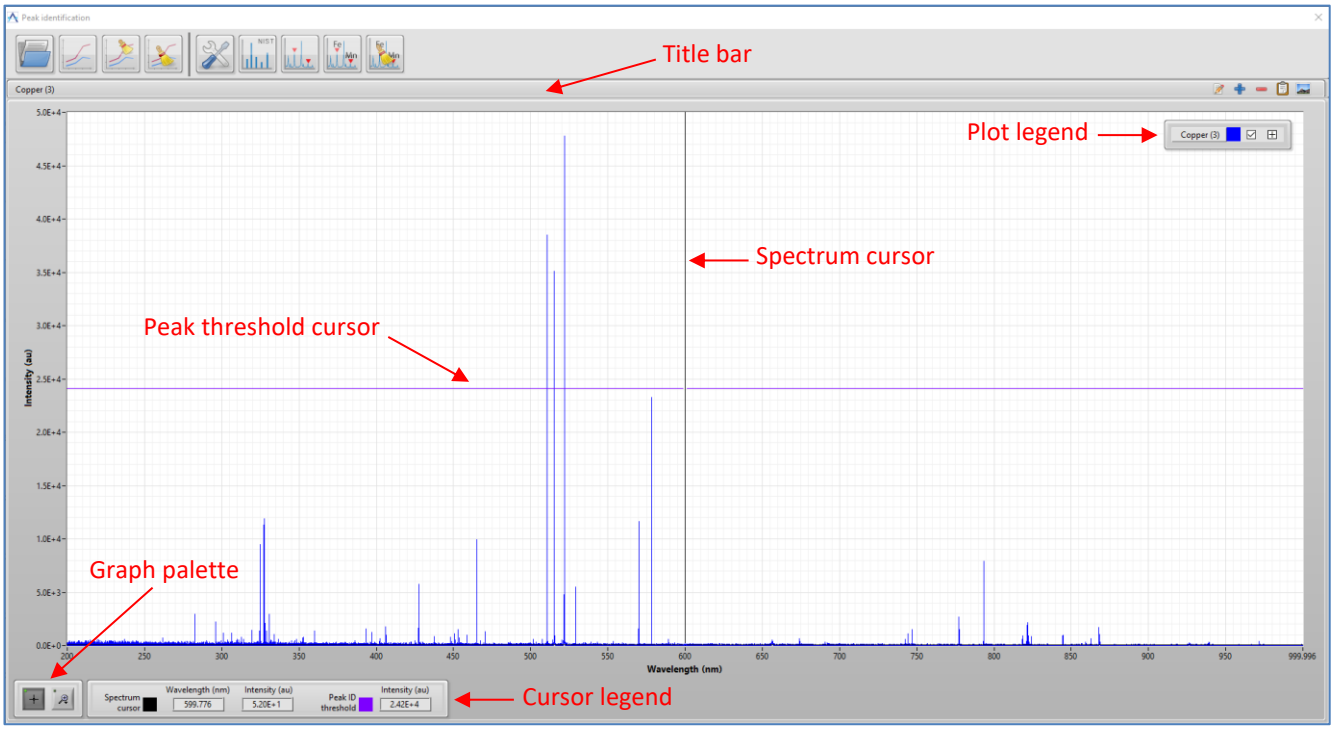
-  : ***Load saved spectra***: select and display spectra previously acquired using *LIBSoft*
-  : ***Compare spectra***: select saved spectra for comparison
-  : ***Clear comparison spectra***: clear spectra loaded for comparison leaving just the spectrum for analysis
-  : ***Clear all spectra***: clear the analysis spectrum and spectra loaded for comparison
-  : ***Open Peak ID configuration***: display the screen used to configure the peak identification parameters

-  : ***Display database lines***: display lines corresponding to the database emission lines for the atoms and ions currently selected on peak identification configuration screen
-  : ***Find peaks***: identify and mark peaks above the threshold intensity in the currently displayed wavelength range
-  : ***Identify peaks***: identify the peaks marked in the currently displayed wavelength range
-  : ***Clear peaks***: clear all peak markers and identifications in the currently displayed wavelength range

### 11.2 Loading spectra for peak identification

If when the peak identification module is opened a spectrum is currently displayed in the main *LIBSoft* application, this spectrum will be automatically loaded into the peak identification module for analysis unless an analysis is already in progress in which case that analysis will be displayed. If when the peak identification module is opened no spectrum is displayed in the main *LIBSoft* application, then a spectrum will need to be loaded for analysis manually.

Spectra can be loaded manually by selecting the  shortcut button in the tool bar and locating the required spectrum file using the file browser that is displayed. As for the display of spectra in the main LIBSoft application, the software will identify if the selected spectrum file contains more than one spectrum. However, in the peak identification module only one of the spectra in the selected file can be loaded at a time for analysis.




The display of spectra in the peak identification module is very similar to the display of spectra in the main *LIBSoft* application. As shown below, the display includes a *title bar*, *plot legend*, *spectrum cursor*, *peak threshold cursor*, *graph palette* and *cursor legend*.

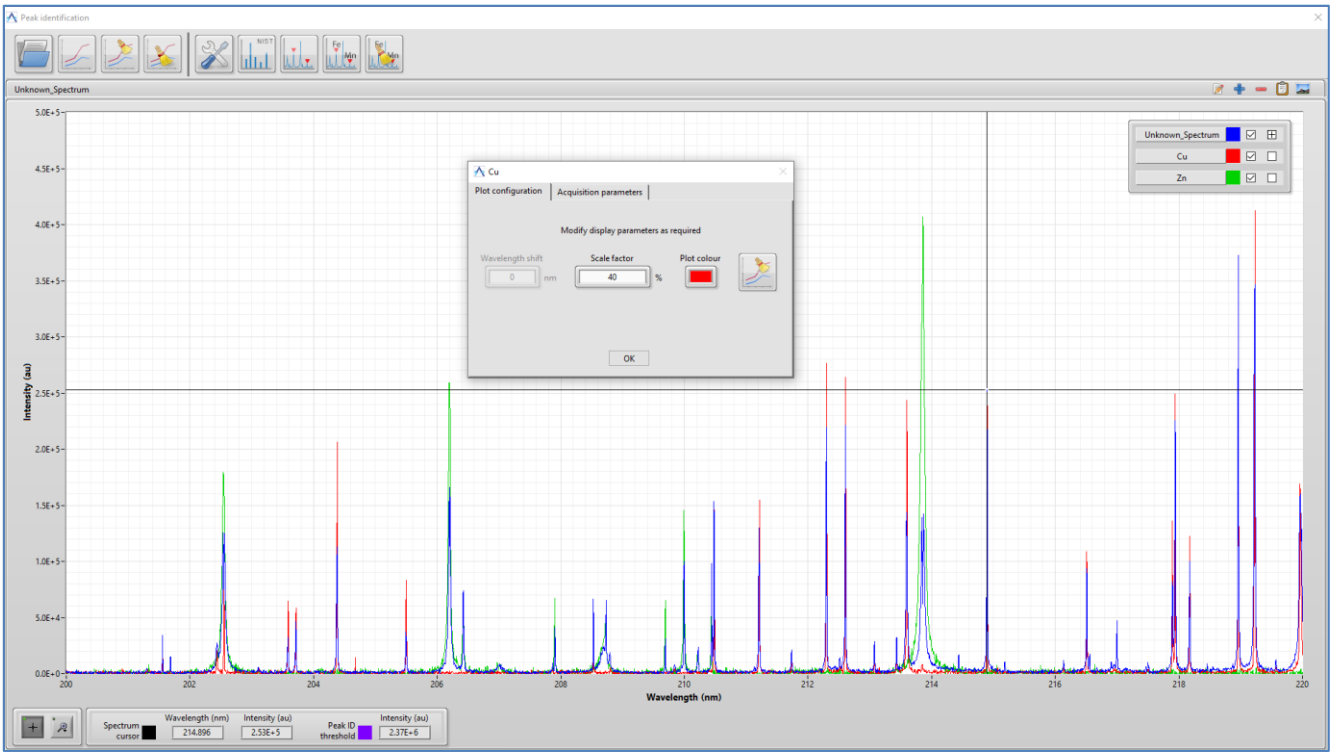
The main differences between the spectrum display in the peak identification module and the main *LIBSoft* application are:

- The title bar does not include the pin icon as the display is already maximised but contains three additional icons that are used to edit the peak identifications (see sections 11.5 and 11.7).
- There is an additional cursor – the peak threshold cursor – which defines the threshold intensity of the peaks in the spectrum which the software attempts to identify (see section 11.5).
- The cursor legend details the position of both the spectrum cursor and the peak threshold cursor.

The functionality of the features common to both the main *LIBSoft* application and the peak identification module is largely as described in section 9. Any exceptions to this are detailed in the following sections describing the operation of the peak identification module.

### 11.3 Loading spectra for comparison

Spectra can be loaded for comparison by selecting the shortcut button in the tool bar and locating the required spectrum file(s) using the file browser that is displayed. The selected spectra will be added to the display and the plot legend. The maximum intensity of the spectra added for comparison will be automatically normalised to the maximum intensity of the spectrum loaded for analysis. However, the comparison spectra can be rescaled as required by right-clicking on the corresponding entry in the plot legend and adjusting the scale factor for the spectrum (see section 9.3). The scale factor for the spectrum under analysis cannot be changed.




The check boxes in the plot legend can be used to set the visibility of each individual spectrum as required (section 9.4).

**TIP**: A set of high purity spectra are included with *LIBSoft* and installed in the folder ***C:\ProgramData\LIBSoft 2020\High purity spectra***. However, the user is not limited to those spectra and can add more spectra to this location or load spectra from a different location for comparison.

### 11.4 Clearing spectra

All comparison spectra can be cleared from the display by selecting the button in the tool bar.

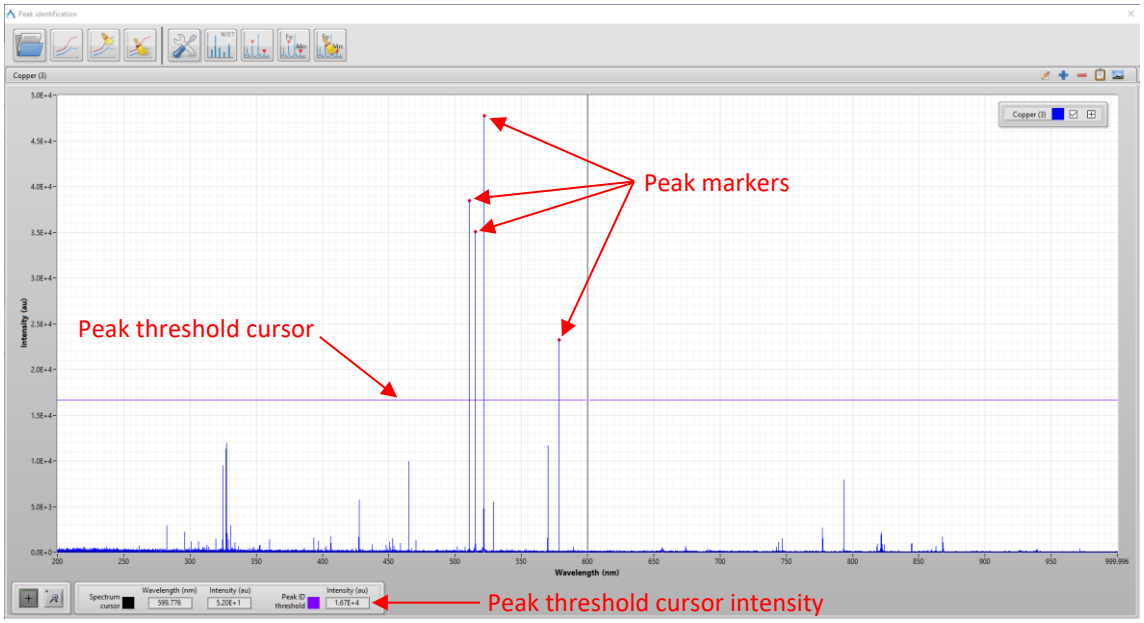
Individual comparison spectra can be cleared from the display by right-clicking on the corresponding entry in the plot legend and selecting the clear comparison spectra button on the *Plot configuration* tab of the window displayed.

All spectra can be cleared from the display by selecting the clear all spectra button in the tool bar. Note that this will also clear any peak identifications.

### 11.5 Marking peaks for identification

Select the shortcut button in the tool bar to automatically find and mark peaks for identification. The software will use a peak detection algorithm to find and mark all peaks in the currently displayed wavelength range with

intensities above the intensity at which the peak threshold cursor is currently set. The peaks identified by the algorithm will be marked with a small, red dot.




To modify the position of the peak threshold value select the button in the graph palette and then left-click and drag the cursor vertically to the required value. The intensity value corresponding to the position of the peak threshold cursor is displayed in the cursor legend at the bottom of the screen. Alternatively, it is possible to left click on the peak ID threshold intensity text box and to enter the required threshold value directly.

The methods available to zoom the display to a specific wavelength and/or intensity range are described in section 9.3.

Note that as the algorithm only marks peaks found in the currently displayed wavelength range each time the button is selected, it is then possible to use different values of peak threshold intensity in different wavelength regions of the spectrum. Also, if the button is selected when peaks are already marked all peak markers, and peak annotations if any are displayed, will be cleared and the peaks remarked according to the current position of the peak threshold cursor.

To manually add a peak marker, move the spectrum cursor to the peak to be marked and then select the button in the spectrum title bar. To manually delete a peak marker, move the spectrum cursor close to the peak marker and then select the button in the title bar. Details of how to move the spectrum cursor are given in section 9.3.

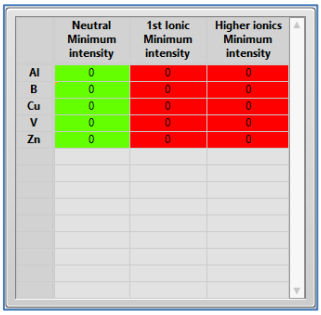
### 11.6 Configuring peak identification

Select the shortcut button in the tool bar to open the peak identification configuration window.


The periodic table in this window allows the selection of the elements that will be used during the peak identification algorithm. Each element has two buttons associated with it: one labelled with the symbol for the element and a second just to the right of the first with no label. When an element is unselected the first of these buttons is grey and the second is dark green. When selected the first button is orange and the second button is bright green (see below).


The button labelled with the symbol for the element, when selected, is used to include database emission lines relating to that element in the peak identification (section 11.7). The second button for each element is used to specify whether the emission lines for that element will be included in the display of database peaks (section 11.8). By default, when an element is first selected, by left-clicking on either of the two buttons, both options are enabled. However, it is possible to disable the inclusion of emission lines relating to the element in the display of database emission lines by clicking on the second button separately after the element has initially been selected.

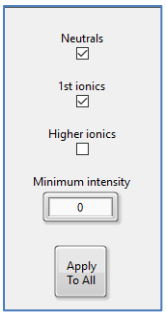
At the bottom left of the configuration screen there is a table that lists the currently selected elements. The table has four columns, one showing the element symbol and one each relating to the emission lines pertaining to the neutrals, first ionics and higher ionics for that element. The elements are listed in alphabetical order.



The value displayed in the each of the three right-hand columns is the minimum intensity of database peaks pertaining to the specified element and ionic that will be included in the peak identification process. This value can be edited by the user if required to filter database peaks with low relative intensities from the peak identification process. Selecting <Ctrl> and left-clicking in a cell in the table will display the maximum relative intensity of peaks included in the database pertaining to the element and ionic specified by the cell, together with the wavelength of the peak with this maximum intensity.

The background colour of each of the cells in the three right-hand columns for each of the selected elements will be either green or red. If it is green, peaks included in the database pertaining to the element and ionic specified by the cell will be used in the peak identification process. If it is red these peaks in the database will be excluded from the peak identification. The background colour of a cell and hence the inclusion in the peak identification process of the element/ionic combination to which it relates can be toggled by right-clicking on the cell.

To the right of the table of selected elements are three check boxes that are used to specify which ionisation states are automatically selected for inclusion in the peak identification process for newly-selected elements. In addition, the user can specify a minimum intensity value that will be applied for newly-selected elements.




Selecting the  button will apply all the parameters above to the currently selected elements.

To the right of these three check boxes is an element selection control and four further buttons.


The element selection control provides an alternative method of selecting/deselecting an element for inclusion in the peak identification process. Enter the symbol for the required element and press enter and the selection status of that element will be toggled. This will update both the periodic table and the table of selected elements.

The  button can be used to select all of the elements in the periodic table for inclusion in the peak identification process. The  button can be used to deselect all elements. In either case both the periodic table and the table of selected elements will be updated accordingly.

The  button can be used to load a saved peak identification configuration. The  button can be used to save the current peak identification configuration for later reuse. Saved peak identification configurations include all of the parameters on the peak identification configuration screen including the selected elements and ionisation states, and the associated minimum relative intensities.

