Practical Organic Mass Spectrometry

J. R. Chapman

Practical Organic Mass Spectrometry

J R CHAPMAN
Kratos Analytical Instruments Ltd

A Wiley–Interscience Publication

JOHN WILEY & SONS
Chichester · New York · Brisbane · Toronto · Singapore

Reprinted October 1986

Reprinted December 1988

Library of Congress Cataloging in Publication Data:

Chapman, J. R.
Practical organic mass spectrometry.

Includes index.
1. Mass spectrometry. 2. Chemistry, Organic.
I. Title.
QD272.S6C43 1985 547.3'0873 84-27132

ISBN 0 471 90696 4

British Library Cataloguing in Publication Data:

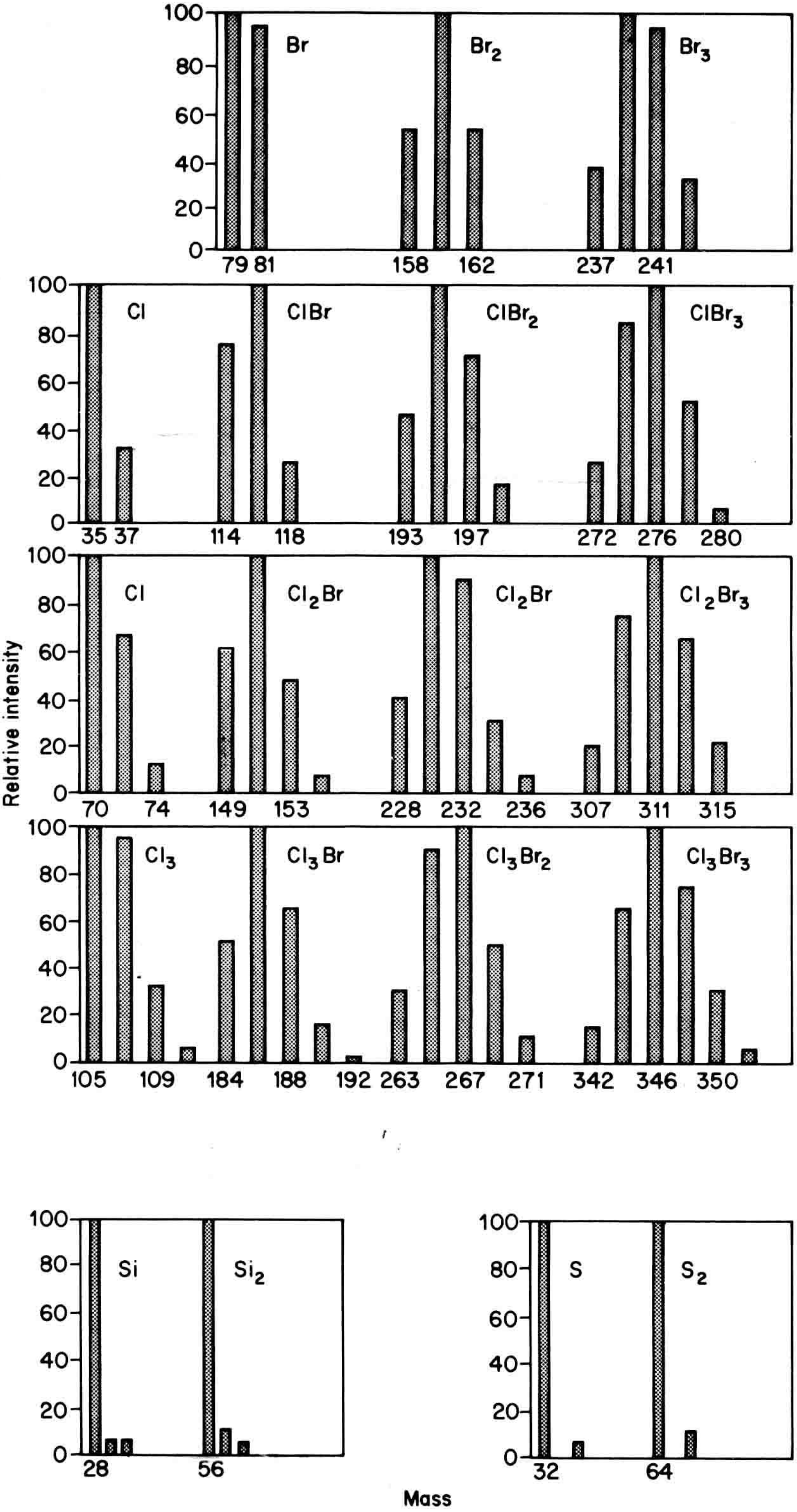
Chapman, J. R.
Practical organic mass spectrometry.
1. Mass spectrometry 2. Chemistry, organic.
I. Title
547.3'0873 QD272.S6

ISBN 0 471 90696 4

Printed and bound in Great Britain.

