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Preface

Applied Spectroscopy Reviews is an international publication dealing with the principles, methods, and applications of spectroscopy in the various fields of science. Chapters will cover the entire field of spectroscopy, from short-wavelength techniques such as gamma-ray and X-ray spectroscopy to long-wavelength methods such as infrared, microwave, and radio-frequency spectroscopy.

Authoritative reviews of the various areas of spectroscopy will be included, as well as critical evaluations of new contributions to the field. The chapters will emphasize the applications of the latest techniques being used in spectroscopy. They will also include brief but pertinent sections on the underlying principles of these techniques and applications. *Applied Spectroscopy Reviews* will serve all researchers who use spectroscopy by informing them of the latest developments occurring in the field.

Of the eight reviews in this first volume of a continuing series, four are devoted to recent advances in the field of infrared spectroscopy. That half of the chapters in Volume 1 deal with infrared studies makes rather apparent the fact that infrared spectroscopy is today one of the most widely used forms of applied spectroscopy. Two chapters discuss important areas of nuclear magnetic resonance spectroscopy, and the remaining two cover flame spectrometry and X-ray analysis.

The review by Dr. Wexler on "Integrated Intensities of Absorption Bands in Infrared Spectroscopy" is one of the most significant chapters on this subject to appear in the literature. He has gathered together and correlated all of the important data in this newly developing field of measurement. "Chemical Far Infrared Spectroscopy" treats

another growing and enlarging field in infrared studies. The results presented in this review must be regarded only as a progress report, because of the rapidly growing number of developments in far infrared spectroscopy.

The review on the examination of small samples by high-resolution NMR reflects very accurately the state of the art and points up the various methods that can be used in such analyses. The procedures given suggest that NMR is approaching infrared in the minimum sample size needed to perform an analysis. The review of polymer studies by NMR illustrates the directness with which NMR has been employed in such studies. Cross-referencing in terms of polymers that have been studied is included to permit easy access to literature on NMR analyses of various polymers.

"Atomic Fluorescence Flame Spectrometry" covers the essentials in the application of this procedure to chemical analysis. Likewise, the review of soft X-ray techniques covers the methods used in soft X-ray excitation, dispersion, and detection, as well as X-ray spectral characteristics of inorganic materials.

A final purpose of this series is to communicate rapidly the latest developments in spectroscopy. The reviews presented will cover a broad range of research, so that all spectroscopists may find information useful in the particular spectroscopic applications and studies in which they are actively engaged.

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Wilmington, Delaware
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Atomic Fluorescence Flame Spectrometry

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Atomic fluorescence flame spectrometry is a new method of chemical analysis. The principles of this method, however, have existed for a number of years. The method is based upon the absorption of radiation by an atomic vapor producing excited atoms and the measurement of the radiation emitted when a fraction of these atoms lose their energy by a radiational process. The emitted energy is called atomic fluorescence.

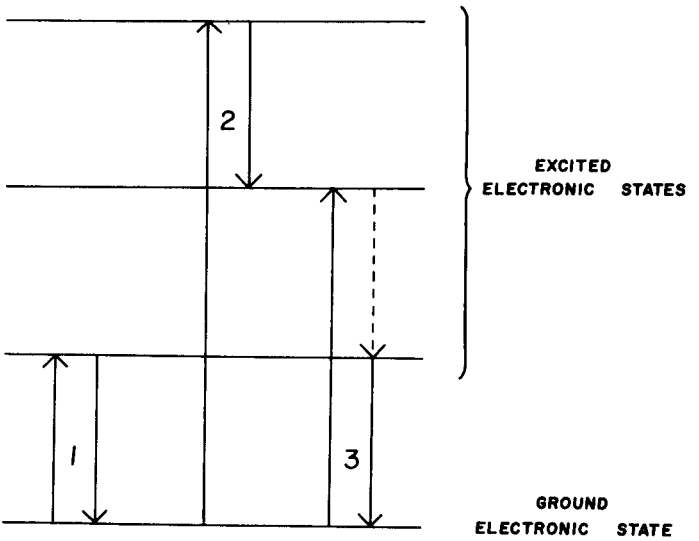

FIG. 1. Types of atomic fluorescence: 1, resonance fluorescence; 2, direct line fluorescence; 3, stepwise line fluorescence.

