Upgrade of diffraction grating spectrometers for multiple purposes

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Abstract

The overall quality of spectroscopic instruments based on diffraction grating monochromators is limited by stray radiation and higher order effects of the employed gratings. Novel variable long- and short-wave pass interference filters have been developed within the framework of the Eurostars Optitune programme between Edinburgh Instruments and Delta of Denmark. These filters, which can be combined to form band-pass filters with a finely tunable center wavelength and bandwidth, are capable of severely reducing the limiting factors of grating spectrometers. Thus, a smaller alternative to double-monochromator systems is provided. In some cases, the use of filters gives advantages in signal to noise ratio due to the avoidance of substantial light losses at multiple grating surfaces. © Edinburgh Instruments Ltd. 2012.

I   Introduction

Spectrometers have proved to be a fundamentally important scientific tool since the time of Hooke and Newton and the first use of prisms. Spectroscopic instruments equipped with replica diffraction gratings are the standard of today with applications ranging from fundamental physics and astronomy to routine testing in chemistry and the life sciences. In principal, the quality of spectral photometry is affected by two factors: Firstly, the occurrence of second and higher order reflections from the grating and, secondly, scattered light reaching the detector. Inaccuracies in a variety of measurements of between 1% and 10% are typical without proper calibration and suppression of stray radiation [1]. This scattered light can arise from any optical surface, from light leaks and insufficient baffles but the dominant source of scattered light is the diffraction grating itself.

Detailed experiments [1] have shown that scattered light reaching the detector from the grating consists of two main components, a Lorentzian type component centered around the primary wavelength and a continuous background. The former can be predicted from diffraction theory of a grating while the continuous background is consistent with Rayleigh scattering from microscopic surface imperfections of the grating itself. Original rulings are subject to error, *e.g.* from the use of a diamond tool on metal. Multiple replicas, as they are typically found in commercial devices, exhibit significantly more scattered light than each preceding replica by factors of up to 2 [1].

Fluorescence and Raman spectroscopy are two of the most demanding applications of grating spectrometers. In particular fluorescence spectroscopy has manifold applications in chemistry and bioscience where the measured signals are frequently orders of magnitude weaker than the excitation intensity. When combined with the need to measure samples with single molecule sensitivity, the necessity for high light grasp and low background sets a challenge to the performance of such instruments.

Edinburgh Instruments (EI) has developed a novel variable-wavelength filter stage as an upgrade to its range of fluorescence spectrometers. By scanning a linear wedge

