Flame Photometry

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PREFACE

This book is intended to provide an introduction to the principles and practice of flame photometry and to serve as a practical handbook of the many experimental aspects of the subject. In a sense, the book is an outgrowth of a series of lectures delivered during the Ninth Louisiana State University Symposium at the invitation of Dr. Philip W. West. Many of those in attendance emphasized the need for a treatise covering the field of modern flame photometry as practiced in the United States. Subsequently, the author undertook the task of assembling and digesting the source material from approximately 2,000 publications.

In the past, inconsistencies among the reported data have arisen because insufficient allowance was made for variations between the different classes of atomizers, for differences arising from the use of different flame temperatures and consequent shifts in the various gaseous equilibria involving the metal and its molecular compounds, and for failure to distinguish properly between purely spectral interferences and those arising from other radiative causes.

The organization of the book will be evident from the Table of Contents. The first 10 chapters are concerned with the theoretical and experimental basis for practical flame photometry. Emphasis in Chaps. 2 to 5 is on basic, essential principles. Practical procedures are considered in Chaps. 6 to 10. The approach is largely expository and analytical rather than historical and discursive. Such historical features as are included are limited to the introductory chapter or to brief introductory paragraphs to provide a general orientation for a given topic. The topics have been discussed at a relatively elementary level but include sufficient treatment to be valuable to the expert, yet so designed to be of equal value for persons whose knowledge of theory may be slight.

Following Chap. 11, the remainder of the book is devoted to the consideration of the individual elements that can be excited to emit radiation in a flame. The nature of the spectrum and the optimum excitation conditions for each element are considered; the purely spectral interferences are enumerated; and the radiation interferences from other cations and anions are discussed. Extensive cross references are given to the first nine chapters so that the practical material and principles can be seen as intimately related. A partial index to the Bibliography is provided by the application sections. The more important areas of clinical analysis, agronomic analysis, and analysis of cement and glass are considered at greater length in the final three chapters. The Bibliography is selective rather than comprehensive; there are rather thorough bibliographical compilations. For convenience, tables for preparation of stock solutions, of analytical factors, and of concentration units are inserted in the Appendix.

I wish to express my appreciation to my graduate students, past and present, and to Dr. Oscar Menis, Theodore C. Rains, and other members of the Analytical Division of the Oak Ridge National Laboratory for the stimulation engendered by many discussions of the divers aspects of flame photometry. I am indebted to Dr. Menis for permission to use his unpublished spectra of the rare earths and certain platinum metals and to Paul T. Gilbert, Jr., for securing certain illustrative matter.

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PART 1

THEORETICAL PRINCIPLE

CHAPTER 1

INTRODUCTION

Probably everyone at some time has observed the characteristic yellow light emitted when a small quantity of a sodium salt is introduced into a flame. For over a century it has been known that flames produced by the combustion of gases were capable of exciting certain elements to emit characteristic radiation. Talbot [711],† in 1826, studied the flame spectra of lithium and strontium. The discovery of cesium in 1860 and of rubidium in 1861 by Bunsen and Kirchhoff was made through observation of their spectra in flames. Emission of such characteristic radiation by each element and the correlation of the emission intensity with the concentration of that element form the basis of the subject matter of flame photometry.

A solution of the sample to be analyzed is sprayed under controlled conditions into a flame possessing the thermal energy required to excite the elements to a level at which they will radiate the observed emissions. In order to isolate the desired region of the spectrum, the light from the flame passes, either directly or indirectly by means of a lens or mirror, into the narrow entrance slit of a monochromator, or, as in the case of less expensive instruments, this isolation is accomplished by the use of a system of filters. The intensity of the isolated radiation is measured by a photosensitive detector and some type of meter or electronic amplifier. After careful calibration of the flame photometer with solutions of known composition and concentration, it is possible readily to correlate the intensity in emission of a given spectral line of the unknown sample with the amount of the same element present in a standard solution.

