Potential problems in collection and data processing of luminescence signals

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A B S T R A C T
Luminescence studies are central to a very wide range of disciplines, both as a primary experiment and in a minor role for additional discrimination between samples. Unfortunately when luminescence studies are not the central objective and expertise the data collection, instrumental corrections and data analysis are not always being totally, or correctly, employed. There are often historical reasons for this but with modern equipment one can readily make the requisite compensations. The problems are outlined with emphasis on spectral and polarisation response of spectrometers and detectors. Typical data processing errors are noted with demonstrations of their consequent effects on the signals. These include the fact that the peak in the wavelength presentation can significantly differ from the true energy centre of a Gaussian emission band. There can be failure to totally compensate for the spectral sensitivity of the detection system, as well as the incorrect use of band de-convolution on the wavelength representation, and energy plots where only the wavelength axis has been corrected; these mistakes all distort the true spectra. Not only are these analyses physically incorrect, but they are misleading, and introduce false features. This brief review indicates why such processing errors can generate spectral differences cited in the luminescence literature that are from measurement, rather than differences between source materials.

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1. Introduction

Luminescence is a ubiquitous property of insulating and semiconductor materials and it has generated immense literature for well over 100 years. The techniques of luminescence spectroscopy have excellent signal to noise sensitivity and they benefit from the detection of a signal against zero, or minimal, background. In extreme cases sensitivity is achieved down to levels of single photon counting. Consequently luminescence equipment is extremely sensitive and methods of luminescence spectroscopy are used in such a wide range of disciplines that it is unlikely that the literature is successfully disseminated between the various types of user. In part this is because the information being sought in areas such as condensed matter science or biology and chemistry have minimal overlap in terms of application and experience. This is unfortunate as the same experimental and data processing problems exist but it is abundantly clear that there is wide diversity of appreciation of the potential errors.

The high sensitivity and ease of equipment operation has attracted users from a wide range of disciplines in materials science related fields such as geology and archaeology, as well as chemists and various branches of physics (from semiconductor processing, ion implantation to colour centre research). For most of these users luminescence detection is merely an extra technique. Such users often had, and have, considerable expertise in their own fields but frequently have not appreciated the methodology and details of the luminescence recording and analysis. Biological applications are frequently termed fluorometry and their luminescence activities are focused on very specific applications that require precise and quantitative signal detection. In such contexts it has been essential to strive for removal of systematic errors in data acquisition and even to attempt to have quantitative data with intensities related to international standards, as well as generating “standard” test samples that can be inter-compared. Refs. [1,2], and the items cited therein, indicate progress in this direction. By contrast, many of the other users of luminescence techniques in the very diverse applications considered in material science have not progressed to this level of standardization. Instead the luminescence is often still used as an exploratory tool, rather than a quantitative one. Unfortunately this has often resulted in a range of systematic errors that have been retained from the historical developments of the methods. The current article aims to re-iterate the more obvious experimental complexities and indicate some of the more common errors in data handling.

In materials science related fields the sensitivity of luminescence measurements is ideal for studies of crystalline defects and impurities as the measurements identify and separate properties
of intrinsic lattice defects, contaminants, controlled dopants, or nanoparticle inclusions with detection limits frequently well below parts per million. This is particularly advantageous if one is seeking evidence for the non-quantitative presence of trace impurities such as rare earth ions, as in these examples there are characteristic sharp line spectra which give a unique indication that a specific rare earth ion is present. A typical luminescence spectrum recorded from say 200 to 1000 nm will use spectrometer resolutions of 1–5 nm in order to have strong signal levels. A focus on rare earth lines requires greater dispersion and when higher spectral resolution is applied one can further identify more subtle changes in the location of the impurities via wavelength and polarisation changes caused by the local crystal field around the impurity. This site specific spectroscopy [3–5] requires higher spectral resolution, typically with 0.1 nm resolution, to reveal site variations that are hidden in the lower resolution of standard luminescence studies. In site specific spectroscopy this high resolution is required both in the choice of excitation wavelength and in the analysis of the emission spectra. Site variations are also apparent for other impurity ions and such data emphasise that impurity inclusion and/or association with intrinsic defects are more diverse and complex than often appreciated. Indeed resolution of such complexity is a major strength of luminescence techniques. By contrast, many of the intrinsic defects, as well as a wide range of other lattice imperfections, generate broader emission bands that subsume the possible variance of the sites. A consequence of such extreme sensitivity is that subtle sample differences are encoded in the luminescence spectra. Therefore, when discussing variations between data from different laboratories it is essential to distinguish between differences that arise from sample variations, or treatments, and those which are artefacts of the signal collection and processing. Precise spectral calibration is required and to decode the details of the component luminescence features it becomes necessary to de-convolute overlapping features. Unfortunately both calibration and de-convolution processes have a number of potential errors and the literature is deeply flawed in many published examples (for obvious reasons, references are not included here). Table 1 attempts to indicate a broad but brief overview of the more common requirements in signal collection and processing.

