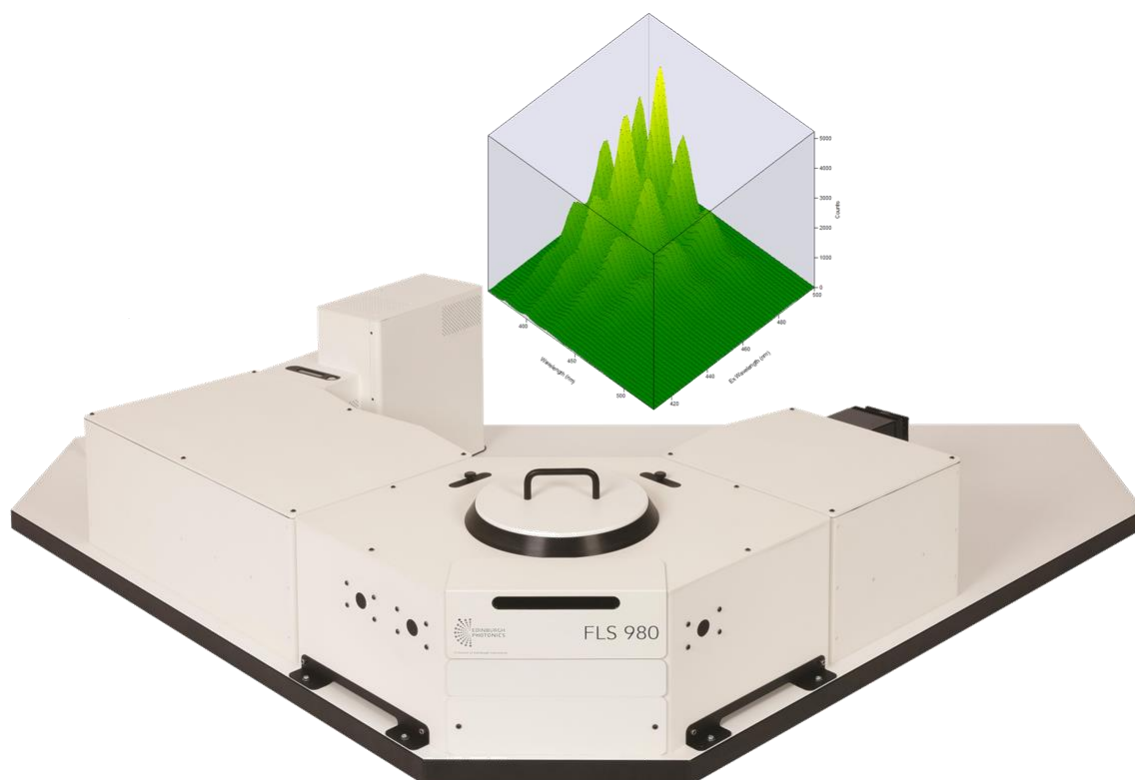


Excitation-Emission Spectroscopy with CCDs and Array Detectors

Maria Tesa, Georgios Arnaoutakis

AN_P36 v.3

July 2016



Edinburgh Instruments Ltd
2 Bain Square,
Kirkton Campus,
Livingston, United Kingdom
EH54 7DQ

Telephone (UK)
+44 (0)1506 425 300
Telephone (North America)
1-800-323-6115

Email
enquiries@edinst.com
Website
www.edinst.com

Introduction

Excitation-emission spectroscopy becomes increasingly useful in the study of photo-luminescent materials. The spectral selectivity of the technique enables the quantification of multiple emitting sites in rare-earth doped crystals¹⁻³ as well as the rapid acquisition of polycyclic aromatic hydrocarbons (PAH) in contaminated water.^{4,5} In order to obtain a complete spectral fingerprint via excitation-emission spectroscopy, scans at multiple excitation wavelengths over the emission spectra are required. Especially in the case of rare-earth materials with narrow emission linewidths, this is extremely demanding in terms of resolution. The acquisition time of such excitation-emission maps (EEM) can be significantly reduced by using Charge Coupled Device (CCD) detectors.