There are four basic types of atomic fluorescence [1,2], and these are illustrated in Fig. 1. Resonance fluorescence results when atoms are excited from the ground electronic state to an excited electronic state and then undergo radiational deactivation to the ground state, reemitting radiation of the same energy which was absorbed. The most intense resonance fluorescence generally occurs from the first excited state of an atom, e.g., the Zn 2139-Å and the Cd 2288-Å lines, because the transition probabilities for this transition are usually much greater than for other transitions. Resonance fluorescence has been and will probably continue to be of the greatest interest to analysts because resonance fluorescence intensities are generally significantly greater than the intensities observed with other types of atomic fluorescence. However, two of the other three types of atomic fluorescence could possibly be used to extend the method's range of application.

Direct line fluorescence results when an atom is raised to an excited electronic state considerably above the ground electronic state and then undergoes a radiational transition to a lower excited state (not the ground state), e.g., the emission of the Tl 5350-Å line after excitation of Tl atoms by the Tl 3776-Å line. Stepwise line fluorescence results when an atom is excited to an electronic state above the first excited electronic state, then undergoes deactivation (usually radiationless) to a lower excited state, and finally undergoes the fluorescence transition to a lower state (often the ground state), e.g., the emission of the Na 5890-Å line after excitation of Na atoms by the Na 3303-Å doublet.

The final type of atomic fluorescence, called sensitized fluorescence, occurs when donor atoms (or molecules) are excited by means of an external light source, the excited donor species collides with the sample atom (acceptor) transferring energy and exciting the sample atom, and then the sample atom undergoes radiational deactivation. For example, if a quartz container has a high concentration of mercury vapor and a low concentration of thallium vapor, mercury atoms excited by means of a low-pressure mercury arc transfer energy quite effectively to thallium atoms, which then emit their 3776- and 5350-Å lines. Unfortunately, as long as flame cells are used, sensitized fluorescence will undoubtedly never be of analytical use because the concentration of the donor species (mercury atoms in the above example) necessary for energy transfer can never be made sufficiently large for efficient transfer of energy. In addition, collisional deactivation of excited sensitizer species in flames is far too great compared to energy transfer. Sensitized fluorescence might, however, be used for analytical purposes if a heated quartz cell or other non-flame cell were used to produce the atomic vapor. It should be mentioned that the lack of efficient energy transfer is an advantage to the flame spectrometric method because the so-called interelement effects, which are prevalent in spark emission spectrometry, should therefore be negligible in this new technique.

I. HISTORY OF ATOMIC FLUORESCENCE

A. Atomic Fluorescence of Metal Vapors in Quartz Containers

Mitchell and Zemansky [1] and Pringsheim [3] have discussed much of the original research on fluorescence of atomic vapors. In the 1890s, the sodium D lines were found to appear when sodium vapor was excited by sunlight or by a sodium flame. Wood [4, 5] observed the emission of the Na D lines from a tube of sodium vapor

excited by the D lines from a sodium flame; the fluorescence radiation obtained consisted of only the D lines themselves and showed a decrease in intensity for higher vapor pressures of sodium.

Dunoyer [6-8] also investigated the fluorescence of sodium vapor. Dunoyer obtained resonance fluorescence from a beam of fast-moving sodium atoms at the point of excitation and showed that the radiation was due to the atoms and that the time between the absorption and the subsequent emission of the light was quite short. He found that the fluorescence was emitted only from the point where the exciting radiation crossed the atomic beam, and little or no spreading of the fluorescence radiation occurred in the direction of motion of the atoms. Dunoyer showed that only the center of the D line is useful for producing fluorescence. Sources with reversed lines gave decreased amounts of fluorescence.