Rather than be overcritical of the failure to correctly analyse earlier data it is helpful to reflect on why such errors have appeared and then become entrenched in the standard techniques for signal processing. Luminescence spectroscopy over a wide spectral range initially used film recording with all the consequent difficulties of non-linear responses, reproducibility and intensity calibration. However, during the late 1950s scanning monochromator and photomultiplier detectors (PM) became routinely available. At that stage the signal output appeared on chart paper. Whilst it was realised that the chart paper spectrum of raw data was distorted in intensity, both by the spectral efficiency of the monochromator and the PM tube, the manual labour to correct for

Table 1
A brief summary of factors that influence luminescence signal data and processing.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Potential problems</th>
<th>Consequences</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Positioning relative to the excitation source</td>
<td>Uncontrolled intensity variations and non reproducibility</td>
<td>Caution in alignment</td>
</tr>
<tr>
<td></td>
<td>Positioning relative to the optics for analysis</td>
<td>Distortion of relative emission band intensities</td>
<td>Caution in alignment</td>
</tr>
<tr>
<td></td>
<td>Crystalline samples need careful orientation as many of the system responses are polarisation sensitive</td>
<td>Spectra from front, rear and side faces will always differ.</td>
<td>Test alternative geometries of sample and beam</td>
</tr>
<tr>
<td></td>
<td>For ion beam and photo-excitation orientation can influence the spectra</td>
<td>NB angle of incidence and polarisation are important</td>
<td>Test these alternatives</td>
</tr>
<tr>
<td></td>
<td>Samples reabsorb luminescence giving signal distortion, with extreme cases of a false double peak.</td>
<td>False intensity data</td>
<td>This is a problem defined by the absorption, test with non-normal incidence</td>
</tr>
<tr>
<td></td>
<td>In photoluminescence different wavelengths excite to different depths</td>
<td>Transmission and polarisation can differ between components</td>
<td>Use during calibration</td>
</tr>
<tr>
<td></td>
<td>Dark current and stray light, (cathodoluminescence filament in or scatter in the spectrometer)</td>
<td>ditto</td>
<td>Use during calibration</td>
</tr>
<tr>
<td>Filters</td>
<td>Essential to avoid higher order diffraction overlap problems</td>
<td>NB these components may be luminescent if excited</td>
<td>Test without a sample</td>
</tr>
<tr>
<td>Polarisers</td>
<td>Essential for anisotropic source materials</td>
<td>Calibrations for unpolarised and polarised usage all differ</td>
<td>All variants need their own calibration curve</td>
</tr>
<tr>
<td>Optics</td>
<td>Incorrect positioning, imaging, or absorption and reflectivity losses</td>
<td>With a photoluminescence double monochromator for analysis this is a factor of 64:1</td>
<td></td>
</tr>
<tr>
<td>Diffraction gratings</td>
<td>2 main problems are a strong wavelength dependence and extreme polarisation sensitivity</td>
<td>Rare earth lines in solids are imprecise for very high resolution data.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Relative polarisations can typically differ by 8.1 across the spectrum from say 200 to 900 nm.</td>
<td>There can be very large variations between nominally identical detectors and they change sensitivity with age and exposure</td>
<td>Calibration of entire system is essential</td>
</tr>
<tr>
<td>Spectrometer calibration</td>
<td>Wavelength calibrations with line spectra and narrow slits.</td>
<td>Temperature uniformity and control can be compromised</td>
<td>Problem in thermoluminescence see Refs 28–31</td>
</tr>
<tr>
<td>Detectors</td>
<td>Mostly photomultipliers and CCD detectors, but photon imaging tubes and semiconductor devices are alternatives. Beware that catalogue descriptions are only generic and replacements require recalibration. Luminescence is predominately of insulators and so samples are poor thermal conductors</td>
<td>There can be very large variations between nominally identical detectors and they change sensitivity with age and exposure</td>
<td>See text and Refs. 1, 2 and 15</td>
</tr>
<tr>
<td></td>
<td>Mostly photons into the PM tube, but photons imaging tubes and semiconductor devices are alternatives. Beware that catalogue descriptions are only generic and replacements require recalibration. Luminescence is predominately of insulators and so samples are poor thermal conductors</td>
<td>There can be very large variations between nominally identical detectors and they change sensitivity with age and exposure</td>
<td>See text and Refs. 1, 2 and 15</td>
</tr>
<tr>
<td>Temperature control</td>
<td>Extremely difficult, even with reference to national standards and interchange of reference standards</td>
<td>There can be very large variations between nominally identical detectors and they change sensitivity with age and exposure</td>
<td>See text and Refs. 1, 2 and 15</td>
</tr>
<tr>
<td>Absolute efficiency</td>
<td>For a correctly calibrated system one records spectra in terms of wavelengths for a fixed wavelength bandwidth</td>
<td>Temperature uniformity and control can be compromised</td>
<td></td>
</tr>
<tr>
<td>Data collection</td>
<td>Only this version is suitable for band deconvolution and separation of components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data analysis</td>
<td>This must be in terms of energy versus intensity with a constant energy bandwidth, ((\Delta E_\text{DE} ) versus (E)).</td>
<td>Many people fail to correctly convert both wavelength and intensity axes; results are then wrong and misleading.</td>
<td></td>
</tr>
</tbody>
</table>
this was considerable. Further, in applications where one was merely monitoring the presence of rare earth impurities in different minerals the absolute intensity values were not of primary importance. Similarly in colour centre studies using various sample treatments one still obtained relative information appropriate to a particular system. Lifetime resolved spectra were also successful (e.g. with lock-in amplifiers) despite distortions of the relative signal intensities. Thus by the time computer data recording was routinely available the pattern of presenting “raw” data as a function of wavelength was still common practice, and was the format that was familiar and accepted by journal referees. This is very obvious in early publications where many spectra clearly reveal the quantum efficiency of the diffraction grating and photomultiplier (PM) tube combination that was used. Indeed, one of the current authors (PDT) progressed through such publication patterns and so he and his contemporaries have made many of the subsequent processing errors discussed in this text.

