

FLUORESCENCE SPECTROSCOPY OF MINERALS: 1—USING A SPECTROMETER

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ABSTRACT

Light interacts strongly with matter with the result that we see a world rich in color. In the case of minerals and gemstones, the color is both beautiful and informative. Shining (invisible) ultraviolet light on minerals can produce a spectacular palette of colors. But what does this tell us and how can we investigate it beyond the stage of being filled with a sense of delight and wonder? The science of spectroscopy allows us to travel deep into the structure of rocks. Here is the first part of an article that explains how to do it. In the second part, we hope to be able to survey in more depth the causes and mechanisms of mineral-light interactions with a greater range of examples of fluorescence spectroscopy.

1. INTRODUCTION

The matter that we see, feel and smell—and indeed are made of—can trace its origins back to the first few minutes of the Big Bang some 13.8 billion years ago. However, as the primordial fireball expanded and cooled, there was only time to form the nuclei of hydrogen, helium and a trace of lithium before these initial products were *frozen* in and there remained insufficient energy (the temperature and density were too low) for further nuclear reactions. The remaining elements that fill the Periodic Table had to be constructed through nuclear reactions that took place slowly and gently in the cores of stars, more rapidly during their violent deaths in supernovae and, in a few cases, in the space between the stars as a result of high energy cosmic rays colliding with atoms in interstellar gas and dust. This process has been going on throughout the Universe for almost its entire history and a fraction of the resulting products have ended up in planets orbiting stars, some of these like our Sun. The most massive elements—the crust on the Periodic Table—have extremely short lifetimes and, although they may have appeared fleetingly in dying stars, today we have to make them to order in particle accelerators. The somewhat hackneyed, but nonetheless true, conclusion is that *we are stardust*.

So, how do we know so much of this remarkable story?

The dominant technique that has enabled us to understand the origin of the chemical elements, the structure of atoms and molecules and a great deal more besides, is spectroscopy.

In the broadest sense, this can be described as the measurement of the color of light where *color* means the distribution of energy with wavelength of electromagnetic radiation and the word *light* is used as a proxy for the entire electromagnetic spectrum, from gamma-rays through to the long wavelength radio waves used to communicate with nuclear submarines. This proxy is useful for us not only because it is a short and familiar word but also because the visible spectrum is generally the place to look when we study the fluorescence of minerals and gemstones.

Spectroscopy is so important for a fundamental reason that lies at the heart of the physics of matter and energy. The relationship between photons (quanta of light) and matter (atoms and their constituents) is an intimate one. Photons are the carriers of the electromagnetic force that helps hold atoms together and directs their structure and chemistry. In the language of physics: *Photons mediate the force of electromagnetism*. The consequence of this is that light and matter interact very strongly with one another and, following such an interaction, the light carries an imprint of what happened. Reading this imprint and understanding what it means is what spectroscopy is all about.

When a sample of a mineral is bathed in light, a rich assembly of physical processes will take place depending on the mineral and the range of colors included in the light impinging upon it. Some of the light will be reflected from the surface. If the mineral is opaque, there may be some interaction with a thin surface layer with the *processed* light emerging from the surface along with the specular reflection. If the sample is transparent or translucent, some of the light will traverse it and emerge carrying the imprint of absorption and scattering processes that have occurred in its interior. If certain colors are present in the light source, usually those of shorter wavelength containing the more energetic photons, there may be evidence of fluorescence where light of one color is absorbed by components of the mineral and re-emitted with another color, usually, but not exclusively, with a longer (redder, lower energy) wavelength.

The phenomenon of fluorescence was studied intensively in the mid-nineteenth century, notably by the Irish physicist Sir George Stokes (President of the Royal Society from

1885–1890). In a wonderfully descriptive (100 page!) paper published by the Royal Society in 1852 (Stokes, G. G. 1852. *On the Change of Refrangibility of Light*, Phil. Trans. R. Soc. Lond. 142, 463–562), Stokes explored the behavior of many different materials—including fluorite—and his work led him, in a following shorter paper, to coin the word *fluorescence* for the phenomenon he was seeing. These papers are freely available from the Royal Society website and are a joy to read. His work was carried out half a century before a revolution in atomic physics gave birth to the *quantum mechanics* that was necessary for fluorescence to be properly understood. It is fascinating to read how close Stokes was able to come to this understanding so long before the theoretical infrastructure was in place.

Stokes made his phenomenological observations and his measurements using his eyes and so, by definition, he was restricted to the *visible* spectrum which is at wavelengths of approximately 400–700nm (a nanometer, *nm*, is a convenient unit for visible spectroscopy and there are a thousand million of them in a meter: 550nm is a good, bright green to most people). While the visible spectrum is particularly useful for our field of interest—electrons in atoms march obediently to the orders given to them by ultraviolet and visible photons—other wavebands certainly have their uses. More than that, fluorescence is not excited only by light. Minerals can be blasted by other sorts of energy and so be made to glow. Beams of electrons are frequently used to encourage atoms to emit light in a technique called *cathodoluminescence*, familiar from the old TV tube. Mechanical and chemical energy can also be used for certain purposes.

However, returning to the electromagnetic spectrum and starting at the high energy end, X-rays can burrow deep into the electron cloud around an atom and reach the ones that longer wavelengths cannot, often exciting fluorescence best studied at X-ray or ultraviolet wavelengths. They are also strongly influenced by the regular arrays of atoms packed closely (around a nm or less) together in a crystal where a beam will produce Bragg diffraction patterns that can be read to determine the crystal structure and atomic spacings.

All atoms will absorb ultraviolet light, resulting in the excitation of electrons to higher energy levels or even to their ejection (ionization). The fluorescence observed in minerals illuminated with ultraviolet lamps originates from the atoms readjusting to these excitations/ionizations. These readjustments can happen in many ways and over different periods of time, resulting in the richness, complexity and diagnostic power of fluorescence spectroscopy. At this point, it should be mentioned that the different timescales of this relaxation of the atoms has powerful diagnostic value in its own right. In addition to the spectrum emitted during the steady-state illumination of a mineral, the response following

the removal of the excitation can be used to follow different paths of de-excitation and it has proved very valuable for identifying the fluorescent activator responsible for a given emission. The useful timescales are often short: from nanoseconds to milliseconds, but systems using lasers can *easily* be configured to do this and there is much literature on the subject (Gaft, Reisfeld, & Panczer, 2005, *Modern Luminescence Spectroscopy of Minerals and Materials*, Springer-Verlag, Berlin, Heidelberg). Longer timescale phenomena are usually referred to as *phosphorescence*.

The infrared is the realm of the molecule. These longer wavelength photons do not often carry sufficient energy to excite electrons directly to higher atomic levels. They can and do, however, incite the molecules to vibrate and rotate, rather like loud rock music influencing the inmates of a disco. The so-called *vibrational spectra* of molecules tend to be excited by light from the red end of the visible spectrum to what is called the *mid-infrared* which is up to around 100,000nm (or 100 microns, μm). Rotational states generally have a lower energy still and so transitions fall at longer wavelengths into the *far-infrared* and microwave range. Rotational and vibrational states are seen in combination and result in extremely complex spectra that can contain millions of transitions (e.g., in water).

As a final topic in our limited tour of the range of spectroscopy, we mention the influence of the states of spin of electrons and nuclei on the spectra of atoms and molecules. While a change in spin state (direction) produces a very small change in the overall energy, it has proved to be extremely important in several branches of science by producing fine- and hyper-fine structure in spectra. Perhaps the most widely known example of hyperfine structure is in the hydrogen atom that can exist with the single electron spin either parallel or anti-parallel to the spin of the proton nucleus. The transition between these two quantum states results in the absorption or emission of radiation with a wavelength of 21cm. Such radiation is used by astronomers to map atomic (neutral, i.e, with its electron in place) hydrogen throughout the Universe.

Particularly in mineralogy, where we are usually dealing with crystalline matter, *polarimetry*—the measurement of the state of linear or circular polarization of light—is often combined with spectrometry into what is called *spectro-polarimetry*. This can be a rich and powerful technique for crystallographers to investigate geometrical properties of crystals. Its successful application is, however, a calibration minefield!

