MASS SPECTRAL STUDIES OF ORGANIC IONS IN THE GAS PHASE

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Mass Spectral Studies of Organic Ions in the Gas Phase.
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Summary.

A single focusing mass spectrometer (Metropolitan Vickers MS2) was adapted to energy studies by adding an electrostatic sector.

The electrostatic sector, spherical and symmetric was calculated to allow focusing of the ion beam received at the end of the magnetic sector and taking into consideration the limited space available in the instrument. Diaphragms to correct for the fringing field were introduced. A plate connected to an electrometer monitored the beam between the two sectors while a channel electron multiplier was used as the final collector.

All the circuits were new and the potentials and currents obtained were stable at least within 0.1%. The resolution obtained was better than 1 Volt in 1000 Volts.

The performance of the instrument was studied, in particular the mass discrimination effect against the lower masses noticed when using the channel electron multiplier in the continuous current mode.

Nitrogen, methane and methanol were studied.

The shapes of the peaks were obtained by plotting the intensity as obtained in the "channeltron" versus the energy determined from the value of the potential applied to the electrostatic sector plates. The following energetic ions were detected:-

i) two groups of energetic ions for peak m/e = 14 from nitrogen;

ii) a particular shape for peak m/e = 14 from methane which could be caused by an energetic ion, or by the presence of some nitrogen mixed with the methane;

iii) a group of energetic ions for peak m/e = 17 from methanol.

All these results are in very good agreement with others previously reported in the literature, obtained using different techniques.

The following metastable transitions, occurring between the monitor and the electrostatic sector, were detected:

i) for Nitrogen $N_2^{+\cdot} \longrightarrow N^+ + N^\cdot$

ii) for Methane $CH_4^{+\cdot} \longrightarrow CH_3^+ + H^\cdot$

$CH_4^{+\cdot} \longrightarrow CH_2^{+\cdot} + 2H^\cdot$

$CH_3^+ \longrightarrow CH_2^{+\cdot} + H^\cdot$

$CH_2^{+\cdot} \longrightarrow CH^+ + H^\cdot$

iii) for Methanol $CH_3\,OH^{+\cdot} \longrightarrow CH_2\,OH^+ + H^\cdot$

$CH_3\,O^+ \longrightarrow CH_2\,O^{+\cdot} + H^\cdot$

$CH_2\,OH^+ \longrightarrow CH\,O^+ + 2H^\cdot$

$CH_2\,O^{+\cdot} \longrightarrow CH\,O^+ + H^\cdot$

These transitions agree with published results obtained with different instruments.

For methane one metastable peak was obtained that was attributed to a transition occurring in the first field free region.

An attempt was made to obtain information about the kinetic energy released in the metastable transition.

A criterion, based on information theory, was developed for the matching of an unknown mass spectrum with that in a computer data bank. The use of the principle of minimum divergence proved adequate in the majority of cases. However, when the same compound is run in various mass spectrometers the divergence between the different spectra of the same compound can be greater than between different compounds on the same instrument.

It was also shown that this criterion, deduced theoretically, approached some of the simpler criterions in use, if the spectra were normalized by making the sum of the ion abundances equal to a fixed value instead of, as is a common practice, making the most intense peak equal to one hundred.

To test the criterion the files were reorganized, to speed the search, and in one case the file on tape was transferred on to a disc. The programmes used are included in an Appendix.

A method was devised to deduce the molecular weight of a compound when the molecular ion does not appear in the spectrum. It is based on the combination of the probabilities of occurrence of the fragment ions and does not involve an a priori knowledge of the compound, except for an estimate of the range of masses that should include the molecular weight.

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Chapter 1.

Introduction.

The beginning of Mass Spectrometry can be traced to Goldstein[1] who, in 1886, was the first to observe rays of positively charged electrical particles and to Wien[2] who later showed that these rays were deflected by a magnetic field.

The first mass spectrograph was built by J.J. Thomson[3] who produced ions using a high voltage discharge tube and deflected the beam of ions by means of a combined electrostatic and magnetic field. The ions emerging from this field were detected on a photographic plate where they impressed a series of parabolas. All ions with the same mass to charge ratio fell on the same parabola and the position of an ion in a parabola depended on its momentum. With his mass spectrograph J.J. Thomson proved the existence of stable isotopes. The instrument had no focusing so it was impossible to increase sensitivity[*] or resolving power[**].

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[*] Sensitivity[4] measures the response of an instrument to ions of a particular component at an arbitrary mass over charge ratio. The response is measured by charge received in a measuring device or blackening of a photographic plate.

[**] Resolving Power[4] or Resolution is usually defined as the largest mass at which two adjacent peaks of equal height, differing by one unit of mass exhibit a valley not greater than a certain percentage (usually 10%) of the peak height.

Aston[5] in 1919, using an electric and a magnetic field in succession built the first mass spectrograph with velocity focusing. Collection was made on a photographic plate placed in the focal plane, that is, the plane where faster ions intersected slower ions for the same mass over charge ratio. Ions with a different mass over charge ratio fell in different lines in the same plane and the masses were determined by comparing with plates from reference compounds.

At about the same time Dempster[6] built the first mass spectrometer which may be considered the predecessor of modern mass spectrometers, the difference in name coming from the methods of collection. Dempster's instrument was based on the principle discovered by Classen[7] that charged particles of a given mass and energy diverging from a slit in a magnetic field were focused after deflection through 180°. This was then the first machine with direction focusing. Ions were collected, one species at a time, in a Faraday cup[8].

After Barber[9] and Stephens[10] showed that the focusing was a property of any wedged shaped magnetic field, a variety of sector angles[11] have been used. In modern instruments a better design, a decrease in the beam width compensated by the use of more sensitive collecting devices, using secondary electron emission (electron multipliers[12]) and much more stable electronics permitted one to improve the resolution from 100 on Dempster's instrument to 10000[13].

Combining the two principles, velocity and direction focusing, Herzog[14] developed the theory of double focusing instruments. The instruments in use nowadays are of two main designs.

In the Mattauch-Herzog[15] geometry the ions are deflected in opposite directions by consecutive electrostatic and magnetic fields, all the ions coming to a focus in the same plane where they are collected generally on a photographic plate.

In the Nier-Johnson[16] design the consecutive electrostatic and magnetic fields deflect the beam in the same direction and the ions are focused at the intersection of the velocity focusing curve with the direction focusing curve. Each mass over charge ratio is focused for a certain value of the magnetic field and the collection is usually made electrically.

By the use of very narrow slits and correction of second[16,17,18] order image aberrations the resolution of the double focusing instruments can increase tremendously though at the expense of sensitivity. An instrument with a resolution of 1,000,000 has been built[18,19].

Various methods are used to produce the ions. The commonest is electron bombardment generally using sources of the Nier[20] type. For all cases where the sample is in the gas or vapour form this type of source produces a beam with a small spread in energy, thus enabling its use with single focusing instruments while its efficiency permits the collection by means of simpler detectors such as the Faraday cup.

Sources using photon impact[21], field ionization[22], high voltage spark[23] and chemical ionization[24] are also currently employed. Some of their applications will be referred to later on.

Other instruments have been developed based on different principles. One of the most common is the time of flight mass spectrometer[25] which uses the different flight times of a pulse of ions of various masses with the same initial kinetic energy travelling along a field free tube. In the Bennett[26] and Redhead[27] types radiofrequency potentials are applied to a series of grids to achieve mass separation. The quadrupole mass spectrometer[28] uses a radiofrequency field in conjunction with a static field. All these instruments by suppressing the magnetic field are less bulky and able to give a faster response. However, the resolution attained is lower and the electronics required is more sophisticated.

Machines using combinations of radiofrequency fields with magnetic fields, such as the omegatron[29], the mass synchrometer[30] and the ion cyclotron resonance[31] mass spectrometer are also used. Of these the last mentioned is the more important by the amount of information provided on ion-molecule reactions.

Initially both mass spectrographs and mass spectrometers could only be used whenever a rather low resolution was needed and the unreliability of electronics made it inadequate for routine analytical purposes. It was after the electronic advances of World War II that it became widely used in industry. Its first analytical application was to the study of hydrocarbon mixtures in the petroleum industry.

The method used in this case[32,33] requires:-

(i) the mass spectrum of a given compound to be reproducible under the same conditions of operation;

(ii) the mass spectrum of a mixture to be a linear superposition of the mass spectra of its components, and

(iii) the intensity of a reference peak from one component to be directly proportional to the partial pressure of that component in the mixture.

The sample in this type of analysis was initially always gaseous. The use of liquid samples of very low vapour pressure became possible with the development of heated inlet systems[34,35]. However, many compounds were too involatile or thermally unstable to be introduced in this way. This difficulty was overcome with the development[36] of methods for the direct insertion of the sample in the ionization chamber. Using vacuum locks it is now possible to put the sample in a probe and insert it in the ionization source without breaking the vacuum of the mass spectrometer. With this method the amount of sample required can be as small as a nanogram (10^{-9} grams).

A method[37] is being developed which will permit the identification of the components of a mixture when it is not possible to separate them. Whenever possible the combination of gas-liquid chromatography with mass spectrometry[38] has been widely applied with very good results. This method requires the use of fast scanning mass spectrometers.

Once a spectrum of a pure compound is obtained it can be compared with files of thousands of compounds previously recorded. Computers are quite frequently used to process the data either on or off line[39]. Computer methods of matching the spectrum of an unknown against those of known compounds in a reference file are also currently employed and will be dealt with in the fourth chapter of this work.

When the spectrum does not compare satisfactorily with any previously recorded, a more detailed analysis is necessary. The same kind of study is also frequently made to determine the structure of known molecules.

It is useful whenever possible to try to recognise the parent ion[40] before comparing the mass spectrum with others of known compounds with similar fragmentation patterns. Empirical rules such as those based on the fragmentation of the isomers of octane[41] have proved to be of very wide application. Specific rules have also been established for the fragmentation of a great number of classes of compounds[42]. This information is in some cases stored so that it can be made accessible by programmes, the more advanced system being, at present, the Dendral[43] program used by the group at Stanford University. Alternatively the "learning machine" theory[44] in which the computer generates all the correlations from a file of reference spectra has been applied. Programmes have also been made to take advantage of information from other analytical methods such as nuclear magnetic resonance[45].

With high resolution mass spectrometry[46] the precise mass measurement permits the use of the differences in the nuclear packing fraction[47] of the elements to determine the elemental composition of an ion.

Precise mass determination is made in the Mattauch-Herzog geometry by measuring with a travelling microscope the distances between the different lines in the photographic plate and relating the masses with those of the reference compound. The process, for a great number of peaks, is very laborious and in general it is impractical to determine every precise mass manually. Biemann[48] introduced a system in which the measurements are made automatically and the results processed by a computer. The data is presented in the form of an "element map" using separate columns for different heteroatom content.

The precise mass measurement with a Nier-Johnson instrument is made usually by peak matching[49] but methods[50] have been devised in which the time interval between the ions is related to their mass difference and a computer can then make the whole "element map". By averaging the results of various scans [39 a)] it is possible to produce this map with an improvement on the basic instrument resolution and the mass measurement accuracy.

The interpretation of high resolution data[51], again requires the consideration of fragmentation patterns. Programmes[52] have been made incorporating all the possible steps a human interpreter would follow to identify a mass spectrum.

One of the remarkable successes of computer aided interpretation of high resolution mass spectra has been in the analysis of peptides[51,53]. This is due mainly to its regular cleavage at the amide bonds.

To rationalize the mass spectral data, a theoretical approach to the reactions occurring in the mass spectrometer was advanced. The Quasi-Equilibrium Theory initially developed by Rosenstock, Wallenstein, Wahrahafting and Eyring[54] assumes that:-

i) The process of ionization of a molecule by electron impact is a Franck-Condon transition.

ii) The time of residence of the molecular ion in the source is sufficient to permit any excess electronic energy to be randomly distributed over the molecular ion.

iii) Owing to the energies normally used in an electron impact source the ions formed are distributed over a very large number of electronically excited states.

iv) Ions with sufficient energy will decompose unimolecularly and if the internal energy is sufficient to allow n decomposition pathways these will usually occur as competing unimolecular decompositions.

The rate constant for each of these pathways can be calculated provided the detailed knowledge of the energetic states of the ion is possible to determine. In spite of the number of approximations that it was necessary to make, quite a good agreement with experimental data was obtained for some small molecules[54 b)]; for larger molecules the method proved too complex.

Recently the theory has been used with success to explain qualitatively spectral features and review critically the methods that have been applied to determine ion structures[55,56].

The calculation of heats of formation of organic ions from ionization and appearance potentials[57] has been used as a method to provide evidence for the identity or non-identity of ion structures. The Quasi-Equilibrium Theory permits one to estimate the errors involved in the assumptions normally made that the ionization or appearance potentials determined correspond to the minimum value and much more attention is being paid to the fact that the released fragments may have excess energy[58].

Metastable ions have become increasingly important because they are a means of determining reaction pathways and also owing to the amount of thermodynamic information they have been shown to provide. McLafferty[59] and co-workers have used metastable ions extensively for the deduction of ion structures, while Beynon and associates[60] have applied metastable data for a variety of kinetic energy studies.

Systems have been devised[61,62,63] which permit the detection of metastable peaks with great sensitivity and independently of the normal ions. In the technique[63] originated by Barber, Elliot and Major the Ion Kinetic Energy Spectrum obtained displays all the metastable peaks. To identify the metastable transitions the Ion Kinetic Energy Spectrum must be mass analysed which requires the setting of the electrostatic and magnetic fields at values related both to the mass of the parent and of the fragment ions. To obtain data for a great number of ions McLafferty[64] used a computer controlled scan and a computer programme to process the data.

More recently the study of the metastable decompositions after the magnetic sector, that is, after mass analysis has been made either using a scintillation collector[65 a)] or an electrostatic sector and this later technique [65 b) c)] was applied in this work.

Another kinetic approach has been the study of substituent effects.

In some cases good correlations were found between changes in ion abundance ratios and the Hammet constant σ for the substituent[66]. A paper by Chin and Harrison[67] confirmed that no direct information on the rate of a specific fragmentation could be obtained in this way. The explanation for the good agreement obtained in many cases seems to be connected with the lowering of the ionization potentials as the substituent becomes more electron-donating[68].

One of the more frequently adopted methods for the study of mass spectrometric reactions has been the use of isotopic labelling. Hydrogen has been replaced by deuterium atoms and carbon -13, nitrogen -15 and oxygen-18 among others have also been employed. The results though of great value should be dealt with with care since scrambling[56] of the labelling isotope is common. When deuterium is used an isotope effect favouring the loss of hydrogen atoms over the loss of deuterium atoms has been reported[69].

Scrambling is explained by means of intermediate isomers resulting from rearrangements. An important proportion of the ions produced in a mass spectrometer involve rearrangements. The interpretation of mass spectrometric reactions using Quasi-Equilibrium Theory[56,70] has led to the conclusion that rearrangement processes will be more frequent in slow reactions (as in low voltage spectra and metastable transitions) than in fast reactions (daughter ions formed in the source, in 70 ev electron impact spectra and especially in field ionization spectra). Scrambling is also minimised in fast reactions and so they permit a more accurate determination of structures.

Though, at present, it is difficult to apply the Quasi-Equilibrium Theory to predict spectra, owing to the number of unknown parameters involved, some semiquantitative prediction is already possible for aliphatic chains[71] and monosubstituted benzenes[72].

The earlier concept of positive charge localization at favoured sites triggering particular decomposition reactions was developed and widely used both by McLafferty[73] and co-workers and Djerassi[74] and co-workers. As a consequence of their success some authors[75] applied the Molecular Orbital Theory to the prediction of mass spectra. As with Quasi-Equilibrium Theory too little is known about the structures and energy states of organic ions produced by electron or photon impact and some authors[76] doubt of the applicability of Molecular Orbital Theory to mass spectrometry at the present time. Meanwhile the experimental results which were once interpreted using the charge localization concept are being looked at more critically[67,73].

Ion structures are also being currently studied using ion-molecule reactions. Either medium and high pressure sources[77] or Ion Cyclotron Resonance[78] are employed. As a particular case of high pressure source Chemical Ionization[24], in which a different substance is used as reactant, provides spectra much simpler than those from electron impact and due to the source conditions the reactions occurring can be treated in a way similar to solution chemistry, employing Arrhenius equation and the Hammett correlations.

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75. a) R.C. Dougherty, J. Amer. Chem. Soc., 1968, 90, 5780, 5788.

b) R.A.W. Johnstone and S.D. Ward, J. Chem. Soc. (C), 1968, 1805, 2540.

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78. a) G. Eadon, J. Dieckmann and C. Djerassi, *J. Amer. Chem. Soc.*, 1969, **91**, 3986 and related papers.

b) R G.C. Good, R.M. O'Malley, K.R. Jennings, *Nature*, 1970, **227**, 1093.

Chapter 2.

Method and Apparatus.

2\. 1. Introduction - Various methods have been used to study the kinetic energy of the ions formed by electron impact in a mass spectrometer. Ions with high kinetic energy were first detected[1] by changing to negative the potential of the ion repeller in the source. Methods, not requiring mechanical modifications in the mass spectrometer include:

i) the study of the peak shape[2,4] or of the change[3] in relative ion intensities with the variation of the accelerating voltage;

ii) the study of the beam width at the collector for various acceleration voltages[5];

iii) the change in relative ion intensities with the voltage in the ion repeller[6];

iv) the comparison of the shapes and positions of peaks with and without kinetic energy, selected with the acceleration voltage and swept with an auxiliary magnetic field[7];

v) the study of the variation in beam intensity with the potential applied to a plate (metastable supressor) placed between the magnet and the collector[8-12].

Other authors used plates placed immediately after the source which deflected the beam in a direction parallel[6,13,14] to the magnetic field and studied the variation of the beam intensity while changing the potential in these plates.

Electrostatic sectors which allowed an energy analysis of the beam before[15] or after[16] mass analysis have also been employed.

The kinetic energy of the ions has also been studied using instruments based on other principles as the trochoidal path mass spectrometer[17], the coincidence time of flight[18] and the time of flight[19].

After Beynon's[20] group studied the relation between the width of the metastable peak and the kinetic energy of the fragment ion this method has been widely applied[21]. In this case the excess kinetic energy measured corresponds to metastable transitions and as expected[22] the excess kinetic energy is smaller than for ions formed inside the ion source.

In the present work an instrument was built with the electrostatic sector following the magnetic sector, to permit the determination of the kinetic energy of the ions after mass analysis and also to study the metastable transitions corresponding to each ion of a known mass to charge ratio.

Instruments with this geometry had previously been built to study ion molecule reactions[16] and to improve the resolving power of a mass spectrometer[23] by reducing the number of scattered particles arriving at the collector.

While this work was proceeding three papers[24,25,26] were published reporting results obtained with instruments having the electrostatic after the magnetic sector.

2. 2. The MS2 - The basic instrument to which the electrostatic sector was to be attached was an MS2 (Metropolitan Vickers No. 11), single focusing, 90° magnetic sector mass spectrometer.

The sector instrument was first described by Nier[27 a)] and descriptions of 90° sector-type instruments had already been published[28,29] when Blears and Mettrick[30] made a detailed study of the resolution and accuracy of the MS2. The source was an electron impact modified Nier type source[27 b)] and the collector a Faraday cup[31].

In this type of instrument the ions formed in the source are accelerated by 2000 V and focused at the defining slit of the collector. The position of this slit inside the tube was taken as the source of ions proceeding to the electrostatic sector.

None of the original electronics of the MS2 was used.

2. 3. Electrostatic Sector - To choose the dimensions of the electrostatic sector, the calculations made by H. Ewald and H. Liebl[32, 33,34,35], for a toroidal sector, were followed. By choosing a toroidal sector, as opposed to a cylindrical one, focusing is obtained in both radial and axial direction.

As represented in the Figure 2.1[32] the two plates forming the toroidal sector are assumed to have a common rotation axis z (in a r, ϕ , z system of cylindrical coordinates) and a common plane of symmetry z = 0.

The radial and axial focusing conditions are calculated by means of the two lens equations:

$$(l' - g_r)(l''_r - g_r) = f_r^2 \quad \text{--------------} \quad (1)$$

$$(l' - g_z)(l''_z - g_z) = f_z^2 \quad \text{--------------} \quad (2)$$

where the subscripts r and z stand for radial and axial respectively and as represented in Figure 2.1

l' - distance from the source to the entrance plane of the sector.

l''_r - distance from the exit plane of the sector to the radial focusing plane.

l''_z - distance from the exit plane of the sector to the axial focusing plane.

The focal distances g_r, g_z and the focal lengths f_r and f_z are given by

$$g_r = \frac{a_e}{\chi} \cot \chi\phi_e \qquad f_r = \frac{a_e}{\chi \sin \chi\phi_e}$$

$$g_z = \sqrt{a_e R_e} \cot \left\{ \sqrt{\frac{a_e}{R_e}}\, \phi_e \right\} \qquad f_z = \frac{\sqrt{a_e R_e}}{\sin \sqrt{a_e/R_e}\, \phi_e}$$

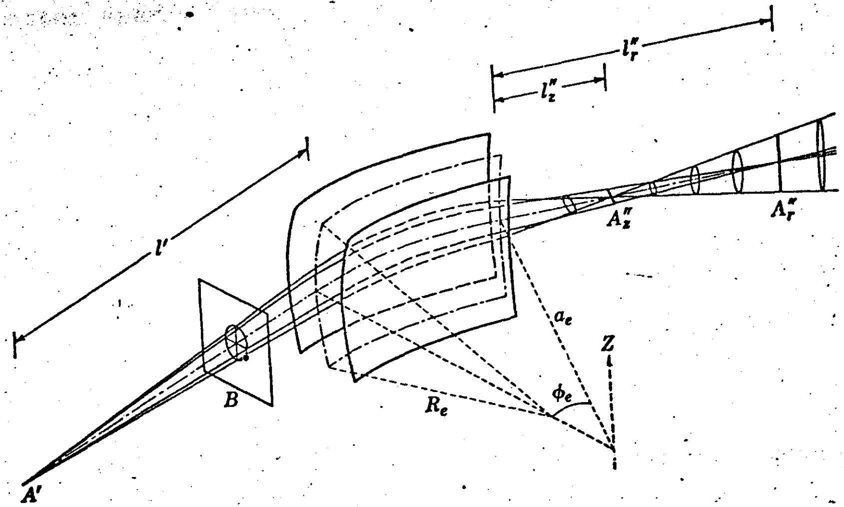


FIG. 2.1.

where a_e - radius of the sector in the radial direction

R_e - radius of the sector in the axial direction

ϕ_e - angle of deflection of the beam

$$\chi = \sqrt{2 - \frac{a_e}{R_e}}$$

While satisfying the conditions (1), (2) for the first order focusing the sector should also have a high velocity dispersion coefficient to permit better energy resolution.

The velocity dispersion factor is given by

$$K_r'' = \frac{2a_e}{\chi^2}\left(1 + \frac{l_r'' - g_r}{f_r}\right) \text{ ------------------------- } (3)$$

It was decided to study first the case of a 60° sector with a 6 inches (152.4 mm) radius a_e. To solve simultaneously equations (1), (2) and calculate K_r'' from (3) a programme (PROGRAM* 1) was written in FORTRAN IV and run on the KDF9 Computer.

