Chapter 1

Applications of Luminescence to Fingerprints and Trace Explosives Detection

Prof. Ismail Mekkaoui Alaoui
Department of Physics, Faculty of Sciences Semlalia
Cadi Ayyad University
BP. 2390 Marrakech 40000, Morocco.
E. mail: mekkaoui@ucam.ac.ma

Abstract Fingerprints and trace explosives detection requires great sensitivity, which is provided by luminescence and appropriate physical and chemical treatments. Ninhydrin, 1,2-indanedione and other chemicals react with the amino acids present in the fingerprint residue. The chemically treated samples, on which the prints are to be detected, are excited with the blue lines 476.5 and 488 nm of an Argon laser, and the sample's fluorescence is observed under orange filters. The detection of common explosives including trinitrotoluene (TNT) may also be carried out using luminescence techniques. Trace explosive and fingerprint detection require sensitivity due to the minute amount of matter left and available on the samples to be detected. Detection sensitivity can be gained by taking advantage of luminescence techniques. To increase the sensitivity of such detection luminescent chemicals are used, and to distinguish among compounds in a mixture of explosives, time-resolved imaging techniques may suppress any unwanted and background luminescence. Explosives are tagged with europium complexes showing long lived luminescence (3 ms) and appropriate for time-resolved imaging. The europium luminescence excitation utilizes a laser operating at 355 nm. Comparison between photoluminescence fingerprints and trace explosives detection will be presented and discussed: common difficulties will be exposed.

key words: Laser, Luminescence, Time-resolved, Explosives, Detection, Fingerprints, 1,2-indanedione, Europium.

1.1 Introduction

Luminescence is a process in which energy is emitted from a material at a different wavelength from that at which it is absorbed. Luminescence covers photoluminescence, electro luminescence, chemiluminescence, etc. We are interested here in photoluminescence (fluorescence and phosphorescence). The principle of photoluminescence transitions is sketched in Figure 1. Fluorescence is a phenomenon in which electron de-excitation occurs almost spontaneously (emission lifetime of a microsecond or less), and in which emission of a photon from a luminescent substance ceases when the exciting source is removed. In fluorescent materials, the excited state has the same spin as the ground state. In phosphorescence, light emitted by an atom or molecule persists some time after the exciting source is removed (emission lifetime of a microsecond or more). It is a quasi stable electron excitation state involving a change of spin state (intersystem crossing) which decays only slowly.

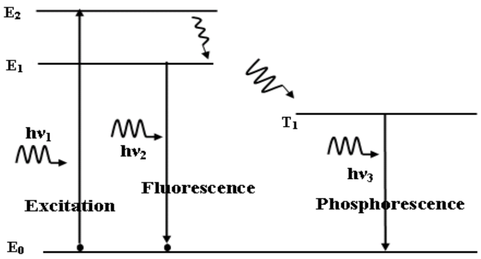

Fig. 1.1 Principle of photoluminescence transitions

The emission decay curve is usually expressed by a single exponential when only one species is emitting.

$$N(t) \;=\; N(0)\exp -(\frac{t}{\tau}), \qquad (1.1)$$

where τ is the lifetime of the emitting species at a given wavelength λ.

Photoluminescence, which includes fluorescence and time-resolved luminescence, has been applied to the detection of explosives (Menzel et al., 2004), and has been used for fingerprint detection since 1980 (Menzel, 1980). This technique helps in identifying the explosive element from the molecules released by exposing a high power laser beam on it or in its vicinity. The excited molecules give off photons (light) of the characteristic wavelength of the material when the light source is removed.

The photoluminescence detection of trace explosives and fingerprints on objects share the same main problems: often there are only minute quantities available or left at the crime scene, and the surface to be screened may fluoresce under laser excitation overwhelming the sample's signal. For explosive detection, there is a broad range of effective explosives that need to be screened for, and most current detection technologies require close proximity to the person or object being screened. In fingerprint and trace explosive detection we have the problem of the surface on which the print/explosive is left: some surfaces are difficult to handle and/or luminesce intensely under laser excitation. Trace explosive and fingerprint detection require sensitivity due to the minute amount of matter left and available on the samples to be detected. Time resolved luminescence is used to suppress the unwanted luminescence background, and may be used to distinguish between explosives that need to be screened.