Bogros [9] obtained fluorescence of an atomic beam of lithium by excitation with the radiation of a lithium flame. In 1912, Wood [10, 11] observed the 2537-Å line by excitation of mercury vapor. Terenin [12, 13] obtained the resonance fluorescence of the cadmium 2288-Å and 3261-Å lines by using a cadmium vacuum arc source. Filters were used to eliminate all but the desired excitation source line. Zinc fluorescence was obtained [14-16] by excitation of zinc vapor.

Many atoms have energy levels of magnitude such that they will exhibit both resonance fluorescence and direct line fluorescence. The fluorescence of thallium, initially investigated by Terenin[12, 13], is an example. Absorption of the 3776-Å line can give either the 3776-Å or 5350-Å lines as fluorescence. The 3776-Å line is the resonance line, and the 5350-Å line is due to a transition to the metastable $6^2P_{3/2}$ state. Similarly, the 2768-Å thallium line can give rise to both the 2768-Å and 3530-Å lines. Terenin also investigated the fluorescence of lead, bismuth, arsenic, and antimony [12, 13].

Strutt [17, 18] and later Christensen and Rollefson [19] excited sodium vapor with the 3303-Å doublet from a sodium vacuum arc and obtained the 3303-Å doublet and the 5890- to 5896-Å doublet (stepwise line fluorescence). Wood and Dunoyer [20] found that excitation with only one of the Na D lines gave only that line as fluorescence. Wood and Mohler [21, 22] later showed that this was true only for pure sodium vapor. The presence of foreign gases results in energy transfer to the other D line.

Fuchtbauer [23] was the first to investigate the absorption of radiation by *excited* atoms and their subsequent fluorescence. In his work on mercury vapor, he showed that after the necessary excitation by absorption of the 2537-Å line, and subsequently by other lines of longer wavelength, considerable fluorescence was observed. Absorption of the 2537-Å line and subsequent absorption of the 3131.5-Å

and 3125-Å lines produced the 5770-Å, 3654-Å, 3131.5-Å, and 3125-Å lines as fluorescence in addition to the resonance radiation. Absorption of the 3131.8-Å line by atoms excited by the 2537-Å line produced the 2967.5-Å, 3131.8-Å, and 3663.2-Å lines with the 2537-Å line. Bender [24] obtained similar effects for cadmium and zinc.

B. Atomic Fluorescence of Metal Vapors in Flames

In 1924, the atomic fluorescence of metal atoms in flames was observed for the first time by Nichols and Howes [25], who reported the atomic fluorescence of calcium, strontium, barium, lithium, and sodium in a Bunsen flame. In 1927, Badger [26] published an excellent paper on the atomic fluorescence of thallium, mercury, magnesium, copper, silver, cadmium, and sodium in a Bunsen flame. Between 1930 and 1960, little research was performed on the atomic fluorescence of metal vapors.

At the 1962 Spectroscopy Colloquium, Alkemade [27] reviewed the methods by which atoms are excited in flames. One of these methods was radiational. Alkemade described the use of atomic fluorescence flame spectrometry for measuring quantum efficiencies and applied this to the measurement of the quantum efficiency for the Na D doublet. He also indicated some possible advantages for atomic fluorescence flame spectrometry.

Winefordner and Vickers [2] first described atomic fluorescence flame spectrometry as a possible means of chemical analysis. Winefordner and Staab [28, 29] applied atomic fluorescence flame spectrometry for the measurement of zinc, cadmium, mercury, and thallium in aqueous solutions. Mansfield et al. [30] used a simple experimental system to measure zinc, cadmium, mercury, and thallium in the part-per-billion concentration range. Veillon et al. [31] used a continuous source for obtaining the analytical curves and limits of detection of thirteen elements by atomic fluorescence flame spectrometry. Dagnall et al. [32] have described the determination of cadmium by atomic fluorescence and atomic absorption flame spectrometry. Armentrout [33] measured nickel in the part-per-million concentration range by atomic fluorescence flame spectrometry, and Prugger [34] has described an experimental system for measurement of zinc by atomic fluorescence flame spectrometry. West [35, 36] has reviewed spectrochemical methods for inorganic analysis and includes an excellent summary of research and results using atomic fluorescence flame spectrometry. Winefordner and co-workers [37-42] have also given several talks summarizing work on atomic fluorescence flame spectrometry. This review article is primarily concerned with the articles cited in this paragraph.