The programme conditions were the following:

i) l_r' should be larger than the distance of the MS2 collector slit to the collector flange - 3.2 inches (81.3 mm) - and less than 12.0 inches (304.8 mm) because of the amount of space available to place the sector and associated pumping system; as a starting value, 4.644 inches (71.52 mm) calculated for a cylindrical sector, was chosen.

---

* The American spelling is used when naming the programmes while the English spelling is used in the text.

```
FORTRAN IV G LEVEL  18                    MAIN                DATE = 72070

C**PROGRAM TO CALCULATE SECTOR**
      IFI=60
      A=6.000
      FI=1.0472
      BL=4.519
      DO 17 J=1,60
      BL=BL+0.125
      X=0.000
      DO 17 L=1,135
      X=X+0.01
      R=A/(2.0-X*X)
      GR=A*COS(X*FI)/(X*SIN(X*FI))
      FR=A/(X*SIN(X*FI))
      GZ=(A*R)**0.5*COS((A/R)**0.5*FI)/SIN((A/R)**0.5*FI)
      FZ=(A*R)**0.5/SIN((A/R)**0.5*FI)
      IF((BL-GR).LT.0.0001)GO TO 17
      RL=GR+FR*FR/(BL-GR)
      IF((BL-GZ).LT.0.0001)GO TO 17
      ZL=GZ+FZ*FZ/(BL-GZ)
      IF((RL.LT.0.0).OR.(RL.GT.15.0))GO TO 17
      IF((ZL.LT.0.0).OR.(ZL.GT.20.0))GO TO 17
      RK=2.0*A/(X*X)*(1.0+(RL-GR)/FR)
      WRITE(6,100)IFI,BL,A,R,RL,ZL,RK
  100 FORMAT(1X,'ANGLE=',I2,1X,'L=',F6.3,1X,'A=',F6.3,1X,
     X'R=',F6.3,1X,'LR=',F6.3,1X,'LZ=',F6.3,1X,'KR=',F6.2)
   17 CONTINUE
      CALL EXIT
      END
```

PROGRAM 1

ii) l_r'' should be positive and less than 15.0 inches (381.0 mm).

iii) l_z'' should be positive and less than 20.0 inches (508.0 mm).

iv) χ should vary between 0.0 ($a_e = 2R_e$) and 1.35 (R_e much larger than a_e; for $R_e \longrightarrow \infty$ the toroid becomes a cylinder).

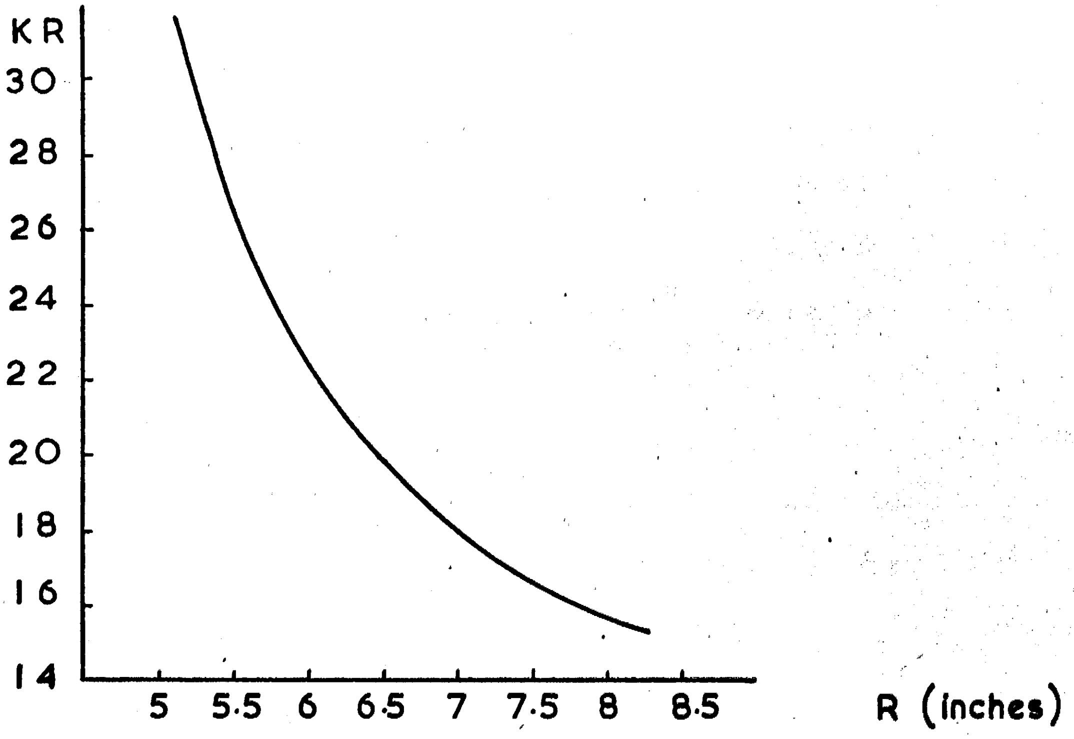
In Table 2.1 are indicated the names in the programme corresponding to the variables in the equations.

Programme	Equations
IFI	ϕ_e (in degrees)
A	a_e
FI	ϕ_e (in radians)
BL	l_r'
X	χ
R	R_e
GR	g_r
GZ	g_z
FR	f_r
FZ	f_z
RL	l_r''
ZL	l_z''
RK	K_r''

Table 2.1

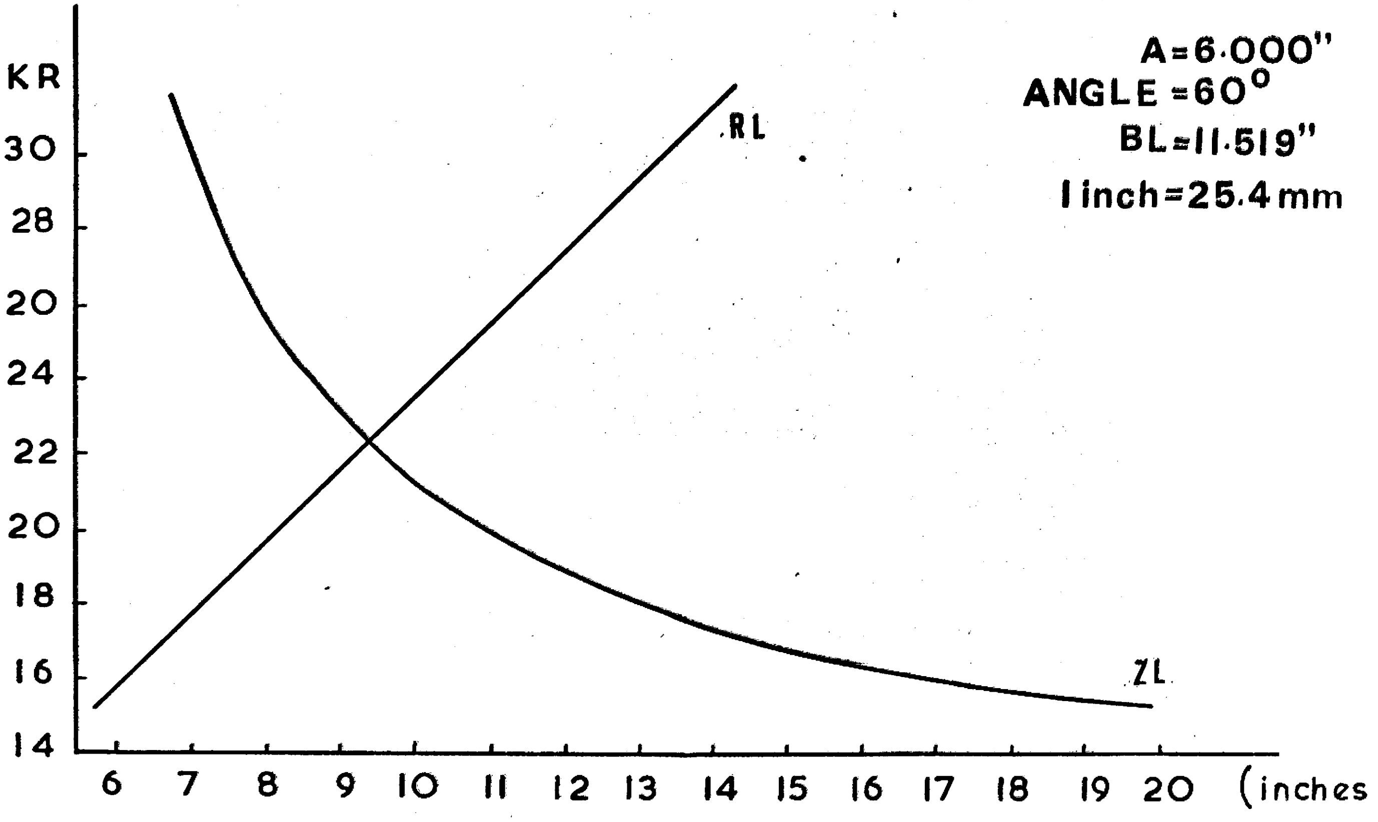
From the results represented in Figure 2.2 and Figure 2.3 it was concluded that for the same radius a_e and angle ϕ_e and for a fixed value of l_r' the velocity dispersion factor decreases with increasing R_e and is

FIG. 2.2.



A = 6.000''
ANGLE = 60°
BL = 11.519''
1 inch =25.4m

FIG. 2.3



A=6.000''
ANGLE =60°
BL=11.519''
1 inch=25.4 mm

directly proportional to l_r''. The first condition R_e small proves the advantage of a toroidal sector over a cylindrical one. The smaller values of R_e correspond to the larger values of l_r'' but they also correspond to the smaller values of l_z''. For the maximum value of K_r'' the difference between l_r'' and l_z'' is rather large.

It was finally decided to choose $l_r'' = l_z''$, that is the case of the spherical sector which for the central point of the beam (focused after the magnetic field) provides first order focusing, after the electrostatic sector, both in the radial and axial directions.

For a spherical sector $R_e = a_e$, $g_r = g_z$, $f_r = f_z$ and $\chi = 1$ so that there is only one lens equation:

$$(l_r' - g_r)\,(l_r'' - g_r) = f_r^2$$

where $g_r = a_e \cot \phi_e$ and $f_r = \dfrac{a_e}{\sin \phi_e}$

The velocity dispersion factor $K_r'' = 2a_e \left(1 + \dfrac{l_r'' - g_r}{f_r}\right)$ is again proportional to l_r''.

The displacement of the image both in the radial and axial direction is given by

$$b_e'' = -\,b_e' \,\frac{l_r'' - g_r}{f_r}$$

where b_e' is the displacement at the entrance slit. $\dfrac{l_r'' - g_r}{f_r} = G$ is the amplification factor[35] and was made equal to 1 as by increasing the amplification the image aberrations are also increased and there is no real gain in resolution.

The condition $G = 1$ corresponds to a symmetric sector, that is, with $l_r' = l_r''$.

The velocity dispersion factor is proportional to the radius of the sector but for a symmetrical spherical sector 6 inches (152.40 mm) was the maximum radius possible for the sector to be placed in the space available; for the same radius the velocity dispersion does not depend on the angle.

However, the angle affects the transmission as smaller sector angles correspond to a longer path between the origin and electrostatic sector and electrostatic sector and final collector. This means that the solid angle α, with origin in the source and defined by the gap between the two plates forming the electrostatic sector, is larger for larger sector angles[36]. To reduce second order aberrations[34] this angle α is kept deliberately small by placing a limiting slit immediately before the sector plates.

When these calculations were made the instruments previously reported with an electrostatic sector following the magnetic sector used in one case[16] a 90° cylindrical sector and in the other[23] a 60° spherical sector.

The sector that was built later on had the following characteristics:

$$\phi_e = 60^\circ$$

$$l'_e = l'_r = 10.394 \text{ inches } (264.01 \text{ mm})$$

$$l''_e = l''_r = l''_z = 10.391 \text{ inches } (263.93 \text{ mm})$$

$$a_e = R_e = 6.000 \text{ inches } (152.40 \text{ mm})$$

$$K''_r = 24.000 \text{ inches } (609.60 \text{ mm})$$

2. 4. <u>Distance between the plates</u> - Once the radius a_e is fixed the two plates will be spherical sectors, one convex and the other concave, separated by a distance 2b and having radii respectively $a_e + b$ and $a_e - b$.

An ion entering the sector in the medium plane and describing an orbit of radius a_e is submitted to a centripetal force[34] given by:

$$\frac{M_o v_o^2}{a_e} = - eE_o$$

Where M_o is the mass of the ion, $\vec{v}_o$ its velocity, e its electrical charge and E_o is the intensity of the radial electrostatic field, between the plates, for a radius a_e. The intensity of the field is given by $E_o = - \frac{\Delta V}{2b}$ where ΔV is the potential difference between the plates. The velocity $\vec{v}_o$ of the ions is calculated considering that the ions are accelerated in the electrostatic field following the source by a potential difference of 2000 Volts.

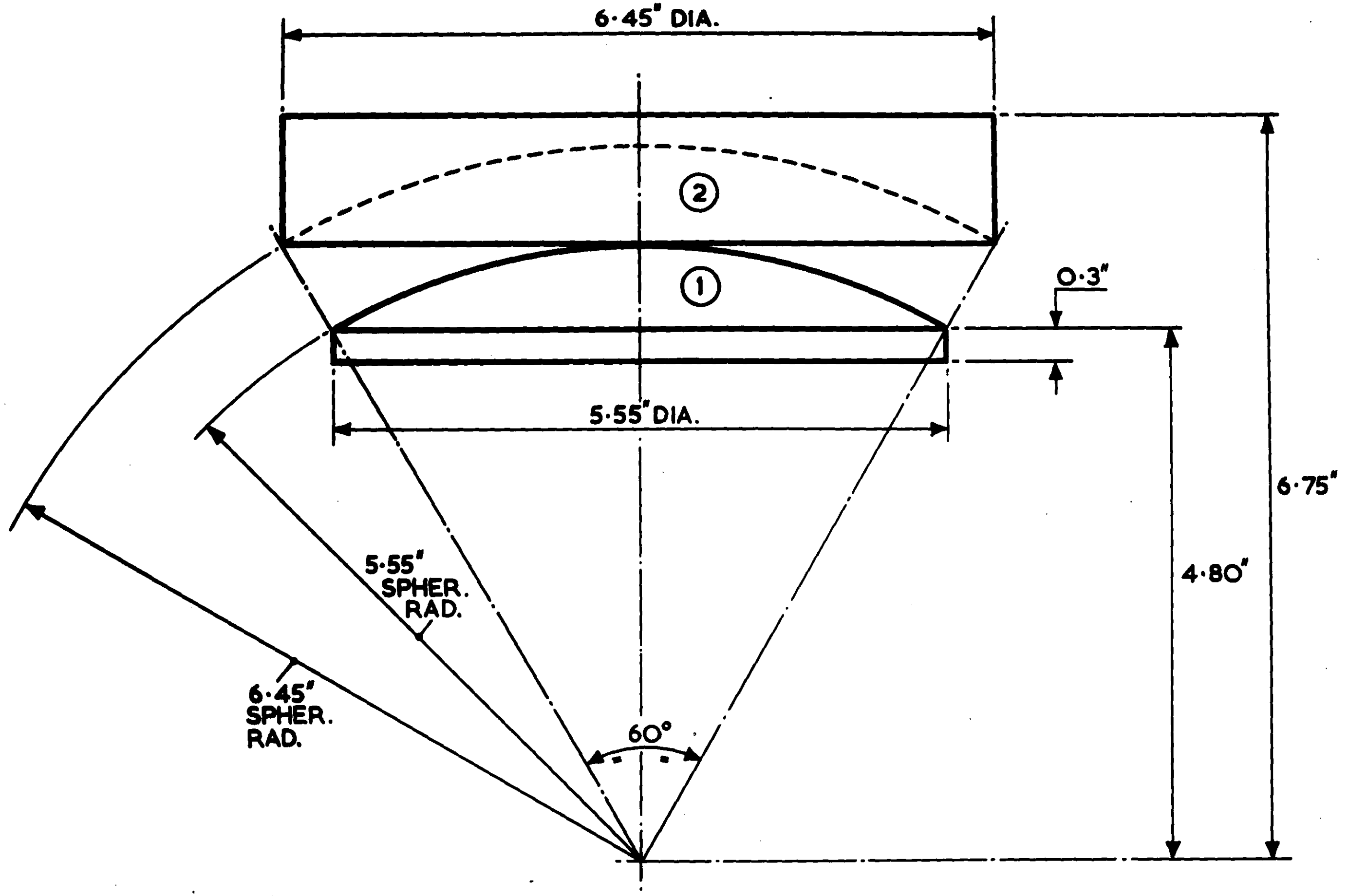
$$\frac{1}{2} M_o v_o^2 = eE \qquad \text{and} \quad E = 2000 \text{ V}$$

The distance 2b between the plates was made equal to 0.9 inches (22.86 mm).

$$\frac{a_e \Delta V}{2b} = 2E$$

The value obtained for ΔV is 600 Volts and the potential applied to each plate will be $\psi_1 = + 300$ V for the concave plate and $\psi_2 = - 300$ V for the convex plate.

The value of the gap was determined essentially by the accuracy which was to be required in the construction. As it was desired to obtain a resolution of better than 2V in 2000 V a precision of 1 in 1000 was required. For a gap of 0.9 inches it corresponds to a precision of 0.9 thousandth of an inch (0.023 mm) in the machining and assembling of the plates. It was thought to be difficult to obtain the same precision for a smaller gap. This also led to the requirement of a stability of 1 in 1000 for the electric circuits.



SPHERICAL SECTOR.

MATERIAL :- NON-MAGNETIC STAINLESS STEEL.

1 INCH = 25.4MM

FIG. 2.4.

The sector was machined* according to Figure 2.4 in non magnetic stainless steel.

2. 5. <u>Fringing field</u> - The field applied to the plates of the sector does not finish abruptly at the end of the plates. The effect of this fringing field is to lengthen the plates so that the analyser would function as though the angle was greater than 60°[36].

The distance at which the electrostatic field would become equal to zero was first calculated in the absence of intermediate slits, considering the origin of the beam as a thin slit and using the expression deduced by Herzog[37] for a parallel plate condenser.

The distance between the real field boundary and the ends of the spherical condenser would be approximately:

$$\eta^* = 2\,\frac{l'_r}{\pi}\ \text{arc tan}\ \frac{b}{l'_r} - \frac{b}{\pi}\ \ln\ \frac{4b^2}{l'^2_r + b^2}$$

$$= \frac{2}{3.1416}\ 10.39\ \text{arc tan}\ 0.0433 - 0.1432\ \ln\ 0.0074$$

$$= 0.99\ \text{inches}\ (25.15\ \text{mm})$$

As is common practice grounded thin slits were used to compress this region. It was intended to make the real field approximately zero outside the condenser and equal to $E = -\frac{\Delta V}{2b}$ inside it so that η^* would be made equal to zero[38]. To use Figure 2.5[38] the values of $\frac{s}{b}$ where s is half the slit width were calculated for the slits to be used at the entrance (0".030 = 0.76 mm) and exit of the sector (0".060 = 1.52 mm); in both cases they were closer to zero than to five tenths so that the curve having $\frac{s}{b} = 0$ was chosen. On this curve the value η^* equal to zero corresponds to approximately 0.52 for $\frac{d}{b}$

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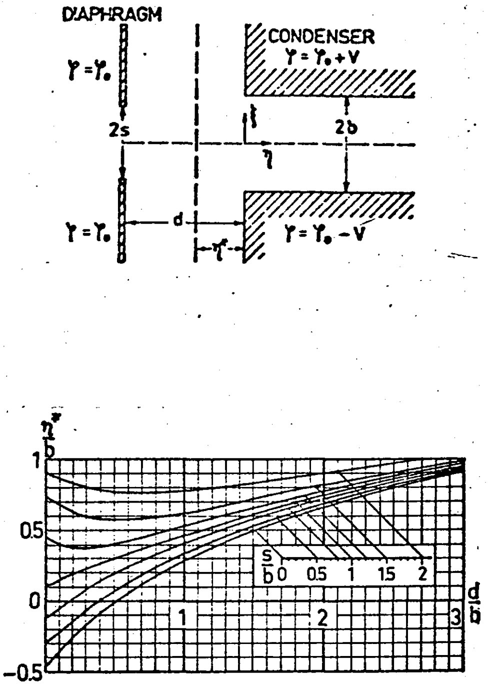
* by Carrick Precision Tools, Stewarton.

FIG. 2.5.


DIAPHRAGM
γ = γ₀
2s
γ = γ₀
d
η*
CONDENSER
γ = γ₀ + V
ξ
η
2b
γ = γ₀ − V
η*/b
1
0.5
0
−0.5
1
2
3
d/b
s/b
0
0.5
1
1.5
2

where d is the distance from the grounded thin slit to the entrance or exit of the sector. This gives d equal to 0.23 inches (5.8 mm). Owing to an error in the positioning the real distances used were 0.15 inches (3.8 mm) for the entrance and 0.25 inches (6.4 mm) for the exit which, on the entrance side, makes the real field equal to zero still inside the sector. However, the value of η^* was determined for a straight electrode boundary; the correction for a circular shaped boundary would have to be determined experimentally in an electrolytic tank and the value used was only an approximation.

The best focusing position was determined experimentally by moving the two bellows situated respectively between the magnetic and electrostatic field and the electrostatic field and final collector. As the fringing field's main effect is the shift of the focusing point it was worth calculating the second order aberrations of the image neglecting the fringing field.

2. 6. Image error and theoretical resolution - The error introduced by second order effects and also the theoretical resolution can be deduced from the expression of the path of the beam after the electrostatic sector.

For a toroidal electrostatic sector this expression was determined by Ewald and Liebl[34]. It is usual to introduce two systems of rectangular coordinates, x', y', z' and x'', y'', z'' with origins respectively at the entrance and exit points, for a beam entering the sector perpendicular to the boundary in the spherical surface equidistant from the two plates, and where x' and x'' are respectively the normal to the entrance and exit points, y' and y'' are the axes in the radial direction contained in the plane of symmetry of the sector (Fig. 2.1) and z' and z'' are perpendicular to this plane and thus parallel to the axis z referred to in paragraph 2.3.

In this system at the origin of the beam x' is equal to l'_e, y' can have the maximum value $a_e\rho_o$, where $a_e\rho_o$ is half the width of the slit after the magnetic field in the y' direction, and z' can have the maximum value $a_e\tau_o$ where $a_e\tau_o$ is the half width of the same slit in the z' direction; at the entrance point x' equal to 0 while y' and z' have the maximum values $a_e\rho_1$ and $a_e\tau_1$ corresponding to the half width of the limiting slit in the directions respectively of y' and z'.