Isotope	Mass	Nat. Ab.	Isotope	Mass	Nat. Ab.
^{1}H	1.00782	99.985	^{32}S	31.97207	95.000
^{2}H	2.01410	0.015	^{33}S	32.97146	0.760
^{4}He	4.00260	99.999	^{34}S	33.96786	4.200
^{6}Li	6.01512	7.420	^{35}Cl	34.96885	75.800
^{7}Li	7.01600	92.580	^{37}Cl	36.96590	24.200
^{10}B	10.01294	20.000	^{36}Ar	35.96754	0.340
^{11}B	11.00930	80.000	^{40}Ar	39.96238	99.590
^{12}C	12.00000	98.900	^{54}Fe	53.93960	5.820
^{13}C	13.00335	1.100	^{56}Fe	55.93490	91.660
^{14}N	14.00307	99.640	^{57}Fe	56.93540	2.190
^{15}N	15.00010	0.360	^{58}Fe	57.93330	0.330
^{16}O	15.99491	99.800	^{63}Cu	62.92980	69.090
^{17}O	16.99913	0.040	^{65}Cu	64.92780	30.910
^{18}O	17.99916	0.200			
^{19}F	18.99840	100.000	^{79}Br	78.91839	50.500
^{20}Ne	19.99244	90.510	^{81}Br	80.91642	49.500
^{22}Ne	21.99138	9.220	^{107}Ag	106.90509	51.820
^{24}Mg	23.98504	78.700	^{109}Ag	108.90470	48.180
^{25}Mg	24.98584	10.130	^{127}I	126.90447	100.000
^{26}Mg	25.98259	11.170	^{133}Cs	132.90543	100.000
^{27}Al	26.98153	100.000	^{197}Au	196.96660	100.000
^{28}Si	27.97692	92.200	^{204}Pb	203.97300	1.480
^{29}Si	28.97649	4.700	^{206}Pb	205.97450	23.600
^{30}Si	29.97375	3.100	^{207}Pb	206.97590	22.600
^{31}P	30.97376	100.000	^{208}Pb	207.97660	52.300

Isotopic masses and abundances



Relative intensities of some common isotopes

Practical Organic Mass Spectrometry

Preface

The aim of this book is to provide a practical guide to the use and utility of some of the alternative ionization and operating techniques now available in mass spectrometry. With this in mind, Chapters 3–6 in particular are each broadly divided into three sections—theory, practical requirements, and applications.

Theory is, of necessity, brief in a book of this size but hopefully presents those aspects that are most relevant for appreciation and application of each technique. Again, detailed practical requirements will vary from instrument to instrument but there is, nevertheless, a body of generally relevant knowledge that this book draws on.

Each section covering applications has been supplemented as far as possible with tabulations of references to published data in order to provide the intending user with a starting point for assessing the utility of a particular method. These tabulations are not completely up to date, mainly because of the labour involved, but I hope that both they and the more general references which follow each chapter will prove to be useful.

I am solely responsible for any opinions expressed within the book and for the emphasis given to any particular aspect of the subject. For example, field desorption, although now no longer a pre-eminent technique, is discussed at length since much of the work that has been published regarding the mechanisms that operate in field desorption provides invaluable background material for an intending user of any of the ionization methods designed for higher molecular weight, labile materials.

In conclusion, I would like to thank my wife for her assistance and encouragement provided throughout this enterprise and acknowledge the co-operation of copyright owners, including my employers, in allowing me to incorporate many of their illustrations in the book.

J. R. Chapman

Contents

Chapter 1

Instrumentation

1.1 Introduction

The first precision measurements of ionic masses and abundances were reported in 1918–19 by F. W. Aston$^{(1)}$ and A. J. Dempster$^{(2)}$ respectively. This work followed the pioneering demonstration of the existence of isotopic forms of stable elements by Sir J. J. Thompson$^{(3)}$ using the first instrument built for positive ray analysis. From these beginnings, using magnetic and electrostatic fields for mass separation, steady improvements in the performance of mass analysers have been made and new forms of analyser, e.g. the quadrupole mass filter, have been introduced. The principles of magnetic sector and quadrupole mass analysers and of ion detection are discussed in this chapter, following a brief description of the standard electron impact ion source.

