MMS Raman Spectrometer

A CENTICE Product

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Installation and Operation Manual

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Ocean Optics offers the most comprehensive, innovative and high-quality line of modular spectroscopy tools in the world. Centice is an essential and valuable partner in this enterprise. We have partnered with Centice because they are committed to the same goals of innovation and quality that inspire us here at Ocean Optics. As always, Ocean Optics conducts its business in an open, honest and technically available fashion. We invite you to contact us at Ocean Optics, Inc. (see front cover for contact information) or Centice with any technical questions, comments, or applications inquiries. Centice can be contacted at the following location:

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Table of Contents

About This Manual

Document Purpose and Intended Audience

This document provides you with installation information to get your system up and running. It also contains an in-depth discussion of Multimodal Sampling technology.

What's New in This Document

This version of the *MMS Raman Spectrometer Installation and Operation Manual* adds clarification to the *Acquiring Spectra* procedure.

Document Summary

Chapter	Description
Chapter 1: *Installation*	Provides a list of system components, and operating requirements. Also contains instructions for installing the MMS Raman spectrometer.
Chapter 2: *Operating the Spectrometer*	Contains instructions for using the MMS Raman spectrometer.
Appendix A: *Specifications*	Provides product specifications for the MMS Raman spectrometer.
Appendix B: *Introduction to Multimodal Multiplex Sampling*	Contains a whitepaper with technical information describing the operation of the MMS Raman spectrometer.
Appendix C: *Remote Interlock*	Contains information on the Remote Interlock feature.

Product-Related Documentation

You can access documentation for Ocean Optics products by visiting our website at **http://www.oceanoptics.com**. Select *Technical → Operating Instructions*, then choose the appropriate document from the available drop-down lists. Or, use the **Search by Model Number** field at the bottom of the web page.

- Detailed instructions for SpectraSuite Spectrometer Operating Software are located at: **http://www.oceanoptics.com/technical/spectrasuite.pdf**.

You can also access operating instructions for Ocean Optics products on the *Software and Technical Resources* CD included with the system.

Engineering-level documentation is located on our website at *Technical → Engineering Docs*.

Upgrades

Occasionally, you may find that you need Ocean Optics to make a change or an upgrade to your system. To facilitate these changes, you must first contact Customer Support and obtain a Return Merchandise Authorization (RMA) number. Please contact Ocean Optics for specific instructions when returning a product.

Laser Safety

Although the MMS Raman Spectrometer is laser-safe, we advise that laser safety eyewear must be worn while operating the system. The MMS Raman uses a Class 3b laser that can cause serious eye injury. The unit contains a remote interlock feature that deactivates the laser when a plug is inserted (see *Remote Interlock* for more information). Safety goggles are available for use with the system. Contact an Ocean Optics Applications Scientist for details.

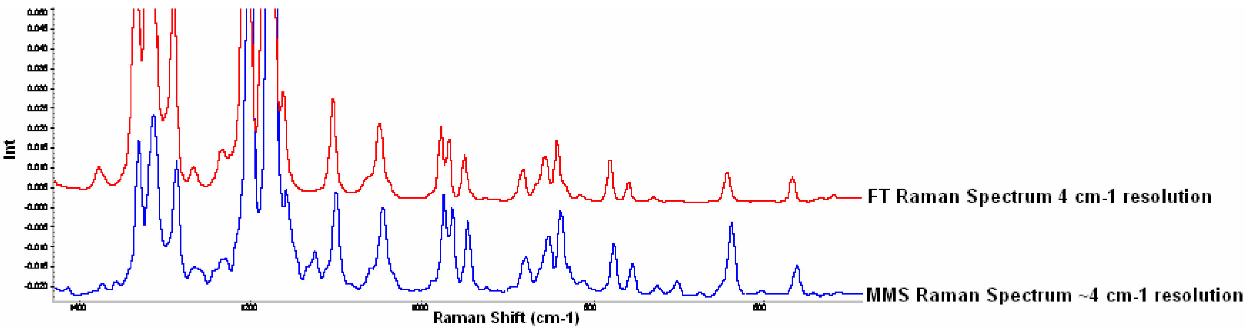
Chapter 1

Installation

Introduction

The Centice Multimodal Multiplex Sampling (MMS) Raman spectrometer provides significantly higher measurement sensitivity than a conventional grating based slit entrance spectrometer due to its unique multimodal multiplex sampling (MMS) technology. An MMS-based spectrometer samples nearly 1,000 optical channels simultaneously through a large area coded aperture – instead of a slit – then applies proprietary algorithms to precisely construct the spectral content of a source. With MMS technology, both high resolution and high light throughput can be achieved simultaneously in a single shot measurement. SpectraSuite software is available with this spectrometer to aid you with your spectral analysis.

The Centice Raman spectrometer is designed to be easy to use and operate with minimal set-up. Follow the detailed step by step instructions described in this chapter to install the spectrometer.



Applications

MMS-based instruments are ideal for measuring weak, scattering and diffuse sources and samples because the spectrometer can collect and process far more light through its wide area aperture, without affecting spectral resolution.

Key applications include material inspection, identification of unknown materials, and quantitative analysis of both intermediates and final products in the chemical and pharmaceutical industries. Any material that is Raman-active and fits within the sample chamber of the instrument can be measured. Typical samples include powders, liquids and polymers. The system is also ideal for teaching and research applications in colleges and universities.

The MMS system uses a wide-area aperture that cannot be illuminated effectively with a fiber input. The aperture should be slightly overfilled to obtain the best spectrum. The wide-area aperture and grating cannot be changed. The MMS aperture and grating are designed specifically for the detector. For fiber-based Raman analysis, consider our QE65000 Spectrometer or the Raman Systems R-3000.

About SpectraSuite

SpectraSuite is a completely modular, Java-based spectroscopy software platform that operates on Windows, Macintosh and Linux operating systems. The software can control any Ocean Optics USB spectrometer and device, as well as any other manufacturer's USB instrumentation using the appropriate drivers. SpectraSuite is a user-customizable, advanced acquisition and display program that provides a real-time interface to a variety of signal-processing functions. With SpectraSuite, you have the ability to perform spectroscopic measurements (such as absorbance, reflectance, and emission), control all system parameters, collect and display data in real time, and perform reference monitoring and time acquisition experiments.