The maximum angle a beam can make with the normal is then given by:

$$\alpha'_r = \frac{a_e(\rho_1 - \rho_o)}{l'_e} \quad \text{in the } x', y' \text{ plane}$$

$$\text{and} \quad \alpha'_z = \frac{a_e(\tau_1 - \tau_o)}{l'_e} \quad \text{in the } x', z' \text{ plane.}$$

In general the ions will have velocities with values between v_o and $v_o \pm \beta v_o$ where β is much less than 1.

On the exit side of the sector the width of the image in the direction y'' is given by:

$$\begin{aligned} y'' = {} & a_e(K_1\alpha'_r + K_2\beta + K_4\rho_o + K_{11}\alpha'^2_r + K_{22}\beta^2 + K_{33}\alpha'^2_z + \\ & + K_{44}\rho_o^2 + K_{55}\tau_o^2 + K_{12}\alpha'_r\beta + K_{14}\alpha'_r\rho_o + K_{24}\beta\rho_o + K_{35}\alpha'_z\tau_o) + \\ & + x''(L_1\alpha'_r + L_2\beta + L_4\rho_o + L_{11}\alpha'^2_r + L_{22}\beta^2 + L_{33}\alpha'^2_z + L_{44}\rho_o^2 + \\ & + L_{55}\tau_o^2 + L_{12}\alpha'_r\beta + L_{14}\alpha'_r\rho_o + L_{24}\beta\rho_o + L_{35}\alpha'_z\tau_o) \end{aligned}$$

where K_1, K_2, K_4, K_{11}, K_{22}, K_{33}, K_{44}, K_{55}, K_{12}, K_{14}, K_{24}, K_{35}, L_1, L_2, L_4, L_{11}, L_{22}, L_{33}, L_{44}, L_{55}, L_{12}, L_{14}, L_{24}, L_{35}, are numerical coefficients related to the geometrical constants of the electrostatic sector.

The first order focusing condition in the radial direction (Equation 1) is obtained by making y'' independent of α'_r that is by making equal to zero the coefficient of the terms in α'_r. The focusing condition in the axial direction (Equation 2) is obtained in the same way by making equal to zero the terms in α'_z in a similar expression giving the width of the beam in the z'' direction.

The first order focusing conditions for the symmetrical sector built are obtained for $x'' = l''_r = l'_e$ and y'' at the distance l'_e from the exit of the sector is equal to:

$$y'' = (a_e K_2 + l'_e L_2)\beta + (a_e K_4 + l'_e L_4)\rho_o + (a_e K_{11} + l'_e L_{11})\alpha'^2_r +$$

$$+ (a_e K_{22} + l'_e L_{22})\beta^2 + (a_e K_{33} + l'_e L_{33})\alpha'^2_z + (a_e K_{44} + l'_e L_{44})\rho^2_o +$$

$$+ (a_e K_{55} + l'_e L_{55})\tau^2_o + (a_e K_{12} + l'_e L_{12})\alpha'_r\beta + (a_e K_{14} + l'_e L_{14})\alpha'_r\rho_o +$$

$$+ (a_e K_{24} + l'_e L_{24})\beta\tau_o + (a_e K_{35} + l'_e L_{35})\alpha'_z\tau_o$$

where

$$K_2 = \frac{2}{\chi^2}(1 - \cos\chi\phi_e)$$

$$K_4 = \cos\chi\phi_e - \frac{1}{\chi}\frac{a_e}{f}\sin\chi\phi_e$$

$$K_{11} = \frac{1}{3\chi}\frac{l'_e}{a_e}\left(\frac{2A}{\chi^2} - 1\right)\sin\chi\phi_e + \left[\frac{1}{3\chi^2}\left(1 - \frac{2A}{\chi^2}\right) - \frac{1}{3}\frac{l'^2_e}{a^2_e}\left(1 + \frac{A}{\chi^2}\right)\right]\cos\chi\phi_e +$$

$$+ \frac{1}{3\chi^2}\left(2 + A\frac{l'^2_e}{a^2_e}\right)\sin^2\chi\phi_e + \frac{1}{3}\left(2\frac{l'^2_e}{a^2_e} + \frac{A}{\chi^4}\right)\cos^2\chi\phi_e +$$

$$+ \frac{1}{3\chi}\frac{l'_e}{a_e}\left(2 - \frac{A}{\chi^2}\right)\sin 2\chi\phi_e + \frac{1}{3}\frac{l'^2_e}{a^2_e}\left(\frac{A}{\chi^2} - 1\right) - \frac{1}{3\chi^2} + \frac{A}{3\chi^4}$$ [39]

$$K_{22} = -\frac{1}{\chi^2}\left(1 + \frac{28}{3\chi^2} + \frac{16A}{3\chi^4}\right)\cos\chi\phi_e - \frac{2}{\chi}\left(1 + \frac{1}{\chi^2} + \frac{2A}{\chi^4}\right)\phi_e\sin\chi\phi_e +$$

$$+ \frac{4}{3}\frac{A}{\chi^6}\sin^2\chi\phi_e + \frac{8}{3\chi^4}\cos^2\chi\phi_e + \frac{16A}{3\chi^6} + \frac{20}{3\chi^4} + \frac{1}{\chi^2}$$

$$K_{33} = \frac{B}{\chi(5c - 2)}\frac{l'_e}{a_e}\sin\chi\phi_e + \frac{1}{\chi^2}\left[1 - \frac{B}{5c - 2} + \frac{l'^2_e}{a^2_e}\left(c - \frac{B}{2}\frac{3c - 2}{5c - 2}\right)\right]\cos\chi\phi_e -$$

$$- \frac{B}{2\sqrt{c}(5c - 2)} \frac{l_e'}{a_e} \sin 2\sqrt{c}\,\phi_e + \frac{B}{4c(5c - 2)} \left(1 - c\frac{l_e'^2}{a_e^2}\right) \cos 2\sqrt{c}\,\phi_e +$$

$$+ \frac{1}{\chi^2}\left[-1 + \frac{B}{4c} + \frac{l_e'^2}{a_e^2}\left(\frac{B}{4} - c\right)\right]$$

$$K_{44} = -\frac{1}{3}\left(1 + \frac{A}{\chi^2}\right) \cos\chi\phi_e + \frac{2}{3}\cos^2\chi\phi_e + \frac{A}{3\chi^2}\sin^2\chi\phi_e - \frac{1}{3}\left(1 - \frac{A}{\chi^2}\right)$$

$$K_{55} = \left[\frac{c}{\chi^2} - \frac{B}{2\chi^2}\frac{3c - 2}{5c - 2}\right]\cos\chi\phi_e - \frac{B}{4(5c - 2)}\cos 2\sqrt{c}\,\phi_e + \frac{1}{\chi^2}\left(\frac{B}{4} - c\right)$$

$$K_{12} = \frac{1}{\chi}\left(1 + \frac{11}{3\chi^2} + \frac{2A}{3\chi^4}\right)\sin\chi\phi_e + \frac{4}{3\chi^2}\frac{l_e'}{a_e}\left(1 + \frac{A}{\chi^2}\right)\cos\chi\phi_e + \frac{l_e'}{a_e} \times$$

$$\times \left(\frac{1}{\chi} + \chi + \frac{2A}{\chi^3}\right)\phi_e \sin\chi\phi_e - \left(1 + \frac{1}{\chi^2} + \frac{2A}{\chi^4}\right)\phi_e\cos\chi\phi_e - \frac{4}{3}\frac{A}{\chi^4}\frac{l_e'}{a_e} \times$$

$$\times \sin^2\chi\phi_e - \frac{8}{3\chi^2}\frac{l_e'}{a_e}\cos^2\chi\phi_e - \frac{2}{3\chi^3}\left(2 - \frac{A}{\chi^2}\right)\sin 2\chi\phi_e + \frac{4}{3\chi^2}\frac{l_e'}{a_e}\left(1 - \frac{A}{\chi^2}\right)$$

$$K_{14} = \frac{1}{3\chi}\left(\frac{2A}{\chi^2} - 1\right)\sin\chi\phi_e - \frac{2}{3}\frac{l_e'}{a_e}\left(1 + \frac{A}{\chi^2}\right)\cos\chi\phi_e + \frac{2}{3}\frac{A}{\chi^2}\frac{l_e'}{a_e}\sin^2\chi\phi_e +$$

$$+ \frac{4}{3}\frac{l_e'}{a_e}\cos^2\chi\phi_e + \frac{1}{3\chi}\left(2 - \frac{A}{\chi^2}\right)\sin 2\chi\phi_e + \frac{2}{3}\frac{l_e'}{a_e}\left(\frac{A}{\chi^2} - 1\right)$$

$$K_{24} = \frac{4}{3\chi^2}\left(1 + \frac{A}{\chi^2}\right)\cos\chi\phi_e + \frac{1}{\chi}\left(1 + \chi^2 + \frac{2A}{\chi^2}\right)\phi_e\sin\chi\phi_e - \frac{4}{3}\frac{A}{\chi^4}\sin^2\chi\phi_e -$$

$$- \frac{8}{3\chi^2}\cos^2\chi\phi_e + \frac{4}{3\chi^2}\left(1 - \frac{A}{\chi^2}\right)$$

$$K_{35} = \frac{B}{\chi(5c - 2)}\sin\chi\phi_e + \frac{1}{\chi^2}\frac{l_e'}{a_e}\left[2c - B\frac{3c - 2}{5c - 2}\right]\cos\chi\phi_e - \frac{B}{2\sqrt{c}(5c - 2)} \times$$

$$\times \sin 2\sqrt{c}\,\phi_e - \frac{B}{2(5c - 2)}\frac{l_e'}{a_e}\cos 2\sqrt{c}\,\phi_e + \frac{1}{\chi^2}\frac{l_e'}{a_e}\left(\frac{B}{2} - 2c\right)$$

$$L_2 = \frac{2}{\chi}\sin\chi\phi_e + \frac{2}{\chi^2}\frac{a_e}{f}\left\{\cos\chi\phi_e - 1\right\}$$

$$L_4 = -\chi\sin\chi\phi_e - \frac{2a_e}{f}\cos\chi\phi_e$$

$$L_{11} = \frac{1}{3\chi}\left[\frac{l_e'^2}{a_e}\left\{A + \chi^2\right\} + \frac{2A}{\chi^2} - 1\right]\sin\chi\phi_e + \frac{1}{3\chi}\left[\frac{l_e'^2}{a_e^2}\left\{A - \frac{\chi^2}{2}\right\} + \frac{1}{2} - \frac{A}{\chi^2}\right] \times$$

$$\times \sin 2\chi\phi_e + \frac{1}{3}\frac{l_e'}{a_e}\left\{\frac{2A}{\chi^2} - 1\right\}\left(\cos\chi\phi_e - \cos 2\chi\phi_e\right)$$

$$L_{22} = \frac{1}{\chi}\left[-1 + \frac{10}{3\chi^2} + \frac{4A}{3\chi^4}\right]\sin\chi\phi_e + \frac{2}{3\chi^3}\left\{\frac{2A}{\chi^2} - 1\right\}\sin 2\chi\phi_e -$$

$$-2\left\{1 + \frac{1}{\chi^2} + \frac{2A}{\chi^4}\right\}\phi_e\cos\chi\phi_e$$

$$L_{33} = \left[\frac{l_e'^2}{a_e^2}\left\{\frac{B(3c-2)}{2\chi(5c-2)} - \frac{c}{\chi}\right\} - \frac{1}{\chi} + \frac{B}{\chi(5c-2)}\right]\sin\chi\phi_e +$$

$$+ \frac{B}{5c-2}\frac{l_e'}{a_e}\left(\cos\chi\phi_e - \cos 2\sqrt{c}\,\phi_e\right) + \frac{B\sqrt{c}}{2(5c-2)}\left\{\frac{l_e'^2}{a_e^2} - \frac{1}{c}\right\}\sin 2\sqrt{c}\,\phi_e$$

$$L_{44} = \frac{\chi}{3}\left\{1 + \frac{A}{\chi^2}\right\}\sin\chi\phi_e + \frac{\chi}{3}\left[\frac{A}{\chi^2} - \frac{1}{2}\right]\sin 2\chi\phi_e$$

$$L_{55} = \frac{1}{2\chi}\left[B\,\frac{3c-2}{5c-2} - 2c\right]\sin\chi\phi_e + \frac{B\sqrt{c}}{2(5c-2)}\sin 2\sqrt{c}\,\phi_e$$

$$L_{12} = \frac{1}{\chi}\frac{l_e'}{a_e}\left\{\frac{5}{3} + \chi^2 + \frac{2A}{3\chi^2}\right\}\sin\chi\phi_e + \frac{2}{3\chi^2}\left\{1 - \frac{2A}{\chi^2}\right\}\cos\chi\phi_e + \frac{l_e'}{a_e} \times$$

$$\times \left\{1 + \chi^2 + \frac{2A}{\chi^2}\right\}\phi_e\cos\chi\phi_e + \left\{\chi + \frac{1}{\chi} + \frac{2A}{\chi^3}\right\}\phi_e\sin\chi\phi_e + \frac{2}{3\chi}\frac{l_e'}{a_e} \times$$

$$\times \left\{1 - \frac{2A}{\chi^2}\right\}\sin 2\chi\phi_e + \frac{2}{3\chi^2}\left\{\frac{2A}{\chi^2} - 1\right\}\cos 2\chi\phi_e$$

$$L_{14} = \frac{2}{3}\chi\frac{l_e'}{a_e}\left\{1 + \frac{A}{\chi^2}\right\}\sin\chi\phi_e + \frac{1}{3}\left\{\frac{2A}{\chi^2} - 1\right\}\cos\chi\phi_e + \frac{\chi}{3}\frac{l_e'}{a_e}\left\{\frac{2A}{\chi^2} - 1\right\} \times$$

$$\times \sin 2\chi\phi_e + \frac{1}{3}\left\{1 - \frac{2A}{\chi^2}\right\}\cos 2\chi\phi_e$$

$$L_{24} = \frac{1}{\chi}\left\{\frac{5}{3} + \chi^2 + \frac{2A}{3\chi^2}\right\}\sin\chi\phi_e + \left\{1 + \chi^2 + \frac{2A}{\chi^2}\right\}\phi_e\cos\chi\phi_e + \frac{2}{3\chi}\left\{1 - \frac{2A}{\chi^2}\right\} \times$$

$$x \quad \sin 2\,\chi\,\phi_e$$

$$L_{35} = \frac{1}{\chi}\,\frac{l_e^{'}}{a_e}\left[B\,\frac{3c-2}{5c-2} - 2c\right]\,\sin\chi\phi_e + \frac{B}{5c-2}\cos\chi\,\phi_e + \frac{B\sqrt{c}}{5c-2}\ x$$

$$x\,\frac{l_e^{'}}{a_e}\sin 2\sqrt{c}\,\phi_e - \frac{B}{5c-2}\cos 2\sqrt{c}\,\phi_e$$

and

$$A = \left[3c - 3 - \frac{c^2}{2}\,(1 + R_e^{'})\right]$$

$$B = \left[c + c^2\,(1 + R_e^{'})\right]$$

with $c = \dfrac{a_e}{R_e}$ and $R_e^{'} = \left(dR/dr\right)_{r = a_e,\ z = 0}$ R being the axial radius of curvature of an equipotential surface adjacent to the zero potential surface in the z = 0 plane; $f = -\,a_e\rho_1/\Delta\alpha$ where $\Delta\alpha$ is the change on the angle of admittance α caused by the fringing field so that in the apparatus built $f \longrightarrow \infty$

The numerical values obtained for this auxiliary variables were $c = 1$, $R_e^{'} = 1$, $A = -1$ and $B = 3$.

From the dimensions of the slits used it was obtained

$$a_e\rho_o = 0\overset{''}{.}004\ (0.10\ \text{mm}) \qquad a_e\rho_1 = 0\overset{''}{.}015\ (0.38\ \text{mm})$$

$$a_e\tau_o = 0\overset{''}{.}05\ \ (1.27\ \text{mm}) \qquad a_e\tau_1 = 0\overset{''}{.}19\ \ (4.83\ \text{mm})$$

The term in ρ_o is equal to $-\,a_e\rho_o$, as expected, since the amplification was chosen to be 1 which makes the image of the entrance slit the same size as the slit itself.

The term in β, representing the dispersion due to the different velocities in the ions entering the sector is equal to $4a_e\beta$.

The numerical value of the second order aberrations is indicated in Table 2.2 except for those including β since this value is still to be determined.

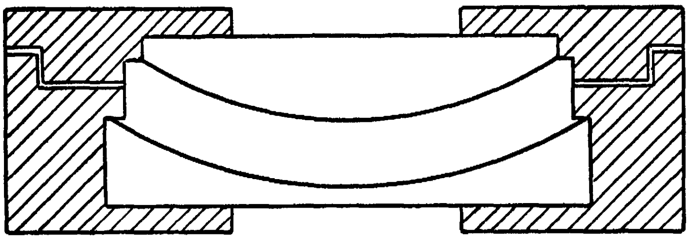
Type	Index	K	L	Numerical value (mm)
$\alpha_r'^2$	11	-2	$-2\sqrt{3}$	-1.26×10^{-3}
β^2	22	-1/2	$-\sqrt{3}/2$	$-304.8 \times \beta^2$
$\alpha_z'^2$	33	3/4	$3\sqrt{3}/4$	$\underline{5.84 \times 10^{-2}}$
ρ_0^2	44	-3/4	$-\sqrt{3}/4$	-9.84×10^{-5}
τ_0^2	55	1/8	0	1.32×10^{-3}
$\alpha_r'\beta$	12	$4\sqrt{3}$	8	$3.36 \times \beta$
$\alpha_r'\rho_0$	14	$-3\sqrt{3}/2$	-5/2	-7.34×10^{-4}
$\beta\rho_0$	24	3	$2\sqrt{3}$	$0.90 \times \beta$
$\alpha_z'\tau_0$	35	$\sqrt{3}/2$	1	$\underline{4.41 \times 10^{-2}}$

Table 2.2

Since the size of the image, without considering the second order aberrations, is equal to 0.1 mm, from the calculated terms, the ones including α_z together are of the same order of magnitude as the image. This is owing to the fact that instead of a small circular hole, a rectangular slit is used and the focusing properties of the sector are only for the centre point of the slit. The wider slit was employed because it made it easier to detect the beam as it did not require such a high precision in the initial setting. As no adjustable slits were available to decrease the size in the z direction it would be necessary to open the machine and replace the plates with the slits. This was not attempted because, at present, it is quite difficult to reassemble the apparatus

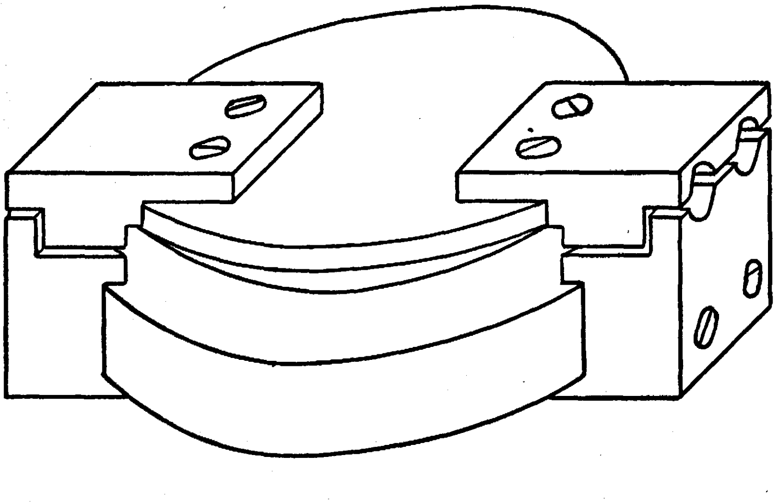
FIG. 2.6.

PLATES ASSEMBLY



Scale 1:2.5

a)



b)

and obtain the same relative positions of all slits.

Two groups of ions entering the sector with different velocities will be distinguishable if the images they form can be separated, that is the term $4a_e\beta$ has to be bigger than the sum of the image with aberrations plus half the width (0.02 mm) of the collector slit since the collection is made electrically[30].

$$4a_e\beta > 0.10 \text{ mm} + 0.02 \text{ mm} + \left[\, 0.10 + 4.26\,\beta - 304.8\,\beta^2 \right] \text{mm}$$

which gives $\beta > 0.0004$

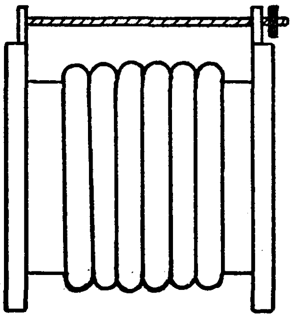
Since $\beta = \dfrac{\Delta v}{v_o} = \dfrac{1}{2}\dfrac{\Delta E}{E_o}$ the energy resolution is of the order of 8 in 10000 which is still better than the limit set by the precision in the construction.

2. 7. <u>Assembling of the sector</u> - The two spherical plates were supported in position using pyrophyllite parts which were machined to size and according to the manufacturer's instructions heated up to 1000°C to gain mechanical strength. After the heat treatment it was noted that there had been no deformation and though they had contracted slightly it did not affect the spacing of the sector.

As shown in the Figures 2.6 a) and 2.6 b) the bottom plate (concave) of the sector was screwed to two pyrophyllite parts and the top plate to the other two. The two pyrophyllite pieces attached to the bottom plate are kept in position inside a brass box by means of small brass bars screwed to the box and insulate electrically the stainless steel plate from the brass box. The distance between the two plates is maintained using small brass cylinders inserted between the bottom and top pieces of pyrophyllite. The spacing between the two plates was measured with a surface micrometer and the error was less than 0.001 inches (0.025 mm).

To the entrance and exit sides of the box are attached metal bellows.

BELLOWS ASSEMBLY

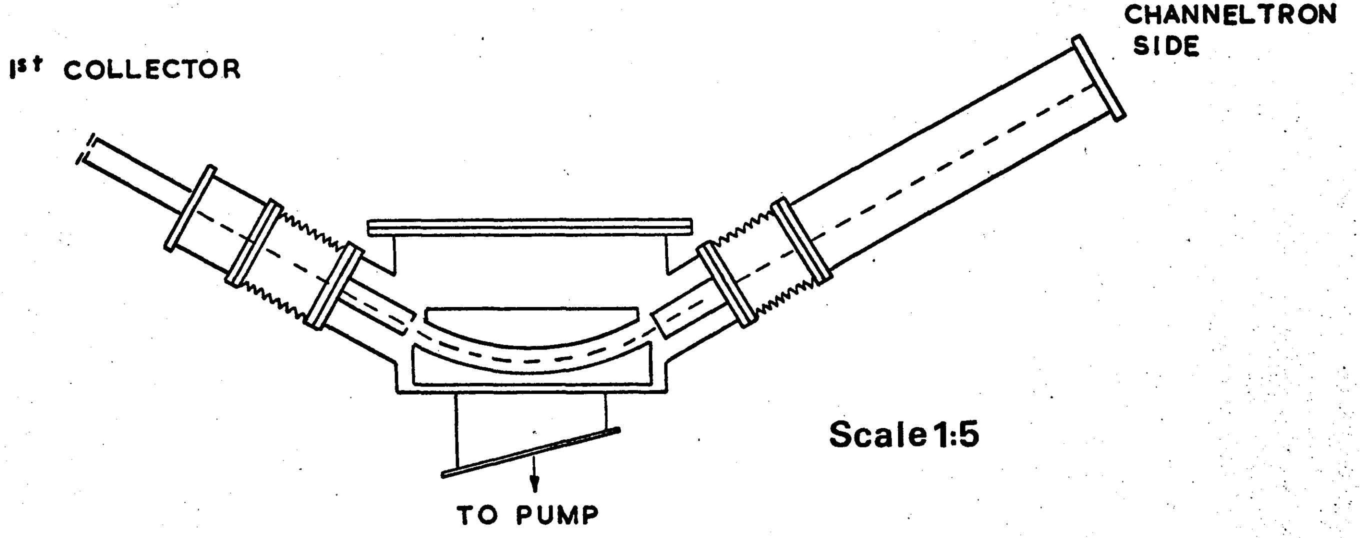


Scale 1:2

FIG. 2.7.