interference filter synchronously with the diffraction grating, a reduction of background intensity by up to two orders of magnitude is achieved. As a consequence, full advantage of the single photon counting capability of the instruments can be taken. A similar reduction in background intensity can be achieved by the double monochromator solution. However, this is achieved only at the price of doubling the size of typical instruments and increased cost. Furthermore, the more complicated optical path in double-pass instruments increases light losses and reduces their signal level due to the cumulative effect of imperfect reflection of blazed gratings. Maximum efficiency is ~70% at blaze angle and falling rapidly to around 10-20% towards the end of the grating range. The use of single-pass instruments with the latest variable filters yields a reduction in background level comparable to double-pass instruments without the cost of signal loss. This leads to a significant increase in signal to noise ratio (SNR). For example, the standard industrial water Raman test (see below) showed an improvement in SNR by factors between 2 and 5 over systems without filters.
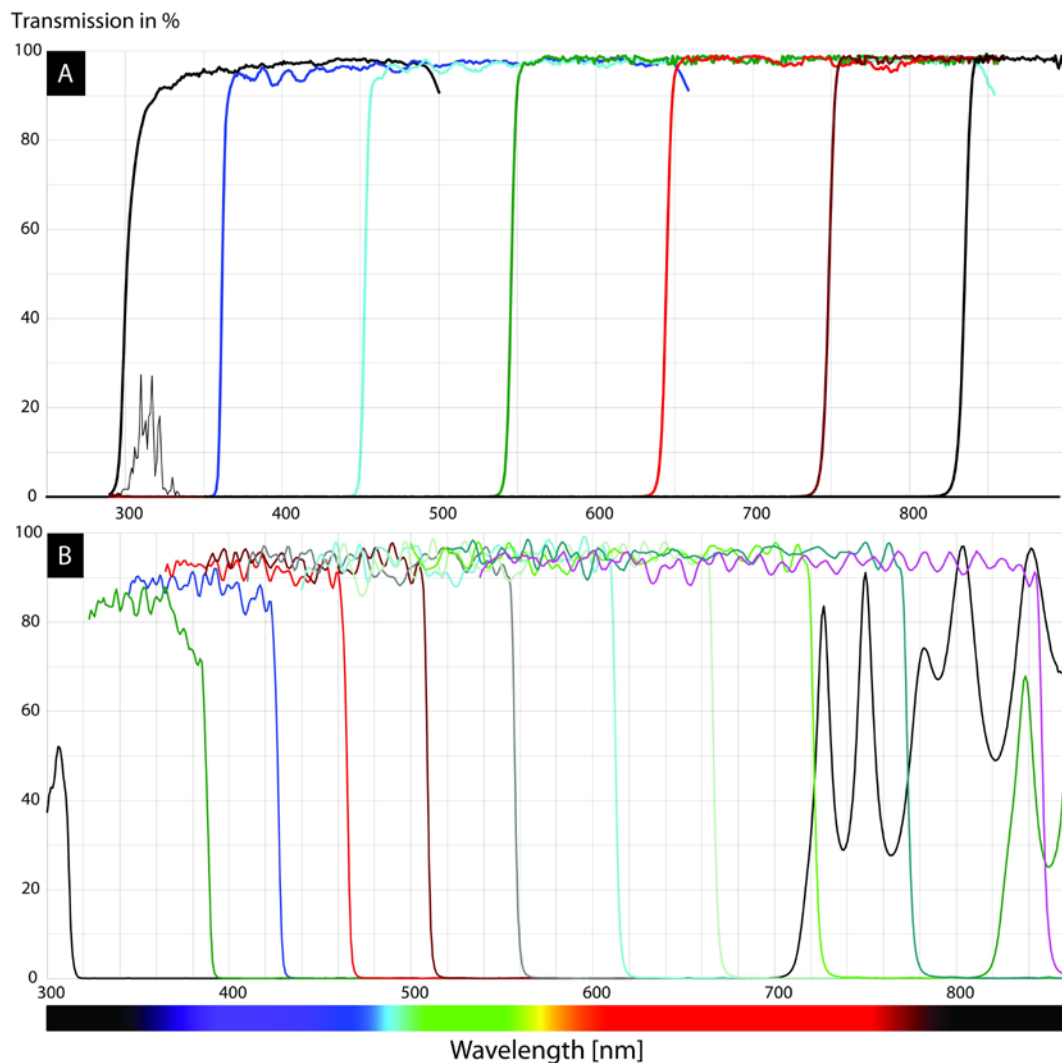

Figure 1: Transmission curves of linear filters at various positions along the filter. A) Long-wave pass filter. B) Short-wave pass filter. *Source: www.delta.dk*

II   Principles of Variable Filters

The variable filter stage comprises a combination of long-wave pass [2] and short-wave pass interference filters, in this case operating in the spectral range from 300 to 850nm. In general, interference filters have a number of advantages in selecting passbands (in principle with greater light grasp [3]) or rejection of various wavelengths. The two most prominent advantages being that the spectral shape and the grade of rejection are designable. They can consist of up to 150 stacked layers of thin films of varying optical thickness nd (where n is the refractive index and d is the thickness of the film). The simplest example is the quarter wave stack in which nd is alternately of high and low index. Such a highly reflecting stack can be designed with 70 or more layers to reduce transmission to ~10^{-4} or 10^{-5}. By variation of layer thickness this can be made to extend over a large wavelength range often supported by a second stack centered at a different wavelength. At the long-wave edge of such a stack the transmission rises very steeply (see Figure 1A). Since the optical thicknesses are always less than a quarter of a wavelength for longer wavelength of incident light the transmission never returns to a low value and indeed can be designed to reach and remain at values as high as 95%.

It is thus possible to create a variable long-wave pass filter by varying the layer thickness along the filter by a linear wedge. Likewise a short-wave pass filter can be constructed by using the short wave cut-off of the quarter wave stack and again modifying thicknesses to give a uniform transmission over a wavelength range limited in this case by the arrival of second order interference effects (see figure 1B). These two outstanding examples of interference filter design and fabrication have been achieved as a result of the Eurostars Optitune programme between EI (leader) and Delta of Denmark.