One of the principal attractions of flame excitation is the high degree of constancy and reproducibility of such sources. Flame photometry provides a precision that is difficult to match by any other spectrographic method. Furthermore, the spectrum of an element, as developed in a flame, is relatively simple, consisting normally of only a few

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† Numbers in brackets are keyed to the Bibliography at the end of the book.

lines. Identification of the line is simple, and spectral interference is less frequent.

Historical Background. Hartley [289] performed remarkable work on the emission spectra of elements excited in flames. He observed and measured the line and band emissions of 17 elements excited in an oxygen-hydrogen flame. Another serious study of the spectra of colored flames is recorded in a series of papers by Hemsalesh and De Watteville [312-315] in the years 1907 to 1910. They blew finely powdered metal into a flame by means of a blowpipe. De Gramont [275] has reviewed their work. Although several minerals, as well as metals, could be analyzed satisfactorily in this manner, as a series of papers by Rusanov and collaborators have shown, there are many types of samples that do not lend themselves to this technique. The use of a solution spray, by contrast, permits the distribution of the sample uniformly throughout the body of the flame.

Early Instruments. The use of a bunsen flame for quantitative analysis was suggested by Janssen [394] in 1870, and the principle was applied by Champion, Pellet, and Grenier [121] in 1873. They constructed an instrument for the determination of sodium in plant ash. The solution containing the sample was introduced into the flame by means of a platinum wire, and the emission intensity of the sodium light was compared with that of a constant-intensity sodium flame by means of a visual spectrometer. The two light paths were at right angles to each other. Light from the reference flame was attenuated until the light intensities were adjudged equal.

Another early flame photometer was designed by Klemperer [420] in 1910. He also employed visual comparison by means of a divided spectroscope eyepiece but varied the concentration of the standard solutions until equality of emission was observed. More recently, Rusanov and coworkers have reported the results of their studies with visual flame photometers.

Lundegardh Method. It was not until the classic studies by Lundegardh, which are contained in his two-volume treatise [450] and later papers [451–453], that the attention and interest of chemists were drawn to the advantages of flame excitation for quantitative analysis. This Swedish agronomist provided needed improvement on atomizer design and burner construction. In the Lundegardh method, the sample solution was sprayed under controlled conditions from a specially constructed atomizer into a condensing chamber and thence the aerosol was conducted into the base of an air-acetylene flame. A quartz-prism spectrograph dispersed the emitted light, and a photographic plate captured the energy emitted. After exposure, the photographic plates were developed and the optical densities of the various spectral lines recorded thereon were measured. With the aid of suitable calibration data, the optical densities could be correlated with chemical concentrations. Relative accuracies were generally 4 to 12 per cent. With the Lundegardh method, it became possible to carry out rapid and accurate analyses for several important microconstituents found in biological media, soil extracts, plant ash, and other types of samples.

Flame Photometers. European chemists were quicker to appreciate the value of flame excitation than were American chemists. A number of applications had been developed by the late 1930s when World War II interrupted the flow of literature between nations. Many early pioneering research studies are discussed in W. Bottger [74] and by Heyes [331]. Equipment was simplified, and the time for analysis was reduced. Colored-glass filters were used to isolate the radiant energy which was measured by a photocell connected directly to a sensitive galvanometer. Such simple, rugged, and economical apparatus constitutes the basis of modern, direct-reading, filter flame photometers.

In the United States it was not until 1939 that the Lundegardh method was introduced by Griggs [277] and by Ells and Marshall [201]. Real impetus was given to flame photometry in the United States with the advent of the work of Barnes et al. [36, 56]. These workers described a simple filter photometer which was subsequently marketed by the Perkin-Elmer Corporation as their model 18 series. This early instrument has been replaced since by improved models using a dual-optical prism system. In 1948, Beckman Instruments, Inc., made available a flame attachment for their well-known, Littrow-type spectrophotometer; subsequent versions incorporated an integral aspirator-burner and multiplier phototube, with recording accessories optional.