FIG. 2.8.

Electrostatic Sector



The bellows* were intended to adjust the focusing position and were chosen with the maximum length advised by the manufacturer, that is, a length equal to the diameter (2 inches = 50.8 mm).

Another bellows was placed between the first collector and the rigid tube to facilitate the connection of the electrostatic to the magnetic sector. Each bellows, as shown in Figure 2.7, had attached to one of the flanges a long screw of short thread which went through the other flange. By adjusting the nut outside this flange, small angular movements were obtained. The lengthening and shortening of the bellows was made by moving the whole assembly relatively to the handy angle structure on which it was mounted.

The bellows were measured under vacuum to determine the length of the rigid parts.

The conductors (nickel wire gage 0.001") supplying the voltage to the plates are introduced in the box through a ceramic to metal seal** to which they are welded.

Figure 2.8 shows the box containing the sector, with mechanical connections. The base of the box makes an angle of 15° with the horizontal to permit the connection of the whole assembly to the old MS2.

2. 8. <u>Vacuum system</u> - Three independent vacuum systems were used all employing A.E.I. "Metrovac" pumps and traps.

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* Supplied by: United Flexible Metallic Tubing Co. Ltd.,
South Street, Ponders End,
Enfield, Middlesex.

** Supplied by: 20th Century Electronics Ltd.,
King Henry's Drive,
New Addington,
Croydon,
Surrey.

The two main ones were formed by a liquid nitrogen trap (MARK III) sitting over a diffusion pump (033C - 130 l/s) backed by a Rotary Pump (GDR1 - 0.72 l/s). The tube of the original MS2, that is, the tube passing inside the magnetic field rested on one of the cold traps while the box containing the electrostatic sector plates sat on the other

The third system which was part of the sample introduction system was formed by a Diffusion Pump (022A - 35 l/s) backed by a GDR1 Rotary Pump.

The vacuum seals used between metal parts were O-rings or rubber cord. The original MS2 tube had heating resistances and the electrostatic sector was surrounded by heating tape. The whole system was usually baked overnight but the baking temperature of the sector was kept under 70°C because of the final collector.

The pressure was measured on the backing lines of the two main systems and on the third one by means of Pirani Gauge Heads (Edwards). At the base of the MS2 tube near to the connection of the sector there was a Penning Gauge Head (Edwards) and on the cover of the box an Ionization Gauge Head (VC20 AE1).

The pressure in the tube and sector varied between 2×10^{-6} torr* to up to 10^{-5} torr during some experiments. In the sample introduction system it was lower than 10^{-4} torr in the absence of a sample.

2. 9. Sample introduction system - As the sample introduction system of the original MS2 had been dismantled a new single inlet system was constructed, similar to the one in the MS9 double focusing mass spectrometer.

The gas or vapour admitted through a small doser[40] was expanded in

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* 1 torr = 1.333×10^{2} N m^{-2} (S.I. units).

a 2 litre reservoir and admitted to the source through a capillary tube and sintered disc to ensure molecular flow and allow a steady pressure in the source for up to 5 minutes. To keep the pressure constant for a longer time it would be necessary to use a sinter of smaller pores or a leak valve. A constant pressure in the source was not important for the experiment using the background and in the others lasting for up to three hours the pressure variation was corrected as will be described in the next chapter.

2. 10. <u>Source</u> - As mentioned before the source used was of the modified Nier type[27 b)], controlled by three electronic units:

i) The first was a stablised power supply for 2000 Volts. For most of the work, to obtain a stability of 0.1 Volts in 2000 Volts, an OLTRONIX regulated high voltage power supply[*] was used.

ii) An electron beam control unit allows the control of the filament current keeping constant the amount of electrons emitted by it. The cage potential was kept constant at 2000 Volts relative to earth which corresponded to + 70 V relative to the filament. The trap current and potential were also supplied by this unit.

iii) A potential divider unit supplied the voltage to the ion repeller, the first slit plate and the two sets of "D" plates according to the practice of the MS2.

The spread in the energy of the ion beam for parent ions can be as low as 0.05 eV[**41]. However this involves using a very low ion repeller

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[*] OLTRONIX A 2.5k - 10HR obtained on loan from the University of St. Andrews.

[**] 1 eV = 1.602 x 10^{-19} J (S.I. Units)

field and space and surface charge decrease the stability and linearity of the source.

According to Blears and Mettrick[30], the thermal energy of the molecules being negligible the main cause of spread in the beam energy is the point of the electron beam where the ion is formed. The width of the electron beam being approximately 0.2 mm and the distance between the ion repeller and the cage d = 4 mm the spread in energy is given by $\Delta V = \frac{V \times 0.2}{4}$ where V is the voltage difference between ion repeller and cage (9 Volts). ΔV should be of the order of 0.5 Volts.

2. 11. Magnetic Field Control Unit - The magnetic power supply provided a current variable between 0 and 350 mA. Since the two coils of the electromagnet were connected in parallel this corresponds to values of mass over charge up to 800. The higher values were never used as the mass resolution of the magnetic sector was much smaller than that.

The stability of this power supply was better than 1 in 1000.

The unit included facilities for scanning the magnetic field either manually or automatically, with three speeds.

2. 12. First collector - The first collector was placed relative to the electrostatic sector as indicated in Figure 2.8 so that when the electrostatic sector is connected to the magnetic sector it occupies the same position as the Faraday Cup in the MS2. The distances between the supporting flange and the defining slit are the same in this collector and in the Faraday Cup.

The top plate at -72 Volts and with a slit of 0.040" (1.02 mm) wide limited the beam to be received in the first collector and set the resolution obtained here at a very low value, and simultaneously repelled secondary electrons produced at the surface of the slit, preventing them from reaching the collector.

The next plate with a slit 0.008" (0.20 mm) wide defines the beam that is going to enter the electrostatic sector. All the ions passing through the 0.040" slit and not through the 0.008" are collected on this plate which is connected through a ceramic leadthrough seal to the electrometer amplifier of the old Faraday Cup placed outside the vacuum line.

The resolution $\frac{\Delta(mv)}{mv}$, that is, the momentum resolution obtained in the first collector is smaller than the resolution in the beam entering into the electrostatic sector.

The signal from the electrometer amplifier is detected in a voltmeter and can be recorded.

As the spherical sector only gives focusing for the central point of the beam, after the beam was first detected in the final collector a new plate with a hole of 0.1" (2.54 mm) diameter was introduced after the 0.008" slit plate and insulated from it. This plate reduced the dimension of the beam in the z direction, as a first step to the replacement of the plates with slits by plates with circular holes. The values calculated in 2.6 refer to the $a_e \tau_o$ obtained this way.

2.13. Electrostatic sector control unit - A power supply unit provides +300 Volts to the lower plate and -300 Volts to the upper plate of the electrostatic sector. There is provision for a small adjustment voltage to be added or subtracted from these potentials. The voltage was stable up to 0.25 Volts and the difference between the absolute value of the potential in the plates was never larger than this. The trimming controls were used as focusing controls to get the highest beam intensity.

The ± 300 Volts can be scanned simultaneously changing the voltage

"CHANNELTRON" ASSEMBLY

Scale 1:2.5

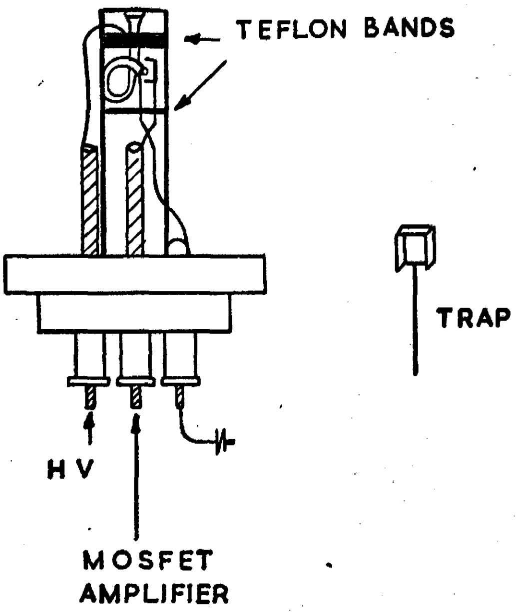

FIG. 2.9.

in both plates by the same amount but in opposite directions. The range of the scan can be changed from zero (fixed voltage) to three hundred Volts. The scan can be made automatically though for wide ranges it was always made manually because the speed of scan available was too high. Values of voltage respectively greater than +310 Volts and less than -310 Volts though obtainable were not used in the experiment.

2.14. Final collector - A channel electron multiplier (type B419 AL No. 456 from Mullard) was used as the final collector.

A channel electron multiplier[42] is formed by a small curved glass tube, the inside wall of which is coated with a resistive material. When a potential is applied between the ends of the tube, the resistive surface works like a continuous dynode in a way analogous to the separate dynodes of a photon or electron multiplier, together with the chain of resistances used to establish the dynode potentials.

An ion entering the negative potential end of the channel multiplier generates secondary electrons when striking the walls of the tube. These are accelerated along the tube until they strike the wall again generating further secondary electrons. When operating on the current amplification mode, as was the case in this work, an open output multiplier is used, with a separate collector electrode(trap).

The "channeltron" assembly is represented in Figure 2.9. Once this assembly is attached to the rest of the system the top plate is situated at the image forming distance (l_r'') from the electrostatic sector plates. The "channeltron" itself was fixed with the cone at about 1 mm from the plate. The "channeltron" is supported and simultaneously insulated from the two brass pillars by means of two teflon

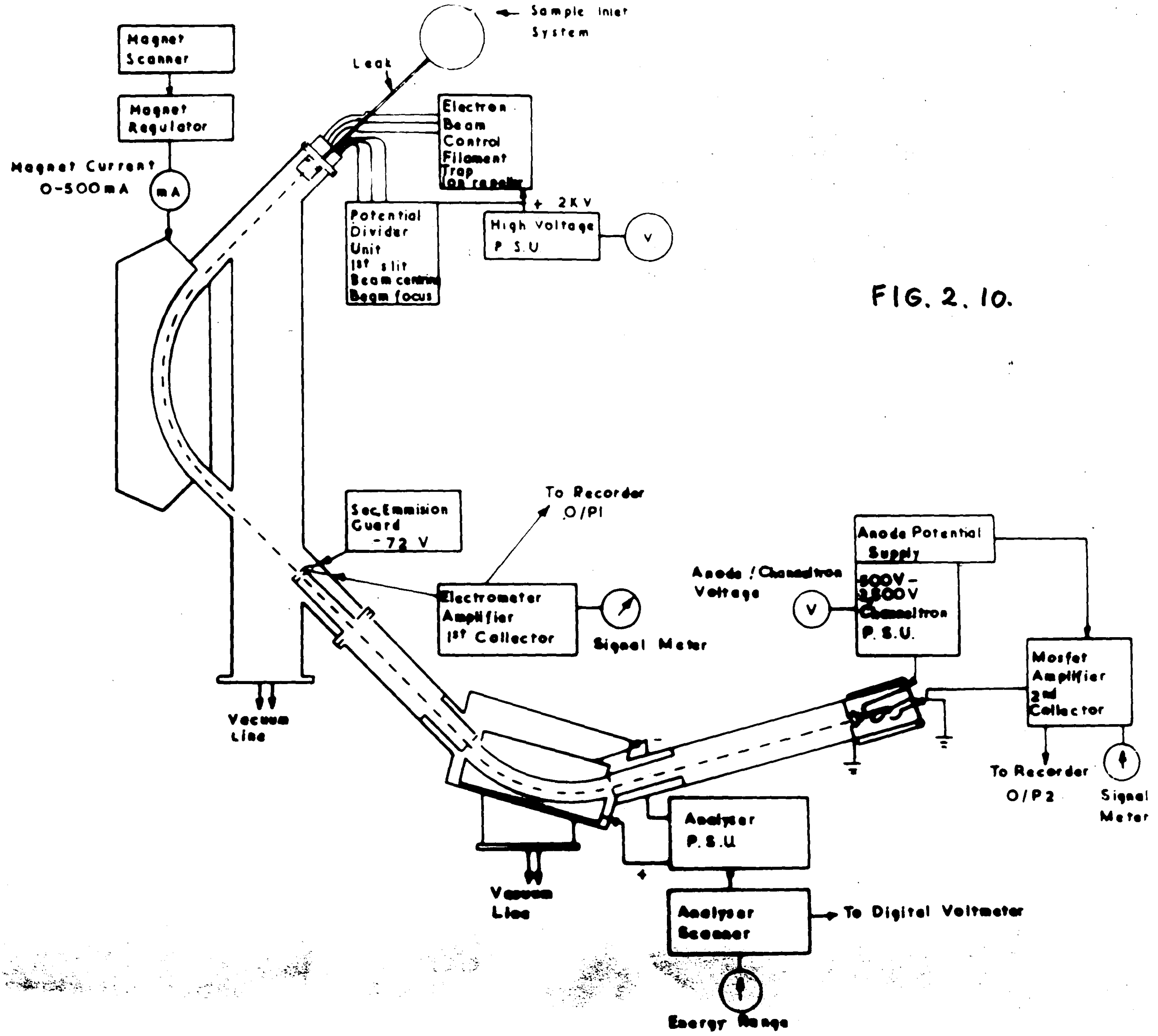
Sample Inlet System
Leak
Magnet Scanner
Magnet Regulator
Magnet Current 0-500mA
mA
Electron Beam Control Filament Trap Ion repeller
+ 2KV
High Voltage P.S.U
V
Potential Divider Unit 1st slit Beam centring Beam focus
Vacuum Line
Sec. Emmision Guard -72 V
To Recorder O/P1
Electrometer Amplifier 1st Collector
Signal Meter
Anode Potential Supply
Anode / Channeltron Voltage
V
500V – 2500V Channeltron P.S.U.
Mosfet Amplifier 2nd Collector
To Recorder O/P2
Signal Meter
Analyser P.S.U
+
Vacuum Line
Analyser Scanner
To Digital Voltmeter
Energy Range

FIG. 2. 10.

pieces screwed together forming a band behind the cone of the channeltron. In front of the opening of the positive end a small trap shaped as indicated in the diagram was also set in position by means of two teflon pieces.

The two brass pillars were screwed to a hollow brass flange which attached to the tube leading to the electrostatic sector. The electrical connections to the exterior of the vacuum system were made by means of a flange with three electrical feedthroughs* which was attached to the hollow brass flange as indicated in Figure 2.9. The three conductors passing through the hole in the brass flange connect respectively to the entrance and exit of the channeltron and to the small trap.

Electronic units supplied the high voltage variable between -500 Volts and -2,500 Volts and the positive potential (relative to the output end of the channeltron) to the trap. This potential difference, variable between zero and two hundred and fifty Volts was set at the value for which an increase in the potential difference did not correspond, any more, to an increase in the signal. This value was +50 Volts. The signal after amplification was read on a meter and, or recorded.

The whole instrument with electronic circuits is schematically represented in Figure 2.10.

2. 15. <u>Measurement of voltages</u> - The acceleration voltage (+2000 Volts relative to earth) was measured, using a SOLARTRON digital voltmeter. The range of this instrument is 1000 Volts. A series of resistances was used to cause a potential drop of 1000 Volts and permit the use of the voltmeter. The value of the resistances changed quickly whenever

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* EFT3 from Vacuum Generators Limited

the circuit was connected and there was also a long time variation. The values measured were for that reason only relative. The instrument allows a precision of 0.25 Volts in 1000 Volts, that is 0.5 Volts in 2000 Volts.

The same digital voltmeter was also used to measure the voltage in one of the plates of the sector. The precision obtained of 0.25 Volts in 300 Volts corresponds however to 1.67 Volts in 2000 Volts and was rather less than required.

Since to change the 2000 Volts involves changes in the source focusing conditions and in the magnetic field, for most applications it is the ±300 Volts supplies that are changed and need to be measured. For further applications it will be necessary to introduce a more sensitive form of voltage measurement.

In the final part of the work, the meter was accidentally broken and a DANA 3800A digital multimeter was used instead. This type of instrument only gave a precision of 1 Volt in 300 Volts and having a lower internal impedance also gave a systematically lower reading.

2. 16. Recording of signals - The signals from the two collectors could be transferred either to a TEKTRONIX TYPE 564 STORAGE OSCILLOSCOPE or to a WATANABE MULTIRECORDER TYPE MC611.

The signals in the oscilloscope were photographically recorded using a TELFORD TYPE P photographic camera.

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Chapter 3.

Performance of the Apparatus and Results.

3. 1. Resolution.

3. 1. 1. Mass Resolution - The resolution of the original MS2, before connecting the electrostatic sector, was determined using a 0.002 inches (0.05 mm) slit in the source and a 0.0065 inches (0.17 mm) in the Faraday Cup. Figure 3.1 shows the group of peaks 139 - 142 from a spectrum of iodomethane taken in these conditions. The resolution obtained was of the order of 150.

After the introduction of the sector, using the same source slit and a slit 0.008 inches (0.21 mm) wide in the entrance of the electrostatic sector, the resolution was obtained from a spectrum of 2 Benzyl Benzoic acid (Figure 3.3) and is of the order of 250. The peaks of 2 Benzyl Benzoic acid were identified by comparison with the spectrum of the same compound run in the MS9 (Figure 3.2).

3. 1. 2. Energy resolution - The resolution in energy was determined by changing the acceleration voltage (2000 Volts) without changing the potentials of the plates of the electrostatic sector. The peaks obtained were recorded in the oscilloscope and photographed (Figure 3.4).

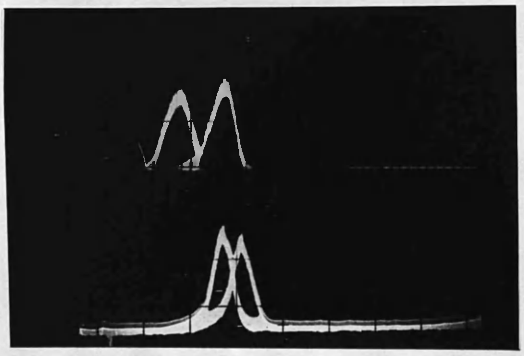


Fig. 3.4.

FIG 3.1.

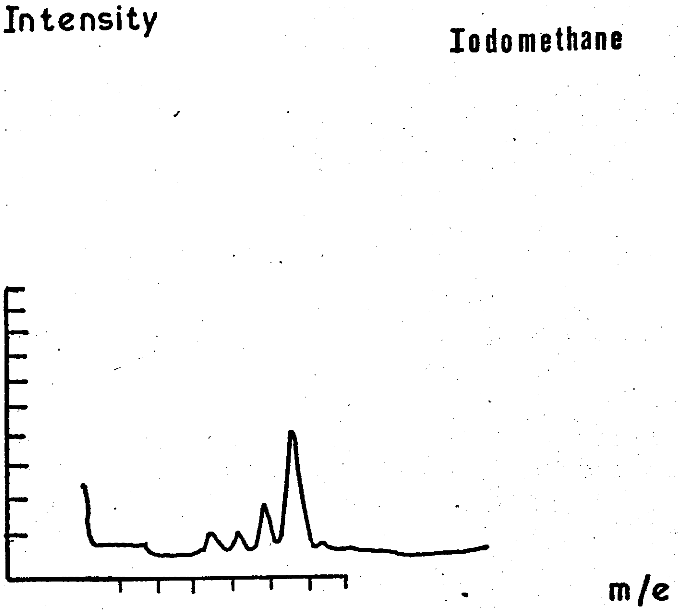
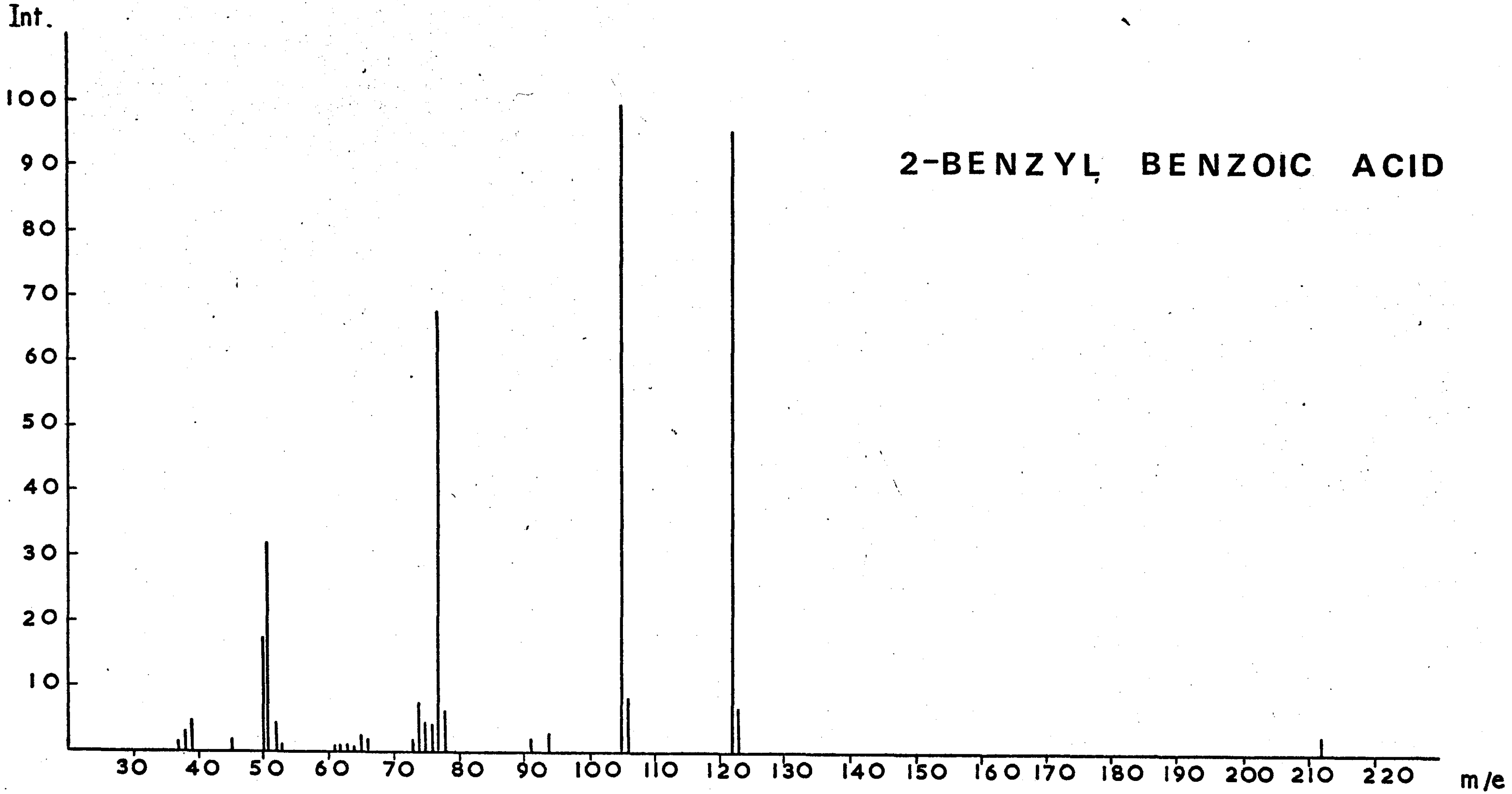


FIG. 3.2.



