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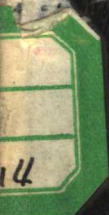


# Mass Spectrometry of Pesticides and Pollutants

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## PREFACE

In the last ten years the uses and applications of mass spectrometry have increased rapidly in many diverse scientific disciplines. The fields of pesticide and pollution analysis and chemistry are not exceptional in this regard and applications of mass spectrometry are probably increasing more rapidly in these fields than in others. The current scientific and political interest in the analysis and monitoring of environmental pollutants has generated a large number of applications of mass spectrometry and in particular gas chromatography-mass spectrometry (GC-MS) is a most powerful analytical method. GC-MS coupled with computer facilities is now routinely used to monitor environmental samples. In addition a number of groups have been increasingly interested in the photochemical and metabolic behavior of pesticides and pollutants and again the analyses and characterization of the products of these processes are facilitated by mass spectrometry.

The main aim of this book has been to collect and discuss all the published information on the mass spectrometry of pesticides and pollutants. These data have been arranged according to their chemical functionality (i.e., carbamates, ureas,

triazines, etc.) and their mass spectra and fragmentations patterns have been presented and discussed in some detail. We have also included and discussed the spectra of many compounds which have recently been run in our laboratory. In addition, the uses of mass spectrometry in the identification of photo and metabolic products have also been included.

We would like to express our appreciation to Dr. W. D. Jamieson for writing the first part of chapter I and for his collaboration in obtaining some of the spectra data. We would also like to thank the following scientists for their assistance: Mr. D. Embree, Mr. M. Cook, Dr. D. L. Stalling, Dr. F. J. Biros, Mr. J. Damico, Dr. E. J. Bonelli, Professor H. Beckey, Dr. J. G. Pomonis, Professor T. R. Majer, Professor B. Munson and Dr. J. M. McGuire. We would also like to acknowledge the help of the Bendix Instrument Co., Finnigan Instruments, Scientific Research Instruments, and numerous publishing companies for allowing us to reproduce some of their material.

S. Safe  
O. Hutzinger

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## INTRODUCTION TO MASS SPECTROMETRY

OPERATING CHARACTERISTICS  
OF MASS SPECTROMETERS

Using suitable apparatus, a sample can be subjected to an ionization process and its mass spectrum determined. This mass spectrum is composed of the relative numbers of ions of different mass/charge ratio ( $m/e$ ) that coexist for the set of conditions defined by the apparatus and by the way the experiment was done.

Mass spectrometers differ in (a) sample introduction systems, (b) sample ionization processes or conditions ("source" characteristics), (c) ionic analysis systems, (d) spectrum recording systems. Characteristic features of a mass spectrum can be affected by any of these instrumental aspects. Some instrumental parameters bias ionic analyses, others affect more the nature of the array of competing and consecutive ionic decomposition reactions defining, in a time-dependent way, the relative members and kinds of coexisting ions — a mass spectrometer is, after all, a chemical reactor.

Modern analytical mass spectrometers typically can yield mass spectral data on samples containing only microgram-range amounts of particular compounds. For many modern instruments the sensitivity limit is in the nanogram range. Consistent with this sensitivity, the most effective sample introduction systems are those by which either a discrete sample is ionized directly (surface ionization, RF spark ionization, laser ionization), sublimates or desorbs directly into an ionization zone (direct introduction with electron-impact or field ionization, field desorption ionization) or, as in the case of coupled gas chromatography-mass spectrometry, all or part of the effluent from a small-sample mixture separator is directed to the ionization zone for a mass spectrometer.

Sample ionization in mass spectrometric analyses for pesticides or other pollutants is usually by electron-impact on sample vapor maintained at a low steady-state pressure ( $\approx 10^{-5}$ – $10^{-6}$  torr) within the "source." This usually results in a coexistent mixture of positive ions complex enough to yield mass spectra characteristic of specific compounds. If electron-impact conditions, especially the electron energy,

are so adjusted that a mixture of coexistent negative ions is available for analysis, then this other simpler type of mass spectral data can be obtained to supplement the positive ion mass spectrum (see Chapter 3).

Spectra of yet another type can be obtained by field-ionization<sup>1</sup> since sample vapor maintained at a low steady-state pressure ( $\approx 10^{-5}$  torr) yields positive ions in an intense electrical field ( $\approx 10^7$ – $10^8$  V/cm) within the source. Ions thus formed possess less excess energy than do those from electron impact ionization and also are much more rapidly extracted from the source for analysis. Unambiguous identification of molecular ions is a major analytical use for these simple spectra while the relatively low yield of ions is a major disadvantage. This sensitivity problem is probably due mainly to low efficiency of sample transport to the small effective ionization zone and has been overcome by the development of field-desorption ionization. In this newer technique the sample is introduced into the source as a coating on the surface of the anode of the ionizing field. Control of the temperature of the anode surface regulates the rate of sample supply, which is by surface migration and desorption, and can also serve to enhance the complexity or information content of the mass spectrum (see Chapter 3).