CW argon-ion lasers are used as excitation of the samples. They deliver continuous wave signals. For time-resolved luminescence purposes, we need to modulate the excitation of the samples as desired depending on the luminescence decay time and also on the background decay lifetime. Two ways of laser modulation were used depending on the decay time range of the compounds: mechanical light chopper for relatively long lifetimes (on the order of milliseconds), and electro-optic modulation for relatively short lifetime decays (on the order of nanoseconds or microseconds). For Eu-RP compounds (3 ms), a mechanical chopper is sufficient when operating at 169 Hz (6 ms).

The rare earth (Eu^{3+}) salts are known for their narrow and weak absorption bands in the UV region coupled with emission bands which have narrow half-widths and long luminescence lifetimes (on the order of ms) in the visible region. The radiative transitions of these elements can be enhanced, when Eu^{3+} is bonded to appropriate organic ligands, via intramolecular energy transfer from the organic ligands to the rare earth ions when excited with the right excitation (Weissman, 1942). Rare earth-RP complexes show emission enhancement of the rare earth ions (Alaoui and Menzel, 1993). RP is the reaction product of glycine with ninhydrin. So far, the only excitations that lead to energy transfer from the organic ligands, RP, to the Eu^{3+} are in the near UV range (200-400 nm) (Alaoui, 1995).

1.2 Fingerprint detection by photoluminescence

1.2.1 Procedures not requiring time-resolved luminescence

Fingerprint reagents, such as ninhydrin followed by ZincChloride treatment (Herold and Menzel, 1982), DFO (Pounds et al., 1990), 1,2-indanedione,(Joullie and Petrovskaia, 1998), fluoresce under Ar laser and develop fingerprints without requiring time resolved luminescence imaging. The reaction product of 1,2-indanedione with glycine (Alaoui et al., 2005) emits yellow under blue-green laser excitation. The emission spectrum is a broad band having its maximum around yellow (560-575 nm). The samples, on which the prints are to be detected, are excited with the blue lines 476.5 and 488 nm of an Argon laser, and observed under orange filters. 1,2-indanedione is a single-step fluorescence way on porous surfaces; on smooth surfaces, the potential of 1,2-indanedione to detect fingerprints depends on how much luminescence is coming from the sample's surface.

1.2.2 Cases requiring time-resolved luminescence

When the routine procedures described above fail to give good results, time-resolved luminescence imaging may be the solution. There are a large number of intensely luminescent surfaces for which conventional detection techniques fail. The basic principle of the time-resolved luminescence technique is described in previous papers (Mitchell and Menzel, 1989; Alaoui, 2006). Undeveloped fingerprints are then treated with chemicals having much longer luminescence lifetimes. The imaging device will only detect this long-lived luminescence and eventually suppress the background.

1.3 Photoluminescence trace explosive detection

Explosives are chemicals (molecules) containing at least two nitro groups (NO_2). When exited with appropriate laser light, the photoluminescence spectrum through a spectrometer will have some peaks characterizing the molecule. Depending on the nature of the transitions the peaks can be more or less sharp. In case of allowed transitions the peaks are usually easy to get while in prohibited transitions the peaks are narrow and hard to find. These electron transitions (peaks) serve as a "fingerprint" for identifying substances. The effectiveness of any trace explosive analysis is dependent on three distinct steps: sample collection, sample analysis, and comparison of results with known standards. All three steps are essential to detect explosives that are present in a crime scene, for example.

It was found recently (Hummel, 2004) that many explosives (TNT, nitroglycerin, etc.) share a common photoluminescence peak at 705 nm when excited with a UV laser source emitting at 325 nm. Common non-explosive substances showed no 705 nm peak under the same experimental conditions (Hummel et al, 2006). Schllhorn's research team (Schllhorn et al, 2007) developed a portable explosives detector based on photoluminescence. The device shines ultraviolet, infrared and visible light onto two sample areas at the same time and then calculates the difference in reflectance between them for each part of the spectrum. If explosives are present at one sample area but not the other, the characteristic signature of reflected light should show up clearly in this difference measurement. This enables easy identification of the explosive by comparing the signature with a database stored in the detector. Three ways of detecting trace explosives using photoluminescence are presented in the following subsections.

1.3.1 Photoluminescence versus colorimetric trace explosive detection

Many reactions with trace explosive residue produce a product that is colored and luminescent. In using a luminescent product for detection, one gains at least one to three orders of magnitude in detection sensitivity (Menzel et al., 2004). To compare colorimetric versus photoluminescence detection of RDX ($C_3H_6N_6O_6$), the following procedure was used by Menzel's team. RDX was solvated in a small amount of acetone, then in a larger amount of methanol and spotted on chromatography paper. The spots were allowed to air dry for about half an hour. Then reagents from an Explosive Testing Kit were spotted on the RDX. The reaction products were immediately visible. The colorimetric product was light purple and visible in room light. The luminescent product was viewed under blue-green laser light using red and orange filters and appeared as a reddish color (Figure 2). At low concentrations (10^{-4} M and lower), the photoluminescence trace explosive detection is superior to the colorimetric method due to its sensitivity.