As will be clear by now, spectroscopy (spectrography, spectrometry, spectrophotometry, ...) is a vast subject and is employed in many different disciplines meaning that, in

an article appearing in the Journal, we can be forgiven in being somewhat selective in our choices of what to discuss. Today, a range of modes of spectroscopy have become key components in the toolkit of the mineralogist endeavoring to determine the composition and structure of a mineral.

2. SPECTROMETRY

2.1 The Spectrometer

So, what is a spectrometer¹ and how is it used to obtain precise and diagnostically useful information? To describe this, let's start with the requirements. We are sitting at our computer with a wish to make a plot of light intensity against wavelength for some illuminated sample. Provided that we know what units we are using and that our device has been properly calibrated, this plot will form the *grist* for our analysis *mill*.

For the measurement of near-ultraviolet, visible and near-infrared light (say 300–1000nm), a modern digital spectrometer is a most powerful device. This will have an electronic detector, which may be a 2048 x 1 *linear array* as in the illustrated example (Figure 1) which either views the optical system directly or has the light concentrated in one direction by a cylindrical lens. The detector may be coated with a filter that prevents certain wavelengths from reaching regions of the detector: for reasons that will become apparent in the calibration section below. The purpose of the spectrometer's optical system is to take the light from an appropriately configured input system and to disperse it (spread the wavelengths in angle) before focusing a straight spectrum onto the linear detector. Most spectrometers today employ a diffraction grating rather than a refracting prism to disperse the light. The grating is placed in the parallel beam of light emerging from a collimating optic focused on the input aperture or slit. The dispersed beams leaving the grating are then brought to a focus on the detector with a camera optic. The input aperture/slit is illuminated with a beam which optimally has the same focal ratio as the collimator and so *fills the beam* within the spectrometer. It is often convenient to bring the light to the input aperture through a flexible optical fiber which can be fed by a small collimating lens. Such a system, supported by software that allows continuous sampling of the light source, is extremely convenient to set up and optimize before acquiring data.

2.2 Light Sources

For our spectrometer to access the properties of a sample, we need to shine light through it, reflect light from

¹ We will use the word *spectrometer* rather than *spectroscope* since we are interested in making measurements and the visual instrument, while favored by many gemologists as a simple aid to identification, has been replaced by electronic instruments for serious mineralogists.

it, scatter light within it or somehow make the sample glow (emit light itself).

For transmission or reflection measurements we usually need a light source that emits continuously over a wide range of wavelengths, ideally over the entire operating range of the spectrometer. It would be best to have a source that emitted approximately that same light intensity at all of these wavelengths. While possible by using the resources of a huge national or international physical laboratory, this is neither cheap nor easy and so we usually have to make do with an incandescent light bulb, i.e., a quartz-halogen lamp running at as high a temperature as possible. The high temperature is needed to produce sufficient blue light for making reasonable measurements at short wavelengths. This is a consequence of the shape of the Planck function which relates the emitted light energy to the temperature of an ideal incandescent body, called a *black body*. For a given temperature, the Planck curve (in power per unit wavelength) peaks at a particular wavelength (966nm in the near-infrared for a 3000K bulb filament) and drops far more precipitately towards the blue than towards the red. Since the spectrometer sensitivity will also decrease for blue and violet light, we are inevitably starved of photons in this region and often suffer an excess at red and near-infrared wavelengths. Filters can help balance this out to some extent but it remains an awkward problem, especially below about 400nm, unless the spectrometer is especially optimized for blue and UV wavelengths.

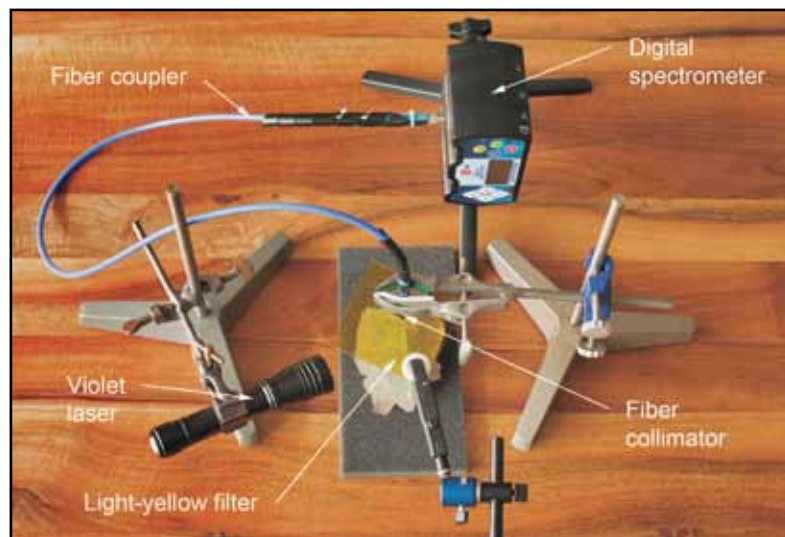


Figure 1. This shows the setup for the fluorescence measurement of a sample of fluorite using a light-yellow filter in front of the spectrometer to remove most of the scattered 404nm violet laser light. The spectrometer is fed by a fiber-optic with a small collimating lens accepting the fluorescent light: note that the filter is placed closer to the fiber than to the sample since this minimizes the possibility of contamination by filter fluorescence from scattered laser light.

For most purposes, scattering measurements can be considered to have similar requirements as for reflection and so we need the continuous spectrum from a glowing filament lamp again. The phenomenon of Raman (inelastic) scattering, however, demands a powerful monochromatic source such as a laser. Note that the subject of Raman scattering is not treated in this article for reasons of space and complexity, although it is a kind of fluorescence.

For the study of fluorescence spectra, we need to think carefully about what we want to achieve and how it can be practically implemented. Ideally we should like a bright monochromatic source whose wavelength could be tuned across the UV-visible spectrum. The closest we can get to this is a monochromator which takes a continuous spectrum as input and selects a narrow wavelength slice of this as output. This sounds great in principle but begs the usual question of what to use as a continuous spectrum source in the UV. As we all know so well, the UV excitation of minerals is usually done with mercury (Hg) discharge lamps with filters that select individual, strong UV emission lines—typically 254nm for SW and 365nm for LW—while rejecting the Hg lines in the visible spectrum with a filter. While these do work for spectroscopy, they have the disadvantage that the filters fail to reject completely many of the lines that the lamps emit at longer wavelengths with the result that the spectra are contaminated by lines that do not arise from fluorescence in the sample. These contaminants can be identified and deleted from spectrometric data but it is not very satisfactory.

A fairly recent development, driven partly by the thirst for *Blue-Ray* disc players, is the manufacture of diodes that emit intermediate width bands of UV light at a number of different wavelengths. Some of these devices, notably those at the *Blue-Ray* wavelength of around 405nm can be made in the form of diode lasers. These are powerful, essentially monochromatic, and are very convenient to use for spectroscopy since the rest of the wavelength range is clean and dark. However, note that the wavelength can vary a little—up to a *nm* or so—from laser to laser and in an individual laser, over time, due to the construction of the diode and its dependence on temperature and ageing effects. Other UV lasers at even shorter wavelengths are made and used for spectroscopy but they are more difficult to acquire and are expensive. A 405nm diode laser with an intermediate power of around 5–50mW is a very useful tool and, with its non-lasing diode counterpart at around 370nm, makes spectroscopy much cleaner and simpler than before. However, a few words of warning are needed here.

These lasers, while extremely useful for fluorescence measurements, are intrinsically dangerous and need to be used with due precaution—the principal one being to absolutely keep them out of the hands of children and

others who don't know what they are! The mineralogist needs to be aware that the eye is not very sensitive to violet light of this wavelength and so the beam appears dimmer than it really is. A laser beam can reflect from almost anything and enter the eye by unexpected routes; so, wear safety glasses that do not transmit violet light. Such (often yellow) glasses can easily be tested by carefully shining the laser beam through them at a piece of white printing paper. Without passing through the yellow filter, the paper will fluoresce a brilliant blue/white; with it in the beam, the laser spot should all but disappear.