For the variable-wavelength filter stage described here we combine these linear filters with a motorized translation stage which is controlled by software to be driven synchronously with the diffraction grating of the monochromator. Thus, when properly calibrated, the filters are always positioned in the beam path in such a way that the wavelength selected by the grating lies near the filter's cut-off wavelength, while still in the region of maximum transmission. In the case of a long-wave pass filter, the very sharp edge and strong reflection then eliminates any stray light at wavelengths shorter than the cut-off. Depending upon the nature of the measurements and the sensitivity to scattered light, we also combine the long-wave with a short-wave pass filter to create a band-pass filter with finely tunable bandwidths as small as ~25 nm without loss in maximum transmission.

Diffraction monochromators inherently select not only one wavelength but also reflect light at higher-harmonics, *i.e.* integer fractions of the selected wavelength. Thus, a diffraction grating selecting light at 600 nm will always also reflect light at 300 nm in the same direction. Usually this component is rejected by inserting a fixed filter with the major disadvantage of being unable to scan a larger range. With the synchronously scanning filters, however, all higher order effects are automatically rejected throughout the whole scanning range.

Figure 2 illustrates the performance of the filters specified and initiated by Edinburgh Instruments and produced in very high quality by Delta of Denmark. The filters show a remarkable performance, as it has to be kept in mind that they consist of up to 150 stacked layers while still maintaining a transmission of >90% across

the whole spectral range required for typical applications. This is to be compared with the rapidly changing efficiency of blazed gratings which at best has 70-80% efficiency at the chosen blaze wavelength (see figure 2). For this reason a single monochromator equipped with a synchronously scanning variable filter shows a significantly improved signal throughput compared with a double monochromator.
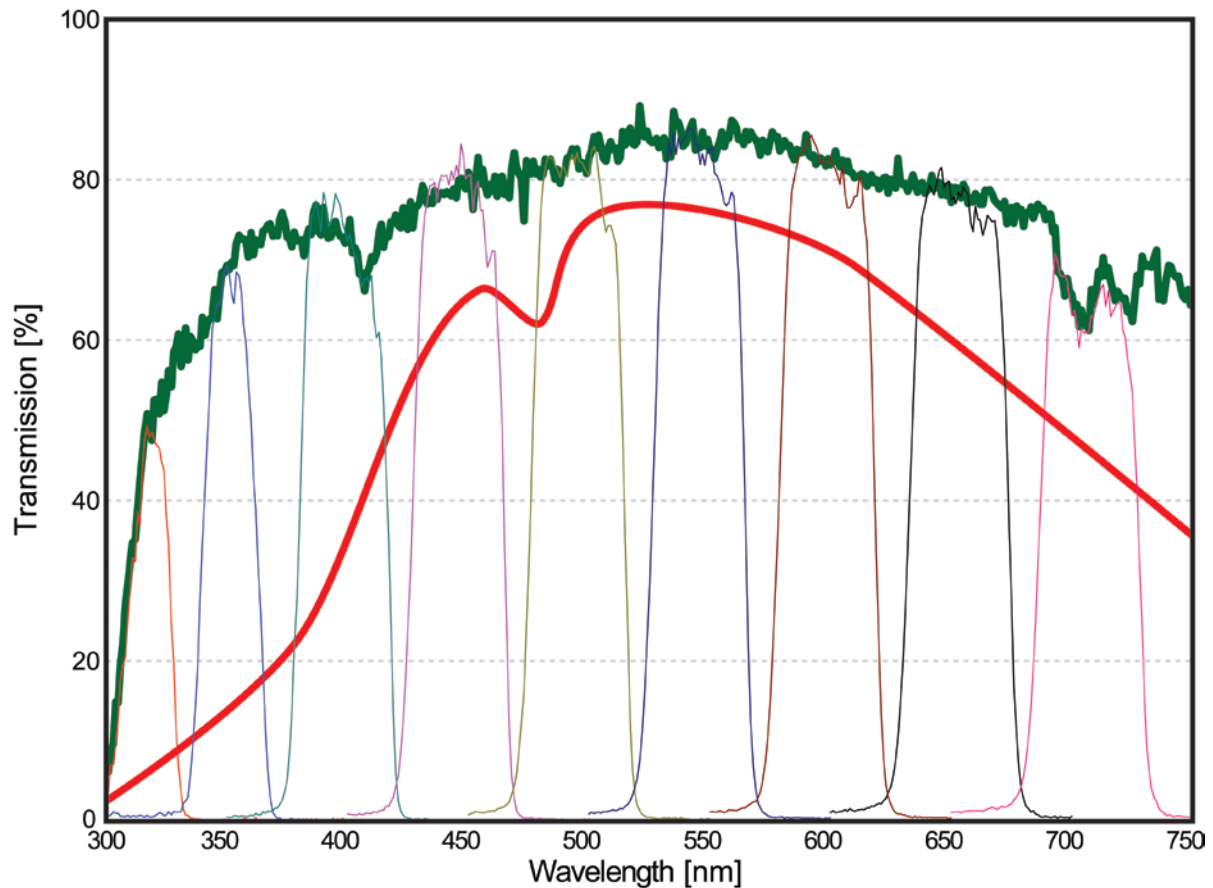