RF spark ionization,<sup>2</sup> applied for many years to elemental analyses of metals and other non-volatile samples, has been particularly useful in determining trace quantities. Minor components of samples can be detected, as elements, at ppb levels. In general, however, such mass spectra are not characteristic of constituent chemical compounds and are of limited usefulness in pollutant studies.

The production of mass spectra by chemical ionization<sup>3,4</sup> of sample vapor is of particular interest in directly coupled gas chromatography-mass spectrometry since operation of the source at the associated high reactant gas pressure ( $\approx 1$  torr) simplifies the interfacing of the two instrument systems. Ions are produced from low partial pressures of compounds of interest by gas-phase reactions in the source with a set of ions derived from ionization of the admixed, predominant reactant gases (see Chapter 3). Analogous to this

technique of ion production is that of high pressure charge exchange mass spectrometry using such reactant gases as nitrogen, nitric oxide, carbon monoxide, carbon dioxide, or oxygen.

Ionic analysis systems resolve, according to mass/charge ratio, the coexistent mixture of ions produced in the source. In many instruments, a sample of the source ionic mixture is extracted by an electrostatic field and accelerated through an electrostatic "lens" system to enter a uniform magnetic field at right angles to the direction of motion. The effect of the magnetic field in ionic optics is analogous to that of a prism in light optics. Ions of different mass/charge ratio are deflected to follow circular trajectories, of different radii, lying in a plane normal to the magnetic field. For magnetic analysis systems, assuming permeability = 1, the relationship between parameters is given by

$$m/e = k H^2 r^2 / V$$

where  $m/e$  is the ionic mass per unit charge,  $H$  is the magnetic field strength,  $r$  is the radius of the ionic trajectory in the magnetic field, and  $V$  is the strength of the electric field used to accelerate ions extracted from the source. Many magnetic analyzer mass spectrometers use a fixed collector electrode to electrically detect ions deflected to follow a specific trajectory -- the mass spectrum is

"scanned" by varying with time either the magnetic field or the electrostatic accelerating field, usually the magnetic field.

The resolution of a mass spectrometer with the capability to distinguish between ions of nearly the same mass/charge ratio, is limited in the case of magnetic analyzer instruments by the width,  $\Delta r$ , of the mass-resolved ionic beam produced by the magnetic field. The smaller this width, the higher the resolution will be. In practice, the minimum beam width is limited by the energy spread,  $\Delta V$ , in the unresolved ionic beam entering the magnetic field. Most double-focusing instruments reduce this energy spread by focusing the ionic beam according to velocity (energy) prior to mass analysis by direction focusing in the magnetic field. The attainable resolution is improved by one to two orders of magnitude.

Commercially available double-focusing instruments are usually of two types of geometry -- Mattauch-Herzog<sup>5</sup> or Nier-Johnson<sup>6</sup> (Figures 1 and 2). Each has advantages for certain kinds of experiments. With Mattauch-Herzog geometry, mass-resolved ionic beams are focused in a plane and it is possible to record mass spectra photographically as an alternative to doing so by electrical detection. In a third type of double-focusing mass spectrometer, the ionic beam from the source is analyzed by crossed electrostatic and magnetic fields. Prolate trochoid ionic paths result

