APPLICATION NOTE

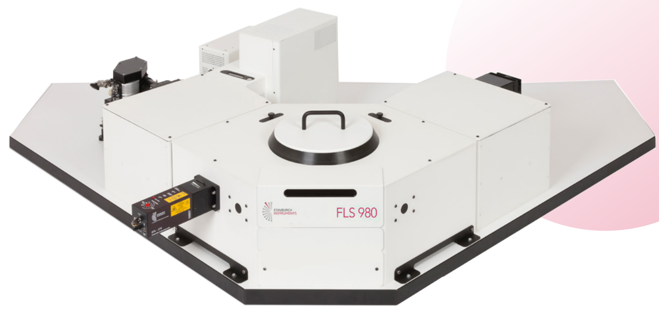
EXCITATION-EMISSION SPECTROSCOPY WITH CHARGE COUPLED DETECTORS

AN_P36 v.2; Jul. 16, Maria Tesa, Georgios Arnaoutakis,

EDINBURGH INSTRUMENTS

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 crystals[1–3] 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 detection, a single emission monochromator is used as a spectrograph that directs the emission from the sample to the input window of the CCD camera. 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 (Figure 1). When acquiring spectral data with the CCD camera, the monochromator is set to the centre wavelength of the emission spectrum.

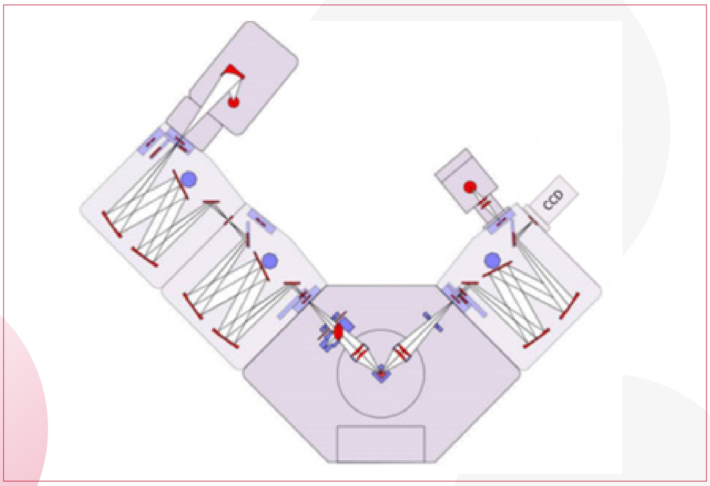


Figure 1: FLS980 fluorescence spectrometer configured with CCD detection. The instrument incorporates a Xe excitation lamp, double excitation monochromator, and single emission monochromator with a PMT and a CCD detector.

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.

Room temperature emission from the 5D4 level to 7F5 and 7F3 levels of Tb^{3+} resulting in strong green emission are displayed in the EEM of LaPO4: Ce, 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.