Figure 2: Band-pass profiles of a combination of long- and short-wave pass linear filters at various wavelengths selected by the diffraction grating. The enveloping green curve illustrates the filter transmission along the whole spectrum for calibrated filters. The red curve shows the reflection efficiency of a typical blazed grating optimized for the same spectral range.

III   Experimental Proof

The measurement of stray light is a somewhat complex procedure and is highly sample dependent. Here, we present several tests to demonstrate the advantages of the synchronously scanning filters. Figure 3B shows a schematic overview of the typical single monochromator setup. The filters are located typically in front of the exit slit of both monochromators in such a way that no stray light can reach the detector. The filters can also be moved out of the beam allowing for easy comparison of spectra with and without the filters.
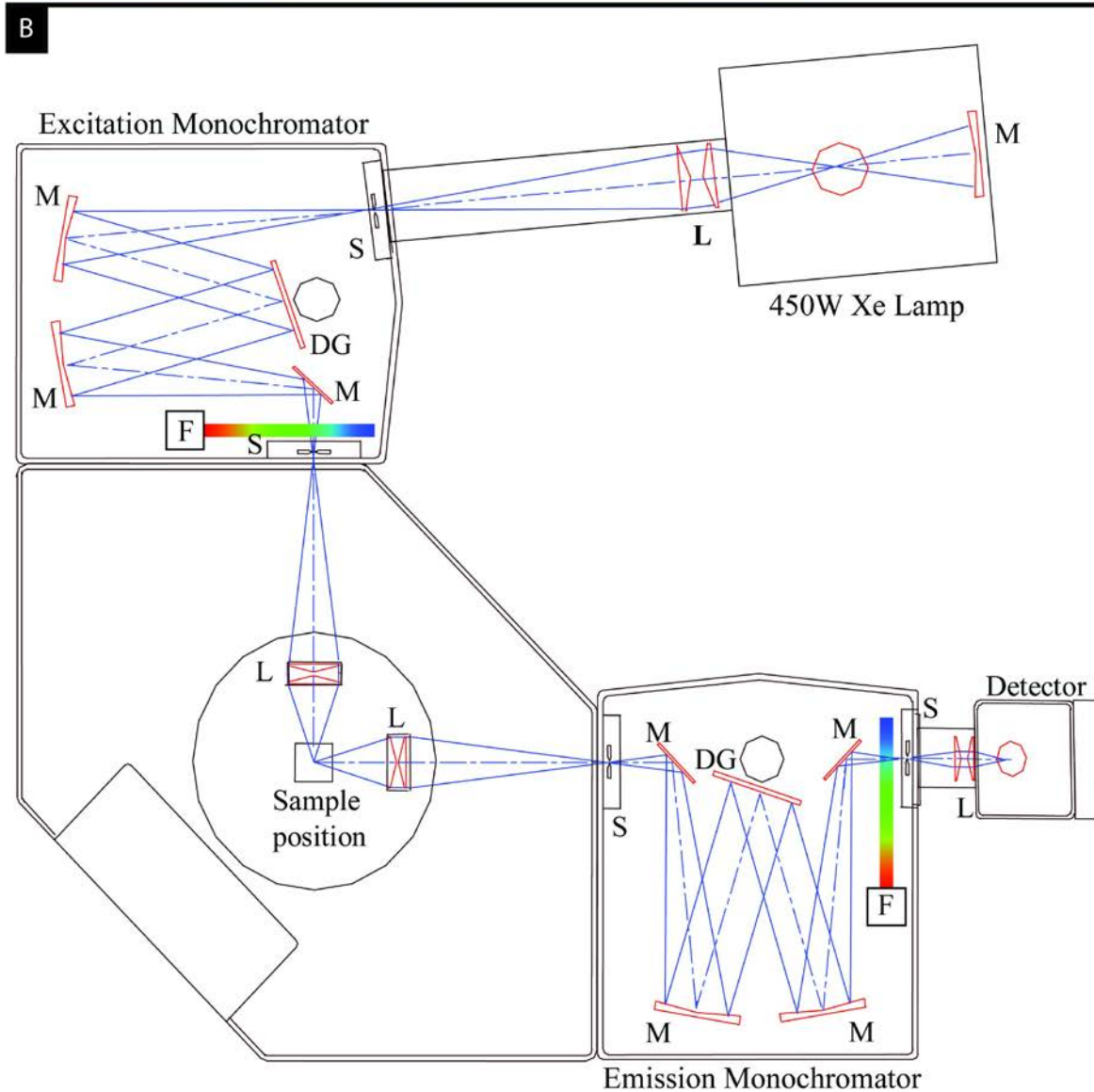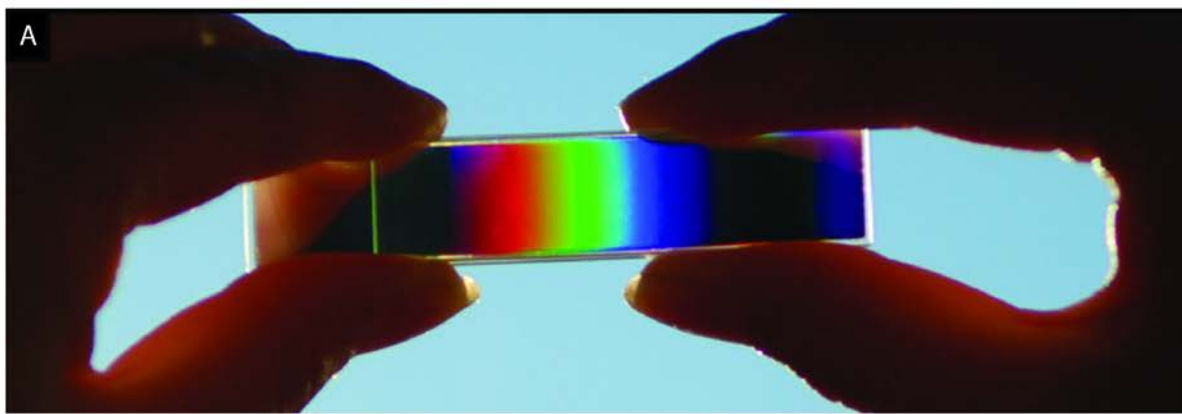
Figure 3: A) Photograph of a band-pass filter realized as a combination of a long- and a short-wave pass filter. *Photo Source: www.delta.dk* B) Typical setup of a single-monochromator spectrometer. M: Mirror, L: Lens, S: Slit, DG: Diffraction Grating, F: New variable filter stage.

