ATOMIC ABSORPTION AND FLUORESCENCE SPECTROSCOPY

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Preface

The decision to prepare this volume was taken at a time (1969) when few texts devoted exclusively to analytical atomic absorption spectroscopy (AAS) had been published, and none concerned specifically with atomic fluorescence spectroscopy (AFS) was available. In the past four years several additional texts on AAS, which also contain sections on AFS, have been written. Despite the appearance of these new volumes, however, we have not been discouraged from preparation of the present volume. It was felt that there was an unfilled need for a general textbook which gave more detailed, though not indigestible, theory of both techniques, and which presented a more exhaustive consideration of instrumentation and practical techniques for the working analytical chemist as well as for the student of analytical chemistry. We recognize that it is dangerous to attempt comprehensive coverage of the theory and practice of techniques at a time when they have been developing rapidly; although it is still possible that the present volume may be rendered rapidly out of date by startling new advances in AAS and AFS, it is the opinion of the authors that while applications of the techniques continue to increase, some stabilization in the fundamentals of the instrumentation and methodology has occurred. Two exceptions which might be mentioned specifically are in the instrumentation and methodology associated with the use of non-flame cells for AAS and AFS and, the application of laser sources in AFS. Atomic fluorescence spectroscopy is considered throughout as a technique which is complementary to AAS and which holds considerable promise for many applications.

The volume deals in detail with the individual components of atomic absorption and fluorescence spectrometers (sources, atom cells, dispersive devices etc.). Sufficient fundamental theory is presented to avoid a misleading and oversimplified approach but the emphasis in the text is placed on the practice of the techniques for analysis. Although the applications literature is not exhaustive the authors feel that sufficient data is given to the reader in search of

AAS or AFS methods for a particular application; he should be able to gain an estimate of the number of alternatives possible and obtain easy access to the pertinent original publications. As mentioned at several points in the text, we consider the advent of the publication 'Annual Reports on Analytical Atomic Spectroscopy', in which comprehensive world-wide coverage of both fundamental and applications literature in both AAS and AFS is presented regularly, has rendered unnecessary any attempt at up-to-date comprehensive coverage of the applications literature in a volume of this type.

During the past decade many workers have made significant contributions to the understanding of the fundamental principles of AAS and AFS and the analytical practice of these techniques. In particular, however, we wish to pay tribute to the work of C.S.I.R.O., Australia, where analytical AAS originated in the work of Alan Walsh and his colleagues, and to Prof. C. Th. J. Alkemade, University of Utrecht, who has so often pointed the way for developments in these techniques and has made many contributions to understanding of their fundamental principles. The extensive contributions of Winefordner and co-workers at the University of Florida, which have so assisted the development of the techniques, must also be acknowledged. Perhaps to a greater extent than for many other instrumental techniques of analysis a very considerable contribution to AAS theory and practice has been made by the instrument manufacturers. In the case of several companies these contributions have been so important and sustained that the work of their employees has received international recognition.

It is a pleasure to acknowledge the encouragement given to us during preparation of this book by Professor Tom West. We wish to express our thanks to the many authors and publishers who have given permission for the reproduction of figures and other material from the original literature. We thank close colleagues for helpful discussions and acknowledge the assistance given by Mike Adams, Dai Bevan, Arthur Ward and P. J. Wilson in collection of much of the applications data given in Chapter 13. We also wish to thank Mike Adams for the preparation of the Subject Index. We are indebted to the Technical Editing staff at Thornton Research Centre, particularly Bob Taylor and Tony Shaw, for help with the preparation of manuscript and diagrams. Many secretaries have been involved with the task of preparation of draft and corrected typescripts. We particularly wish to thank Mrs. Janet Broome and Miss Maureen Coleman for their efforts in this respect. We also should thank our families for their patience and forebearance during the preparation of this book.

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CHAPTER 1

Introduction

1.1 HISTORICAL ASPECTS

The techniques to be described in this book are concerned with one small region of the electromagnetic spectrum: the wavelength range extending from approximately 180 nm to 800 nm and embracing the region of visible light. Within the restrictions imposed by these somewhat arbitrary limits to "the spectrum" it may be said that the history of spectroscopy dates back over two and a half centuries to the discovery of the visible spectrum by Newton.[1] Since that time, spectroscopists at any given period have concentrated their efforts on one of two fields: analytical chemistry or the interpretation of physical and atomic properties. At the present time atomic absorption spectroscopy in particular represents a major area of interest and growth in the former field.

