Analytical Atomic Spectroscopy

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ANALYTICAL ATOMIC SPECTROSCOPY

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Preface

This textbook is an outgrowth of the author's experience in teaching a course, primarily to graduate students in chemistry, that included the subject matter presented in this book. The increasing use and importance of atomic spectroscopy as an analytical tool are quite evident to anyone involved in elemental analysis. A number of books are available that may be considered treatises in the various fields that use atomic spectra for analytical purposes. These include areas such as arc–spark emission spectroscopy, flame emission spectroscopy, and atomic absorption spectroscopy. Other books are available that can be catalogued as "methods" books. Most of these books serve well the purpose for which they were written but are not well adapted to serve as basic textbooks in their fields.

This book is intended to fill the aforementioned gap and to present the basic principles and instrumentation involved in analytical atomic spectroscopy. To meet this objective, the book includes an elementary treatment of the origin of atomic spectra, the instrumentation and accessory equipment used in atomic spectroscopy, and the principles involved in arc–spark emission, flame emission, atomic absorption, and atomic fluorescence.

The chapters in the book that deal with the methods of atomic spectroscopy discuss such things as the basic principles involved in the method, the instrumentation requirements, variations of instrumentation, advantages and disadvantages of the method, problems of interferences, detection limits, the collection and processing of the data, and possible applications. Since the book is intended to serve as a textbook, principles are stressed. Detailed methods of analysis for specific elements are not included. It is the hope of the author, however, that the presentation of basic information is sufficiently detailed so the students can develop their own methods of analysis as needed.

Included in the textbook are several appendixes that should be valuable to the student as well as to atomic spectroscopists. These include a compilation of frequently used spectroscopic terms and units, tables of sensitive spectral lines of 70 elements abridged from National Bureau of Standards publications, absorbance values and the Seidel function calculated from percentage transmittances, and a table of elemental detection limits for flame emission and atomic absorption spectroscopy.

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Mr. Allan Childs, a graduate student in chemistry, aided in preparing a number of the spectral plates used as illustrations in the text and Mr. Truman Waugh of the Kansas Geological Survey, Lawrence, Kansas, was very helpful with the preparation of Appendix IV, which shows wavelength positions of some 50 elements together with a reference iron spectrum.

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Chapter 1

Historical Introduction

The use of atomic spectroscopy in chemical analysis requires, in addition to knowledge concerning the origin and production of spectra, a knowledge of the intrumentation required to produce, record, and measure the wavelengths of spectral lines and their intensities. These requirements therefore make necessary a knowledge of (1) the basic laws of optics, including characteristics of lenses and mirrors, (2) spectral dispersion elements, such as prisms and gratings, (3) methods of recording spectral wavelengths and intensities, such as photographic plates, photomultipliers, and strip chart recorders, and (4) methods of producing, under controlled conditions, spectra of the desired substances, as may be accomplished with arc, spark, or flame excitation techniques. Thus, a short history of atomic spectroscopy should include the major historical developments in each of these areas.

1. EARLY DEVELOPMENTS

Probably the first optical device of present-day spectroscopy to be discovered and used was the lens. There is archeological evidence of the existence of convex quartz lenses many years B.C. Though no early writings describing such objects have been discovered, it seems most likely that the properties of such lenses to magnify an object and/or to gather light rays from some object such as the sun were known to ancient peoples. In fact the possibility of using a lens to concentrate rays from the sun was mentioned by Aristophanes about 423 B.C.

Euclid, about 300 B.C., treated mathematically the size relations of the object and the image for plane and spherical mirrors. He located the focal point of concave mirrors and laid a foundation for the study of convergence and divergence of light beams reflected from mirrors. About 100 B.C., Hero presumably laid the basis of the law concerning the equality of the angles of incidence and reflection from a plane mirror when he stated that light takes the shortest path possible between two points.

The earliest recorded rainbow spectrum using glass as the dispersing medium is that of Seneca, about 40 A.D., who observed that the colors produced by passing sunlight through a three-cornered piece of glass produced colors similar to those of the rainbow. About 100 A.D., Ptolemy summarized knowledge of optics to that time and measured angles of incidence and refraction between air/glass, glass/water, and water/air.