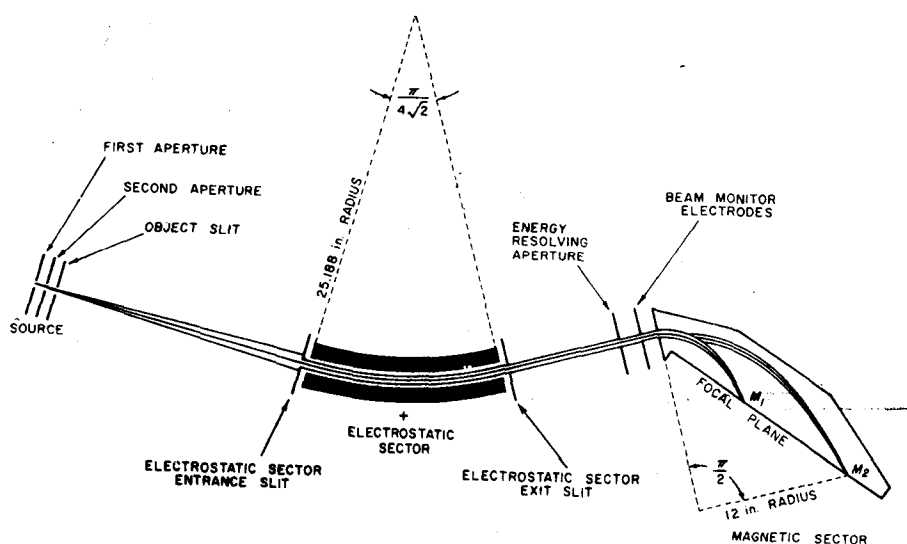


FIGURE 1. Mattauch-Herzog optics. (From DuPont Instrument Division, Monrovia, Cal. With permission.)

and a collector electrode is used to detect ions which have followed the critical cycloidal path.

The linear time-of-flight mass spectrometer<sup>7</sup> (Figure 3) does not use a magnetic field to mass-resolve the ionic beam. Ions produced in the source are accelerated along a drift tube by a pulsed electric field in such a way that all of the

ions formed acquire nearly identical kinetic energies and, therefore, velocities dependent on their mass/charge ratios. At the end of the drift tube ions are detected by an electron multiplier. Mass/charge ratio determination is by measurement of the flight time of the different ions in the beam. Although these instruments are useful in

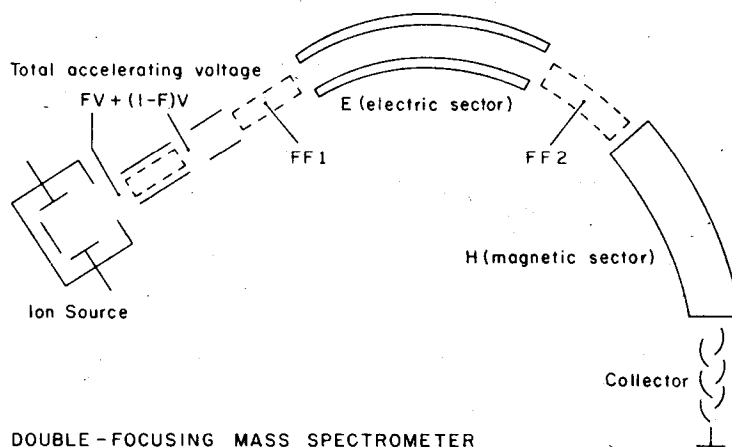


FIGURE 2. Niers-Johnson optics.