Features

- Novel Multimodal Multiplex Spectroscopy (MMS)
- Spectral resolution of ~4 cm^{-1}
- Spectral range of 220-2000 cm^{-1}
- Integration times ranging from 50 ms-100 seconds
- Sample holder for cuvettes and test tubes
- Rapid analysis, with no sample preparation

Parts Included

- Digital Raman Spectrometer with integrated sample holder (holds up to 10-mm cuvettes and test tubes)
- Power supply for the Spectrometer CCD Camera
- Key for turning the laser on/off
- Removable Remote Interlock plug to automatically disable the laser (see *Remote Interlock* for more information)
- USB cable to interface to the PC
- Ocean Optics *Software and Technical Resources* CD with this user manual

Caution

You must first install the software before you power up the spectrometer.

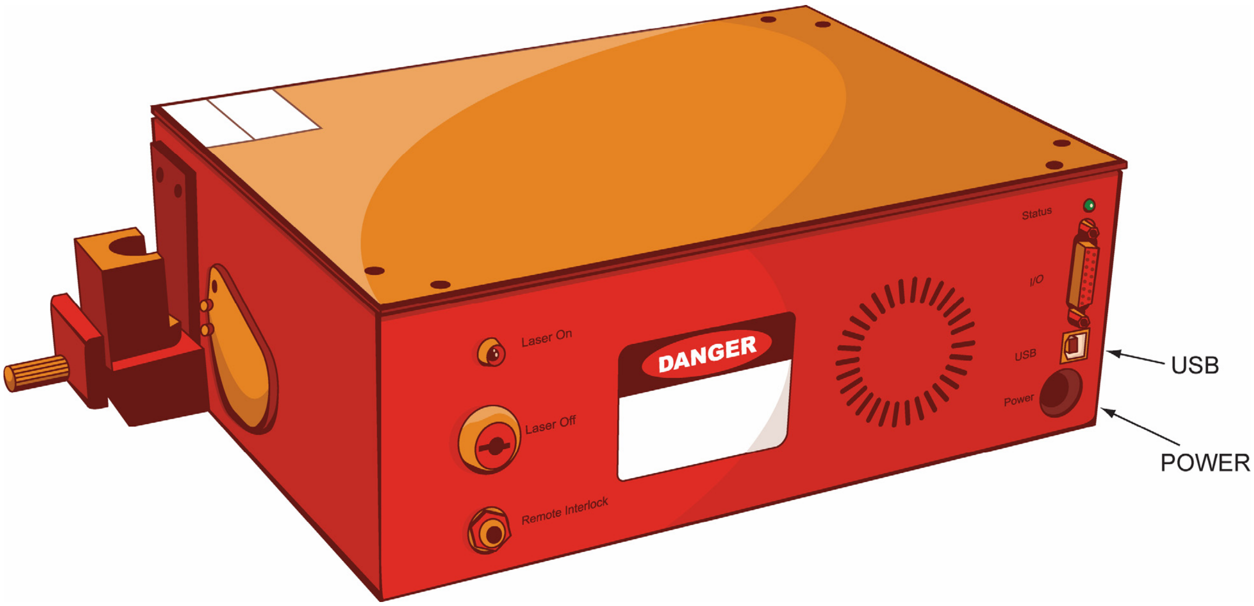
Other Equipment Needed

In addition to the parts you received with your spectrometer, you will need the following equipment to run your experiments:

- Ocean Optics' SpectraSuite Spectrometer Operating Software
- A computer to run the software. See the *SpectraSuite Spectrometer Operating Software Installation and Operation Manual* for SpectraSuite system requirements.
- Safety goggles (such as the R-2001-GL goggles from Ocean Optics)

Installation Procedure

Before you power up your Raman spectrometer, you must install the software. See the *SpectraSuite Spectrometer Operating Software Installation and Operation Manual* for software installation instructions. See [Product-Related Documentation]() for more information on accessing this document.



► ***Procedure***

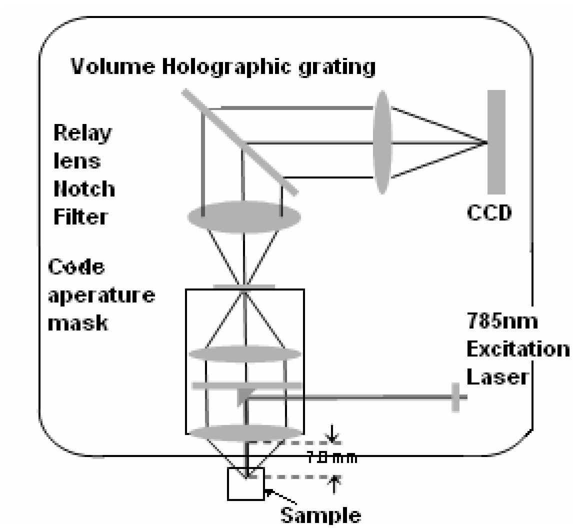
1. Install SpectraSuite on the destination computer. See the *SpectraSuite Spectrometer Operating Software Installation and Operation Manual* for information on SpectraSuite.
2. Connect the camera power supply to the power interface of the device, and plug the power supply into an AC outlet. All functions of the spectrometer are operational when it is powered on except for the laser.
3. Locate the USB cable provided with the spectrometer. Connect one end of the USB cable to the USB interface of the spectrometer camera and the other end into the computer. Your computer system should detect the new hardware. Follow the instructions for your computer system for it to recognize the new hardware device.

CHAPTER 2

Operating the Spectrometer

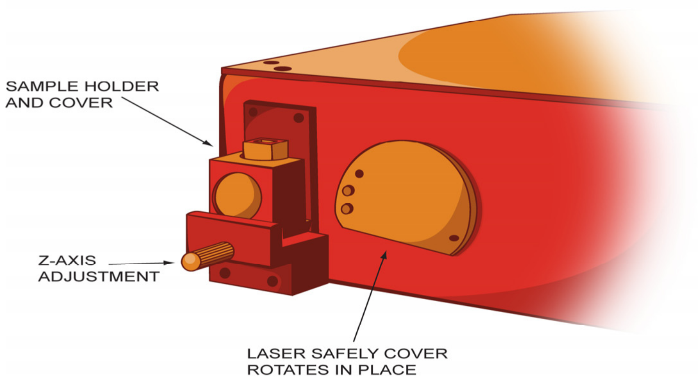
This chapter describes the procedure to operate your MMS Raman spectrometer. Follow these instructions carefully for optimum results.