Following Newton's study of the spectrum of the sun was a period of almost one hundred years entirely concerned with *emission* spectroscopy. However, in 1802 Wollaston[2] reported the presence of dark bands in the continuum emission spectrum of the sun and, after a more detailed study by Fraunhofer (1814), Brewster[3] (1820) was able to ascribe them to *absorption* of radiation within the sun's atmosphere. Another forty years passed before Kirchoff and Bunsen[4,5,6]

showed that one of these dark bands in the emission spectrum of the sun corresponded exactly to the yellow emission band obtained when sodium vapour is heated in a flame. Their work enabled Kirchoff to enounce the fundamental relationship between emission and absorption spectra: any species that can be excited to emit radiation at a particular wavelength will also absorb radiation at that wavelength. Thus a new technique could be added to the already well-established one of emission spectroscopy and the work of Bunsen and Kirchoff was continued and placed on a sound theoretical basis by the physicists and astronomers of the early twentieth century. Their research, which has been summarized by Mitchell and Zemansky,[7] was mainly performed with atoms at low pressures in enclosed vessels and was primarily concerned with the interpretation of atomic structure and spectra.

Although there were occasional practical applications to the study of elements present in solar and stellar atmospheres, virtually no attempt was made to apply the discoveries to practical chemical analysis; only the determination of mercury vapour in air[8] was reported as a rather exceptional example. This striking contrast with emission spectroscopy, which by the 1920s was an important analytical tool in the form of arc and spark spectrography, must be viewed in the light of two important factors. Firstly, before about 1930 the emission technique was mainly used for qualitative analysis, and there was no advantage to be gained from using absorption spectra for this purpose (in fact the reverse is true, as is witnessed by the present-day applications of the absorption technique). Secondly, even after 1930 the difficulty of making absorption measurements for quantitative analysis was considerably greater than that experienced with emission. Not only was the photographic recording of the absorption spectra more tedious, but the theory seemed to indicate that they would only prove useful for quantitative analysis if observed under very high resolution. Thus, when atomic absorption spectrometry was introduced as an analytical tool by Walsh[9,10] in 1953 and Alkemade and Milatz[11,12] in 1955, emission methods of analysis were firmly established and difficult to replace. However, these workers were able to overcome two major problems which twenty years earlier had seemed almost insuperable. The technique proposed by Walsh of measuring only the peak absorbance at the centre of the spectral line (see Section 3.5.2) removed the practical difficulty of making quantitative absorption measurements with a

simple monochromating device, and the availability of photoelectric light detectors of very high sensitivity meant that it was no longer any more troublesome to record absorption rather than emission signals. By presenting this new "simple" absorption technique in combination with modern instrumentation and a high-temperature flame as the atom reservoir, Walsh in particular was able to demonstrate the advantages of atomic absorption spectrometry over emission spectrometry and flame photometry for many elements. Today a wide range of instruments is available commercially, atomic absorption is widely used in a greater range of routine determinations than the arc, spark and simple flame emission techniques, and new publications on atomic absorption spectrometry greatly outnumber those on the emission methods.

The re-emission by an atom of radiation as *fluorescence* after the absorption of light from a suitable source was first reported in 1905 when Wood[13] succeeded in exciting atomic fluorescence of the D lines of sodium vapour. He used an evacuated test tube containing sodium vapour as the atom reservoir and a gas flame containing sodium chloride as the illuminating source. The result was predicted by the classical theory of light in the same way as the resonance of standing waves observed for sound, vibrating strings, etc. Wood, therefore, termed this fluorescence "resonance radiation" and the name is still encountered today for the atomic fluorescence of resonance lines such as the D lines. Similar work was carried out with other readily volatile elements, enclosed cells again being used to contain the atomic vapour, and was mainly concerned with fundamental studies of atomic spectra. This work has been described in some detail by Mitchell and Zemansky[7] and by Pringsheim.[14]