2. Standard luminescence equipment

2.1. Diffraction gratings

Although very early spectral studies used prism monochromators and spectrometers the normal practice is now to disperse the spectrum with a diffraction grating. Gratings have the major advantage that the signal appears on a linear wavelength axis. The theory of diffraction gratings is well documented [6,7] and gratings can be produced to cover different spectral ranges with line densities that offer different levels of spectral resolution. A variety of coatings have been used on diffraction gratings for different spectral regions and the grating diffracts power into a central (mirror direction) and a set of side bands. By controlling the shape of the grating lines one can concentrate power into a single side band to optimise grating efficiency. The line shape defines the peak wavelength efficiency and this is the “blaze” wavelength (also termed apodization). Higher order diffraction cannot of course be totally suppressed and if one is covering a wide spectral range line it is essential to introduce blocking filters so that second or third order diffraction is not detected. For example a grating blazed for ~400 nm is typically used to span a wavelength range from say 200 to 900 nm. So at a wavelength setting of 600 nm one will also detect 2nd order light at 300 nm and 3rd order light at 200 nm. Lower order blocking filters are thus needed to define detection of a single wavelength. Blocking filters are rarely neutral components but have absorption distortions which modify the signals and require correction. Further, they are rejecting higher energy photons and can contribute their own fluorescence signal. Less common is that they add polarisation effects. Surprisingly, not all research groups use order blocking filters, so some potential consequences will be mentioned.

Fig. 1 shows a typical pattern of grating efficiency with wavelength. In this example the grating was blazed near 450 nm. The normally cited response is for un-polarized light (Fig. 1a) and this displays a maximum value with an asymmetric pattern extending to long wavelengths. Response usually falls to an efficiency of say 10–20% of the peak value by ~1/2λblaze and ~2λblaze. This defines the useful spectral range of the grating. If we plan to cover the region that includes the UV/visible spectrum, and where there are reasonably good detectors, we need to span say 200–900 nm and this implies a single grating with a blaze set for say 400–450 nm can be adequate. Different spectral ranges differ in the choice of blaze wavelength. For many situations the signal source is nominally unpolarised (e.g. if the source is from a glassy amorphous material, or from random powder). However, the light reaching the spectrometer can be directed by mirrors or other optical components which impose different degrees of polarisation and these experimental artefacts must be accounted for.

For crystalline material light may be polarized either because the lattice structure is anisotropic, or because there is an imbalance in the excitation of differently oriented sites. This is particularly relevant for photoluminescence where the light from monochromators or lasers is invariably polarized solely from the grating contribution; Fig. 1b contrasts the separate responses of light polarized parallel to the grating lines (P type) and light polarized perpendicular to them (S type). There is an extensive and long established literature on the polarisation performance of diffraction gratings and their efficiency varies across the spectrum. Details vary with grating construction but in all cases the P wave response shows a strong peak at the optimised blaze angle (as intended to give a peak performance at λblaze). But the S response is more complex as the result of surface plasmon interactions. The S response is sustained further to long wavelengths and has a number of resonances. (The problems in part relate to surface plasmon responses on the metal reflection surface and historically have been discussed as Wood’s anomaly.)

2.2. Grating effects on polarisation measurements

Detailed information from the luminescence of crystalline lattices benefits from analysis of the polarisation of the emission. This is obvious in anisotropic materials such as sapphire, where the intensity and spectra of light polarised parallel to the crystal c axis differ from that of light perpendicular to the axis. The axes and relative intensities offer data on the local crystalline field of the emission site. Even in cubic structures, such as alkali halides or MgO, one can use
polarised excitation to alter the balance between polarisations contributing to isotropic emission. Overall this implies that for crystalline materials it is valuable to record signals at different polarisations as their differences help in modelling the structure of the emission sites. Nevertheless the recorded signal is a combination of source, optics, and diffraction grating polarisation responses and the use of the “standard” unpolarised grating performance is inadequate as it significantly distorts the information.

