ADVANCES IN
SPECTROSCOPY

VOLUME II

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INTRODUCTION TO THE SERIES

A hundred years ago, Bunsen pointed the way to the use of characteristic wavelengths in atomic emission spectra for the qualitative or quantitative analysis of metals. Fifty years before that Herschel had discovered the infra-red, and Abney later predicted the correlation between some characteristic absorption bands in this spectral region and special features of molecular structure. It is a sobering thought that the wider implications of these discoveries have only been fully realized during the past forty years. Delay in their development and application was due, perhaps, not so much to difficulties on the technical side as to the lack of a convincing background framework of spectral theory such as became possible by the application of quantum theory to the interpretation of the spectra of atoms and molecules.

However that may be, it is generally accepted that spectroscopy now occupies a leading place among the modern physicochemical techniques, not only in pure and applied research, but also for many routine scientific operations. The applications in physics, chemistry and biochemistry cover a wide range; they bear upon questions of atomic and molecular structure, of qualitative and quantitative analysis, and they lead to data about the energy levels of atoms, molecules, ions or aggregates which are useful in relation to physical and chemical properties of materials.

It is increasingly evident that the variety of spectroscopic work is now such that few workers in the field can deal directly with more than a limited part of it. On the other hand, more of us need to maintain contact with other branches than our own, not only to follow the advances in technique, but also because of a common interest in atomic and molecular energy levels and the information derived from them. For these reasons, there is a need for periodic authoritative surveys on recent progress in different branches, written by experts who themselves have contributed to it, and

collected together in one place. A series of volumes has therefore been planned along these lines, of which this is the first. It is intended to cover in this series all important aspects of spectroscopy, pure and applied, atomic and molecular, emission and absorption, relating to physics, chemistry, biology, astrophysics, meteorology and general technique.

It is hoped to publish the first few volumes quickly with reviews of the present position in most important fields. Subsequently, volumes will be planned as seem to be required by the state of the subject.

My thanks are due to Professors Dieke, Herzberg, Lord and Swings, to Dr. R. N. Jones and to many other colleagues for their helpful suggestions.

OXFORD   H. W. THOMPSON
May 12 1959

PREFACE TO THE SECOND VOLUME

The popularity of the first volume has left no doubt that the experiment of introducing this series was fully justified. Very gratifying comments have been received not only about the high standard set by the authors of the articles, but also as regards the variety of subjects covered. It was perhaps not surprising that some critics should have drawn attention to the absence so far of a progress report on emission spectrographic analysis. It is, indeed, hoped to deal with this appropriately in the near future, but expert advice suggested that at the present stage it might be more desirable to give preference to newer developments on the atomic side, such as atomic absorption or x-ray emission methods. Both these topics are discussed in this second volume. Moreover, it is generally admitted that during the past fifteen years the emphasis on studies of molecular spectra of one sort or another has been considerable.

In this present volume the topics again cover a wide range, including atomic and molecular spectra—x-ray, ultra-violet and infra-red—with special reference in some cases to particular directions of application, such as flames or crystals. Some subjects of biological interest are discussed, such as the ultra-violet spectra of proteins and the infra-red spectra of bacteria, and an account from a chemist's point of view of the significance of nuclear magnetic resonance is obviously opportune.

The third volume, which is now in preparation, should make it possible to complete a survey of other established fields, and to include a few of the very recent developments. Also, it may be possible to include reviews of a number of the current industrial applications which are not covered by earlier articles.

My apologies are due to several authors for the delay between receipt of their articles and the date of publication, but here, as in a complex chain reaction, the rate of the over-all process is governed

by that of its slowest step. Our thanks are due to the publishers and printers for their continuous and tolerant help, and for the excellence of the printing and photographs.

St John's College, Oxford   H. W. THOMPSON

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APPLICATION OF ATOMIC ABSORPTION SPECTRA TO CHEMICAL ANALYSIS

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CONTENTS

I. INTRODUCTION

The first application of atomic absorption spectra to chemical analysis was reported 100 years ago by Kirchhoff,[21] who used the atomic absorption lines in the Fraunhofer spectrum to deduce the

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presence of certain elements in the solar atmosphere. Shortly afterwards, Kirchhoff and Bunsen [22-24] described their celebrated experiments which clearly showed that atomic spectra, either in emission or absorption, could be the basis of powerful methods of chemical analysis. From that time onwards emission methods of spectrochemical analysis were steadily developed and during the last 20 years these have culminated in direct-reading spectrographs which provide multicomponent analysis of remarkable accuracy at high speed.

