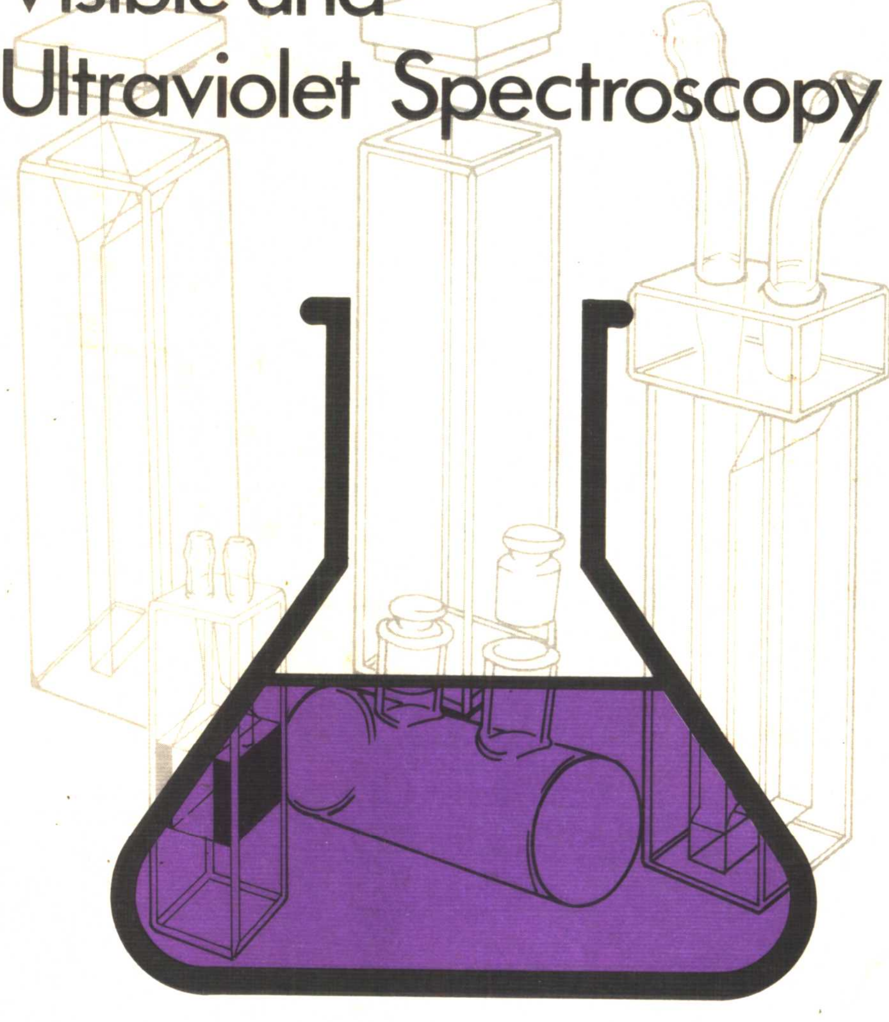
ANALYTICAL CHEMISTRY BY OPEN LEARNING

Visible and Ultraviolet Spectroscopy



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Visible and Ultraviolet Spectroscopy

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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.

Study Guide

This Unit has been written to provide a knowledge of the theory and practice of ultraviolet/visible spectrometry for both qualitative and quantitative chemical analysis.

Of all the areas of analytical chemistry it is fair to say that either directly or indirectly most laboratory workers encounter some form of ultraviolet/visible spectrometry at some stage. This may be in such simple things as checking the amount of an impurity in water using a colour comparator, or the more complex multi-sample absorption measurements using an automatic analyser in a clinical laboratory. This Unit seeks to enable the non-specialist to acquire sufficient knowledge about the scientific rules, techniques, procedures and equipment used in ultraviolet/visible spectrometry to appreciate its role and value as an analytical tool.

In order to achieve these objectives the Unit first deals with the simple concepts of the production of coloured substances in various reactions and the relationship of these colours with characteristic wavelengths of light in the visible region of the spectrum. It shows how colour is related to chemical structure and the manner in which various chemical groups can lead to changes in maximum absorption values. The Unit deals in some detail with the quantitative aspects of ultraviolet/visible absorption spectra and the laws governing the development and use of calibration curves for quantitative analysis. This aspect is well illustrated with fully worked examples showing how such curves may be plotted from experimental data.