A considerable impetus to the development of organic mass spectrometry has also come from advances in sample handling and in methods of ion formation which have both enormously increased the range of samples amenable to mass spectrometric analysis. Sample handling techniques, particularly the combination of mass spectrometry with on-line chromatographic separation, are the subject of Chapter 2, whilst Chapters 3–5 cover alternative ionization techniques in some detail.

The observation of the further fragmentation of ions formed in the mass spectrometer has added another dimension to the measurement of ionic masses and abundances and has proved to be particularly fruitful as a basis for methods for the analysis of specific compounds in complex mixtures. The quantitative aspects of this so-called metastable ion analysis and of other techniques are discussed in Chapter 7 following a general survey of metastable ion analysis in Chapter 6.

1.2 The electron impact ion source

In the electron impact (EI) source first used by Dempster,$^{(4)}$ and subsequently developed by Nier,$^{(5)}$ sample vapour at a reduced pressure flows through a

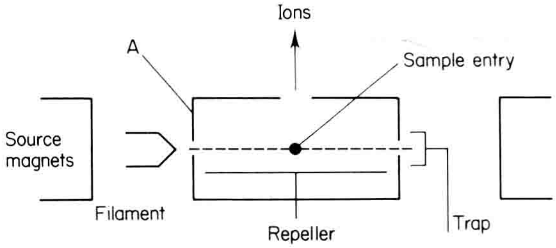


Fig. 1.1 Schematic diagram of electron impact ion source

region traversed by an electron beam. A schematic diagram of the ion source is shown in Fig. 1.1.

Electrons formed by heating a tungsten or rhenium ribbon filament are accelerated by a voltage of from 5 to 100 volts towards plate A (Fig. 1.1). Some of these electrons pass through the slit in plate A and traverse the ionization region. The ionizing beam current may be controlled by monitoring total filament emission or, with more accuracy, by feedback control from the current reaching the trap plate in the EI mode. A magnetic field of the order of a few hundred gauss is maintained along the length of the electron beam to confine it to a narrow helical path. Alternatively the beam may be confined by the use of a focusing electrode.

Gas molecules entering the ionizing region interact with the electrons. Some of these molecules lose an electron to become positively ionized and often subsequently undergo fragmentation. Only about 1 in 10^4 of the molecules present in the source is ionized. The ionization probability differs among substances, but it is found that the cross-section for most molecules is a maximum for electron energies from approximately 50 to 100 eV. A typical plot of ion current versus electron energy is shown in Fig. 1.2. Note the dramatic fall in sensitivity at low electron energies.

The total ion current and the fragmentation pattern both depend on the electron energy. Fig. 1.3 shows the variation in the mass spectrum of ethyl acetate obtained using nominal electron energies of 14, 20, and 60 eV. Most existing compilations of electron impact mass spectra are based on spectra recorded with approximately 70 eV electrons, since sensitivity is here close to a maximum and fragmentation is unaffected by small changes in electron energy about this value.

Ions formed in the ionization volume are extracted through the ion exit slit by a small potential applied to the ion repeller plate (Fig. 1.1) and partly by penetration of the accelerating voltage field through the ion exit slit in the case of magnetic sector instruments.

Most electron bombardment sources are reasonably gas-tight apart from the small electron entry hole and ion exit slit necessary for their operation, so that a high sample pressure and consequently a high sensitivity is maintained. At the same time, fast pumping is maintained in the source housing and analyser regions (Fig. 2.1 and cf. section 2.1). A high pumping speed in the source