A schematic layout of the MMS Raman spectrometer is shown below:



Sample Placement

The MMS Raman spectrometer contains an attached sample holder. Remove the sample holder cover and place the cuvette with your sample into the sample holder. You can adjust its distance from the lens using the z-axis knob. In general, liquid samples should be placed as close to the lens as possible; solid samples should be placed as far from the lens as possible.



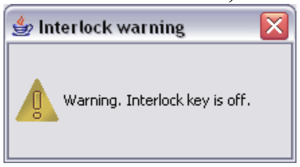
Acquiring Spectra

► *Procedure*

1. Remove the sample holder cover.
2. Place the sample cuvette in the sample holder and adjust its distance from the lens using the Z-axis knob. Then, replace the cover.
3. Turn the laser safety key to the On position (vertical) to activate the laser. The laser is not active at this point. A signal is sent to the spectrometer's processor requesting activation of the laser. The LED on the spectrometer lights. Two seconds after the processor receives the laser activation request, the processor sends the activation signal to the laser controller. The laser is now operating.

Note

If you attempt to take a scan with the laser off, a warning appears in SpectraSuite:



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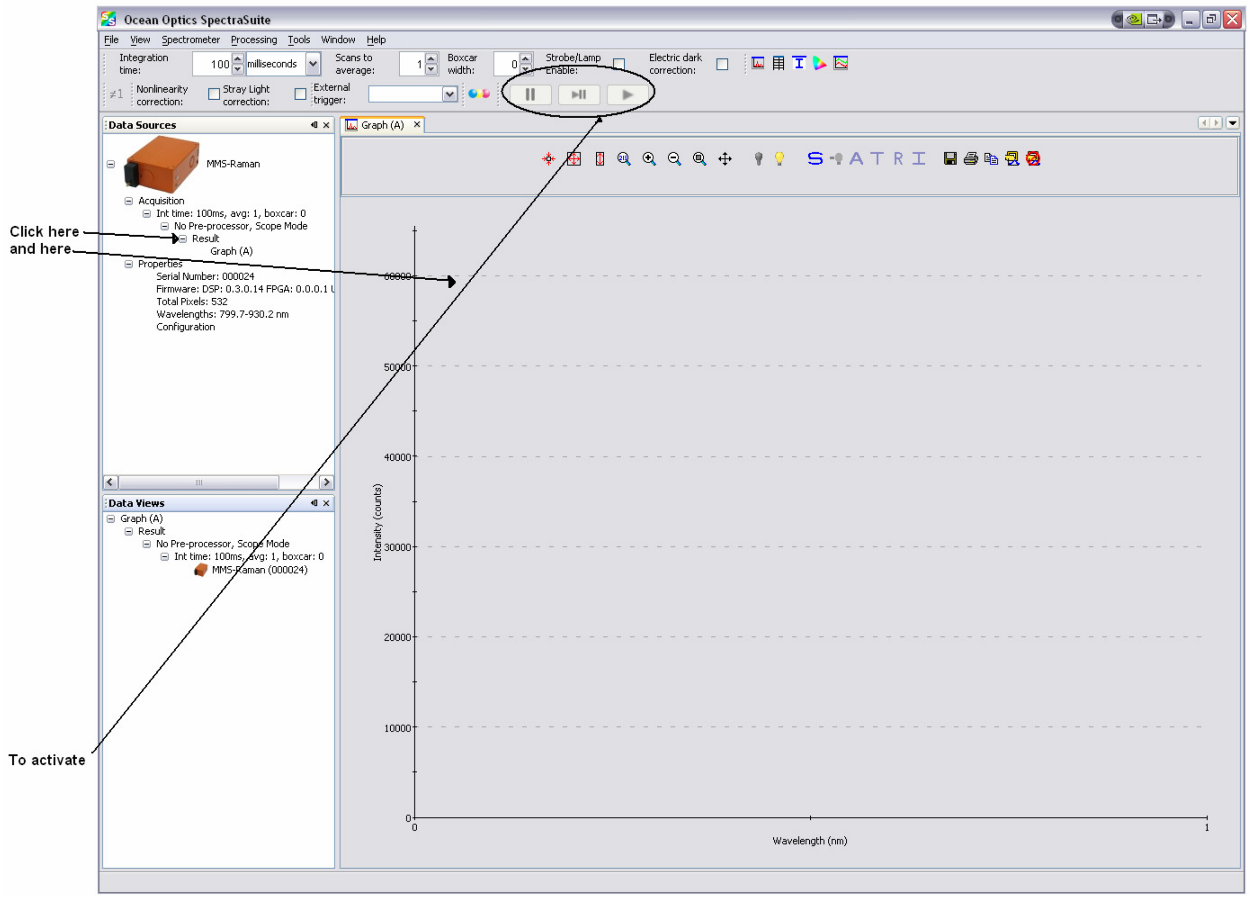
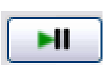
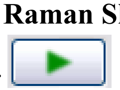
4. If you have not already done so, start the SpectraSuite software application.

   SpectraSuite should now recognize the spectrometer (a picture of the spectrometer appears in the Data Sources pane of the SpectraSuite window).

5. Click on the line under the MMS Raman Spectrometer's Acquisition node (expand the node if necessary) in the Data Sources pane, then click on the spectrum graph to activate the acquisition controls at the top of the screen.