2-BENZYL BENZOIC ACID

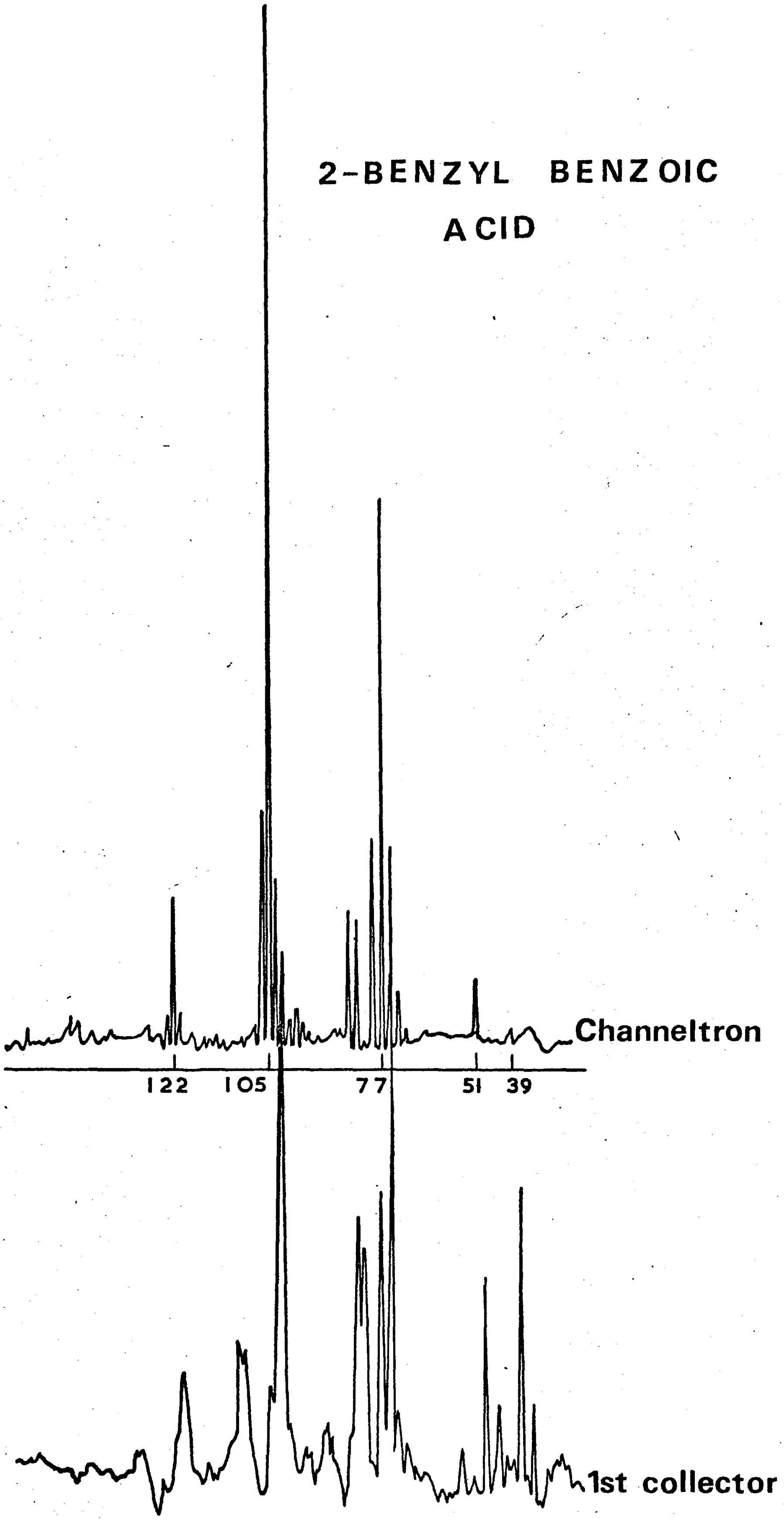

2-BENZYL BENZOIC ACID
Channeltron
122
105
77
51
39
1st collector

FIG. 3.3.

The two peaks in the upper part of the photo differ by 2 Volts while the ones on the lower part differ by 1 Volt. The resolution was better than 1 Volt in 1000 Volts.

After this photo was taken the resolution was marginally improved by using a pen recorder which permitted a thinner trace and a more convenient scale.

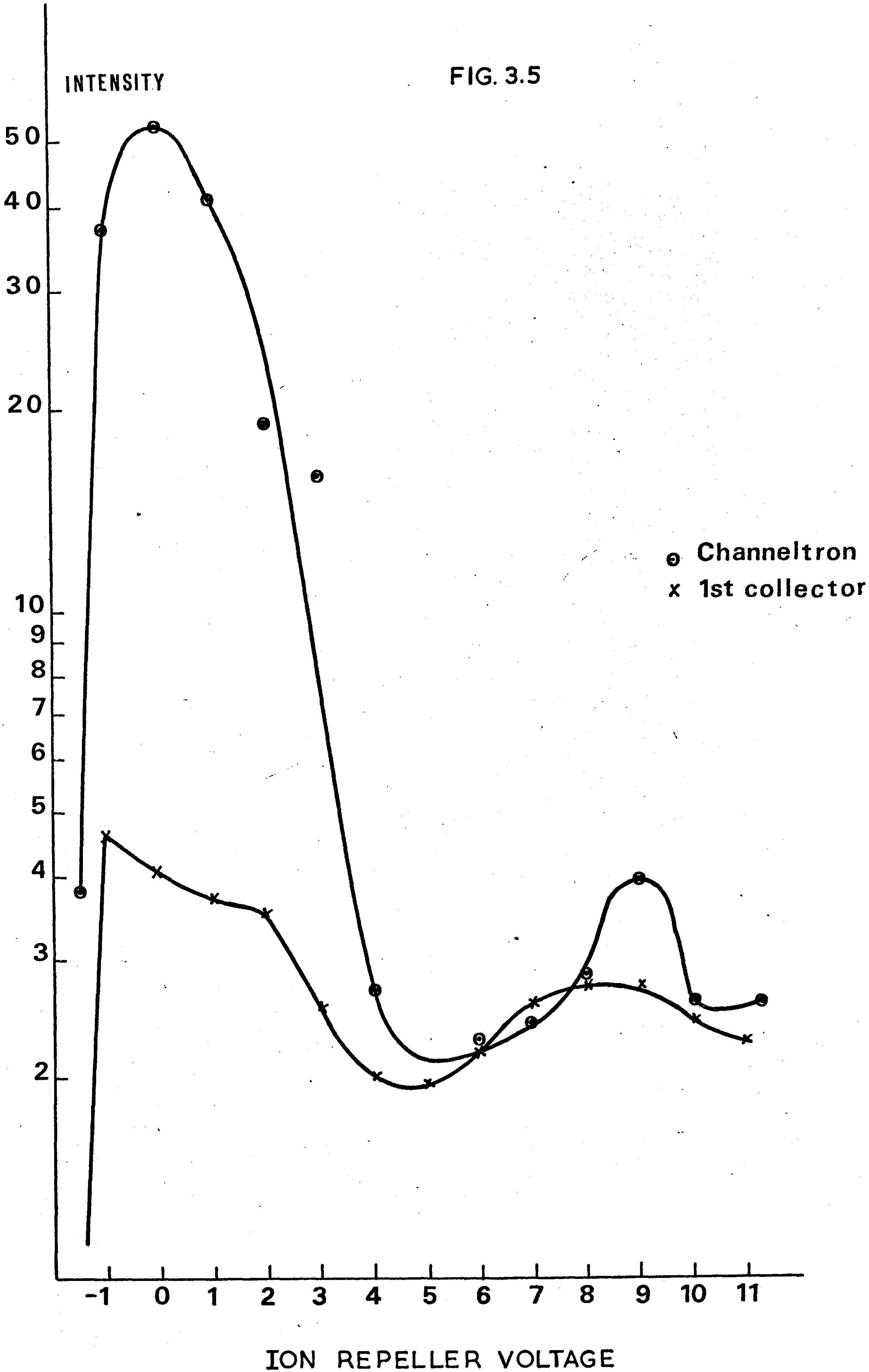
Since the exit slit of the electrostatic sector is less wide than the entrance one, to deduce[1] the intensity of the ionic beam per unit energy interval, the peak height will have to be divided by the mean value of the energy in the interval. For ions of energy 2000 ± 2 Volts when calculating relative intensities the correcting factor is of the order of 0.1%.

Once the electronic instabilities were solved the main limitation in resolution is coming from the spread in energy of the ionic beam. The change of the plates with slits to ones with holes may improve the resolution. A similar effect may also be obtained by a better alignement of the magnetic sector. Further improvement will have to come from modifications in the source or the use of a source of different design.

3. 2. Ion Repeller characteristic - The curves corresponding to the variation of peak height with the ion repeller voltage (relative to the ionization chamber) were obtained both for the first collector and the channel electron multiplier. The curves represented in Figure 3.5 were obtained with the focusing controls of the source set to give the maximum value of the ion current on the second maximum of the ion repeller ($\sim + 9V$).

In the case of the "channeltron" for each setting of the ion repeller voltage, the potential in the plates of the electrostatic sector

FIG. 3.5

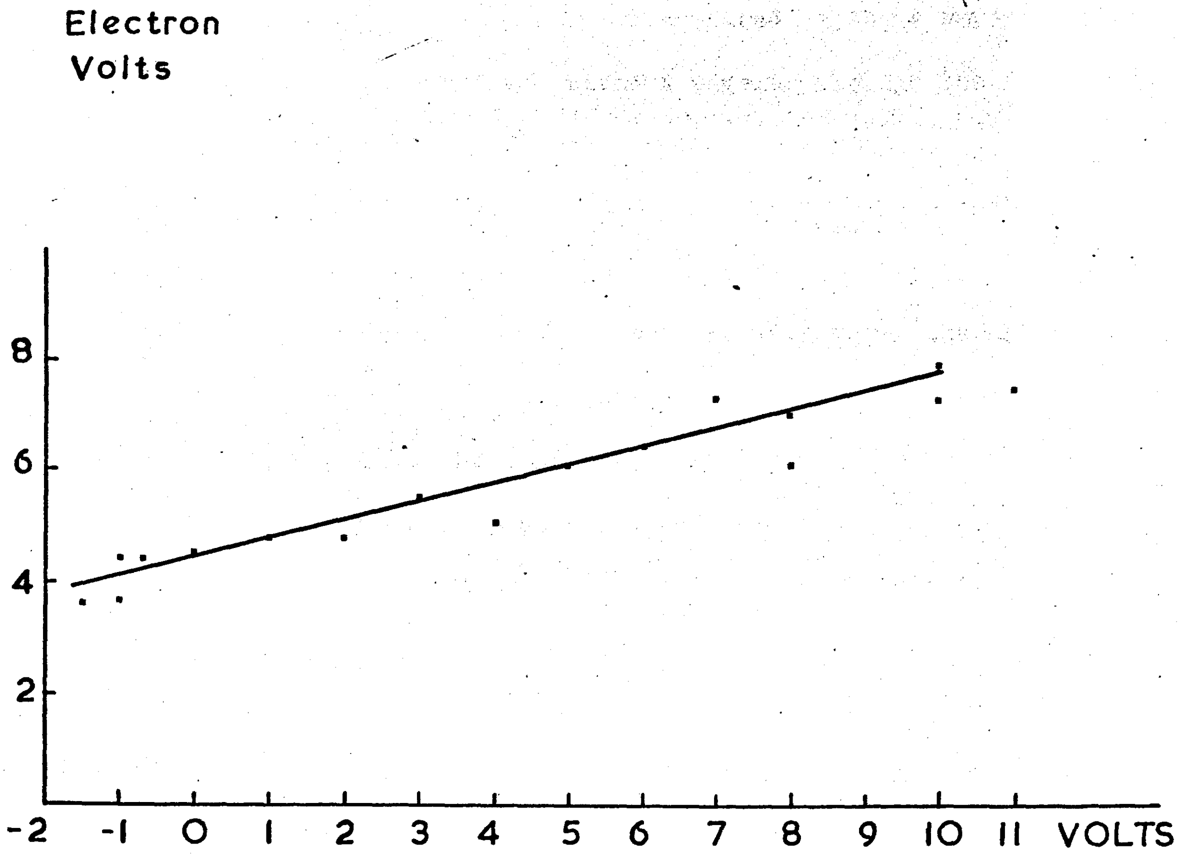


INTENSITY
50
40
30
20
10
9
8
7
6
5
4
3
2
Channeltron
1st collector
-1
0
1
2
3
4
5
6
7
8
9
10
11
ION REPELLER VOLTAGE

Peak 28

Energy Versus I.R. Voltage.

FIG. 3.6.



was also changed to give a maximum value of the ion current. The relation between the variation in the ion repeller voltage and plate potential (calibrated in ion energy) is indicated in Figure 3.6 and, as expected, is linear.

The first maximum[2] corresponds to a more nearly monoenergetic beam since practically all the ions formed with velocity components in the opposite direction of the electrostatic field are not going to leave the ionization chamber; all the ions with velocity components in the direction of the acceleration field would still be transmitted. However, owing to the instability over the first maximum the second one was chosen.

The curves were obtained using peak 28 from the background.

3. 3. <u>Performance of the channel electron multiplier</u> - The channel electron multiplier was used in the continuous current mode.

The initial amplification was not measured as there were no means of comparing the signal with and without passing through the "channeltron". The "channeltron" suffered a rather rough treatment since it was used during the whole positioning and focusing of the instrument often with rather intense signals.

No appreciable change in amplification, with time, was noted during the first part of the work, during which the ion repeller characteristic was determined and curves of intensity versus energy were drawn for background, methane and methanol.

According to the manufacturer's instructions[3] to obtain some proportionality between input and output a gain of less than 10^7 should be used. This corresponded to an applied voltage of less than 1.7 kV. In this part of the work the applied voltage was 1.25 kV except to determine the energy curves of peaks 14 to 18 in the background in which case 1.5 kV were used to obtain the necessary amplification. In this last case instability in the form of afterpulses superimposed to the basic current was observed, in a way similar to the one described by D.S. Evans[4].

The power supply for the electrostatic sector, employed during this part, made use of batteries which discharged slowly requiring frequent replacement or the introduction of new batteries to readjust the potentials of the plates.

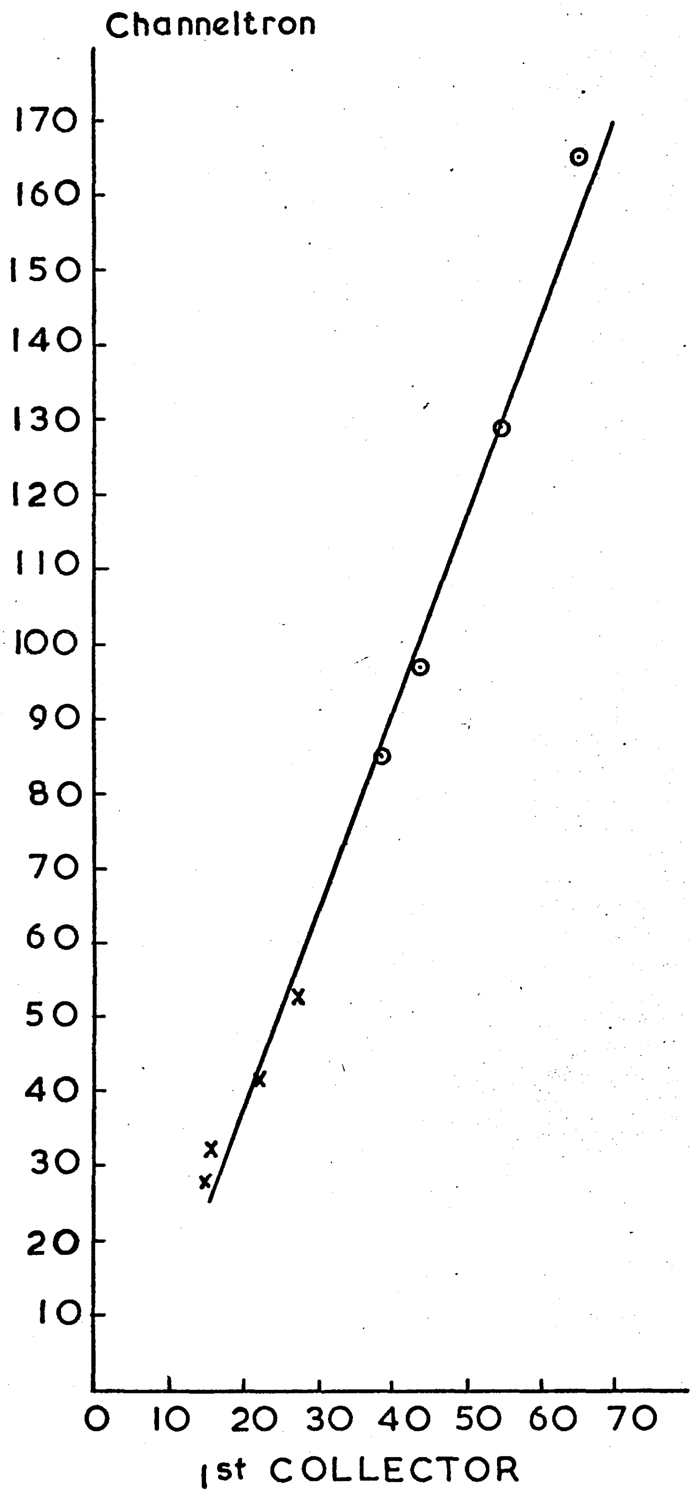
When the new stabilized power supply was introduced and methane and methanol were run again in the apparatus it was noticed that the gain of the multiplier was much lower and it continued to decrease steadily with time. Short lived improvement was obtained by switching off or simply decreasing to a minimum the applied voltage. Baking in vacuum overnight had a slightly longer lasting effect. Degradation of the gain with use in the pulse counting[4,5] mode had previously been observed.

To increase the gain a higher potential difference was applied. For voltages over 1.6 kV saturation effects due to field distortion were observed. In this case owing to wall charging[4] or positively charged particles[6] the multiplication process stops. After a "dead time" the current is restored. When operating in this mode the signal was observed as pulses, that lasted long enough to be detected in the oscilloscope but not in the pen recorder.

As some of the samples took about three hours to run it was necessary to correct for pressure variation. From the manufacturer's instructions[3] and from Figure 3.7, it was assumed that the variation with pressure as measured by the intensity of the signal in the first collector, was linear.

SAMPLE OF AIR.

FIG. 3.7



As previously noted[5] in the pulse counting mode, there was a strong mass discrimination effect against ions of lower mass. To study the change in amplification with the mass of the ion it was however, necessary to consider the variation in peak height of different masses m_1, m_2 with energies between E and E + dE.

Considering the energy distribution to be Maxwellian[7] the number of molecules with the velocity component in the x direction, having a value between v_x and $v_x + dv_x$ is given by[8]

$$dN = N \left(\frac{m}{2\pi kT} \right)^{\frac{1}{2}} \left(\exp - \frac{mv_x^2}{2kT} \right) dv_x$$

Since the component of energy being measured is also in the x direction reference to the direction will be omitted from here on.

The energy of the ions is given by

$$E = \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

where m_1, m_2, v_1, v_2 are the masses and velocities of the ions of species 1 and 2.

$$dE = m_1 v_1 dv_1 = m_2 v_2 dv_2$$

The number of ions in a certain energy interval is given by

$$dN_1 = N_1 \left(\frac{1}{4\pi EkT} \right)^{\frac{1}{2}} \left(\exp - \frac{E}{kT} \right) dE$$

and is therefore independent of the mass, depending only on the total number of ions of species 1, N_1, present.

The value N_1 was taken to be proportional to the height of peaks as obtained from the intermediate collector. It was assumed that a fraction, always the same (for the same speed of scan), of the ions impinging on the collector plate went through the slit, into the electrostatic sector.

From these ions, those with energy in the interval dE were collected at the "channeltron" and the current produced was amplified by a factor X_1. The value measured after the "channeltron" was taken as equal to $X_1 dN_1$. $X_1 \frac{dN_1}{N_1}$ is a function of the energy but the ratio $X_1 \frac{dN_1}{N_1} \Big/ X_2 \frac{dN_2}{N_2}$ should be independent of energy in the interval where the scan is being made[1] and if different from 1, the difference should be due to mass discrimination.

The ratios obtained are indicated in the Tables.

Table 3.1. - Background

m/e	14	18	28	29	32
Ratios[a)]	0	0	1.0	3 ± 1[b)]	1.6 ± 0.2[b)]

a) the ratios indicated are relative to m/e = 28,

b) the error indicated results from the estimated maximum values of the error in measuring peak heights; 29 is very small in the intermediate collector.

Table 3.1 refers to the complete spectra of the background represented in Figure 3.8. The ratios were calculated using the heights of the peaks. Another set of peaks run at a lower speed was used to compare the ratios obtained by measuring either the heights or the areas of the peaks and the results compared well considering the experimental error in the measurement.

