What's new in luminescence spectroscopy: applications and recent trends

J. J. Aaron

Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7-Denis Diderot, associé au CNRS (ESA 7086), 1, rue Guy de la Brosse, 75005 Paris, France

Luminescence phenomena have attracted the attention of man for several centuries. Puzzling questions were related to the observation of emission of visible light by a number of living organisms including fireflies, insects, fishes, mushrooms and luminescent bacteria. How can an animal or a plant produce light? What is the energy source of this light? Nowadays, this kind of cold light is called chemiluminescence; it occurs when a chemical reaction yields an electronically excited species which produces electromagnetic radiations in the visible. When the chemiluminescent reaction occurs within living organisms, it is known as bioluminescence.

Other related emissive processes are: electroluminescence, produced by electrical discharges in gases or electrochemically in the solid state, and photoluminescence (fluorescence and phosphorescence), generated by the absorption of light by organic or inorganic molecules and ions.

Although the various types of luminescence have been classified and investigated as early as the nineteenth century [1], basic knowledge on photoluminescence has only been established in the 1940s and 1950s with the fundamental works of P. Pringsheim [2] and T. Förster [3]. Besides academic research, the applications of luminescence to various fields such as biology, medicine, materials science, polymers, environmental sciences, analytical chemistry, have developed tremendously in the last three decades. This is because of the inherent high sensitivity, selectivity and versatility of luminescence and also because of major improvements in instrumentation (laser technology, ultrashort time-resolved spectroscopy, fiber optics, fluorescence probes, imaging techniques, fluorescence microscopy…). Many books and review articles covering both principles and applications have been published, demonstrating the growing interest for a number of aspects of luminescence spectroscopy. A representative, but of course not exhaustive, list of these works is given in the bibliographic section for the interested reader [4-26]. Several international conferences series specialized in luminescence show also the recent and various developments of these methods; special mention should be made of the International Symposium Luminescence Spectrometry in Biomedical and Environment Analysis (IXth Meeting held in Montpellier in May 2000) [27] and the International Conference on Methods and Applications of Fluorescence Spectroscopy (5th Meeting held in Paris, in September 1999) [28].

The various contributions given in this issue of Analusis-EurJAC present the different facets of luminescence spectroscopy, a multidisciplinary field which is concerned by instrumental development, use of organized media, combination of luminescence detection with separation methods such as chromatography and capillary electrophoresis, and applications to the biomedical, pharmaceutical and environmental sciences. It has been attempted to give here some representative examples of the most recent instrumental improvements and major analytical applications involved in fluorescence, phosphorescence and chemiluminescence.

The two first contributions are devoted to an overview on the usefulness of the organized media for analytical applications of fluorescence. D.A. Lerner and M.A. Martin describe the nature of supramolecular inclusion complexes formed with cyclodextrins and the structure and properties of micelles. They show that the main advantage of these organized media for analytical applications is to enhance considerably the fluorescence of drugs; the scope of the technique can even be extended to non-emitting chromophores, such as retinoids, which are found to fluoresce when they are included in cyclodextrines. P. Prognon *et al* demonstrate the analytical interest of native cyclodextrins and their hemisynthetic derivatives in fluorescence spectroscopy, either for direct detection of guest molecules or as a detection mode after separation by chromatography or electrophoresis; several examples, including the improved fluorimetric determination of antipsoriatic drugs (psoralens) and environmental pollutants (aflatoxins) in liquid chromatography are detailed.

In the third contribution, A. Muñoz de la Peña *et al.* present a related topic, *i.e.* a survey on the room temperature phosphorescence (RTP) of a number of organic compounds in organized media such as micellar solutions, cyclodextrins and their mixtures. The authors show that strong RTP signals are obtained for halogenated as well as non-halogenated guest organic molecules, permitting to determine by phosphorimetry a variety of aromatic and heteroaromatic derivatives.

B. Gooijer *et al.* illustrate, in the fourth contribution, the applicability of laser-induced fluorescence (LIF) combined with capillary electrophoresis (CE) to natively fluorescent analytes by employing either UV laser systems or multiphoton excitation. The authors report that, very recently, the introduction of high-repetition rate, femtosecond Ti :

Article available at http://analusis.edpsciences.org or http://dx.doi.org/10.1051/analusis:2000280647

sapphire lasers has paved the way for two- and three-photon excited LIF detection of a wide variety of native biological fluorophores at the ultra-trace (amol to zmol) levels.

The fifth contribution, coauthored by A.M. Garcia-Campaña and W.R.G. Baeyens, focusses on the potentials and possibilities offered by chemiluminescence in analytical chemistry. As pointed out by the authors, the chemiluminescence applications in flowing streams such as flow injection analysis (FIA), high performance liquid chromatography (HPLC) and capillary electrophoresis have increased exponentially in the last two decades, as well as the development of sensors and micromachining (sub-droplet-sized CE).

