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Der Schweizerische Chemiker-Verband veranstaltete vom 15. bis 20. Oktober 1962 in der Schweizer Mustermesse in Basel die zweite ILMAC (Internationale Fachmesse für Laboratoriumstechnik, Meßtechnik und Automatik in der Chemie). Gemeinsam mit der Schweizerischen Gesellschaft für Automatik* führte er wissenschaftliche Fachtagungen durch. Die dem SChV zufallenden drei Tage waren der Laboratoriums- und Meßtechnik gewidmet. Die achtzehn gehaltenen Vorträge kommen – bis auf zwei – in den folgenden Heften der *Chimia* zum Abdruck.

Methoden der Konstitutions- und Strukturaufklärung (I)

Application of High Resolution Mass Spectrometry in Organic Chemistry**

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Summary

High resolution techniques combined with accurate mass measurement enable more precise information to be obtained on the atomic composition of ions in the mass spectrum of an organic compound than has previously been possible with the more usual single focusing mass spectrometers.

A description of these high resolution techniques and of a method for the rapid and precise measurement of mass is given and their application to the examination of organic compounds illustrated with examples. A brief description is also given of a double focusing mass spectrometer that has been specifically designed for this work and which incorporates these techniques; the instrument has a resolving power in excess of 10,000 and an accuracy of mass measurement better than 1 part in 10^5.

1. Introduction

Mass Spectrographs with a resolving power of several thousand and capable of measuring mass with an accuracy of at least 10 parts per million have been known for more than thirty years. However, it is only recently that high resolution mass spectrometry has been applied in organic chemistry and this in spite of the fact that single focussing mass spectrometers of somewhat lower resolution have been used for analysis in organic chemical laboratories for the last twenty years.

At first sight then, it seems surprising that high resolution techniques were not used in organic analysis much earlier, but there are probably two reasons for this. Firstly, the interest in applying high resolution mass spectrometry grew primarily from the desire to use the technique for the qualitative analysis and structural identification of organic compounds; this interest is of much more recent origin. Secondly, it is only in the last few years that high resolution double focusing mass spectrometers haye become commercially available; this has put into the hands of organic chemists instruments that only a few years ago were considered capable of operation only by teams of highly skilled physicists and engineers.

It is worthwhile to consider briefly the development of the use of mass spectrometry in organic chemistry.

In the nineteen forties a considerable amount of work was done in studying organic applications of mass spectrometry but this was almost entirely directed towards developing the technique for the accurate analysis of multi-component mixtures of organic compounds such as hydrocarbons, alcohols, etc. Little if any work was done towards understanding the fundamental theory of mass spectra and it is only in the last five or six years through the work associated with names such as MC LAFFERTY and BIEMANN in the U.S.A., STENHAGEN in Sweden and BEYNON in the United Kingdom, that definite correlations have been established between the mass spectra and molecular stucture of a wide range of organic compounds. Once correlations of this kind are established, the technique can be applied with confidence to the structural analysis of organic compounds, and it is hardly surprising that there is now an increasing demand tu use the technique in this way.

However, with the exception of BEYNON and O'NEAL, workers in this field have used single focusing mass spectrometers which at best have only unit mass reso-

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** Lecture presented by J.D. WALDRON at the Technical Congress of the 2nd International Exhibition of Laboratory Measurement and Automation Techniques in Chemistry (ILMAC), October 15th to 20th 1962, in Basel (Switzerland).

lution. This has limited the work somewhat since it is not usually possible with such instruments to determine unequivocally the atomic composition of ions in the mass spectrograph. For example, a benzthiophene and an alkyl benzene have the same molecular weight and it is difficult to distinguish these in the mass spectrum of an oil fraction in which both may be present. Again to take an example of fragment ions, $C_3H_7^+$ and CH_3CO^+ would occur at mass 43 and yet both ionic species could conceivably be present in the mass spectrum of an oxygenated compound. However, the masses of atoms are not precisely whole numbers and advantage can be taken of this fact to distinguish between different combinations of atoms of the same apparent mass if the resolving power of the mass spectrometer is sufficient. Table 1, for example, lists various atomic combinations possible at mass 44.

Table 1: Different Atomic Combinations Possible at Mass 44

Ions	Mass
N_2O	44.0151
CO_2	44.0038
CH_2NO	44.0277
CH_4N_2	44.0515
C_2H_4O	44.0403
C_2H_6N	44.0641
C_3H_8	44.0767

In this simple case an instrument of resolving power 4,000 would distinguish and identify unambiguously the ion species responsible for the peak at mass 44 in the mass spectrum of any organic material. Although the number of atomic combinations possible at any one mass increases rapidly as the molecular weight increases, the advantages of high resolution in facilitating the interpretation of mass spectra are obvious.

The object of this paper is to give a brief account of a high resolution mass spectrometer specifically designed for organic work, to describe the technique used in the high resolution studies of organic compounds, and to indicate the applications to which these might be employed.

2. Instrumental

Double focusing mass spectrometers suitable for organic work have been described previously by Robinson, Perkins and Bell[1] and by Craig and Errock[2]. In this paper a brief description will be given of the instrument with which the author is most familiar, namely the MS 9 mass spectrometer. Some of the techniques and applications which will be described would be applicable to the other instruments.

The MS 9 mass spectrometer is a high resolution, double focusing instrument specifically designed for the examination of organic compounds. It is, in fact, a new

[1] C.F. Robinson, G.D. Perkins and N.W. Bell, *Instruments and Measurements*, Vol. 1, p. 260, Academic Press, London 1961.