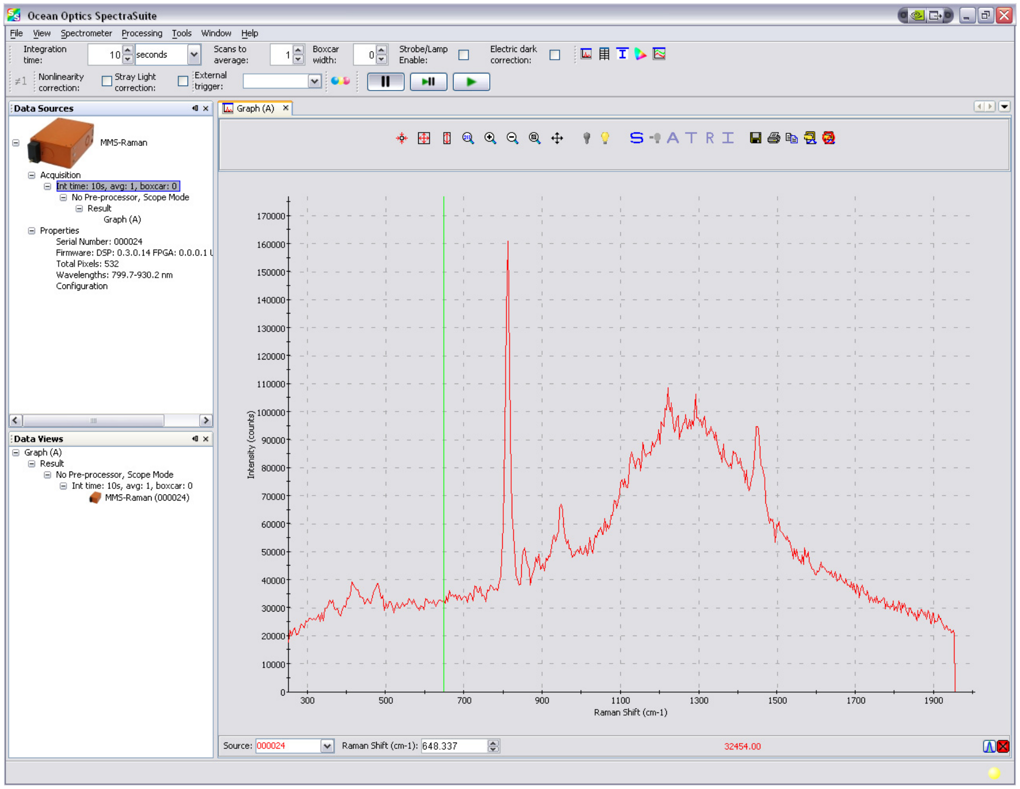


6. Click  (single shot) to start a scan after installing the MMS Raman Spectrometer. Unlike other Ocean Optics spectrometers, you must first click an acquisition control to start a scan after installing the MMS Raman Spectrometer. This precaution is taken since the MMS Raman Spectrometer uses an internal laser.

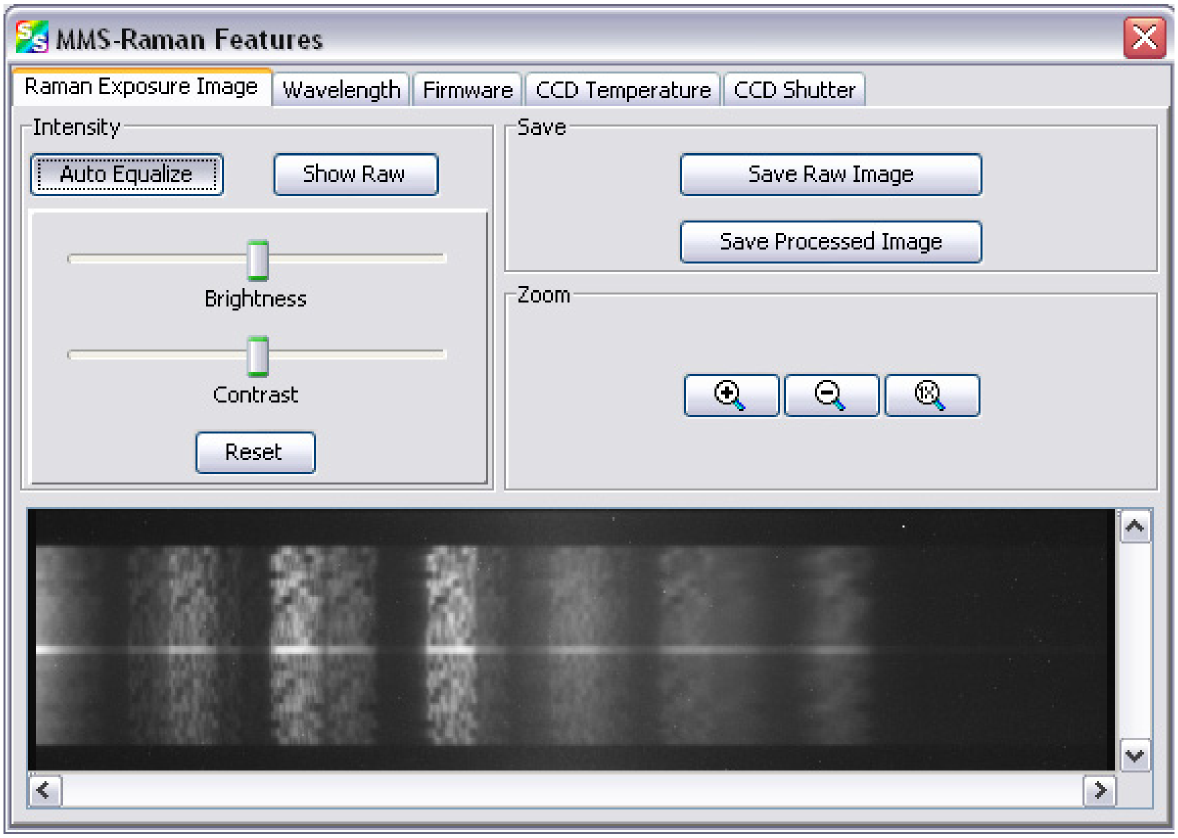
7. The spectrum graph appears in wavelength units. Select either **Processing | Processing Mode | Raman Shifts** or **Processing | x-axis Units | Raman Shifts.** The next acquisition appears in Raman Shifts. Click  (single shot) or  (continuous) acquisition control on the SpectraSuite screen to take your Raman spectrum.

Note

SpectraSuite automatically takes a dark reading for you.



8. You can display the CCD image, if desired. Either right-click on the spectrometer in the Data Sources pane and select **Spectrometer Features** or select **Spectrometer | Spectrometer Features** from the menu. Use **Auto Equalize** to adjust the contrast and brightness.