III-i) Water Raman Test

The water Raman test yields a figure of merit for an instrument and has become and industry-wide standard. At EI, single monochromator spectrometers are manufactured to achieve a signal to noise ratio of 6000:1 or better. Here, this test is conducted under identical conditions, once employing the new variable filter stage and once in the standard configuration without filters (see figure 4). The result of background reduction is an increase in signal to noise ratio by a factor of 2 or greater, depending on the sample (see table 1).

Sample	Without Filter		With Filter		Improvement ratio	
	SNR	Background	SNR	Background	SNR	Background
S1	4980:1	35770	20629:1	1250	4.14	28.6
S2	15224:1	2989	29904:1	499	1.96	6.0

Table 1: Results of two standard water Raman tests on different samples. S1 is aged water with a scattering component. The effect of this additional component is removed by the filters. S2 is a highly purified sample of water without additional scattering.
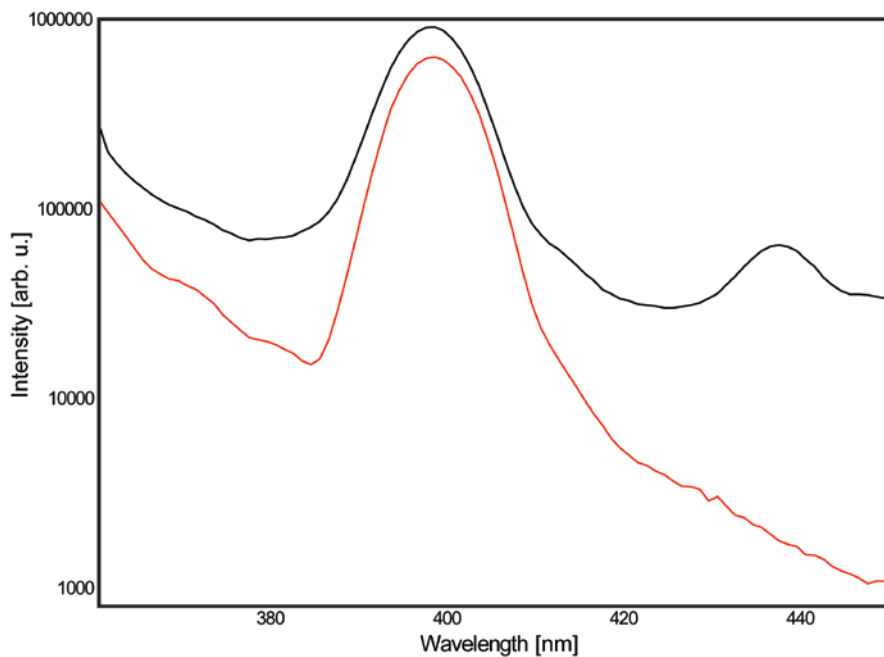

Figure 4: The standard water Raman test conducted with (upper) and without (lower) linear filters.

III-ii) Background reduction

In this context it is also important to address the pure noise/background reduction capabilities of the filters without any signal present. Polytetrafluoroethylene (PTFE) only exhibits a very weak fluorescent background while scattering light evenly across the whole visible spectrum including near UV and IR radiation. Thus, under ideal conditions, no light should reach the detector when the diffraction grating of the emission monochromator is tuned away from the excitation wavelength. However, stray light from the grating surface and other imperfections result in a considerable background level. Figure 5 shows the effect of the filters on background levels when a PTFE block is illuminated by 350 nm radiation.
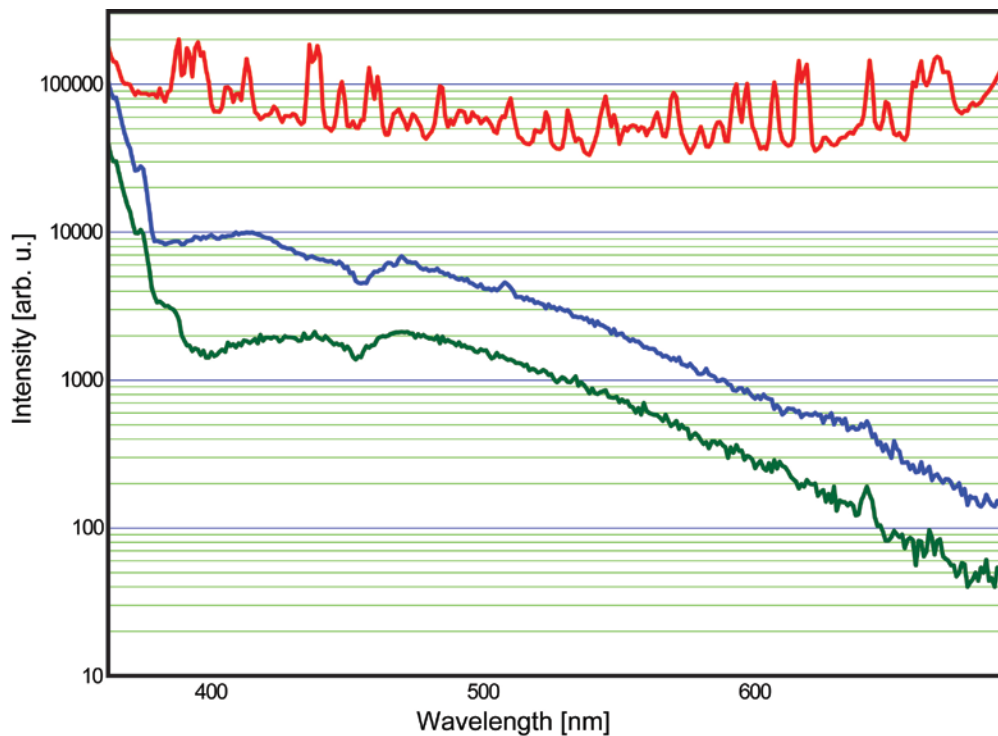

Figure 5: Detected light of 350 nm wavelength Rayleigh scattered from a PTFE block at the sample position. Red (upper) curve denotes a spectrum without any filters present. Note the constantly high background level and spurious peaks. Blue (middle) and green (lower) curves are spectra taken with the filter on the emission side and filters on both emission and excitation side present, respectively. Employing both filters, any effects of stray radiation are eliminated and a reduction in background level by 2 orders of magnitude is readily achieved.

