Atomic Absorption and Emission Spectroscopy

Analytical Chemistry by Open Learning

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Analytical Chemistry

This series of texts is a result of an initiative by the Committee of Heads of Polytechnic Chemistry Departments in the United Kingdom. A project team based at Thames Polytechnic using funds available from the Manpower Services Commission 'Open Tech' Project has organised and managed the development of the material suitable for use by 'Distance Learners'. The contents of the various units have been identified, planned and written almost exclusively by groups of polytechnic staff, who are both expert in the subject area and are currently teaching in analytical chemistry.

The texts are for those interested in the basics of analytical chemistry and instrumental techniques who wish to study in a more flexible way than traditional institute attendance or to augment such attendance. A series of these units may be used by those undertaking courses leading to BTEC (levels IV and V), Royal Society of Chemistry (Certificates of Applied Chemistry) or other qualifications. The level is thus that of Senior Technician.

It is emphasised however that whilst the theoretical aspects of analytical chemistry can be studied in this way there is no substitute for the laboratory to learn the associated practical skills. In the U.K. there are nominated Polytechnics, Colleges and other Institutions who offer tutorial and practical support to achieve the practical objectives identified within each text. It is expected that many institutions worldwide will also provide such support.

The project will continue at Thames Polytechnic to support these 'Open Learning Texts', to continually refresh and update the material and to extend its coverage.

Further information about nominated support centres, the material or open learning techniques may be obtained from the project office at Thames Polytechnic, ACOL, Wellington St., Woolwich, London, SE18 6PF.

How to Use an Open Learning Text

Open learning texts are designed as a convenient and flexible way of studying for people who, for a variety of reasons cannot use conventional education courses. You will learn from this text the principles of one subject in Analytical Chemistry, but only by putting this knowledge into practice, under professional supervision, will you gain a full understanding of the analytical techniques described.

To achieve the full benefit from an open learning text you need to plan your place and time of study.

- Find the most suitable place to study where you can work without disturbance.
- If you have a tutor supervising your study discuss with him, or her, the date by which you should have completed this text.
- Some people study perfectly well in irregular bursts, however most students find that setting aside a certain number of hours each day is the most satisfactory method. It is for you to decide which pattern of study suits you best.
- If you decide to study for several hours at once, take short breaks of five or ten minutes every half hour or so. You will find that this method maintains a higher overall level of concentration.

Before you begin a detailed reading of the text, familiarise yourself with the general layout of the material. Have a look at the course contents list at the front of the book and flip through the pages to get a general impression of the way the subject is dealt with. You will find that there is space on the pages to make comments alongside the text as you study—your own notes for highlighting points that you feel are particularly important. Indicate in the margin the points you would like to discuss further with a tutor or fellow student. When you come to revise, these personal study notes will be very useful.

Π When you find a paragraph in the text marked with a symbol such as is shown here, this is where you get involved. At this point you are directed to do things: draw graphs, answer questions, perform calculations, etc. Do make an attempt at these activities. If necessary cover the succeeding response with a piece of paper until you are ready to read on. This is an opportunity for you to learn by participating in the subject and although the text continues by discussing your response, there is no better way to learn than by working things out for yourself.

We have introduced self assessment questions (SAQ) at appropriate places in the text. These SAQs provide for you a way of finding out if you understand what you have just been studying. There is space on the page for your answer and for any comments you want to add after reading the author's response. You will find the author's response to each SAQ at the end of the text. Compare what you have written with the response provided and read the discussion and advice.

At intervals in the text you will find a Summary and List of Objectives. The Summary will emphasise the important points covered by the material you have just read and the Objectives will give you a checklist of tasks you should then be able to achieve.

You can revise the Unit, perhaps for a formal examination, by re-reading the Summary and the Objectives, and by working through some of the SAQs. This should quickly alert you to areas of the text that need further study.

At the end of the book you will find for reference lists of commonly used scientific symbols and values, units of measurement and also a periodic table.

Study Guide

This Unit is designed to introduce you to the basic theory and practice of atomic spectroscopy. The emphasis is on the practical and instrumental aspects and the use of mathematics and theoretical spectroscopy is kept to a minimum.