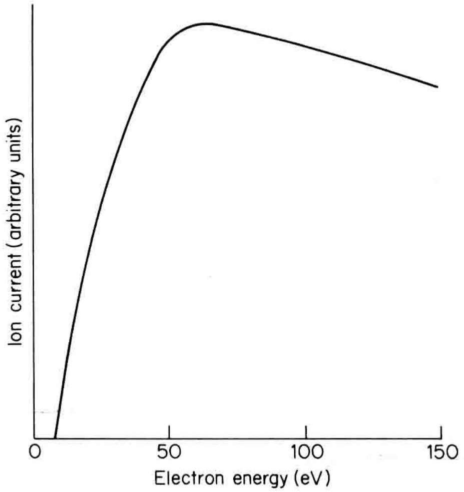


Fig. 1.2 Plot of ion current versus electron energy

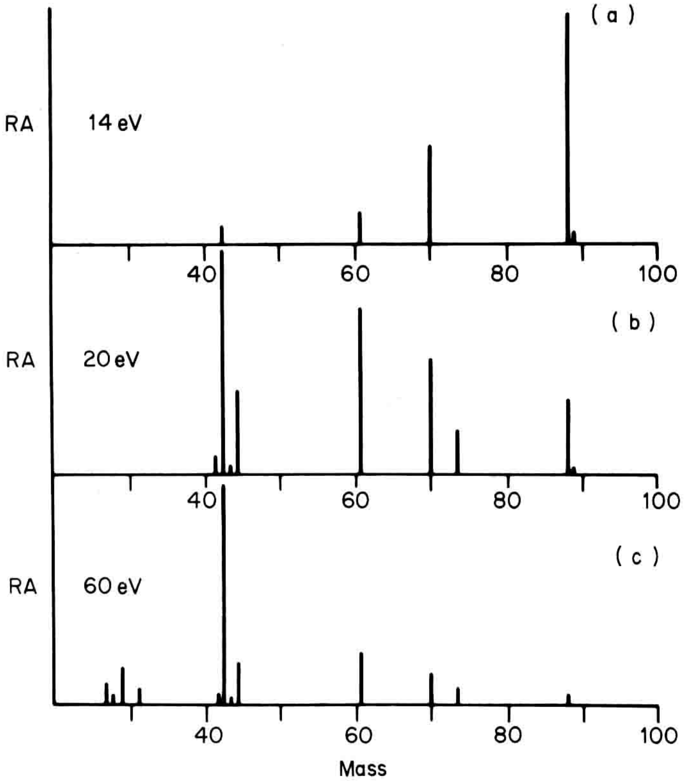


Fig. 1.3 Mass spectrum of ethyl acetate as a function of electron energy: (a) 14 eV; (b) 20 eV; (c) 60 eV (Reproduced with permission from *Techniques of Combined Gas Chromatography/Mass Spectrometry* (ref. 23))

housing reduces the sample pressure in the region of the hot filament so as to prolong filament lifetime and minimizes the possibility of sample molecules re-entering the ionization chamber. A high pumping speed in the analyser and source housing regions also minimizes the possibility of unwanted ion-molecule collisions, although fragmentation of ions can be deliberately induced by ion-molecule collisions with a high pressure gas in a specially constructed collision cell (section 6.2.3). Too high a pressure in the analyser can have a number of other undesirable consequences, e.g. loss of sensitivity, loss of resolution and a shortening of electron multiplier lifetime.

Despite its relative gas-tightness, the half-life for sample molecules which are continuously pumped from the small volume of the source and attached sample lines is only a fraction of a second. Thus the mass spectrometer as a detector has a very rapid response, entirely compatible with the rapid changes in sample concentration experienced in high resolution chromatography. The effective pumping speed is, however, dramatically reduced by any cooler surfaces which can trap less volatile materials (cf. section 2.2.4.2). Even heating of the source block and adjacent areas is therefore essential. Adjustment of the source block temperature by cooling as well as by heating is a useful facility. In this connection, it should be appreciated that the heat of the filament alone will maintain an ion source temperature of 100–150°C.

Although the electron bombardment source was the first source developed and used in organic mass spectrometry, it is still the most popular. Several factors contribute to its popularity. Thus, its stability, ease of operation and control of beam intensity, lack of contamination problems, and relatively high sensitivity are practical advantages. The lack of selectivity under electron impact conditions is a further advantage when a wide range of compounds is to be analysed.

Some groups of isomeric compounds give very similar mass spectra, but generally an electron impact mass spectrum is specific and characteristic of the chemical structure of the sample. Furthermore the major compilations of mass spectral reference data presently available consist entirely of electron impact spectra.

1.3 Mass analysers

Several forms of mass analyser which separate ions according to their mass-to-charge ratio exist,(6) e.g. magnetic sector analysers,(6,7) quadrupole mass filters,(6,8,10) time of flight analysers,(6,11) and ion cyclotron resonance instruments.(12,13,14) The first two types, which account for the great majority of instruments used in organic analysis, are discussed in more detail in the following sections.

1.3.1 Magnetic sector analyser(6,15 p.9–13)

The principle of the single-focusing magnetic deflection mass spectrometer is illustrated in Fig. 1.4. Ions formed in the source are accelerated through a

