HORIBA Scientific

Detection of Explosives with Fluorescence

FL-21

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Introduction

International terrorism, security concerns, and the remains of forgotten landmines throughout the world have increased interest in detection of explosive materials. Most mines contain TNT (2,4,6-trinitrotoluene). Many techniques for detecting explosives detection assume that landmines are encased in metal. Other techniques require expensive instruments or can be unreliable. The best methods for plastic mines involve detection of vapors escaping from landmines. These gases are impurities or degradation products, e.g., 2,4-dinitrotoluene, which are more volatile than TNT.

Nitroaromatic explosive compounds have weak fluorescence, because of high intersystem crossing causing radiationless decay. Thus these compounds need to be converted into fluorescent materials to be detected via fluorescence spectroscopy.[1] A group of scientists at the University of Idaho, including Dr. C.M. Wai, his Scientific Assistant, Delyle Eastwood, and his graduate student Chrystal Sheaff, have been researching effective fluorescence detection of such explosive compounds when they are reduced to aromatic amines via Pd-nanoparticle catalysis, and combined with the fluorescent compound fluorescamine.[2]

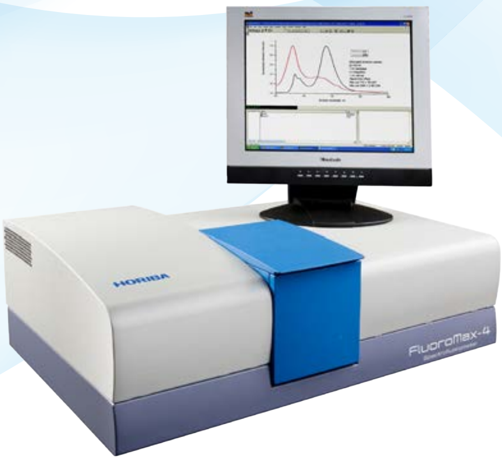

Fig. 1. FluoroMax®-4 benchtop spectrofluorometer.

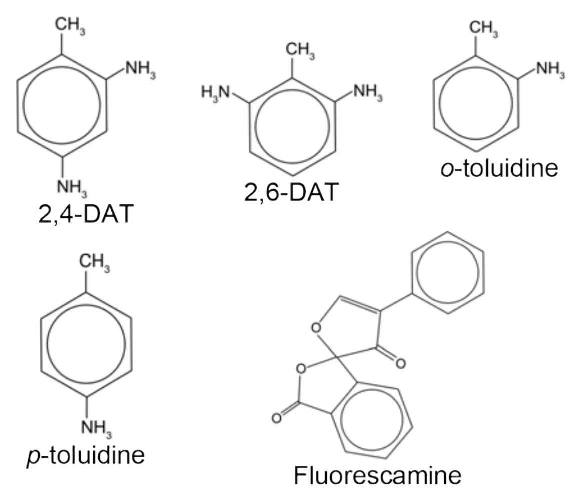

Fig. 2. Molecular structures of reagents used.

Experimental procedure

A FluoroMax® spectrofluorometer (Fig. 1) containing a 150 W Xe lamp, controlled by our FluorEssence™ software, was used. Increments were 1 nm, with bandpasses of 3 to 10 nm as noted in the data. Pure ethanol was the solvent

[1] G. G. Guilbault, Ed., *Practical Fluorescence* (Marcel Dekker, New York, 1990), 2nd ed., rev. and expanded, pp. 99–100.

[2] D. Eastwood, et al., *Appl. Spectroscopy*, **60**(9), 2006, 958–963; C.N. Sheaff, et al., *Appl. Spectroscopy*, **61**(1), 2007, 68–73.

JOBIN YVON Technology

for all compounds, which themselves were the highest purity commercially available. Compounds examined were 2,4-diaminotoluene (2,4-DAT), 2,6- diaminotoluene (2,6-DAT), o-toluidine, and *p*-toluidine. Fluorescamine (98%) was used to create nitroaromatic derivatives. (See Fig. 2.) Derivatives' purities were checked by thin-layer chromatography and ^{1}H-NMR. Concentrations down to 10^{-12} *M* were reached in ethanol. Solutions were stored in amber glass containers wrapped in aluminum foil to protect against photodecom-position.