No ratios were determined for the background peaks 14 and 18 for

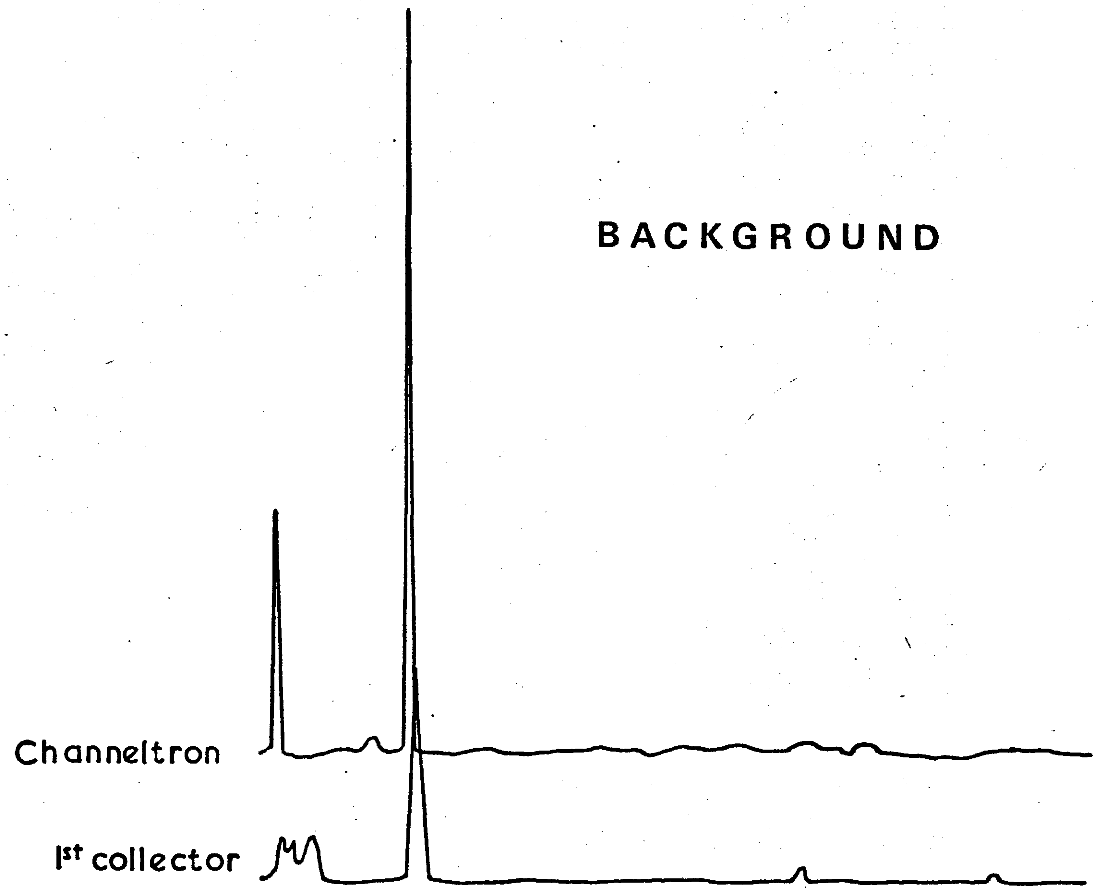


FIG.3.8.

even increasing the signal in the "channeltron" (by increasing the applied voltage) they would still be affected by a very big error as the height of the peaks as measured in the intermediate collector was very small. An error would also be introduced on considering peak 14, since, as will be seen further on, it is not a Gaussian peak and so the dependence on energy is different from that of peak 18.

The mass discrimination effect was then studied with the samples of methane and methanol.

The results obtained for methane are indicated in Table 3.2. The values referred are mean values obtained for various energy intervals (dE), chosen in the medium part of the Gaussian curve, as the error in the measurement of the height is smaller in this part than on the sides of the curve. Values obtained in one energy interval only, showed the same average but smaller dispersion of results.

Table 3.2 - Methane a)

m/e	13	14	15	16	17	18
1st run	0.05 ± 0.02	$0.3_8 \pm 0.0_9$	$0.51 \pm 0.0_9$	1.00	$0.2_o \pm 0.0_2$	$0.2_8 \pm 0.0_3$
2nd run	0.07 ± 0.03	$0.4_1 \pm 0.1_4$	$0.5_o \pm 0.0_2$	1.00	$1.3_1 \pm 0.0_8$	$1.3_8 \pm 0.1_o$

a) ratios relative to m/e = 16.

Both runs of methane (Table 3.2) were made with no noticeable change of gain in the multiplier. A strong discrimination effect against the water peaks 17, 18 was observed for the first run.

For methanol the spectrum had to be divided in two parts that were studied with different amplifications. The results are indicated in Tables 3.3 a) and 3.3 b). From Table 3.3 a) it can be concluded that in this range 28 - 32 the mass discrimination effect is much less important than for lower masses which is in agreement with previous results[5]. The difference in the ratio for peaks 29,30 obtained between the first and second run, is not due only to experimental error but no suitable explanation for it has been found so far.

Table 3.3 a)

Methanol - Higher masses [a)]

m/e	28	29	30	31	32
1st run	0.89±0.03	0.90±0.04	1.32±0.22	1.00	0.99±0.03
2nd run	0.83±0.09	0.72±0.06	0.89±0.13	1.00	1.06±0.10

a) ratios relative to m/e = 31.

Table 3.3 b)

Methanol - Lower masses [b)]

m/e	14	15	17	18
	0.56±0.10	1.00	0.64±0.17	2.10±0.62

b) ratios relative to m/e = 15.

For lower masses the ratio recorded for peak 17 is lower than should be expected but, as will be seen later, peak 17 has a non-Gaussian distribution and the value of the ratio will therefore be a function of the energy interval.

3. 4. <u>Study of the peak shapes</u> - To detect the presence of ions with kinetic energy it was first tried to scan automatically the electrostatic field but the method had to be abandoned due to instability in the

initial circuits which could mislead in the interpretation of the curves.

The method used consisted in setting the potentials of the electrostatic plates manually, by means of a calibrated potentiometer and scanning the magnetic field. Plots of intensity versus ion energy, as obtained from the settings of the potentiometer, were made for a group of peaks. The shapes could then be compared since, in general, instability would affect more than one peak in one setting and could therefore be distinguished from differences in peak shape.

Molecular ions are expected to give rise to Gaussian curves characteristic of Maxwell-Boltzman distributions[7], at the ion source temperature. For this type of function, the distribution obtained for the ions received at the collector[9] is equal to the component in the x direction of the initial distribution.

Peaks corresponding to groups of ions of higher kinetic energy will appear either superimposed on, or as satellites to the one with thermal or quasithermal energy[9,10,11].

For ions coming from secondary reactions between ions and molecules the kinetic energy distribution is connected with the reaction mechanism[12].

Though the absolute value of the energy of the ions could not be measured with a precision better than that indicated in the previous chapter, energy differences could be determined to about one tenth of an electron Volt by calibrating the scale of the potentiometer in electron Volts of ion energy.

The relation between the voltage on a plate of the sector (V_1) and the energy of the ions is given by

$$\frac{a_e 2V_1}{2b} = 2E$$ as indicated in the previous chapter.

A small variation of the energy of the ions δE will correspond to a change δV_1 with

$$\delta V_1 = \frac{2b}{a_e} \delta E \qquad \text{and} \qquad \frac{2b}{a_e} = 0.15$$

and 1 Volt variation in the energy of the ions will correspond to 0.15 Volts of change (with different signals) to each plate.

The first part of the work was done using batteries to supply the stabilized ± 300 Volts and the potentiometer permitted a change of 2 Volts using the 10 turns, so that 0.75 divisions in the potentiometer corresponded to 1 eV of difference of energy in the ionic beam.

The final circuits which included a stablized power supply had the potentiometer set for 3 Volts corresponding to 10 turns. In this case 0.5 divisions corresponded to 1 eV.

3. 5. Detection of metastables - The new power supply for the electrostatic plates had associated a circuit which permitted the scanning manually or automatically in a variable range of voltages. This facility was used to detect metastable transitions[13].

Once a peak of a determined $m/e = m_1$ is focused using ± 300 Volts in the plates, these voltages are changed by the same amount but in opposite directions, decreasing the potential difference, while keeping all the other conditions constant. Such a technique was previously described[14] and is called direct analysis of daughter ions (DADI)[15]. If the ions of mass m_1 decompose between the magnetic and electrostatic field, the new species of $m/e = m_2$ will be detected for new potentials in the plates of value $\pm V_2$ and the mass m_2 will be given by $m_2 = m_1 \times V_2/V_1$.

If the ions m_1 are not stable enough it may happen that no ions are detected for ± 300 V in which case the magnetic field will be set precisely at the value corresponding to mass m_1 and the daughter ions will be searched for in the same way. For all the metastable transitions detected in this work there was a very abundant ion of $m/e = m_1$.

The time taken by an ion from its formation in the source until it crosses the first collector is equal to the time spent in the source plus the time taken along the path in the magnetic sector.

The time spent in the source was determined, using J.A. Hipple's[16] calculations, and is given by $t_1 + t_2$ where t_1 is the time spent inside the ionization chamber and t_2, the time spent between the first slit and the final source slit.

$$t_1 = (2s_1/\alpha_1)^{\frac{1}{2}}$$

$$t_2 = (v_2 - v_1)/\alpha_2 + t_1$$

$$\alpha_1 = E_1\, e/300m$$

$$\alpha_2 = E_2\, e/300m$$

$$v_1 = (2\alpha_1\, s_1)^{\frac{1}{2}}$$

$$v_2 = (2\alpha_2\, l_2 + 2\alpha_1\, s_1)^{\frac{1}{2}}$$

where E_1 is the intensity of the field between the ion repeller and the first slit (volts/cm)

E_2 - intensity of field between first slit and exit plate of source (volts/cm)

e - charge of the ion in e.s.u.

m - mass of the ion in grams

l_1 (cm) - distance between ion repeller and cage (0.3 cm)

l_2 (cm) - distance between cage and exit plate of ion gun (2.1 cm)

s_1 (cm) - distance between middle plane of the electron beam and cage (0.07 cm).

The values obtained for t_1 and t_2 were respectively $t_1 = 7.0 \times \sqrt{m} \times 10^{-8}$s and $t_2 = 1.36 \times \sqrt{m} \times 10^{-7}$s where m is the mass of the ion in atomic mass units.

The ions that decompose after the first collector and before the electrostatic sector travel, after the ion gun, a distance between 53.6 cm and 80.0 cm with an energy of 2000 eV. This corresponds to a travelling time between $8.6 \times \sqrt{m} \times 10^{-7}$s and $1.2 \times 10^{-6}\sqrt{m}$ s where m has the same meaning as before.

The total life-time in this instrument of the metastable ions detected by this method (DADI) is between $1.1 \times \sqrt{m} \times 10^{-6}$s and $1.4 \times \sqrt{m} \times 10^{-6}$s.

3. 6. Background.

3. 6. 1. Results - The background spectrum was taken simultaneously on the first collector and "channeltron" at a pressure of approximately 2×10^{-6} torr (Figure 3.8.) The potential difference between the entrance and exit of the "channeltron" was 1.25 kV.

The largest peak present was peak 28 and the second largest 32. Two small peaks corresponding to mass over charge 14 and 18 were recorded on the first collector only. The two peaks appearing before 32, in the first collector, are metastables to which were assigned the apparent masses 31.1 and 31.7. They were attributed to the decomposition of ions of higher masses coming from the cracking of the pump oil. The low resolution obtained in the first collector did not permit their identification.

Since the amplification obtained for the group of peaks 14 - 18 was much lower than that for peak 28 and 32 the two groups were studied separately using different gains of the "channeltron".

The plots on Figure 3.9 were obtained for a voltage of 1.25 kV between the terminals of the "channeltron". The plots of intensity versus kinetic energy give, as expected, curves very near Gaussian both for m/e = 28 and m/e - 32. A slight asymmetry was attributed to an error in mechanically setting the focusing position, either in the magnetic or electrostatic field.

For peaks 14 and 18 curves of energy distribution were also obtained (Figure 3.10). In this case the voltage applied to the "channeltron" was 1.5 kV. For this potential the instability was noticeable. The dispersion of points relative to the curves drawn is greater than for the case of peaks 28 and 32. No attempt was made to draw the curves corresponding to peaks 15, 16 and 17 since the uncertainty was about the same size as the signal.

From the curves drawn simultaneously for mass 18 and 14 while m/e = 18 presents a Gaussian distribution, for m/e = 14 a small high energy peak (about 3.3 eV) was detected while the existence of another (at about 1 eV), not completely resolved from the thermal one was suspected. A curve similar to the one for peak 14 in Fig. 3.9 was obtained when running methanol which, since such a feature is not a property of peak 14 in methanol[17], was attributed to the background. A sample of nitrogen obtained from the chemistry store and with no further purification, was run at the end of the experimental work. The "channeltron" had by then lost most of its gain and it was necessary to apply a potential voltage of 1.5 kV to obtain a small signal. In spite of the instability it was possible to confirm the presence of two not completely resolved peaks.

At the end of the life of the "channeltron" using the circuits to

FIG. 3.9.

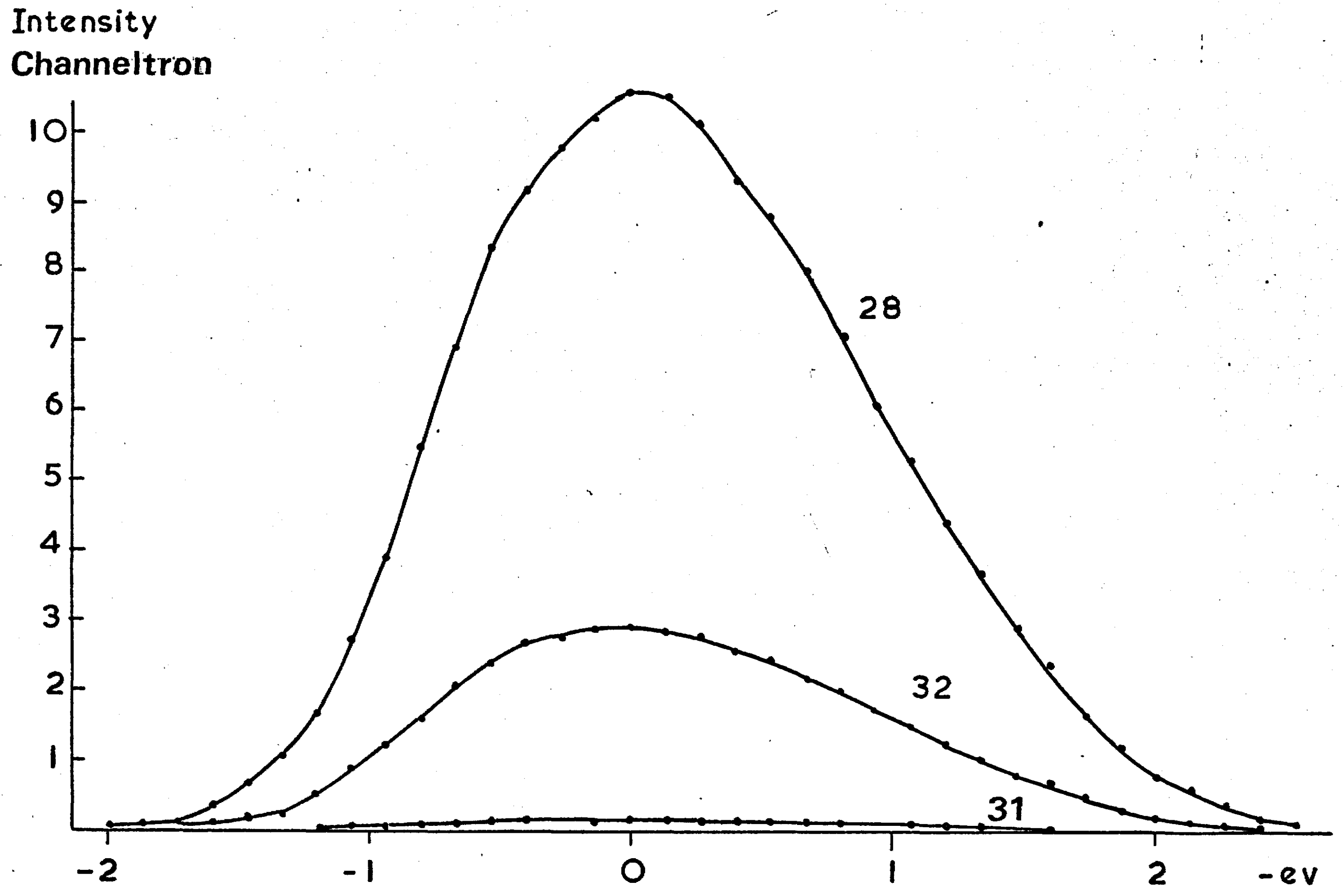
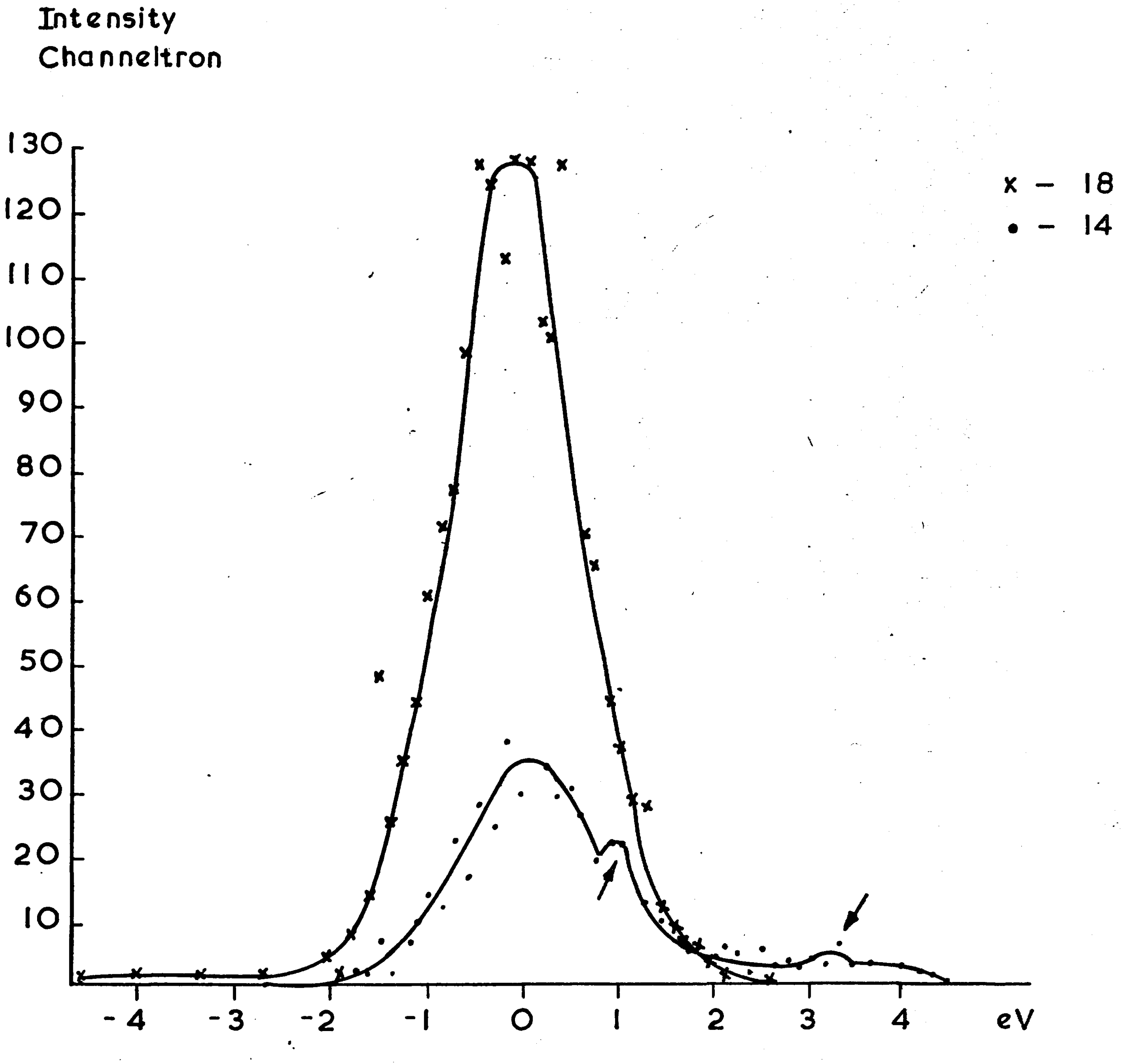


FIG. 3.10.


Intensity
Channeltron
130
120
110
100
90
80
70
60
50
40
30
20
10
x – 18
• – 14
-4
-3
-2
-1
0
1
2
3
4
eV

detect metastable transitions peak 28 was scanned. While the main peak was obtained with ± 298 Volts* on the plates, another peak was obtained for the potential ± 150 Volts. This corresponds to the transition of the parent ion twenty-eight to a daughter ion of mass $\frac{150}{298} \times 28$, i.e. 14.1 ± 0.5.

The signal was obtained with field saturation of the "channeltron", Figure 3.11. shows the photograph of the signal (thrice) obtained from the oscilloscope. The whole energy scale was scanned and for no other energy could any signal be observed. In saturation conditions the

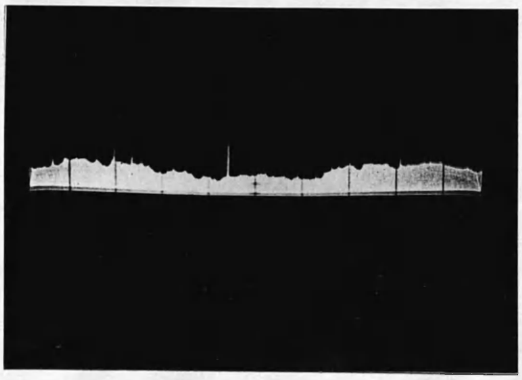


Fig. 3.11.

---

* This value was obtained with the DANA digital voltmeter and corresponded to a reading of 300 Volts on the solartron meter. The systematic error due to the low impedance of the DANA meter does not affect the ratios of the potentials. The absolute error committed in the readings using this voltmeter was ± 1.

pulse height is not proportional to the input signal[3].

A metastable transition for peak twenty-eight corresponds to a lifetime of the ion between 5.8×10^{-6}s and 7.4×10^{-6}s.

3. 6. 2. <u>Discussion</u> - The presence of ions with excess kinetic energy for mass fourteen, when nitrogen is bombarded with electrons of over 50 eV was first reported by Vaughan[20] and studied by Tate and Lozier[18].

Table 3.4 - Energetic ions for m/e = 14.

1st peak	2nd peak	3rd peak	References
1 - 2 eV	2 - 7 eV	4 - 8 eV	a)
0	~ 1.3	~ 3.2	b)
0	1	4	c) d) e)
0	~ 1	~ 3.3	This work

a) J.T. Tate and W. W. Lozier, Phys. Rev., (1932) <u>39</u>, 254.

b) O. Osberghaus and R. Taubert, Angew Chem. (1951) <u>63</u>, 287
also referred by
J. Durup and F. Heitz, J. Chim. Phys. (1964) <u>61</u>, 470.

c) P.M. Hierl and J.L. Franklin, J. Chem. Phys. (1967) <u>47</u>, 3154.

d) 1st and 2nd peak
L.J. Kieffer and R.J. Van Brunt, J. Chem. Phys. (1967) <u>46</u>, 2728.

e) 1st and 3rd peak
J.W. McGowan, L. Kerwin, Proc. Phys. Soc. (1963) <u>82</u>, 357.

This, with other results of previous observations are indicated in the Table 3.4. The results reported for this work correspond to the medium points of the satellite peaks. There seems to be good agreement between the results in this work and those reported in the literature.

In this work the peak with thermal energy only, corresponds simultaneously to ions coming from the dissociation of N_2^+ giving N^+, to N_2^{++} and since the work was done with the background spectrum possibly to ions CO^{++}. Since no CO^{++} ions with excess energy have been reported it was assumed they contribute only to the thermal energy peak.