Whereas emission methods have become firmly established and widely adopted, it is a curious feature of the history of spectrochemical analysis that the potentialities of absorption methods have been almost completely overlooked. It is only during the past few years, [32, 37, 41] that the use of atomic absorption spectra for general analytical purposes has been shown to possess fundamental advantages over emission methods. Previously, the analytical applications of atomic absorption spectroscopy had been largely confined to astrophysical work on the determination of the compositions of the solar and stellar atmospheres, and to the special case of estimating the contamination of laboratory atmospheres by mercury vapour, which has an appreciable vapour pressure at room temperature. This neglect of the techniques of atomic absorption spectroscopy in analytical work is all the more surprising when one recalls that they have been widely used in research work, particularly in studies of the hyperfine structure of atomic spectral lines, and in investigations of the resonance radiation from atoms. There is little doubt that the spectacular successes of emission methods have tended to obscure some of their fundamental limitations, and it also seems to have been tacitly assumed that the latter would necessarily have their counterparts in absorption methods. A further contributing factor may have been the difficulties often associated with atomic absorption measurements.

In this review the factors governing the relationships between atomic absorption and atomic concentrations will be discussed and a description given of the experimental methods which have been developed for carrying out chemical analyses by the absorption technique. A brief survey will then be given of recent analytical applications: these will not be discussed in detail, but only in so

far as they help to illustrate the advantages and limitations of the absorption method. Finally an assessment will be made of the present status of this method of spectrochemical analysis.

II. CHARACTERISTICS OF ATOMIC ABSORPTION SPECTRA

A. Variation of Atomic Absorption with Atomic Concentration

The relationships between atomic absorption and atomic concentration, under various physical conditions, are fully discussed in several papers, mainly in astrophysical journals, and in standard reference books. [30, 34, 39] For the purpose of this review it is sufficient to consider only the most fundamental of these relationships and to restrict the discussion in the first place to the case of atomic absorption lines possessing no hyperfine structure.

Consider a parallel beam of radiation of intensity I_0, at frequency ν incident on an atomic vapour of thickness l cm. Then if I_ν is the intensity of the transmitted beam, the absorption coefficient K of the vapour at frequency ν is defined by

$$I_\nu = I_0 \exp\{-K_\nu l\} \tag{1}$$

The dependence of K_ν on ν, i.e. shape of the absorption line, is determined by the nature of the transition involved in the absorption, and on the physical conditions such as temperature, pressure and electrical fields, to which the atoms are subjected during the measurement. This subject is discussed further in Section IIB.

According to classical dispersion theory, the relationship between integrated absorption coefficient and concentration is given by

$$\int K_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f \tag{2}$$

where e is the electronic charge, m the electronic mass, c the velocity of light, N_ν the number of atoms per cm³ which are capable of absorbing in the range ν to $\nu + d\nu$, and f the oscillator strength, which is the average number of electrons per atom that can be excited by the incident radiation. Equation (2) is only

strictly valid when the refractive index can be considered equal to unity over the breadth of the absorption line, and thus becomes inaccurate at high absorption.

For an absorption line involving a transition from an initial state i of excitation energy E_i, the number of atoms per cm^3 capable of absorbing is related to the total number of atoms per cm^3 N by

$$N_\nu = N \frac{P_i \exp\{-E_i/kT\}}{\sum P_j \exp\{-E_j/kT\}} \tag{3}$$

where P_i and P_j are the statistical weights of the initial and other energy states, respectively, and the summation in the denominator extends over all possible energy states.

In order to illustrate the magnitudes involved in equation (3), Table I gives the fraction of atoms in the first excited state for various elements at different temperatures.

It will be seen that the fraction only becomes appreciable for atoms with low energy levels and at high temperature. Since most elements have their strongest resonance lines at wavelengths below 6000 Å (see Table III), and atomic absorption measurements in spectrochemical work are usually made on atomic vapours in flames at temperatures below 3000°C, the number of atoms in the ground state can generally be assumed to be equal to the total number of atoms. Thus in (2) N_ν can usually be replaced by N, and in such cases there is a simple linear relationship between the integrated absorption coefficient and concentration. It would therefore be ideal if spectrochemical methods could be based on