In addition to the safety issues for eyes, we also need to take care of the spectrometer: the reflected/scattered light from a bright laser can flood our sensitive device with more photons than it knows what to do with. For most, but not necessarily all, samples it will be necessary to remove as much as possible of the laser light from the beam leaving the illuminated sample before it enters the spectrometer. This appears simple, just use a light yellow filter at the right location. It sounds good, but the problem is that most yellow filters will fluoresce a beautiful, brilliant orange when illuminated by a violet laser! Even though the filter will not be placed directly in the laser beam, the reflected/scattered light from the sample can stimulate enough fluorescence to add an unwanted signal to the spectrometer output. While this can be subtracted from the signal in subsequent processing, it is best to try to avoid it as much as possible. Now, I'm not sure I know the best solution to this problem but this is what I do. I avoid the yellow glass filters generally used for photography: while they result in a nice sharp wavelength cut somewhere in the blue/green part of the spectrum, they do fluoresce strongly. I have a light-yellow plexiglas filter (made by Cokin for photography, see Figure 1) that does not cut so sharply and does allow a small fraction of the laser light to pass, and it fluoresces only very weakly at a level that is generally not a problem. While not a perfect solution, it works; and, by measuring the transmission spectrum of the filter, I can, to some extent, correct the measured fluorescence spectrum during data processing.

While a violet laser will excite fluorescence in many minerals, it clearly is insufficient for a general study of the phenomenon which requires an understanding of the dependence of fluorescent emission on the exciting wavelength (an *excitation spectrum*). The SW (254nm) Hg lamp works quite well but most of the data longward of 680nm has to be thrown away because of contamination. Diodes, and possibly lasers, at other UV wavelengths are of great value if they can be procured. We should not neglect the uses of lasers at longer wavelengths since they can be used to excite different energy levels in some minerals. I use lasers at 532nm and a 633nm, but both of these are slightly contaminated by the pumping light and so need to be used

with circumspection and possibly extra filters. For example, I use a Schott BG38 red-absorbing filter between the 532nm laser and the sample to remove the ~800nm pumping light.

2.3 Calibration

2.3.1 Wavelength

Commercial spectrometers usually have a reasonably good wavelength calibration provided by the manufacturer. For a typical wide-wavelength spectrometer, say 400–1000nm this should be accurate over most of the range to about 1nm. Depending on the design and construction of the spectrometer, this may not remain stable either over short periods due to temperature changes or over longer periods due to mechanical *drift*. It is therefore worthwhile to check the scale fairly regularly.

This is done by observing a lamp which emits atomic lines of known wavelength, e.g., discharges of mercury, argon, helium, neon, etc. The individual lines can be identified from wavelength lists that are widely available on the Web, taking care to avoid *blended* groups of lines which will not yield a clean measurement. The manufacturers will usually make a *least-squares* polynomial fit to the relationship between pixel number and wavelength for a few tens of emission lines distributed as evenly as possible over the wavelength range. This is straightforward to do using, say, a spreadsheet program and it will yield a set of polynomial coefficients that can be uploaded into the spectrometer firmware. A third-order polynomial is usually sufficient. In practice, what I do is to make this polynomial fit to the difference between my lamp measurements and the predicted wavelengths from the original manufacturer's calibration. I then apply the resulting correction to an observed dataset during analysis rather than try to upload data to the spectrometer itself. In this way, I can obtain a wavelength accuracy of typically a few tenths of a nm over the entire 350–1000nm wavelength range.

2.3.2 Power vs. Wavelength

Before starting this story, I should make clear that this calibration is most pertinent to the measurement of fluorescence (emission) spectra. The calibration of transmittance and reflectance is considerably easier (but see the next subsection) since the measurements are made relative to the actual lamp being used. So, for instance, the transmittance of a sample is defined as the ratio of (the light traversing the sample minus the dark counts² for the same integration time)/(light from the illuminating lamp minus the same dark count). This assumes that the illumination geometry is the same for the observation of the sample as for

² Note that it will always be necessary to subtract the *dark* background signal from a measurement made with a spectrometer. This dark signal must be measured with no light entering the spectrometer and with an integration time the same as that used for the sample measurement.

that of the direct lamp (the reference signal). The calibration is then an integral part of the measurement and is done every time you make one.

So here comes the tricky, very important and often the most neglected part of the process. A spectrometer actually measures the number of *counts* produced by each pixel of the detector in a given interval of time. The number of these counts in relation to the amount of light energy entering the spectrometer depends on a number of factors:

1. The sensitivity of the detector to light at each wavelength.
 2. The efficiency of the dispersing element (grating) to put light into the appropriate diffraction order.
 3. The efficiency of the entire optical system which depends on optical anti-reflection coatings, absorption in transmitting or reflecting optical elements (lenses, fibers, mirrors, . . .).
 4. The geometrical matching of the optical system, i.e., the matching of focal ratios of fibers, collimators and cameras.
 5. The response of any grating-order sorting filter.
 6. The number of *dark* counts arising from the detector not coming from detected light.
- . . . and probably other factors that I have not thought of!

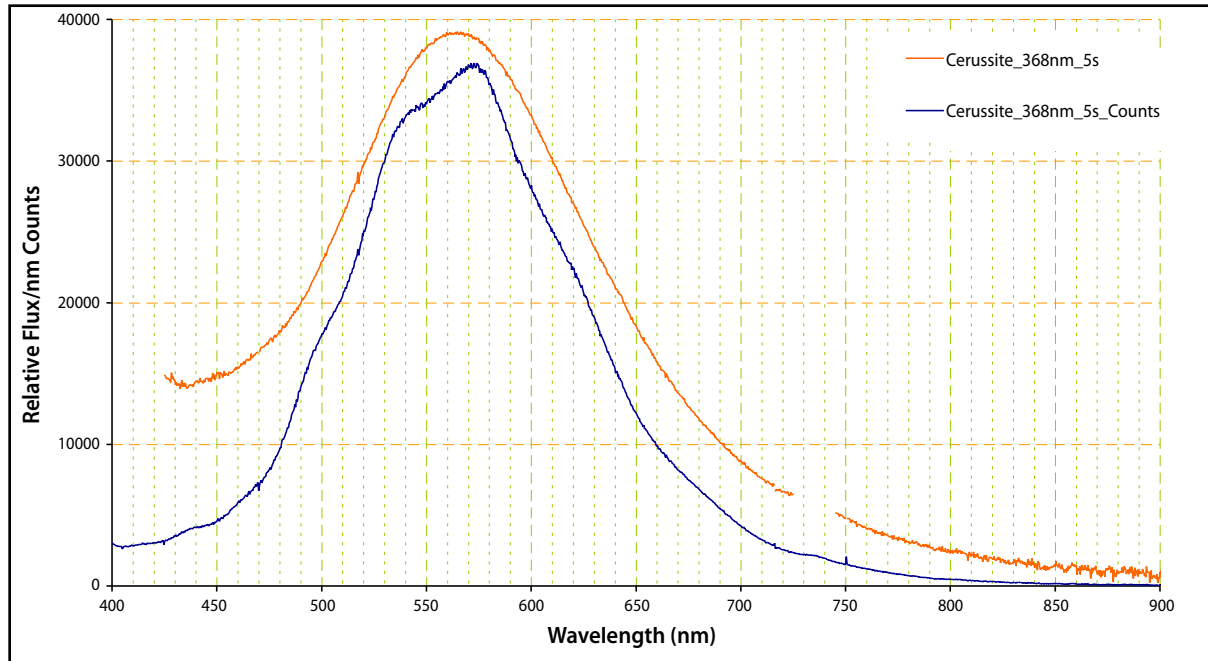
The net result of this is that a *raw* spectrum (counts vs. wavelength) collected by the spectrometer bears little relation to the energy spectrum (I will use the energy flux per unit wavelength)³ that you really want to measure. You can get away with it over short wavelength intervals where the sensitivity changes only by a small amount, but over a wider wavelength ranges you will see fluctuations and *ripples* that are certainly not produced by the sample. This is a MAJOR problem for fluorescence spectroscopy since so many of the fluorescence activators produce broadband emission. Figure 2.