The knowledge of the translational energy permitted[19], by using the potential energy curves for the various states of the N_2^+ ion[21,22] to determine the probable processes originating the first and second peaks:

Process 1 $\quad N_2^+\ (D^2\Pi g) \longrightarrow N(^4S^o) + N^+(^3P)$

Process 2 $\quad N_2^+\ (C^2\Sigma_u^+) \longrightarrow N(^2D^o) + N^+(^3P)$

The group of ions with higher kinetic energy is attributed by the same authors[19], to Process 3 i.e.

$$N_2^{2+}\ (A^3\Pi g) \longrightarrow 2\ N^+(^3P)$$

in which case the kinetic energy is due to the coulombic repulsion of the two ions, and was calculated[19] to be at least 4 eV. This value which agrees with the experimental results obtained by Hierl and Franklin[19] is however higher than the one obtained in this work and also by O. Osberghaus and R. Taubert[23]. McCulloh and Rosenstock[24] suggest the decomposition of N_2^{++} from a lower lying state[25].

The metastable dissociation of N_2^+ giving N^+ has previously been reported both as a collision induced[26] and a unimolecular[27] process. Since the transition was detected on saturation conditions no attempt was made to study the variation of intensity with pressure. A "channeltron" during its "higher gain" period or alternatively working on a pulse counting mode would permit one to decide on the contributions of each of the two processes. The transition was detected as a pulse so no peak shape could be determined, and the pulse was assumed to correspond to the medium of a possible peak. The pulse was detected at 150 V and not at 149 V, as would be expected. This could be due to an excess kinetic energy, but the difference 1 Volt is of the order of the error in the measurement of the voltage and quantitative values, determined from it would be meaningless.

3. 7. Methane.

3. 7. 1. Results - Methane obtained from the Chemistry Store and with no further purification was run using 1.25 potential difference in the "channeltron". The spectra recorded simultaneously in the first collector and the "channeltron" are represented in the photo (Figure 3.12).

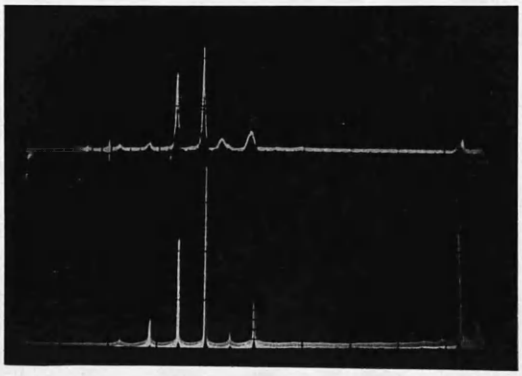


Fig. 3. 12.

The study of the variation of intensity of peaks in the "channeltron" with the energy was again made. The background was not accounted for since it was extremely small in the first collector and as had been seen previously in these conditions it was not recorded in the "channeltron".

The presence of a small percentage of water mixed with methane, was noted in the spectra. To calculate the effect of water on peak sixteen it would be necessary to run a sample of water and plot peak sixteen coming from water versus energy. This was not attempted. It was assumed that peak sixteen from methane, corresponding to a molecular ion should have a Gaussian distribution. If the fragment ion sixteen (coming from water) also had a similar distribution the resulting curve would also have the same shape while any features of the curve for the fragment ion would appear superimposed on the Gaussian shape. The curves obtained for masses sixteen, fifteen and fourteen are represented in Figure 3.13. Both masses sixteen and fifteen show Gaussian distributions while mass fourteen is asymmetric with an increased number of ions on the high kinetic energy side. The heights of the ions of mass thirteen and twelve were too small to allow the plotting of meaningful curves.

Table 3.5. - Metastables from methane.

MAIN PEAK		METASTABLES		Transition
E.S. Voltage*	Mass	E.S. Voltage	Mass	
298	16	275 - 281 a)	14.9	$[CH_4]^{+\cdot} \longrightarrow [CH_3]^{+} + H^{\cdot}$ 1)
		256 b)	13.7	$[CH_4]^{+\cdot} \longrightarrow [CH_2]^{+\cdot} + 2H^{\cdot}$ 2)
298	15	278 - 280 a)	14.0	$[CH_3]^{+} \longrightarrow [CH_2]^{+\cdot} + H^{\cdot}$ 3)
298	14	279	13.1	$[CH_2]^{+\cdot} \longrightarrow [CH]^{+} + H^{\cdot}$ 4)

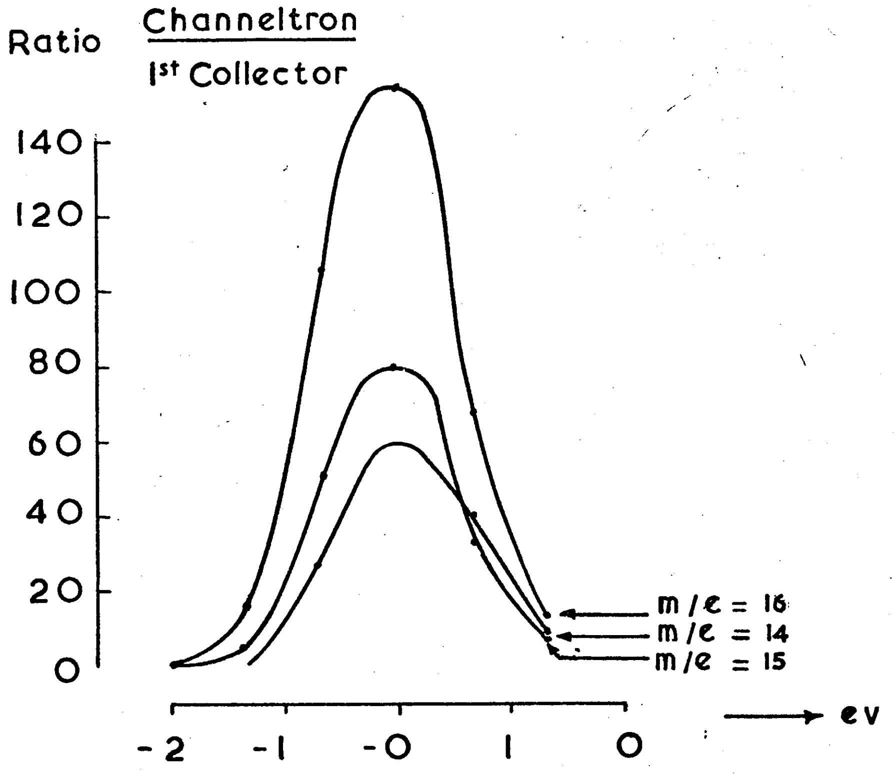
* E.S. voltage indicates half the potential difference between the plates.

a) Pulses were detected over a wide range of voltages. See Discussion.

b) Much less intense than the others.

With the "channeltron" working in saturation conditions and the

FIG. 3.13


Ratio
Channeltron
1st Collector
140
120
100
80
60
40
20
0
m / e = 16
m / e = 14
m / e = 15
-2
-1
-0
1
0
ev

peaks showing up as pulses, the metastable transitions indicated in Table 3.5 were detected. While scanning peak fifteen a smaller satellite peak appeared for ± 296 V in the plates of the electrostatic sector. This peak was big enough (about 1% of the main peak) to be possible to detect with the pen recorder after lowering the gain in the "channeltron" and is represented in Figure 3.14. The difference of 2 Volts relative to the main peak, in the potential applied to the plates, corresponds* to a difference in mass of 0.1 a.m.u. or to a difference in energy of 13 eV relative to the main beam. Since the 0.1 a.m.u. may be affected by up to 50% of error it is possible that it is a group of ions, part of the main beam and not resolved by the magnetic sector or otherwise a metastable transition occurring in the field free region between the magnetic and electrostatic sector.

3. 7. 2. <u>Discussion</u> - The excess kinetic energy of methane ions as determined by Morrison and Stanton[10] could not be detected in this work

---

* $mv = k$ where k is a constant for the ions entering the electrostatic sector

$$\frac{1}{2} mv^2 = E$$

$$\frac{1}{2} mv \times \frac{mv}{m} = E$$

$$k^2 = 2m E$$

$$2\Delta mE + 2m\Delta E = 0$$

$$\frac{\Delta m}{m} = - \frac{\Delta E}{E}$$

$$\Delta V_1 = 0.15 \Delta E$$

$$0.15 \frac{\Delta m}{m} = - \frac{\Delta V_1}{E}$$

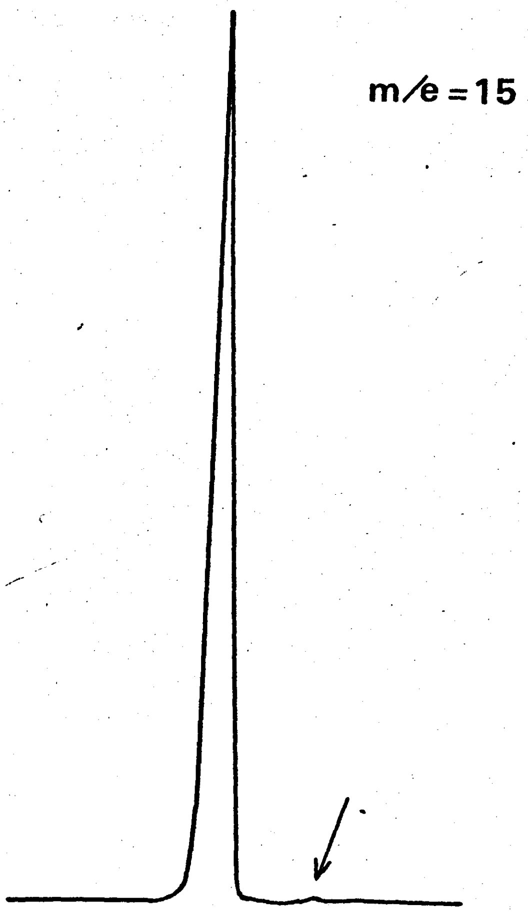


FIG. 3.14.

as half the beam width due only to thermal energy is greater than the maximum value of kinetic energy they recorded. The particular shape of the energy distribution curve for mass fourteen could be due to the presence of some air mixed with methane[28], though peak fourteen coming from air shows an energetic peak at about 1 eV which seems higher than the possible centre of an energetic peak causing the bump on the curve The peculiar shape of the energy curve for mass fourteen was noticed previously by R. Fuchs and R. Taubert[29].

The satellite of peak fifteen showing up for ± 296 Volts in the electrostatic sector plates was not included in the table since it was considered very unlikely that its formation should be due to a loss of kinetic energy without loss of mass from the ion m/e = 15. Such a process could be caused by collision with the slits in which case it should be observed for other ions.

Another origin could involve its formation in the first field-free region of the mass spectrometer in which case it would be a metastable of nominal mass approximately 15.1. The transitions $CH_5^+ \longrightarrow CH_4^{+\cdot} + H^\cdot$, or $^{13}CH_4^{+\cdot} \longrightarrow {}^{13}CH_3^+ + H^\cdot$ would originate metastables of mass 15.06. The first reaction has been observed at higher pressures[30] and for both of them the resulting metastables would be much smaller than 1% of peak fifteen. Various metastable transitions from the ions coming from oil could be responsible. In this case, the real mass of the fragment ion being higher than fifteen would justify the higher relative intensity of the peak due to the discrimination effect of the "channeltron".

Collision induced metastable transitions in normal methane have been known[31,32] for a long time while in 1965, Öttinger[33] followed by other authors[34,35] confirmed the existence of unimolecular processes.

No study of variation of intensity with pressure was made but since Process 2) in Table 3.5 was considered by L.P. Hills <u>et al</u> [35] as being exclusively collision induced, all the other transitions are assumed to be the result at least in part of collision induced processes.

For processes 1) and 3) pulses could be detected over a wide range of energies. It was impossible to distinguish between one wide peak and various single peaks. The possible meaning of a wide peak in energetic terms was studied in more detail for methanol.

3. 8. <u>Methanol</u>.

3. 8. 1. <u>Results</u> - Two spectra of methanol (BDH Analar) are shown in Figures 3.15 and 3.16.

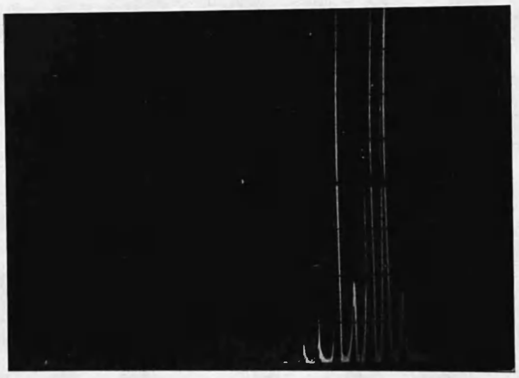


Fig. 3.15.

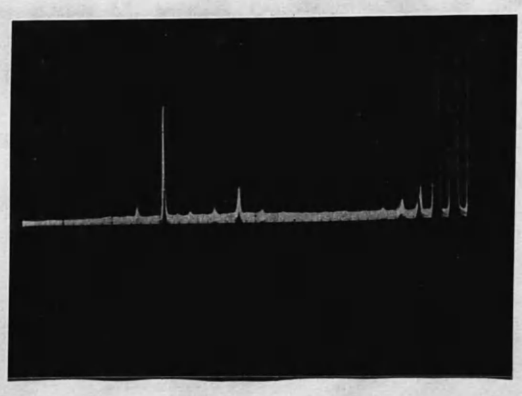


Fig. 3.16.

Figure 3.15 shows the relation in intensity between m/e = 15 on the left side of the photo and the group of peaks around m/e = 32 that are off scale. Figure 3.16 shows the region around m/e = 15 in a different scale. The first photo was obtained using 1.25kV on the "channeltron" while for the second one the applied voltage was 1.5 kV.

As for nitrogen and methane the shapes of the peaks were studied. The curves corresponding to m/e = 28, m/e = 29, m/e = 31 and m/e = 32 were Gaussian.

For m/e = 17 the ratio between the heights of the peak in the "channeltron" and first collector, necessary to correct for pressure variation, could not be determined as the peak was too small in the first collector. The height of peak fifteen (in the first collector) was used instead assuming that the ratio between the heights (in the first collector) of peaks seventeen and fifteen was constant. The curves for m/e = 15 and m/e = 17 are represented in Fig. 3.17. For m/e = 17 two peaks were recorded with a distance of about 1.9 eV between the central parts. The dispersion of the points between about 2.5 eV and 4 eV was attributed to the instability of the "channeltron". The same was considered as the explanation for the peak on the lower energy side of fifteen. This small satellite peak is only defined by a very low intensity in the "channeltron" while scanning for -1.2 eV. To confirm these data it would be necessary to repeat the scans but when this was tried the gain of the "channeltron" was too low.

Working again in a saturation mode the metastable transitions indicated in Table 3.6. were detected.

Table 3.6. /

FIG. 3.17.

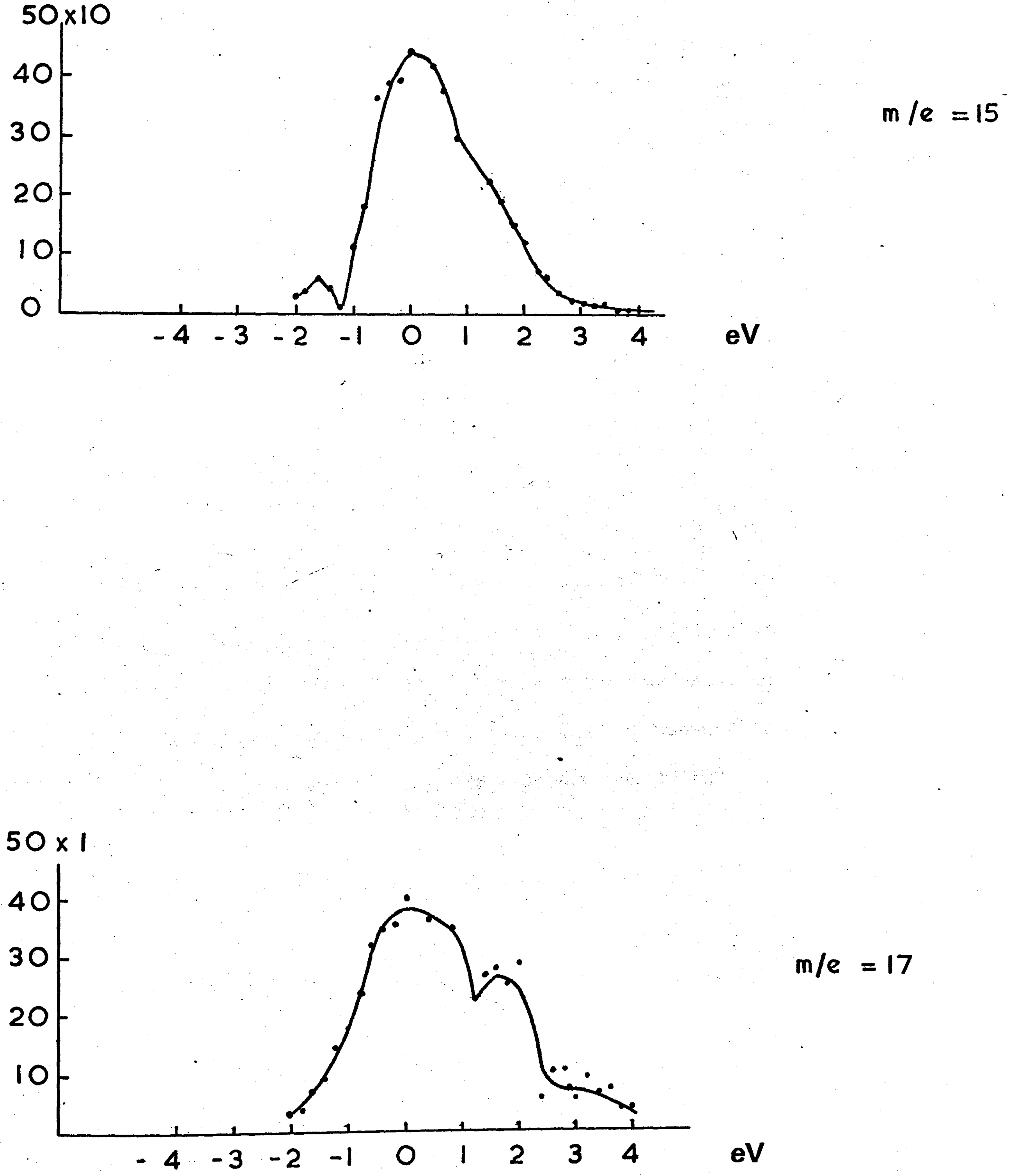

50x10
40
30
20
10
0
-4
-3
-2
-1
0
1
2
3
4
eV
m /e =15
50 x 1
40
30
20
10
-4
-3
-2
-1
0
1
2
3
4
eV
m/e = 17

Table 3.6. Metastables from Methanol.

Main Peak		Metastables		Decomposition
E.S. Voltage*	Mass	E.S. Voltage	Mass	
298	32	288	31	$CH_3OH^{+\cdot} \longrightarrow CH_2OH^+ + H^\cdot$ 1)
298	31	288	30	$CH_3O^+ \longrightarrow CH_2O^{+\cdot} + H^\cdot$ 2)
		275-278[a)]	29	$CH_2OH^+ \longrightarrow CHO^+ + 2H^\cdot$ 3)
298	30	288	29	$CH_2O^{+\cdot} \longrightarrow CHO^+ + H^\cdot$ 4)

* E.S. Voltage indicates half the potential difference between the plates.

a) Very wide peak?

3. 8. 2. <u>Discussion</u> - From the results reported in the literature[17] peak fifteen has a satellite peak with 2.7 eV of kinetic energy but its intensity is less than 1% and, in this work, the error in the points due to instability is greater than this so that it was not possible to detect. For peak seventeen the energy determined is the same as obtained by Tsuchiya[17] while the ratios of the abundances of the peaks with and without kinetic energy were $\frac{1.3}{2.0}$ from Tsuchiya's work and $\frac{1.4}{2.0}$ from this work.

Tsuchiya attributes the formation of energetic OH^+ ions to three processes:

$$\begin{tikzcd} CH_3OH \arrow[r] & CH_3OH^+ \arrow[r] \arrow[dr] & OH^+ + CH + 2H \\ & & OH^+ + C + 3H \end{tikzcd}$$

$$CH_3OH \longrightarrow CH_3OH^{2+} \longrightarrow CH_3^+ + OH^+$$

The difference in the kinetic energies detected by him for CH_3^+ and OH^+ compared with the values expected from the conservation of momentum was attributed to the loss of total energy as rotational by the OH^+ ion.

Two[36,37] very thorough papers have been published recently, discussing, for normal and deuterated methanols, the metastable peaks and their use to energetically study the fragmentation of the molecular ion.

The metastable transitions in the Table 3.6. are the same detected by C. Lifshitz et al[37] and the most abundant in Beynon's[36] paper with the exception of the one resulting from process 2 the abundance of which was not indicated as it is obscured by the transition of the heavy isotope ions $^{13}CH_2O \longrightarrow {}^{13}CHO$.

In both works process 3) is characterized by a wide metastable peak so it was assumed that the wide range of energies (275V - 278V) of the sector over which the process could be detected corresponded to a wide peak.

It was necessary to establish the relation between the width of the peak, in energy, as detected after the electrostatic sector and the kinetic energy released in the dissociation. The calculation made parallels that of Beynon et al[38].

Consider an ion m_1^+ which passes through the first collector slit with a kinetic energy equal to $\frac{1}{2} m_1^+ v_a^2 = eV$ where v_a is its velocity and eV the acceleration potential of the electrostatic field just after the source.

Before entering into the electrostatic sector the ion dissociates into an ion m_2^+ and a neutral fragment $m_1 - m_2$, i.e.

$$m_1^+ \longrightarrow m_2^+ + (m_1 - m_2)$$

The velocities of m_2^+ and $(m_1 - m_2)$ are v_b and v_c respectively and T represents the total decrease of internal energy. The law of conservation of energy requires

$$T + \frac{1}{2} m_1 v_a^2 = \frac{1}{2} m_2 v_b^2 + \frac{1}{2} (m_1 - m_2) v_c^2 \text{ ----------(1)}$$

and the conservation of momentum

$$m_1 v_a = m_2 v_b + (m_1 - m_2) v_c \text{ -----------------------(2)}$$

Eliminating v_c between equation (1) and (2) and putting $v_b/v_a = x$ the following equation is obtained

$$x^2 - 2x + \left[\frac{m_1}{m_2} - \frac{m_1 - m_2}{m_2} \left(1 + \frac{T}{eV} \right) \right] = 0$$

Making $(m_1 - m_2) / m_2 = \mu$ it gives

$$x^2 - 2x + (1 - \mu T/eV) = 0$$

$$x = \frac{v_b}{v_a} = 1 \pm \sqrt{\mu T/eV}$$

When entering the electrostatic sector the ions are deflected according to the equation

$$a_e E_1 = m_1 v_a^2$$

$$a_e E_2 = m_2 v_b^2$$

where E_1 and E_2 are the values of the field between the plates and a_e is the radius of the sector.

The potential of one plate V_1 which was the quantity measured as the potentials were equal but with opposite signals is given by

$$V_1 = \frac{E}{4b}$$ where 2b is the spacing between the plates.