A description of the basic principles of atomic spectroscopy is given in Parts 1 and 2 of the Unit.

The basic instrumentation and practice of the (currently) most widely used technique in atomic spectroscopy – flame atomic spectroscopy – is described in Parts 3 and 4 of the Unit. In order to use atomic spectroscopy as an effective analytical tool it is important to understand the problems which can arise, and to know how to combat these problems by sample treatment or instrumental methods.

Thus the first four Parts of the Unit are designed to give you a basic grounding in the theory, instrumentation and practice of atomic spectroscopy.

The more specialised techniques of atomic absorption are described in Parts 5 and 6. Emission spectroscopy, which has been less widely used than absorption spectroscopy in the past, has become an increasingly more attractive method in recent years for reasons described in Part 7. Part 8 describes the relative merits of what may, to the newcomer, be a bewildering variety of methods, in order to give an overall perspective on the Unit.

Supporting Practical Work

The range of atomic spectroscopy instrumentation available will vary widely from one laboratory to another. The experiments which follow are designed to illustrate basic procedures and will not require particularly sophisticated instrumentation.

Aims

(*a*) To provide experience in the preparation and pre- treatment of samples in a form suitable for analysis.

(*b*) To provide experience of operating and otpimising appropriate instrumentation.

(*c*) To select a suitable working range for a given element, and construct and use calibration cu ves.

(*d*) To demonstrate the interferences which can arise, and methods of combating these interferences.

(*e*) To demonstrate the use of the method of standard additions.

Suggested Experiments

The experiments suggested here are designed to be carried out without the use of particularly specialised or expensive equipment.

(*a*) Optimisation of an atomic absorption spectrometer.

(*b*) The determination of potassium in tomato puree. (Using calibration curve and method of standard additions).

(*c*) The determination of magnesium in tap water. (With and without EDTA).

(*d*) The determination of iron in beer. (Using APDC/MIBK extraction).

(*e*) The determination of sulphate. (Precipitation with barium).

Experiments (*a*) to (*e*) can be carried out on flame atomic absorption spectrometers. Experiments (*b*) and (*e*) can also be carried out on flame photometers.

If a graphite furnace accessory is available, the following experiments are suggested:

(*f*) Optimisation of ashing and atomisation for cadmium and copper.

(*g*) Determination of arsenic using nickel chloride as a matrix modifier.

Note

In addition to selecting some of the above experiments, you may wish to use the computer simulation program provided by the CALM project.

Bibliography

1. ATOMIC SPECTROSCOPY TEXTBOOKS

(*a*) L Ebdon, *An Introduction to Atomic Absorption Spectroscopy*, Heyden, 1982.

(*b*) G F Kirkbright and M Sargent, *Atomic Absorption and Fluorescence Spectroscopy*, Academic Press 1974.

(*c*) W J Price, *Spectrochemical Analysis by Atomic Absorption*, Heyden, 1979.

(*d*) M Slavin, *Atomic Absorption Spectroscopy*, Wiley, 2nd Edn, 1978.

(*e*) M Thompson and J N Walsh, *A Handbook of Inductively Coupled Plasma Spectrometry*, Blackie 1983.

(*f*) B Welz, *Atomic Absorption Spectroscopy*, Verlag Chemie, 1976.

Notes

Reference (*a*) is readable, comprehensive and fairly up to date.

References (*c*) and (*d*) are practically-orientated.

Reference (*e*) is a specialist text.

2. 'STANDARD' ANALYTICAL TEXTBOOKS

Most comprehensive analytical chemistry texts will contain a chapter on atomic spectroscopy. Examples include:

(*a*) T Kuwana (Ed), *Physical Methods in Modern Chemical Analysis*, Vol 1, Academic Press, 1978.

(*b*) G Svehla (Ed), *Wilson and Wilson's Comprehensive Analytical Chemistry*, Elsevier, 1975 (several volumes).

(*c*) H H Willard, L L Merit, J A Dean and F A Settle, *Instrumental Methods of Analysis.* Van Nostrand, 1981.

