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SELECTED METHODS

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Preface

This book was conceived to appeal to the practicing analyst. Theory is presented in a very descriptive, nonrigorous fashion. Citations have been kept to a minimum to improve the flow of material and to avoid the impression that the reading of these references is essential. The general principles of atomic absorption spectroscopy are now well-established, and it seems desirable to cease the referencing of each point of theory.

The procedures were selected with a view to their reliability. Emphasis was placed on choosing thoroughly tested methods, preferably ones that were evaluated by using standard reference samples or inter-laboratory comparison. Unfortunately, this process and the personal bias of the author will inevitably have resulted in the exclusion of good procedures. The methods are given, as much as possible, in the words of the original author. This has been done to avoid misinterpretations, which can often negate the usefulness of a method.

There will inevitably be gaps in the chapters where the analyst might feel a procedure should have been given. A conscious attempt has been made to recognize the strengths and weakness of atomic absorption spectroscopy and thereby avoid including procedures for elements and applications for which the technique is poorly suited. Good examples of the latter are the omission of most major element analyses, analyses better done by flame emission and indirect methods. Other gaps will exist. In spite of the burgeoning atomic-absorption-methods literature, a critical review has shown that no reliable procedure has been published for many applications. Again, I am painfully aware of omissions that may occur due to the subjective nature of such a process.

Analytical methods have been grouped into chapters in a manner that minimizes overlap and repetition. However, there are instances where procedures useful for several sample types have been placed in the most suitable chapter and reference is then given in text to other applications.

In addition to the conventional chapters, a short section has been presented on elemental speciation using atomic absorption spectroscopy. This latter field, so crucial to the solution of environmental, biological, and health related problems, is in its infancy. Few tested procedures yet exist in this area. However, the study of elemental speciation is a very important new direction being taken by atomic absorption spectroscopy. Therefore, the available work has been included here, to introduce analysts to the power and simplicity of the approach.

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General Principles

INTRODUCTION

The phenomenon of the absorption of radiation by atoms has been used for investigations in physics since the early part of the nineteenth century, when Frauenhöfer observed a number of dark lines in the sun's spectrum. The first analytical application of atomic absorption was to the determination of mercury by Müller (1). Not until 1955, when Walsh (2) discovered the general usefulness of the approach to elemental analysis, was real analytical atomic absorption spectroscopy born. In the relatively short period of two and one-half decades since this development, atomic absorption spectroscopy has become one of the most important techniques for the analysis of the elements.

During the early commercialization of atomic absorption spectroscopy, extravagant proclamations were made concerning the general lack of interferences encountered with this technique. This is peculiar in that Walsh, in his original paper, limited his claims for superiority to a simpler pattern of atomic spectral interference and a greater tolerance to thermal fluctuations in the atomizer compared to emission spectroscopy. Another rather amusing characteristic of early research in this field was the great deal of wasted time spent by many workers, including the present author, in rediscovering interferences in flames which had been known to emission spectroscopists for up to 50 years.

Emission spectra are usually produced thermally using high-energy sources such as high-temperature flames, arcs, or sparks, and they are usually very complex. For a given element only a small fraction of the atoms obtained is in an excited state and this fraction is highly temperature dependent. Hence, small temperature fluctuations cause appreciable variations in emission. The ground-state atom population, important in absorption, is much less affected by small temperature fluctuations. Many atomic species generated in high-energy thermal sources

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emit radiation. This results in a complex spectrum that must be resolved using an expensive, high-resolution spectrometer.

Absorption spectra are relatively simple, requiring the use of a low-priced monochromator. The likelihood of atomic spectral overlap is high with emission spectroscopy, whereas this possibility is much reduced with atomic absorption spectroscopy.

Few techniques of chemical analysis have the inherent simplicity of atomic absorption spectroscopy. Thus, the technique is commonly used by those with limited knowledge of analytical chemistry or atomic spectroscopy. It is important to emphasize the potential consequences of this fact. The present author is frequently confronted with manuscripts and theses written by researchers in biological, health, geological, and metallurgical sciences that are based on results obtained by atomic absorption spectroscopy. In many cases it is impossible to judge the validity of the data presented. These workers seldom give sufficient procedural detail to indicate whether precautions have been taken to avoid common sources of interference (e.g., nonspecific absorption). Standard reference materials are seldom analyzed.