A CCD detector contains an array of photo-sensors which enables the detection of light with spatial resolution. CCD detectors for the visible and NIR range can be integrated into the Edinburgh Instruments range of fluorescence spectrometers. Consequently, multiple wavelengths are recorded simultaneously with this approach, so that an entire emission spectrum can be acquired in a single shot. Measurements such as excitation-emission maps are therefore much faster with a CCD compared to standard photomultiplier tube (PMT) detectors. In addition, this enables the acquisition of highly resolved excitation emission maps in a rapid manner compared to traditional PMT detectors used in spectroscopy, as will be outlined in this application note.

Experimental setup

In an FLS980 Fluorescence Spectrometer configured for CCD or array detection, a single emission monochromator is used as a spectrograph that directs the emission from the sample to the input window of the detector.

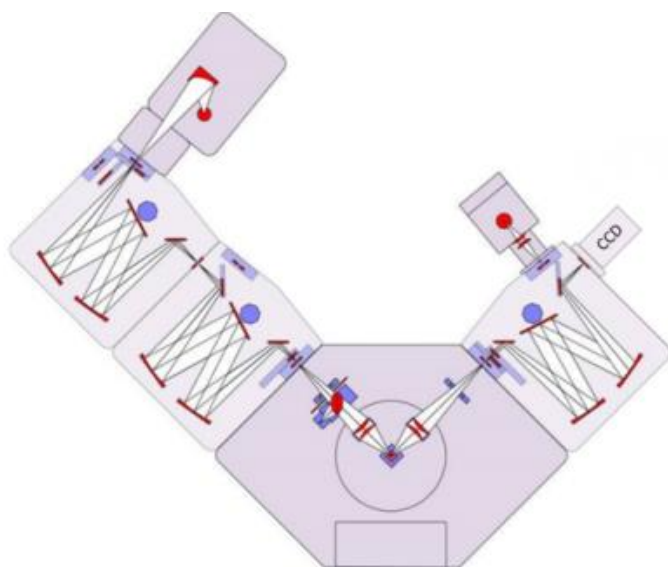


Figure 1: FLS980 fluorescence spectrometer configured with CCD detection. The instrument incorporates a Xe excitation lamp, double excitation monochromator, and single emission monochromator with a PMT and a CCD detector.

The monochromator has one port with a computer-controlled slit for PMT detection, and a second imaging port with a wide aperture for the CCD or array (Figure 1). When acquiring spectral data with the CCD camera, the monochromator is set to the centre wavelength of the emission spectrum.

Results - Discussion

In the following Figures 2-4, excitation-emission maps acquired with CCD detectors are shown. Both visible and near-infrared (NIR) detectors based on InGaAs arrays are fully controlled from the spectrometer's software, F980. The software allows the user to display the data as 2D, contour maps and 3D plots.