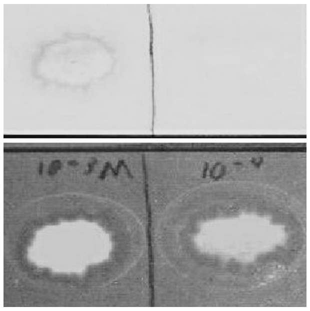

Fig. 1.2 Colorimetric versus photoluminescence detection of RDX

1.3.2 Trace Explosive detection by time-resolved luminescence

The luminescence time-resolved approach records the luminescence intensity in a specific time at a given delay after the excitation pulse, where both delay and gate width are carefully chosen based on the characteristic decay of the explosive signal and the background luminescence, on which the explosive is to be detected. The photoluminescence trace explosive detection approach may employ Eu^{3+} lanthanide tagging for time-resolved detection due to the fact that the photoluminescent properties of its compounds depend slightly on the nature of the ligands (Alaoui and Menzel, 1996). The observed decay time of its main peak (616 nm) is 3 ms, which is suitable for time resolved imaging (Figure 3). The ground state for europium trivalent ions is an ^7F state. The lowest excited states inside the 4f-shell for Eu^{3+} are $^5D_0$ (about 17267 cm^{-1}), the main emissive level, and $^5D_1$ (about 19025 cm^{-1}).

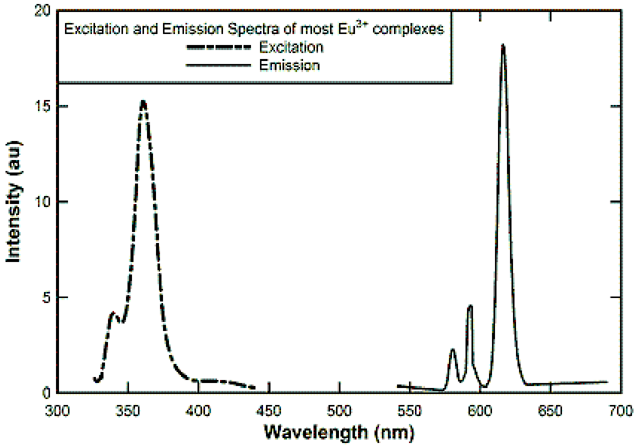

Fig. 1.3 Excitation and emission spectra of Eu^{3+} compounds.

To detect trace explosives on a high background surface, Eu^{3+} compounds (long lifetime) are needed, so that time-resolved imaging could be utilized. In the study done by Menzel's team (Menzel et al., 2004), several $EuCl_3$ complexes were tested on a variety of different explosives (NG, RDX, and two kinds of smokeless powder). The explosive was rubbed on filter paper, then the lanthanide complex was spotted on the explosive. A control, with solvent and no explosive, was also spotted with the lanthanide complex. The luminescence intensities were then compared between the samples and the controls. There was a change in luminescent intensity and a slight color shift for these tests when viewed immediately (under both near and deep UV) after spotting. There are possible reactions taking place, which is a good sign: Eu^{3+} is probably forming complexes with the explosive molecules. But further study and research would be necessary for Eu^{3+} and time-resolved luminescence to become a trace explosives detection method.

1.3.3 Trace Explosive detection with luminescent polymers

Luminescent polymers were used (Toal et al., 2006) as sensors for TNT. When a molecule of an explosive binds to a polymer it can 'turn off' the luminescence of the polymer. This change can be used to sense very low concentrations of explosives. The Toal team has made a silicon-containing polymer that glows blue or green under illumination with a UV light, and dims in the presence of TNT. This could be used to detect trace explosives left by the fingerprints of a bomb maker. Usually, fingerprint residue does not hold much matter, as stated in the introduction. Other studies using photoluminescent metallole-containing polymers (Toal et al., 2007) reported detection of trace explosives limits observed to be as low as 5 ng for TNT, and 20 ng for DNT (2,4-dinitrotoluene).