The fluorescence of atoms in flames was first reported in 1923 by Nichols and Howes[15] for calcium, strontium, barium, lithium and sodium in a Bunsen flame. Similar observations were also reported by Badger[16] and by Mannkopff[17] for a number of other volatile elements. Further interest in the subject then appears to have lapsed until the use of atomic fluorescence spectrometry in 1956 by Boers, Alkemade and Smit[18] to study quenching processes in flames. Following this, a further report was given by Alkemade[19] in 1962 on sodium fluorescence in flames together with the suggestion that it might have analytical possibilities. This suggestion was followed up by Winefordner, Vickers and Staab[20,21] who reported the first successful analytical application of atomic fluorescence spectrometry

with the determination of zinc, cadmium, and mercury. Since that time the number of publications on the technique has increased rapidly.

1.2 FUNDAMENTALS

It is worthwhile initially to outline the instrumental arrangement most commonly used for analytical absorption and fluorescence measurements, and to define some of the more widely used terms. This should avoid confusion when these terms arise in subsequent chapters.

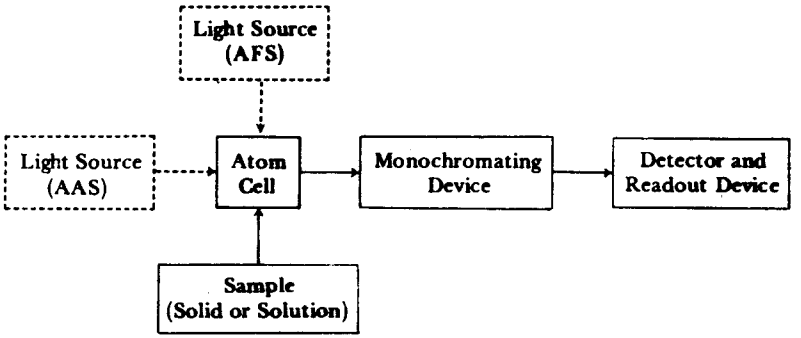

Fig. 1-1. Basic apparatus for analytical atomic spectroscopy.

The basic apparatus required is shown diagrammatically in Fig. 1-1, and a typical commercial atomic absorption spectrophotometer conforming to this arrangement is illustrated in Fig. 1-2. In order to observe atomic absorption or fluorescence signals it is necessary to have a population of free, neutral atoms of the element of interest. Thus, the most important component of the instrument is the *atom cell* or reservoir. This may take a wide variety of forms, ranging from a simple quartz cell at room temperature (for mercury) to a high-temperature flame or plasma with its ancillary equipment. If the atoms contained in this cell are to absorb radiation, and possibly to re-emit a fraction of this as fluorescence, they must be irradiated with light of the same wavelength as that of a strong absorption spectral line of the element that has been atomized. This radiation is obtained from a *light source* which may emit the spectrum of a single element, the spectra of several elements whose common analysis is frequently required or a continuum spectrum (see Section 5.1). As

with the atom reservoir, the complexity of the light source and its ancillary equipment can vary considerably.

The light transmitted after the atomic absorption process has occurred, or the fluorescence emission stimulated from the atoms in the reservoir, will often be composed of radiation of both the required wavelength (i.e. the absorption line(s)) and a number of unwanted wavelengths. The latter may simply take the form of stray daylight, or may arise from other spectral lines emitted by the light source or the atom cell. It is usually necessary, therefore, to select the wavelength of the radiation from the atom cell before an attempt