3. JOURNALS

It is particularly true of atomic spectroscopy that text books soon date, because of the rapid developments in the subject. Some of the journals which contain reviews and original papers are given in the following list:

(*a*) *Analyst*

(*b*) *Analytica Chimica Acta*

(*c*) *Analytical Chemistry*

(*d*) *Annual Reports on Analytical Atomic Spectroscopy*

(*e*) *European Spectroscopy News*

(*f*) *International Laboratory*

(*g*) *Journal of Analytical Atomic Spectroscopy*

(*h*) *Spectrochimica Acta*

Journals (e) and (f) contain occasional review articles aimed at the general reader. The other journals contain original research papers, although some, such as (c) and (g) also publish general review articles. Journal (d) contains detailed and comprehensive reviews.

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The frontispiece is two colour plates provided by Mr A Batho of the Analytical Instrument Division, Thermoelectron, Birchwood, Warrington, Cheshire WA3 7QZ.

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Figures 7.2a and 7.2b are redrawn from the Corning catalogue: *A guide to Flame Photometer Analysis*. Permission has been applied for.

Contents

1. Atomic Spectroscopy – General Introduction

Overview

After a short historical introduction, some basic spectroscopic ideas essential to this Unit are revised. The main features of the different types of atomic spectroscopy are then reviewed. The scope of atomic spectroscopy is then discussed in terms of which elements are most conveniently determined.

1.1. INTRODUCTION

Atomic spectroscopy has its origins in the flame test in which many elements can be identified by the characteristic colours which their salts give to a flame.

Talbot, in 1826, saw that a wick impregnated with table salt (sodium chloride) burnt with the emission of an intense yellow light, and that the same colour was obtained with other sodium salts. Potassium salts, on the other hand, gave a different colour, a bluish tinge, to flames. The metals present in salts could in many cases be identified from the colours which they gave to flames.

Simple visual observation of flame colours was, however, rather limited. For example both lithium and strontium give red flames which are not easily distinguished. An improvement was to use a prism to disperse the light emission from the flame into its component wavelengths (Fig. 1.1a). Lithium and strontium are then easily identified since in the red region of the spectrum, lithium emits only one wavelength while strontium emits several different wavelengths.

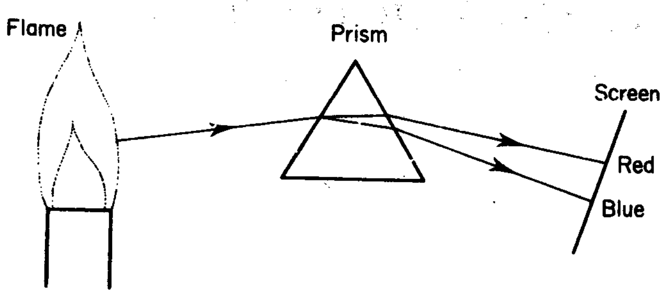

Fig. 1.1a. *Dispersion of light emitted from a flame*

With the development of the bunsen burner, giving a relatively hot and colourless flame, Bunsen and Kirchoff improved the technique. Several previously unknown elements were identified using the technique, for example caesium and rubidium (1861) and helium (1895).

As we shall see in this Unit atomic spectroscopy has made tremendous advances and is now a very widely used technique for both the identification and quantitative determination of many elements present in samples. There are many variations of the technique, but all share two main characteristics:

(*i*) *specificity* – individual elements in given sample can be reliably identified.

(*ii*) *sensitivity* – the amounts of an element that can be detected are very small. Levels of around 1 ppm (part per million) can be measured with straightforward procedures. Even smaller levels of 0.001 ppm or less can be measured with more sophisticated procedures.

1.2. SOME BASIC CONCEPTS IN SPECTROSCOPY

The Unit requires a good understanding of three basic concepts in spectroscopy, namely

(*i*) the wave nature of light;

(*ii*) the particle properties of light;

(*iii*) the absorption and emission of light.

This section covers material which may already be familiar to you. If you can answer the following three SAQs, you may skip the rest of this section and move on to Section 1.3. If you have some difficulty in answering these SAQ's you will need to study this section and then attempt the questions again.