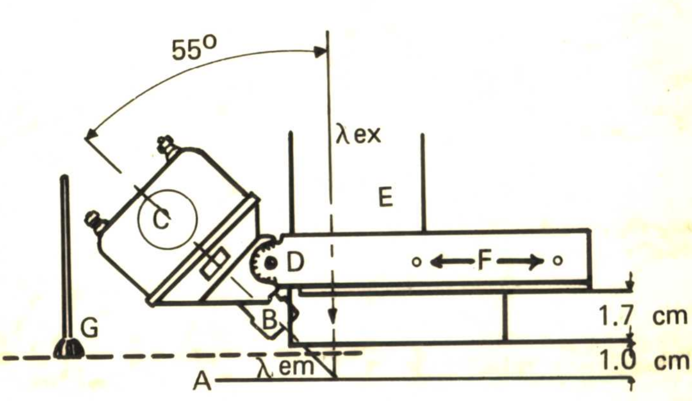
Modern Monographs in Analytical Chemistry / 1

SOLID SURFACE LUMINESCENCE ANALYSIS

THEORY, INSTRUMENTATION, APPLICATIONS

ROBERT J. HURTUBISE



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Foreword

Tremendous advances have been made in the field of analytical chemistry in the past ten years--new techniques, improved instrumentation, sophisticated automation, and new methods of data processing and handling. In an attempt to keep analytical chemists abreast of these rapidly changing developments the idea of the current series was conceived.

Modern Monographs in Analytical Chemistry will be a series of books, each devoted to a special treatise of a particular subject or field. Subjects to be presented will cover a large area from lasers to automation, piezoelectric crystals to fluorescence assays in biology and medicine. Each book will give an informative introduction to the field for the nonexpert, present a thorough description of the types of research currently being conducted, and conclude with a discussion of the future of this area. It will appeal to the expert as well as the novice. It is anticipated that monographs will appear in the developing areas of current research.

George G. Guilbault

Preface

Solid surface luminescence analysis has been applied to the trace analysis of elements and compounds, but mainly to the analysis of organic compounds. The versatility of solid surface luminescence analysis is illustrated by the variety of samples that have been analyzed. Several commercial instruments are in use and many modified or laboratory-constructed instruments have appeared for solid surface luminescence analysis. The theoretical understanding of luminescence scattered from solid surfaces has been developed partially and remains to be expanded. With the advent of room temperature phosphorescence from solid surfaces and high-performance thin-layer chromatography, new dimensions have been added to solid surface luminescence analysis. Some exciting developments should be seen in these two areas in the future.

Detailed consideration of solid surface luminescence analysis is given in this book in the areas of theory, instrumentation, and applications. To the author's knowledge no other book has appeared on the subject that specifically treats solid surface luminescence analysis. Two chapters are devoted to instrumentation, one to theoretical aspects of luminescence scattered from solid surfaces, another to interactions responsible for room temperature phosphorescence, one to some analytical procedural considerations, seven to analytical applications, and one to future trends.

The beginner, the practicing analyst, and the researcher should all find this book useful in their work. Also, the nonanalytical chemist who wishes to use luminescence analysis or who already uses luminescence analysis will find the book helpful. In addition, the book should be useful as a textbook to teach the theoretical, instrumental, and applied aspects of solid surface luminescence analysis. Basic theory on luminescence was not presented because of the ready availability of several fine textbooks that consider luminescence theory.

Appreciation is extended to Dr. J. D. Winefordner for the use of some prepublication material on room temperature phosphorescence. Also, I am indebted to Agnes Kennington and Karen Singer, who typed the original manuscript, and to Sharon Breitweiser, who typed the final version.

Robert J. Hurtubise

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Introduction

Solid surface luminescence analysis involves the measurement of fluorescence or phosphorescence of components adsorbed on solid materials. A variety of solid materials has been employed in analysis, such as silica gel, aluminum oxide, filter paper, silicone rubber, sodium acetate, potassium bromide, sucrose, and cellulose. Both inorganic and organic species can be analyzed using solid surfaces. Many of the arguments advanced for sensitivity and selectivity for solution luminescence analysis are applicable directly to solid surface luminescence analysis (1-3). Luminescence spectrometric methods are among the most sensitive methods available for trace analysis. Because many excellent books have already been written on solution luminescence analysis which include a discussion of the theoretical distinction between fluorescence and phosphorescence (1-3), those aspects will not be considered here.