Further to the right on the configuration screen are the *Peak match tolerance* and the *ID window* controls. The *ID window* is used by the peak detection algorithm and the default value of 2 is typically suitable for most spectra. Depending on the resolution of the spectrometer employed, the user will need to adjust this value to improve the performance of the peak detection algorithm. When spectra obtained using Avantes spectrometers are analysed, the ID window value can be reduced to 1. If EMU spectra are analysed, the ID window can be increased to 3 - 5. Occasionally if a spectrum is particularly noisy this value can be increased to reduce the number of peaks that the algorithm detects due to noise. The Peak match tolerance specifies how closely the wavelength of a marked peak

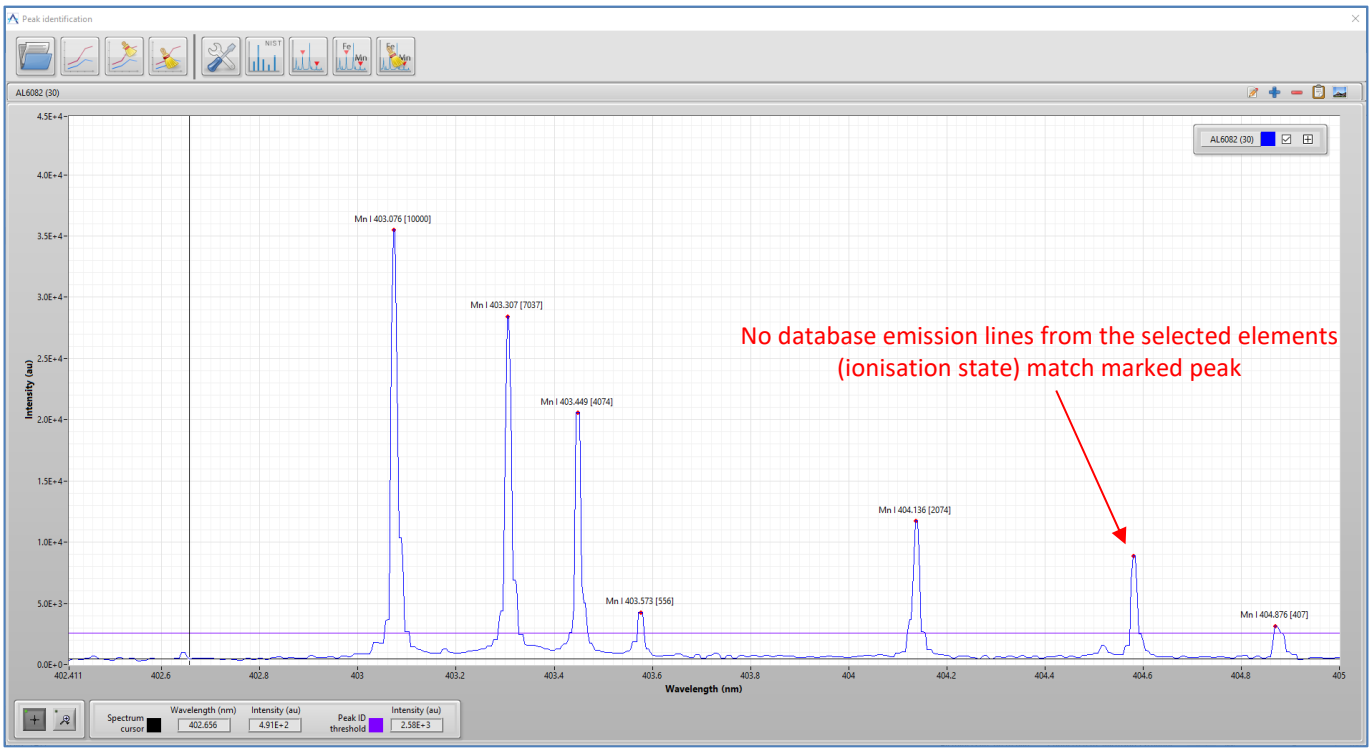
in the spectrum must match the wavelength of the emission lines listed in the database for it to be identified. The lower this value the fewer emission lines in the database will be identified as matching a peak in the spectrum. The higher this value the more lines in the database will be identified, perhaps erroneously, as matching a peak in the spectrum. This value should be adjusted as required and the optimum value will again depend on the spectrometer used to acquire the spectra. Typical values for Avantes spectrometers are 0.1 - 0.2 nm and typical values for EMU spectrometer are 0.01 - 0.02 nm.

Finally, on the far right of the peak identification configuration window are two further checkboxes. The first of these, labelled *Annotate NIST lines*, determines whether the database lines are labelled with the element and wavelength to which they correspond when they are displayed (section 11.8). The check box labelled *Online identification* determines whether the software will attempt to automatically attempt to identify peaks in spectra as they are acquired based on the currently configured peak identification parameters.

### 11.7 Identifying peaks

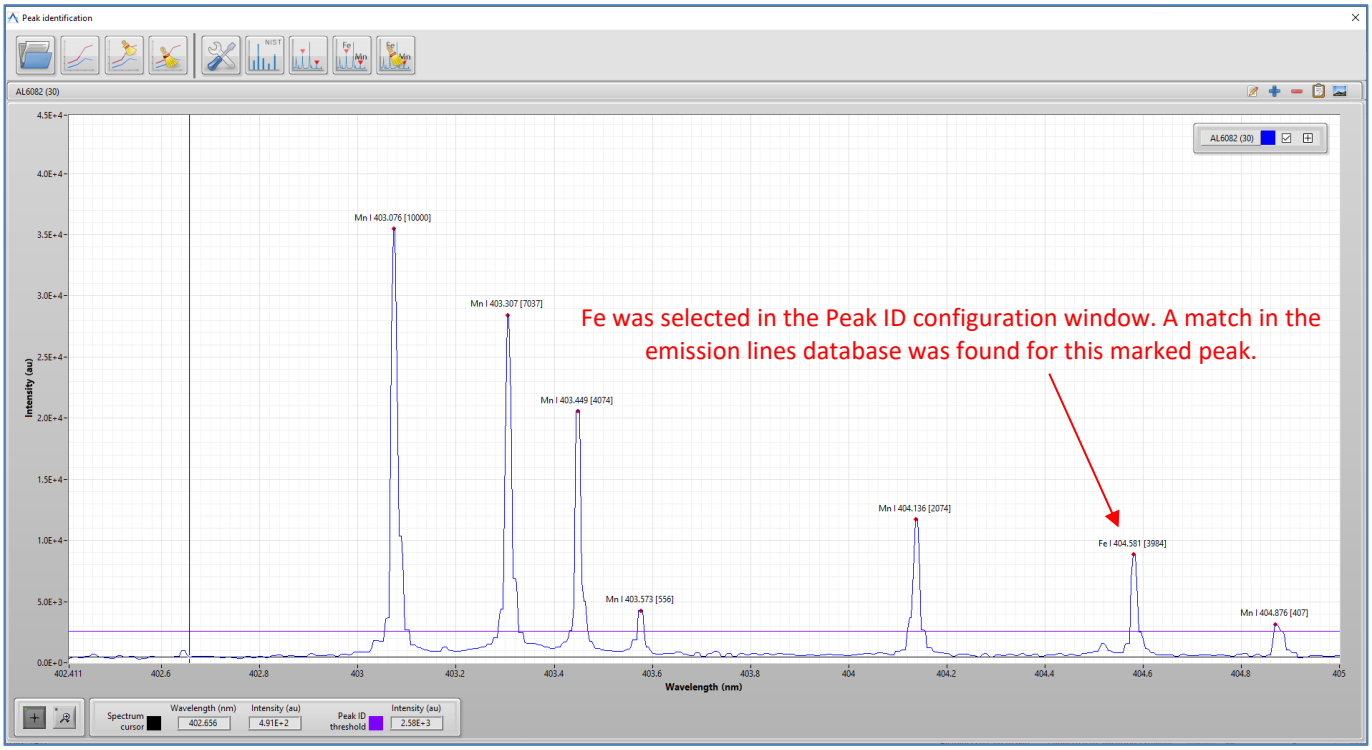
Selecting the  button in the tool bar will identify all marked peaks in the currently displayed wavelength range using the parameters set in the peak identification configuration window. Each marked peak will be compared to the emission lines in the database for the selected element/ionisation state combinations and be annotated with the element, ionisation state, wavelength and relative intensity as listed in the database of those that match within the specified *Peak match tolerance*. Note that, depending on the configuration settings, there may be more than one database emission line that matches each marked peak. In this case the marked peak will be annotated with the details of all database lines that match it. If no database lines match the marked peak then it will be left unannotated. Note also that the relative intensity of a peak in the database, although generally indicative of the intensity of a peak that might be seen in a LIBS spectrum, should not be taken as an absolute guarantee of the intensity of any peak that is observed.

Identification of individual peaks, for example those that haven't previously been marked, is also possible. To do so, move the spectrum cursor to the peak to be identified, select the  button in the spectrum title bar to mark it, then click the  button again. The selected peak will be identified using the parameters set in the peak identification configuration window. If no emission lines in the database match the selected peak within the specified parameters, the peak will remain unannotated.

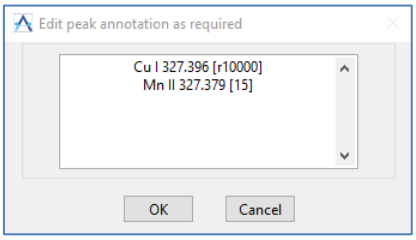



To refine the identifications either the configuration parameters can be adjusted as appropriate and the identification repeated or the displayed annotation can be edited manually. Note that if the identification process

is repeated then any existing peak annotations in the currently displayed wavelength range will be cleared first. However, the user will be warned of this and given the option to cancel the operation.




To edit an annotation manually first move the spectrum cursor to the peak whose annotation is to be edited. Then select the  button in the spectrum title bar. A window will be opened that displays the current annotation allowing it to be edited as required. Select *OK* in the editing window to accept and display any changes or select *Cancel* to leave the annotation as it was.

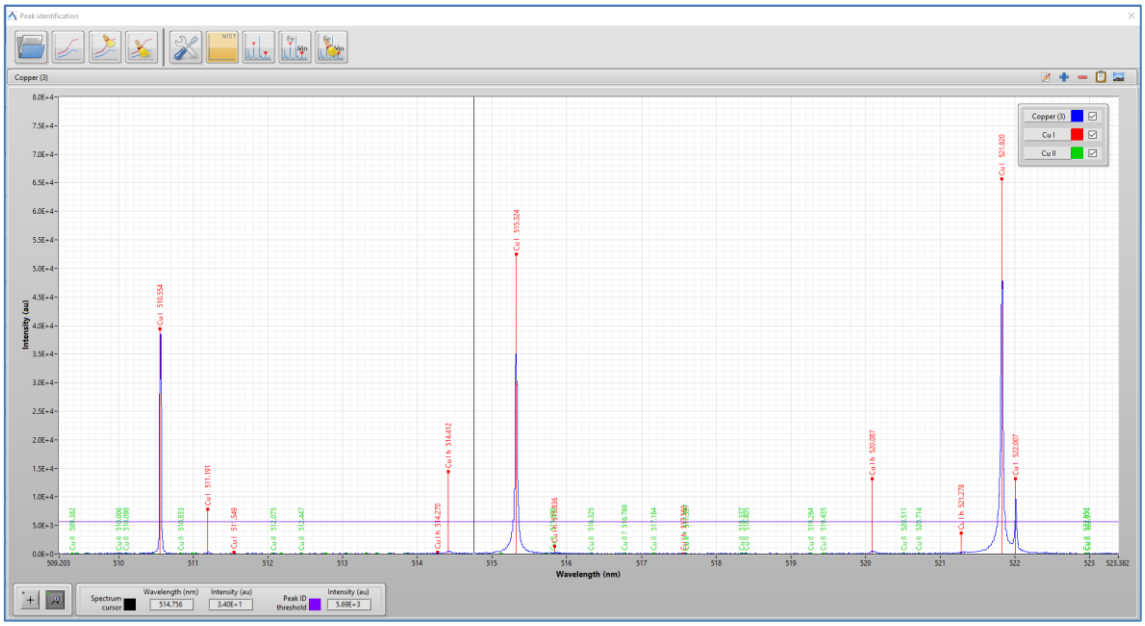



Note that selecting the  button will actually display the annotation of the nearest annotated peak to the spectrum cursor so the cursor does not need to be positioned precisely on the annotated peak.

### 11.8 Displaying database emission lines

Selecting the  button in the tool bar will overlay on the spectrum under analysis vertical lines corresponding to the wavelengths and intensities of the database emission lines for the selected elements/ionisation states see section 11.6 for details about how to select elements/ionisation states). The length of each line is scaled to the relative intensity for the emission line as listed in the database. This tool provides a powerful visual way to compare the position of the spectrum peaks with the emission lines in the Atomic Emission NIST Database helping the user in the identification of the peaks. In addition, the possible interferences with the emission lines of other elements can be evaluated.

**TIP**: If the *Annotate NIST lines* check box is ticked (section 11.6) then these lines will also be annotated with the details of the lines that they represent (see below). Note that for clarity only a certain number of the most intense lines for each element/ionisation state are annotated. To view the annotations for less intense database lines, zoom in to the relevant section of the spectrum.




## 11.9 Online peak identification

The peak identification function can be used to annotate peaks in spectra as they are acquired by selecting the Online identification option on the peak identification configuration screen. To enable this option, one or more elements must be selected for identification.

**TIP:** This option is only enabled for selection if a spectrometer is connected to the system and has been detected and correctly initialised by *LIBSoft*, i.e., the system is capable of acquiring spectra.

When enabled, the acquired spectrum is automatically passed to the peak identification module before it is displayed. A peak threshold value is automatically calculated based on the spectral data in order to identify a reasonable number (typically between 5 and 20) of the most intense peaks in the acquired spectrum. These peaks are marked and annotated and the spectrum displayed in the usual way. If further analysis is required using, for example, a user-specified peak threshold or the selection of different elements for identification, the acquired spectrum can be loaded directly into the peak identification module as described in the preceding sections and the configuration adjusted as required.

# 12 Element Identification

## 12.1 Introduction

*LIBSoft 2020* includes a module to assist with element identification in acquired spectra. This module is only available in *LIBSoft Full* and the corresponding USB key is required to activate and utilise its functions.

The element identification module facilitates the determination of the likely presence of specified elements in the material analysed by matching peaks in the acquired spectra to known characteristic emission lines for each element. *LIBSoft* includes a selection of emission lines for most elements in the periodic table chosen from a combination of available databases of atomic emission spectra, e.g., the NIST Atomic Spectra Database, and practical experience of the analysis of spectra acquired from a wide range of materials. For each element up to five primary emission lines and up to five secondary emission lines are included in this reference database. The primary emission lines are used to provide the initial identification of the presence of an element in the material analysed and the secondary emission lines are used in certain circumstances, for example when the primary emission lines for the element in question are known to be prone to self-reversal, and the initial identification is inconclusive.

The results provided by the element identification module are categorised in three levels based on the percentage of reference emission lines identified in the sample spectrum:

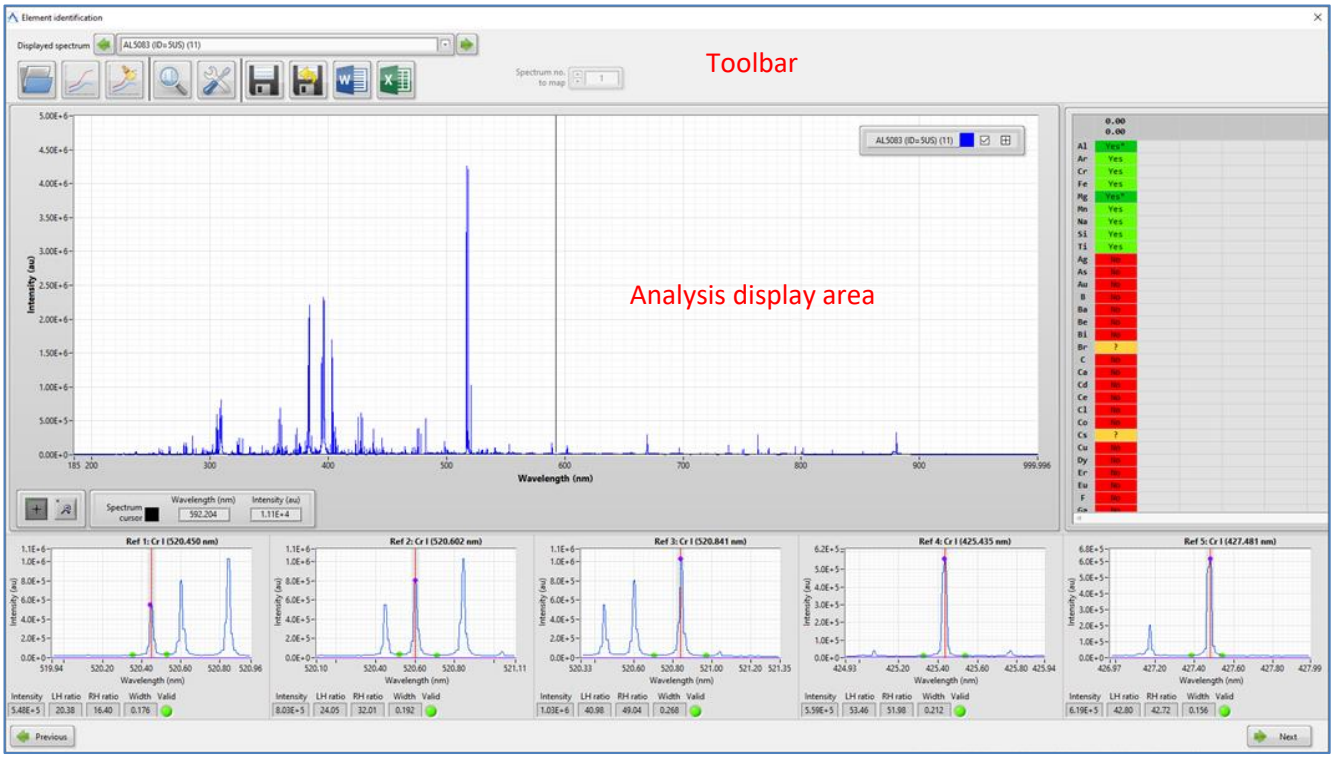
- the element is almost certainly present in the material
- the element may be present
- the element is almost certainly absent from the material analysed

Where multiple measurements have been made at different positions on a sample, the element identification module also provides the facility to generate maps of both the identification result and the raw spectral intensity for individual elements, provided that these acquisitions have been made using *LIBSoft* and the positional data is included in the file names (see section 8).

The element identification module can be opened from the main *LIBSoft* application screen by selecting the 

shortcut button. This causes the element identification module main screen to be opened and maximised in front of the main *LIBSoft* application screen which remains open in the background. The element identification module can be closed at any time to return to the main *LIBSoft* application by left-clicking on the ***X*** in the top right-hand corner of the screen. Any data currently loaded in the element identification module will however be retained in this instance and will be redisplayed if the module is reopened, provided that the main *LIBSoft* application has not been closed in the meantime.

The element identification module main screen is shown below and consists of a tool bar and an analysis display area.




## 12.2 Element identification tool bar

The shortcut buttons in the tool bar are, from left to right, as follows:

-  : ***Select spectra for analysis***: select and display spectra previously acquired using *LIBSoft*.
-  : ***Add comparison spectra***: select saved spectra for comparison with the analysis spectrum.
-  : ***Clear comparison spectra***: clear spectra loaded for comparison leaving just the spectrum for analysis.
-  : ***Analyse spectra***: analyse the currently loaded spectra using the current configuration.
-  : ***Open Element ID configuration***: display the screen used to configure the element identification parameters (a detailed description of the configuration window is given is section 12.4).
-  : ***Save results***: save the results of an analysis to file.
-  : ***Load saved results***: load previously saved analysis results.
-  : ***Export results to Microsoft Word***: export the analysis results to a Microsoft Word document.
-  : ***Export results to Microsoft Excel***: export the analysis results to a Microsoft Excel workbook.