As the value of the data from ultraviolet/visible spectrometry depends very much on the type of equipment used, the Unit also deals with the different types of instruments available. These range from the simple optical comparators through to highly sophisticated high resolution double beam spectrometers.

The Unit has been designed to provide a sound working idea of ultraviolet/visible spectrometry. But it does not cover the more obscure and abstruse mathematical concepts and calculations more generally associated with advanced physical chemistry. We are concerned here with the importance of ultraviolet/visible spectrometry in analysis for the measurement of real, everyday things encountered in many walks of life. This is applied chemistry for quality control, chemical purity, medical diagnosis and new product development.

Throughout the Unit there is a range of problems devised to enable you to gain a working knowledge of the procedures used to carry out quantitative determinations and to relate certain structures with calculated absorption wavelengths. But this is all really only a beginning and ideally the knowledge contained here needs reinforcing with practical experience of the methods and instrumentation wherever possible.

Bibliography

1. ANALYTICAL CHEMISTRY TEXTBOOKS

All books in this subject area contain major chapters dealing with ultraviolet/visible spectrometry. The following are used extensively:

(*a*) J. Bassett, R. C. Denney, G. M. Jeffery and J. Mendham, *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edn., Longmans, 1978.

(*b*) F. W. Fifield and D. Kealey, *Principles and Practice of Analytical Chemistry*, 2nd edn., International Textbook Company Ltd, 1983.

(*c*) H. H. Willard, L. L. Merritt, J. A. Dean and F. A. Settle, *Instrumental Methods of Analysis*, 6th edn., Wadsworth Publishing Co., 1981.

(*d*) D. C. Harris, *Quantitative Chemical Analysis*, W. H. Freeman & Co, 1982.

2. TEXTBOOKS ON ABSORPTION SPECTROMETRY

These books deal with the theory and practice of spectrometry with special chapters on ultraviolet/visible spectra treated in some depth.

(*a*) J. M. Hollas, *Modern Spectroscopy*, J. Wiley & Sons, 1987.

(*b*) C. N. Banwell, *Fundamentals of Molecular Spectroscopy*, 3rd edn., McGraw-Hill Book Co, 1983.

(*c*) D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to Spectroscopy*, Holt, Rinehart and Winston, 1979.

Practical Objectives

1. GENERAL CONSIDERATIONS

Even in a modestly equipped laboratory it is possible to carry out simple experiments to illustrate the basic concepts of ultraviolet/visible spectrometry. Many of the examples given in the early part of the text can be easily repeated in practice in order to gain experience. However, the application of your knowledge will be that much easier if you have access to a simple optical comparator or to a spectrometer.

2. AIMS

(*a*) To provide a basic experience of using

(*i*) a simple spectrometer or colorimeter for quantitative analysis.

(*ii*) a spectrometer for recording ultraviolet/visible spectra

(*b*) To give experience in the use of ultraviolet/visible spectrometry in quantitative analysis, with the emphasis on good analytical practice.

3. SUGGESTED EXPERIMENTS

(*a*) The operation of a recording and a non-recording ultraviolet/visible spectrometer to record spectra, determine λ_{max} values. The data to be used to calculate molar absorptivities and to plot Beer-Lambert Law calibration graphs.

(*b*) The determination of iron in potable waters.

(*c*) The enzymatic determination of glucose in a food stuff.

The three experiments suggested are closely linked to the content of this Unit. Other similar experiments could, however, be equally appropriate in realising the aims given above.

Acknowledgements

– Extracts in Section 3.1.1 on the determination of iron in raw and potable waters are taken from *Iron in Raw and Potable Waters by Spectrometry* (1977 version), published by H.M.S.O.

– The method reproduced in Section 3.1.2 for the determination of sucrose/glucose is reproduced by permission of Boehringer Mannheim GmbH.

– Extracts in Section 3.1.3 on the determination of trace amounts of iron are taken from the *Analyst*, **101**, 974–81, 1976 and reproduced by permission of the Royal Society of Chemistry.

Contents

1. Introduction

The foundations of quantitative chemical analysis can be traced back to the development of titrimetric analysis in which titration end-points depended on the change of colour of either the species being analysed or of that of a specially added chemical indicator. These colour transitions arise due to molecular and structural changes in the substances being examined, leading to corresponding changes in the ability to absorb light in the visible region of the electromagnetic spectrum. In various ways absorption spectroscopy in the visible region has long been an important tool to the analyst. Many important and sensitive colour tests have been developed for the detection and determination of a wide range of chemical species, both inorganic and organic in nature, and were first used long before the development of ultraviolet and visible spectrometers.