The expectation is that the luminescence and optical absorption in anisotropic materials will contain a mixture of polarised and unpolarised features. In optical absorption one can resolve these components by using a polariser during the measurement (for both the reference and transmitted beams). Such absorption data, with a mixture of polarisations, do not cause problems in subsequent de-convolution of overlapping absorption bands. Unfortunately this is not the case for luminescence studies if the signals are fed directly into a grating monochromator or grating spectrometer. In this situation the spectrometer response is polarisation sensitive. So correction of the raw data for grating response is not feasible if the input signal has a mixture of differently polarised and/or un-polarised input emission bands. De-convolution of such emission spectral is thus impossible with a polarised input directly into the grating analyser.

Note the distortions in signal intensity caused by the grating response vary with wavelength and in the current example (Fig. 1b) the relative S/P sensitivities differ by around 1–8 times across the spectral range 200–900 nm. Quite similar patterns are noted both for ruled and holographic gratings. Since there are often several peaks in the S polarisation response these further distort the data, and then the consequences of both problems can be misinterpreted as evidence for additional luminescence bands.

In many modern luminescence experiments light is commonly delivered to the spectrometer via an optical fibre and, in general, such fibres do not preserve polarised inputs. Rather than this being a problem it might be a solution if the fibre randomises the output polarisation. If the signal that is to be analysed is selected by a polariser at the input to the fibre system then not only does one know the polarisation of the light relative to the sample, but the light transmitted by the polariser is also randomised by the time it reaches the spectrometer. Hence in all measurements one has a constant spectrometer response. With such data it is then possible to separate emission bands of different polarisations by noting the responses as a function of polariser/sample orientation. Such signal collection geometry also implies that the spectral dependence of the system need only be made with unpolarised light. Nevertheless, one must still make corrections for the wavelength sensitivity and transmission of the polariser (i.e. in the same manner as is needed for the blocking filters that remove higher order diffraction).

2.3. Grating effects in photoluminescence

One further complexity, which is strongly influenced by the polarisation dependence of the diffraction grating, occurs in photoluminescence experiments if one uses an intense broad band light source and an initial monochromator for the selection of the excitation wavelength. In spectral scans of the excitation wavelength the input is not unpolarised but steadily varies across the spectrum. Even if the excitation source is unpolarised the monochromator used to select the excitation wavelength introduces polarisation effects, so experimentally the light reaching the sample is partially polarised and this condition varies with wavelength. This is the result of mirror or optical surfaces and the diffraction grating used to select the illuminating wavelength. The grating therefore gives steadily changing polarisation content where the S/P components can alter by ~8:1 across a wide excitation range. Not only is this a source of intensity distortion but it also produces a false impression of the number of features that are present. There may similarly be conflicts in the analysis stage with a subsequent single or double monochromator analyser, since in many commercial instruments the two sections are physically coupled. Throughout materials science the normal photoluminescence strategy is to use a double monochromator for analysis to minimise the scattered primary excitation source light. Polarisation distortions occur in this analysis step and because it is a double monochromator the S/P distortion term rises to ~64:1 for the double monochromator. Correction for such equipment responses is not trivial, not least because such large dynamic effects may totally mask the presence of weaker signals, or skew our perception of the wavelength regions where signals are important.

2.4. Spectral efficiency of detectors

For some commercial systems it is possible to purchase a spectrometer package that has been individually calibrated and therefore it comes complete with a wavelength dependent correction factor. Ideally such systems should allow access to the raw collected data as well as a wavelength corrected version of it, as such systems require calibration adjustments whenever blocking filters or polarisers are added to the system. Hence access to the raw data with a separate calibration package is preferable to one where the corrections are automatically applied within the data collection system. It is not acceptable to use generic correction factors based on catalogue examples of the transmission efficiency of the spectrometer and the typical quantum efficiency of the detector. This is because it is not uncommon that replacement of components, with say nominally the same model of spectrometer or detector, can produce significant changes in the appearance of the collected spectra. Changes can be dramatic with gains, or loss, of apparent emission features. Hence a unique calibration is required for every variant of the spectrometer and detector combination. Unfortunately both components will show ageing effects. In terms of signal one also assumes that any background signals are removed before signal processing and interpretation are attempted.

2.5. Photomultiplier detectors

Photomultiplier detection of the light is convenient for higher energy photons (UV to green, from ~6 to 3 eV) as the PM photocathodes are moderately effective in terms of quantum efficiency (QE) for generating photoelectrons. The state of the art is cited in the major manufacturer's catalogues and the underlying science is noted in earlier review articles [8,9]. PM tubes operate over a very wide dynamic range and have fast time responses, and in these responses they are often preferable to CCD detectors. Nevertheless, the QE values change dramatically across the spectrum and there are large variations between individual tubes of the same generic type. Fig. 2 shows data from an early PM catalogue. For broad spectral coverage from ~200 to wavelengths near 900 nm the option is often a variant of the trialkali type photocathode (termed S20). The inset emphasises that at the longer wavelengths QE values can differ by more than 10 times for nominally very similar trialkali photocathodes. The underlying problem at the long wavelengths is that the photocathode material is transparent and so does not absorb the light. Some manufacturers have compensated for this by using thicker photocathodes, but the layer is then too thick for electron escape for photoelectrons generated by UV/blue light. The overall effect in these thick cathodes is dramatic and the QE at ~300 nm can drop to ~4% in attempts to raise the QE at 800 nm towards 10%.