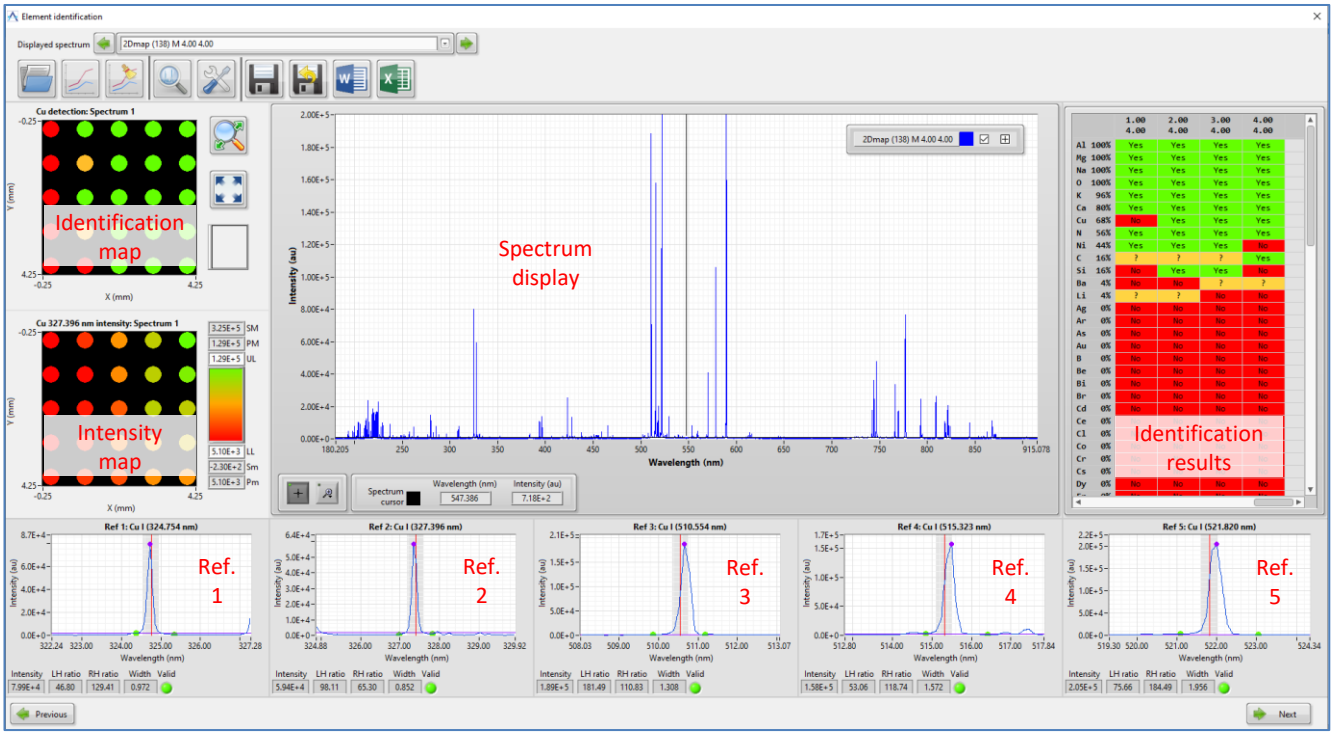
**TIP**: A set of high purity spectra are included with *LIBSoft* and installed in the folder ***C:\ProgramData\LIBSoft 2020\High purity spectra***. These spectra can be loaded for comparison with acquired spectra to aid in the identification of elemental emission lines. However, the user is not limited to those spectra and can add more spectra to this location or load spectra from a different location for comparison.

In addition to the shortcut buttons there are the following controls at the top of the screen:

- ***Displayed spectrum***: provides a list of the spectra loaded for analysis allowing the user to select which of these to display (the green arrows either side of this control allow the user to step forwards and backwards through the list)
- ***Spectrum no. to map***: where a loaded file includes multiple spectra, this control allows the user to select which of these spectra to display and map

## 12.3 Analysis display area

The analysis display area is divided up into a number of panels as shown below.




These panels are as follows:

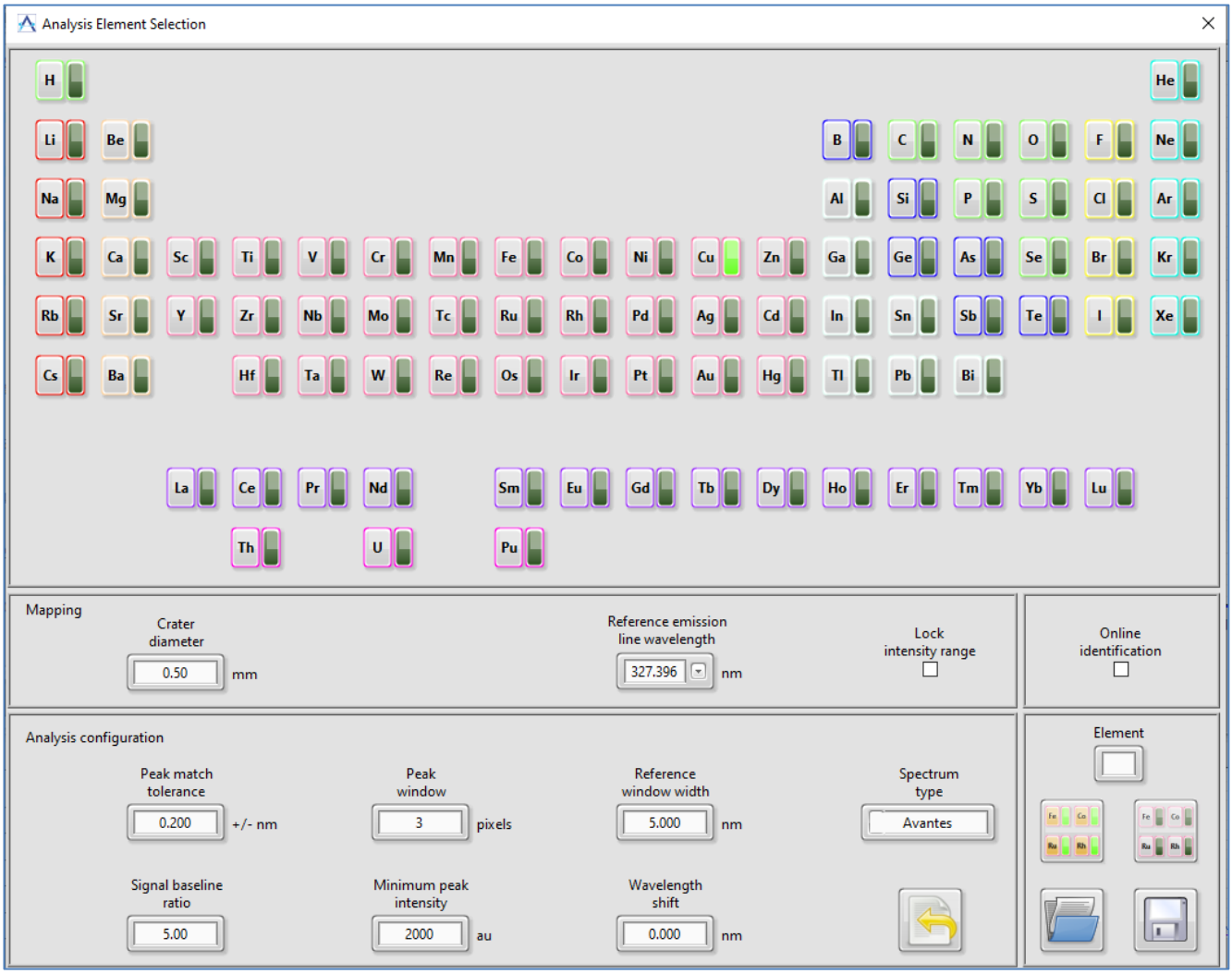
- ***Identification map***[1]: map of the identification results (only displayed for multi-measurement acquisitions).
- ***Intensity map***[1]: map of the peak intensities (only displayed for multi-measurement acquisitions).
- ***Spectrum display***: display of the currently selected spectrum.
- ***Identification results***[1]: the table of identification results.
- ***Reference emission line panels***[2]***:*** panels for the display of the wavelength region of the reference emission lines for the currently selected element in the displayed spectrum. Use the Previous and Next buttons at the bottom to display all of the reference emission lines.

[1] These panels will initially be empty until the first analysis has been performed.
[2] If no element is currently selected then these panels will be empty.

Further details about the different features and function of these panels can be found in section 12.6.

## 12.4 Element identification configuration window

To configure element identification, select the shortcut button in the tool bar. The element identification configuration screen will be displayed as shown below.




The upper part of this screen displays a representation of the periodic table showing all the elements for which characteristic emission lines are included in the reference database and which *LIBSoft* can therefore be used to identify. Each element has two buttons associated with it. The labelled buttons are used to select the elements that will be included in the analysis. The unlabelled button for each element is used to specify the element selected for display, i.e., the one for which the characteristic emission lines and map data (if any) are displayed in the main window of the module.


Element not included in analysis


Element included in analysis


Element included in analysis and selected for display

In the middle of the screen are the mapping configuration parameters. These parameters are only applicable if the element identification module is used to map data acquired from different positions on a sample (see 12.6.2 and 12.6.3). The parameters are as follows:

- ***Crater diameter***: this is the size of the marker used in th Emission line wavelength to represent the approximate size of the crater on the surface of a sample created by the interaction of the laser with the sample material.

  **NB** The crater diameter is intended to be an indicative representation only so that any likely overlap between analysis sites can be easily identified from the maps. The actual size will vary depending on the experimental conditions and the samples analysed and it is up to the user to set this value appropriately.
- ***Reference emission line wavelength***: this parameter allows the user to select which of the primary characteristic emission lines for the currently selected element should be used to generate the intensity map.

- ***Lock intensity range***: This parameter allows the range of intensity values used in the intensity map to be locked when changing the spectrum number to map instead of updating the range based on the new spectrum. This can make it easier to see variations between spectra.

To the right of the mapping configuration parameters is a checkbox to allow ***Online identification*** to be selected. This checkbox is only enabled if a suitable spectrometer has been detected and initialised by *LIBSoft* on start-up, i.e., the system is capable of acquiring spectra. When enabled, the table of identification results (see 12.6.1) will be displayed on the *LIBSoft* main screen to the right of the main spectrum display and each spectrum acquired will be analysed using the current analysis configuration.

At the bottom of the screen are the analysis configuration parameters. These parameters are as follows:

- ***Peak match tolerance***: Range of wavelengths centred on the reference emission line wavelength in which the analysis software searches for a candidate peak.
- ***Peak window***: The interval either side of the candidate peak in which it must be a maximum to be defined as a peak.
- ***Reference window width***: The interval either side of the candidate peak in which the analysis software searches for the limits of the peak, i.e., the minima either side of it.
- ***Signal baseline ratio***: the minimum value of the ratio between the peak intensity and baseline intensity either side of the peak for it to be deemed valid.
- ***Minimum peak intensity***: the minimum intensity of an identified peak for it to be deemed valid.
- ***Wavelength shift***: this parameter allows a linear wavelength shift to be applied to the spectrum to account for a shift in the spectrometer calibration,
- ***Spectrum type***: this allows the spectrometer used to acquire the spectrum under analysis to be selected and thus automatically select the analysis configuration parameters suitable for that type of spectrum.

**TIP**: The identification process is automated based on the configuration parameters set here. In the majority of cases the default configuration parameters can be used very successfully but the user can tailor these as required. The  button will restore the default analysis configuration parameters for the currently selected spectrum type.

In the bottom right-hand corner of the screen there are additional controls to help with the analysis configuration. These are as follows:

- 

: this control allows the user to enter the chemical symbol for an element directly, e.g., *Al*, and is equivalent to selecting the element in the periodic table. Doing so will toggle the selection state of that element.
-  : ***Select all***: this button will select all elements in the periodic table for inclusion in the analysis.
-  : ***Deselect all***: this button will deselect all elements in the periodic table from inclusion in the analysis.
-  : ***Save configuration***: opens a file browser to allow the current configuration including the element selections and both mapping and analysis configurations to be saved for later use if required.
-  : ***Load configuration***: opens a file browser to allow a saved configuration to be selected and loaded for use.

### 12.5 Loading spectra for analysis

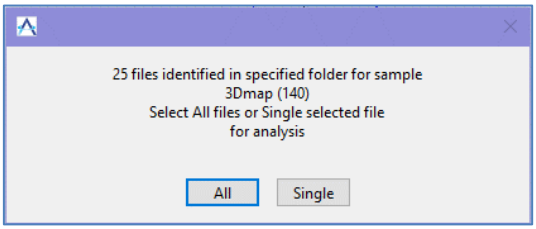
To load a spectrum for analysis, select the  button from the tool bar on the element identification module main screen. A file browser will open allowing the selection of a saved spectrum file.

If the selected file contains a single spectrum, that spectrum will be displayed and the file added to the *Displayed spectrum* list.

If the selected file contains more than one spectrum (denoted by the addition of an ***S*** suffix to the file name – see 8), the first spectrum in the file will be displayed and the root file name will be added to the *Displayed spectrum* list.

**TIP**: The *Spectrum no. to map* control allows the user to select a specific spectrum from the selected file.

If the selected file has an ***M*** suffix in the file name denoting that it is part of a multi-measurement acquisition (see 8), *LIBSoft* will check to see if there are any other files in the same folder that are part of that multi-measurement acquisition, i.e., that have the same root file name. If there are, then the user will be offered the choice of either loading all of the related files or just the single file selected.




If the user chooses to load a single file, the software will behave as described in the previous paragraphs. If the user chooses to load all files, then each of the files will be added to the to the *Displayed spectrum* list allowing the user to select which of them is displayed by selecting from the list or moving forwards and backwards through the list using the green arrows either side of the list control. As before, if each file contains multiple spectra, then the *Spectrum no. to map* control will be enabled allowing the user to select which spectrum in each file to display.

## 12.6 Elemental identification example

The analysis spectra from a multi-measurement acquisition will be used to illustrate the function of the Element Identification module and describe its features in more detail. The data from this multi-measurement acquisition consist of 5 spectra acquired at each of 25 different sample positions, i.e., a total of 125 spectra. The default analysis configuration parameters have been used and all available elements selected for analysis.

Once the analysis parameters have been configured and the spectra loaded the analysis can be initiated by selecting the  in the tool bar. Each of the loaded spectra is analysed in turn and the table of results and maps (if any) are updated as this is done. An indicator in the tool bar labelled *Spectra remaining for analysis* indicates the progress of the analysis process (see below).
**NB** The reference peaks are not displayed during the analysis process to minimise the processing time but each spectrum is displayed in the spectrum display panel. The data displayed in the table of analysis results and the maps corresponds to the currently selected *Spectrum no. to map* if there is more than one spectrum per measurement file loaded.

**TIP**: When the analysis is complete the user will be presented with the option to save the result data so that it can be reloaded later if required. However, it is not necessary to do so at this point as the  button can be selected from the tool bar to do this as required.

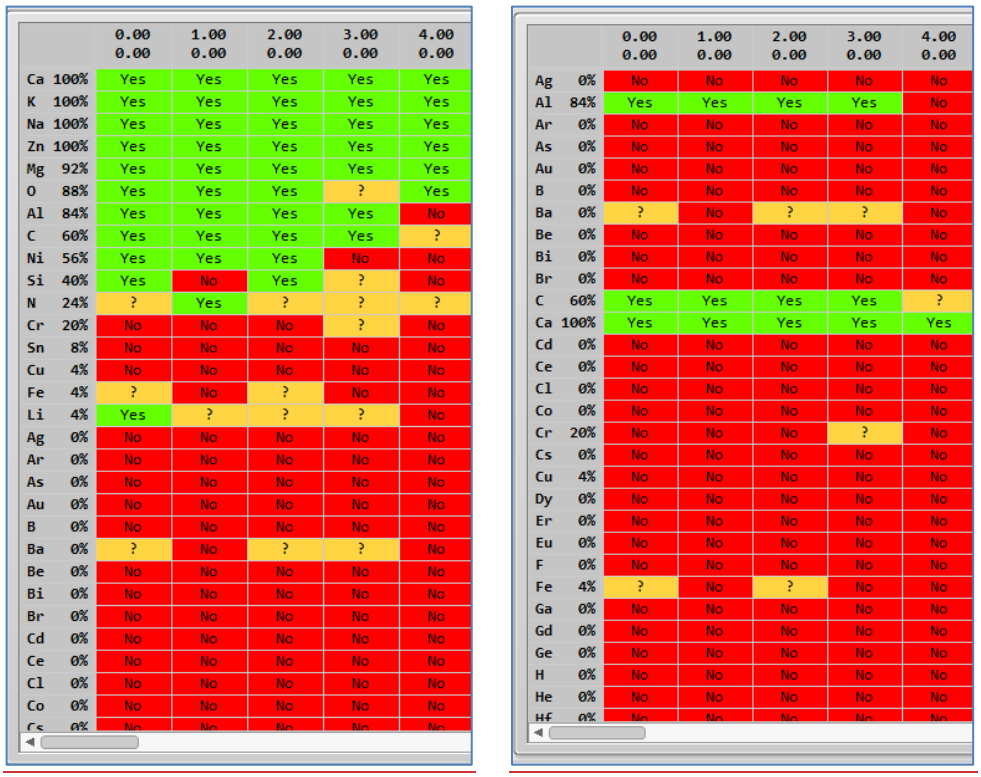
On completion of the analysis all panels in the analysis display area (see section 12.3) will be populated as appropriate. These panels are described in further detail in the following sections.

### 12.6.1 Identification results table

The table of identification results (shown below) is located at the right side of the analysis display area. This table displays the results of the identification algorithm, i.e., if an element is present or not in each analysed spectrum. The row headers list the element symbols and alongside each is a percentage value which indicates the percentage of the measurements in which the element was identified as being present.

The column headers indicate the X and Y co-ordinates of the measurement extracted from the file name.