In about 1038 A.D., Alhazen treated, in more detail, reflection of light from curved mirrors and the refraction of light through two different media. He also was aware of the atmospheric refraction of light but did not detail the laws of light refraction.

Roger Bacon, about 1250 A.D., refined the circular concave mirrors into parabolic surfaces and determined their precise focal points. He also studied lenses and observed the magnification possibilities of convex lenses.

About 1600 A.D. combinations of lenses were used and the telescope was invented about 1609 in Holland. News of this development reached Galileo in Italy and he improved on the telescope and demonstrated his own in 1610. This is also about the time that Snell (1591–1626) made his observation of the sine relationship between the angles of incidence and reflection as light passed between two different media.

2. THE NEWTONIAN ERA

Sir Isaac Newton (1642–1727) performed many experiments on the nature of light, the best known being those using a glass prism to study color. He noted that blue light was refracted a greater amount than was red. Thus, when sunlight was allowed to pass through a small hole, through the prism, and fall on a screen, he observed the resulting series of colored images of the hole. This Newton called a *spectrum*. A second prism did not further disperse the light but merely caused additional refraction. Newton had proved that the light from the sun was a heterogeneous mixture of rays that could be separated by a dispersion device.

Newton also felt that the separation of the light rays from the sun could be improved by the use of a lens. By using a lens to focus the sun's rays from the entrance hole onto the screen, he was able to produce a solar spectrum about 10 in. long. Newton realized that the ability of the prism to sort out the colors in sunlight depended on the fact that different colors of light possessed different indices of refraction and he measured indices of refraction of various substances. He was aware of Snell's law of the index of refraction; thus this work was an extension of Snell's observations.

Newton's study of combinations of lenses in telescopes led him to the conclusion that he could compensate for spherical aberration but that chromatic aberration could not be corrected. As in many cases, Newton's prestige as a scientist thus probably delayed further developments in optics for a number of years.

3. THE EARLY 1800'S (TO KIRCHHOFF AND BUNSEN)

The early 1800's produced a number of important developments related to spectroscopy. In 1800 Herschel discovered the infrared spectrum by using thermometers to measure energy beyond the visible red of the spectrum. In 1802 Wollaston observed dark lines in the sun's spectrum but failed to explain their presence. Also in 1802 Thomas Young made the first wavelength measurements of light using the theory of interference of wave motion as a basis. His measurements showed the visible spectrum to extend from 675×10^{-6} to 424×10^{-6} mm, remarkably close to presently accepted limits.

Fraunhofer, about 1814–15, observed the dark lines in the sun's spectrum that had been observed earlier by Wollaston (1802). He observed the fixed positions of the dark lines and improved the optics used for his observations. His use of a narrow slit and a telescope mounted behind the prism allowed him to carefully observe and locate the lines. Fraunhofer catalogued over 700 dark lines in the sun's spectrum. His study, using very narrow slits, led to his observation of diffraction patterns and in 1821 Fraunhofer invented the diffraction grating. Subsequently, he used a grating to determine the wavelengths of the dark lines in the sun's spectrum; eventually, the lines were to be named after him. For example, Fraunhofer measured the wavelengths of the *D* lines of sodium as 588.6×10^{-6} and 589.0×10^{-6} mm. These lines are the doublet and are now assigned wavelengths of 589.0×10^{-6} and 589.6×10^{-6} mm, respectively. These measurements made possible, for the first time, results in terms of wavelength rather than angles of refraction, a property dependent on the nature of the dispersing medium, rather than a fundamental property of light.

In 1823, J. F. Herschel published the first pictures of emission spectra and in 1831 suggested for the first time that the colors of an alcohol flame, as solutions were placed on the wick, produced "a ready and neat way of detecting extremely small amounts of them." He described how an alcohol flame could be made very bright when certain materials were placed in the flame.

Talbot, in 1825, also observed an orange color in a flame and ascribed its appearance as due to strontium added to the flame. He pointed out that this was the same color observed by Herschel when Herschel added a different