This is not just a problem of the gradual fall in spectrometer sensitivity towards the ends of the spectral range. Several of the effects listed above can introduce apparent but unreal spectral features into the raw spectrum which appear as a series of only partially regular *ripples* that can easily be interpreted as real spectral structures.

So, what can we do about this? The easiest but least satisfying and most expensive way is to ask the manufacturer of the spectrometer to provide you with a so-called flux calibration. They will do this using a carefully controlled

³ There are many units for the measurement of the brightness of light as a function of wavelength but we do not really need to go there unless we are interested in the measurement of absolute energy flux in units of, say, Watts/square meter/nm/steradian. Fortunately, we will usually only be interested in the relative energy flux spectrum, i.e., Watts/nm multiplied by some unknown but constant factor. Our aim is to ensure that this relative spectrum has the correct *shape*. This is much easier to achieve but tricky nonetheless.

**Cerussite, Morocco; 368nm Fluorescence
Raw Counts and Flux Calibrated**



*Figure 2. An observation of the fluorescence of cerussite ($PbCO_3$, courtesy of G. Barmarin) with 368nm diode excitation. This shows a very broad-band, smooth, fluorescence signal arising from Pb^{2+} (Waychunas, G., "What causes mineral fluorescence? Activators of luminescence in minerals," *FMS Journal*, Vol. 20, 1998.). The plot compares the raw counts spectrum (blue) with the flux-calibrated spectrum (orange). The gap between 720 and 750 nm is in the region that shows some second (grating) order leakage from the UV diode emission. Note that all the low-frequency ripples in the counts spectrum, resulting mostly from light interference within the CCD detector, are removed by the calibration.*

standard lamp that has a known energy spectrum output. They provide you with a curve which gives the ratio between counts (measured with YOUR spectrometer) and the power transferred from the lamp to the spectrometer input (fiber). This is great but it will change with time and you may have to have it redone every year by re-mortgaging your house.

What I do with my spectrometer depends on the fact that a simple quartz-halogen filament lamp in the presence of a simple metal reflector and a ground-glass diffuser (not one of these fancy, highly-colored dichroic reflectors!) emits a pretty good *black body* spectrum (Planck function) over most of the visible spectrum—especially at the longer wavelengths. The color temperature (CT) of these lamps obviously depends on the current you put through it but is normally around 2600–2800K.

How do you figure out the CT of your lamp? You can measure it with a photographer's CT meter. This is actually not too bad and probably gets you there to within a few tens of K. What I do (I'm an astronomer and know how to do this!) is to use an observation of the Sun in a clear sky. Since the Sun is so bright, I have to use a neutral diffuser: a piece of especially white opalized glass manufactured to be color-neutral over the visible spectrum to about 1000nm. I correct the solar flux spectrum for absorption in the Earth's

atmosphere dependent on the solar altitude at the time of the observation. This allows me to construct a curve of the ratio of solar flux/nm to the number of counts from the solar observation. If I keep proper account of the integration times of the observations, this gives me a curve that I can multiply into my fluorescence observations. The problem with this is that the solar spectrum contains lots of what we call *telluric* spectral absorption features produced by oxygen, water and ozone in the atmosphere leaving uncalibrated *gaps* in my calibration curve—especially at longer wavelengths.

Here is where the lamp observation comes in. I form a similar ratio curve for the lamp data using a computed Planck function to represent the flux. I adjust the temperature in this calculation until the shape of this curve matches the shape of the uncontaminated regions of the solar observation—which is essentially a measurement of the lamp CT. I then use this lamp-derived curve as my calibration function to be multiplied into any emission measurement. This has the advantage that all the irregularities in the spectrometer response, from pixel-to-pixel scale to broad ripples, are removed. Although in principle I have an absolute energy flux calibration, I almost always only use it as a relative (spectral shape) calibration. Figure 3.

I know this sounds complicated (it is quite!) but it makes a huge difference to the utility of the spectrometer and allows the production of publishable quality results.

2.3.3 Straylight

Just to finish this rather lengthy, hopefully useful but admittedly tedious section, I will add a word about the effects of straylight in the spectrometer. Although some manufacturers do offer some kind of correction algorithm for this, it is best to understand what causes it and how it can be recognized and, possibly, corrected.

Not all of the light that enters the otherwise light-tight box of a spectrometer ends up in the appropriate pixel of the detector. Some gets smeared into the wrong place by the diffraction grating and some just misses the optics and bounces around before ending up on a pixel that does not represent its correct color. Just to put this in the correct perspective, the typical scale of this effect is that about a millionth part of the total light entering the spectrometer ends up as a random background on each detector pixel. It does not sound like much but there are a few circumstances where it introduces a substantial error.

The most severe effect is at the blue end of the spectrum in a transmission or reflection measurement. A filament lamp produces few photons at this wavelength and so both the reference and the sample spectra contain low counts here. When dividing the sample by the reference spectrum (both dark count corrected), the addition of only a few extra straylight counts can make a big difference, especially when the sample shows very little blue light. This appears in the transmittance/reflectance spectrum as a sharp, entirely artificial, rise at the blue end of the spectrum (and to a much smaller extent at the red end). It can be corrected by the application of a simple, empirically-guided, algorithm that subtracts some fraction of the total counts from both the sample and reference spectra. Figure 4.

Perhaps the most obvious straylight effect to be seen when doing fluorescence (emission) spectroscopy is if you let too much laser light into the spectrometer. Depending on how much light there is, you can see a range of different effects. The first is the appearance of the laser line in another order of the diffraction grating, e.g., for a 404nm diode laser you will see a line at 808nm from the grating second order spectrum. Manufacturers generally include a filter into their broad wavelength coverage spectrometers to attenuate this