1.4 Conclusion

Even though the chemistry is different, photoluminescence fingerprints and trace explosive detection share many common difficulties: scarcity of the materials left at the crime scenes, sensitivity, high power excitation, and high background signal. When the luminescence signal from explosive materials is strong, luminescence can be used as a main technique for explosive materials detection and identification. In the case of a weak signal and/or high background luminescence under a laser excitation source, time resolved luminescence and other techniques (Raman spectroscopy and laser-induced luminescence spectroscopy) may solve the problem. In any case luminescence may be used as a complimentary property; it serves as a "fingerprint" for identifying explosive materials. The distinct photo luminescent peak at 705 nm (if confirmed by further studies), common to all explosive materials, opens new windows: luminescence may become an excellent and extremely sensitive trace explosive identification tool.

1.5 Acknowledgments

Part of this work has been done at the Center for Forensic Studies (E.R. Menzel, Director) and the Physics Department, Texas Tech University.

References

1. Alaoui, I. M., and Menzel E. R. (1993) Spectroscopy of Rare Earth Ruhemann's Purple Complexes. J. Forensic Sciences, 38(3), 506-520.
2. Alaoui, I. M. (1995) Non-Participation of the Ligand First Triplet State in Intramolecular Energy Transfer In Europium and Terbium Ruhemann's Purple Complexes. J. of Physical Chemistry, 99, 13280-13282.
3. Alaoui, I. M., and Menzel, E. R., (1996) Constituent Effects on Luminescence Enhancement in Europium and Terbium Ruhemann's Purple Complexes, J. Forensic Science International, 77, 3-11.
4. Alaoui, I. M., Menzel, E. R., Farag, M., Cheng, K. H. and Murdock, R. H. (2005) Mass spectra and time-resolved fluorescence spectroscopy of the reaction product of glycine with 1,2-indanedione in methanol. Forensic Science International, 152, 215-219.
5. Alaoui, I. M., (2007) Time-resolved luminescence Imaging and Applications, ASI-Imaging for Detection and Identification, 243-248.
6. Herold, D. W. and Menzel, E. R., (1982) Laser detection of latent fingerprints: ninhydrin followed by zinc chloride. J. Forensic Sci. 27 513-518.
7. Hummel, J. (2004) Photoluminescence spectroscopy: New technique for detecting explosives. www.buzzle.com/editorials/10-11-2004-60363.asp.
8. Hummel, R. E., Fuller, A. M., Schllhorn, C., Holloway, P. H. (2006) Detection of explosive materials by differential reflection spectroscopy. Applied Phys. Letters, 88, 23.
9. Joulli, M. M. and Petrovskaia, O., (1998) A better way to develop fingerprints. ChemTech , 28(8), 41-44.
10. Menzel, E. R. (1980) Fingerprint Detection With Lasers. Marcel Decker Inc., New York.
11. Menzel, E. R., Menzel, L. W. (2004) Ordinary and time-resolved photoluminescence field detection of traces of explosives and fingerprints. J. Forensic Ident.54, 560-571.
12. Menzel, E. R., Bouldin, K. K., Murdock, R. H. (2004) Trace explosives detection by photoluminescence. The Scientific World JOURNAL 4, 55-66.
13. Menzel, E. R., Menzel, L. W., Schwierking, J. R., (2004) A photoluminescence-based field method for detection of traces of explosives. The Scientific World JOURNAL 4, 725-735.
14. Mitchell, K. E. and Menzel, E. R. (1989) Time resolved luminescence imaging: Application to latent fingerprint detection, Fluorescence Detection III, SPIE Proceedings, E. R. Menzel, Ed., 1054, 191-195.
15. Pounds, C. A., Ggrigg, R., Mongkolaussavaranta, T., (1990) The use of 1,8-diazafluoren-9-one (DFO) for the fluorescent detection of latent fingerprints on paper. J. Forensic Sci. 35(1), 169-175.
16. Schllhorn, C., Fuller, A. M., Gratier, J. and Hummel, R. E., (2007) Developments on standoff detection of explosive materials by differential reflectometry. Appl. Opt. 46, 6232-6236.
17. Toal, S. J., and Trogler, W. C. (2006) Polymer sensors for nitroaromatic explosives detection. J Mater Chem. 16, 2871-83.
18. Toal, S. J., Sanchez, J. C., Dugan, R. E. and Trogler, W. C., (2007) Visual Detection of Trace Nitroaromatic Explosive Residue Using Photoluminescent Metallole-Containing Polymers. J. of Forensic Sciences 52(1), 79-83.
19. Weissman S. I., (1942) Intramolecular energy transfer, the fluorescence of complexes of europium. J. of Chemical Physics, 10, 214-217.