The multiplier phototube provided the sensitivity and, consequently, the selectivity needed in direct-reading flame photometry. The increased sensitivity enabled the less strongly emitting elements to be determined, and the improvement in detection limits permitted, in turn, a greater degree of spectral selectivity.

The utility of flame photometry for the analysis of sodium and potassium is well established, and these analyses constitute the bulk of the determinations performed at this time. However, the method is slowly displacing more troublesome methods for other elements, especially in laboratories conscious of the cost of analyses and the savings that can be effected through the adoption of flame methods for routine control purposes.

ORGANIZATION OF THE SUBJECT MATTER

The theoretical principles of flame photometry are considered in Chaps. 2 to 5. The use of organic solvents forms the subject matter of Chap. 5. It greatly increases sensitivity and thereby selectivity without increasing the complexity of the flame method. In Chap. 6, the components of the flame photometer are described along with their inherent characteristics and limitations. A discussion of interferences, evaluation methods, and optimal working conditions follows in Chaps. 7 to 9.

Chapter 10 describes absorption flame photometry. The flame is interposed between a monochromatic source and the receptor. Absorption of light from the monochromatic source by components in the test sample, rather than the emission of the test elements, is measured. The method overcomes to some degree the limitations and difficulties of emission measurements.

A discussion of the individual elements forms the subject matter of Chaps. 11 to 20. The elements are grouped according to their appearance in the Periodic Table. For each individual element, the emission spectrum, the excitation conditions, and the spectral and radiation interferences suffered are discussed.

Chapters 21 to 23 treat specific areas of applied analyses in which the flame method has been widely employed.

Although an extensive bibliography is appended, only selected references are included. For more comprehensive bibliographies devoted to flame photometry, the reader is directed to the bibliographies on analytical flame spectroscopy compiled by Mavrodineanu [482, 482a] and published in 1956 and in 1959–1960, or to the bibliographies included in the monographs written by Herrmann [326] or by Burriel-Marti and Ramirez-Munoz [104].

CHAPTER 2

ATOMIZATION

Early methods of introducing the test material into the flame have been well described by Mavrodineanu and Boiteux [483], Mitchell [509], and Twyman [725]. They included feeding the solution into the flame from a glass tube along a spiral or bundle of platinum wires [271, 272, 310, 513] and rotating a platinum-gauze disk through the solution and into the flame [191]. Several groups of workers [113, 312–315, 619, 620, 627] have blown finely ground powders into the flame. In the Ramage method [593], a small roll of filter paper—a spill, on which a fraction of a milliliter of the sample solution has been evaporated—is fed into the flame at a uniform rate. Mitchell [507] and Steward and Harrison [692] have shown that the method is not adequate for analysis of several cations simultaneously. Its main advantage is that only 0.05 to 0.1 ml of solution is required. Roach [608] has fully described the technique as evolved by workers in England. Kent [409] has shown that the maximum accuracy to be expected is only ±9 per cent.

The present trend is to prepare solutions of known concentrations and to spray these into the flame, using some form of aerosol production. Use of an aerosol permits the distribution of the sample throughout the body of the flame rather than its introduction at a single point. Morton [517] seems to have been the first to propose the atomizatiom of a solution with a jet of air and the conduction of the resulting aerosol into the high-temperature zone of a flame. However, his atomizer lacked stability and constancy, and it is to Gouy [273] that we owe the development of an atomizer similar in form to the discharge type of atomizer in use today.

Other methods of spray production have been proposed, but they have not been adopted into practice. Kirchhoff and Bunsen [419] swept a spray from an acidified solution, to which zinc was added, into the flame with the gas stream. Torok [719, 720] used aluminum and potassium hydroxide as a source of a hydrogen spray, and acid and ammonium carbonate for a carbon dioxide spray. In the electrolytic method used by Beckmann [43] and Klemperer [420], droplets were produced by electrolysis of the test solution, and these were swept into the flame by the air stream.