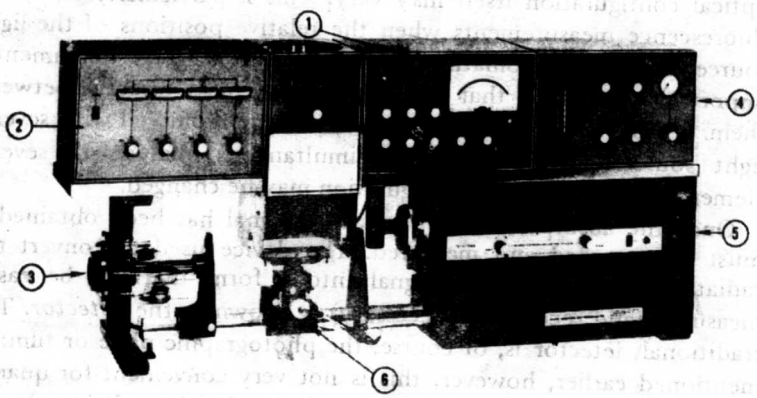

Fig. 1-2. Commercial atomic absorption spectrophotometer. 1, amplifier; 2, lamp power supply; 3, lamp turret; 4, gas control unit; 5, monochromator; 6, burner and sample nebulizer.

is made to measure the absorption or fluorescence signal. This is done with a *monochromating device*, the design of which will depend on the complexity of the instrument and the type of work to be carried out with it. For simple instruments intended only for measurements with one or two elements giving single strong spectral lines at wavelengths that can be detected a simple optical filter may suffice. On the other hand, most commercial instruments designed for maximum versatility utilize relatively complex diffraction grating monochromators (see Chapter 9).

Whatever monochromating device is employed, it must be placed in the correct position with respect to the light source and the atom cell. In Fig. 1-1 it is shown to lie in the direct optical path from the source to the cell for absorption measurements (so that the amount

of radiation absorbed is easily determined) and at 90° to this optical path for fluorescence measurements (so that fluorescence emission may be detected without interference from any radiation received direct from the light source). Although these configurations are frequently adhered to in commercial instruments for the *optical path* between light source and monochromating device, it must be remembered that the arrangement of the individual components may not be as straightforward as in Fig. 1-1; in many cases the light beam may be deflected by several mirrors or prisms so that a practically convenient instrument design is obtained. Less frequently, the optical configuration itself may vary. This is particularly true with fluorescence measurements when the relative positions of the light source and monochromating device are not of great fundamental importance provided that radiation cannot pass directly between them. Thus, if it is necessary to irradiate the atom cell with several light sources, perhaps for the simultaneous analysis of several elements, the 90° optical configuration may be changed.

Once the absorption or fluorescence signal has been obtained it must be recorded and measured. The device used to convert the radiation constituting the signal into a form that can be easily measured (and recorded if necessary) is known as the *detector*. The traditional detector is, of course, the photographic plate or film; as mentioned earlier, however, this is not very convenient for quantitative measurements and quite impracticable for absorption measurements. Hence almost all modern instruments use photoelectric devices (see Chapter 10). These convert the optical signal to an electrical signal so that a *readout device* is required in order to measure the signal. Again, this may vary considerably in complexity to range from a simple meter to measure the voltage generated by a photoelectric cell to elaborate electronic assemblies using computing techniques.

In addition to the instrumental components discussed above other more general terminology is in use the early definition of which is worthwhile. The analytical techniques utilizing the measurement of atomic absorption and fluorescence are usually referred to as respectively *atomic absorption spectrometry, spectroscopy or spectrophotometry* (*AAS*) and *atomic fluorescence spectrometry, spectroscopy or spectrophotometry* (*AFS*). The instruments used for the measurements are referred to as *spectrophotometers or spectrometers*. These different derivatives of spectr- are often used quite interchangeably in the literature but there is usually little danger of

confusion arising. The observation of the presence of an element by its absorption or fluorescence spectrum is referred to as its *detection* whereas the quantitative analysis is known as its *determination*. The actual element detected or determined is frequently termed the *analyte* and it is present in the *analytical sample*, the actual composition of which may be referred to as the *sample matrix*. The word *sample* is also generally used for the solid or solution added to the atom cell, even though this may have been obtained by complicated treatment of the original analytical sample. Thus, care is sometimes necessary to avoid confusion, especially when mention is made of the *analyte concentration* in the sample. As absorption measurements in particular are made as the difference between two signals it is usually necessary to have a sample giving zero signal, that is, a *blank* which contains no analyte element. Finally, other species present in the sample or the atom cell can sometimes cause an erroneous determination of the analyte; these are known as *interferences* and are revered by analytical chemists.