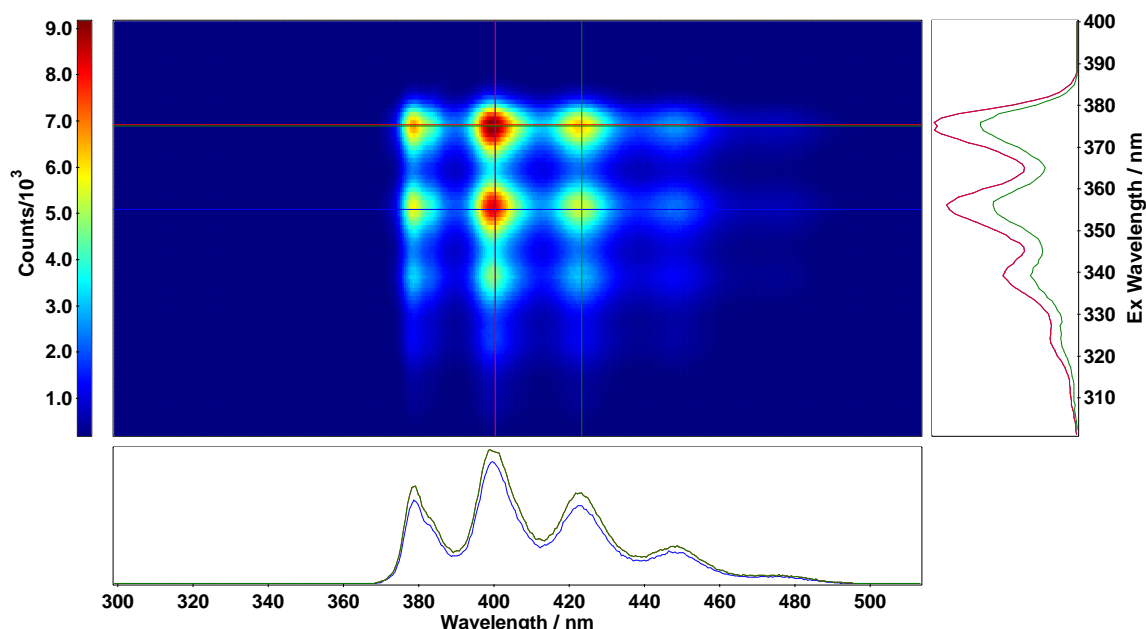


Figure 2: Excitation-emission map of anthracene in cyclohexane acquired with a visible CCD camera (1024x255 pixels, 26x26 μm pixel size) cooled down to $-40\text{ }^{\circ}\text{C}$. Measurement conditions: $\Delta\lambda_{\text{ex}}=5\text{nm}$, $\text{step}_{\text{exc}}=1.00\text{nm}$, $\lambda_{\text{em}}=500\text{nm}$, $\Delta\lambda_{\text{em}}=1\text{nm}$, $\text{step}_{\text{em}}=0.553\text{nm}$, $t_{\text{int}}=0.5\text{s}$, $t_{\text{acq}}=15\text{min}$. The cross sections correspond to blue: $\lambda_{\text{exc}}/\lambda_{\text{em}}=355\text{nm}/400\text{nm}$, red: $\lambda_{\text{exc}}/\lambda_{\text{em}}=375\text{nm}/400\text{nm}$ and green: $\lambda_{\text{exc}}/\lambda_{\text{em}}=375\text{nm}/423\text{nm}$.

Room temperature emission from the $^5\text{D}_4$ level to $^7\text{F}_5$ and $^7\text{F}_3$ levels of Tb^{3+} resulting in strong green emission are displayed in the EEM of $\text{LaPO}_4: \text{Ce}, \text{Tb}$ of Figure 3. To obtain a map with this resolution an acquisition time of 58 min was required, compared to 90 h needed when a PMT is used. Estimated acquisition times for EEM of anthracene and Nd: YAG with a PMT were 15 h and 2 h, respectively.