Methods of Atomization. Atomization refers to the process of breaking a large mass of liquid into small drops. Of the different methods of atomizing liquids, only gas-stream, or pneumatic, atomization and impingement atomization are employed in flame photometry. Pneumatic atomizers are more suitable than other types of atomizers for producing very fine sprays and sprays with a small cone angle. Atomization by means of supersonic vibrations has been considered, as well as atomization by high-voltage electrical energy [698].

The construction of typical pneumatic atomizers is shown schematically in Fig. 2-1. In type *a*, the two annuli are concentric about a center and the liquid emerges from the inner annulus, usually a palladium capillary. Air or oxygen forced through the outer annulus creates sufficient suction in the central feed tube to lift the solution through a height of about a foot, so that, by using a relatively short tube, small variations in the depth to which the tube is immersed in the solution lead to insignificant variations in the amount of spray delivered to the flame. In type *b*, the two nozzles are positioned at right angles to each other. The liquid may flow into the atomizer by gravity or by suction produced by the flow of the gas stream issuing from the other nozzle. The flow of the stream of air or oxygen at a high velocity past the top of the vertical tube in dip-type atomizers creates a reduced pressure at this point, which causes liquid to flow up the tube and into the high-velocity gas stream. Atomizers operate with gas pressures ranging between 5 and 15 lb per sq in.

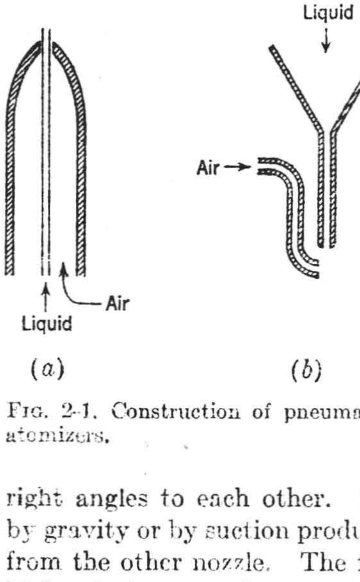

FIG. 2-1. Construction of pneumatic atomizers.

Mechanism of Pneumatic Atomization. The formation of an aerosol through atomization by high-velocity gas streams has been studied by many workers [116, 440, 446, 471, 536, 633]. A two-step process has been postulated: (1) the formation of ligaments of liquid and the disruption of these to form drops and (2) the shatter of the drops under the continuing influence of the gas stream.

Several stages can be distinguished as the liquid leaves the orifice of a capillary (Fig. 2-2) when the sequence of events is followed by high-speed photography [471]. By proper design of nozzle diameters and choice of velocity of the atomizing gas stream, the velocity of the gas stream is high relative to the liquid at the point where it encounters the liquid jet. A portion of the liquid jet is caught up at a point where its surface is ruffled by the action of the gas stream and, being anchored at the other end, is drawn out into a fine ligament. The continuing action of the air pressure and other forces initiate periodic disturbances along the ligament, and it starts to neck down. At each node the liquid ligament, being quite small in diameter, collapses and is swiftly drawn up into spherical drops whose diameter is approximately twice the diameter of the original ligament. Interspersed among the drops are small satellite drops formed from the liquid at the point of necking down. The higher the velocity of the gas stream, the finer the ligaments, the shorter their lives, and the finer the drops formed.

The motion-picture studies by Marshall show several other interesting phenomena. Immediately after formation, the larger drops oscillate between the shape of an elongated cylinder and that of a flat disk. Drops seldom recombine or coalesce on collision with one another but usually bounce away. The ratio of large drops to the smaller satellite drops is approximately 2.8.