The discussion of AAS and AFS necessitates frequent mention of the emission technique, and much of the nomenclature given above applies to this also. The corresponding names *atomic emission spectrometry, spectroscopy or spectrophotometry* (*AES*) are widely used; it is also common to find the technique referred to as *flame emission spectrometry, spectroscopy or spectrophotometry* (*FES*), as the flame is a widely used atom cell (in the present discussion we shall exclude traditional arc or spark emission spectrography from our definition of AES).

1.3 COMPARISON OF TECHNIQUES

It is readily recognizable from the preceding pages that essentially the same equipment and techniques may be applied to both AAS and AFS. In fact, apart from the spectral light sources, this may also apply to AES. Thus, in an analytical laboratory where inorganic trace analysis is frequently carried out by atomic spectroscopy, sufficient equipment and expertise may be available for all three techniques. It is then possible to select one of the techniques on its own merits as the most suitable for a particular determination. In view of this, it is intended to make a brief comparison of techniques by discussion of their individual advantages and disadvantages, and then to make a general comparison of all three techniques with other instrumental methods of inorganic analysis.

1.3.1 Comparison of AES, AAS and AFS

It is important first to emphasize the opinion of the authors implied above that the three techniques are complementary and no one has outstanding advantages over the other two. This is true whether comparison is based on the criterion of "limit of detection" or that of ease and convenience of analysis. First, at the time of writing there exists for each technique a group of elements for which it may provide the most sensitive method of analysis. There also remain many elements whose determination may be undertaken with equal sensitivity by two or even all three techniques. Secondly, each technique has its own instrumental and experimental advantages and disadvantages. Many are common to more than one technique, and a direct comparison may be made by detailing favourable and unfavourable points for each technique. This approach should assist when a decision is to be made concerning the technique best suited to a particular analytical service.

Advantages of AES

1. No spectral light sources are required.
2. For many elements a wide choice of sensitive analytical lines exists; many of these lines may lie in the visible region of the spectrum where intensity measurements are less complicated than in the ultraviolet region.
3. The technique can provide flexibility in dealing with a wide range of sample concentrations.
4. Qualitative as well as quantitative analysis is readily carried out.
5. Simultaneous multi-element analysis is possible.

Disadvantages of AES

1. Large changes in the intensity of the analytical signal result from small temperature changes in the atom cell.
2. Background and other line or band spectra emitted from the atom cell may cause greater interference than in the other two techniques.
3. Considerable operator skill is required routinely to obtain reliable results.
4. A high quality monochromator is essential if the technique is to be reliable and versatile.

Advantages of AAS

1. The instrumentation is simple to set up and operate because of the useful wavelength and intensity reference provided by the background light source.

2. The technique is easily automated.
3. Double-beam operation is readily arranged to provide for reduction of the effect of variation in intensity of the light source.
4. Sharp-line light sources provide better spectral selectivity than is usually obtainable with AES.
5. The analytical signal in AAS for many elements is less sensitive to temperature changes in the atom cell than it is in AES.

Disadvantages of AAS

1. A large number of relatively expensive spectral light sources are usually required. High sensitivity cannot be obtained when continuum or broad-line light sources are used with low resolution commercial instrumentation.
2. Many of the most useful absorption lines are quite far into the ultraviolet region of the spectrum where measurement is more difficult; for most elements only a few analytical lines are available.
3. When spectral interferences do occur they are less apparent than in AES and can therefore cause a more serious chance of error.
4. It is relatively difficult to obtain a long range of concentration over which linear calibration is possible.

Advantages of AFS

1. Sensitivity attainable is controlled by the intensity of the light source employed.
2. The technique is less sensitive to temperature changes in the atom cell than AES is.
3. Much of the equipment required can be less complex than that needed for AES or AAS.
4. Continuum or fairly broad-line light sources can be used with a less serious loss of sensitivity than for AAS.
5. High sensitivity is available far into the ultraviolet region of the spectrum where AES is insensitive.

Disadvantages of AFS

1. A spectral light source is required, usually one for each element, as in AAS.
2. Quenching of the fluorescence signal is greatly affected by the gas species present in the atom cell.
3. The very hot flames needed as atom cells for the determination of elements such as the refractory metals and to avoid some chemical interferences favour AES rather than AFS.