In the sixth paper, J.J. Aaron and A. Coly present an overview on the current luminescence-based methods for determining pesticides in different types of samples. Some of the methods which have recently gained widespread importance for the fluorimetric analysis of pesticides, such as chemical and photochemical derivatization and fluorescence detection in HPLC and FIA are described in more detail. Environmental applications are also given.

In the seventh and last contribution of this issue, J.J. Santana Rodríguez and C. Padrón Sanz review the application of various fluorescence techniques, including conventional fluorescence, synchronous fluorescence, low temperature and Shpol'skii fluorescence spectroscopies, and HPLC with fluorescence detection, to the quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) in marine environments; the simplicity, sensitivity and reliability of these methods for determining these potentially cancinogenic and mutagenic pollutants in marine waters, sediments and organisms are emphasized by the authors.

References

1. Harvey, E.N. *A History of Luminescence from the Earliest Times until 1980;* Philadelphia: American Philosophical Society, 1957.
2. Pringsheim, P. *Fluorescence and Phosphorescence*; New York: Interscience, 1949.
3. Förster, T. *Fluorescence Organisher Verbidungen*; Göttingen: Van den Bröeck and Ruprecht, 1951 and 1982.
4. Hercules, D.M. (ed) *Fluorescence and Phosphorescence Analysis*; New York: Wiley Interscience, 1966.
5. Parker, C.A. *Photoluminescence of Solutions*; Amsterdam: Elsevier, 1968.
6. Becker, R.S. *Theory and Interpretation of Fluorescence and Phosphorescence*; New York: Wiley Interscience, 1969.
7. Udenfriend, S. *Fluorescence Assay in Biology and Medicine*; Vols 1 and 2, New York: Academic Press, 1962 and 1971.
8. Berlman, I.B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; New York: Academic Press, 1971.
9. Guilbaut, G.G. (eds) *Practical Fluorescence*; New York, Marcel Dekker, 1990.
10. Chen, R.F.; Edelhoch, H. *Biochemical Fluorescence Concept*; Vols 1 and 2, New York: Marcel Dekker, 1976.
11. Wehry, E.I. (ed), *Modern Fluorescence Spectroscopy*; New York: Plenum, 1981.
12. Zander, M. *Fluorimétrie*; Berlin: Springer, 1981.
13. Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*; New York: Plenum, 1983.
14. Schulman, S.G. (ed) *Molecular Luminescence Spectroscopy. Methods and Applications*; Vols 1, 2 and 3, New York: John Wiley, 1985, 1988, 1993.
15. Krasovitskii, B.M.; Bolotin, B.M. *Organic Luminescent Materials*; Weinheim: VCH, 1988.
16. Goldberg, M.C. (ed) *Luminescence Applications in Biological, Chemical, Environmental and Hydrological Sciences*; Washington DC: ACS Symposium Ser. Vol. 383, Am. Chem. Soc. 1989.
17. Dewey, T.G. (ed) *Biophysical and Biochemical Aspects of Fluorescence Spectroscopy*; New York: Plenum, 1991.
18. Baeyens, W.R.G.; De Keukeleire, D.; Korkidis, D. (eds) *Luminescence Techniques in Chemical and Biochemical Analysis*; New York: Marcel Dekker, 1991.
19. Hemmila, I.A., *Applications of Fluorescence in Immunoassays*; New York: John Wiley, 1991.
20. Lakowicz, J.R. (Ed.) *Topics in Fluorescence Spectroscopy*; Vol. 1, 2 and 3, New York: Plenum Press, 1991 and 1992.
21. Czarnik, A.W. (Ed.) *Fluorescent Chemsensors for Ion and Molecule Recognition;* Washington DC: ACS Symp. Series, Vol. 538, J. Amer. Chem. Soc. 1992.
22. Wolfbeis O.S. (Ed.) *Fluorescence Spectroscopy, New Methods and Applications;* Berlin Heidelberg: Springer, 1993.
23. Slavik, J. *Fluorescent Probes in Cellular and Molecular Biology;* Boca Raton: CRC Press, 1993.
24. Rettig, W.; Strehmel, B.; Schrader, S.; Seifert, H. (Ed.), *Applied Fluorescence in Chemistry, Biology and Medicine;* Berlin: Springer, 1998.
25. Blum, L.J. (Ed.) *Bio- and Chemi-Luminescent Sensors;* Singapore: World Scientific, 1997.
26. Soper, S.A.; Warner, I.M.; Mc Gown, L.E.; *Anal. Chem*. **1998,** *70*, 477R-494R.
27. Lerner, D. (Coord.), Abstracts and extended abstracts of the IXth ISLS 2000 Luminescence Symposium held at Montpellier, France on 15-17 May 2000, *Luminescence*, **2000**, *15*, 59-130.
28. Brochon, J.C.; Valeur, B. (Coords.) Special Issue: Sixth International Conference on Methods and Applications of Fluorescence Spectroscopy, Paris, France, September 12-15, 1999, *J. Fluoresc.* **2000**, *10*, 69-216.