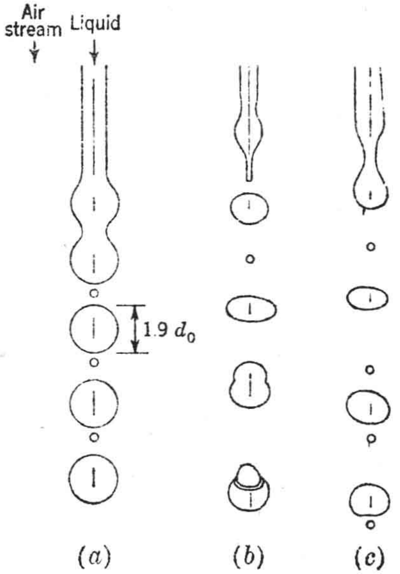

FIG. 2-2. Breakup of a water jet. (*a*) An idealized drawing; (*b* and *c*) as drawn from high-speed photographs. (*From W. R. Marshall, Jr., Atomization and Spray Drying, Chem. Eng. Progr. Monograph Ser. 2, vol. 50, American Institute of Chemical Engineers, New York,* 1954, *page* 4. *By permission of the author and publisher.*)

Further breakup of these drops occurs during their movement under the influence of the gas stream. Again the breakup has been studied by rapid photographic registration [440, 471]. The sequence of events is reproduced in Fig. 2-3. Impaction between the air and the drops causes the drop to become increasingly flattened and, at a critical velocity of the air, it is blown out into the form of a hollow bag attached to a roughly circular rim. Bursting of this bag produces a shower of very fine droplets and leaves a necklace of droplets where the rim of the bag had existed. The rim contains about 70 per cent of the mass of the original spherical drop.

The breakup phenomenon demonstrates a feature that is characteristic of aerosol production: a distribution of droplet sizes with only a comparatively small fraction of the liquid mass ultimately appearing as the finest droplets. The latter either are produced by the collapse of the hollow bag or originate as satellite drops.

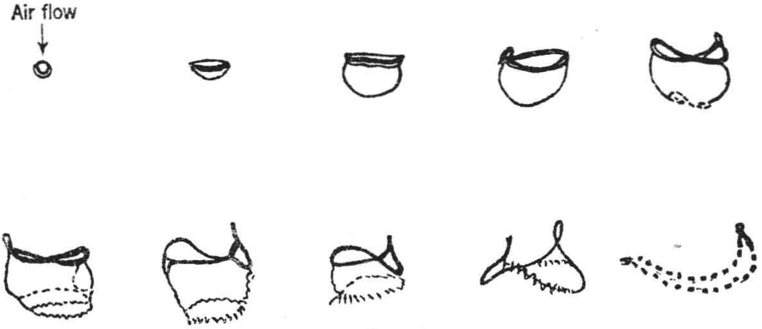

FIG. 2-3. Breakup of a drop. [*Adapted from W. R. Lane, Ind. Eng. Chem.*, **43**, 1313 (1951).]

Impingement Atomization. Mechanical impingement was adopted by Rauterberg and Knippenberg [598] and others [516, 764]. It consists in directing the liquid jet against a solid target (brise-jet) or a solid surface. A small glass ball is often placed in the path of the liquid stream, or the liquid is directed against the walls of the condensing chamber. The resulting impact and liquid attenuation caused by the sudden change of direction of the jet bring about additional disintegration. A distinctly larger fraction of droplets possess smaller mean diameters. The position of the target, relative to the liquid orifice, is important; breakup is effected better if the liquid jet has started to neck down just before impacting the target.

Use of mechanical impingement is confined to the discharge type of atomizer, type *b* of Fig. 2-1.

Drop-size Distribution. Since the atomization process produces a range of drop sizes, it is important to know the size distribution of drops. With discharge atomizers and their attendant condensing chambers only the finest droplets will actually reach the burner and contribute to the emission intensity.

Several distribution equations have been developed which fit experimental data with reasonable precision. These have been ably reviewed by Mugele and Evans [522]. None of the distribution equa-