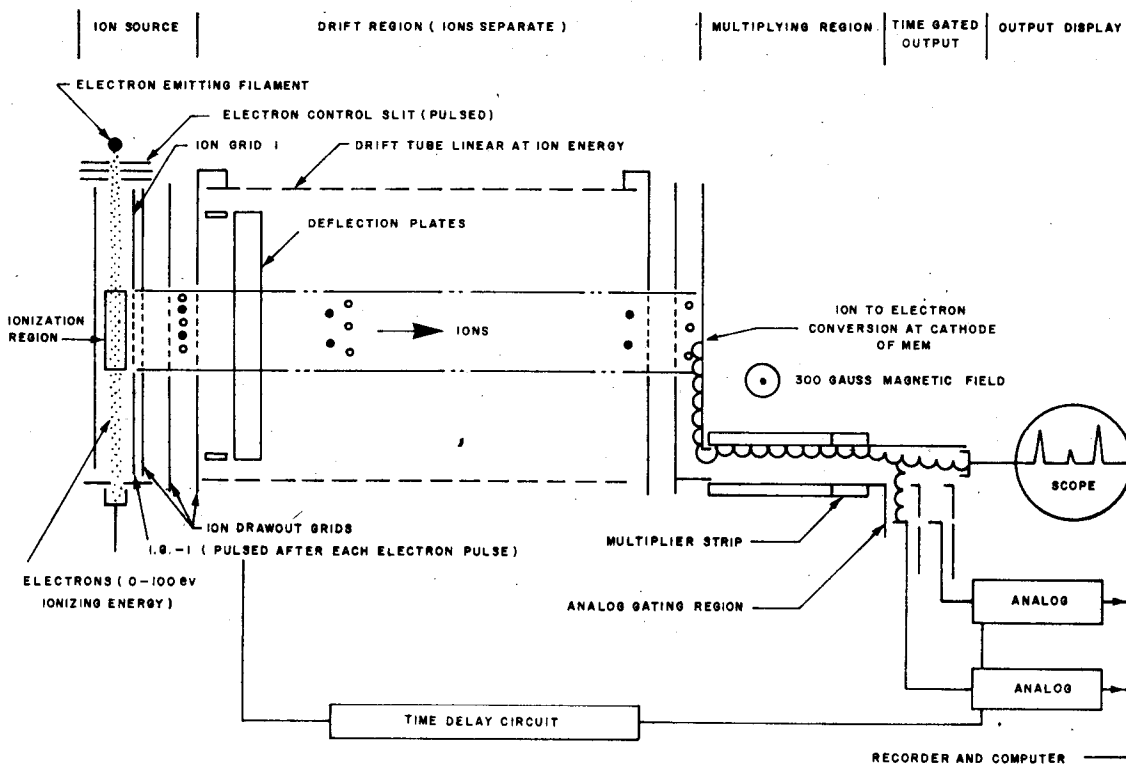


FIGURE 3. Bendix time-of-flight mass spectrometer. (Courtesy of Bendix Instrument Co.)

analyzing rapidly changing samples (scan time  $\approx 100$  sec), in comparison to magnetic analyzer instruments they lack resolving power and sensitivity.

In the ion cyclotron resonance mass spectrometer<sup>8</sup> (Figure 4), another type of time-of-flight instrument, ions are analyzed by use of a magnetic field crossed with a radio-frequency electric field. A collector electrode detects ions spiraling out of the magnetic field when the radio-frequency field is in resonance with the mass/charge dependent oscillating frequency of the ions. Such instruments have usually been used as residual gas analyzers in high vacuum technology.

The quadrupole mass spectrometer is another instrument not using a magnetic field (Figure 5).<sup>9</sup> Opposing pairs of electrodes in a quadrupole filter system maintain an electrostatic field upon which is superimposed a radio-frequency field. An unresolved ionic beam is injected into these fields parallel to the direction of the electrodes and the ions oscillate in directions determined by the electrostatic field but with an amplitude increasing exponentially with distance in the direction of injection. Suitably chosen electrostatic and radio-frequency fields allow ions of a given mass/charge ratio to escape from the quadrupole filter and be detected while other ions strike a surface and are lost. These instruments are not as sensitive as others to source conditions and contamination.

This and their rapid-scan capability have led to their wide use directly coupled to gas chromatographs in application not requiring resolving power above 750.

Most mass spectrometers use a collector electrode to detect mass-resolved ionic beams. Because the collected currents are low ( $10^{-9}$  to  $10^{-17}$  amp), those designed to scan rapidly use electron multipliers. Instruments designed to record relative ionic abundance data with the best accuracy usually use Faraday cup detector systems followed by either electrometer-dc amplifier or vibrating reed electrometer-ac amplifier systems and must be scanned slowly. Electron multiplier detectors discriminate, by lower sensitivity, against ions of higher mass and, in addition, the sensitivity is not independent of the chemical nature of the ion. With magnetic-scanning instruments the electron multiplier amplification may also be affected by the magnetic field changes. Many standard reference spectra were recorded on instruments using Faraday cup detectors but employing electrostatic scanning of the mass spectrum — a scanning method which discriminates strongly, by lower sensitivity, against ions of higher mass. It is interesting (and helpful) that the mass discrimination effects inherent in electrostatic scanning are approximately equivalent to those inherent in the use of electron multiplier detectors.