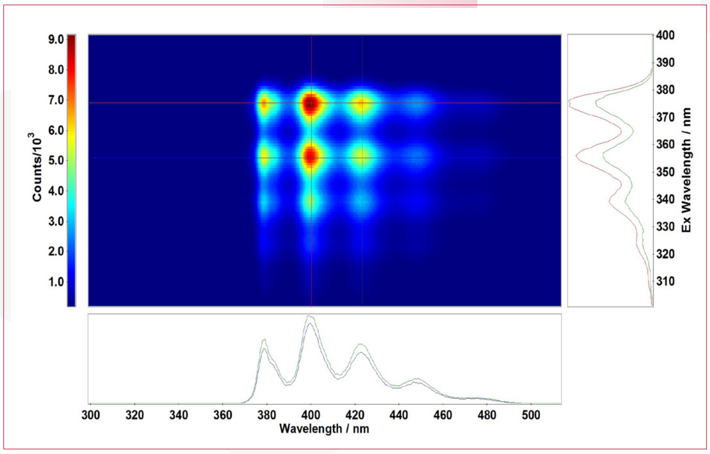


Figure 2: Excitation-emission map of anthracene in cyclohexane acquired with an iDus DU420A camera cooled down to -40 °C. Measurement conditions: $\Delta\lambda_{ex}$=5 nm, $step_{exc}$=1.00 nm, λ_{em}=500 nm, $\Delta\lambda_{em}$=1 nm $step_{em}$=0.553 nm, t_{int}=0.5s, t_{acq}=15min. The cross sections correspond to blue: $\lambda_{exc}/\lambda_{em}$=355 nm/400 nm, red: $\lambda_{exc}/\lambda em$=375 nm/400 nm and green: $\lambda_{exc}/\lambda_{em}$=375 nm/423 nm.

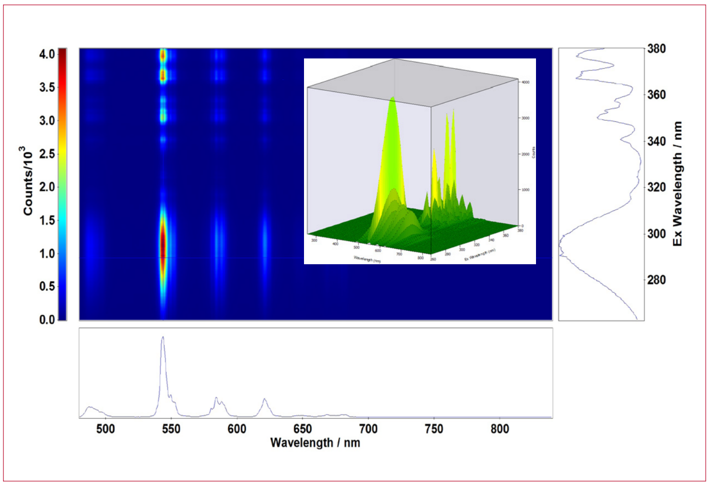


Figure 3: *Excitation-emission map of $LaPO_4$: Ce,Tb acquired with an iDus DU420A camera cooled down to -70°C. Measurement conditions: $\Delta\lambda_{ex}$=0.50 nm, $step_{exc}$=0.20 nm, λ_{em}=550 nm, $\Delta\lambda_{em}$=0.3 nm, $step_{em}$=0.568 nm, t_{int}=0.5s. t_{acq}=58min. The cross section is at $\lambda_{exc}/\lambda_{em}$=290 nm/544 nm and a 3D map is shown in the inset.*

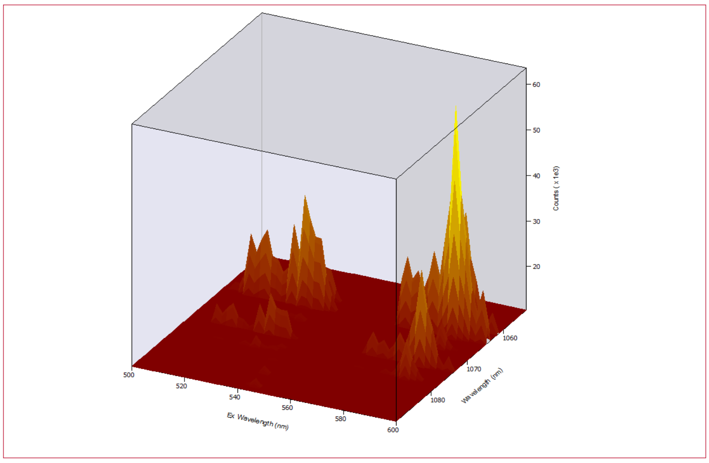


Figure 4: *Excitation-emission 3D map of Nd: YAG acquired with an iDus DU491-A 1.7 camera cooled down to -70 °C. Measurement conditions: $\Delta\lambda_{ex}$=0.50 nm, $step_{exc}$=2 nm, λ_{em}=1100 nm, $\Delta\lambda_{em}$=0.5 nm, $step_{em}$=0.118 nm,*

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For more information, contact:

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

T: +44 (0)1506 425 300
F: +44 (0)1506 425 320

E: sales@edinst.com
W: www.edinst.com