No technique of chemical analysis is universally applicable. Figure 1 is a periodic table showing only those elements that can be analyzed directly by atomic absorption. Of those shown, osmium, wolfram, zirconium, hafnium, niobium, tantalum, and the rare earths are better

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	NOBLE GASES
Li	Be											B					
Na	Mg											Al	Si				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se		
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		
Cs	Ba	La	Hf	Ta	W		Os	Ir	Pt	Au	Hg	Ti	Pb	Bi			

						Eu		Tb	Dy	Ho	Er	Tm	Yb	Lu

Fig. 1. Periodic table showing elements determinable by atomic absorption.

handled by other techniques. These refractory elements present difficulties and exhibit poor sensitivity in flame atomizers. Alkali metals are easily handled by flame emission and many workers still prefer this approach. Below the parts per million (ppm) level, neutron activation and related nuclear techniques, when available, must be considered competitive. In the percentage range, x-ray fluorescence spectroscopy is superior. There is a tendency among analysts to force atomic absorption spectroscopy to do analyses for which it is poorly suited. The meteoric rise in popularity of atomic absorption must not be allowed to obscure the niche it best fills among other analytical techniques.

ATOMIC SPECTROSCOPY

Techniques commonly referred to as atomic spectroscopy usually include atomic emission, atomic absorption, and atomic fluorescence spectroscopy. These involve valence electron transitions yielding radiation with wavelengths in the ultraviolet–visible region of the spectrum. X-Ray fluorescence and neutron activation, although atomic techniques, are not usually referred to as atomic spectroscopy. An abundance of analytical procedures exist that involve either atomic emission or absorption spectroscopy, but little analytical use has been made of atomic fluorescence spectroscopy.

Atomic Spectra

Electron orbits in an atom are characterized by the major and azimuthal quantum numbers n and l, respectively. When an electron undergoes a transition from a higher energy level (E_{nl}) to a lower energy level ($E_{n_1 l_1}$), light of frequency

$$\nu = (E_{nl} - E_{n_1 l_1})/h = \Delta E/h$$

is given off. In terms of wavelength,

$$\lambda = c/\nu = hc/\Delta E$$

The constants h and c in these questions are Planck's constant and the velocity of light, respectively. Thus, electronic transitions can be discussed in terms of frequency ν, energy E, and wavelength λ. The latter is most frequently used in atomic absorption spectroscopy. The parameters ΔE, ν, and λ have unique values for a given electronic transition. An element can undergo many electronic transitions. This results in a
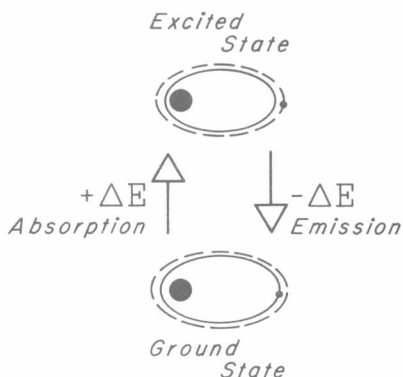
Fig. 2. Relationship between emission and absorption of energy by a valence electron.

series of sharp lines—a spectrum—which is uniquely characteristic of each element.

Emission and absorption can be related as shown in Fig. 2. An electron of an atom in its lowest energy state, the ground state, can absorb a quantum of energy ($+\Delta E$) and undergo transition to a low-lying excited state. Emission occurs when this quantum of energy is released ($-\Delta E$) and the electron returns to the ground state. A transition to and from the ground state, as illustrated in this example, is called a resonance transition. Resonance lines are the most useful analytical lines for atomic absorption spectrometry.

An energy level graphical representation of an atom is usually given by a Grotian diagram (3). A Grotian diagram for sodium is shown in Fig. 3. Sodium has one valence electron. When this electron is in the ground state (3s), the energy-of-transition-scale (vertical, electron volts) shows zero. Resonance transitions emanate from this energy level, with the most commonly used analytical line for absorption measurements being 5889.9 Å. This transition from the $3s^2_{1/2}$ to the $3p^2_{3/2}$ energy level is the lowest energy transition for sodium and represents an energy gain by the electron of 2.2 eV.

The horizontal axis of the Grotian diagram shows the term symbol. This shows that p levels have two terms, $3p^2_{3/2}$ and $3p^2_{1/2}$. The detailed discussion of this aspect of the Grotian diagram is beyond the scope of this book. However, it should be pointed out that this indicates that transitions from p levels for one-valence-electron elements result in doublets. In the case of sodium, the 5895.9 Å transition represents only a slightly different energy than the 5889.9 Å line and these two are the well-known D line doublets of the sodium spectrum.
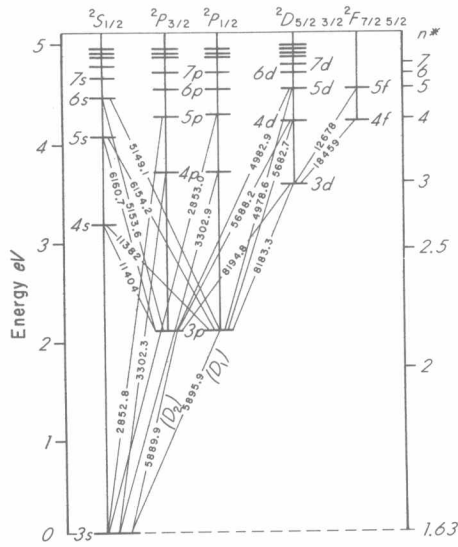
Fig. 3. Grotian diagram (3) for sodium.