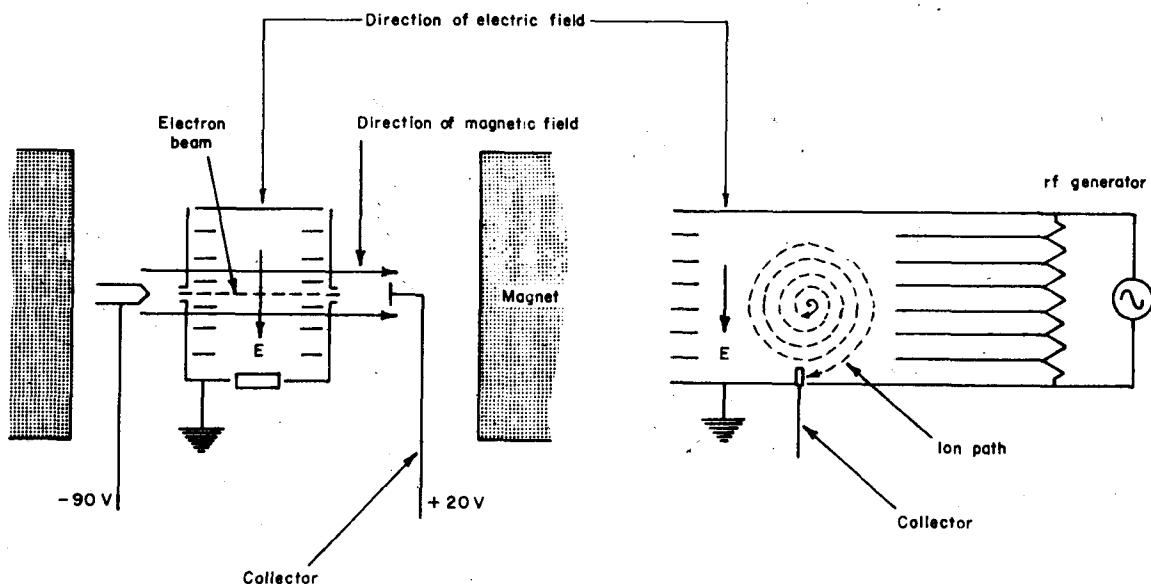


FIGURE 4. Schematic representation of ion cyclotron resonance mass spectrometer. (From Hamming, M. C. and Foster, N. G., *Interpretation of Mass Spectra of Organic Compounds*, Academic Press, New York, N.Y., p. 43. With permission.)

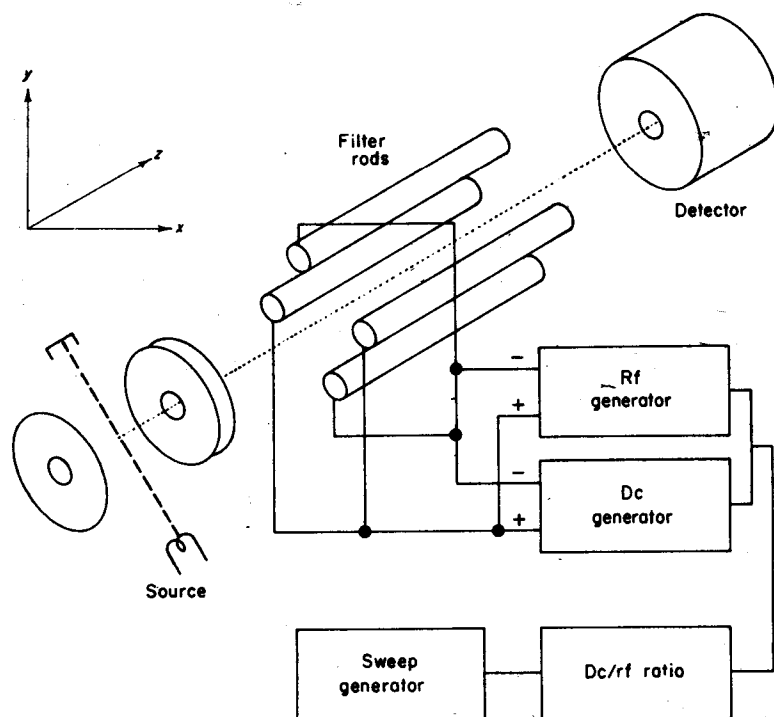


FIGURE 5. Schematics of ion quadrupole resonance mass spectrometer. (From Lawson, G. and Todd, J. F. J., *Chem. Br.*, 8, 373, 1972. With permission.)

Ion currents detected by electron multipliers<sup>10</sup> have usually been amplified and recorded as analog data with a dynamic range of  $10^7$ . This technology requires, too, that automatic data acquisition systems feeding into digital computers be interfaced to ion current output amplifiers in such a way that analog-digital conversion is achieved. An alternative technology directly counts the electron multiplier output pulses and not only avoids, therefore, any analog-digital conversion step but also makes possible data with a dynamic range of 10. This technology will probably prove useful in analyses of mixtures for trace components.

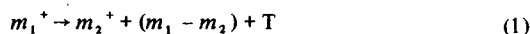
Among modern mass spectrometers, double-focusing instruments with Mattauch-Herzog-type ion optics are usually fitted with photographic plate ion detection systems either as the only detection system or as an alternative to an electrical detection system. Photoplate detection, an "integrating" method, is the only useful method for cases where the rate of ion production can fluctuate seriously in a time interval less than the minimum required to record a mass spectrum — it is, therefore, commonly used with such ion production methods as an RF spark.