Modern PM tubes may offer slightly higher QE values but they are still variable between individual detectors. There are also many
ways in which one can enhance the PM sensitivity ranging from external anti-reflective layers, which allow standard placement of the tubes, to less familiar examples of non-normal incidence of light onto the photocathode, structured surfaces and antireflective techniques within the window to photocathode layer. Overall these can improve detection of luminescence by factors of more than 2 in the blue and as much as 15 times by normal head-on illumination or redirected by using a silica prism to waveguide the light within the tube window. The “prism” guided light offers more sensitivity as the absorption is greater into the photocathode at non-normal incidence and the waveguiding offers more chances of a successful absorption interaction.

2.6. Effects of second order signal contamination

Figs. 1 and 2 both show that grating and multi-alkali PM responses often peak near 400 nm. Hence the net performance at say 400 and 800 nm may be considerably different with the grating response falling by ~10 times and the PM response by as much as ~20 times. Indeed one of our Sussex systems with an excellent trialkali photocathode showed a net sensitivity difference of ~200 times between blue and red performances. Such a variation underlines why it is critically important to remove both background dark current noise and second order diffraction. The second order problem requires blocking filters. Since this problem is ignored by some research groups it is worth considering a detailed example. We have chosen the case of a red to blue sensitivity difference of 200:1 and an overall system blue QE of 20%. For two emission bands at 400 and 800 nm with equal initial signal intensity (say 10,000 photons per collection interval) the detected photon count will be 2000 from the blue signals, but only 10 for the red. We therefore need compensating correction factors of 5 and 1000 to redress the signals to the true values. The small number of red counts also implies the final red signal will statistically be far noisier.

The problem is seriously compounded if we have failed to totally block higher order diffraction. Even if we assume that the second order diffraction of the blue signal is only 5% of the main blue peak, then at the red 800 nm setting there will be a contribution from 2nd order diffraction of the blue light which will generate 10,000 x 20% x 5% = 100 counts. This is 10 times greater than the true 800 nm peak. If we have failed to block the second order but still apply the red correction factor of 1000 times we will compute an intense false peak with an intensity of 20,000 counts. Not only will this totally overshadow any true feature but it will distort our perception of the emission spectrum.

When recording transient spectra it is inconvenient to record full spectral and filtered data sequentially. Therefore, in our own attempts to record wavelength multiplexed luminescence during thermoluminescence over a wide temperature span, and with a large dynamic intensity range, we needed to simultaneously reduce these problems. This was achieved with a pair of spectrometers, one with a UV/blue blazed grating and a blue sensitive photon imaging PM tube, and a second red blazed grating with detection by a red sensitive imaging PM tube (and a red transmitting filter to reject higher order blue signals). This design has proved very effective in terms of sensitivity, resolution and dynamic range. It has not only allowed detection of the temperature dependent spectra seen during thermoluminescence, but has also revealed a wide range of phase transitions by changes in the luminescence signals [13].

2.7. CCD spectral systems

Performance of CCD detectors has improved steadily and they offer good spectral coverage to longer wavelengths than most PM tubes. They are well suited in scale to many compact spectrometers but have weaknesses in terms of dynamic range if a spectrum has a mixture of very weak and very intense signals. Also they lack the inherent speed and detector gain of a PM tube. There are many CCD designs with differences in spectral response and, in particular, light may enter either the front surface or a specially thinned back surface of the CCD. Anti-reflective coatings can further improve performance, albeit often with interference problems in sensitivity across the spectrum. Anti-reflective coatings are widely used but the literature on their spectral performance shows considerable diversity (as indicated by manufacturers’ specification sheets), and it is therefore essential to make a spectral calibration of each package of CCD plus spectrometer,
optics and filters, etc. As in all such cases a calibrated lamp system offers a convenient route to monitor the spectral response. Overall a CCD can offer excellent sensitivity and good response from the UV to beyond 1 μm. However the response curves are rarely a monotonic function of efficiency versus wavelength. This can introduce many peak type features in uncorrected data (i.e. as initially recorded). Fig. 4 shows two examples of CCD responses. In Fig. 4 the sensitivity peaks are broadly spaced but this is not always the case. Changing detectors for nominally equivalent ones can also reveal that “identical” CCD sensors have significant differences both in terms of sensitivity and spectral response. Note that the thinning and coating methods used to enhance CCD performance can introduce thin film interference effects in the CCD response. If they are not successfully corrected for on the measured data then their presence distorts the luminescence signal and may give a false impression that the sample is generating thin film type oscillations in the signal.