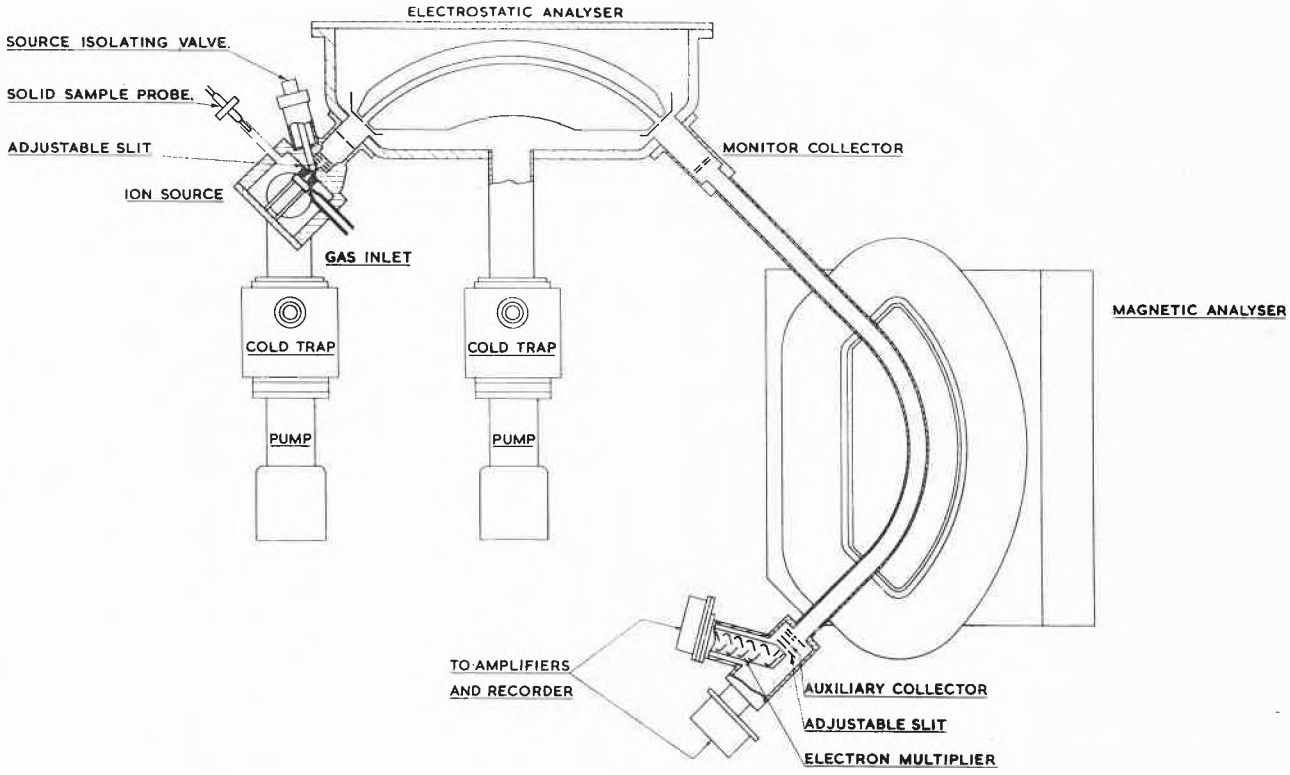


Fig. 1. Schematic Diagram of the Tube Unit of the MS9 Mass Spectrometer

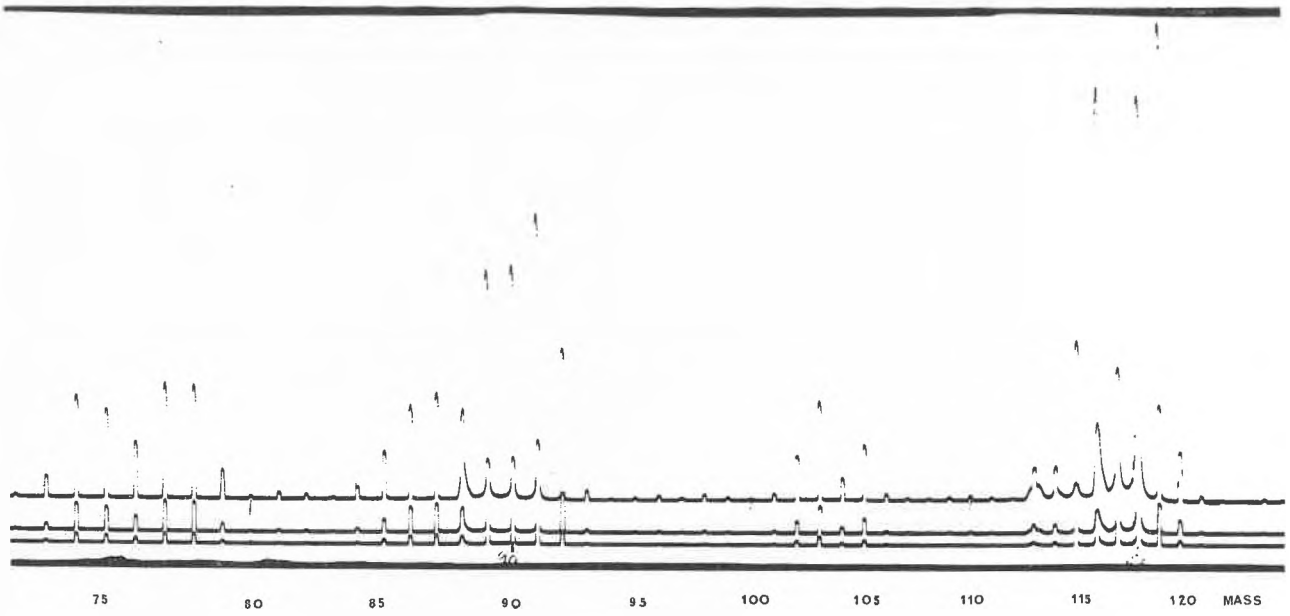


Fig. 2. Partial Mass Spectrum of a mixture of coumarone, indane and 7 aza indole

and improved version of the double focusing mass spectrometer, type MS 8, which was described previously[2].