In other cases, too, however, photoplate detection, if available, is often the best way to record a mass spectrum. High resolution data can be quickly and economically recorded on a photoplate for most or all (typically, up to five octaves of mass) of the mass range of a spectrum — this data can then be processed later as warranted, "off-line," either manually or automatically. In cases where the instrument resolution must be the maximum attainable, photoplate recording can yield higher resolution than an electrical detection system since, having no ion collector slit system, optimizing the photoplate-focal plane relationship can have the effect of reducing to "zero" the width of the collector slit used with an electrical detection system. Perhaps the most important advantage of photoplate detection, however, is that this method is in the limit about two or more orders of magnitude more sensitive than electrical detection methods. This is often very important when significant ions are of low relative abundance and can be critical when minor components of a mixture are of interest or when only very small or thermally unstable samples are available. Background noise and statistical considerations limit

the useful sensitivity of electron multiplier detectors to ion currents of about  $10^{-16}$  amperes or about 1,000 ions/sec assuming a scan speed slow enough to provide 0.1 sec per spectrum "peak." When required, however, a photoplate can be exposed for 2,000 sec or longer and lines can be detected which have been due to arrival of less than 10,000 ions over the period of exposure.

## METASTABLE IONS

Electron bombardment of a sample in the ion source of a mass spectrometer leads to a large array of positive ions with different internal energies. Ions with sufficient stability or lifetimes are accelerated out of the ion source and after several energy filtering stages reach the ion collector. These ions make up the conventional primary ion mass spectra. Many of the ions decompose prior to reaching the collector and those which undergo unimolecular decompositions in the mass spectrometer analyzer tube (second field-free region, FF<sub>2</sub>; see Figure 2) appear in the primary ion mass spectrum as weak, somewhat broadened, diffuse peaks called metastable ions. Ionic decompositions which produce metastable ions (Equations 1 and 2) involve the release of kinetic



$$m_2^* = \frac{m_2^2}{m_1} \left[ 1 \pm \sqrt{\frac{uT}{eV}} \right] \quad (2)$$

energy (T eV) and this contributes to the shape of the metastable peak. The parent ( $m_1$ ) and daughter ions ( $m_2$ ) which have not undergone decomposition appear in the mass spectrum at  $m_1/e$  and  $m_2/e$  respectively whereas the metastable ion ( $m_2^*$ ) appears at a mass considerably lower than  $m_2/e$ . The position of the metastable

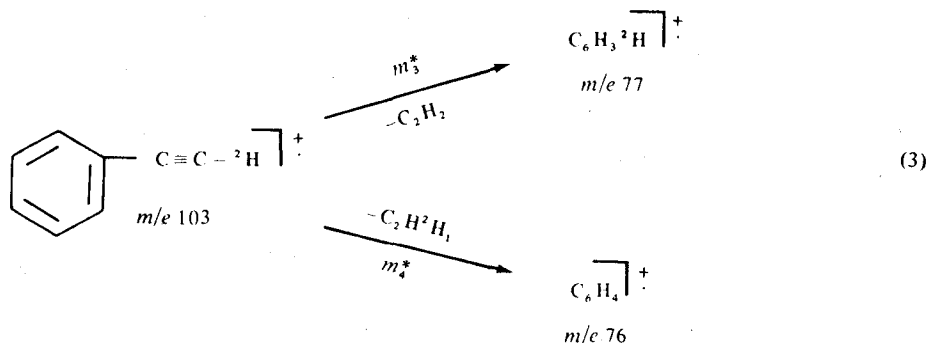
ion can be calculated from the equation where V is the accelerating voltage and  $u = m_2 - m_2^*/m_1$ . When the energy release factor T is small the equation simplifies to  $m_2^* = m_2^2/m_1$  which can be used to calculate the position of a specific metastable transition. More detailed descriptions of the origins of metastable ions have been reported in the literature.<sup>11-14</sup>

Although metastable ions contribute only a small portion of the ion current in a mass spectrum, they play a major role in several applications of this spectrometric technique.

1. The location of a metastable peak in a mass spectrum is essential in determining the fragmentation pattern of a particular ion. Most of the decomposition pathways discussed in this book have been confirmed by the presence of the appropriate metastable ions.

2. Metastable ions can also be used to study the degree of isotopic enrichment of a specific molecule. This application was recently reported by Beynon and co-workers in an investigation of a mixture of toluene and toluene-d<sub>1</sub> species. In this work they were also able to obtain a metastable ion spectrum by slowly scanning the mass spectrum of the toluene mixture while simultaneously changing the electric sector voltage. The spectrum thus obtained was observed without interference from the more intense primary ions and provided a useful and sensitive technique for examining metastable transitions.

