

Nuclear Magnetic Resonance 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 have 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 four reference lists of commonly used scientific symbols and values, units of measurement and also a periodic table.

Study Guide

This short course is designed to introduce you to some of the most important aspects of nuclear magnetic resonance that are in widespread use in both industrial and academic laboratories. Proton and carbon-13 are by far the most widely used nuclei in nmr spectroscopy, and as such are dealt with almost exclusively. The principles of nmr are common to all nuclei and hence if, for example, you are interested in using fluorine-19 or phosphorus-31 nmr, little further study would be needed.

From our experience of teaching nmr spectroscopy over a number of years, we have found that the major difficulty students experience is the large number of new ideas. Hence a course such as this, which allows you to study at your own pace, is particularly beneficial.

The course is biased towards applications at the expense of some theory. In this respect it differs from many other publications on the subject. You will find, however, it provides an adequate theoretical basis for dealing with spectral interpretation and quantitative analysis. If you get a chance to carry out some laboratory work in conjunction with this course, do so. It will help a great deal in developing your understanding and expertise.

Although you do not need any prior knowledge of nmr before embarking on this course, it is advantageous for you to have studied chemistry since leaving school. Typically, you will have studied chemistry for a further two or three years together with supporting studies in physics and mathematics. More specifically you will need to be familiar with structural organic chemistry, the electromagnetic spectrum, any branch of spectroscopy, and basic analytical chemistry.

Practical Objectives

A short laboratory course in nmr spectroscopy would benefit any student studying this Unit.

The successful attainment of the three objectives given below would take a minimum of six hours of practical work. Such work would directly support Parts 2, 4 and 5 of the text. Practical work is not of direct relevance to the other Parts, 1 and 3.

By the end of a practical course the student should be able to:

1. Prepare a solid or liquid sample for nmr analysis by selection of a suitable solvent, etc.
2. Obtain a routine CW nmr spectrum and its integration curve from an analytical sample, by selecting appropriate instrumental conditions.
3. Analyse quantitatively, via integration data, samples such as those examined in Part 5 of the text.

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NOTE References 1–4 are books immediately useful at this level: Reference 1 gives three books which contain a single chapter devoted to nmr. References 5–8 are more advanced, but some chapters are directly relevant; Reference 9 and 10 are of Honours level and beyond; Reference 11 is the source of the carbon-13 data used in this Unit.

Acknowledgements

Fig. 3.1d redrawn with permission from F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, John Wiley & Sons Ltd, Chichester (1976).

Fig. 4.3c redrawn with permission from J. K. Akett, *NMR and Chemistry*, 2nd Edn, Chapman & Hall (1983).

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1. Background and Theory of NMR Spectroscopy

Overview

In this first part of the course we are going to study quite a number of ideas about nuclear magnetic resonance spectroscopy. As you will appreciate later in this course and if you go on to study this fascinating and wide-ranging technique at higher levels you need to have a sound knowledge of the physical origin of the nmr phenomenon and its associated parameters. So we start off by looking at spin-active nuclei and how nuclei can absorb radiofrequency radiation—the physical basis of nmr.

We shall encounter a couple of fundamental equations which govern some nmr processes and we will explore the information that nmr spectroscopy can give us in terms of four parameters measurable from an nmr spectrum: chemical shifts, coupling constants, relaxation times, and integrations. You will be able to explain and exemplify all these terms by the end of this part of the Unit.

We shall see that all of these parameters are closely linked with molecular structure. Chemical shifts of protons and carbon-13 nuclei in organic structures will be explained in terms of bonding and electronic effects and you will encounter the mysteries of magnetic anisotropy (pronounced an-isotropy).

The fine structure associated with many nmr spectra will be seen to be related to spin-spin coupling and can give information about neighbouring nuclei. An important rule—the $2nI + 1$ rule—will be introduced and developed.

When it comes to relaxation times you won't be doing any relaxation—only the spin-active nuclei. This parameter affects the width of nmr signals and has other far reaching consequences.