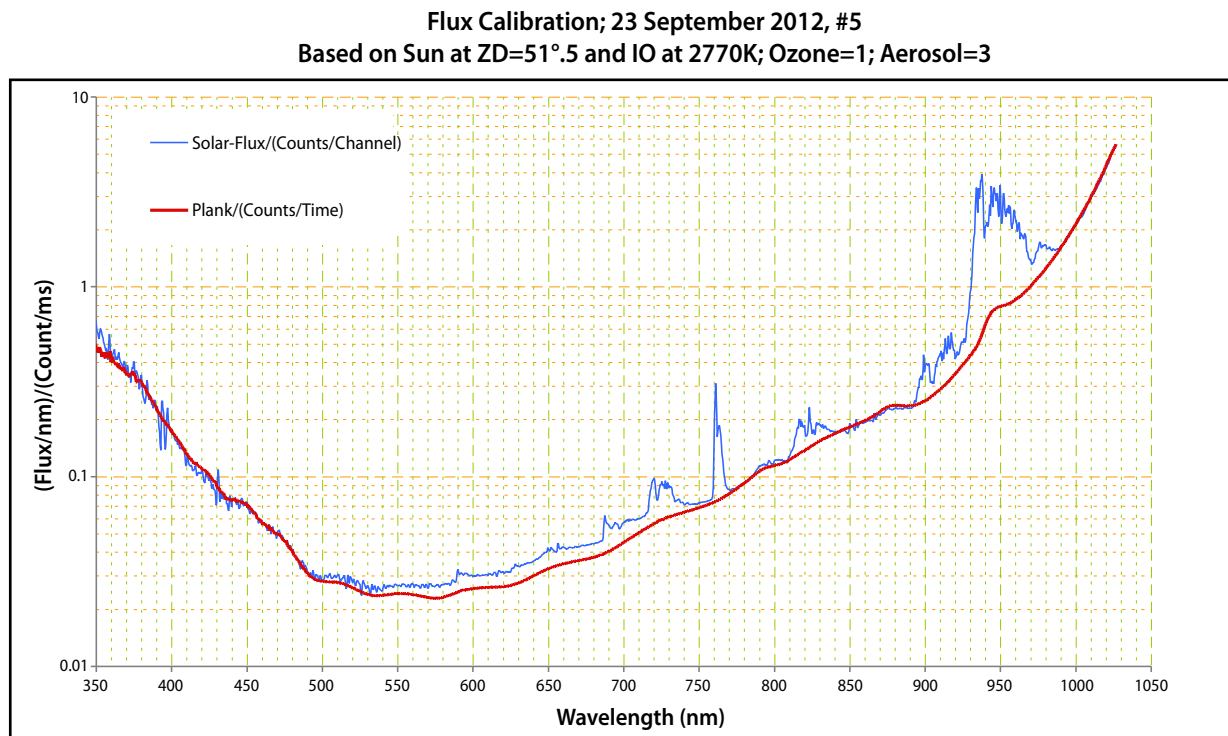


Figure 3. This shows the flux calibration curve that I currently use. It was determined from observations of the Sun (corrected for atmospheric scattering and ozone absorption—but not for molecular oxygen or water absorption). The ordinate is the ratio of power/nm from the Sun (known) and from the lamp (assuming a black body spectrum) divided by the number of spectrometer counts per unit time in each spectral channel. The best fit between the two curves is for an assumed lamp color temperature (CT) of 2770K. Any emission spectrum observed with the spectrometer is multiplied with the red curve after subtracting the dark counts; this gives a result which represents the relative flux/nm. I redo this calibration every year or so. The upward deviations in the blue (solar) ratio represent absorption by O_2 and H_2O in the atmosphere. There remains also a small, unexplained offset between 500 and 750nm.

but, if you are cavalier enough with your laser beam, you will see it! If you do see it, you should also be on the lookout for other *ghost* lines caused by slight irregularities in the grating rulings or from low level internal *specular* reflections outside the nominal optical path. These effects begin to appear when you look about a factor of a thousand below the strongest spectral feature. They are hard to correct but it is important to be aware of them in case they are interpreted as real features from the sample. In some cases, it is possible to see *ghosting* from a very bright fluorescence line in the sample spectrum.

3. OBSERVING FLUORESCENCE SPECTRA

Before moving on to a few examples of fluorescence spectra, we should give at least a brief summary of the physics of fluorescence. I won't go into too much detail here because the basics are reasonably straightforward and there are many books and articles that will take you as deep as you need and probably deeper than you want.

When a photon of light with sufficient energy (blue or UV say) interacts with an atom, a molecule or a *defect* in a crystal—which can itself act a bit like an atom, an electron can be excited from the lowest level, *the ground state*, to an excited state. This electron sometimes decays

almost immediately back to where it started by emitting a photon of the same wavelength. This is called resonance fluorescence and is interesting for quantum physicists but less so for mineralogists.

The electron can, however, do more exotic things. Within a crystal, it can bounce around a bit—emitting a little heat on the way—to reach a lower lying excited state from which it can make a radiative transition to a yet lower and possibly, ground state by emitting a photon that is redder than the original exciting one. In a molecule there can be an analogous process where the excited electron can first decay to the lowest vibrational level of the excited state and then make a radiative transition to one of the vibrational levels associated with the ground state: such a process can produce a *rippled* fluorescence emission band due to the availability of many vibrational levels associated with the ground state.

Sometimes the excited electron can end up in a lower excited state (by an intersystem crossing) that has no easy path for a radiative transition back to the ground state. It can hang around there for seconds or even hours and longer before it finally drops down to radiate what is called *phosphorescence*. Such processes provide plenty of opportunities for the production of complex fluorescence spectra.

Straylight Correction for a Transmission Measurement, Schott RG715 (3mm)
1.35 e-6 * Total Counts

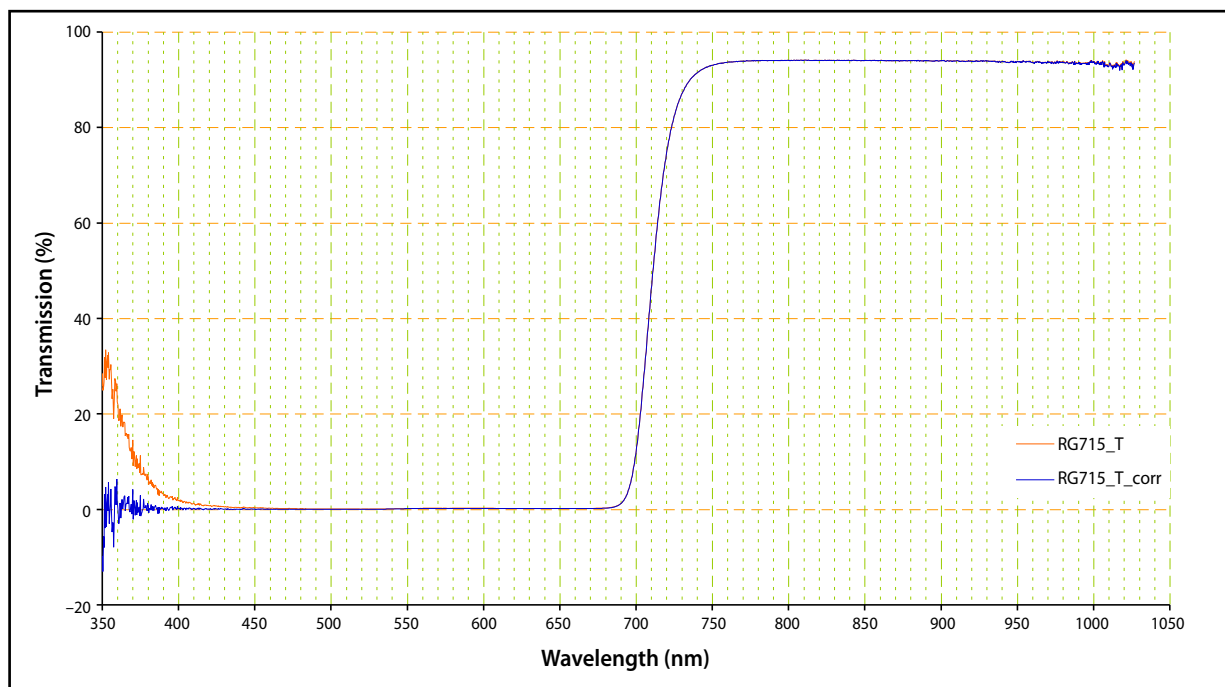


Figure 4. An example of the effect of straylight in the transmittance measurement of a photographic infrared filter that cuts all light bluer than around 700nm (orange curve). The blue curve shows the result of a simple correction where about 1.4 millionths of the total sample count is subtracted from each pixel in the sample spectrum. A subtraction is also made for the reference spectrum but this is not so important.

Scheelite, Italy (Small Sample); GB/RAEF; 9 September 2011 and 24 March 2013
Transmission and Fluorescence; Excitation by Laser at 532 and 404nm and Hg Emission at 254nm

