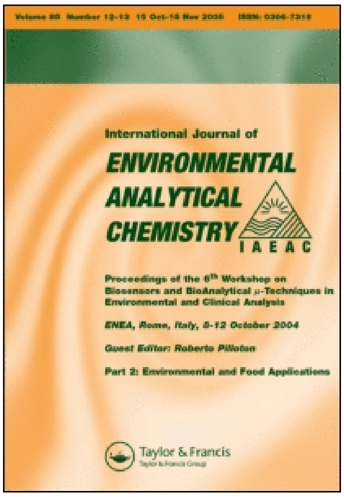

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Recent Advances in Phosphorimetry[†]

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Recent progress in phosphorimetry is reviewed briefly. Special emphasis is placed on areas of application, including pharmaceuticals, pesticides, air pollutants, etc. Various modes of instrumentation and operation and a critical assessment of their advantages and disadvantages are given.

The use of phosphorescence emission spectra for identification of organic substances was first suggested by Lewis and Kasha.[1] In 1957, Keirs, Britt and Wentworth[2] published their fundamental paper on the basic principles of phosphorescence analysis. In the following years several groups were active in this field. Phosphorescence spectroscopy as an analytical method for organic compounds is very well established and has been used frequently in such varied disciplines as biochemistry, pharmacology, food chemistry, pollutant analysis, tar chemistry, petrochemistry, polymer chemistry, and others.

The literature on theory, instrumentation and application of phosphorimetry through early 1967 is covered in a book by Zander.[3] Developments in this field since then have been discussed in detail by McCarthy.[4] The present paper should be regarded only as a bibliography of newer important papers on phosphorimetric techniques and applications, at which the discussion of application is restricted to the field of pollutant analysis.

U.v. spectral analysis, fluorescence analysis and phosphorescence analysis are not exclusive, but rather complement each other. Recently, a comparison

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[†] Extract of a plenary lecture presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

of these techniques as analytical methods for polycyclic aromatic hydrocarbons has been given.[5] The points of view from which the methods have been compared were breadth of application, selectivity, sensitivity, and accuracy.

For several of the methods of phosphorescence analysis described in the earlier literature relative standard deviations of 2–10% are quoted. The accuracy of phosphorescence measurements, however, can be increased considerably by using the rotating sample cell technique. This method, which is very well known in n.m.r. spectroscopy has been introduced in phosphorescence spectroscopy by Winefordner *et al.*[6,7] With the Winefordner technique the accuracy of phosphorescence analysis becomes comparable to that of fluorescence and u.v. spectroscopy.

Pulse source-time resolved phosphorimetry has been established by Fisher and Winefordner.[8] The pulsed source phosphorimeter has a number of advantages compared to the conventional continuously operated source-rotating can phosphoroscope phosphorimeters, including increased sensitivity and selectivity and applicability to fast-decaying phosphors.

The sensitivity and selectivity of phosphorimetry can also be improved by the application of external heavy-atom spin-orbit coupling effects. This method has been introduced in phosphorimetry independently by Hood and Winefordner[9] and Zander [10,11] (for reviews see McCarthy[4] and Zander[12]). A comparison of several solvents showing the external heavy-atom effect in phosphorimetry has been given.[13] A mixture of C_2H_5Br and C_2H_5OH (1 : 1, v/v) seems to be the most useful solvent system.[5] The use of the external heavy-atom effect in fluorimetry has also been described.[12,14,15]

Phosphorimetry in aqueous solution at 77°K has been described recently and is a very useful method, especially in the area of drug analysis.[16,17] Only a few per cent (by weight) of sodium chloride, sodium bromide, or sodium iodide in water resulted in phosphorescence signals at 77°K several orders of magnitude greater than the phosphorescence signal for the same compound in pure water solution.[17]

Phosphorimetry has already been used widely in the field of pollutant analysis.[3] Sawicki[18] has pointed out that phosphorescence spectroscopy should be of great service for the investigation of airborne dust samples. In addition to earlier papers (for these see Zander[3]) more research has been done on the phosphorimetric characterisation and analysis of pesticides.[19–21] A quantitative phosphorimetric procedure for the analysis of organophosphate pesticides has been developed.[22] It is possible to determine these substances with a sensitivity varying from 0.0025 to 5 mcg/ml. The phosphorimetric analysis of chlorinated pesticides[23] and of some pesticides derived from *p*-nitrophenol[24] has also been described. The determination of parathion on celery by phosphorimetry has been compared with the Averell-Norris and electron capture methods.[25] The phosphorimetric procedure proved to be simple, faster than the Averell-Norris method and less subject to interference than electron capture gas chromatography. Among the chloro- and nitro-aromatic fungicides 2,6-dichloro-4-nitroanaline (DCNA), Dyrene, tetrachlorisophthalonitril (Daconil 2787), 1,4-dichloro-2,5-dimethoxybenzene (Chloroneb) and 1-chloro-2,4-dinitronaphthalene can be estimated phosphorimetrically with high sensitivity.[26] The application of phosphorimetry to pesticides has been briefly reviewed.[27]

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