Compared with conventional single focusing mass spectrometers the main difference in the MS 9 is the addition of an electrostatic analyser in order to obtain the higher resolution, although the opportunity has been taken to provide a number of additional features such as a wide range of sample introduction facilities not generally found on single focusing instruments. Compared with the MS 8, the chief differences in the new instrument are the use of a resolving system of twice the previous dimensions, the provision of an electron multiplier detector and faster scanning, a more versatile and accessible ion source and improved facilities for rapid and accurate mass measurement. Details of the design of the MS 9 have already been reported[3] and, therefore, only those features of the instrument important for its use in organic analysis will be considered here.

A schematic diagram of the tube unit of the instrument is shown in Fig. 1. The sample to be examined enters the ionization chamber of the ion source through the gas inlet or via the solid sample probe at a pressure of 10^{-6} torr. (The method of introduction gaseous, liquid and solid organic compounds to the mass spectrometer will be described in detail later.) As in conventional instruments, collisions take place in the ionization chamber between low voltage electrons, of 5 to 75 volts energy, and molecules of the sample and a series of positive ions are formed, characteristic of the compound from which they originate. The ions are then accelerated through a present voltage of 2 to 8 kV in the ion source, pass through the electrostatic analyser followed by the magnetic analyser and are focused on to the collector. With a given setting of ion accelerating voltage, ions of gradually increasing mass are focused on to the collector in turn by gradually increasing the magnetic field and the mass spectrum, so obtained, recorded as a series of peaks on a recorder.

Fig. 2 is a reproduction of a portion of the mass spectrum of a mixture of cumarone, indane and 7 aza indole recorded at only moderate resolution (~ 800). The three tracings shown were obtained simultaneously at different sensitivities, namely $\times 1$, $\times 3$, and $\times 10$.

Fig. 3 is a high resolution scan of the parent peak at mass 118 in the mass spectrum, which shows the three components completely resolved.

The analyser system used in the MS 9 is similar to that of NIER and JOHNSON[4] in which first order double focusing and second order angular focusing are achieved by suitable choice of dimensions. The angle of both electric and magnetic sectors is 90° and the radii of curvature are 15″ and 12″ respectively.

The ion source is arranged so as to provide maximum accessibility, easy removal of ionization chamber and filament and line of sight access to the ionization region. The source isolating valve in Fig. 1 is a metal ball valve which closes off the source from the analysers at a point immediately beneath the object slit and enables the source to be removed without admitting air to the analyser region. The source region can be baked out at a temperature of 300 °C and the analyser region baked and operated at a temperature of 100 °C.

[2] R. D. CRAIG and G. A. ERROCK, in *Advances in Mass Spectrometry* J. D. WALDRON, ed.), pp. 68–85, Pergamon Press, 1959.

[3] R. M. ELLIOTT, R. D. CRAIG and G. A. ERROCK, in *Proceedings of the International Instrument and Measurement Conference*, Stockholm (Sweden) 1960.

[4] E. G. JOHNSON and A. O. NIER, *Physic. Rev. 91* (1953) 10.

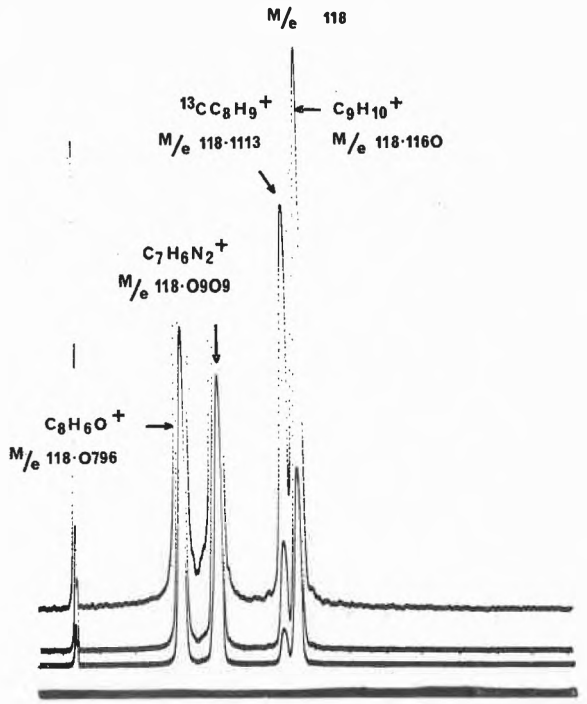


Fig. 3. Parent peak spectrum of a mixture of coumarone, indane and 7 aza indole

The monitor collector situated between the analysers, intercepts and measures a fraction of the total beam passing through the system. Since at this point, no mass separation has taken place, the monitor current provides a measure of the total ion beam intensity. The monitor collector has two functions, namely, to assist in setting up the instrument for maximum resolving power and to provide an indication of the total quantity of sample admitted to the spectrometer.

There are two completely independent final collector systems, both of which are provided with variable slits. The principal collector incorporates a high sensitivity electron multiplier and is used for high resolving power work with very narrow slits or for fast scanning with a wide collector slit. The auxiliary collector system is standard and is intended for routine work at low resolving power. The principal collector slit can be varied between 0.0003″ and 0.030″ and the auxiliary collector slit between 0.002″ and 0.016″.

Two features of the design of the instrument are somewhat novel and of special significance for organic work. The first is the provision of variable source and collector slits which enable the instrument to be operated at different resolving powers. Reference has already been made to the variable collector slits and, with regard to the source, the ion beam is defined by a slit whose width is variable from 0.0003″ to 0.008″. Adjustments to the width of both source and collector slits can readily be made by means of calibrated micrometer controls situated outside the vacuum system without the necessity of admitting atmosphere to the source and collector regions in order to make a change.