One fundamental difference between solution luminescence and solid surface luminescence is that in solid surface luminescence the luminescent components are usually adsorbed on small particles of the solid material, and this results in the scattering of both source and luminescent radiation. The radiation, whether it is source radiation or luminescent radiation, can be reflected from the solid material or transmitted through the solid material. Of course for transmitted radiation, the experimental system has to allow for transmission and measurement of the radiation such as with a plastic-backed thin-layer chromatoplate. Wendlandt and Hecht (4) discussed the differences between specular reflection and diffuse reflection. These concepts are important in solid surface luminescence analysis. *Specular reflection* or mirror reflection occurs from a very smooth surface and is described by the Fresnel equations. *Diffuse reflection* of exciting radiation results through penetration of the incident radiation into the interior of the solid material and multiple scattering occurs at the boundaries of individual particles. Ideal diffuse reflection is defined by the condition that the angular distribution of the reflected radiation is independent of the angle of incidence (5). Several theories have been developed to describe diffuse reflection. Kortum (5) has emphasized that specular reflection and diffuse reflection are two important limiting cases, and all possible variations are found in practice between these two extremes. However, with solid surface luminescence analysis diffuse luminescence is measured normally. Generally, in solid surface luminescence analysis, a fraction of the sample penetrates into the solid matrix, and the sample luminescence is excited at the surface and within the solid matrix. The excited luminescence is scattered diffusely. As will be discussed in Chapter 4, the theoretical aspects of scattered luminescence in a solid matrix are not fully developed. In this book, *reflected luminescence* refers to diffusely reflected luminescence, and it appears at the same side as the excitation source. Any specular reflection is considered unimportant. *Transmitted luminescence* refers to diffusely transmitted luminescence, or luminescence that appears at the unexcited surface. Wendlandt and Hecht (4) and Kortum (5) have treated in detail the diffuse reflectance of external source radiation used in absorption measurements. They have given a brief treatment of luminescence generated within a solid medium (4,5). In Chapter 4, a discussion of recent theoretical equations useful in solid surface luminescence analysis will be considered.

A variety of commercial and laboratory-constructed instruments are used to measure solid surface luminescence. Commercial instruments and accessories are available for simple routine analysis, and more sophisticated models are used for fundamental research. The laboratory-constructed instruments are such that the design principles employed by the researchers can be used for further developing instrumentation in solid surface luminescence analysis.

Hundreds of applications have appeared in the literature since the introduction of commercial instrumentation for solid surface luminescence analysis. Several commercial instruments became available about 1968. The applications have appeared in such areas as environmental research, forensic science, pesticide analysis, food analysis, pharmaceutical process control, biochemistry, medicine, and clinical chemistry. The many examples to be considered in this book illustrate the simplicity, accuracy, sensitivity, and versatility of solid surface luminescence analysis. Recently room temperature phosphorescence from compounds adsorbed on solid surfaces has been shown to be feasible analytically (6-17). This approach will expand substantially the versatility of solid surface luminescence analysis, and many applications which use room temperature phosphorescence will appear in the future.

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2

Commercial Instruments

Instruments for quantitative thin-layer chromatography (TLC) have been available since about 1968. The commercial instruments can be employed for quantitative and qualitative analysis of a variety of luminescence components adsorbed on several solid surfaces, such as silica gel, alumina, filter paper, gels, potassium bromide, silicone rubber, and sodium acetate. Reviews on commercial instruments have appeared that describe self-contained units and motorized thin-film scanners as attachments to spectrofluorometers (1-7). Only a few commercial instruments will be considered here.

The Schoeffel SD 3000 is a spectrodensitometer that can be used in several different spectral modes. The instrument is shown in Fig. 2.1, and an optical diagram is given in Fig. 2.2. Either a 200-W xenon-mercury lamp or a 150-W xenon lamp can be used as the exciting source. The solid surface such as a TLC plate with fluorescent components on it is positioned on the stage of the spectrodensitometer and quartz optics focus the source radiation onto the solid surface, after dispersion by a prism monochromator. The area illuminated can be controlled in both width and length. Figure 2.2 shows the instrument in several modes of operation. When fluorescence or phosphorescence is measured, the single-beam mode is employed because the only reference available is

FIG. 2.1 Schoeffel SD 3000 spectrodensitometer. (Reproduced with permission from Kratos, Inc., Schoeffel Instrument Division.)

the nonfluorescent background of the solid surface. Transmitted or reflected luminescence can be measured with detectors either from underneath a transparent surface or at a 45° angle to the incident source radiation for measurement from a solid surface. Interference wedge monochromators covering the range from 400 to 650 nm graduated into 10-nm divisions can be employed in the reflection and transmission emission modes, or else appropriate filters can be used. To obtain luminescence emission spectra, a grating emission monochromator that can detect radiation from 180 to 720 nm can be attached to measure reflected luminescence. Also, the SD 3000 can be employed in the fluorescence quenching mode, and a paper strip, cylindrical gel, and gel slab scanning attachments are available.