The identification result for each element is displayed in the corresponding cell. If the element is identified as being present the cell background is coloured green and labelled ***Yes***. If the identification is inconclusive the cell is coloured orange and labelled ***?***. If the element is identified as being absent then the cell is coloured red and labelled ***No***.



| | 0.00 0.00 | 1.00 0.00 | 2.00 0.00 | 3.00 0.00 | 4.00 0.00 |
|---|---|---|---|---|---|
| Ca 100% | Yes | Yes | Yes | Yes | Yes |
| K 100% | Yes | Yes | Yes | Yes | Yes |
| Na 100% | Yes | Yes | Yes | Yes | Yes |
| Zn 100% | Yes | Yes | Yes | Yes | Yes |
| Mg 92% | Yes | Yes | Yes | Yes | Yes |
| O 88% | Yes | Yes | Yes | ? | Yes |
| Al 84% | Yes | Yes | Yes | Yes | No |
| C 60% | Yes | Yes | Yes | Yes | ? |
| Ni 56% | Yes | Yes | Yes | No | No |
| Si 40% | Yes | No | Yes | ? | No |
| N 24% | ? | Yes | ? | ? | ? |
| Cr 20% | No | No | No | ? | No |
| Sn 8% | No | No | No | No | No |
| Cu 4% | No | No | No | No | No |
| Fe 4% | ? | No | ? | No | No |
| Li 4% | Yes | ? | ? | ? | No |
| Ag 0% | No | No | No | No | No |
| Ar 0% | No | No | No | No | No |
| As 0% | No | No | No | No | No |
| Au 0% | No | No | No | No | No |
| B 0% | No | No | No | No | No |
| Ba 0% | ? | No | ? | ? | No |
| Be 0% | No | No | No | No | No |
| Bi 0% | No | No | No | No | No |
| Br 0% | No | No | No | No | No |
| Cd 0% | No | No | No | No | No |
| Ce 0% | No | No | No | No | No |
| Cl 0% | No | No | No | No | No |
| Co 0% | No | No | No | No | No |
| Cs 0% | No | No | No | No | No |

| | 0.00 0.00 | 1.00 0.00 | 2.00 0.00 | 3.00 0.00 | 4.00 0.00 |
|---|---|---|---|---|---|
| Ag 0% | No | No | No | No | No |
| Al 84% | Yes | Yes | Yes | Yes | No |
| Ar 0% | No | No | No | No | No |
| As 0% | No | No | No | No | No |
| Au 0% | No | No | No | No | No |
| B 0% | No | No | No | No | No |
| Ba 0% | ? | No | ? | ? | No |
| Be 0% | No | No | No | No | No |
| Bi 0% | No | No | No | No | No |
| Br 0% | No | No | No | No | No |
| C 60% | Yes | Yes | Yes | Yes | ? |
| Ca 100% | Yes | Yes | Yes | Yes | Yes |
| Cd 0% | No | No | No | No | No |
| Ce 0% | No | No | No | No | No |
| Cl 0% | No | No | No | No | No |
| Co 0% | No | No | No | No | No |
| Cr 20% | No | No | No | ? | No |
| Cs 0% | No | No | No | No | No |
| Cu 4% | No | No | No | No | No |
| Dy 0% | No | No | No | No | No |
| Er 0% | No | No | No | No | No |
| Eu 0% | No | No | No | No | No |
| F 0% | No | No | No | No | No |
| Fe 4% | ? | No | ? | No | No |
| Ga 0% | No | No | No | No | No |
| Gd 0% | No | No | No | No | No |
| Ge 0% | No | No | No | No | No |
| H 0% | No | No | No | No | No |
| He 0% | No | No | No | No | No |
| Hf 0% | No | No | No | No | No |

**TIP**: Left-clicking in the top left-hand corner of the table will toggle the display of the list of elements between being ordered by the percentage of measurements in which they were found (shown on the left) and being ordered alphabetically (shown on the right).

If desired, the user can edit/manually overwrite an automated identification result by left-clicking in the corresponding cell in the table and entering ***Y***, ***?*** or ***N*** as appropriate.

In this example 5 spectra were acquired at each analysis position and *LIBSoft* calculates a table of identification results for each spectrum. The *Spectrum no. to map* control (see section 12.5) can be used to select the spectrum for which the table of identification results is displayed.

**TIP**: Left-clicking on one of the row headers will update both the reference emission line panels (see 12.6.4) and the maps (if any) (see 12.6.2 and 12.6.3) to display data for the corresponding element.
**NB** This can also be achieved by opening the element identification configuration panel and selecting the required element in the periodic table (see 12.4).

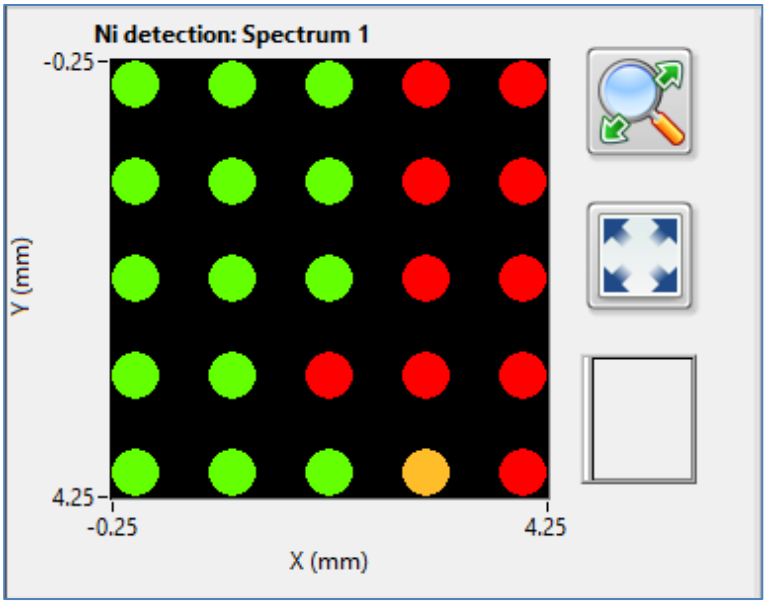
**TIP**: Right-clicking on the top left-hand corner of the table will hide the spectrum display panel and expand the table of identification results in its place. Right-clicking again on the top left-hand corner of the table will return the display to its original form.

**TIP**: Right-clicking anywhere on the table except the top left-hand corner will display options allowing the table data to be copied to the Windows clipboard or exported to Microsoft Excel.

### 12.6.2 **Identification map**

The identification map (shown below) is a visual representation of the identification results table for each element. It can be used to identify areas in the analysed sample in which a given element is present. This map

is only generated if a multi-acquisition file is analysed, i.e., spectra have been acquired from several positions on the sample.




The map is headed with the element and the spectrum number to which it relates. In the example above the identification results for nickel in the first spectrum acquired at each location are displayed. The identification result at each measurement location is marked using a coloured, circular dot. The colour of the dot marker corresponds to the identification result and is the same as that indicated in the table of identification results. The diameter of this dot marker corresponds to the crater diameter specified in the mapping configuration (see 12.4). In the example above, nickel has been identified mainly in the left-hand side of the sample.

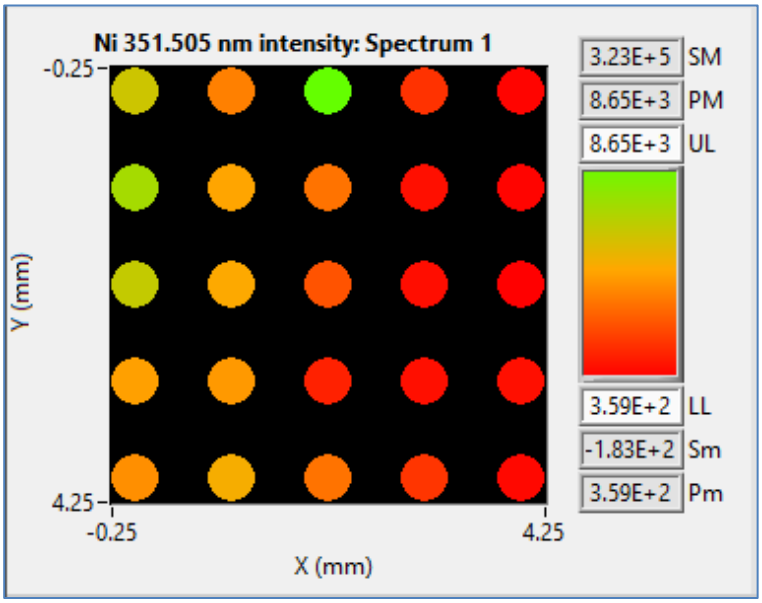
**TIP**: Left-click on the axis limits to edit the maximum and minimum scale values as required. To return the map to the initial scale select the  button displayed to the right of the map.

**TIP**: Let-clicking on any point of the mapped results will display the measurement co-ordinates, identification result and the peak intensity for the selected element at that location in the small window to the right of the map for as long as the mouse button is depressed.

**TIP**: Selecting the  button to the right of the map will display both the identification and intensity maps full-screen. Selecting the  button on the full-screen display will return to the maps to the main element identification screen.

### 12.6.3 **Intensity map**

The intensity map provides a visual representation of the intensity of a given peak in the spectrum as a function of the analysed position. A typical intensity map is shown below.




The map is headed with the element name and wavelength of the reference peak selected for mapping and the spectrum number to which it relates. The reference peak mapped can be changed in the element identification configuration window (see 12.4). The peak intensity at each measurement location is marked using a coloured, circular dot. The diameter of this dot marker corresponds to the crater diameter specified in the mapping configuration (see 12.4).

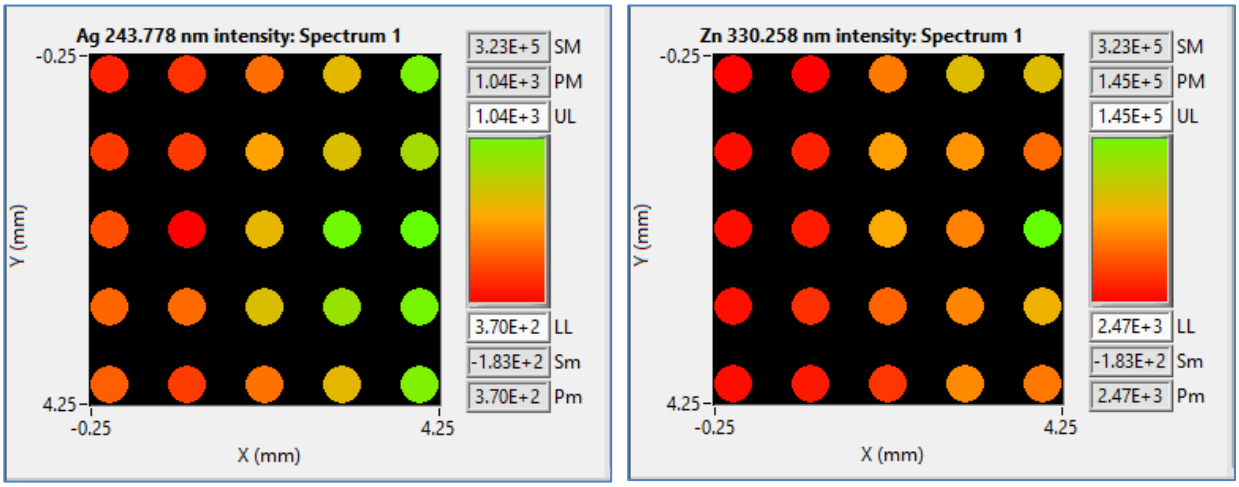
The colour of each marker is defined by the scale to the right of the map. A number of values are specified with the scale. These are as follows:

- ***SM***: ***S****pectrum* ***M****aximum*: the maximum intensity in the currently selected spectrum number.
- ***PM***: ***P****eak* ***M****aximum*: the maximum intensity of the currently selected peak in the currently selected spectrum number.
- ***UL***: ***U****pper* ***L****imit*[1]: the intensity corresponding to the upper end of the colour scale (blue).
- ***LL***: ***L****ower* ***L****imit*[1]: the intensity corresponding to the lower end of the colour scale (red).
- ***Sm***: ***S****pectrum* ***m****inimum*: the minimum intensity in the currently selected spectrum number.
- ***Pm***: ***P****eak* ***m****inimum*: the minimum intensity of the currently selected peak in the currently selected spectrum number.

[1] Values are user-editable

The spectrum and peak range values can be used to provide important information about the peak and the spectrum. For example, if the SM value is 60,000 and the PM is 100 the intensity of the selected peak is very low and probably close to noise levels. In addition, if the PM and the Pm values are similar, the variability of the intensity at different locations is unlikely to be due to changes in the composition of the sample at different analysis positions but to the intrinsic variability of the LIBS measurement.

In the images below two intensity maps are shown. On the left the Ag 243.778 nm intensity map for spectrum 1 is shown and the values of PM and Pm are of the same order or magnitude indicating that the variability in this map is just due to spectral noise. The Zn 330.258 nm intensity map for spectrum 1 on the right however clearly indicates that Zn is more abundant on the right-hand side of the sample. The PM value is of the same order of magnitude as the SM value while the value of Pm is two orders of magnitude lower.

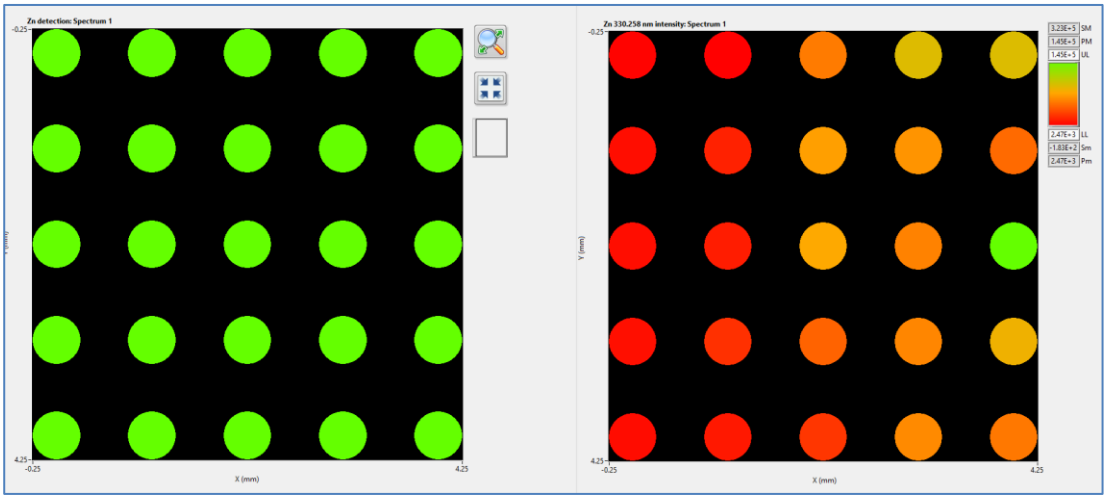



**TIP**: Initially, the upper limit of the scale is set to the peak maximum intensity, i.e., UL = PM and the lower limit of the scale is set to the peak minimum intensity, i.e., LL = Pm.

**TIP**: The user can adjust the Upper Limit and Lower Limit values (within the limits of defined by the spectrum maximum and minimum respectively) and doing so can sometimes enhance the map to more clearly distinguish the presence of an element.

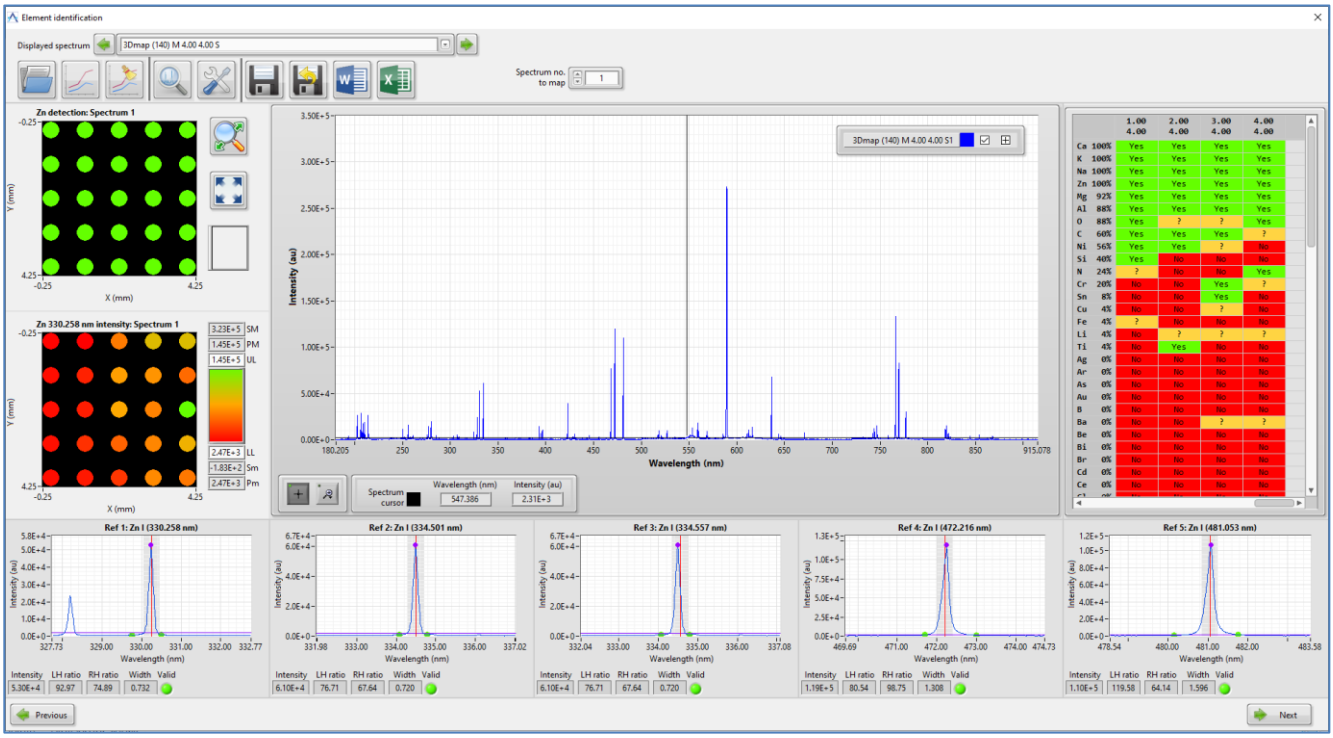
**TIP**: When the *Spectrum no. to map* value is changed to display results for a different spectrum the Upper Limit and Lower Limit values are updated automatically based on the new data. However, the *Lock intensity range* option can be enabled on the configuration screen (see 12.4) to fix these values if required. This can be useful when comparing the mapped intensities for different spectra.

**TIP**: Information provided by the identification and intensity maps is complementary. The identification maps provide information on the presence of a given element while the intensity maps provide an indication of the abundance of the element. While the identification algorithm employs several emission lines to confirm the presence of an element, the intensity map is created using a single emission line and therefore attention should be paid to possible interferences with emission lines of other elements. The image below displays both maps for the same sample. Zn is found in the whole of the scanned area, however from the intensity maps it is obvious that the concentration of Zn on the right-hand side of the sample is higher than that on the left.