A further feature of the design is the differential pumping which has been provided between the source and analyser regions. The only connection between the two regions is the narrow source slit and this ensures that the sample pressure in the analysers is at least 10,000 times less than that in the source. It is hoped in this way that contamination of critical surfaces in the analysers by organic compounds will be avoided. Experience with the MS 9 is somewhat limited and it is too early yet to say how effective this arrangement will be. However, a similar system was provided on the MS 8

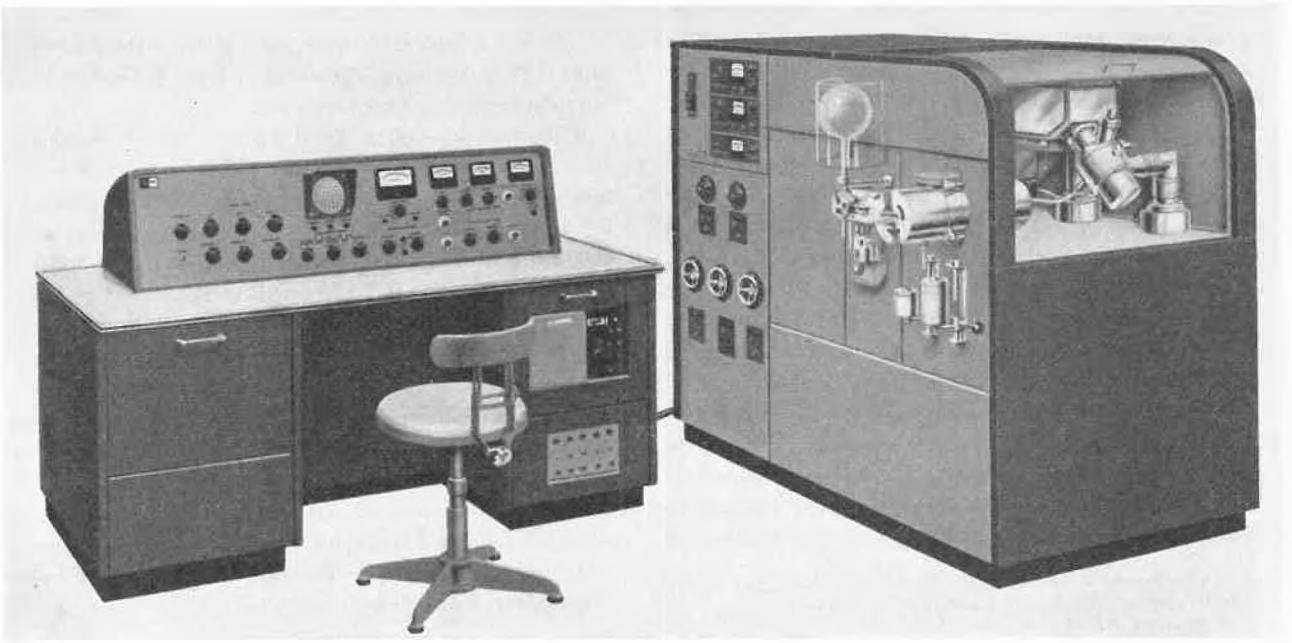


Fig. 4. Photograph of the MS 9

and has proved highly satisfactory; it has been unnecessary to remove the electrostatic analyser plates for cleaning during four years operation.

The general arrangement of the instrument is such that controls for the adjustment of source conditions, the recording of mass spectra, mass measurements, etc. are conveniently placed for the operator. A photograph of the complete instrument is shown in Fig. 4.

3. Techniques for the Examination of Organic Compounds

Several different techniques must be employed, frequently on the same sample, if a wide range of organic compounds is to be examined and the maximum information obtained on any one sample. Some of these techniques as they relate to the operation of a high resolution mass spectrometer have been discussed by BEYNON[5], but, in general, they have received surprisingly little attention. Opportunity has been taken, therefore, to summarise and discuss these techniques here in relation to the MS 9 mass spectrometer, although it should be remembered that many could be adapted to other instruments.

3.1. Sample Introduction Techniques

The range of organic compounds that can be examined by high resolution mass spectrometry need not be limited on a correctly designed instrument by the mass range of the spectrometer itself. On the MS 9, for example, ions in the range mass 6 to 2,000 can be scanned with an accelerating voltage of 3,000 volts and even higher masses could be focused, if required, by reducing this voltage. The problem, then, is to develop suitable sample introduction techniques to cover the whole range of gaseous, liquid and solid compounds with their widely different volatilities. This can only be done by providing several introduction systems two of which are shown as examples in Fig. 5. The two methods shown are:

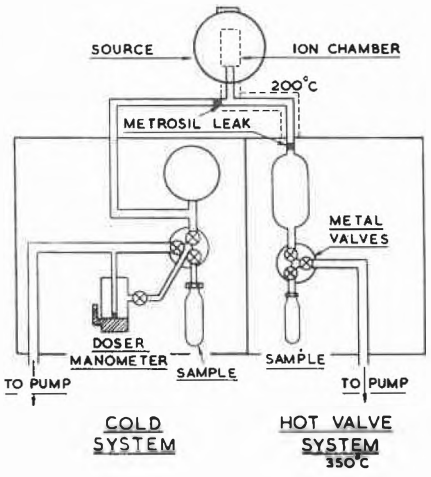


Fig. 5. Schematic diagram of two typical inlet systems

(1) Admission of a vapourised liquid or solid sample through the hot valve system.

The advantage of this particular system is that it enables samples to be introduced from atmospheric pressure. Liquid or solid samples contained in, for example, melting point tubes are inserted directly into the sample bottles shown. Air above the sample is then removed, the sample being frozen during this operation if necessary, and the sample evaporated into the glass reservoir. Ideally, the pressure of sample in the reservoir is about 0.1 torr, although advantage can be taken of the high sensitivity of the electron multiplier to examine samples at a pressure one-thousend times smaller if necessary. From the reservoir, the sample flows through the sintered disc leak, which reduces the pressure by a factor of about 10^5, through the heated glass inlet line and into the ionization chamber.

The whole system can be heated to 350 °C and all metal surfaces with the exception of the valve seatings are coated with glass to minimise catalytic decomposition of the sample. This method of introduction is generally suitable for compounds which can be heated without decomposition to a temperature where the vapour pressure is greater than 0.1 torr. The quantity of sample can be as little as a few micrograms.