Genuine thin film interference effects that produce intensity oscillations across the spectrum occur in many luminescence samples. For example oxide films on silicon that have been modified or doped to act as semiconductor light sources show such features (in addition to raw data oscillations from thinned CCD detectors). The signals generated in thin films will differ from those of the detectors as they tend to be equally spaced in wavelength and cover the entire spectral range. Therefore one can often separate the sample interference problems from the detector ones. Fig. 5 shows data obtained during excitation of an alumina film on a silica substrate. The thin film effects occur across the entire recorded spectral range and their spacing alters with the film thickness [14].

2.8. Overall system calibration

Calibration of spectrometer systems is not trivial [1,2]. Ideally one requires a light source at the sample position which has a known and reproducible emission spectrum. The recorded signal response across the spectrum can then be used as a monitor of the spectral response of the entire system. Calibrated light sources that quote radiance values as a function of wavelength are commercially available and for any systematic and quantitative data these are essential. Despite the long history of such measurements it is still a topic of current research [1,2,15]. However, within this caveat one can achieve a reasonable set of correction curves for the spectral responses of the system (including polarisation). For fluorometry type applications detailed prescriptions are offered to not only improve the calibration in terms of relative system efficiency, but even to approach absolute intensity data [1,2]. This has been achieved by using reference sources with traceable intensity calibrations and/or reference samples that are compared in all laboratories undertaking related measurements. Nevertheless it is to be noted that components and detector responses alter with time and ambient conditions.

2.9. Unexpected experimental errors in intensity measurements

One normally assumes that recording luminescence signals is a passive process and indeed in some cases this is correct, but in other situations the act of sample stimulation can noticeably modify the intensity and emission spectra. Whilst the perturbations are not experimental errors they are features that run across the range of materials science applications which employ luminescence data and so some examples will be briefly cited here. For example, with ion beam excited luminescence (IL) there will always be some radiation damage generated and so every sample is changing with beam exposure as new defect sites are formed, and there are rearrangements into new defect complexes and charges are transferred between sites. These effects modify the intensity and spectra and associated excited state lifetimes of the processes. Therefore one tries to minimise the radiation dose and acquire the spectra with minimal damage and redistribution of charge between the various emission sites. Ion beams are an extreme example as they have the interaction energy needed to damage the structure but for insulators there is also a possibility that electrons, X-rays or even light can introduce new defect sites and/or relocate the electron distributions between existing defects and impurities. On the positive side the luminescence spectroscopy offers insights into these dynamic processes and probe techniques may include simultaneous combinations of excitation methods to follow transient events [16].

A second type of problem arises when the detector sensitivity is modified by incoming signals. This fact is rarely discussed but one such example exists with the red sensitive S20 type PM tubes when used with a scanning monochromator, as exposure to high photon energy UV light can enhance the sensitivity for subsequently detecting long wavelength red signals (enhancements as large as six times have been noted). Hence spectra scanned in different wavelength directions may appear to differ. PM sensitivity may also differ as the result of exposure to different light intensities and both the S20 and S1 (red and near infrared sensitive) photocathodes can display such effects e.g. [8,9].
3. Potential errors in signal processing and spectral deconvolution

The intrinsic shapes of luminescence emission bands are variously Lorentzian or Gaussian when displayed in terms of photon electron energy. This matches the early discussions [17–21] of transitions between parabolic ground and excited states of electrons at imperfections in insulating materials using the standard configurational co-ordinate diagram description. (Note that more structured spectra also exist in the case of emission centres with zero phonon type features.) Nevertheless, rather than recording data in terms of photon energy the data obtained from the grating spectrometer systems are dispersed in terms of wavelength (\(\lambda\)), and are collected with a fixed slit, so the signals are recorded with a fixed wavelength band width (\(d\lambda\)). The first stage after data acquisition is to process the signals to compensate for the spectral efficiency of the collection system (i.e. to account for background signals, filters, polarisers, grating and detector distortions etc.). Ideally this provides the true values of wavelength dispersed luminescence signals.

For many applications and research activities this is the signal which is considered (e.g. fluorometry [1,2,15]) and considerable experimental care is taken to quantify these wavelength spectra for subsequent discussion and applications. Inter-comparisons of emission spectra in terms of wavelength are equally valuable for initial research studies throughout the field of luminescence spectroscopy. However to proceed to more quantitative materials science one requires the data be transformed into the energy domain (i.e. from wavelength (\(\lambda\)) signals of \(I(\lambda)d\lambda\) versus \(\lambda\) to the energy view of \(I(E)dE\) versus \(E\)) as only from this viewpoint can one make deconvolution of the signals into their components. In theoretical modelling of the underlying science the predictions will normally be presented in terms of the energy picture.

Unfortunately, because of the universal appeal of luminescence data, many users are expert in their specific disciplines, but follow historical precedents on both band deconvolution and the wavelength to energy conversions, which are often incorrect. Rather than cite specific papers one can summarise the typical consequences. These are (i) that even the peak position of a single emission band (in wavelength terms) differs from the wavelength equivalent value of the energy plot and (ii) one cannot correctly use a curve fitting programme to deconvolute the data into component features.