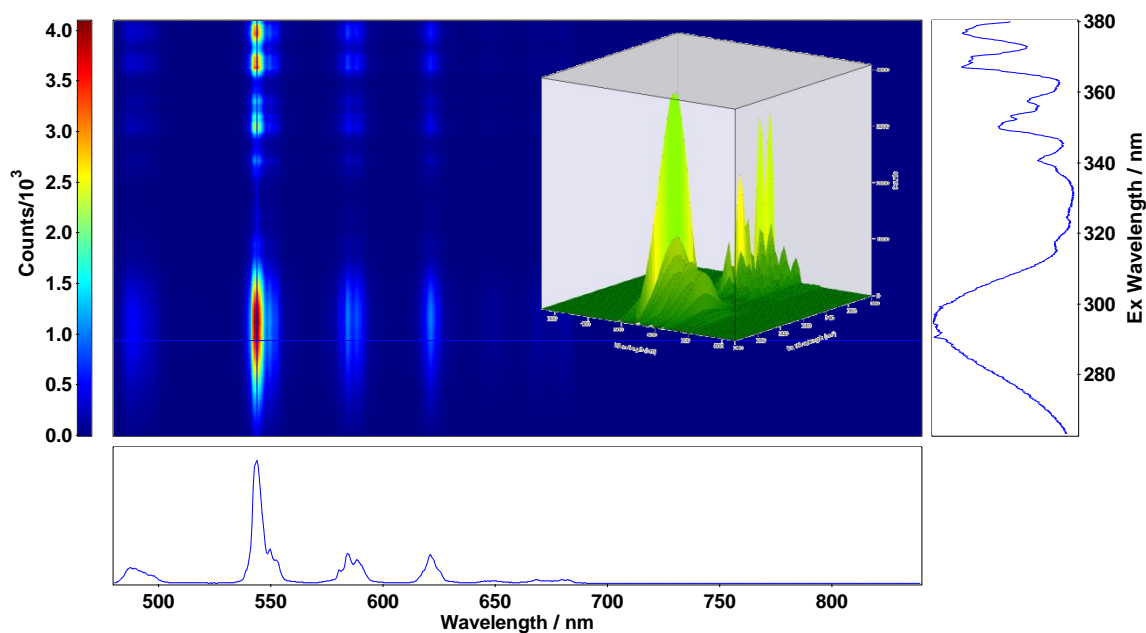


Figure 3: Excitation-emission map of LaPO₄: Ce,Tb acquired with a visible CCD camera (1024x255 pixels, 26x26 μm pixel size) cooled down to -70°C. Measurement conditions: $\Delta\lambda_{\text{ex}}=0.50\text{nm}$, $\text{step}_{\text{exc}}=0.20\text{nm}$, $\lambda_{\text{em}}=550\text{nm}$, $\Delta\lambda_{\text{em}}=0.3\text{nm}$, $\text{step}_{\text{em}}=0.568\text{nm}$, $t_{\text{int}}=0.5\text{s}$, $t_{\text{acq}}=58\text{min}$. The cross section is at $\lambda_{\text{exc}}/\lambda_{\text{em}}=290\text{nm}/544\text{nm}$ and a 3D map is shown in the inset.

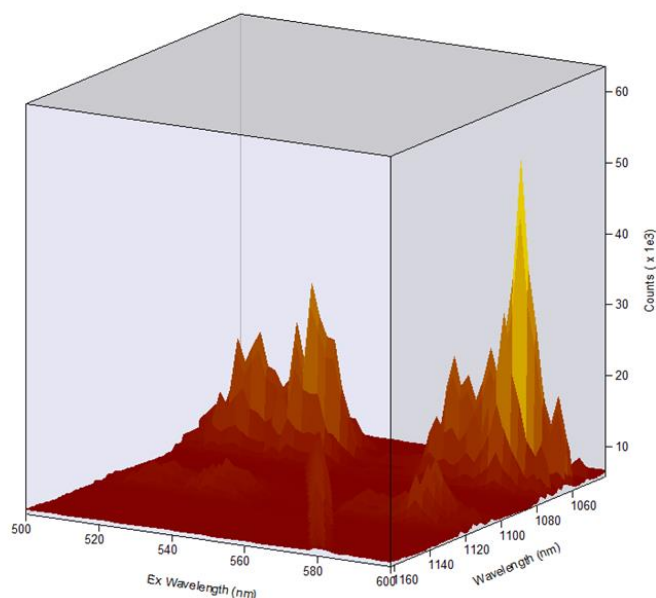


Figure 4: Excitation-emission 3D map of Nd:YAG acquired with a 1.7 μm InGaAs array detector (1024 pixels) cooled down to -70 °C. Measurement conditions: $\Delta\lambda_{\text{ex}}=0.50\text{ nm}$, $\text{step}_{\text{exc}}=2\text{nm}$, $\lambda_{\text{em}}=1100\text{nm}$, $\Delta\lambda_{\text{em}}=0.5\text{nm}$, $\text{step}_{\text{em}}=0.118\text{nm}$, $t_{\text{int}}=0.5\text{s}$, $t_{\text{acq}}=10\text{min}$.

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