(2) Admission of a gas or volatile liquid through a conventional cold inlet system.

This type of system has been described frequently in the literature (for example, see reference[6] and, therefore, will not be discussed in detail here. The amount of sample normally required is approximately 1 cc of gas at S.T.P. or 1 to 2 microlitres of liquid, although with the electron multiplier detector a high resolution analysis would be carried out satisfactorily with as little as onethousandth of these quantities. In addition to the more obvious applications, this system is particularly useful for the admission of reference compounds for mass measurement.

In addition to the methods similar to those described above, other techniques of sample introduction have been used which involve the direct introduction of the sample into the inlet line of the mass spectrometer (see reference[3]).

3.2. Mass Measurement

The use of precise mass measurement to help establish the atomic composition of ions is perhaps one of the most neglected techniques in mass spectrometry. The principle of the method is simple. Measurement of the mass of an «unknown» ion is made with reference to that of a «known» ion by comparing the ion accelerating voltage necessary to bring the ion beams on to the

[5] J. H. BEYNON, in *Advances in Mass Spectrometry*, Vol. II, (R. M. ELLIOTT, ed.), Pergamon Press, to be published 1962.

[6] J. D. WALDRON, in *Applied Mass Spectrometry*, Institute of Petroleum, London 1954, p. 71.

collector slit at a constant magnetic field. The «known» ion can form part of the mass spectrum of the same material as that of the «unknown» ion, although it is more usual to admit a compound of reference when making mass measurements.

On the MS 9, the comparison between the mass of the «known» and «unknown» ions is made by a modification of the method described by NIER[7] and is illustrated in Fig. 6. A sawtooth signal is applied to a pair of auxiliary coils on the magnet and to the X plates of an oscilloscope the output of the electrometer amplifier being connected to the Y plates, and a portion of the mass spectrum is displayed on the screen. The amplitude of the sawtooth voltage is restricted so that only a single

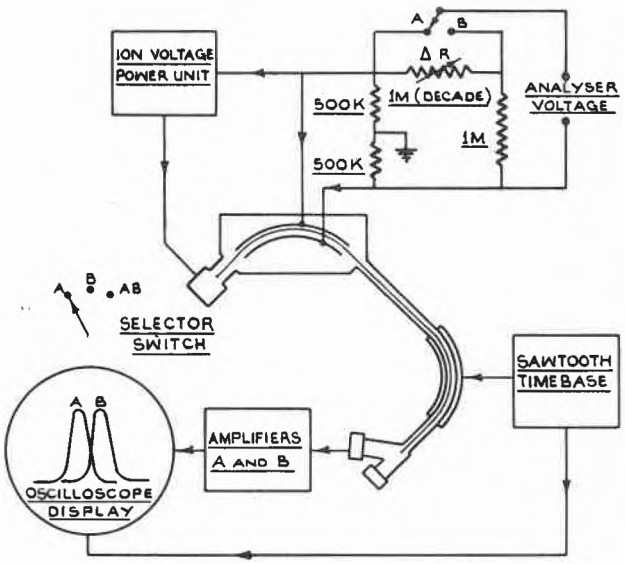


Fig. 6. Peak switching circuit of mass measurement

peak appears. With the selector switch in position A, the peak of lower mass is tuned in by adjusting the magnet current. With the switch in position B, the decade ΔR is adjusted to bring the peak of higher mass on to the screen. In position AB, the two peaks are displayed alternately every few seconds. With the switch in position AB, the heights of the two peaks are adjusted to be approximately the same by varying the separate sensitivity controls of amplifiers A and B and the two peaks are then brought into coincidence by a final adjustment of the decade. The ratio of the two masses is then obtained directly from the reading of the decade; there are six individual decade potentiometers and the ratio is read off simply as 1. *xxxxxx*, where the values x are the individual decade readings.

This is a particularly easy and convenient method of measuring mass and the accuracy of the technique depends on the difference between the masses of the «known» and «unknown» ions. Accuracy increases as the difference in the mass of the two ions decreases. For example, in experiments designed to test the accuracy of mass measurement on the MS 9, the results shown in Table 2 were obtained.

Table 2: Accuracy of Mass Measurement

"Unknown" Ion	Reference Ion	Reference Mass	Measured Mass of "Unknown"	Literature Values
Cl_2^+	$C_5H_{10}^+$	70.1005290	69.959945 ± 35	69.9599440 ± 22 [8]
$^{84}Kr^+$	$CH_2Cl_2^+$	83.9800502	83.938199 ± 42	83.93820 ± 3 [9] 83.938178 ± 3 [10]

Theses results indicate the high accuracy obtainable when comparing the masses of doublet peaks. In practice, this is rare but, provided the masses of the two ions do not differ by more than 10%, the stability of the circuits and resolving power of the instrument is sufficient for the measurement of mass ratios with a precision of a few parts in 10^6. This means that, provided some care is taken in the choice of reference compounds, it is possible to be certain of the third decimal place in the mass of an organic ion and to obtain a rough indication of the fourth decimal.

In order to illustrate what this means in practice Table 3 lists the various atomic combinations of carbon, nitrogen, oxygen and hydrogen possible at mass 100. This tabulation, which has been taken from BEYNON[11] lists the atomic combination of the type $C_wH_xN_yO_z$ with the restrictions that $y \leqslant 4$, $z \leqslant 4$, and $y + z \leqslant 6$.

It is seen from Table 3 that provided the third decimal place can be established with certainty the different atomic combinations can be unequivocally identified and distinguished. Of course, the situation becomes more complex as the molecular weight increases but with accurate mass measurement the choice can usually be reduced to two or three alternatives at any one mass and the decision between the alternatives made easily on chemical grounds.