9. Save the spectrum or export it to an ASCII text file.

Appendix A

Specifications

Specification	Value
Spectral Range	220-2200 cm^{-1}
Spectral Resolution	~4 cm^{-1}
Grating (*)	1200 lines/mm Transmissive Volume phase grating
CCD specifications:	
Chip	Hamamatsu CCD
Pixel Array	512 x 122 Active pixels
Pixel Size	24 x 24 microns
Well Capacity	300,000 electrons
Quantum Efficiency	85% at 250 nm
Dark Noise	200 e^-/pixel/sec @ 0^o C
A/D resolution	16 bits
Exposure Time	50ms to 100 s
Detector readout noise	8 e^- RMS
Gain	4.7 e^-/ADC count
Cooling	to 20^o C below ambient temperature
Laser Source Requirements:	
Lasing Wavelength:	785 nm
Power Output:	> 70 mW
Spectral Line-width:	< 0.2 nm

Specification	Value
General Specs:	
Operating temperature range	-10^{o} to 35^{o} C
Operating Voltage	120 VAC, 50-60Hz
Power Consumption (Maximum)	25 W
Computer Interface	USB 2

Appendix B

Introduction to Multimodal Multiplex Sampling

Introduction

This appendix describes a new generation of spectrometer technology that employs multimodal multiplex sampling (MMS). The performance of a spectrometer based on MMS is then compared to conventional slit and fiber input spectrometers.

Dispersive spectrometers come in two basic designs: scanned-grating monochromators and static grating designs with detector arrays. With the availability of inexpensive linear detectors and charge coupled devices (CCDs) in the UV/Visible/NIR region, dispersive spectrometers are moving away from scanned-grating designs to static implementations. Static implementations are preferred for their single shot measurements, fast data acquisition times and high mechanical reliability. A typical static grating design is shown in Figure 1.

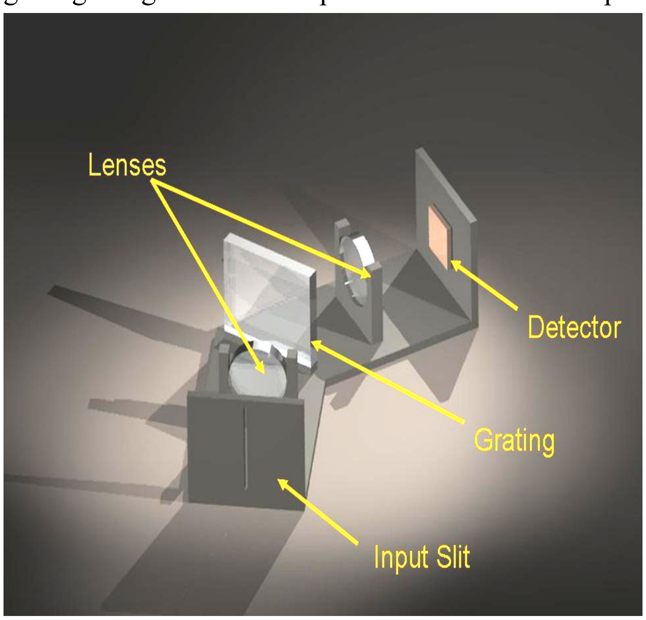


Figure 1: A traditional static grating spectrometer

Most dispersive designs use a fiber based input while some implement a vertical slit which is binned on the detector to increase sensitivity. In such traditional designs, there is an inherent tradeoff between resolution and light throughput. While spectral resolution increases as slit width decreases, a narrow input slit greatly limits photon throughput and likewise, measurement sensitivity.

Centice is introducing a new patent pending spectrometer design based on an optical sensing technology originally developed at Duke University called Multimodal Multiplex Sampling (MMS).

An MMS-based spectrometer samples nearly 1,000 optical channels simultaneously through a coded aperture – instead of a slit – then applies proprietary algorithms to precisely construct the spectral content of a source. With MMS technology, both resolution and throughput (aka etendue) can be maintained and optimized in a single-shot measurement. Interestingly, while the exact performance advantages of MMS vary with the particular circumstances, in no case can a fiber or slit input spectrometer outperform an identically configured MMS system.

The most dramatic MMS performance advantage is realized when making difficult measurements such as measuring weak, scattering and/or diffuse sources commonly occurring in life science applications as well as field or portable use. Diffuse and scattering samples are particularly challenging for conventional sensors to measure because light collection is extremely low and thus, spectral features of interest are flattened or are not detected at all. MMS systems inherently alleviate this problem. Furthermore, MMS technology can be used for UV-Visible, NIR, Fluorescence and Raman spectroscopy. In this whitepaper, we will provide an overview of MMS and compare its performance to slit/fiber based spectrometers.

Theory of Operation

The layout of a typical MMS spectrometer is shown in Figure 2. This particular design uses a dispersive grating geometry with a coded aperture in place of a traditional slit/fiber. Light enters the system through the coded aperture and is collimated onto the grating by a collimating lens. The grating spectrally disperses the light which is then mapped to a 2-D detector array such as a CCD. The dispersive element could be a transmissive volume phase hologram or a reflective holographic grating depending on the spectral range and other system design parameters. It is important to note that the MMS technology platform can be implemented using a wide variety of optical designs and be applied to any spectral range.