TABLE I. Values of N_j/N_o for Various Resonance Lines

Resonance line	Transition	$\frac{P_j}{P_o}$	N_j/N_o			
			$T=2000°K$	$T=3000°K$	$T=4000°K$	$T=5000°K$
Cs 8521 Å	$^2S_{1/2}-^2P_{3/2}$	2	4.44×10^{-4}	7.24×10^{-3}	2.98×10^{-2}	6.82×10^{-2}
Na 5890 Å	$^2S_{1/2}-^2P_{3/2}$	2	9.86×10^{-6}	5.88×10^{-4}	4.44×10^{-3}	1.51×10^{-2}
Ca 4227 Å	$^1S_0-^1P_1$	3	1.21×10^{-7}	3.69×10^{-5}	6.03×10^{-4}	3.33×10^{-3}
Zn 2139 Å	$^1S_0-^1P_1$	3	7.29×10^{-15}	5.58×10^{-10}	1.48×10^{-7}	4.32×10^{-6}

measurements of integrated absorption coefficients. These measurements would have the important advantage of being independent

of the physical conditions, such as temperature, pressure, electric fields, etc., to which the atomic vapour is subjected. Unfortunately this ideal method cannot be used owing to the experimental difficulties associated with the accurate measurement of the integrated absorption coefficients of atomic spectral lines. Since these difficulties have their origin in the small widths of atomic lines, and in order to appreciate the characteristics and limitations of the present methods of atomic absorption measurement, it is necessary to consider the factors governing the shapes and widths of atomic lines. For a detailed discussion of this subject the reader is referred to the reviews by Margenau and Watson[27] and by Ch'en and Takeo.[9]

B. Shapes and Widths of Atomic Spectral Lines

1. Natural Width

Corresponding to the probability distribution associated with each energy level of an atom there is a corresponding intensity distribution in a spectral line due to transitions between two of these levels. For resonance lines this natural width is of the order of 10^{-4} Å and for the experimental conditions of interest in this review this width is negligible compared with that due to other causes.

2. Doppler Width

The Doppler width D_λ, of a line of wavelength λ, due to the absorbing or emitting atoms having different component velocities along the line of observation, is given by

$$D_\lambda = 1 \cdot 67 \frac{\lambda}{C} \left(\frac{2RT}{M} \right)^{\frac{1}{2}} \tag{4}$$

where R is the universal gas constant, M the atomic weight, and T the absolute temperature. Typical values for different atomic species at various temperatures are given in Table II, from which it can be seen that over the temperature range 1500–3000°K, in which we shall be interested, the Doppler width is of the order of 0·01 Å.

TABLE II. Values of D_λ at Various Temperatures

Element	λ	M	D_λ		
			1000°K	2000°K	3000°K
Na	5890 Å	22·3	0·028 Å	0·039 Å	0·048 Å
Cu	3247 Å	63·6	0·0092 Å	0·0113 Å	0·016 Å
Zn	2139 Å	65·4	0·0060 Å	0·0085 Å	0·010 Å

3. Pressure Broadening due to Foreign Gases

Another important cause of broadening of atomic spectral lines is perturbation of the absorbing or emitting atom by foreign gas atoms. As the pressure of foreign gas is increased the line is broadened and the shape of the line becomes asymmetrical with the peak of the line shifting, in most cases to longer wavelengths. To a first approximation the magnitude of each of these effects is linearly proportional to pressure, and varies for different elements, for different foreign gases, and for different atomic lines. In view of these various factors on which pressure-broadening effects depend it is not surprising that it has so far proved impossible to calculate, accurately, the magnitude of the effect in any specific case. A useful working rule is that for the strongest resonance lines the broadening at one atmosphere of foreign gas is in the range 0·01–0·1 Å. Since the experimental methods described later are concerned with measuring the absorption by flames, having temperatures of 1500–3000°C, it can be seen that in such cases the pressure broadening is of the same order as Doppler broadening (see Table II). For example, in a sodium flame the pressure broadening has been found [40] to be approximately one-half that due to Doppler broadening.

4. Resonance Broadening

A special type of pressure broadening, which is much more severe than that due to foreign gases, is known as resonance broadening and occurs when the emitting or absorbing atom is perturbed by an atom of the same type. In this case the broadening may be appreciable at pressures as low as 0·1 mm Hg and it is only at pressures below 0·01 mm that resonance broadening may be assumed to be negligible (see Section III).