3.3. *High and Variable Resolving Power*

The provision of facilities for the easy and rapid variation of resolving power is almost as important as high resolving power itself. Although high resolution is important, there is no point in working at a higher resolution than is absolutely necessary, because both the time required to scan through a mass spectrum and the sen-

[7] A.O. NIER, in *Nuclear Masses and their Determination*, H. HINTENBERGER, ed.), pp. 185–193, Pergamon Press, 1957

[8] C.F. GIESE and J.L. BENSON, *Bull. Amer. Physic. Soc. II, 2* (1957) 223.

[9] J.T. KERR, G.R. BAMBRIDGE, J.W. DEWDNEY and H.E. DUCKWORTH, *Advances in Mass Spectrometry* (Waldron), Pergamon Press, 1959, p. 1.

[10] R.R. RIES, R.A. DAMEROW and W.H. JOHNSON, *Proceedings of the International Conference on Nuclidic Masses, 1960*, University of Toronto Press.

Table 3: Atomic Combinations Possible at Mass 100

Ion	Mass
$C_2H_2N_3O_2$	100.0466
$C_2H_4N_4O$	100.0705
$C_3H_2NO_3$	100.0354
$C_3H_4N_2O_2$	100.0592
$C_3H_6N_3O$	100.0831
$C_3H_8N_4$	100.1069
$C_4H_4O_3$	100.0480
$C_4H_6NO_2$	100.0718
$C_4H_8N_2O$	100.0956
$C_4H_{10}N_3$	100.1195
$C_5H_{12}N_2$	100.1321
$C_5H_8O_2$	100.0844
$C_6N_{10}NO$	100.1082
$C_6H_{12}O$	100.1208
$C_6H_{14}N$	100.1446
C_7H_2N	100.0507
C_7H_{16}	100.1572
C_8H_4	100.0633

sitivity of the instrument are directly proportional to the resolving power used.

The adjustable source and collector slits provided on the MS 9 have already been mentioned and the variation in resolving power they permit is from approximately 500 to the maximum resolution of the instrument itself which is in excess of 10,000. This facility is used with almost every sample. It is usual to scan the whole mass spectrum very rapidly at relatively low resolving power, say 1,000 to 2,000 and then to repeat parts of the spectrum that are of particular interest at the highest resolving power. Also when only sub-microgram quantities of material are available then the spectrum will be scanned with only unit mass resolution in order to obtain the maximum sensitivity.

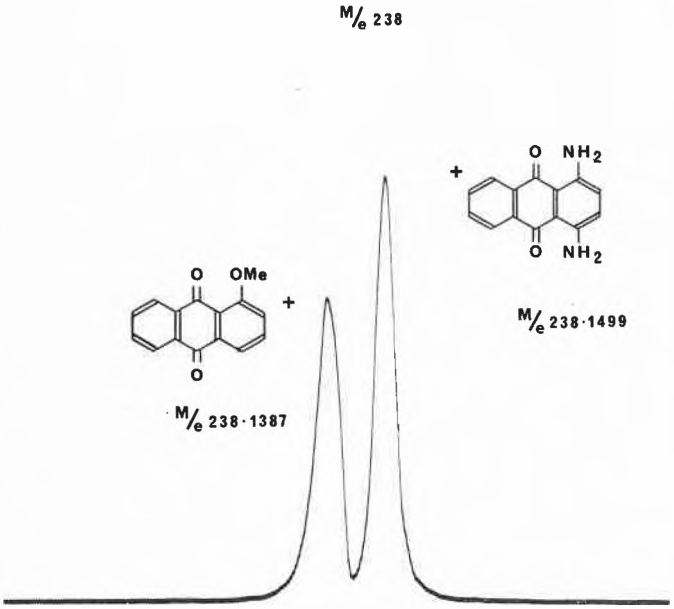


Fig. 7. Parent peak spectrum of 1-methoxy-anthraquinone and 1–4 diamino-anthraquinone, recorded on the MS9 mass spectrometer

Fig. 7 is a reproduction of the parent peak spectrum of a mixture of 1-methoxy- and 1-4 diamino-anthraquinone and represents perhaps one of the highest resolution spectra observed on organic compounds. The mass difference between the two parent ions is only 0.0112 in 238 and the resolution corresponds to approximately 22,000, on the definition that would give a 10% valley between peaks of equal height separated by this mass difference. Whilst this represents one of the highest resolutions observed, it is quite practical to think in terms of obtaining a resolution of at least 10,000 on the 10% valley definition, in every day operation.

It is important to consider, therefore, how far resolving powers of this order of magnitude can be useful in assisting the interpretation of the mass spectra of organic compounds. The importance of high resolving power lies primarily in the ability to separate multiplet peaks which otherwise would not be identified and might lead to errors in the interpretation of the mass spectrum and in mass measurement. In Table 4 are listed some of the more common doublets, likely to be encountered in organic chemical work, to which most problems of separation can be reduced.

Table 4: Some Common Doublets

Mass	Doublet	Separation ΔM	Maximum mass at which doublet could be identified
14	$N–CH_2$	– 0.01258	315
16	$O–NH_2$	– 0.02381	595
16	$O–CH_4$	– 0.03639	910
32	$S–O_2$	– 0.01776	445
32	$S–CH_4O$	– 0.05415	1352
32	$S–C_2H_8$	– 0.09055	2262
28	$CO–N_2$	– 0.01123	280
30	$NO–C_2H_6$	– 0.04897	1225

Of course, a particular doublet need not necessarily occur at the mass given in column 1 of the table, which represents the lowest mass at which the combination could conceivably occur, and, in fact, it more usually arises at higher mass. For example, the doublet $O–CH_4$ arises at mass 32 form the parent ions of methanol (CH_4O) and oxygen O_2, at mass 44 of the parent ions of acetaldehyde (C_2H_4O) and carbon dioxide CO_2, at mass 60 from the parent ions of acetic acid ($C_2H_4O_2$) and propanol (C_3H_8O) etc. The particular point of significance is the maximum mass at which the doublet could be recognised and this is tabulated in column 4.