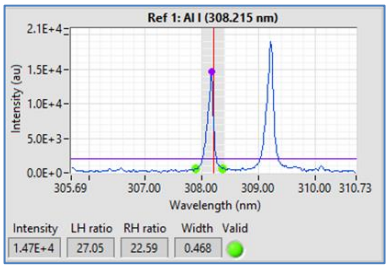
### 12.6.4 **Reference emission line panels**

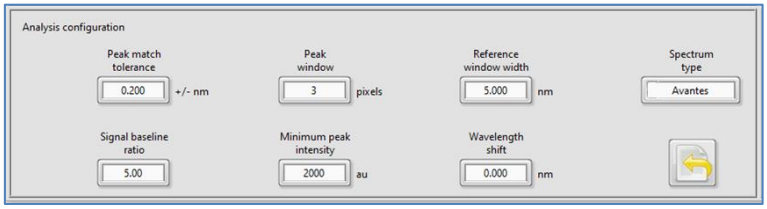
The reference emission line panels are shown at the bottom of the analysis display area. The graphs in these panels can be used to confirm the identification results found by the algorithm. In the image below, Zn reference emission lines are shown for the spectrum 3Dmap (140) M 4.00 4.00 S1.




**TIP**: The data displayed in the reference emission line panels corresponds to the spectrum specified by the *Displayed spectrum* and *Spectrum no. to map* controls (in the tool bar at the top of the screen) and will be updated if either of these values is changed.

Each reference emission line panel is titled with the element, ionisation state and wavelength of the reference emission line that it represents. The wavelength position of the reference emission line is marked with a vertical red line. *LIBSoft* attempts to find a peak in the spectrum in a region either side of the characteristic peak that fulfils the conditions set in the configuration window. For clarity, an image showing the relevant analysis configuration parameters is shown alongside the example reference emission line panel below (further details can be found in 12.4).




The region shaded in grey in the reference emission line panel is defined by the *Peak match tolerance* parameter, i.e., the range of wavelengths centred on the reference emission line wavelength in which the analysis software searches for a candidate peak. The *Peak window* parameter specifies the interval either side of the candidate peak in which it must be a maximum to be defined as a peak. This is to eliminate candidate peaks at the edge of the defined search region which are not true maxima. A purple dot is used to mark the location of the peak if one is found.

*LIBSoft* also identifies the minima in a region either side of the identified peak. This region is defined by the *Reference window width* parameter. The minima identified are marked with green dots. The intensities of the identified peak maximum and these minima and their wavelengths are used by *LIBSoft* to determine the "validity" of each peak, i.e., whether a sufficiently significant and distinct peak is present at the expected location to suggest the presence of the element.

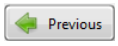
The peak is assessed in terms of its absolute intensity, its signal to baseline ratio, width and how closely the wavelength of the maximum matches that of the known characteristic peak for the currently selected element.

If all of these values are within the limits specified by the analysis configuration then the peak is deemed to be valid and is marked as such using a green indicator at the bottom of the panel. If a peak is deemed to be invalid it is marked as such using a red indicator.

Each of the five peak panels also includes various additional diagnostic data. For example, a horizontal purple line indicates the *Minimum peak intensity* specified in the analysis configuration. The intensity of the maximum and the signal to baseline ratio either side of the maximum are indicated at the bottom of each panel together with the calculated peak width. From these values it is generally possible to identify why a peak has been determined by *LIBSoft* to be either valid or invalid.

Occasionally a slight wavelength offset may be seen between the peaks in the spectrum and the marked characteristic peaks for the elements to be identified. This could be due to a small drift or offset in the spectrometer calibration. If this is the case a linear wavelength shift can be applied to the loaded spectra using the *Wavelength shift* parameter on the configuration screen (see 12.4).

There are up to ten characteristic peaks for each element in the *LIBSoft* database – five primary and five secondary peaks. To display additional peaks, select the 

button at the bottom of the screen. This will cause the displayed peaks to scroll to the left and any additional peaks to be displayed on the right. The 

button can be used to scroll the peaks back to the right.

Secondary peaks are identified by the addition of a * in the title, e.g., *Ref 6: Al I* (305.714 nm)*. Secondary peaks are not generally used in the identification process but can be useful in certain scenarios to confirm the presence/absence of an element in the sample. They are however used for certain elements whose primary peaks are known to be subject to self-reversal. In this case, due to self-reversal, the primary peaks could be falsely identified as being invalid, hence if the initial analysis is inconclusive using the primary peaks, the analysis is repeated using the secondary peaks.

### 12.7 Saving results

On completion of each analysis the user is given the option to save the results of the analysis. However, the results can be saved at a later time if required by selecting the  button in the tool bar. The identification results and intensities for each spectrum analysed are saved in separate text files, e.g., for an analysis of multiple measurements each comprising three spectra the files generated would be as follows:

*3Dmap (140) IDs Spectrum 1*
*3Dmap (140) IDs Spectrum 2*
*3Dmap (140) IDs Spectrum 3*
*3Dmap (140) Intensities Spectrum 1*
*3Dmap (140) Intensities Spectrum 2*
*3Dmap (140) Intensities Spectrum 3*

The identification results files include the *Yes*/*No*/*?* result for each element included in the analysis at each measurement location and the percentage of the measurement locations at which each element was identified as being present. The intensity results files include the peak intensity at each of the primary wavelengths for each element at each measurement location. The primary use of these result files is so that they can be loaded back into *LIBSoft* for display of the table of identification results and maps (if any) as described in 12.8. They can be opened in any suitable text editor or loaded into Microsoft Excel as delimited files, however, there are other options within *LIBSoft* that can be used for generating a Microsoft Word report or exporting the analysis results to Microsoft Excel (see 12.9 and 12.10 respectively).

### 12.8 Loading results

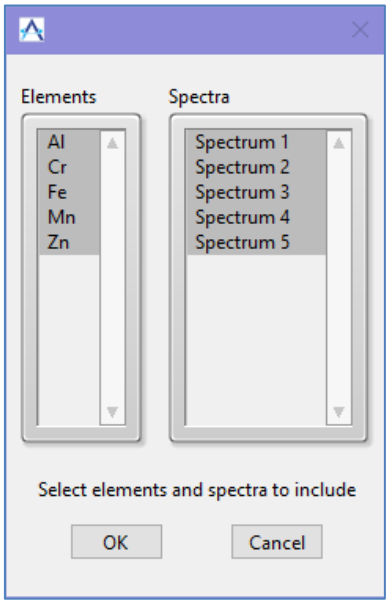
To load previously saved analysis results for redisplay of the table of identification results select the  button in the tool bar and use the file browser to select one of the files corresponding to the analysis data to be loaded. *LIBSoft* will automatically load all of the files relating to the selected analysis, i.e., both identification results and

intensity files for all spectra included in the analysis. The table of identification results and maps (if any) will be displayed.
**NB** As the raw spectral data used to generate the analysis results are not included in the files, neither the full spectra or the peaks used for identification will be displayed.

The table of identification results can be ordered and edited and the mapped element changed as described in 12.6.1.

### 12.9 Generating a Microsoft Word report

A basic report of the analysis results can be generated by selecting the button in the tool bar. Doing so will display a dialogue allowing the user to select which data to include in the report.




By default, all elements and spectra analysed are selected for inclusion in the report but a subset of these can be selected. Highlight the required items by holding down the *Cntrl* or *Shift* key as appropriate and left-click on the chosen items. When the elements and spectra have been selected click on ***OK*** and *LIBSoft* will generate the report by opening a new Microsoft Word document then displaying each of the results specified for inclusion and copying them to that document. When the report is complete the user will be presented with a dialogue allowing it to be saved.

The report produced includes a title page detailing the date/time, sample name, number of measurements, number of spectra per measurement, the analysis configuration used, the elements analysed and the elements and spectra included in the report. On subsequent pages details of the analysis of each spectrum for each element are displayed, including any maps that have been generated.

### 12.10 Exporting results to Microsoft Excel

The analysis result data can be exported to Microsoft Excel files by selecting the in the tool bar. Doing so will display a dialogue allowing the user to select which data to include in the report in the same way as for the generation of a Microsoft Word report (see 12.9).

The identification and intensity results are exported to separate Excel files. The identification results file includes the *Yes*/*No*/*?* result for each element included in the analysis at each measurement location and the percentage of the measurement locations at which each element was identified as being present. The intensity results file includes the peak intensity at each of the primary wavelengths for each element at each measurement location. In both cases the data for each spectrum included in the file is displayed on a separate worksheet.

### 12.11 Online element identification

The element identification function can be used to identify elements in spectra as they are acquired by selecting the *Online identification* option on the element identification configuration screen.

**TIP:** This option is only enabled for selection if a spectrometer is connected to the system and has been detected and correctly initialised by *LIBSoft*, i.e., the system is capable of acquiring spectra.

When enabled, the table of identification results is displayed to the right of the acquired spectrum display on the LIBSoft main screen and, if the number of measurements specified in the acquisition configuration is greater than 1, the identification and intensity maps are also displayed below the table.

As spectra are acquired they will be analysed automatically using the current element identification configuration and the results will be displayed in the table and the maps (if appropriate).

If the online quantitative calibration analysis is also enabled (see 10.5.6), buttons will be displayed at the top of the table allowing the user to toggle between the display of the online quantitative calibration results and the online element identification results.

**Appendix A**

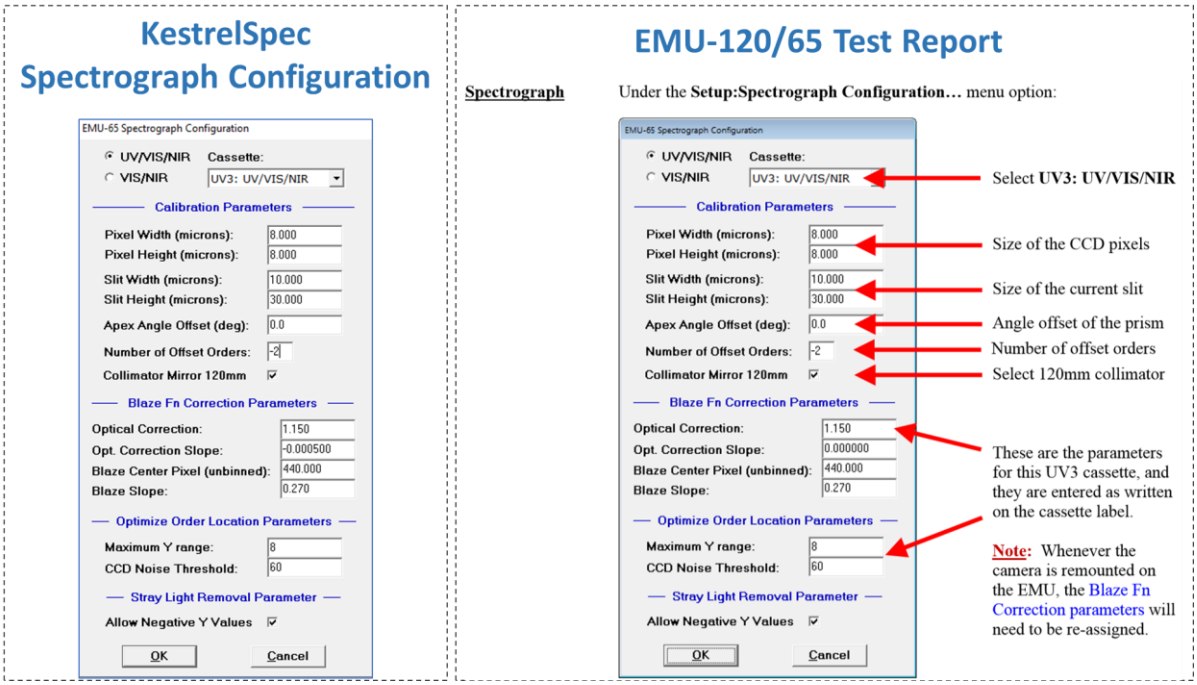
**EMU spectrometer calibration**

The EMU spectrometer should be recalibrated periodically, preferably before each daily use to account for possible wavelength drift due temperature variations and to check that the system is operating correctly. This can be done quite simply using a mercury-argon calibration lamp and the KestrelSpec application. It is assumed that the Imperx Framelink card has been installed in the system computer together with the corresponding software drivers (section) and that the Catalina Scientific KestrelSpec application has been installed (section 3.8). The calibration procedure is as follows.

Power on the mercury-argon calibration lamp and leave it to warm-up and stabilise for about 5 minutes.

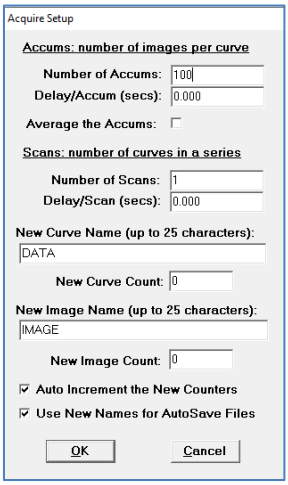
Open the KestrelSpec application (see section 4.1) and configure the application parameters as described below. Note that these parameter values are retained by KestrelSpec and should therefore already be correct if the dispersion cassette has not been changed since the previous calibration was performed, but it is best to check anyway.

Select ***Setup*** and then ***Spectrograph configuration*** from the menu to display the spectrograph configuration window. Check that the dispersion cassette that is currently installed in the spectrometer is selected in the configuration window and that the parameter values match those detailed in the corresponding dispersion cassette test report shipped with the system, updating them if necessary. Then select ***OK*** to close the configuration window.



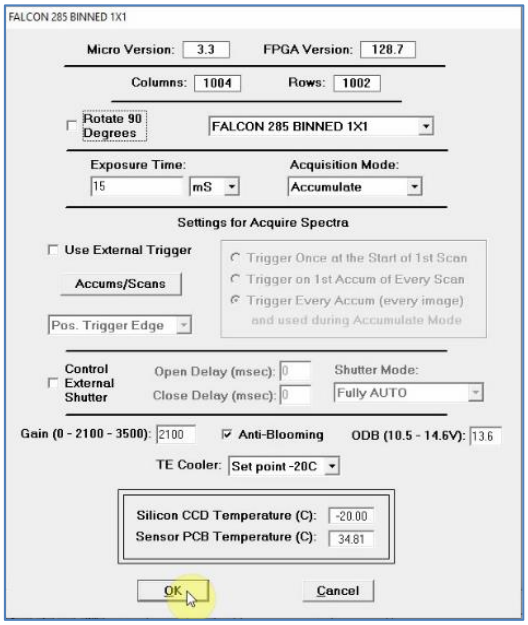

**NB** The dispersion cassette and parameter values may be different to the ones shown here.

Select ***Setup*** and then ***Acquire setup*** from the menu to display the acquisition configuration window. Set the ***Number of Accums*** = 100 and then select ***OK*** to close the configuration window.




Select ***Setup*** and then ***Camera configuration*** from the menu. There are four important parameters in the configuration window displayed.

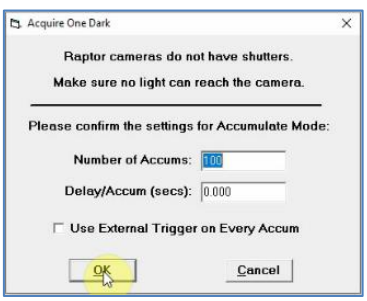
- The ***Exposure time*** should be selected such that the maximum intensity of an image pixel is close to but less than the saturation value of 55,000. Typically, the exposure time will be 10 – 20 ms and so an initial value of 15 ms is suggested but this may need to be modified once the calibration image has been acquired and the maximum pixel intensity has been determined.
- The ***Acquisition mode*** should be set to ***Accumulate***.
- The ***Gain*** should be set to ***2100***
- ***Use external trigger*** should be unchecked, i.e., use internal trigger.



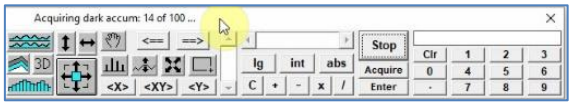

When the camera configuration parameters have been set select ***OK*** to close the configuration window.

The application parameters required for the acquisition of the background and calibration images.

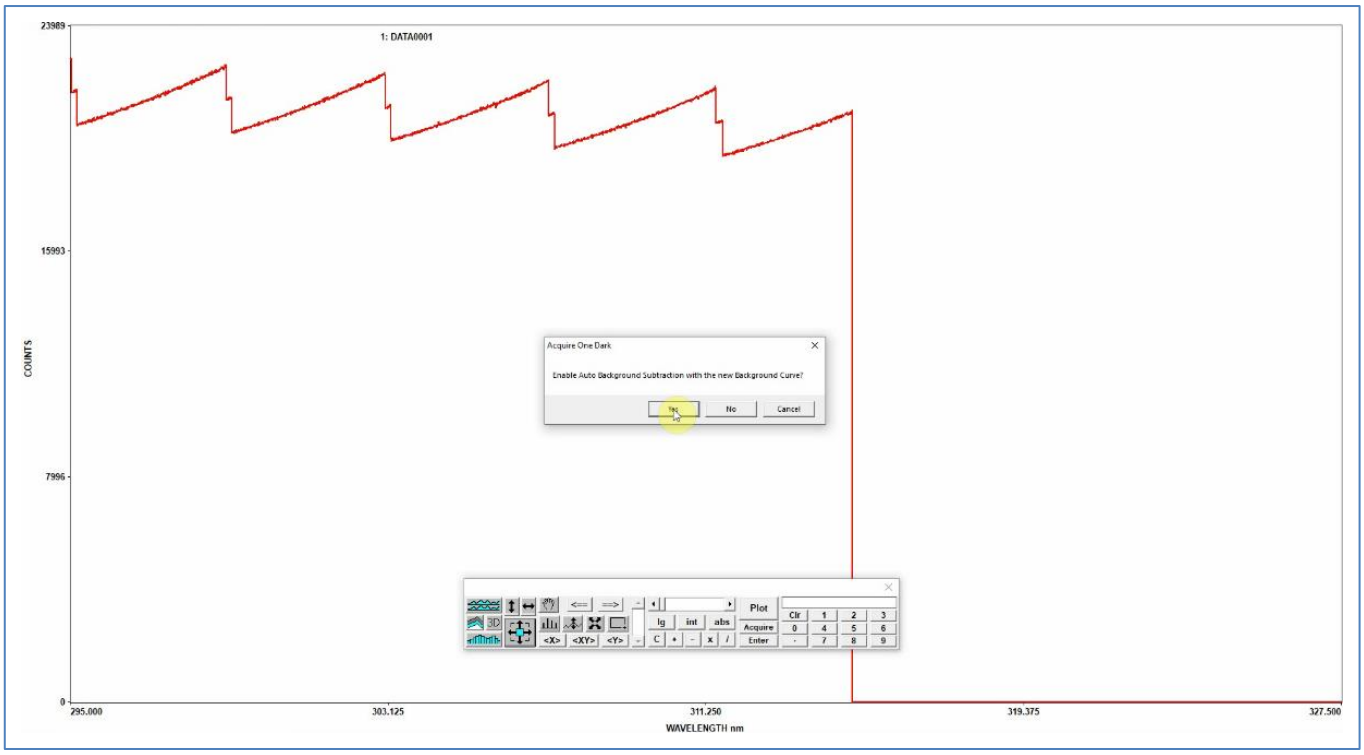
To acquire a background curve, select ***Acquire*** and then ***Acquire one dark exposure*** from the menu. Select ***OK*** to close the dialogue box displayed and start the acquisition.