Results and discussion

An example of the FluoroMax®'s sensitivity to a nitroaromatic compound attached to fluorescamine is shown in Fig. 3, with a detection limit of 10^{-12} *M* 2,4-DAT.

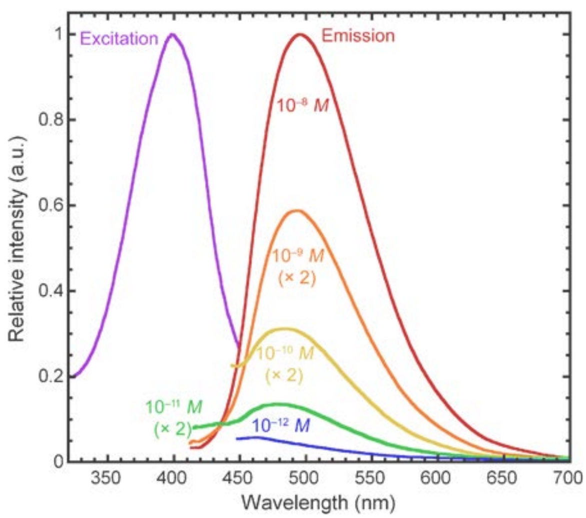

Fig. 3. Excitation and emission spectra of 2,4- DAT + fluorescamine at various dilutions, blank-subtracted, and all bandpasses = 10 nm.

Synchronous scans, in which the excitation and emission monochromators are simultaneously scanned, keep a constant interval (offset) between the two monochromators. Synchronous spectra were measured at a 9 nm offset with bandpasses = 3 nm and integration time = 1 s. A comparison of excitation, emission, and synchronous scans is shown in Fig. 4. The top plot shows how similar all the emission scans are for four different compounds. Note the much narrower peak for the synchronous scan of 2,4-DAT compared with its excitation and emission scans.

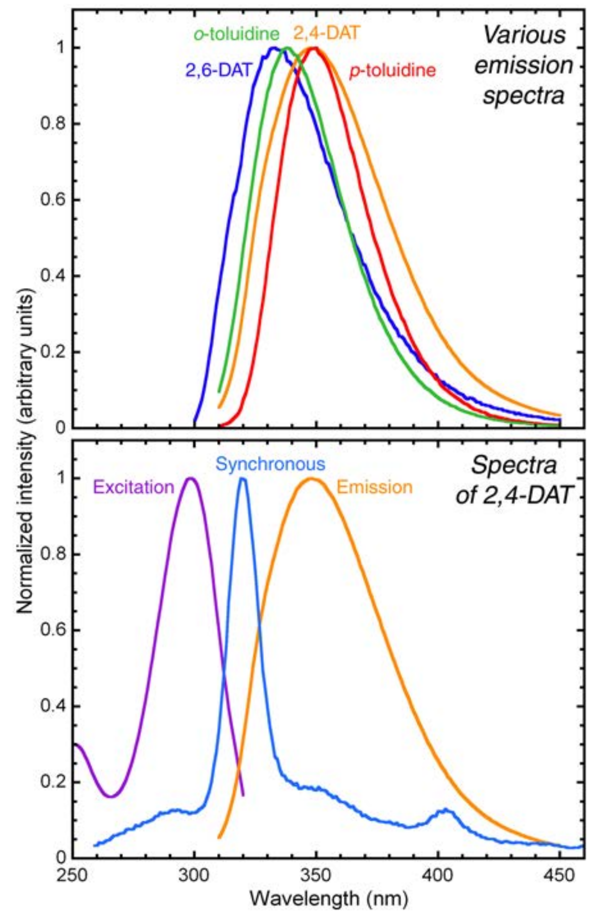

Fig. 4. (Top) Emission spectra of 4 × 10^{-4} *M* 2,6- DAT, 4 × 10^{-5} *M* 2,4-DAT, 4 × 10^{-5} *M* *o*-toluidine, and 4 × 10^{-5} *M* *p*-toluidine. (Bottom) Comparison of excitation, synchronous, and emission spectra of 4 × 10^{-5} *M* 2,4-DAT. All spectra are blank-subtracted in EtOH, with 3 nm bandpass.

Similar emission, excitation, and synchronous spectra were taken of several decomposition products of TNT. Results are shown in Table 1. Notice how even the peaks scanned with synchronous monochromators, while narrower and distinguishable, are still very similar in wavelength.