The values in column 4 of Table 4 have been calculated on the basis of $M/\Delta M = 25{,}000$ because it is felt that with a resolving power of 10,000 on the 10% valley definition, doublets which are separated in mass by 1 part in 25,000 should at least be recognised, although not completely separated, and this may well be an underestimate. Thus, with the resolving power available under routine conditions all of the commonly occurring doublets can be recognised up to at least mass 280 and many

at much higher values. This covers a considerable range of molecular weight.

Of course, there are some doublets which would not be separated with this resolving power, though in general, these are of rare occurrence. Perhaps the most important exception is the isotope doublet $^{12}CH-^{13}C$ which would only be distinguished up to mass 110, with a resolving power of 10,000 (calculated on the same basis as Table 4). As a general rule, the most difficult doublets to separate are those involving the heavy isotopes. Fortunately, this does not give rise to serious difficulty since the presence of the heavy isotope can always be predicted from the lower mass 'peaks' at which the more abundant isotopes occur.

3.4. Fast Scanning

As indicated above, for a given amplifier system, the speed of scanning must be decreased as the resolving power is increased. There is every incentive therefore to increase the response of the whole collector and amplifier system on a high resolution instrument and this was one reason why the principal collector system on the MS 9 was designed with an electron multiplier feeding an amplifier with a 98 % response time of 0.05 seconds.

The manner in which scanning speed varies with slit width is indicated in two example in Table 5. If the source and collector slits were widened beyond the values given in the table, even faster scans would be possible, though at the sacrifice of signal-to-noise ratio, and this might find some application in the observation of rapidly changing phenomena, e.g. scanning a portion of the mass spectrum of the output of a gas chromatographic column.

Table 5: Typical Scanning Speeds with the Electron Multiplier Collector

Application	Fast Low Resolution Scan	High Resolution Scan (R.P. ~ 5,000)
Slit Widths – source	0.003″	0.001″
– collector	0.016″	0.001″
Scanning speed	0.6 minutes/octave	9.6 minutes/octave
Examples	At 8 kV, mass 20 to 400 in approximately 3 minutes	At 8 kV mass 40 to 400 in approximately 35 minutes

Note: An octave is taken to be a factor of two in mass.

3.5. Routine Investigations

Although the emphasis is on high resolution, it is important that routine measurements are not neglected. For quantitative analysis it is essential that the mass spectra should be accurately reproducible, and there is an additional source of variation of mass spectra on instruments that employ electron multipliers, namely that the gain of the multiplier can vary with time and also be mass dependent. It is important, therefore, that a standard collector system is provided, even if this is only used to give spectra of reference and to calibrate the electron multiplier.

It was for this reason that the auxiliary collector, mentioned above, was incorporated into the design of the MS 9. This collector can be used at a resolving power of approximately 800 to provide scans of mass spectra from mass 40 to 800 in about 20 minutes that are entirely comparable with the standard spectra observed on single focusing instruments. Somewhat faster scans could again be obtained with this collector though at the sacrifice of signal-to-noise.

4. Applications of High Resolution Mass Spectrometry

It is not the object of this paper to review in detail all the applications of high resolution mass spectrometry, but merely to indicate one or two possibilities. A detailed treatment of this subject has been given by BEYNON.

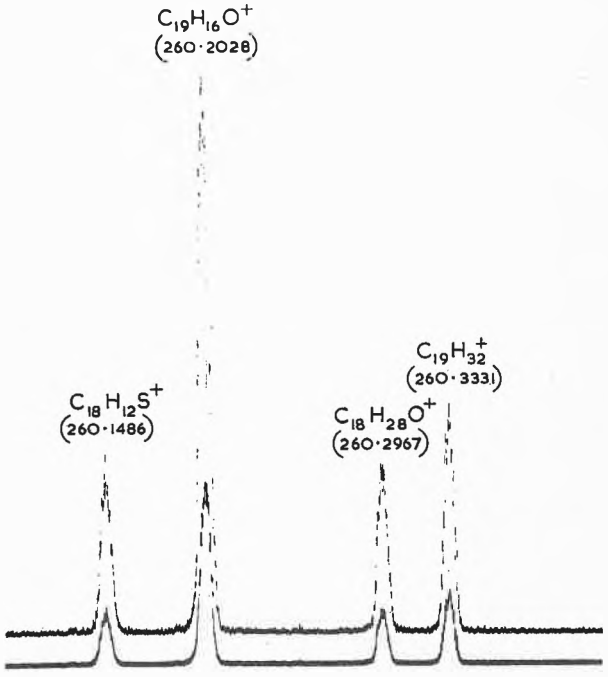


Fig. 8. Parent peak spectrum of tri-decyl benzene, phenyl undecyl ketone, 1.2.dimethyl 4 benzoyl naphthalene, 2.2′ naphthyl benzo thiophene (the upper tracing is recorded at 3 X the sensitivity of the lower record)

4.1. Molecular Weight and Atomic Composition

Perhaps the most useful single piece of information which can be derived from the mass spectrum of a compound is its molecular weight, from the mass of the molecular ion or parent peak; from this, in turn, information about the atomic composition of the molecule can be deduced. The parent peak is particularly easy to

identify in the mass spectrum because apart from the isctope peaks it is the peak of highest mass.

The technique can be used on almost any mass spectrometer, but a high resolution instrument gives added precision and accuracy to the method. In order to illustrate the application of high resolution and precise mass measurement to this problem, a mixture of four compounds, each of molecular weight 260, was made up and admitted to the MS 9 mass spectrometer. The mixture consisted of:

tri-decyl benzene, $C_{19}H_{32}$
phenyl undecyl ketone, $C_{18}H_{28}O$
1.2. dimethyl 4 benzoyl naphthalene, $C_{19}H_{16}O$
2.2′ naphthyl benzo β thiophene, $C_{18}H_{12}A$

and the parent peak spectrum is reproduced in Fig. 8. Measurement of the mass of the four ions was made with reference to the mass 238 peak in the spectrum of dibromobenzene, which was admitted as a reference compound, and the results are shown in Table 6. The figures in column 3 are calculated from the mass of the individual atoms.