III-iii) Raman Spectrum of Cyclohexane

A typical experiment shall be illustrated at the example of the cyclohexane (C_6H_{12}) Raman spectrum measured with the *EI FLS920 single monochromator fluorescence spectrometer*. The measurement of high-resolution Raman scattering requires very high sensitivity and a clean background level as the probability for a Raman scattering event is only in the order of 10^{-6}. Cyclohexane (C6H12) exhibits several Raman active modes at shifts between 300 and 3000 cm^{-1} (see table 2).

Raman shift [cm^{-1}]	Wavelength [nm]	Intensity
384.1	509.8	Weak
426.4	510.9	Weak
801.3	520.8	Medium
1028.3	527.1	Medium
1157.6	530.7	Weak
1266.4	533.8	Medium
1444.4	538.9	Medium
2664.4	576.8	Weak
2852.9	583.2	Strong
2923.8	585.6	Strong
2938.3	586.1	Strong

Table 2: Raman modes of cyclohexane, their respective wavelength when excited at 500 nm and observed intensity.

A significant level of general background is readily observable in the spectrum measured without filters (figure 6, red/upper curve) and photonic noise renders the weak peaks almost unobservable. The introduction of the synchronously tuned variable filter shows a significant reduction of the background (figure 6, green/middle curve) by one order of magnitude without reducing the signal strength. The resulting reduction in photonic noise renders the weak peaks observable (see e.g. the weak peak at 2664.4cm^{-1}/576.8 nm). The signal to noise ratio improves by a factor of 3.4 for the strongest peak. Obviously, even better ratios are achieved for the weaker peaks. For comparison reasons the same experiment was repeated on a double-monochromator system (figure 6, blue/lower curve). The use of two additional diffraction gratings in the beam path severely reduces the signal strength which – despite the reduction in background levels – renders the weaker peaks unobservable.
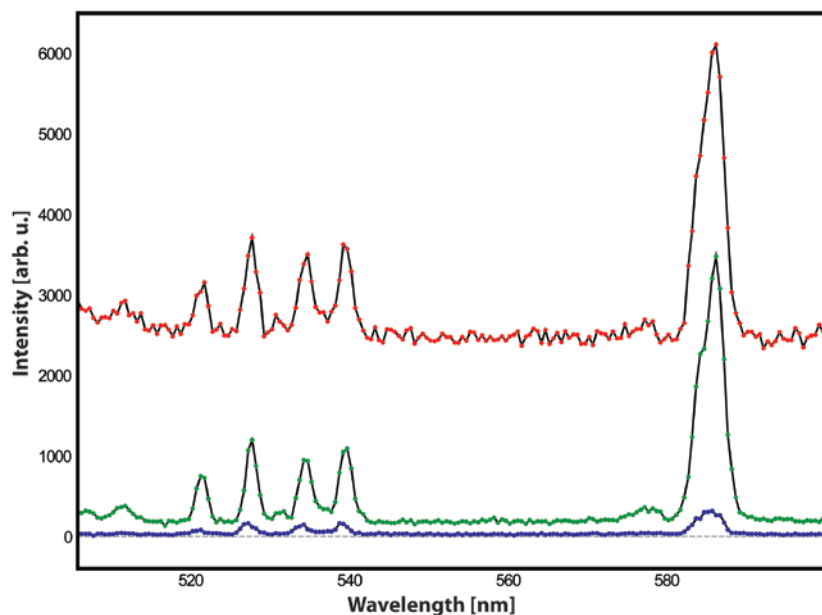

Figure 6: Raman spectrum of cyclohexane measured at an excitation wavelength of 500 nm. The red curve (upper) denotes a spectrum taken at 1 nm spectral resolution without the use of variable filters. The green spectrum (middle) is taken with the variable filters in place. For comparison, the same measurement was repeated on a double-monochromator spectrometer (blue – lower). The signal is severely reduced.