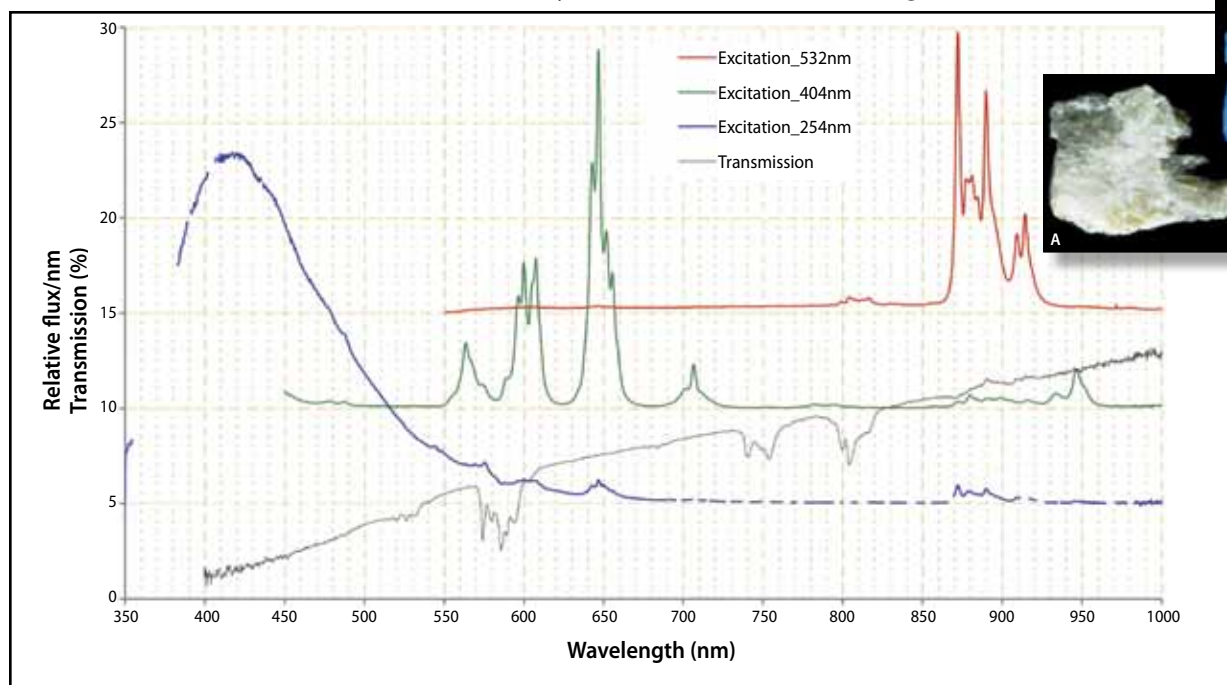


Figure 5. Fluorescence and transmission (gray line) spectra of a sample of Italian scheelite (courtesy of G. Barmarin) illuminated with a 254nm SW Hg lamp (blue line: the gaps are due to contamination by Hg emission in the lamp) a 404nm laser (green line) and a 532nm laser (red line). The images are in white light (A) and SW UV (B). Note the relatively weak lanthanide emission with the SW lamp and the large difference between the two laser-excited spectra. Even the transmission spectrum shows weak red fluorescence around 890 and 915nm. The blue, green and red spectra are shifted up the flux scale by 5, 10 and 15 units respectively. (Photos enlarged on page 17).

3.1 Scheelite

For a first example, let's take a look at scheelite, the name for calcium tungstate (CaWO_4). This is closely related to powellite which has molybdenum replacing the tungsten. The notable behavior of scheelite, when irradiated with SW UV is its emission of a remarkable deep sky-blue fluorescence (Figure 5) that is intrinsic to the WO_4 in the pure mineral.⁴ This can be seen as the blue line in the figure which results from excitation with the 254nm Hg lamp. The violet (404nm) and the green (532nm) lasers excite trivalent (three positive charges from the absence of three electrons) lanthanide rare earth ion impurities in the natural mineral (Dy, Sm, Nd etc.). Since these elements have many absorption bands throughout the visible and near-UV spectrum, the lasers can excite very different looking fluorescence spectra (red and green lines in the figure). The figure includes the transmission spectrum of the sample (gray line) which shows some of the absorption bands.

⁴ Fluorescence resulting from a process taking place in an essential ingredient of the mineral structure— WO_4 in this case—is called *idiochromatic*. When the fluorescence results from an impurity in the mineral, however, it is called *allochromatic*.

3.2 Chromium Fluorescence

An example of an allochromatic mineral is ruby, which is sapphire (Al_2O_3) with a percent or so of the Al replaced by chromium. Sitting comfortably in place of an aluminum ion, the chromium ion (Cr^{3+}) provides three *unpaired* electrons which can do wonderful things for the color and the fluorescence. The crystal can absorb light in the violet and in the green leaving the crystal a deep red tinged with blue. The electron which is affected by such an absorption is lifted to one of two excited states lying at 3 and 2.2 electron volts (eV) respectively above the ground state. This electron then drops down to a doublet (split into two close levels) state around 1.8eV where it sits for a little while before dropping back down to the ground state by emitting a red photon—at one of two closely spaced wavelengths called the *R lines*. This is the transition that makes the ruby laser.

The positions of the energy levels involved in this process depend on the electric field felt by the Cr^{3+} ion and provided by the symmetrically placed surrounding ions. This is called the *crystal* or, more correctly, the *ligand* field. Different crystallized minerals containing a replacement chromium ion,

e.g., emerald, have different ligand fields and so have different colors and fluorescence behavior. Figure 6 shows a set of ten chromium containing allochromatic crystals which, when

illuminated by short wavelength light (a violet laser in this case) emit rather similar, but far from identical, fluorescent spectra with *R lines* at slightly different wavelengths and

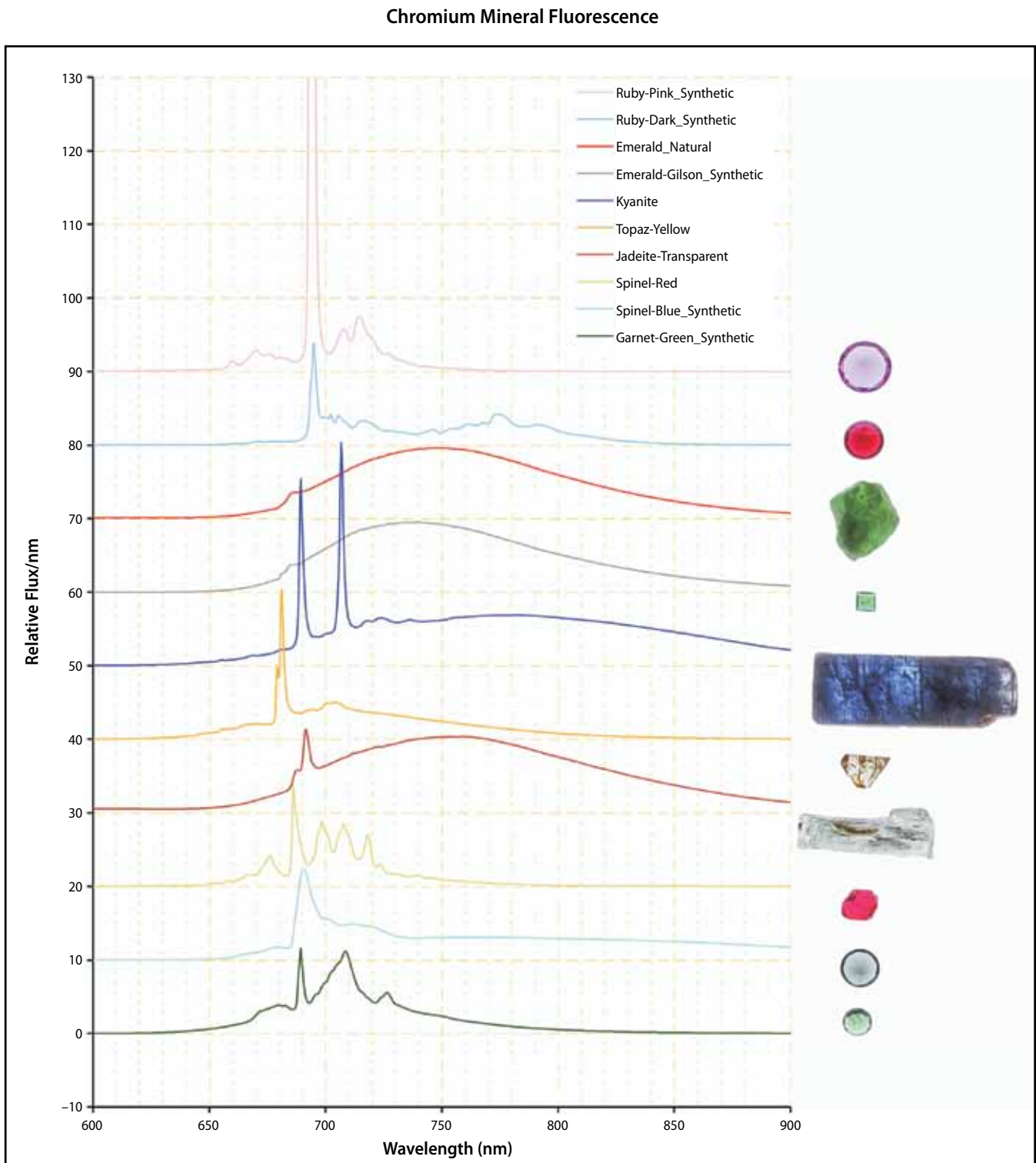


Figure 6. A set of ten allochromatic crystals that contain chromium in the form of the Cr^{3+} ion. They are excited by a violet laser in this set of measurements. These all show fluorescent line emission in the deep red around 700nm but the detailed structures differ due to the different crystal (ligand) field strengths and symmetries. Note that in the dark red ruby (second from top), the 'R line' doublet is self-absorbed and relatively much weaker than in the pink crystal above it.

with different doublet splitting. Such spectra are clearly very valuable diagnostics since they are so easy to distinguish. Kyanite in particular stands out with a large splitting. Crystals like this react differently to incident light with different polarization directions and show strong dichroic behavior.