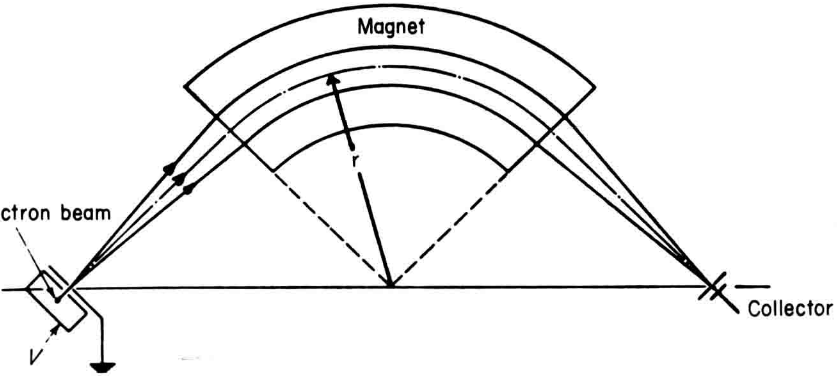


Fig. 1.4 Schematic diagram of single-focusing magnetic sector instrument

voltage V (V = 2000–8000 V) towards the source slit which is at earth potential. The fall in potential energy for the ions is equal to their gain in kinetic energy and this is summarized in equation (1.1) where e is the charge on an electron, z is the number of such charges on the ion, m is the mass of the ion, V is the accelerating voltage and v is the velocity of the ion.

For an ion to reach the collector slit and be recorded, it must traverse a path of radius of curvature r through the magnetic field of strength B. The equation of motion of the ion (1.2) then expresses the balance between the angular momentum and the centrifugal force caused by this field. Note that rearrangement of Equation (1.2) in the form $mv = Bzer$ demonstrates the fact that a magnetic sector is a momentum analyser rather than a mass analyser as is commonly assumed. Combining Equations (1.1) and (1.2) gives the basic mass spectrometer Equation (1.3).

$$zeV = \frac{1}{2} mv^2 \tag{1.1}$$

$$mv^2/r = Bzev \tag{1.2}$$

$$\frac{m}{z} = \frac{B^2r^2e}{2\,V} \tag{1.3}$$

$$M = 4.83 \times 10^3\,(B^2r^2/V) \tag{1.4}$$

Expressed in practical units the atomic mass (M) of a singly charged ion is given by Equation (1.4) where r is in centimetres, B is in tesla (1 tesla ≡ 10^4 gauss) and V is in volts. For example a maximum field strength of 1.5 tesla gives a maximum mass of just over 2400 daltons for an instrument of 30 cm radius operating with an accelerating voltage of 4000 V.

Thus, by varying either B or V, ions of different m/z ratio separated by the magnetic field can be made to reach the collector. The most common form of mass scan is the exponential magnet scan, downward in mass. It has the advantage of producing mass spectral peaks of constant width. The equations appropriate to this form of scan are (1.5) and (1.6) where m_0 is the starting mass at time $t = 0$, m is the mass registered at time t, t_p is the peak width between its 5% points, t_{10} is the time taken to scan one decade in mass (e.g. m/z 200 to 20, or m/z 500 to 50) and R is the resolving power measured by the 10% valley definition (see section 1.6).

$$m = m_0 \exp^{(-kt)} \tag{1.5}$$

$$t_p = t_{10}/2.303R \tag{1.6}$$

Scanning of the accelerating voltage V would, at first sight, appear to be advantageous because of the ease of rapid scanning and the ease of scan control. Change of the accelerating voltage over even a two-fold range, however, causes defocusing and loss of sensitivity and is consequently little used as a method of scanning.

The magnetic field may be sensed by a Hall effect probe(16) and the Hall effect voltage induced used to provide a reliable mass indicator. In addition the Hall voltage may be used in feedback control both to provide more reproducible magnet scanning and to allow linked scanning, e.g. of the magnetic field and electrostatic sector voltage, in double focusing instruments (section 6.3.2).

1.3.2 Double focusing magnetic sector analyser(6,7,15 pp.13-18)

Since a magnetic sector is a momentum rather than a mass analyser, ions of the same mass but of differing translational energy are not brought to a point focus in a single-focusing magnetic deflection instrument. The translational energy spread of the ions formed in an electron impact source will therefore limit the available resolution, and the existence of charging effects and contact potentials as source contamination builds up in use causes some worsening of this situation. Other ion sources, e.g. the field desorption source, produce ions with a much greater translational energy spread.

The inability of a single magnetic sector instrument to provide more than a limited resolution under practical conditions can be overcome by the addition of an electrostatic sector (Fig. 1.5). The combination of the two sectors can then be designed to have velocity focusing properties.

An ion entering the electrostatic field travels in a circular path of radius R such that the electrostatic force acting on it balances the centrifugal force. The equation of motion is then (1.7) where E is the electrostatic field strength. Hence the radius of curvature of the ion path in the electrostatic sector is dependent upon its energy, but not its mass.

$$\frac{mv^2}{R} = eE \tag{1.7}$$

A narrow slit placed in the image plane of an electrostatic sector could be used to transmit a narrow band of ion energies. If such an energy filter were used as the