Compound	Excitation peak, FWHM (nm)	Emission peak, FWHM (nm)	Synchronous peak, FWHM (nm)
2,6-DAT	287, 27	335, 51	309, 10
o-toluidine	282, 32	340, 49	314, 16
2,4-DAT	290, 39	350, 50	319, 14
p-toluidine	285, 42	349, 50	325, 15

Table 1. Peak values with full-widths at half-maximum from emission, excitation, and synchronous scans of TNT-decomposition products.

Therefore, to further enhance sensitivity and selectivity to specific compounds in explosives, second derivatives were applied to the spectra. Among the mathematical functions included with our exclusive Origin®- based FluorEssence™ software are Savitzky-Golay smoothing and derivative calculations by averaging slopes between two adjacent data points. Professor Wai and coworkers found that five-point smoothing gave the best resolution with second derivatives. An example of a four-componentmixture of 2,6-DAT, *o*-toluidine, 2,4- DAT, and *p*-toluidine in ethanol with concentrations in the 10^{-5} *M* range is shown in Fig. 5. (These were found to have detection limits via synchronous scanning of 2.6×10^{-6} *M*, 2.3×10^{-6} *M*, 6.7×10^{-7} *M*, and 1.7×10^{-7} *M*, respectively.) While the synchronous spectrum (upper plot) has only a single visible peak, the second derivative (lower curve) reveals the presence of each component clearly.

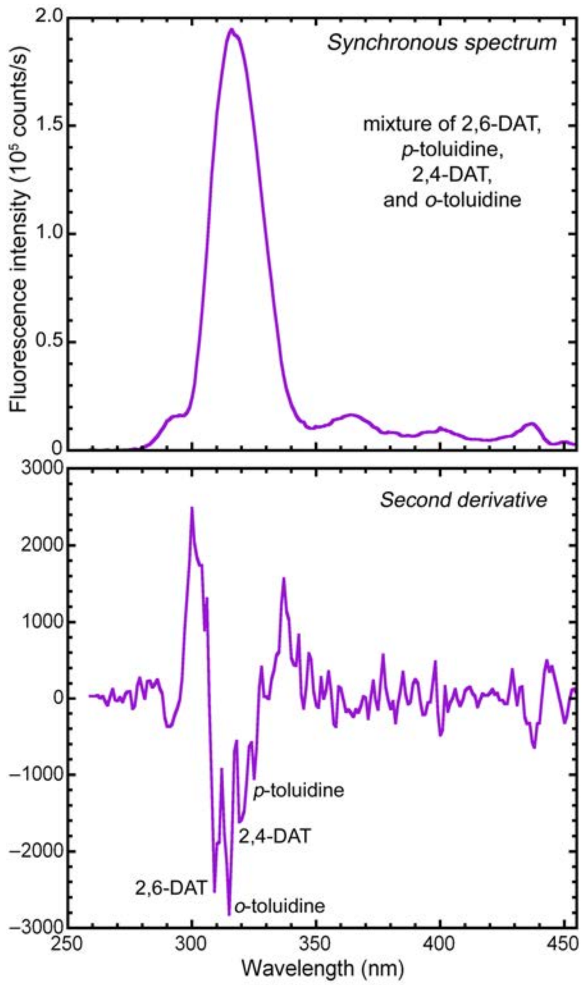

Fig. 5. (Top) Synchronous spectrum of a mixture of 2,6-DAT (4 x 10^{-5} *M*), *o*-toluidine (1 x 10^{-5} *M*), 2,4-DAT (2 x 10^{-5} *M*), and *p*-toluidine (1 x 10^{-5} *M*) in EtOH; bandpasses = 3 nm, blank-subtracted, integration time = 1 s. (Bottom) Second derivative of the top graph, with components identified at 309, 314, 319, and 325 nm.

Conclusions

Professor Wai's research is the first to show that synchronous scanning plus the second derivative can distinguish among four likely reduction products in a TNT-based explosive mixture. Synchronous scanning itself has advantages over other identification methods, because it is rapid, sensitive, and selective. Taking the second derivative helps, in addition, to distinguish various products whose spectra overlap. The use of an agent (fluorescamine, in this case) to form a derivative compound reaches a lower limit of detection. HORIBA Jobin Yvon spectrofluorometers are capable of recording and analyzing weak fluorescence such as that presented here.

Acknowledgments

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