3.3 Lapis Lazuli

Lapis lazuli is a mineral that has been of enormous significance in the history of art by providing the source of the voluptuous blue pigment *ultramarine*. Coming to Venice from far over the seas (ultra marine) in Afghanistan, the rock was ground to a powder and refined by a long manual process to provide a paint that cost up to thousands of times more than an equal amount of some of the other colors.

The deep blue color of the lazurite in lapis lazuli arises from the presence of sulfur in the form of a polysulfide consisting of three sulfur atoms with a single negative charge. It is the charge transfer between orbitals that produces the strong, broad absorption band at 600nm producing such a rich red-tinged blue. The orange fluorescence spectrum, however, comes from disulfide: two sulfur atoms again with a single negative charge. Such LW excited rippled fluorescence is typical for sodalite and its variety hackmanite and is a good example

the appearance of a fluorescent transition in a *molecule* with vibrational levels in the ground state. Figure 7.

The blue fluorescence in hackmanite comes from the negative dioxide ion O_2^- as an alternative to S_2^- in the same crystal *cage*. (Emmermann, A. 2011. *It's never 'Just and Activator!'* FMS Journal, Vol. 31, p. 5). The blue SW fluorescence in this lapis lazuli is, however, spatially uncorrelated with the orange disulfide emission.

3.4 Fluorite

My final example is a mass of blue/green fluorite crystals of unknown origin excited with a 404nm laser. Fluorite (CaF_2) has, of course, a special place in the history of the study of fluorescence since its name was given to the phenomenon by Sir George Stokes in 1852. Fluorine also has a unique position in the story of the origin of the chemical elements in stars over the history of the Universe. The fluorine we have around us today and use in our toothpaste is thought to be made during the explosive events that arise at the end of the life of stars more massive than the Sun. Such *core-collapse* supernovae emit a huge burst of neutrinos (about 10^{58} of them in a few seconds!) as the trigger of the collapse and, as they emerge through the outer layers of the doomed

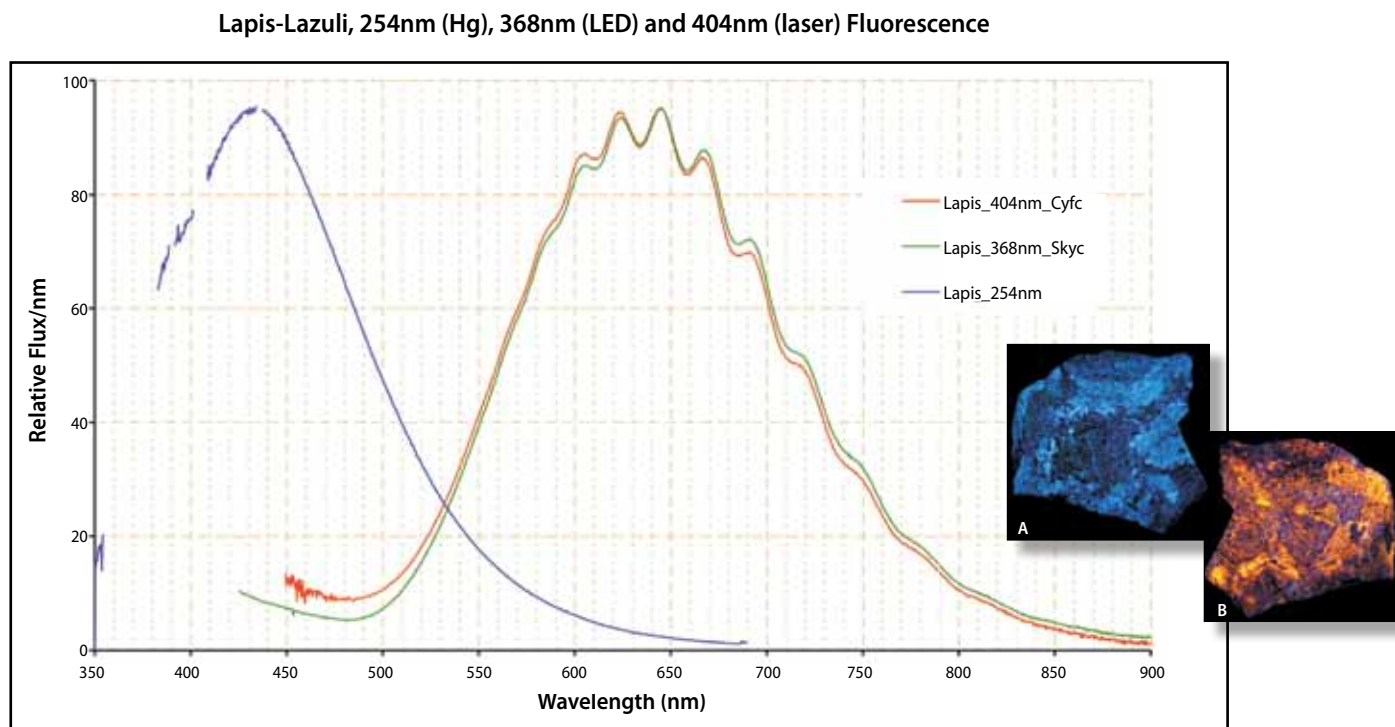


Figure 7. The fluorescence of Lapis lazuli under SW (A: 254nm; left image and blue line spectrum) and under LW (B: 368nm LED and 404nm laser; right image and green and orange line spectra) excitation. The LW illuminations excite the orange disulfide fluorescent transitions to a series of vibrational levels in the electronic ground state. The blue fluorescence excited by the SW lamp is not yet determined. (Photos enlarged on page 17).