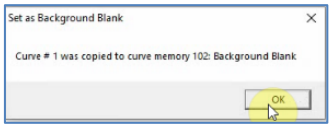
A background curve consisting of 100 accumulations will be acquired.




When the acquisition is complete the background curve will be displayed together with a further dialogue box. Select ***Yes*** to enable auto Background Subtraction and close the dialogue box.



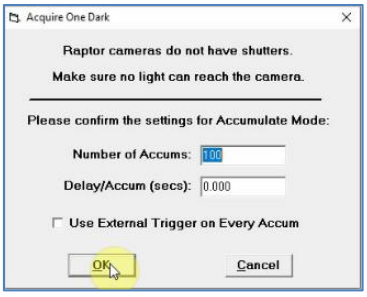

A further information window will be displayed. Select ***OK*** to close it.



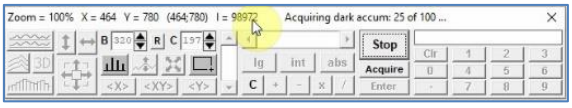

**NB** A background curve has been acquired but a background image is required for the calibration. A background image can only be acquired once a background curve has been acquired and the active image is selected.

Select ***Window*** and then ***Active image*** from the menu to display the active image window.

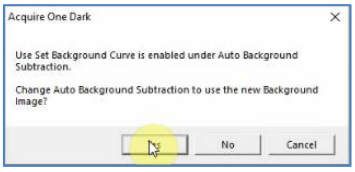
To acquire a background image select ***Acquire*** and then ***Acquire one dark exposure*** from the menu again. Select ***OK*** to close the dialogue box displayed and start the acquisition.



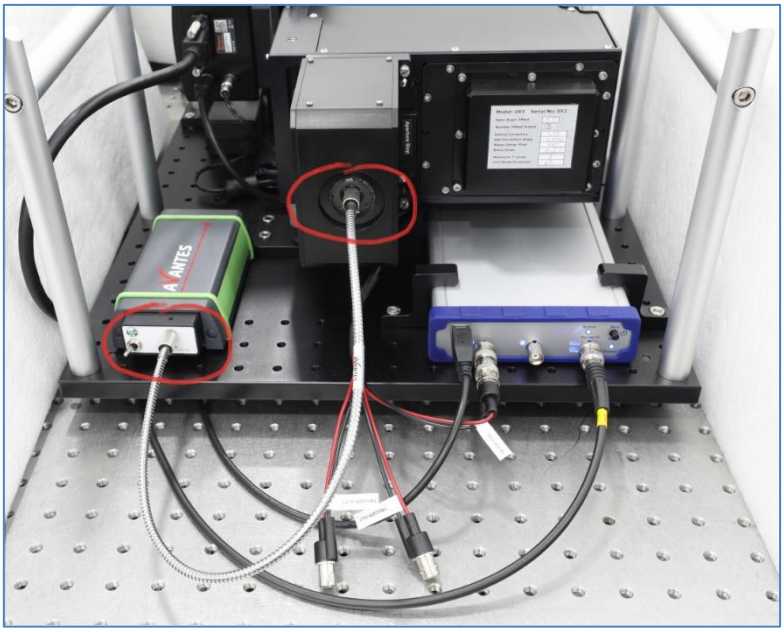

A background image consisting of 100 accumulations will be acquired.



When the acquisition is complete a dialogue box will be displayed. Select ***Yes*** to Change Auto Background Subtraction to use the new Background Image and close the dialogue box.

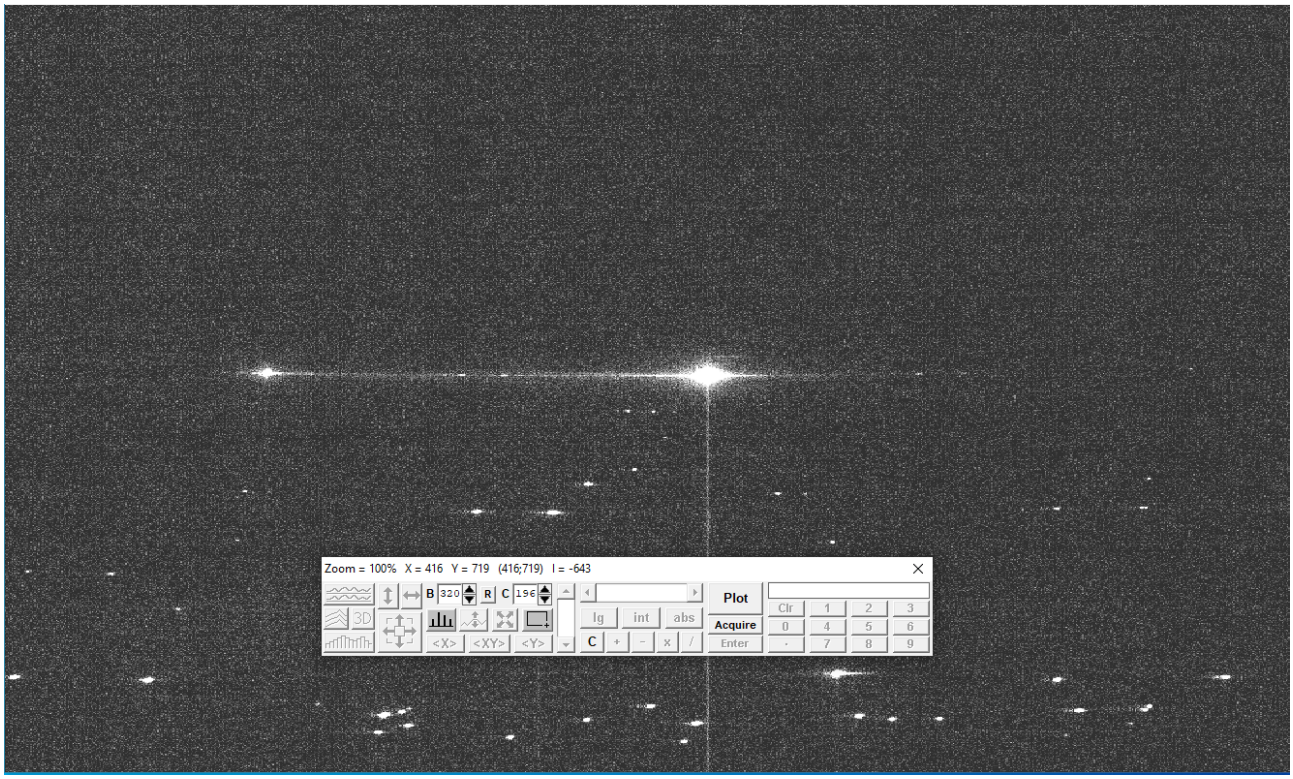



Connect the mercury-argon calibration lamp to the SMA entrance port on the EMU spectrometer using the optical fibre provided.

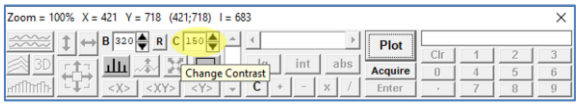


When the calibration lamp has been connected the calibration image can be acquired. Select ***Acquire*** and then ***Acquire one exposure*** from the menu. A calibration image consisting of 100 accumulations will be acquired.

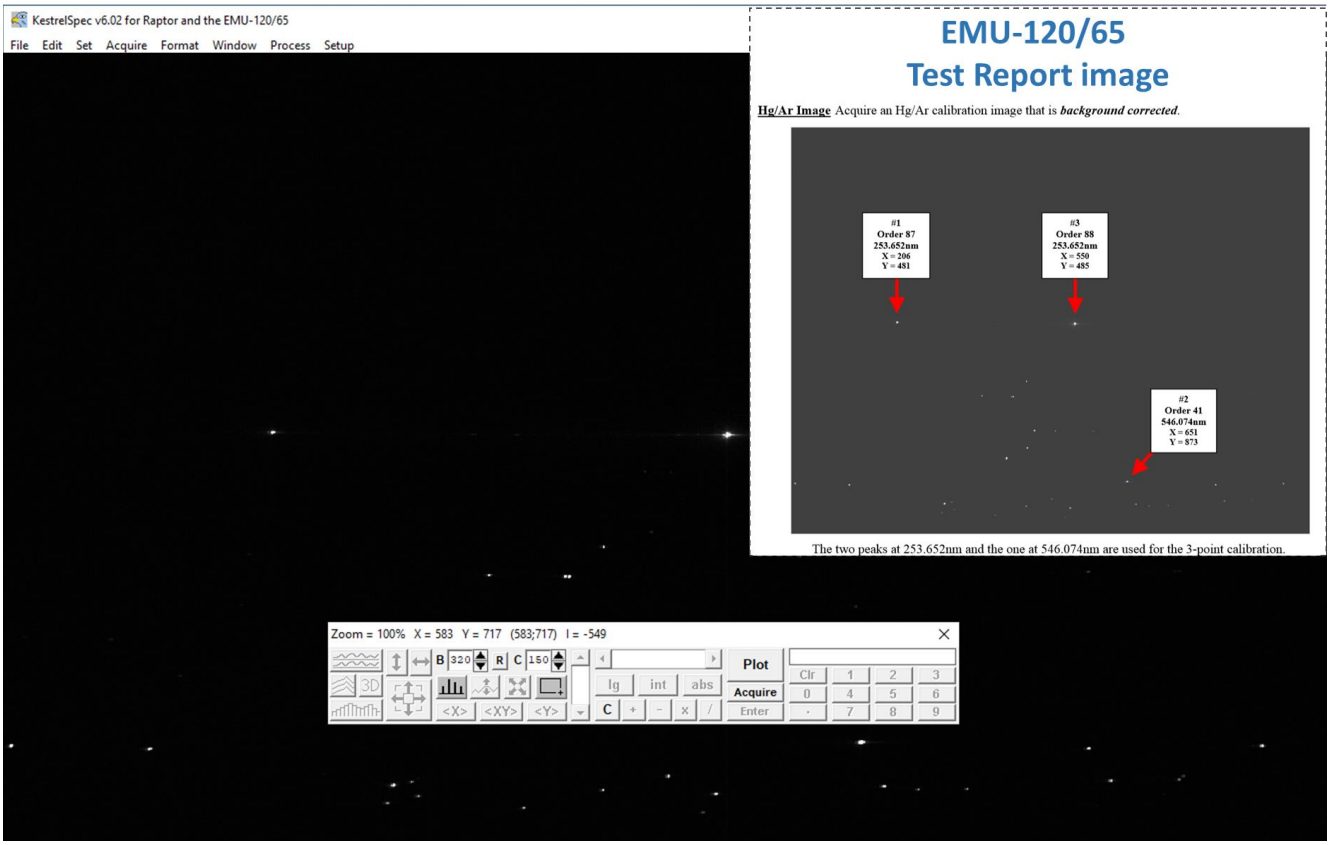

When the acquisition is complete the image will be displayed.



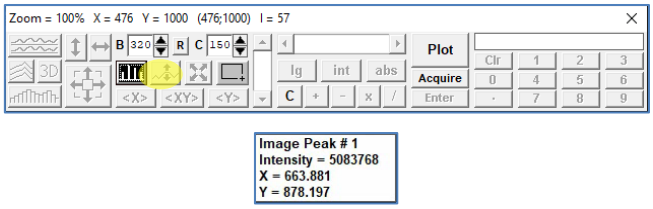

Adjust the contrast if necessary, to optimise the image.




The acquired image should look like the one shown in the test report for the dispersion cassette currently installed in the spectrometer.

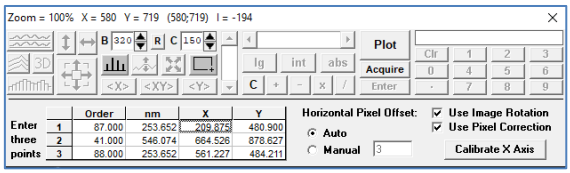


Ideally the maximum intensity in the image should be in the range 50,000 – 55,000 per accumulation. Therefore as 100 accumulations have been acquired the value should be between 5,000,000 and 5,500,000. The ***Peak finder*** button (see below) can be used to find the most intense pixel in the image and display its intensity.

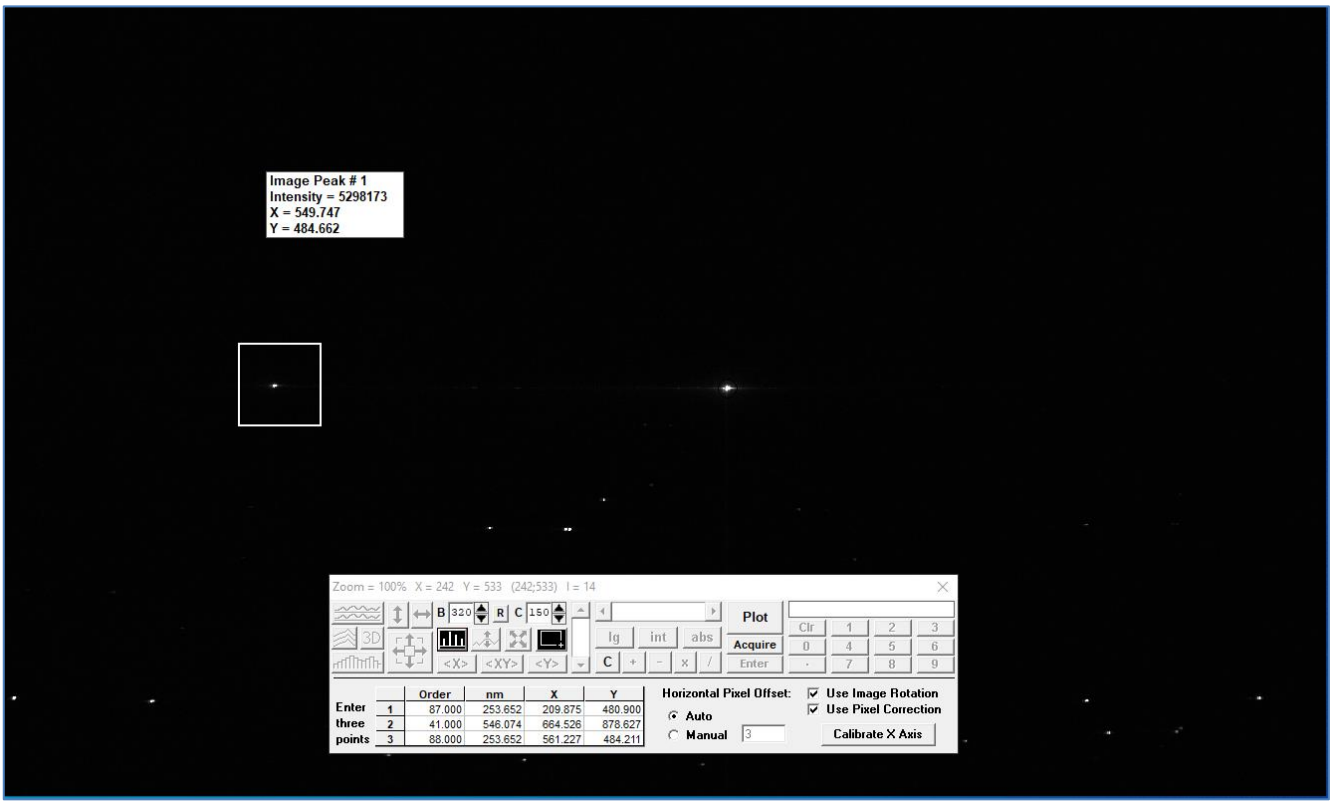



If the displayed value is in the required range continue with the calibration procedure. If it is outside the required range adjust the *Exposure time* in the camera configuration window accordingly, i.e., increase the Exposure time to increase the intensity or reduce it to reduce the intensity, and then repeat the acquisition of the background and calibration images until the maximum intensity is in the required range.

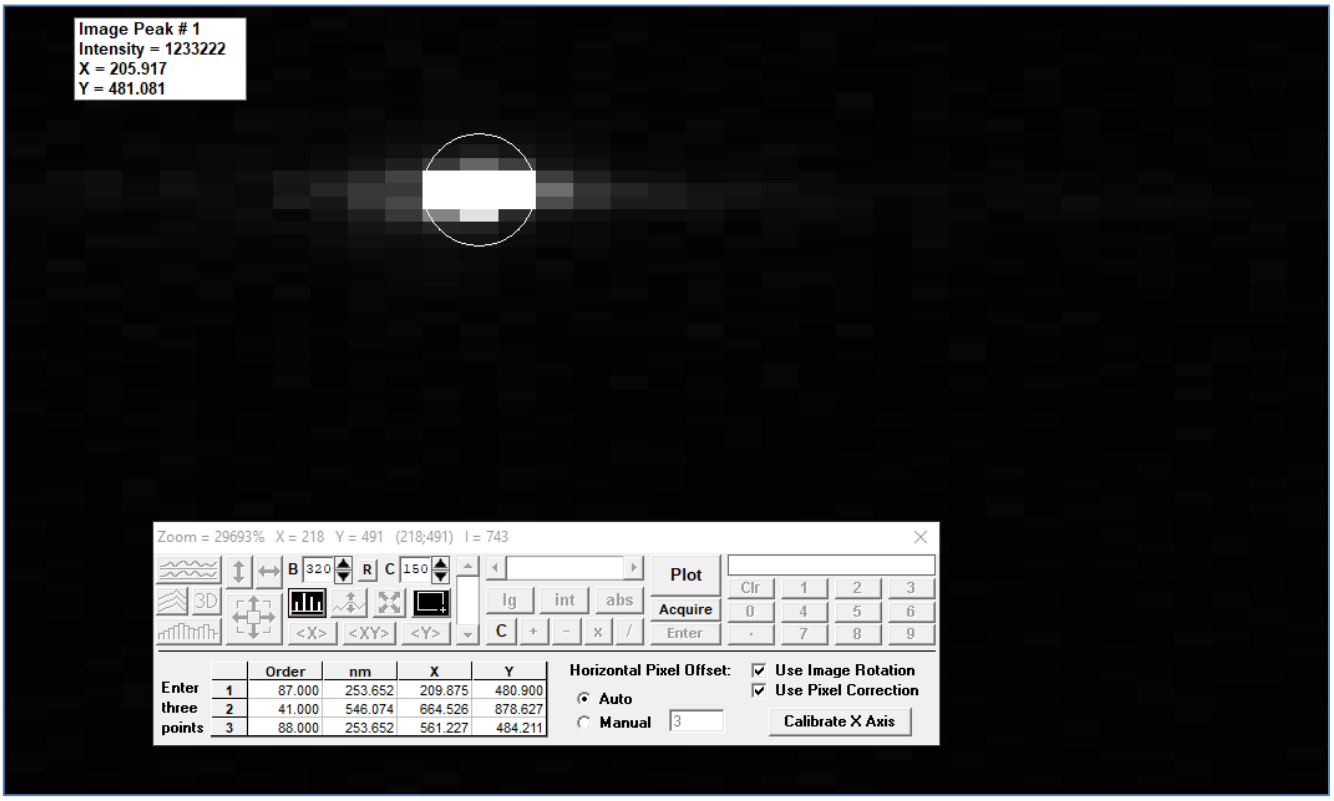
Select ***Window***, ***Spectrograph setup***, then ***Calibrate X axis*** from the menu to open the calibration window.