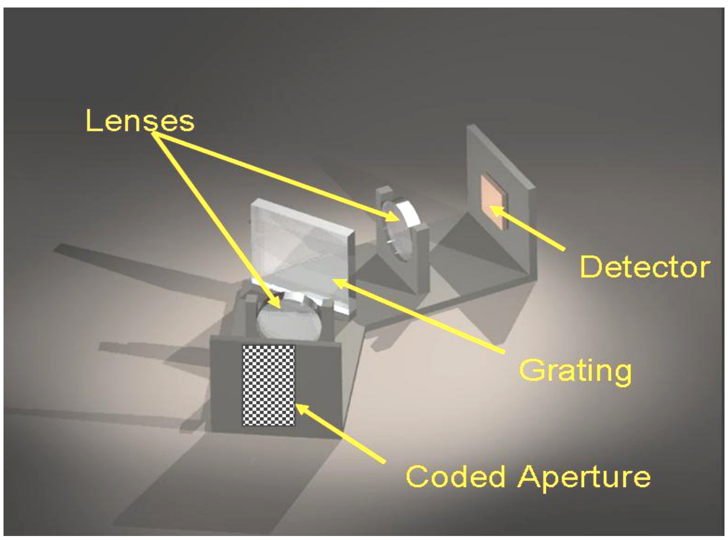


Figure 2: Schematic of a MMS spectrometer

Coded Aperture

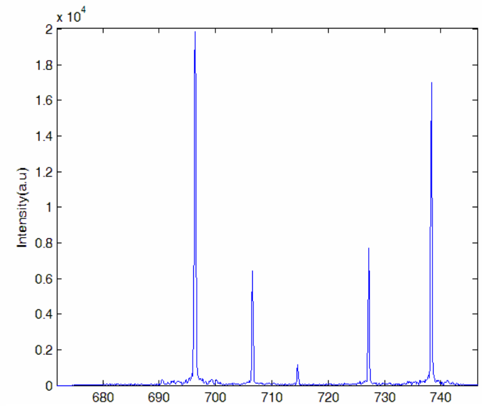


Figure 3: Spectrum of Argon lamp obtained with an MMS spectrometer

The coded aperture is fabricated in such a manner that it has transmissive and blocking apertures. MMS allows for the flexible use of these aperture codes and custom codes can be implemented to optimize the performance for any specific application. To estimate a spectrum, place the source at the input to illuminate the whole aperture. For ease and convenience, a fiber bundle can also be attached to the aperture if the sample is physically remote from the spectrometer. By the use of collimating and focusing lenses, the input aperture is spectrally imaged onto the CCD. The CCD measures multiplexed patterns of the aperture depending on the spectral content of the source. The CCD measurements are then inverted by the use of appropriate algorithms and the source spectrum is reconstructed. It is important to know the particular aperture code that is implemented in the system for the inversion algorithms. Figure 3 illustrates the spectrum from an Argon lamp obtained with a MMS spectrometer. Some key differentiators for this technique include the following:

Multiplex (SNR) Advantage

A slit/fiber spectrometer measures each spectral channel separately onto a pixel in the detector. However in MMS, each pixel in the detector measures several spectral channels of the source in tandem. This is the multiplex advantage of MMS; resulting in a substantial improvement in signal-to-noise ratio (SNR) (see *Signal to Noise Ratio*).

Multimodal (Etendue) Advantage

MMS spectrometers offer an etendue advantage (see *Etendue*). Every spectral source radiates into numerous spatial modes. For fiber or slit based systems, only a few modes can be coupled into the system. Since the aperture area of the MMS input is comparatively large, many modes of the source can be simultaneously coupled into the optical system.

Imaging Aspect of MMS

Inherently, MMS is an imaging spectrometer design. So this technique can be easily adapted to simultaneously measuring many spectral inputs using a single detector array.

MMS and Conventional Multiplex Spectroscopy

Multiplex design has been applied to spectroscopy for over 50 years, including both Fourier and Hadamard transform designs. In general, these designs have been applied to infrared spectroscopy and have emphasized minimizing the number of electronic detectors used. For example, dynamic mask Hadamard transform spectrometers employ spatial light modulators (SLM) such as MEMS based devices or electro-optic elements to temporally multiplex spectral channels. SLM is a device that controls the transmission or reflection of light electronically and is placed between the grating and the detector. The SLM spectrally encodes the dispersed light from the grating and combines them in coded fashion (like a Hadamard transform) onto the detector, one row at a time. Since the coding is done between the grating and the detector, there is no real etendue advantage in such spectrometers. Furthermore, data acquisition is performed serially.

In contrast, MMS is a true 2-dimensional parallel acquisition and processing system that captures both spatial and spectral information simultaneously throughout the entire aperture. This leads to a number of performance advantages (not the least of which is higher etendue and SNR) as well as unique features such as multi-input and hyperspectral imaging. These important differences enable MMS designs to outperform conventional multiplex as well as fiber and slit entrance spectrometer designs. In addition to its performance advantages, MMS can be implemented using commonly available low cost components.

Performance Comparison

In this section, the performance of MMS spectrometer is compared with that of a conventional slit and fiber input spectrometers. System components for each system (f number, grating, lenses, filters, detector etc.) are identical. For these experiments, a Raman spectrometer with an excitation wavelength of 663 nm is used as the test-bed.

This system implements an f/2 optical design and a Kodak CCD detector, cooled to -18oC. The system was set up to accommodate each of three entrance designs: 1) pin hole, 2) vertically binned slit, and 3) coded aperture. To provide a fair performance comparison of the three sampling methods, the width of the pin hole, slit width and feature size of coded aperture are equivalent. Thus the optical resolution of each configuration is equal. Additionally, the height of the slit and aperture are equal.

Etendue

Etendue is a well accepted measure for optical throughput as it specifies the geometric capability of an optical system to transmit radiation. The numeric value of the etendue is a constant of the system and is calculated as the product of the entrance aperture (or slit area) and the solid angle through which light is accepted.

Assume that the input aperture implements an order N matrix. Such an aperture typically has 2N x N aperture elements, with each element proportional to the pixel size. The etendue of such a spectrometer is given by:

$$\text{Etendue (MMS)} = 0.5 \times 2N \times N \times \Omega$$

where Ω is the input solid angle and the factor of 0.5 takes into account the fact that only 50% of the aperture elements are transparent.

The etendue for a slit based spectrometer achieving the same resolution is:

$$\text{Etendue (Slit)} = 2N \times 1 \times \Omega$$

and for a fiber input-based spectrometer, the etendue is:

$$\text{Etendue (Fiber)} = 1 \times 1 \times \Omega$$

Therefore,

$$\frac{E_{MMS}}{E_{Slit}} = N/2 \quad \text{and}$$

$$\frac{E_{MMS}}{E_{Fiber}} = N^2$$

Typical MMS implementations use proprietary coding schemes that range in order from N=16-48. That translates to an etendue advantage of 8-24X compared to slit based spectrometers or 256-2304X compared to fiber based spectrometers. This is illustrated in Figures 4 and 5.