3. The metastable ion concentrations are valuable in the investigation of electron impact-induced rearrangements. The relative intensities of metastable ions can be readily used in the study of H/D and C rearrangements which are frequently observed. Phenylacetylene<sup>15</sup> expels C<sub>2</sub>H<sub>2</sub> from its molecular ion whereas phenylacetylene-d<sub>1</sub> expels both C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>DH (Equation 3). This former



reaction is accompanied by the corresponding metastable ions at  $m/e$  57.5 ( $m_3^*$ ) and 57.1 ( $m_4^*$ ) with the  $[m_3^*]/[m_4^*]$  ratio being 2:1. For 100% H/D randomization in the decomposing molecular ions the calculated value for  $[m_3^*]/[m_4^*]$  was also 2:1 as obtained experimentally.

4. The shapes of metastable ions, and in particular their width at half-height can be used to study the energetics of ionic decomposition reactions and this is directly related to possible structures of the decomposing ions.

## ION KINETIC ENERGY SPECTROSCOPY<sup>1,5-21</sup>

Both metastable ions and ion kinetic energy (IKE) spectra have their origin in those ions which decompose after leaving the ion chamber and prior to reaching the collector. Decompositions which take place in the second field-free region (between the electric sector and magnetic sector) give rise to metastable ions which are seen in the mass spectra as weak diffuse peaks. Those ions which decompose in a similar manner between the accelerating region and the electric sector (the first field-free region,  $FF_1$ ) are not normally transmitted through the energy resolving  $\beta$  slit (Figure 2). The electric sector voltage  $E$  is set to transmit only those ions which have the full accelerating energy of the main ion beam and any ionic decompositions which occur in the first field-free region of the mass spectrometer would necessarily yield daughter ions without the requisite energy to pass through the electric sector. The main ion beam for the DuPont CEC 21-110B mass spectrometer is transmitted at an electric sector voltage of 400 V (at 8 kV accelerating voltage). However, if the electric sector voltage  $E$  is scanned from 400 to 0 V those daughter ions with only a fraction of the energy of the main ion beam ( $E$ ) will be transmitted through the  $\beta$  slit and can be duly detected and recorded. The results thus obtained are called the IKE spectra.

In a unimolecular reaction [e.g.,  $m_1^+ \rightarrow m_2^+ + (m_1 - m_2)$ ] occurring in the first field-free region the daughter ions,  $m_2$ , will appear at  $m_2/m_1 E$  of the main ion beam and when the electric sector is scanned from 0– $E$  only daughter ions of that specific fractional energy are transmitted at  $m_2/m_1 E$ . In some cases there are possible overlaps and an IKE peak will be the sum of two or more ionic decompositions. An example

of this coincidence of peaks occurs in the IKE spectra of the isomeric dichloroanilines;<sup>22</sup> the expulsion of Cl from the molecular ion ( $m/e$  161  $\rightarrow$   $m/e$  126) and the expulsion of HCN from the  $[M-Cl]^+$  ion ( $m/e$  126  $\rightarrow$   $m/e$  99) both give overlapping ionic decomposition peaks at 0.786  $E$ . One possible solution to this problem is the use of the photoplate technique in which the peak at 0.786  $E$  is allowed to impinge on the photoplate and the ratio of the two daughter ions can be readily calculated from the relative intensities of these species on the photoplate using conventional microcomparator techniques (see photoplate section). Thus the IKE spectrum gives a series of peaks which are directly related to the masses of the daughter and parent ions and the intensities of the observed IKE peaks are proportional to the frequencies of their corresponding ionic decomposition reactions. In most cases there is excellent agreement between the IKE peaks and the metastable ions observed in the primary ion mass spectra.

The IKE spectra observed between 0 and  $E$  are referred to as low energy IKE spectra whereas the spectra observed between  $E$  and  $2E$  are referred to as high energy IKE spectra and reflect the ionic decompositions of doubly-charged ions in the first field-free region. For the transition  $m_1^{x+} \rightarrow m_2^{y+}$  the corresponding IKE peak occurs at  $x/y (m_2/m_1)E$  and, if the above transition involves the decomposition of a doubly-charged ion ( $m_1^{2+}$ ) to give a single-charged species ( $m_2^+$ ), the peak for this reaction occurs at 2.0 ( $m_2/m_1$ ) $E$  in the high energy IKE spectrum. A large number of the reactions of doubly-charged and triply-charged ions can be studied using this technique. It is thus apparent that IKE spectroscopy can be applied to many different aspects of mass spectral analysis and these can be summarized as follows:

1. IKE spectra can be used in most of the same applications noted for metastable ion data<sup>23</sup> (i.e., confirmation of fragmentation pathways,<sup>24</sup> isotopic composition studies, determination of degree of atomic scrambling, and energetics of decomposing ions).<sup>25</sup>

2. The IKE spectrum of a molecule provides a characteristic fingerprint spectrum which can be used in structural and analytical studies. IKE spectra are characteristically more sensitive to stereochemical differences between molecules and this application can be noted in the mass spectra



of isomeric polychlorinated biphenyls (see Chapter 6). The mass spectra of most isomers are virtually indistinguishable whereas their IKE spectra usually show significant differences.