Three lines are used for calibration corresponding to pixels in different regions of the image. These are highlighted in the image shown in the test report (as shown above). The X and Y co-ordinates corresponding to these lines need to be entered into the table displayed in the calibration window.
Select the ***Zoom tool*** and then left-click and drag a zoom window around the pixels corresponding to the first line.

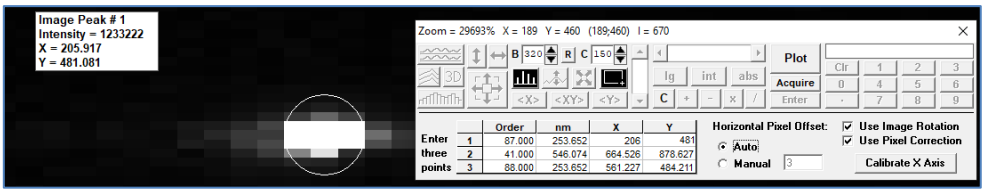



The *Peak finder* should still be enabled and the co-ordinates of the most intense pixel for the selected line will be displayed together with its intensity.



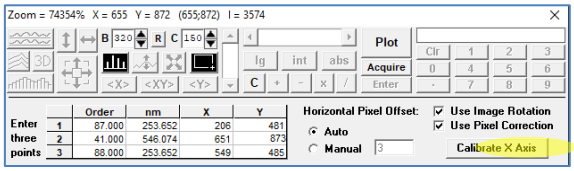

**NB** If for any reason the co-ordinates are not displayed it is likely that the *Peak finder* is disabled so reselect it.

Copy the X and Y values into the table cells corresponding to peak 1 in the calibration window. Note that it is only necessary to use the integer component of the co-ordinates.

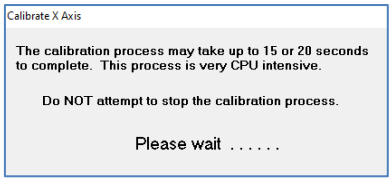



Right-click to zoom out to view the full image and then repeat this process to determine and enter the X and Y co-ordinates for the second and third lines.

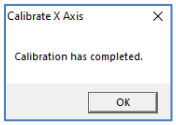
When the co-ordinates for all three lines have been entered into the table select ***Calibrate X Axis*** in the calibration window.




Wait for the calibration to complete.



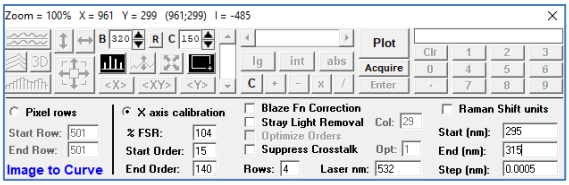

Select ***OK*** to close the calibration completion dialogue.



The calibration is now complete but now needs to be checked.

Select ***Window***, ***Spectrograph setup***, then ***Image to curve*** from the menu. In the configuration window that is now displayed make sure that:

- The ***Step value*** is set to ***0.0005 nm***.
- ***Rows*** = 4
- All checkboxes except ***X axis calibration*** are unchecked.




Find the table of calibration results in the test report for the dispersion cassette currently installed in the spectrometer.

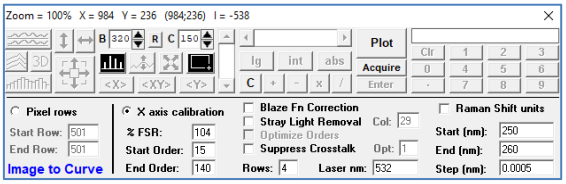
## EMU-120/65
## Test Report values

**Calibration:** The following calibration results were achieved using a step size of **0.0005nm**:

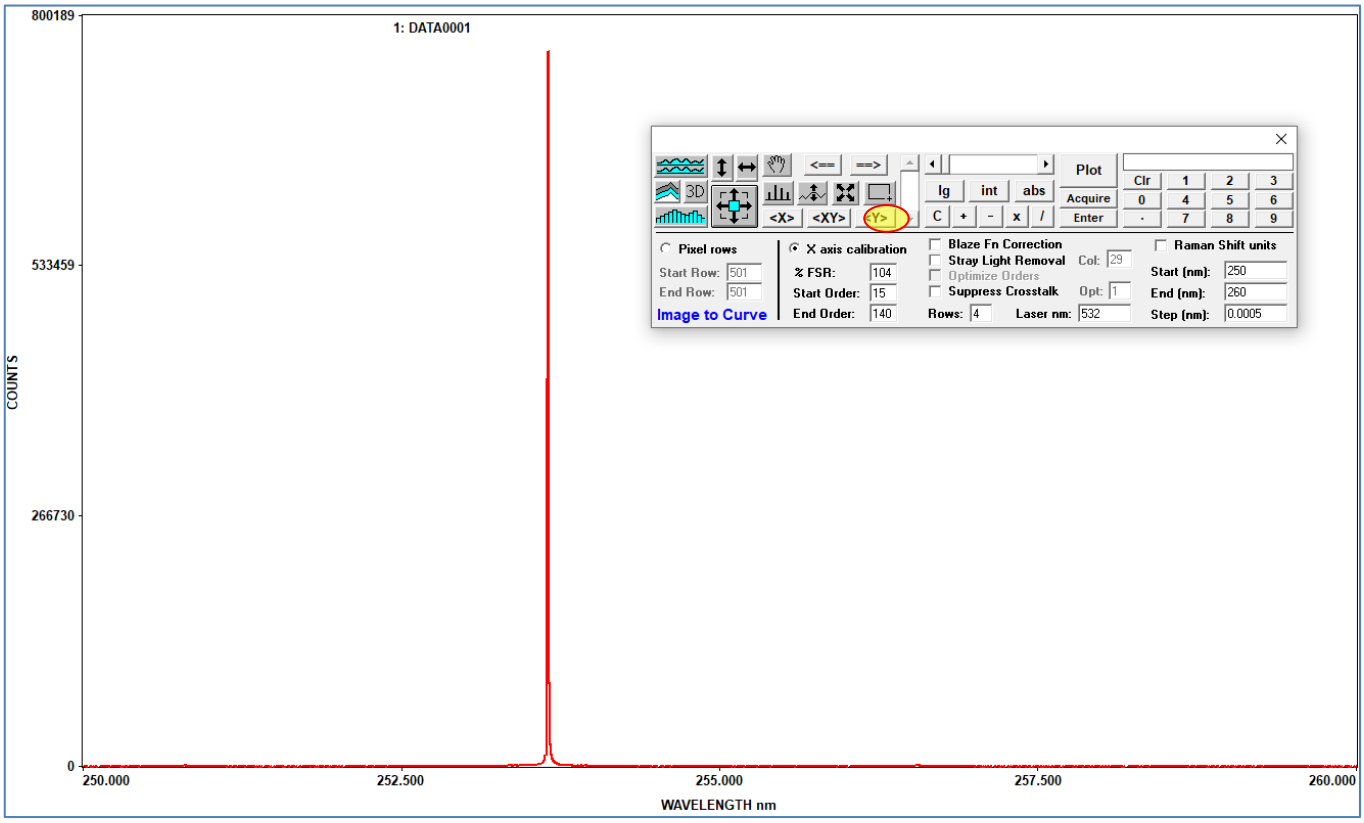
EMU-120/65 UV3:UV/VIS/NIR Cassette #052: 10x30u slit: 8x8u pixels: 16mm AS: 0.0005nm step size

| Actual WL (nm) | Calibrated WL | Difference (nm) | Difference (%) | FWHM | λ / Δ λ |
|---|---|---|---|---|---|
| 253.652 | 253.651 | -0.0010 | -0.0003942409 | 0.0165 | 15373 |
| 296.728 | 296.728 | 0 | 0 | 0.0100 | 29673 |
| 312.567 | 312.569 | +0.0020 | +0.0006398628 | 0.0110 | 28415 |
| 365.015 | 365.019 | +0.0040 | +0.0010958454 | 0.0120 | 30418 |
| 365.484 | 365.483 | -0.0010 | -0.0002736098 | 0.0125 | 29239 |
| 404.656 | 404.660 | +0.0040 | +0.0009884939 | 0.0135 | 29975 |
| 435.833 | 435.387 | -0.4460 | -0.1023327743 | 0.0285 | 15277 |
| 546.074 | 546.078 | +0.0040 | +0.0007325015 | 0.0170 | 32122 |
| 576.960 | 576.964 | +0.0040 | +0.000693289 | 0.0170 | 33939 |
| 579.066 | 579.069 | +0.0030 | +0.0005180757 | 0.0210 | 27575 |
| 750.387 | 750.382 | -0.0050 | -0.0006663228 | 0.0430 | 17451 |
| 763.511 | 763.511 | 0 | 0 | 0.0260 | 29366 |
| 801.479 | 801.482 | +0.0030 | +0.000374308 | 0.0240 | 33395 |
| 826.452 | 826.454 | +0.0020 | +0.0002419983 | 0.0260 | 31787 |
| 922.450 | 922.444 | -0.0060 | -0.0006504418 | 0.0610 | 15122 |
| | | Mean of Difference (%): | -0.006602201 | Mean of FWHM | Mean of λ / Δ λ |
| | | Std. Dev. of Difference (%): | 0.0264889867 | 0.0226 | 26608 |

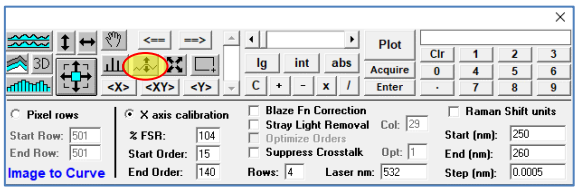
Ideally the values of ***Actual wavelength*** and ***Full Width Half Maximum*** for each of the peaks listed in the table should be checked against the calibrated spectrum. The first peak to be checked is at approximately 253 nm. So, in the Kestrel Spec configuration window, set the ***Start*** wavelength to be 250 nm and the ***End*** wavelength to be 260 nm to generate a spectrum that includes this line.



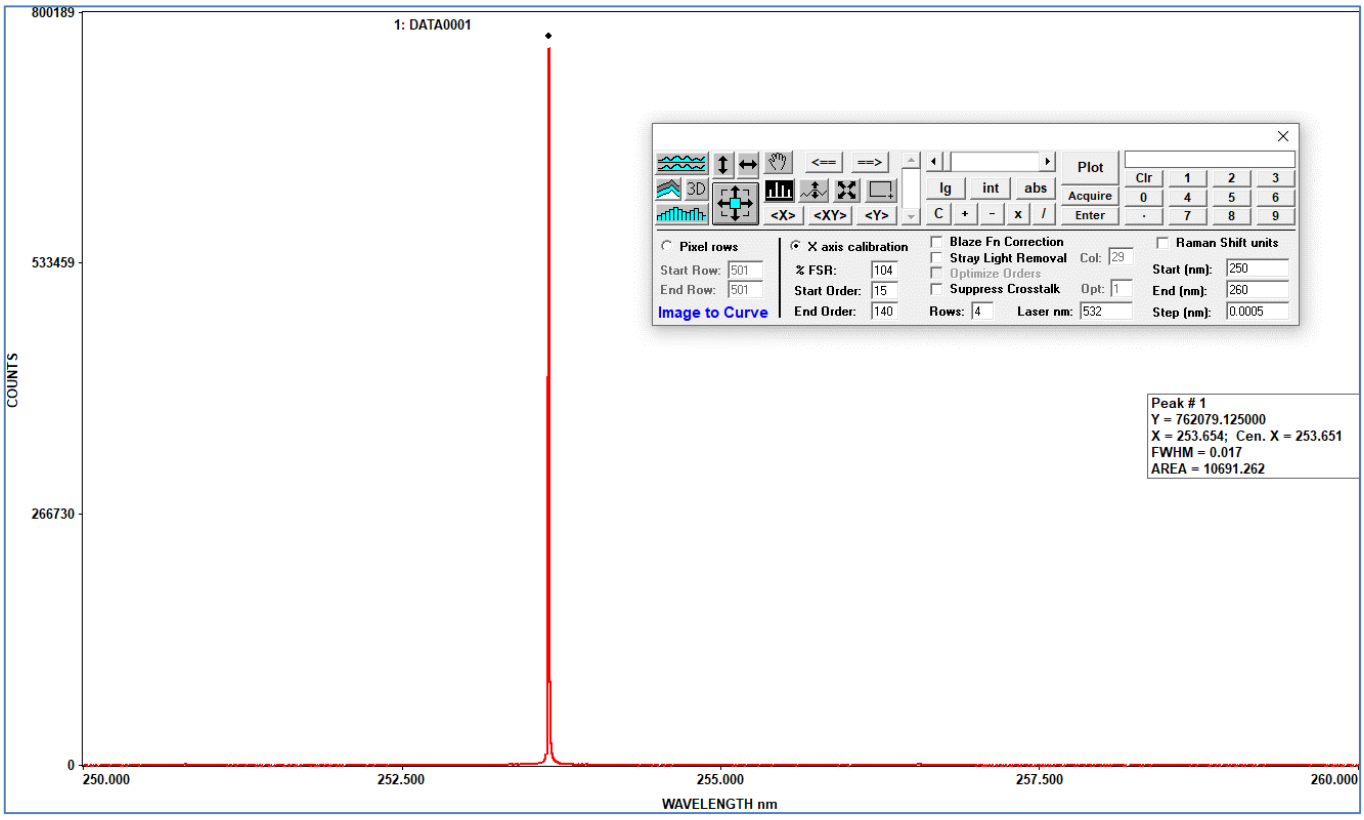

Select ***Process*** and then ***Copy Image to Curve*** from the menu to display spectrum and select the ***Autoscale X and Y*** button to display the specified wavelength range.



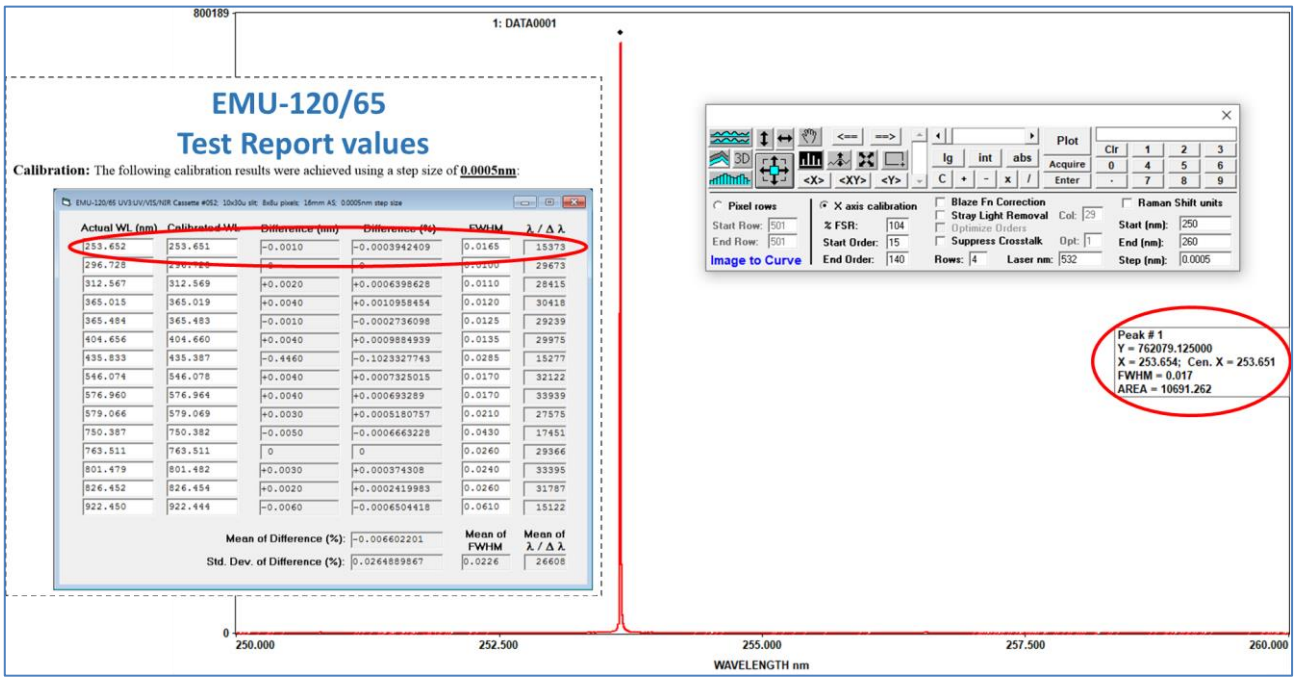

Select the ***Peak finder*** button.



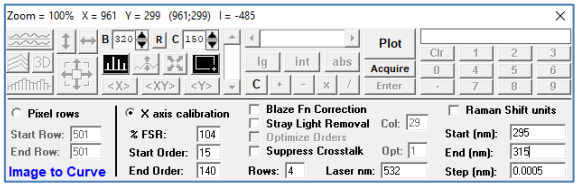
The most intense peak in the displayed range will be marked and a window displayed showing the parameters associated with it.