II. THEORETICAL CONSIDERATIONS

A. Intensity of Atomic Fluorescence [43]

The intensity of atomic fluorescence depends upon the intensity of exciting radiation; the ratio of the excitation source line or band half-width, $\Delta\nu_S$, in sec^{-1}, to the absorption line half-width, $\Delta\nu_A$, in sec^{-1}; the diameter of the absorption cell and the solid angle over which excitation occurs (see Fig. 2); the atomic concentration of the absorbing atoms; the efficiency of converting the absorbed energy to fluorescence energy; and the spectral parameters, such as frequency of the absorption line, the transition probability, the types of line broadening, etc. Because the measured photodetector signal and the shape of analytical curves depend directly upon the intensity of atomic fluorescence, expressions for intensity will be given in Section III.B. For the conditions necessary for the intensity expressions to be valid, refer to the paper by Winefordner et al. [43].

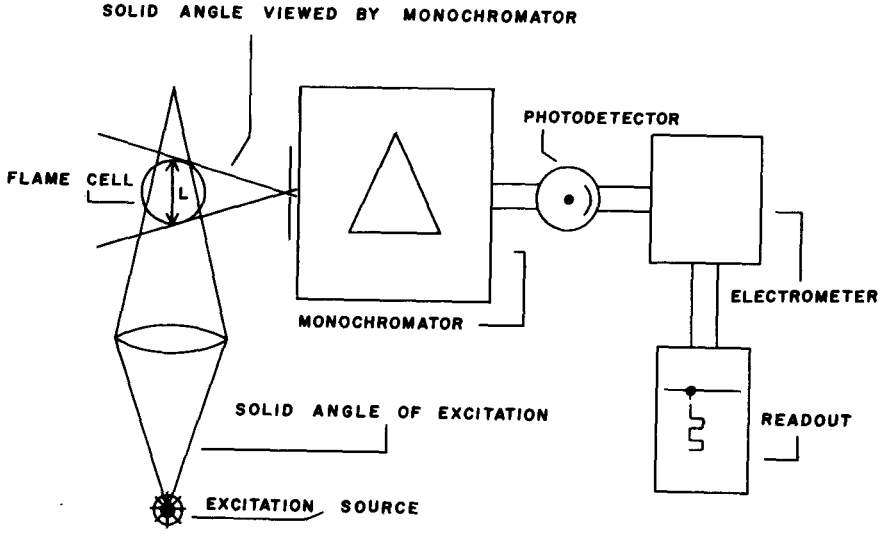

FIG. 2. Schematic diagram of atomic fluorescence flame spectrometer.

The integrated atomic fluorescence expression for an isolated spectral line is given [43] by

$$I_F = I_A(\Phi/4\pi) \qquad (1)$$

where I_F is the fluorescence intensity in watts/cm^2 ster, I_A the total

intensity absorbed by the spectral line(s) which result in activation of the fluorescent state (the upper level involved in the fluorescence process), and Φ the total power efficiency of the fluorescence transition, i.e., watts emitted by the fluorescence process to watts absorbed causing fluorescence process.

The intensity absorbed I_A is given [43], in general, by

$$I_A = \Omega_a \sum_i I_i^0 A_{T_i} \tag{2}$$

where Ω_a is the solid angle over which excitation occurs and is determined by the entrance optics of the monochromator, I_i^0 and A_{T_i} are the incident intensity of the exciting radiation, in watts/cm² ster/sec, and the total absorption factor, in sec^{-1}, respectively, for the absorption line i causing the fluorescence process. If the only process of concern is resonance absorption-resonance fluorescence, such as Zn 2139 Å and Cd 2288 Å, then

$$I_A = \Omega_a I^0 A_T \tag{3}$$

where I^0 and A_T are for the resonance absorption process.