3. Beynon and co-workers have used the high energy IKE spectra in calculating interatomic distances between the charges in doubly-charged ions.<sup>25-27</sup> Using this approach they have shown the presence of linear, cyclic, and coiled ions in the IKE spectra of toluene.

4. Beynon and Cooks<sup>23</sup> have also recently described a further advance in this field obtained by interchanging the magnetic and the electric sector. Thus the ions can be initially separated according to their mass and the fragmentation of each ionic species can be studied. This technique of mass analyzed IKE spectra (MIKES) will offer in the future an even more refined technique for the study of ionic decompositions in the first field-free region of the mass spectrometer.

## THE LITERATURE OF PESTICIDES AND MASS SPECTROMETRY

With the rapid growth in the use of mass spectrometry in pesticide chemistry a number of researchers who may not be familiar with either mass spectrometry or pesticide chemistry are drawn into this field. The following two sections contain information on the more important recent literature for both subjects.

### Pesticides and Related Compounds

Guides to the literature of pesticides are available in three articles<sup>28-30</sup> and in the biannual literature reviews in *Analytical Chemistry*.<sup>31</sup>

Extensive lists of journals and books dealing with pesticides and related compounds are available from the sources mentioned above; only the more recent literature will be discussed in the following section.

Several collections of information on pesticides<sup>32-39</sup> give common and chemical names, formulae, and other useful data such as physical properties, toxicity, source for samples, etc.

Comprehensive volumes on the chemistry of pesticides are available,<sup>40-42</sup> as are books dealing with individual classes of compounds such as fungicides,<sup>43</sup> herbicides,<sup>44</sup> organophosphorus insecticides,<sup>45,46</sup> and organochlorine insecticides.<sup>45,47</sup>

An established series<sup>48</sup> and two newer publications<sup>49,50</sup> feature reviews dealing with the chemistry of pesticides and related environmental chemicals and toxic compounds.

Metabolism and environmental breakdown of pesticides are reviewed in several books.<sup>51-55</sup>

Information on recent developments in the field of pesticide and pollution chemistry can often be obtained from conference proceedings.<sup>56-58</sup>

### Mass Spectrometry

Mass spectrometry has become a well established technique and several books, some of them considered "classical," give the reader an excellent introduction to the subject.<sup>59-68</sup> All aspects of mass spectrometry are reviewed biannually in the review issue of *Analytical Chemistry* (for the latest article see Reference 69) and in a newly established Specialist Report Series of the Chemical Society.<sup>70</sup> A literature survey on mass spectrometry and allied topics is given by the *Mass Spectrometry Bulletin*.<sup>71</sup>

Several books containing articles on special topics in mass spectrometry have appeared recently<sup>72-75</sup> and published proceedings give information on topics of conferences on mass spectrometry.<sup>76-79</sup> Since several classes of pesticidal compounds contain heterocyclic moieties a book devoted to the mass spectrometry of heterocyclic compounds<sup>80</sup> is of interest.

Mass spectra of pesticides, related compounds, and their metabolites now appear regularly in most journals dealing with the analysis, chemistry, and biochemistry of these compounds. Many mass spectra of compounds structurally related to pesticides are reported in journals dealing with organic chemistry and several journals are devoted entirely to research in mass spectroscopy.<sup>81-83</sup>

Collections of mass spectral data have been evaluated.<sup>84,85</sup> The most important ones are the compilation of Cornu and Massot<sup>86</sup> (with two supplements) which gives the ten most intense peaks; the *Atlas of Mass Spectral Data*<sup>87</sup> and *Archives of Mass Spectral Data*<sup>88</sup> (quarterly) both of which compile complete spectra; the *Index of Mass Spectral Data*<sup>89</sup> which gives the six most intense ions and the *Eight Peak Index of Mass Spectra*.<sup>90</sup> The Aldermaston Data Centre<sup>71,90</sup> also issues mass spectral data sheets.

Other useful information particularly for high