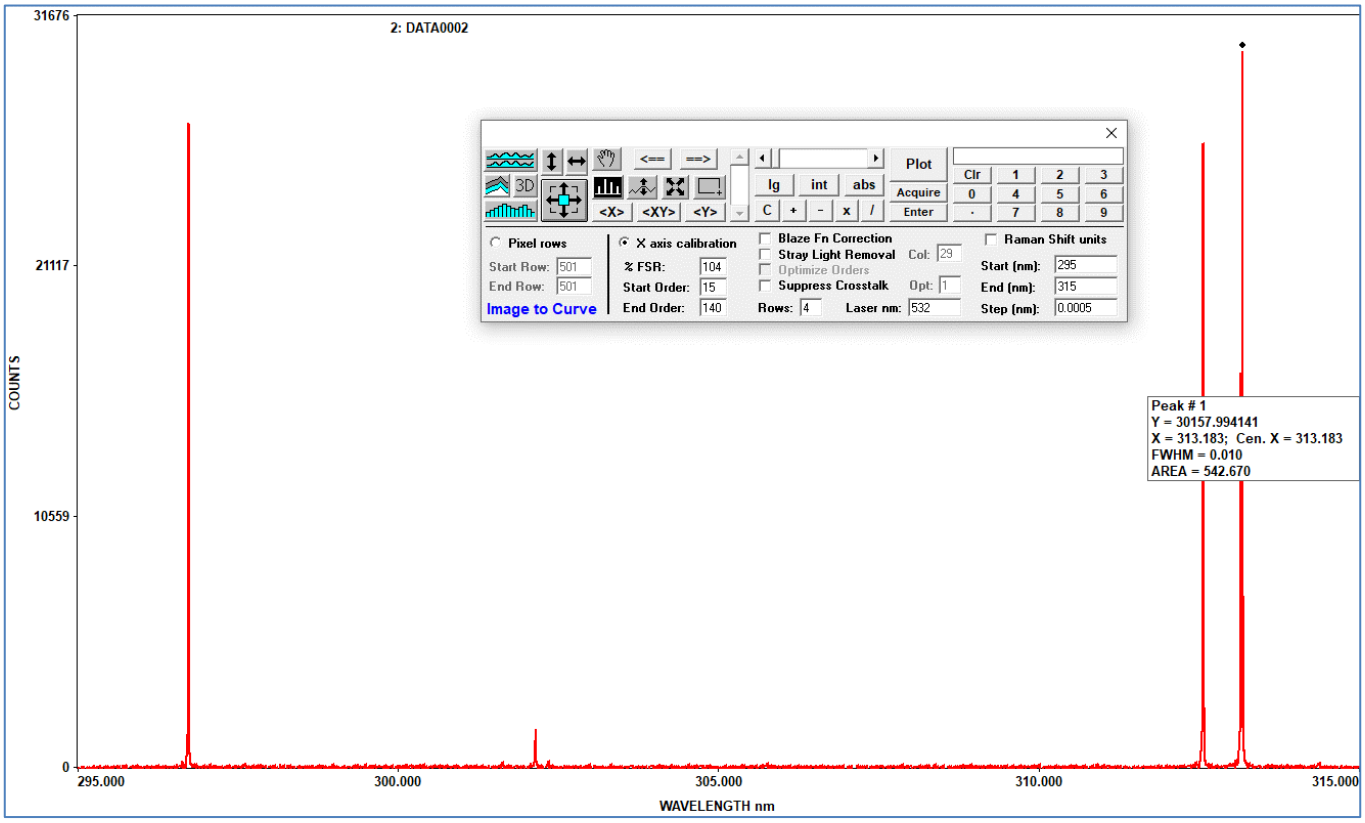
Compare the wavelength of the peak centroid with the *Actual wavelength* listed in the table of calibration results. The maximum difference between these values should be of the same order of magnitude as the corresponding *Difference* value listed in the table of calibration results. Compare the *FWHM* value for the identified peak with the value listed in the table of calibration results. These values should also be the same but can be different by a factor of 2, or occasionally 4.




Change the values of *Start* and *End* wavelengths in the configuration window to specify a new region of the spectrum to display in order to check more of the peaks listed in the table of calibration results contained in the dispersion cassette test report. If the wavelengths of the peaks listed in the table of calibration results are reasonably close together it is possible to specify a range that includes more than one peak. For example, for the dispersion cassette used for demonstration in this manual the next two peaks listed in the table of calibration results are at approximately 296 nm and 312 nm. Therefore, a *Start* wavelength of 295 nm and an *End* wavelength of 315 nm can be specified.




As before select ***Process*** and then ***Copy Image to Curve*** from the menu and then select the ***Autoscale X and Y*** button to display the specified wavelength range.




Select the ***Peak finder*** button. The most intense peak in the displayed range will be marked and a window displayed showing the parameters associated with it. If the peak marked does not correspond with one of the peaks listed in the table select the ***Peak finder*** button again and the next most intense peak will be marked. Repeat this process until one of the peaks listed in the table of calibration results is marked. Compare the wavelength of the peak centroid with the *Actual wavelength* listed in the table of calibration results. Compare the *FWHM* value for the identified peak with the value listed in the table of calibration results.

Select the ***Peak finder*** button again until the next peak listed in the table of calibration results is marked. Compare the wavelength and *FWHM* values for this peak with those listed in the table.

Repeat this process of displaying regions of the spectra and checking the peak values until all of the peaks listed in the table of calibration results have been checked.

Note that with experience this calibration check procedure will become quicker and easier to perform. Also, it is probably not necessary to check every peak every time a calibration is performed. By checking a number of peaks across the full wavelength range it should quickly become obvious whether there is an issue with the calibration. It is unlikely that the parameter values for all peaks will match exactly with those listed in the table of calibration results but the values for the vast majority of peaks should be within the limits described.
If in any doubt about the calibration validity contact APL for further advice.

Once the calibration has been completed and checked, the calibration image and parameters can be saved if required.

**NB** These files are only required if the data acquired using the current calibration needs to be retrieved and further manipulated at a later date. This is not generally necessary.

To save the calibration image select ***Window*** and then ***Active Image*** from the menu to redisplay the calibration image. Select ***File*** and then ***Save Current Image*** from the menu. Use the file browser to select a suitable folder for the calibration image and name the image file appropriately. For example, ***Hg-Ar UV3 (28-Jul-20)*** to identify the calibration source and dispersion cassette used and the date of the calibration.

To save the calibration configuration parameters, select ***File***, ***Archive EMU Setup*** and then ***Archive Current Setup…*** from the menu. The current setup parameters will be displayed. Select ***Archive*** and specify a suitable name for the

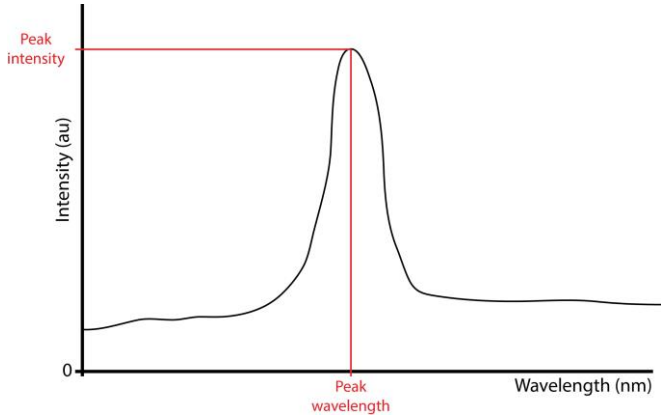
archived parameters. For example, ***Hg-Ar UV3 (28-Jul-20)*** can again be used to identify the calibration source and dispersion cassette used and the date of the calibration. Select ***Save*** to save the parameter file.

Finally, the KestrelSpec initialisation file should be updated so that the correct parameters are loaded automatically when the application is next started. To do this select ***File*** and then ***Update INI File*** from the menu to update the initialisation file.

The EMU calibration is now complete.

**Appendix B**
**Quantitative calibration types**

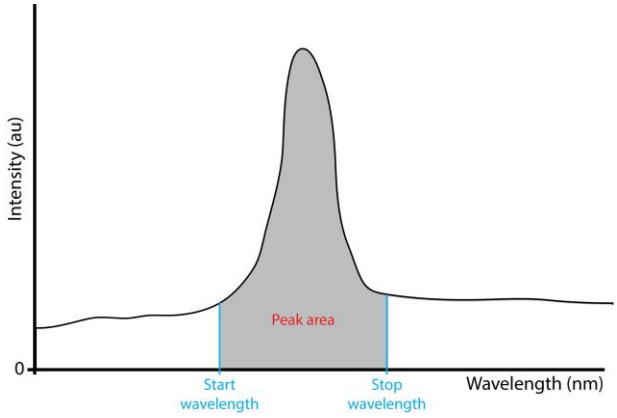
***Peak intensity*:**
Parameters used: *Analyte peak* wavelength, *Peak tolerance*
This is the most basic metric used for calibration and uses just the wavelength of the analyte peak and a peak tolerance value to specify the number of pixels either side of the specified peak wavelength that the software will search to find the maximum intensity value. This maximum intensity is used as the calibration metric.



**Determination of peak intensity**

***Peak intensity ratio*:**
Parameters used: *Analyte peak* wavelength, *Matrix peak* wavelength*, Peak tolerance*
This is essentially the same as the *Peak intensity* calibration except that a matrix peak is also specified and the two peak intensities are ratioed to generate the calibration metric in order to reduce the effect of variability between spectra.

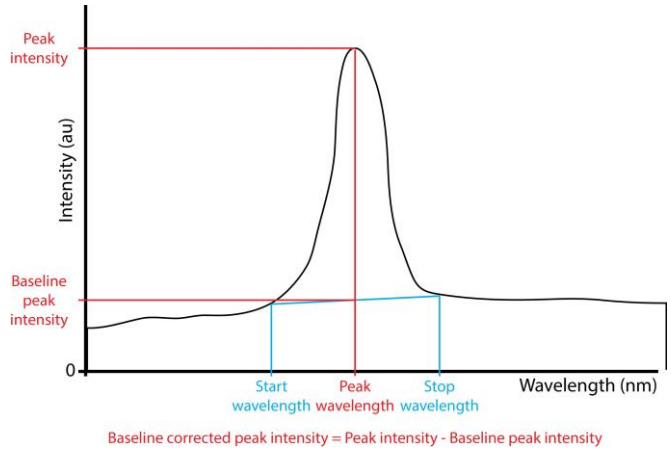
***Peak area*:**
Parameters used: *Analyte start* wavelength*, Analyte stop* wavelength
In this instance the limits of the analyte peak are specified by a start wavelength and a stop wavelength and the area under the peak is calculated. This full area under the peak is used as the calibration metric.



**Determination of peak area**

***Peak area ratio*:**
Parameters used: *Analyte start* wavelength*, Analyte stop* wavelength*, Matrix start* wavelength*, Matrix stop* wavelength
This is essentially the same as the *Peak area* calibration except that start and stop wavelengths are also specified for a matrix peak and the two calculated peak areas are ratioed to generate the calibration metric in order to reduce the effect of variability between spectra.

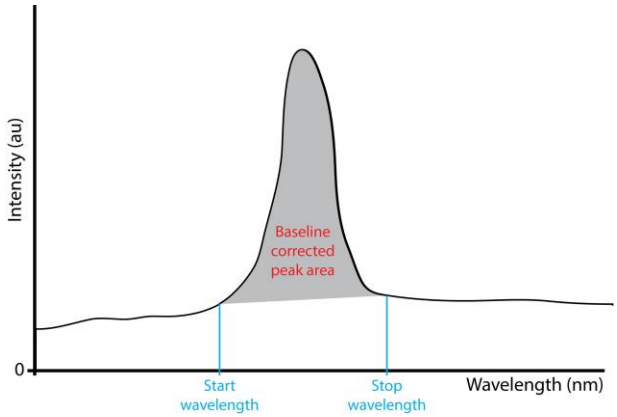
***Baseline-corrected peak intensity*:**
Parameters used: *Analyte peak* wavelength*, Analyte start* wavelength*, Analyte stop* wavelength*, Peak tolerance*
For this calibration type the maximum intensity of the analyte peak is calculated in the same way as for the basic peak intensity calibration. However, peak start and stop parameters are also used to determine a measure of the baseline intensity at the wavelength corresponding to the peak maximum and this is subtracted from the maximum peak intensity to determine the calibration metric.



**Determination of baseline-corrected peak intensity**

***Baseline-corrected peak intensity ratio*:**
Parameters used: *Analyte peak* wavelength*, Analyte start* wavelength*, Analyte stop* wavelength*, Matrix peak* wavelength*, Matrix start* wavelength*, Matrix stop* wavelength*, Peak tolerance*
This is essentially the same as the *Baseline-corrected peak intensity* calibration except that peak start and stop wavelengths are also specified for a matrix peak and the two calculated baseline-corrected peak intensities are ratioed to generate the calibration metric in order to reduce the effect of variability between spectra.

***Baseline-corrected peak area*:**
Parameters used: *Analyte start* wavelength*, Analyte stop* wavelength
This calibration type is similar to the basic *Peak area* calibration except that the specified start and stop wavelengths are also used to determine the area of the trapezoid between the base of the analyte peak and the wavelength axis and this area is subtracted from the full area below the peak to determine the calibration metric.



**Determination of baseline-corrected peak area**

***Baseline-corrected peak area ratio*:**
Parameters used: *Analyte start* wavelength*, Analyte stop* wavelength*, Matrix start* wavelength*, Matrix stop* wavelength
This is essentially the same as the *Baseline-corrected peak area* calibration except that start and stop wavelengths are also specified for a matrix peak and the two calculated baseline-corrected peak areas are ratioed to generate the calibration metric in order to reduce the effect of variability between spectra.

**Appendix C**
**Grubbs test for outlier removal**

A gross error is one due to an error/mistake during the measurement that usually leads to an outlier point. The Grubbs test can be used for the detection and elimination of such outliers. A value, *G*, can be calculated for each measurement value according to the following equation:

$$G_{calculated} = \frac{|x - \overline{x}|}{s}$$

where:

$x$ = measurement value to be assessed
$\overline{x}$ = mean of the data set
$s$ = standard deviation of the data set.

This calculated value can then be compared to the corresponding critical value at the specified significance level as tabulated below. If $G_{calculated}$ is greater than the critical value, then the measurement value should be discarded.

**TABLE 1 Critical Values for *T* (One-Sided Test) When Standard Deviation is Calculated from the Same Sample[A]**

| Number of Observations, *n* | Upper 10 % Significance Level | Upper 5 % Significance Level | Upper 1 % Significance Level |
|---|---|---|---|
| 3 | 1.1484 | 1.1531 | 1.1546 |
| 4 | 1.4250 | 1.4625 | 1.4925 |
| 5 | 1.602 | 1.672 | 1.749 |
| 6 | 1.729 | 1.822 | 1.944 |
| 7 | 1.828 | 1.938 | 2.097 |
| 8 | 1.909 | 2.032 | 2.221 |
| 9 | 1.977 | 2.110 | 2.323 |
| 10 | 2.036 | 2.176 | 2.410 |
| 11 | 2.088 | 2.234 | 2.485 |
| 12 | 2.134 | 2.285 | 2.550 |
| 13 | 2.175 | 2.331 | 2.607 |
| 14 | 2.213 | 2.371 | 2.659 |
| 15 | 2.247 | 2.409 | 2.705 |
| 16 | 2.279 | 2.443 | 2.747 |
| 17 | 2.309 | 2.475 | 2.785 |
| 18 | 2.335 | 2.504 | 2.821 |
| 19 | 2.361 | 2.532 | 2.854 |
| 20 | 2.385 | 2.557 | 2.884 |
| 21 | 2.408 | 2.580 | 2.912 |
| 22 | 2.429 | 2.603 | 2.939 |
| 23 | 2.448 | 2.624 | 2.963 |
| 24 | 2.467 | 2.644 | 2.987 |
| 25 | 2.486 | 2.663 | 3.009 |
| 26 | 2.502 | 2.681 | 3.029 |
| 27 | 2.519 | 2.698 | 3.049 |
| 28 | 2.534 | 2.714 | 3.068 |
| 29 | 2.549 | 2.730 | 3.085 |
| 30 | 2.563 | 2.745 | 3.103 |
| 35 | 2.628 | 2.811 | 3.178 |
| 40 | 2.682 | 2.866 | 3.240 |
| 45 | 2.727 | 2.914 | 3.292 |
| 50 | 2.768 | 2.956 | 3.336 |

[A] Values of *T* are taken from Grubbs (1),[3] Table 1. All values have been adjusted for division by $n - 1$ instead of $n$ in calculating $s$. Use Ref. (1) for higher sample sizes up to $n = 147$.

**NB** Values in this table are for a one-tailed test, as recommended by ASTM E178-02 Standard Practice for Dealing with Outlying Observations.

*LIBSoft* uses this procedure iteratively to identify all outliers in the data set in question. For example, if ten replicated spectra are acquired from a calibration sample with a particular concentration of analyte to be used in a calibration based on analyte peak intensity, this will generate a data set comprising ten intensity values:

$$Int_1, Int_2, Int_3 \ldots .Int_{10}$$

*LIBSoft* calculates the mean and standard deviation of these ten intensity values and from this a value of $G_{calculated}$ is determined for each intensity. The maximum absolute value of $G_{calculated}$ is then compared to the corresponding critical value and if it is greater than this critical value the corresponding intensity value is marked as an outlier and removed from the data set. The remaining nine intensity values are then used to determine revised values of mean and standard deviation and hence revised values of $G_{calculated}$ for each of the intensity values. Again, the maximum absolute value of $G_{calculated}$ is then compared to the corresponding critical value to identify any further outliers. This process is repeated until no further outliers are found, i.e., the maximum absolute value of $G_{calculated}$ is less than or equal to the critical value.

If the number of values in a data set is outside the range for which critical values are tabulated, i.e., < 3 or > 50, the no outliers will be identified. If the number of values in a data set is not uniquely specified in the tabulated data LIBSoft will interpolate between the critical values corresponding to the tabulated values immediately above and below the number of values.

**Appendix D**
**Calculation of LOD and LOQ**

One of the figures of merit commonly used to illustrate the analytical performance of a LIBS instrument is the limit of detection (LOD), i.e., the lowest concentration of analyte that can be detected in a sample matrix. In the literature, several methods of calculating the LOD can be found.

*LIBSoft* calculates the LoD using a method which uses the standard deviation of the "blank" measurement[1,2] ("blank" meaning the sample containing zero concentration of the analyte). This is perhaps the most commonly used method in LIBS. The methodology for this calculation is as follows.

**Linear calibration curve:** $y = a + mx$

$$LOD_{Sbl} = \frac{3s_{bl}}{m}$$

**Quadratic calibration curve:** $y = ax^2 + bx + c$

$$aLOD^2_{Sbl} + bLOD_{Sbl} = 3s_{bl}$$

where:

$s_{bl}$ is the standard deviation of the blank (or the sample with the lowest analyte concentration if a blank is not available)

*LIBSoft* calculates the Limit of Quantitation (LOD) as:

$$LOQ \ \ 3.3 \times LOD$$

Whenever the LOD of a given analytical instrument needs to be precisely calculated, a dedicated experiment and the procedure described in the ISO standards should be followed[3].

[1]A.W. Miziolek, V. Palleschi, I. Schechter, *Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications*, Cambridge University Press, (2006), p. 153.
[2]R. Noll, *Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications*, Springer, (2012), pp. 214-215.
[3]British standards, BS ISO 11843, *Capability of detection*.