Electronic transitions in an atom are governed by selection rules that designate which possible transitions are permitted and forbidden. For a good discussion of this and other more fundamental aspects of spectroscopy, the reader is referred to Mitchell and Zemansky (4) and Herzberg (5).

ABSORPTION EXPRESSION

An Absorption Line

When a parallel beam of continuous radiation of intensity I_0 passes through a cell containing atomic species of an element, the transmitted radiation I_ν will show a frequency distribution as given in Fig. 4 (4). The atomic species is said to possess an absorption line at frequency ν_0, where ν_0 is the frequency at the center of the line. The absorption coefficient of the atomic vapor k_ν is defined by

$$I_\nu = I_0 e^{-k_\nu b}$$

where b is the thickness of the absorbing layer, and the integrated absorption
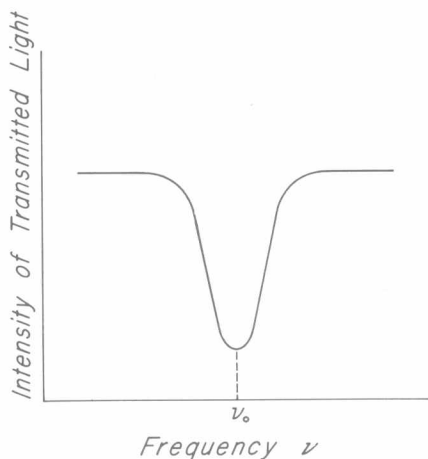
$$\int k_\nu \, d\nu = \frac{\pi e^2}{mc} N_\nu f$$

Fig. 4.   Frequency dependence of transmitted radiation.

where N_ν is the number of atoms per cubic centimeter that can absorb in the frequency range ν to $\nu + d\nu$, f is the oscillator strength (the average number of electrons per atom that can be excited by the incident radiation), e is the charge on an electron, c the velocity of light, and m the mass of an electron. Tables of oscillator strength are available to allow a comparison of transition probabilities for a given line and a given element. Figure 5 (4) depicts the variation in k_ν with frequency. The maximum value of the absorption coefficient is k_{max} and its value at half-height is designated $k_{max}/2$.

Relation between Emission and Absorption and Linewidths

Natural linewidths are of the order of 10^{-4} Å. Broadening occurs due to self-absorption, the Doppler effect, and collisional processes. In the majority of cases the most important collisional broadening is due to collisions of the analyte atoms with foreign gases (Lorentz broadening). Line sources such as hollow-cathode lamps are generally used in atomic absorption spectroscopy. Hollow-cathode lamp emission occurs in an inert gas atmosphere at a reduced pressure of about 1 torr. Flames or furnaces are used as absorption cells in atomic absorption spectroscopy. In contrast to line sources, atoms in flames or furnaces are at or near ambient pressures and much collisional broadening occurs. Thus the emission linewidth from a hollow-cathode lamp is narrow compared to the absorption line. With reference to Fig. 5, the width of an absorption
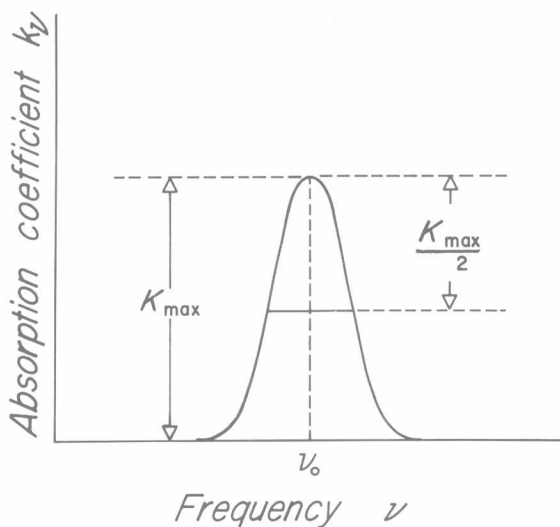
Fig. 5. Variation of absorption coefficient with frequency.

line is taken to be the frequency interval at $k_{max}/2$. It is therefore possible in conventional atomic absorption analysis to measure absorption at the center of the absorption line.