The reason for these difficulties is that in the transformation from wavelength (\(\lambda\)) signals (\(I(\lambda)d\lambda\) versus \(\lambda\)) into the energy plot (\(I(E)dE\) versus \(E\)) the transformation of the wavelength axis into terms of energy is obvious (i.e. using \(E=hc/\lambda\)). However for the intensity axis a correct transformation requires the intensity correction from wavelength to energy units of \((I(E)\ dE)\). The change from the fixed wavelength bandwidth to a fixed energy bandwidth is related by \(dE=-hc/\lambda^2\ d\lambda\). Particularly for broader luminescence features the \((1/\lambda^2)\) term has a major distortion effect on the curve shapes.

3.1. Apparent differences in peak positions of wavelength and energy data

To emphasise the inherent problems Figs. 6 and 7 display examples of the same idealised luminescence signals but from the different viewpoints of the energy and wavelength domains. The energy plots are for Gaussian shaped emission bands and different full width half maximum (FWHM) values are contrasted. In all cases when such Gaussian features are transformed to the wavelength views the wavelength bands are asymmetric with extended tails at longer wavelengths. The influence of the \((1/\lambda^2)\) term is more obvious wider bands which are centred at lower photon

![Fig. 6. Energy and wavelength plots of a Gaussian shaped energy band centred at 4.75 eV but with different values of full width half maximum.](image)

![Fig. 7. Energy and wavelength plots of a Gaussian shaped energy band centred at 2.0 eV but with different values of full width half maximum.](image)
energies. The example Fig. 6 displays values for a UV band centred at 4.75 eV (equivalent to a true peak wavelength of 261 nm) but the wavelength views of the data have intensity maxima which vary with wavelength as a function of the FWHM. The problem is emphasised by the choice of large FWHM values. The problem is not uniform across the spectrum and it is even more obvious in the case of longer wavelength signals, as shown in Fig. 7 for an orange band at 2.0 eV (with a wavelength equivalent value of 620 nm).

In both these examples it is apparent that for wider bands the wavelength “peak” is shifted relative to the original energy value; the wavelength domain band shapes are very asymmetric. The literature widely cites the peak in the wavelength recorded spectra in terms of nanometres and frequently attributes to this an energy in eV which is implied to mean the peak intensity of the emission feature. As seen in these figures this is obviously inaccurate for wider emission bands, but in practical terms (especially with wider band width entrance slits) the error is relatively minor for emission features with an FWHM less than say 0.25 eV. Table 2 indicates the scale of errors for four emission bands within the visible spectrum with FWHM values of 0.65 eV.

This is a signal distortion which is rarely mentioned. In part this is because in spectral calibrations with laser lines or line spectra the band widths are so small that no errors are apparent, as they may be less than the wavelength bandwidths used in the measurement. We therefore tend to forget that such errors can exist. Luminescence bandwidths vary considerably from the very narrow line emissions seen with rare earth transitions to normal defect and impurity bandwidths of maybe 0.2–0.5 eV, to examples in excess of 1.5 eV (absorption band data do not have this experimental problem and are generally slightly narrower.). For narrow luminescence bands in the UV the misreading of peak positions from wavelength data is relatively minor, but for broader features at long wavelengths (e.g. for say iron impurity bands recorded near 800 nm in many minerals and other insulators) the error in wavelength assignment could be as much as ~100 nm relative to the value seen in the energy plots of the data. With a mixture of narrow and broad bands, even the sequence along the wavelength axis may be misinterpreted.

One of the hidden problems with the wavelength peak assignments is that the values are often quoted in terms of electron energy so as to be consistent with other references, and subsequently it is rarely obvious whether system corrections have been applied and the true energy values are cited. This is unfortunate as one of the strengths of luminescence spectroscopy is that it is responsive to small differences in the lattice environments and distortions of the emission sites, both from short and long range interactions. These shifts are typically on the same scale as the differences between the energy quoted based on the wavelength spectra (Eₜₐₜ) and the true energy plot values obtained where intensity transformations were made (Etrue). Distortions, impurity content and long range interactions are precisely the key features of interest in many applications. The entire literature of site selective spectroscopy underlines how even for rare earth ions there are wavelength shifts in absorption and emission that are the result in local crystal fields around the rare earth ion e.g. [3–5]. These offer a sophisticated probe of the local distortions. A classic example of lattice distortions and charge separation for electron–hole pairs was discussed by Hayes and Stoneham [22] in which the sets of excitonic energy levels giving luminescence varied with the separation of the electron and hole sites. The line sets were measurably distinct to more than 50 atomic shells around the core of the defect and agreed with theoretical computations. A more familiar mineralogical example shows the manganese emission bands in the calcium carbonate lattice scale in wavelength with the lattice parameter of the various CaCO₃ isomorphs [23]. Spectral shifts span ~50 nm for the various Mn–O distances found in different carbonates. In quartz and silicate examples the intrinsic emission bands (e.g. from oxygen vacancy type sites) are also sensitive to impurities and, because many impurities associated as immediate neighbours with the vacancies the emission band shifts are pronounced [24,25]. For example the vacancy type emission band moves from ~370 to 450 nm for samples ranging from ultra-pure to H, Ge or Al contaminated samples. Other reviews summarise similar shifts in luminescence wavelength with distortions and defect complexes for many materials e.g. [26]. The information is valuable in modelling the defect sites and so it is essential to be sure whether one is comparing Eₜₐₜ or Etrue values.