Massive Blue/Green Fluorite; Fluorescence 404nm Laser

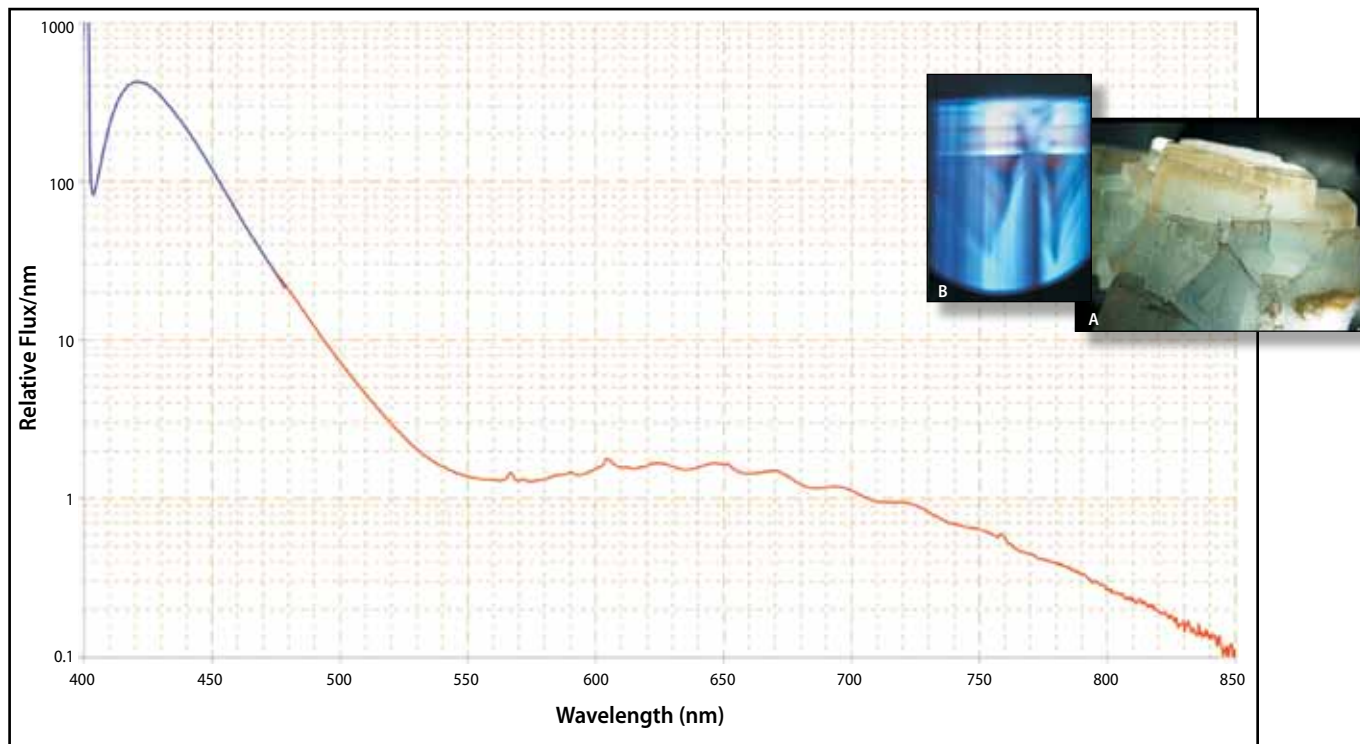


Figure 8. The high dynamic range spectrum of a sample of blue/green fluorite of unknown origin which shows distinctive yellow/brown crystal edges to a depth of 2–3mm. The spectrum was measured with and without the yellow filter with different integration times, allowing the blue Eu^{2+} peak to be faithfully recorded even in the presence of the 404nm laser line. The combined spectrum, plotted here on a logarithmic intensity scale, covers a flux range of over 4000:1. The right (A) image is a white light photograph of the crystals while the photomicrograph on the left (B) shows the defocused laser illuminating the colored edge of one of the crystals. (Photos enlarged on page 17).

star, a very few of them interact with a neon nucleus causing it to emit a proton or a neutron to create a fluorine nucleus, either directly or after a neon-19 isotope beta-decay. Many other heavier elements are produced in such an explosion but by neutron capture rather than neutrino interactions.

The characteristic strong blue fluorescence of fluorite is known to be the result of the rare earth element europium as Eu^{2+} which is a common impurity. The mineral often also hosts a number of other lanthanide rare earths and the laser can excite even tiny quantities of these activators. In this sample, the edges of the crystal faces are a light yellow/brown color to a depth of 2–3mm. Figure 8. When the laser is shone through this layer, it excites a red fluorescence that is not seen strongly in the bulk of the crystal (see the left-hand micrograph in the figure). The defocused laser shines from the top and produces the pinkish glow mostly in this surface layer which shows horizontal zoning. The spectrum of this glow, extending from about 550 to 900nm shows weak lanthanide lines, the strongest at 567, 604 and 758nm but it also exhibits a series of ripples that very closely match

the sodalite/hackmanite peaks seen in the lapis lazuli above. Since the disulfide ion cannot sit comfortably within the fluorite crystal structure, it is presumably contained in micro-inclusions that cause or are associated with the yellow/brown color.

This behavior appears to be unusual, though I have seen evidence for it at a lower amplitude in one and possibly two English fluorite samples. Many fluorite crystals also show a broad-band emission centered at 730nm which is ascribed to an *M*-center.

This section has given just a flavor of the kind of measurements that can be made with a modern digital spectrometer. It is a rich field and, with cheap, powerful lasers, I suspect that there are many discoveries yet to be made. In Part II of this article (*FMS Journal*, Vol. 34), we hope to provide a more comprehensive description of the spectra produced by different fluorescence activators and what it can tell us about the host mineral.

Figure 5. Scheelite. The images (courtesy of G. Barmarin) are in (A) white light and (B) illuminated with a 254nm SW Hg lamp.

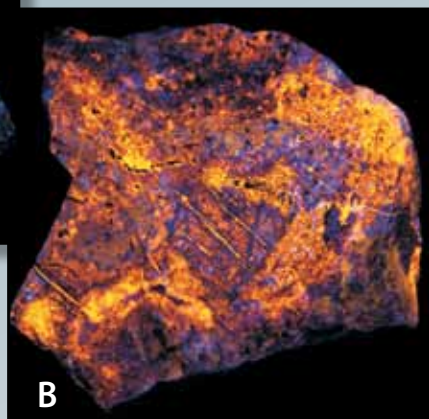
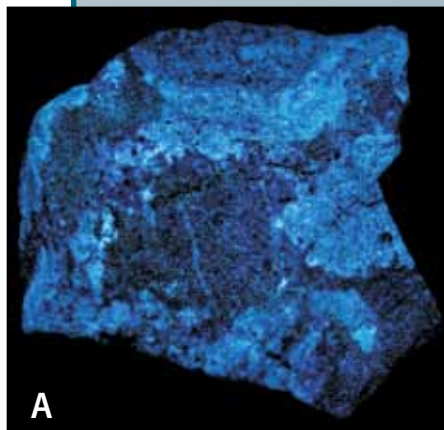
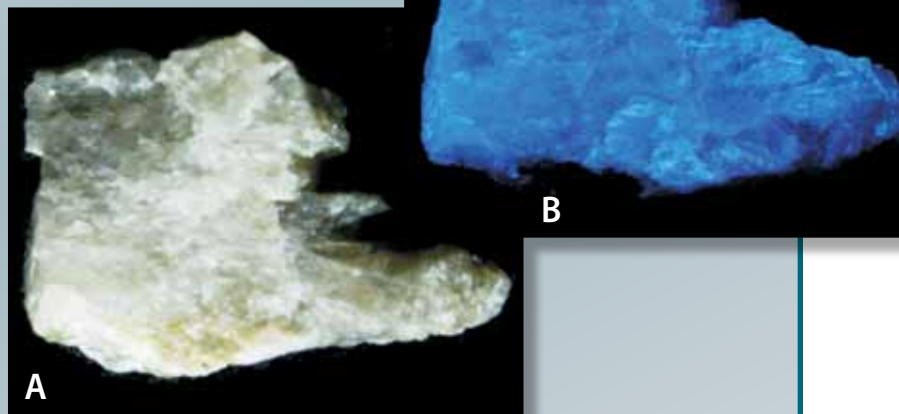


Figure 7. Lapis Lazuli. Fluorescence under SW, 254nm; left image (A) and under LW, 368nm LED excitation; right image (B).

Figure 8. Fluorite. The right image (A) is a white light photograph of the crystals while the photomicrograph on the left (B) shows the defocused laser illuminating the colored edge of one of the crystals.



ACKNOWLEDGMENTS

My spectroscopic interests and experience were assembled during the professional use of spectrometers on large astronomical telescopes on the ground and in space and from my love of nature and its colors. The latter pursuits resulted in me becoming also an amateur spectroscopist. Without the help and encouragement of my relatively new-found friends and colleagues in the field of mineralogy, I would not have attempted to write this article. In particular, I should say that my effort was inspired and instigated by

Karl Russ. I should also like to thank Gérard Barmarin, Axel Emmermann and Cran Cowan for our frequent dialogues. Gérard generously provided me with many interesting samples to supplement my original meager collection. My knowledge of mineralogy is growing but is nowhere near as deep as theirs! See the spectroscopy set at: www.flickr.com/photos/bob_81667 ■