III-iv) The Diamond Raman Signal

Single crystal diamond exhibits a Raman active mode at a shift of $1333cm^{-1}$, corresponding to the sp^3 vibrational mode of the carbon atoms in the crystal lattice. Raman-spectroscopy is often employed in quality control in synthetic diamond production and requires very sensitive instruments. When excited by a 500nm light source, the Raman mode emerges at 535.7nm. However, the unique properties of diamond as a highly refractive material in the visible range dictate that the Raman mode is only conveniently observable under direct reflection geometry. This in turn leads to primary radiation being reflected directly into the analysis path and onto the emission monochromator. Stray light and imperfect reflections from the grating thus become a dominant constituent of the light reaching the detector, rendering the weak Raman peak impossible to observe without using variable filters. Figure 7 shows a comparison of two spectra taken with and without the filter. Note the very high background level and spurious peaks arising from grating imperfections and surface contamination.
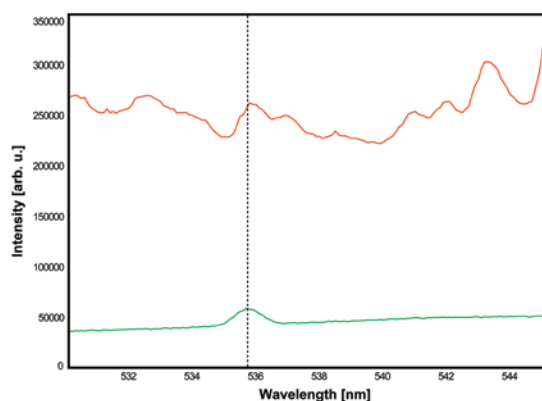

Figure 7: The sp^3 Raman peak of diamond. The red curve shows the measured spectrum without filters, green with filters. The spectra were taken under identical conditions with a spectral resolution of 0.5 nm. The increasing background level of the lower curve is in fact fluorescence from the diamond.

III-v) Fluorescence from Zinc Oxide

Zinc Oxide (ZnO) exhibits a strong fluorescence peak at 383nm and a continuous luminescent background at higher wavelengths. ZnO powder furthermore shows strong scattering of primary radiation which would lead to a high background level, similar to what is observed in diamond and scattering from PTFE (see above). Figure 8 shows a measurement of the fluorescence peak again once with and once without variable filters. In this example, light at 320nm excites the fluorescence but scattered light causes a significant background level below 383nm (red line). When using the filters, the average noise level dropped in average by one order of magnitude, increasing the signal to noise ratio by a factor of 2.5
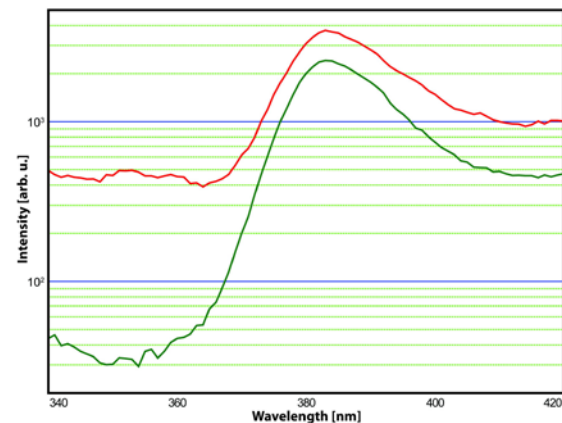

Figure 8: Fluorescence spectrum of ZnO powder. The red (upper) spectrum was taken without filters, the green (lower) with synchronous filters in place. Note the significant drop in background intensity almost to the electronic noise limit of the detector.

IV Conclusion

- We have shown that a combination of linear short- and long-wave pass interference filters can be used to realize a variable band-pass filter. This filter can be scanned synchronously with the wavelength selected by the diffraction grating in a monochromator to severely reduce the influence of higher order effects and stray light. Thus the performance of the spectrometer is greatly improved.

- We have demonstrated the capability to reduce background levels by 2 orders of magnitude and increase the signal to noise ratio by up to a factor of 5 in various situations and at least a factor of 2 in the standard water Raman test.

- A monochromator equipped with synchronous filters thus can achieve a background reduction comparable with a double monochromator system (which gives higher spectral resolution) without the cost of increased size and signal loss at multiple gratings.

References:
[1]   T. N. Woods *et al.*, Appl. Optics **33**, 4273 (1994)
[2]   J. S. Seeley, S. D. Smith, Appl. Optics **5**, 81-85, (1966)
[3]   H. A. MacLeod, *Thin-Film Optical Filters, 4th edition*, Taylor & Francis (2010)