The intensity, I^0, for a continuous source is merely the watts emitted/cm² ster frequency interval. Intensities of line sources are generally listed as integrated intensities, i.e., watts/cm² ster, and so to obtain I^0 for a line source, the integrated intensity for the line in concern is simply divided by the source line half-width, $\Delta\nu_S$. In other words, the intensity I^0 which is substituted in Eqs. (2) or (3) must be in terms of watts/cm² ster/sec, i.e., steradiancy, in watts/cm² ster frequency interval. The total absorption parameter, A_T, for an absorption line is given [44] by

$$A_T = \int_0^\infty [1 - \exp(-k_\nu L)]\, d\nu \tag{4}$$

where the integration is over the entire absorption line, and k_ν is the atomic absorption coefficient, in cm^{-1}, which is a complex function of frequency and line-broadening factors. It is difficult to solve Eq. (4) for any value of $k_\nu L$ (except by numerical analysis or graphical methods), but fortunately A_T has been evaluated for several limiting but analytically useful cases, as will be illustrated below.

If $\Delta\nu_S \gg \Delta\nu_A$, i.e., a continuous or very wide line source of excitation is used, and if $k_\nu L \ll 1$ at all frequencies, i.e., the absorbing gas is sufficiently dilute that $k_\nu L$ is much less than unity at all frequencies, then it can be shown [43] that

$$I^0 A_T = C_1 I^0 \lambda_0^2 NLA \tag{5}$$

where λ_0 is the peak wavelength of the absorption or fluorescence transition (the wavelength of absorption and fluorescence transition are essentially the same), N the number of ground-state atoms per cm^3 of flame gases, A the transition probability of the transition, and C_1 a constant composed of spectral parameters characteristic of the resonance line. The integrated fluorescence intensity, I_F, is therefore given by

$$I_F = (C_1\Omega_a/4\pi)I^0\lambda_0^2NLA\Phi \tag{6}$$

If $\Delta\nu_S \gg \Delta\nu_A$ and if $k_\nu L \gg 1$ at the line center, i.e., the absorbing gas is essentially opaque at the line center frequency, then it can be shown [43] that

$$I^0A_T = C_2I^0\lambda_0(aNLA)^{1/2} \tag{7}$$

where C_2 is different from C_1 but is determined by similar parameters, and a is approximately given by

$$a = (\ln 2)^{1/2}(\Delta\nu_C/\Delta\nu_D) \tag{8}$$

where $\Delta\nu_C$ is the collisional half-width, in sec^{-1}, of the absorption line, and $\Delta\nu_D$ is the Doppler half-width, in sec^{-1}, of the absorption line. The integrated fluorescence intensity in this case is therefore given by

$$I_F = (C_2\Omega_a/4\pi)I^0\lambda_0(aNLA)^{1/2}\Phi \tag{9}$$

Growth curves of log I_F vs. log N if $\Delta\nu_S \gg \Delta\nu_A$ would then be expected to have a slope of 1.0 at low N's, i.e., low $k_\nu L$ values at the line center, and 0.5 at high N's, i.e., high $k_\nu L$ values at the line center (see Fig. 3).

If $\Delta\nu_S \ll \Delta\nu_A$, i.e., a narrow line source is used, and if $k_\nu L \ll 1$ at all frequencies, then it can be shown [43] that

$$I^0A_T = C_3I_L\lambda_0^2NLA/\Delta\nu_D \tag{10}$$

where C_3 is different from C_1 and C_2 but is determined by similar parameters, I_L is the integrated intensity of the exciting line, in watts/cm^2 ster, and $\Delta\nu_D$ is the Doppler half-width, in sec^{-1}, of the absorbing atoms at the flame temperature. The integrated fluorescence intensity, I_F, is therefore given by

$$I_F = (C_3\Omega_a/4\pi\ \Delta\nu_D)I_L\lambda_0^2NLA\Phi \tag{11}$$