Today the uv/visible spectrometer is often referred to as the workhorse of the analytical laboratory, and is applied to many thousands of determinations which have been developed over the years. Uv/visible spectrometry has proved particularly useful in biochemical analysis, and is of vital importance in the clinical laboratory attached to most of our modern hospitals where various components of blood and/or urine in particular are determined and monitored on a 24-hour basis. It plays a part in environmental studies on pollutants, in forensic science work on drugs, and in maintaining the quality of the food we consume. In all of these realms analytical chemists and laboratory technicians regularly use uv/visible spectrometry as an essential tool in the identification and quantification of a very broad range of chemical and biological substances. The equipment for these purposes ranges from very simple colour comparators through to large computer controlled automatic scanning instruments covering the whole of the uv/visible region of the electromagnetic spectrum. But in all instances these studies involve measurement of radiation intensity at the spectral wavelengths which are characteristic for the substances under investigation.

1.1 COLOUR TESTS AND CHEMICAL ANALYSIS

One of the earlier tests you may have encountered in your study of chemistry is the change in colour of anhydrous copper sulphate crystals from white to blue when water is added, or the colour change of litmus paper from blue to red when the paper is dipped into a solution of an acid. These, and similar observations of colour and colour change, would probably have been your first experiences of the principles of absorption spectroscopy applied to the study of chemical systems. Thus a material will appear coloured if it shows selective absorption of radiation within the visible region of the electromagnetic spectrum and any change in that absorption will be associated with a change in colour.

The observation of colour or colour change has often captured the imagination of research workers and has led to significant discoveries in the field of chemistry and the development of new materials and dyestuffs. You should be able to think of a number of situations from your own experience where the generation of a coloured species or a sudden change of colour has caused you to observe the reaction system more carefully.

1.1.1 Colour Tests and Qualitative Chemical Analysis

For those responsible for the analysis of materials, simple colour tests have often provided useful preliminary or confirmatory evidence for the presence of particular chemical species. Thus in the early stages of your training in chemical analysis you will have already encountered a number of characteristic colour tests. Some possible examples are listed below:

(*a*) Use of litmus or indicator paper to test acidity/alkalinity.

(*b*) The yellow colour imparted to a gas flame when testing for sodium.

(*c*) The blue colour produced when testing for iodine with starch solution.

(*d*) The change in the colour of the crystals from yellow to green in the tube-and-bag breathalyser test, indicating the presence of ethanol.

No doubt some of these tests will be familiar to you. Six further well known tests are listed below.

Π Can you identify which of these tests involve an observation of colour or colour change? If you find this an easy question to answer then perhaps you could try to indicate the chemical reaction involved in each test!

(*a*) The test for halide ions using silver nitrate solution.

(*b*) The test for Mn^{2+} ions in aqueous solution with hydrogen sulphide gas.

(*c*) The test for Fe^{3+} ions with aqueous potassium thiocyanate solution.

(*d*) The test for aldehydes with Fehling's solution.

(*e*) The test for ketones with 2,4-dinitrophenylhydrazine.

(*f*) The Lassaigne test for nitrogen in organic compounds.

The correct response is that the appearance of a characteristic colour is the main observation in tests (*c*), (*d*) and (*f*). But with (*a*), (*b*) and (*e*) the main observation is the formation of a precipitate, although the colour of the precipitate may also be of some significance as indicated below. As for the nature of the chemical reaction involved this is indicated in the following notes.

Test a

The presence of a halide (X^-) is indicated by a precipitate of AgX which for chloride is normally white, for bromide is a very pale yellow colour and for iodide is distinctly yellow. Hence the colour of the precipitate is a useful part of the test.

$$X^- + AgNO_3 \rightarrow AgX + NO_3^-$$

Test b

A number of metal sulphides including copper, cadmium and lead are readily precipitated in acid solution, however manganese ions are precipitated under alkaline conditions, the precipitate being a pale creamy pink colour, which aids identification.

$$Mn^{2+} + H_2S \rightarrow MnS + 2H^+$$

Test c

Iron(III) gives a characteristic blood red colour with potassium thiocyanate, and this is a sensitive test for low concentrations of iron in the 3+ state. The formula of the complex ion can vary depending on the reaction conditions although the principal species will be the one shown.

$$Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)_3$$

Test d

Fehling's solution is an alkaline solution of copper (II) complexed with tartrate ion which is initially blue in colour, but in the presence