An example of the uncertainty for this problem is typified by a review of emission bands from silicon dioxide polymorphs [27] where nearly 40 peaks are cited from different research groups within the range of 1.65–4.5 eV (nominally 750–275 nm). One suspects that many of the minor differences are experimental or data processing artefacts. A similar diversity of peak positions exists in the luminescence literature ranging through that of many minerals, to thin films and nanoparticles on silicon.

### Table 2

Table 2 Differences in the position of maxima between energy and wavelength data for visible emission bands that have an FWHM value of 0.65 eV.

<table>
<thead>
<tr>
<th>Energy plots, peak values</th>
<th>Wavelength plots, peak values</th>
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</tr>
</thead>
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<td>nm</td>
<td>eV</td>
</tr>
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<td>500</td>
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</tr>
<tr>
<td>1.77</td>
<td>700</td>
<td>1.839</td>
</tr>
</tbody>
</table>

3.2. Deconvolution of component signals

Because of the sensitivity of luminescence measurements most samples show a number of emission features and the experimental challenge is to record them, correct for the spectral sensitivity of the collection apparatus, and then transform them to an energy presentation in order to attempt deconvolution. To demonstrate the various steps and the influence of the corrections and transformations we have considered an idealised set of 4 Gaussian shaped emission bands of equal intensity that are incident on the system. The 4 bands are spaced across the spectrum each with an FWHM of ~0.7 eV, as shown in Fig. 8a for the energy view, and Fig. 8b for the wavelength transformed view of the signal.

The diffraction grating conversion to a wavelength axis, with a fixed d/λ bandwidth, emphasises the UV components and spreads the longer wavelength signals, so our impression is that the UV signals are dominant. As a next step we can now introduce the signal distortions imposed by the grating and detector. These will be specific to the chosen pair. We are using a grating response as sketched in Fig. 1a, multiplied by the response of a standard normal S20 PM tube (Fig. 3) and this gives a delivered signal approximating to the view shown in Fig. 8c. This same pattern would be noted either with a monochromator and PM tube or a spectrometer and a photon imaging detector of the S20 photocathode type. Very different output signals are recorded if we have instead used CCD detectors and Fig. 8d gives the examples for detectors of responses such as those of Fig. 4. The figures have been normalised to the same maximum intensity.

At this stage the four original bands are still apparent but in different intensity ratios; however they are not centred at exactly the same values and, as a result of fluctuations in the detector responses, there are shoulders and other features which one will
be tempted to interpret as evidence for additional emission bands. It is therefore unwise and misleading to consider raw data spectra, but instead one should always use views of the spectra after they have been corrected for all the factors of the system response. The corrections for the system response produce the intensity pattern in terms of wavelength for a fixed wavelength bandwidth. For some applications e.g. [1,2] this view of the data may be sufficient; however for a deeper insight into the relative intensities of the component features it is necessary to make a transformation into the energy format. The latter needs both \(x\) and \(y\) axes transformations and so moves to the fixed energy bandwidth which introduces the \(1/\lambda^2 \text{d}\lambda\) that enhances the long wavelength signals and generates symmetric emission bands. Unfortunately many authors only convert the \(x\) axis so the spectra are distorted and unsuitable for deconvolution. The problem is highlighted in Fig. 9 which shows a pair of Gaussian energy bands, their wavelength transformation and an incorrect wavelength to energy conversions where only the energy axis was processed. As expected, the incorrect processing has minimised the intensity of the low photon energies of the red signal, and also distorted both peaks. Consequently any attempts to use a Gaussian fit programme will generate incorrect positions, band widths and additional false minor peaks. These are precisely the same type of error involved by those who attempt curve fitting on the wavelength data. Unfortunately both mistakes are widely made.

4. Final comments on corrections and sources of error

The preceding article has focussed on the need to make accurate calibrations for all luminescence data and in particular to recognise that this is done to varying degrees between different applications in materials science. The methods of excitation include photo-, cathode-, electron, X-ray or ion beam luminescence and this situation applies to all such data. There are other experimental pitfalls with each of the techniques but they are not discussed here. Instead our aim is to encourage correction of the system responses and manipulation of the data so that modelling and deconvolution of overlapping features can be compared. One present problem is that there is no uniformity in defining peak positions and many articles do not specify if they are citing \(E_{\text{peak}}\) or...
E. This seriously undermines the conclusions that can be drawn and adds confusion when comparing data from different sources.

In some sense this situation is worse than that which exists in the related topic of radiation dosimetry, where the entire community tends to discuss the intensity peaks in terms of the experimentally measured temperature of the heater, rather than the actual temperature of the sample. The two values are significantly different but purely for dosimetry this is not a problem (hence the continued acceptance of a systematic error). For the deeper level of scientific analysis it is critical and the associated corrections have been presented by many authors [28–31].

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References