The Kontes Glass Company has available an inexpensive densitometer that is useful for routine quantitative fluorescence analysis in the visible region for components separated on TLC plates (Fig. 2.3). The instrument can be used in the fluorescence and

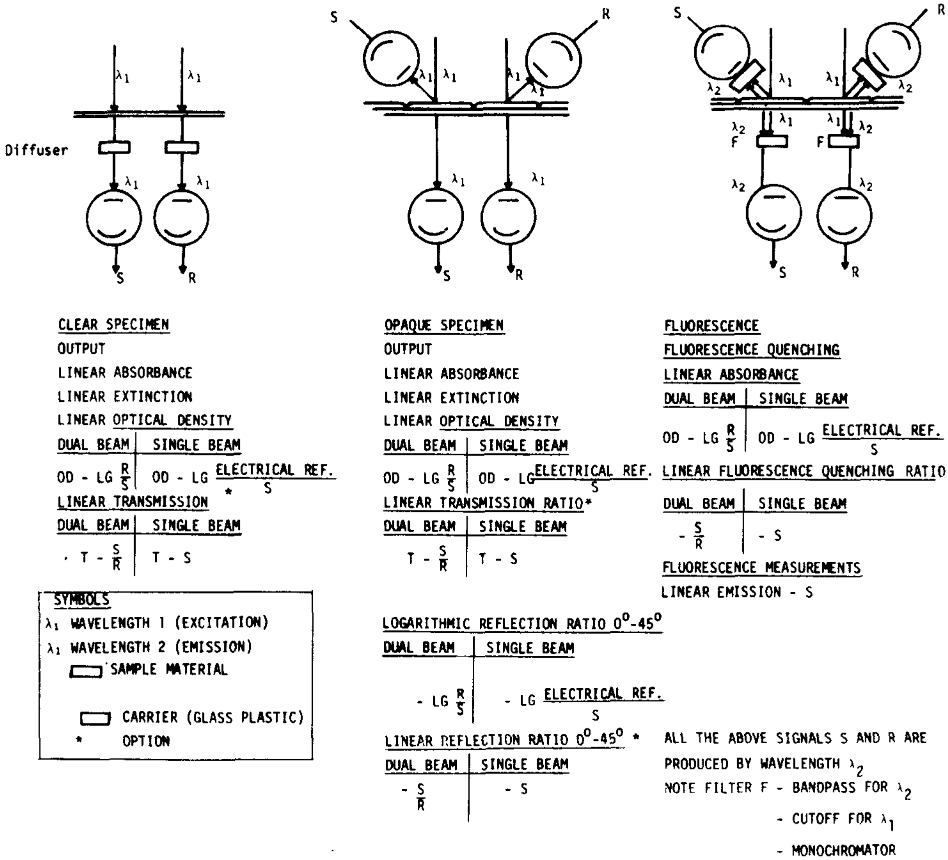

FIG. 2.2 Schoeffel SD 3000 spectrodensitometer modes of operation. (Reproduced with permission from Kratos, Inc., Schoeffel Instrument Division.)

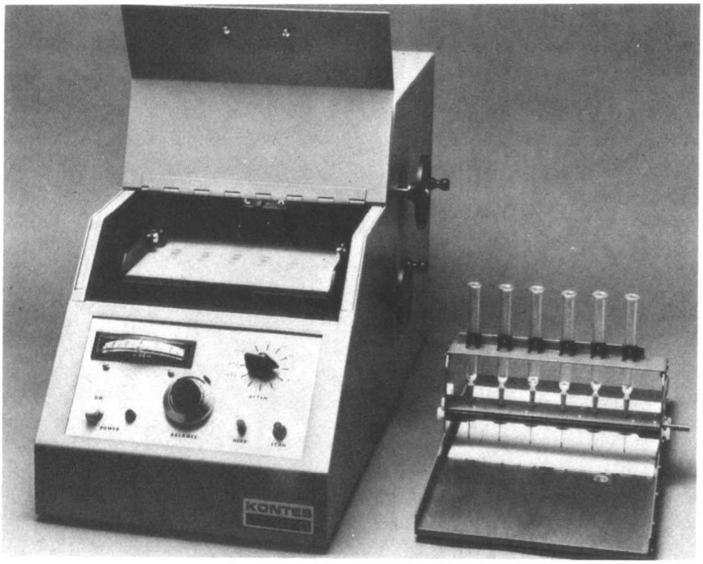

FIG. 2.3 Kontes densitometer. (Reproduced with permission from Kontes Glass Company.)

fluorescence quenching modes, or diffuse reflectance and transmission modes for absorption analysis. In the fluorescence mode either longwave or shortwave ultraviolet lamps, which are underneath the plate carriage, are used for excitation. An ultraviolet transmitting filter, a filter holder, and a quartz cover plate are needed for operation of the fluorescence mode. They are not provided with the instrument and have to be purchased separately. In actual use the filter and holder are positioned over the ultraviolet sources to prevent the passage of visible light. The developed chromatoplate is placed on top of the quartz cover plate with the adsorbent side face down. This assembly is placed on the plate carriage and the fluorescent components are excited in single-beam operation with either shortwave or longwave ultraviolet radiation. The visible fluorescence of the components passes through the chromatoplate's glass or plastic backing and is transmitted by fiber optics to a photodetector. A choice of