Relation between Absorption and Concentration

Absorption of monochromatic radiation is governed by the following two laws:

Lambert's law. Light absorbed in a transparent absorption cell is independent of incident light intensity. An equal fraction of the light is absorbed by each successive layer of absorbing medium.

Beer's law. Absorption of light is likewise exponentially proportional to the number of absorbing species in the path of the light beam.

Referring to Fig. 6, the incident beam of monochromatic radiation I_0 falls on an absorption cell of length b. The transmittance is given by $T = e^{-kbc}$. Then since

$$\log_{10}(1/T) = \log_{10}(I_0/I) = abc$$

and

$$\log_{10}(I_0/I) = A$$

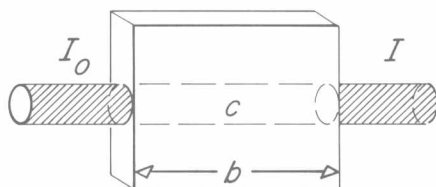where A is the absorbance, then $A = abc$, where a is a constant for a

Fig. 6. Atomic absorption cell of length b.

given system and c is the concentration of the analyte atoms in the flame.

This expression, known as the Beer–Lambert law, predicts a linear relationship between absorbance and concentration as long as a and b remain constant. The linear relationship is between the concentration of analyte atoms in the atomizer and not necessarily analyte in the sample solution. To obtain the latter it is necessary to carefully avoid interference problems outlined in subsequent sections.

It is important to note that the atomic absorption instrument must compute $\log (I_0/I)$, that is, $\log I_0 - \log I$ rather than a small emitted signal as is the case in emission spectroscopy. Failure to appreciate that different parameters, with no direct relationship between them, are being measured has led many workers to claim a fundamental improvement in sensitivity of absorption over emission spectroscopy.

Figure 7 shows a linear calibration graph. Three solutions of known concentration 1, 2, and 4 μg/ml of an element are nebulized into an atomic absorption flame and the absorbances are found to be A_1, A_2, and A_3, respectively. As can be seen, this yields a straight line as
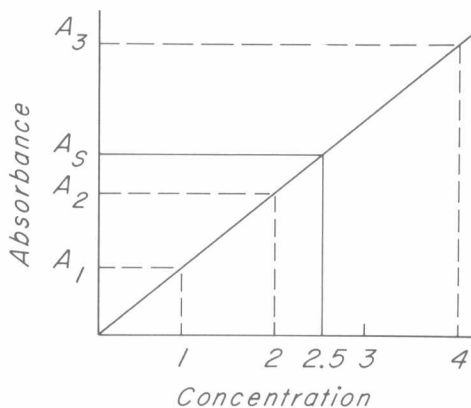

Fig. 7. Linear calibration graph.

predicted by the Beer–Lambert law. A sample to be analyzed is then nebulized. The absorbance obtained is A_s. By interpolation on the calibration graph a concentration of 2.5 μg/ml is obtained for the sample.

It is common to obtain calibration graphs with departures from ideality. The curves in Fig. 8 summarize frequently encountered problems. Curve A does not pass through zero absorbance-concentration. This problem, due to nonspecific absorption, is discussed in detail on p. 39.

Nonlinearity in Analytical Calibration Graphs

The concentration working range for an element determined by atomic absorption spectroscopy is generally 4 to 5 orders of magnitude. At the upper end of the concentration range, it is common to have the graph bend toward the concentration axis (Fig. 8, curve B). Less frequently, the calibration graph curves throughout the whole working range (curve D).

The Beer–Lambert law is valid for monochromatic radiation. Reasons for the bending of curves have been postulated by a number of researchers. de Galan and Samaey (6) indicate two common causes of this problem. Both result from failure of the monochromator and slit system to prevent multiple, close-spaced lines from reaching the detector. If several lines of differing absorption coefficient (e.g., unresolved multiplets or nonabsorbing lines) fall on the detector, a nonlinear relationship will result between absorbance and analyte concentration. The calibra-
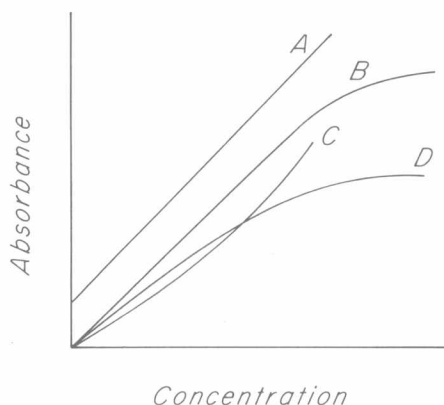

Fig. 8. Calibration graph showing departures from ideality.