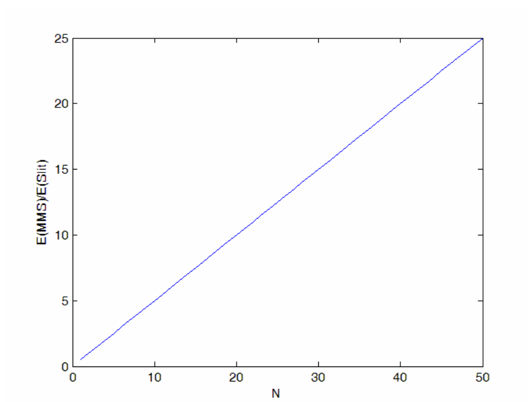


Figure 4: Etendue advantage of MMS compared to a binned slit.

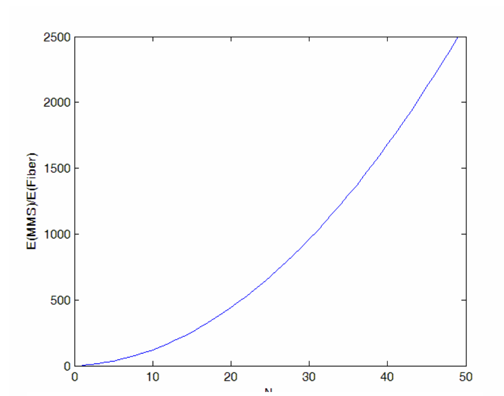


Figure 5: Etendue advantage of MMS compared to a pin hole.

Signal to Noise Ratio

A better understanding of the performance advantage of MMS spectroscopy can be obtained by comparing spectra from real samples. Raman spectra of Toluene are measured with three different configurations and an integration time of 2 seconds: fiber-input (Figure 6), vertically binned slit (Figure 7), and MMS (Figure 8), where all other system parameters are equivalent. These data show a noticeable signal to noise ratio advantage of MMS. The specific advantage depends on the source noise characteristics, detector noise characteristics and the spectral content of the source, and therefore cannot be generalized for all cases. However, MMS spectrometers always offer superior signal to noise performance versus these conventional designs.

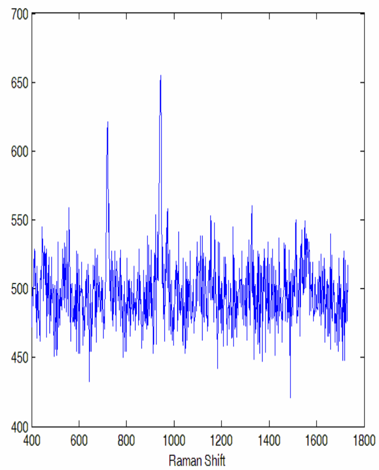


Figure 6: Raman spectrum of toluene with a pinhole aperture.

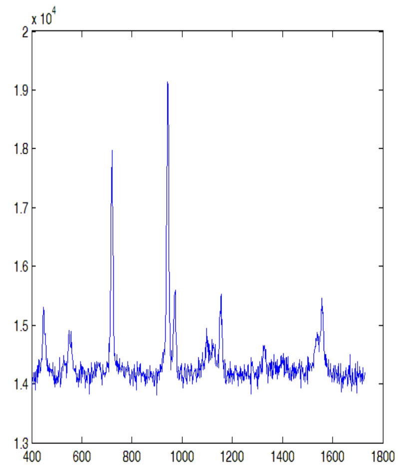


Figure 7: Raman spectrum of toluene measured with a slit.

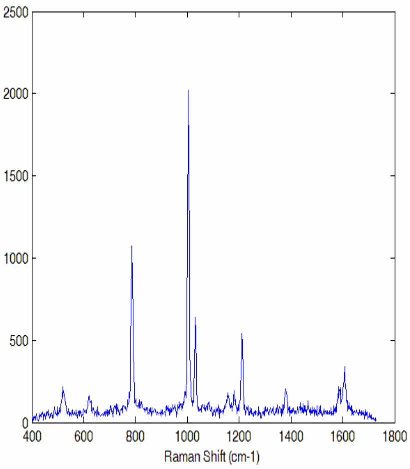


Figure 8: Raman spectra of toluene measured with MMS.

Additional Raman spectra obtained with the MMS spectrometer are shown in Figures 9 and 10.

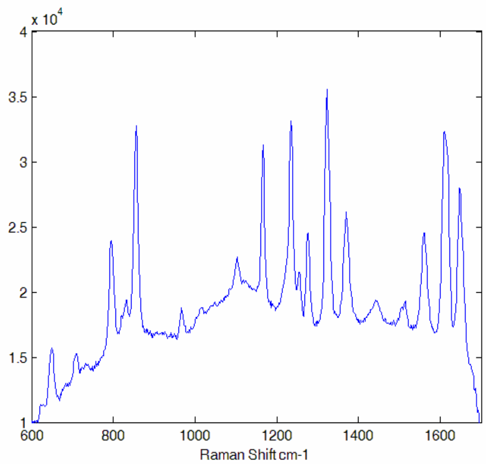


Figure 9: Raman spectrum of Tylenol with MMS spectrometer (20s integration)

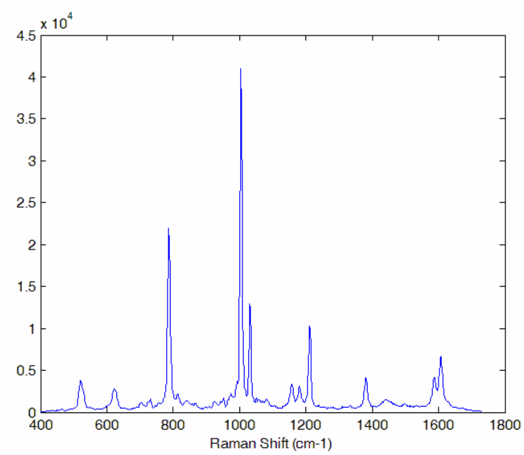


Figure 10: Raman spectrum of toluene with MMS spectrometer (20s integration)

Measuring in Scattering Media

High etendue MMS systems perform extremely well when measuring scattering samples such as blood or tissue. For comparative purposes, we measure the Raman spectrum of ethanol in lipid. Lipid is a blood emulating medium which offers scattering properties similar to that of blood. The Raman spectra are shown in Figures 11, 12 and 13. A higher percentage of Raman scattered photons – the signal of interest – is entering the wide area aperture of the MMS system as evidenced by the stronger primary ethanol peak in these figures. The spectra have been zoomed in to 800-1100 cm-1 range. Note that this is a 663 nm excitation system, so some of the Raman ethanol peaks are lost in the background fluorescence.