Finally, in this part of the Unit you will learn about integration of nmr signals and how the area under a signal is proportional to the number of spin-active nuclei causing the signal. This lays the basis for quantitative analysis (Part 5) as well as being an aid in qualitative work (Part 3).

Don't worry if you find this first part tough going because, like all of the Units of the Analytical Chemistry series, you can study at your own pace and come back to parts you do not follow, later on.

1.1 NUCLEAR MAGNETIC RESONANCE AND SPIN-ACTIVE NUCLEI

When certain types of nuclei like protons, carbon-13 and fluorine-19 are placed in a strong magnetic field they can absorb electromagnetic radiation in the radiofrequency range. Such nuclei are said to be *spin-active* and to *resonate*. The precise frequencies at which spin-active nuclei resonate can be picked up and displayed by instruments called *nuclear magnetic resonance* (nmr) spectrometers.

To explain the phenomenon of nmr we must look at the nature of a spin-active nucleus such as a proton. As well as having an electrical charge associated with it, a nucleus behaves as if it were *spinning* about an axis (a bit like a gyroscope in motion or the Earth spinning on its axis). Fig. 1.1a shows the idea. Now, charged spinning particles generate a magnetic field around them, so that we can think of protons and so on as tiny spinning magnets (microscopic compass needles). In the absence of any external magnetic field these nuclei are spinning at random in their atomic or molecular environment, but when placed in a strong external field (B_0) these nuclear mag-

nets orientate themselves with respect to the direction of the magnetic field, again just like compass needles align themselves in the Earth's magnetic field. Unlike compass needles, though, spin-active nuclei can orientate themselves in more than one way. For protons there are two possible alignments, either with the field, or against it (Fig. 1.1a).

The two orientations of our example are also known as the α and β spin states, and these states differ very slightly in energy. It is this energy difference that can be supplied by the radiofrequency radiation allowing the nuclear spins to change their state. (Fig. 1.1b).

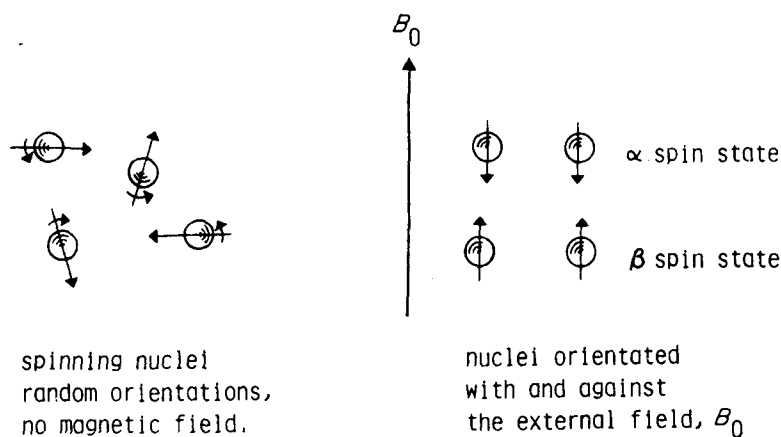


Fig. 1.1a. Nuclear spin

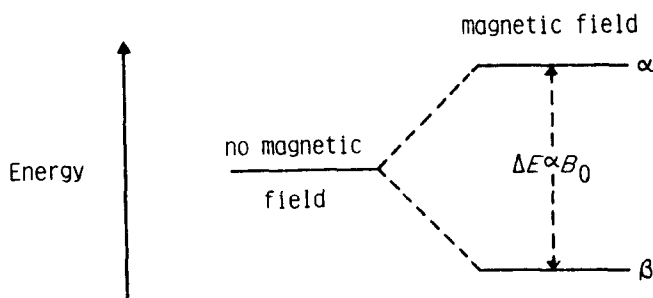


Fig. 1.1b. Energy description of the nmr phenomenon