5. Self-Absorption Broadening

For sources of extended depth, such as the hollow cathode tubes described later, an important cause of broadening of the emitted resonance lines is self-absorption, which results in the centre of the line being absorbed to a greater extent than the wings of the line (see Section III). Broadening of this type can only be avoided by using combinations of source length and vapour concentrations which ensure that the maximum absorption along the length of the source is negligible. Self-reversal is a special type of such broadening which occurs when the source is surrounded by a cooler sheath of vapour, and results in selective absorption of the centre of the line. A detailed discussion of the effects of self-absorption and self-reversal has been given by Cowan and Dieke.[10]

6. Stark Broadening

Since a uniform electric field will split an atomic spectral line into its Stark components, the separation of which increases with the field strength, a non-uniform field will produce a whole series of Stark components and thus result in a broadening of the line. The Stark components of the hydrogen line H_α, for example, have a separation of 3 Å for a field of 10,000 V/cm. Since similar effects can be caused by the electric fields due to neighbouring ions, it is apparent that if Stark broadening is to be avoided it is important to avoid large concentrations of ions or electrons, and current densities must therefore be kept low (see Section III). In an arc in air at atmospheric pressure, for example, the high charge density results in the diffuseness of many of the lines in the emitted spectrum.

7. Zeeman Broadening

Corresponding to Stark broadening, there may also be Zeeman broadening due to magnetic fields. The effects, however, are only appreciable for strong externally applied fields and are negligible under all the experimental conditions considered in this review.

8. Hyperfine Structure

In the above discussion the hyperfine structure of atomic lines due to nuclear spin, or to the presence of several isotopes, has been

neglected. It is clear that each of the hyperfine components will be broadened by the processes described above, and that as regards absorption each component can be treated as an independent line. The possibility of using the absorption method for the determination of isotopic composition is discussed in Section V.

III. EXPERIMENTAL TECHNIQUES

A. Principle

It will be apparent from (2) that an ideal experimental technique would be one which measured the integrated absorption coefficient, $\int K_\nu d\nu$, since this is directly proportional to concentration and is independent of line shape and line width. It would, therefore, be independent of the physical conditions of the absorbing atomic vapour, assuming that these conditions are not so severe as to alter the oscillator strength of the line in question. Unfortunately the accurate measurement of integrated absorption coefficients for atomic lines presents severe experimental conditions, since under the conditions suited to the production of atomic vapour the widths of the absorption lines are in the range 0·01–0·1 Å. Accurate intensity measurement over the profile of such a line would require a spectral slit-width of the order of 0·005 Å, which is beyond the performance of most spectrographs or monochromators. Furthermore, if it is desired to use photo-electric methods of intensity measurement, then it is scarcely feasible to use a continuous source, since the energy emitted over such a small spectral slit-width would be too small to give an adequate signal–noise ratio. In astrophysical work this difficulty is overcome by the method of 'total absorption'[25] in which the energy removed from the incident beam is measured. This method has the advantage that the measurement is independent of the resolution of the monochromator, but suffers from the disadvantage of giving a complicated relationship between the quantity measured and concentration, according to the region of the curve of growth in which the measurement is made.

For spectrochemical work the atomic absorption methods which have been developed [1–3, 6, 11, 19, 32, 35, 37, 38] consist essentially in measuring peak absorption. In these methods the difficulties of obtaining high resolution are overcome by using light sources

which emit lines of much smaller width than those of the absorp-
tion lines to be measured. A further feature of the experimental
technique is the provision of means for compensating for any
radiation emitted by the vapour whose absorption is to be
measured.

The principle of the method [1, 2, 32, 41] is shown in Fig. 1. The
light source emits, under conditions which ensure the production
of extremely sharp lines, the spectrum of the element to be
estimated and this emitted radiation is modulated, either by
modulating the electrical supply to the lamp or by a mechanical
chopper in the light beam, before it passes through atomic vapour
of the sample. The monochromator isolates a given line, usually
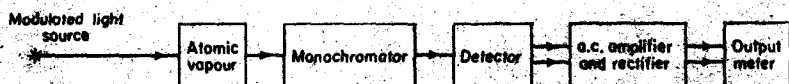

FIG. 1. Schematic diagram illustrating operation of an atomic absorption
spectrophotometer.

the strongest resonance line, and this falls on to a photo-electric
detector. The output from the latter is passed to an amplifier
tuned to the same frequency as the light-source modulator, so
that only the signal due to the radiation from the source is
amplified; any radiation emitted by the atomized sample is not
modulated and thus produces no signal at the output of the
amplifier. After amplification the signal is rectified and passed to
a meter or recorder which indicates the signal with and without
the absorbing sample in the radiation path.

B. Description

A typical arrangement [6] which has been used in several investi-
gations[11, 43-46] is shown in Fig. 2. Modulated radiation from a
sealed-off hollow cathode tube, [15, 20, 35, 38] containing a cathode of
the element to be determined, passes through the flame into which
is sprayed the solution for analysis, and the appropriate resonance
line is selected by the monochromator. The absorption of the
resonance line by the flame is measured by means of a photo-
multiplier tube. The power pack on the left supplies the hollow