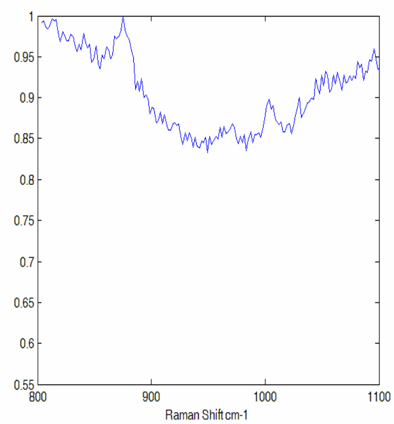


Figure 11: Raman spectrum of ethanol in lipid with pinhole

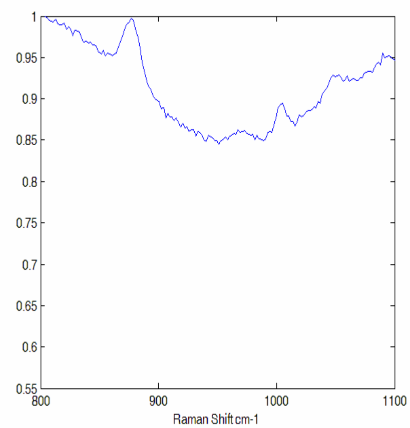


Figure 12: Raman spectrum of ethanol in lipid with a binned slit.

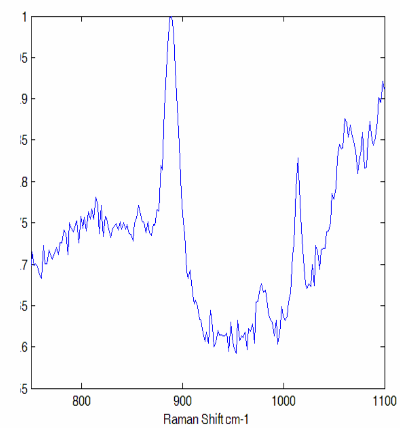


Figure 13: Raman spectrum of ethanol in lipid with MMS

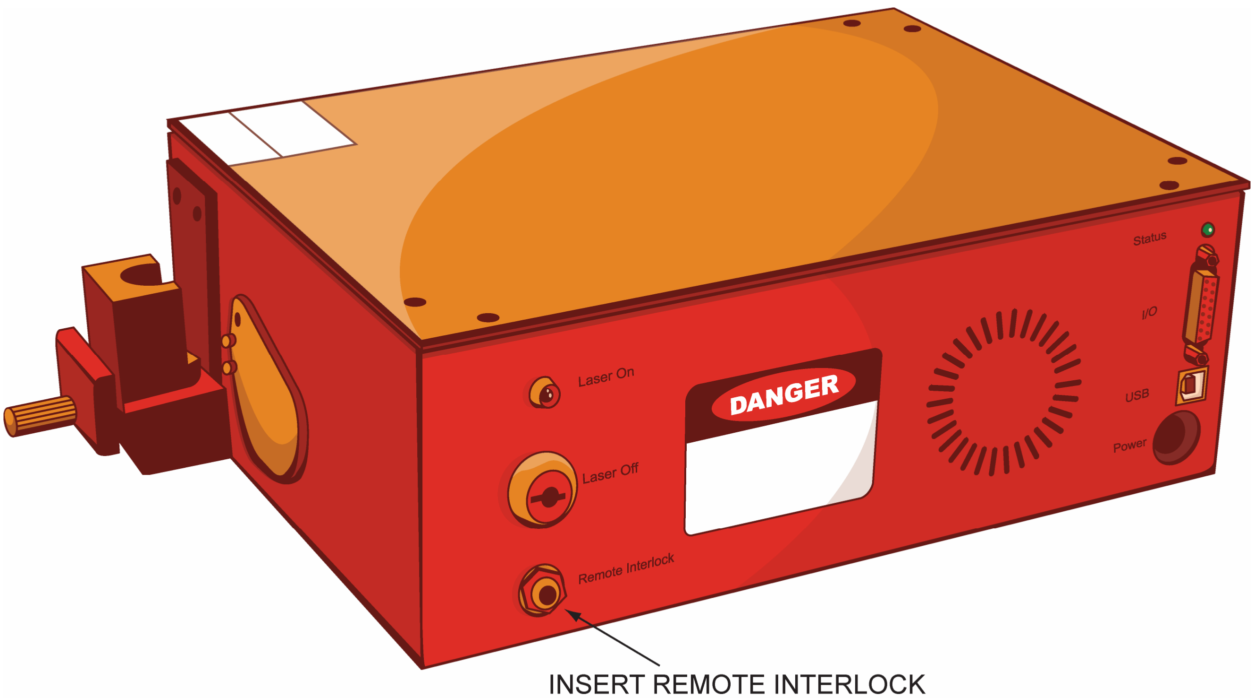
Conclusion

Multimodal multiplex spectroscopy is an example of how digital instruments can be adapted to specific measurement tasks, in this case efficient signal collection from wide area sources. Of course, sensors are evaluated in practice by how well they perform specific tasks. For MMS systems, attractive applications focus on molecular recognition and imaging for life and chemical science applications. While we have shown in this white paper that MMS systems offer performance advantages over conventional systems, the use of MMS systems as embedded biological and chemical sensors will perhaps be more significant than their application as general purpose bench top spectrometers.

Appendix C

Remote Interlock

The laser activation request signal passes through the Remote Interlock, a 0.25" phone jack on the panel of the spectrometer. The Remote Interlock feature has been designed to pass this signal with no plug inserted into the jack. An unwired plug (0.25" phone plug, 3 conductor type: Tip, Ring, and Shield, provided) inserted into the jack opens this signal path. The spectrometer processor will no longer receive the activation request and will stop sending the activation signal to the laser controller, shutting off the laser. This will also cause the Laser On LED to turn off.



Connecting the Tip and Ring conductors of the plug to the normally closed (NC) contacts of an external user-specified switch maintains the laser activation request signal path when the plug is inserted into the Remote Interlock jack. Opening the external switch contacts disables the laser.

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