Table 6: Mass Measurements on the Peaks in Fig. 8

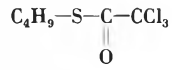
Ion	Measured Mass	Calculated Mass	Difference
$C_{18}H_{12}S^+$	260 · 1482	260 · 1486	0.0004
$C_{19}H_{16}O^+$	260 · 2026	260 · 2028	0.0002
$C_{18}H_{28}O^+$	260 · 2964	260 · 2967	0.0003
$C_{19}H_{32}^+$	260 · 3329	260 · 3331	0.0002

Although the reference peak differed in mass by almost 10 % from that of the unknowns, it is seen that the third decimal place in the molecular weight of each compound can be definitely established and the maximum error in the fourth decimal is only 4. This accuracy would almost certainly have been sufficient to identify the compounds and establish their atomic composition had they been present as «unknowns».

4.2. Structural Analysis

In a similar way, by making precise mass measurements on the principal fragment peaks, the atomic composition of the major fragment ions in the mass spectrum of a compound can be established. Since, under electron bombardment, groups of atoms tend to break off as whole units, information about the structure of the molecule then can be frequently deduced.

Again, this is a technique which has been used on single focusing instruments of somewhat lower resolving power, but the advantages of high resolution and precise mass measurement are that identification can be made much more positively. In fact, there are instances where the absence of high resolution might lead to a faulty interpretation and the example of the thioester



will serve to illustrate this point. The mass spectrum of this compound contains a peak at mass 117, which in

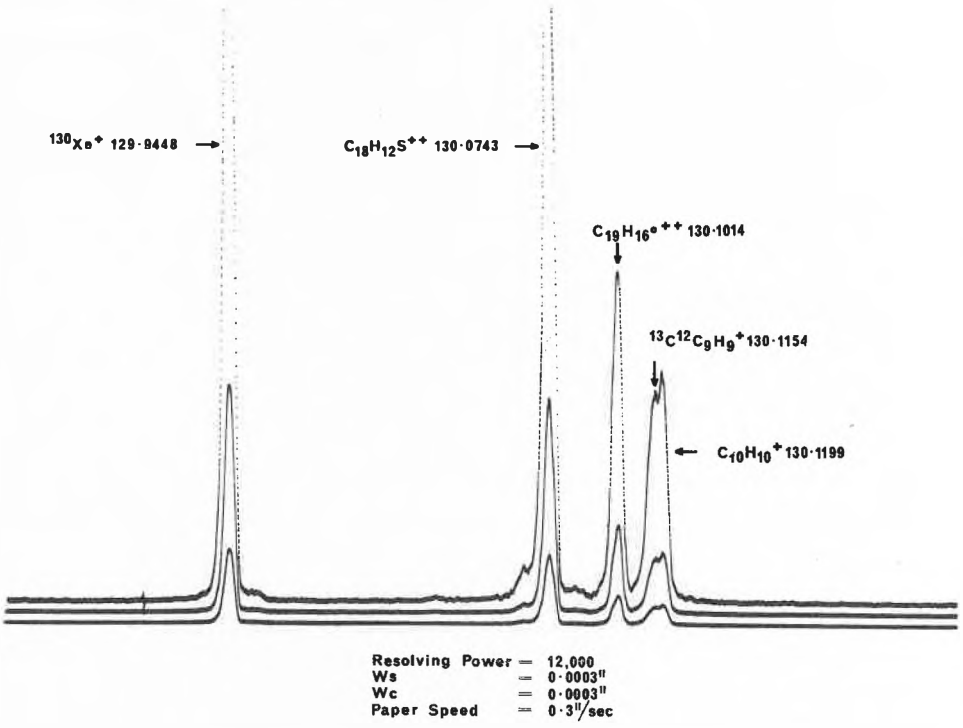


Fig. 9. Mass 130 multiplet from a four component mixture in which Xe was used as a reference (the three recordings correspond to three different sensitivities, namely $x1$, $x3$ and $x10$)

the absence of high resolution would probably have been assigned to the ion

$$C_4H_9-S-\overset{\overset{O}{\|}}{C}{}^+$$

on the grounds that the isotope ratios of neighbouring peaks were wrong for CCl_3^+ alone. In fact, the high resolution spectrum shows the 117 peak to be a doublet of about equal height and mass measurements indicate that both the $C_4H_9 \cdot S \cdot CO^+$ and the CCl_3^+ ions are present.

It seems likely that the interpretation of the mass spectrum of many compounds may have to be modified in the light of high resolution.

4.3. Quantitative Analysis

It is too early yet to say with certainty whether high resolution mass spectrometry will find much application in quantitative organic analysis. Of course, high resolution does not preclude quantitative analysis and the same analyses which are carried out now on low resolution single focusing mass spectrometers could also be made with high resolution double focusing instruments. However, routine quantitative analysis does not usually demand high resolution.

There are, however, a few notable exceptions to this generalisation which have already been found, particularly in the oil industry. For example, a problem in the analysis of lubricating oils is that alkyl benzenes and benzthiophenes have the same molecular weight and it is impossible to separate these in a complex mixture by conventional single focusing mass spectrometry. A possible way in which high resolution mass spectrometry may help to solve this problem is indicated in Fig. 9 which shows the high resolution spectrum of the fragment peak at mass 130 in a synthetic mixture of tridecyl benzene, phenyl undecyl ketone, 2–2′naphthyl benzo thiophene and 1–2 dimethyl 4 benzoyl naphthalene. (Xenon has been added as a reference compound for mass measurement.) This shows a clear separation of the hydrocarbon from both the sulphur compound and the oxygenated compound and although a synthetic mixture of simple compounds indicates the possible separation that might be achieved with a more complex lubricating oil.

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