$E_1 = kV_1$ and $E_2 = kV_2$ where k is a constant.

$$\frac{v_b^2}{v_a^2} = \frac{V_2/m_2}{V_1/m_1} = \left[1 \pm \sqrt{\mu T/eV} \right]^2$$

$$V_2 = V_1 \frac{m_2}{m_1} \left[1 \pm 2\sqrt{\mu T/eV} + \mu T/eV \right]$$

and the width of the peak in Volts is

$$d(\text{Volts}) = 4V_1 \ \frac{m_2}{m_1}\sqrt{\mu T/eV}$$

For transition $31^+ \longrightarrow 29^+ + 2$

$m_1 = 31$

$m_2 = 29$

$d = 3$ - peak width was made equal to the range over which the peak was detected

$V_1 = 298$

$\mu = 0.69$

$eV = 2000$

$\times\left(\frac{V}{E}\right) \cdot 1.41$

The value obtained for T, kinetic energy released is 0.209 eV. This value is much smaller than the value 1.42 determined by Beynon et al[36] and 1.33 by C. Lifshitz et al. The difference could be due to the different geometry of the apparatus. The determination of peak width in this work was very arbitrary as the peak profile was not available and as d is susceptible to a great error, nothing can be concluded with confidence.

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Chapter 4.

Criterion for the Identification of Low Resolution Mass Spectra by Retrieval from a Data Bank.

4. 1. Introduction - The rapid increase in the number and variety of mass spectra of organic compounds has created a problem in information retrieval. There are currently some seventeen thousand five hundred spectra available in various collections, which number will increase rapidly.

Searches are now generally made using computer methods, keeping the information stored either on a magnetic tape or on a disc. There have been many different approaches to this problem and these may be broadly split into two classes: those which try and identify the particular compound by some internal properties of the molecules, as is exemplified by the studies of Tal'roze *et al*[1], and the larger group, in which some aspects of the spectrum of the unknown are sought in a known compound embedded in a data bank. The latter, in general, has involved the matching of a certain number of peaks in the compound analysed with those of the spectra on file. Several methods have previously been employed, using the five largest peaks,[2] six,[3] the largest, or two largest in each successive fourteen units[4,5] and so on. One additional difficulty which is encountered is the fact that the spectrum of the same compound may vary from one mass spectrometer to another, often significantly so[6]. Many such variations have appeared in the literature during the past nine years and the whole of this literature has been recently examined by Grotch[7].

The method to be discussed is a statistical one. As such it is unreasonable to expect a single definite solution. Often the use of wider confidence limits will admit of more than one solution.

4. 2. Calculation of the divergence - Information theory which in its modern form may be traced back to the classical communications of Shannon[8] and Wiener[9] was used in the development of the present method. The treatment of Kullback[10] was closely followed.

The "divergence" is used to measure the difficulty in discriminating between two spectra coming from the same compound or from different compounds.

The "divergence" J(1,2) is calculated by means of the formula

$$J(1,2) = N_1 \sum_{i=1}^{c} (p_{1i} - p_i) \ln(p_{1i}/p_i) + N_2 \sum_{i=1}^{c} (p_{2i} - p_i) \ln(p_{2i}/p_i) \qquad \text{----------} \ (1)$$

where N_1 and N_2 are the sums of the abundances of the ions respectively in the mass spectrum of the unidentified compound and in that of the member of the data bank, c is the total number of categories of ions in both spectra, that is total number of different m/e values. The logarithms used throughout are to the base e (Naperian); p_{1i} and p_{2i} refer to the "probabilities" of the various mass to charge ions in the spectra 1 and 2 respectively while i refers to the running number of mass in each; p_i is the probability of occurrence of an ion of species i coming either from spectra 1 or 2. The quantities x_i and y_i refer to the abundance of the i^{th} ion in the unknown and reference compounds. If spectra 1 and 2 were different spectra of the same compound and if there were no differences due to experimental conditions, $p_{1i} = p_{2i} = p_i$ and the "divergence" $J(1,2) = 0$. In the calculations p_{1i}, p_{2i} and p_i are replaced by their best unbiased estimates in the observed spectra which will be from here on referred as p_{1i}, p_{2i} and p_i their values being:

$$p_{1i} = \frac{x_i}{N_1} \quad ; \qquad p_{2i} = \frac{y_i}{N_2} \quad ; \qquad p_i = \frac{x_i + y_i}{N_1 + N_2}$$

Not all the ions in the spectra were used. It is common to find in nearly all spectra some twenty to thirty ions of a reasonable abundance, the remainder being insignificant. As experimental data was considered these small values were also likely to be affected by relatively larger errors.

When the complete spectrum was available a compromise was reached by using the twenty five peaks; later on only eight peaks were used to appreciate how this affected the results as only eight peaks were available in the second tape used. The maximum number of categories $\underline{c}$ was then 50 or 16 respectively.

Considering the comparison between the unknown (U) and reference (R) spectra as a problem in the theory of sets, one is concerned with the intersection of these which, if they prove disjoint $U \cap R = \phi$, yield ϕ, an empty set. However, some electrical noise is always present and although this may be of a very low level it has the important result of ensuring that this intersection is not empty. The level of noise was chosen to be below the lowest peak height recorded, 0.01 and all peaks that were not used in the calculation were treated as noise. The level of noise was considered to be very low and the same for both spectra, the first condition being essential for the approximations that were made. Two values for the noise level were tried $\phi = 0.00001$ and $\phi = 0.0001$ and as the results showed very little difference the latter was chosen.

The maximum value of the divergence corresponds to the particular case in which none of the peaks has a match and was calculated as follows:-

For two nearly disjoint sets of mass-to-charge values, it can be seen from equation (1) that to each mass number in the unknown corresponds a term:

$$N_1 \left(\frac{x_i}{N_1} - \frac{x_i + \phi}{N_1 + N_2}\right) \ln \left(\frac{x_i}{N_1} \Big/ \frac{x_i + \phi}{N_1 + N_2}\right) + N_2 \left(\frac{\phi}{N_2} - \frac{x_i + \phi}{N_1 + N_2}\right) \ln \left(\frac{\phi}{N_2} \Big/ \frac{x_i + \phi}{N_1 + N_2}\right)$$

where ϕ represents the noise level.

For $\phi \sim 0$ this reduces further leading to

$$N_1 \left(\frac{x_i}{N_1} - \frac{x_i}{N_1 + N_2}\right) \ln \frac{N_1 + N_2}{N_1} + N_2 \left(- \frac{x_i}{N_1 + N_2}\right) \ln \left(\frac{N_1 + N_2}{N_2} \cdot \frac{\phi}{x_i}\right) =$$

$$= \frac{N_2 x_i}{N_1 + N_2} \left[\ln (N_1 + N_2) - \ln (N_1 + N_2) - \ln \frac{N_1}{x_i} + \ln N_2 - \ln \phi \right]$$

Making $\dfrac{x_i}{N_1 + N_2} = q_{1i}$ the above becomes

$$N_2 \; q_{1i} \cdot \ln \left(p_{1i} \cdot \frac{N_2}{\phi}\right)$$

When considering the terms from the second spectrum - the reference y_j represents the ion abundance at a particular mass number while the corresponding ion in the first spectrum $x_j = \phi$. For each mass the corresponding term in the divergence is

$$\frac{N_1 \, y_i}{N_1 + N_2} \cdot \ln \left(\frac{y_i}{N_2} \cdot \frac{N_1}{\phi}\right)$$

Making $\dfrac{y_j}{N_1 + N_2} = q_{2j}$ the expression simplifies to

$$N_1 \; q_{2j} \cdot \ln \left(p_{2j} \cdot \frac{N_1}{\phi}\right)$$

For all the masses extracted from spectrum one, the unknown,

$$\sum_x = \frac{N_2}{N_1 + N_2} \sum_{i=1}^{c'} x_i \; \ln \left(\frac{x_i}{N_1} \cdot \frac{N_2}{\phi}\right)$$

and for those originating in spectrum two, the reference,

$$\sum_{y} = \frac{N_1}{N_1 + N_2} \sum_{j=1}^{c''} y_j \ \ln \left(\frac{y_j}{N_2} \cdot \frac{N_1}{\phi}\right)$$

The divergence for these two, nearly disjoint sets is equal to

$$DIV = \sum_{x} + \sum_{y} = \frac{N_2}{N_1 + N_2} \sum_{i=1}^{c'} x_i \ \ln \left(\frac{x_i}{N_1} \cdot \frac{N_2}{\phi}\right) + \frac{N_1}{N_1 + N_2} \sum_{j=1}^{c''} y_j \ \ln\left(\frac{y_j}{N_2} \cdot \frac{N_1}{\phi}\right) \qquad (2)$$

$$c' = c''$$

The criterion, although it seems rather elaborate, would become quite simple if the spectra were normalized for the sum of ion abundances instead of, as is common practice, for the highest peak. In such a case $N_1 = N_2$ and the expression for the divergence would be reduced to

$$J(1,\ 2) = \sum \left(\frac{x_i - y_i}{2}\right) \ln \frac{x_i}{y_i} \approx \sum \frac{(x_i - y_i)^2}{x_i + y_i}$$

4. 3. <u>Experimental</u> - Two sets of data were available, the first a tape containing spectra 1 to 3000 from the M.S.D.C. series and the second the eight peak index (1971 Edition Magnetic Tape MS0075). Both tapes were kindly loaned by the Mass Spectrometry Data Centre, Aldermaston, Berkshire, England.

The spectra used as unknown were from the A.P.I. and Dow Collections.

Since the most difficult to identify are usually isomers, mostly chain or position isomers the same molecular weight was chosen as a pre-requisite for identification. To speed the search, the tapes were reorganized by increasing molecular weight as detailed in the Section 4.5.

A different pre-filtering step like a certain range of molecular weights or the same most abundant peak could have been chosen; this last one for practical reasons would require a different way of ordering the tape. The pre-filtering step though affecting the way the search was conducted, would not influence the criterion for identification which was the main point of our study.

The two programmes first written SR and R2 (see Appendix) included a pre-requisite of the same formula that was suppressed in latter programmes.

It was also required that the largest peak in the unknown should also be present in the nine (when the divergence was calculated for twenty-five peaks) or eight (when calculated for eight peaks only) largest peaks for the compound on the tape and also that the largest peak on the tape should be present within the same limits in the unknown.

Once these pre-filtering conditions were satisfied the programme called sub-routine Diver. This sub-routine calculates simultaneously the first term of expressions (1) and (2) using the information from the unknown and searching the reference and then the second term of both expressions using data from the reference and searching the unknown. The total for expression (1) is then divided by that for expression (2) so that the result is the normalized divergence with the maximum value 1.

This calculation finished, the search proceeded for a second match in the reference file and so on until all the compounds of the same molecular weight had been tested. In two cases the whole file (900 compounds) was searched. The compound name, spectrum origin, divergences and, if required, the spectra are printed out. Identification is made in general by the minimum value of the divergence, the divergence varying between 0 and 1. The programmes written in Fortran IV are included in the Appendix. The investigation was carried out upon a 360/50 I.B.M. computer sited in Edinburgh with an I.B.M.

2780 terminal at the University of Glasgow.

4. 4. Results and Discussion - Table 4.1 refers to the first 900 spectra of the M.S.D.C. file of complete spectra.

Table 4.1

NAME OF COMPOUND	M.W.	DIV 25 a)	Minimum Div.25	DIV 8 b)	Minimum DIV 8	N
Trimethylamine	59	0.0184	C	0.0834	C	1
2-Pentanol	88	0.0243	C	0.0394	C	3
3-Pentanol	88	0.0321	C	0.1064	C	2
2-Ethyl-1-butanol	102	0.0220	C	0.1333	0.1239(1)	11
3-Heptanol	116	0.0018	C	0.0001	C	9
2, 5-Hexane-diol	118	0.0174	C	0.0464	C	2
2-Ethyl-Hexanol-1	130	0.0222	C	0.0783	C	18
2-Methylnaphthalene	142	0.0407	C	0.0542	C	2
2, 6-Dimethyl-4-heptanol	144	0.0436	C	0.1060	C	15
1, 6-Dimethylnaphthalene	156	0.0136	0.0029(2)	0.0345	0.0309(2)	9
1-Decanol	158	0.0127	C	0.1707	0.1142(1)	8
1-Tetradecanol	214	0.0012	C	0.1410	C	3
1-Hexadecene	224	0.0463	C	0.0917	0.0089(1)	2

a) Divergence calculated using 25 peaks

b) Divergence calculated using 8 peaks

C - indicates that the minimum value for the divergence is the one in the column on the left and the compound was correctly identified. The number between brackets indicates the number of compounds with divergence less than the correctly identified compound.

N - Total number of times the divergence was calculated for each compound.

Using twenty-five peaks (DIV 25) all compounds, but one, were identified. This one, 1,6-dimethylnaphthalene could only be "confused", using Grotch's expression, with 2,7 or 2,6-dimethylnaphthalene and it is known to be impossible to distinguish them by their mass spectra only. As would be expected when using less information, that is, eight peaks only, there were more cases of "confusion" but the true compound was still the second most probable, in the three new cases.

Table 4.2 refers to the Eight Peak Index; the first thirteen unknown spectra are the same as in Table 4.1 and the other twenty-two are different and are also ordered by increasing molecular weight.

Table 4.2

NAME OF COMPOUND	M.W.	DIV 8 Limits-Same Compound	Degree of Ambiguity$^+$	DIV 8 Limits-Other Compounds	$N^a(N')^b$
Trimethylamine	59	0.0362	A	0.1801	6(2)
API-1127				0.2572	
2-Pentanol	88	0.0001	C1, F1	0.0027	44(5)
API-654		0.1108		0.4499	
3-Pentanol	88	0.0899	A	0.1614	17(4)
DOW 176		0.1055		0.4101	
2-Ethyl-1-butanol	102	0.0450	C1	0.0713	63(5)
DOW 275		0.1450		0.6737	
3-Heptanol	116	0.0001	A	0.1825	27(4)
API 1057		0.0899		0.5312	
2,5-Hexane-diol	118	0.0468	A	0.2224	25(2)
DOW 435				0.5238	
2-Ethyl-hexanol-1	130	0.0010	C3, F3	0.1369	51(6)
DOW 556		0.1823		0.5681	

Table 4.2 contd.

NAME OF COMPOUND	M.W.	DIV 8 Limits-Same Compound	Degree of Ambiguity$^+$	DIV 8 Limits-Other Compounds	$N^a(N')^b$
2-Methylnaphthalene	142	0.0270	C1	0.0528	26(6)
API 855		0.0531		0.6701	
2, 6-Dimethyl-4-heptanol	144	0.0965	A	0.1145	19(2)
DOW 781				0.4870	
1, 6-Dimethylnaphthalene	156	0.0336	C3	0.0298	34(2)
DOW 978				0.6302	
1-Decanol	158	0.1706	C2, F1	0.0783	20(5)
DOW 997		0.2722		0.6460	
1-Tetradecanol	214	0.1402	A	0.1604	8(2)
API 882				0.6190	
1-Hexadecene	224	0.0917	C1, F1	0.0089	17(3)
API 1013		0.1638		0.7841	
Carbon dioxide	44	0.0036	A	0.0795	23(6)
DOW 27		0.0300		0.3178	
Methyl chloride	50	0.0205	A	0.2287	7(5)
DOW 33		0.1015		0.2355	
1-Butene	56	0.0001	C3	0.0005	23(8)
DOW 39		0.0280		0.3020	
Isopropyl alcohol	60	0.0257	A	0.1896	28(8)
DOW 58		0.0522		0.4498	
Tert-butylamine	73	0.0344	A	0.1670	12(4)
DOW 99		0.0706		0.4170	
1-Hexyne	82	0.0362	A	0.1116	33(4)
API 332		0.0578		0.4454	

Table 4.2 contd.

NAME OF COMPOUND	M.W.	DIV 8 Limits-Same Compound	Degree of Ambiguity$^+$	DIV 8 Limits-Other Compounds	$N^a(N')^b$
2, 3-Butanedione	86	0.0277	F1	0.0342	39(3)
API 782		0.1300		0.5221	
Methyl-2-methyl-allyl Ether	86	0.00	A	0.1154	34(1)
DOW 148				0.6004	
3-Methyl-1-butanol	88	0.0087	P1, C1	0.0001	15(4)
DOW 178		0.1965		0.4805	
Toluene	92	0.0001	C2	0.0468	15(10)
DOW 208		0.1449		0.3262	
Cyclohexanone	98	0.0004	C1	0.0687	57(7)
DOW 224		0.0915		0.5152	
3-Methyl-2-pentanone	100	0.0007	A	0.0799	84(3)
API 663		0.0266		0.4974	
o-Xylene	106	0.0002	P2	0.0001	27(5)
DOW 1311		0.0632		0.4974	
1, 2-Dichloro-1-fluoroethane	116	0.0	A	0.1277	11(1)
DOW 397				0.6662	
1, 4-Dichloro-2-butyne	122	0.0292	A	0.6094	5(3)
DOW 480		0.0378		0.6174	
1,1,2-Trichloroethane	132	0.0367	A	0.3170	10(5)
DOW 580		0.1077		0.3616	
1-Decyne	138	0.0005	A	0.0986	20(2)
API 535				0.6797	

Table 4.2 contd.

NAME OF COMPOUND	M.W.	DIV 8 Limits-Same Compound	Degree of Ambiguity+	DIV 8 Limits-Other Compounds	$N^a(N')^b$
2-Methyl-1,2,3,4-tetrahydronaphthalene	146		A	0.3486	5(2)
API 1211		0.1201			
m-Tert-butyl phenol	150	0.000	A	0.0269	23(1)
DOW 879				0.4555	
2,2'-Bipyridyl	156	0.0426	A	0.0445	25(2)
API 630				0.5616	
Benzyl benzoate	212	0.0294	A	0.3858	4(3)
DOW 1641		0.0338			
2,4,6-Tri-tert-butylphenol	262	0.0228	A	0.2799	8(5)
DOW 1874		0.0584		0.4009	
Perfluoromethylcyclohexane	350	0.0231	A	0.0820	6(3)
DOW 1951		0.0551		0.1734	

a) N - Total number of times the divergence was calculated for each "unknown".

b) N'- Total number of times the divergence was calculated with spectra of the same compound as the "unknown" but from different origins

+ The number after the letter indicates the number of other compounds that had divergences included within the limits of the divergence for the same compound.

A - compounds in which there was complete identification

C - chain isomers had DIV 8 values within the limits of DIV 8 for the same compound

P - position " " " " " " " " " " " "
compound

F - functional " " " " " " " " " " " "
compound

In every case the minimum value for the divergence, 0.00, was obtained since the spectra used as unknowns were included on the tape. This result is not indicated in the table unless the divergence was not calculated on any other occasion and in this instance N' is equal to one (see, for example, 1,2-dichloro-1-fluoroethane). With the exceptions of 3-methyl-1-butanol and o-Xylene, the minimum value of the divergence - neglecting the value obtained when the unknown and reference are in fact the same spectrum - gives the correct identification.

The number of compounds with which there can be an error of identification, indicated in Table 4.2, differs from those used by Grotch since they refer to the worst possible value for the divergence comparing the tested compound with all the spectra of a similar compound on the tape. For the best value of the divergence confusion only exists for 3-methyl-1-butanol with 2-methyl-1-butanol and for o-Xylene with p- and m-Xylene. For the last case it would be more practical to follow the custom of Grotch and merely identify the set of isomers; the very low value (0.0001) for the divergence with 2-methyl-1-butanol was obtained for a spectrum with the same origin (DOW catalogue) and consecutive serial number to the one of 3-methyl-1-butanol used as "unknown" (DIV 8 = 0.0000) which seems to suggest they were probably run in the same mass spectrometer. Spectra of the same origin as the unknown were also responsible for all the cases of possible mis-identification for 1-butene and 2-ethyl-1-butanol and partially for 2-ethylhexanol 1,2-pentanol and 1-decanol which confirms that very often spectra of different isomers run in the same mass spectrometer are more similar than spectra of the same isomer run in different instruments.

While, as was demonstrated by Tal'roze <u>et al</u>[1] using the same instrument the ratios between the heights of three peaks can be enough to identify most compounds, when comparing the same compound run in different instruments the problem is far more complicated. One would normally expect[6] that for similar experimental conditions the probability that a repeat scan would yield the same result is: for the same instrument > for a different instrument of the same design > for an instrument of differing design > for an instrument working on a different principle.

The range of values for the divergence where it may be calculated upon various separate spectra, as in the case of toluene, may yield one very discordant value. This suggests that some consideration should be given to the origins and quality of the spectra.

The maximum value of the disagreement between divergence values for the same compound was 0.2722. With this exception no values over 0.2 were recorded and the value rarely exceeded 0.15. The spectra (2-ethyl-hexanol 1 and 1,6-dimethylnaphthalene) were compared without prefiltering steps and with all the 900 spectra in the first file. 2-Ethylhexanol 1 was again identified and the divergence had values between 0.0 and 0.2 for 88 compounds three-quarters of which were alcohols. The molecular weights were ranging from 84 (dihydropyran) to 424 (nonacosanol). For 1,6-dimethylnaphthalene there were again two spectra (2,7- and 2,6-dimethylnaphthalenes) with smaller divergences. Values between 0-0.2, in this case all less than 0.1, were obtained for 9 isomers, all dimethyl or ethylnaphthalenes. It seems from these results that a lower value for the divergence means in many cases the presence of similar chemical functions.

The criterion of minimum divergence yielded a very large percentage of successful identifications even when the calculations are restricted to eight peaks. The dependence upon noise accompanying the signals will, by increasing the noise level, allow a study of noisy signals which may be expected with rapid scanning techniques.

4. 5. Reorganization of files:

4. 5. 1. MSDC File of Complete Spectra - The first file used was the M.S.D.C. tape containing 3000 complete spectra. Owing to the computer time taken to make the comparison between an unknown and the compounds in this tape it proved necessary to reorganize it. As a first step it was decided to keep only the twenty-five largest peaks of each spectrum, or all if there were less than that and order them in decreasing order of intensity. This was made using PROGRAM* A1. As the main interest was to see the effect on the running time of a reorganized tape only the first 900 spectra were used.

This new tape was again transferred (using PROGRAM A2) replacing columns 73 to 80 at the end of each record where a source reference was contained previously by three code numbers which indicated the number of order of the spectra in the collection, the number of order of the record in the spectrum and the molecular weight of the compound. The source reference was still indicated in the second record of each spectrum columns 10-71. The 900 spectra were then reordered by increasing molecular weight using the SORT facility of the I.B.M. 360/50. The PROGRAM SR used to calculate the divergence from the original tape was replaced by PROGRAM R2. The main programme now includes the prefiltering step, that is, it checks for the presence of the largest peak of each spectrum on the other before calling the subroutine DIVER. The subroutine BIG that orders the peaks by decreasing intensity is the

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* The same convention of Chapter 2 is used. The American spelling PROGRAM is used for the name of the programmes only.

same as used by PROGRAM SR.

The new tape content was then transferred to a disc (File 10). To use the disc it was necessary to organize an extra file (File 9) which for each molecular weight gave the exact position of the first compound with this molecular weight in File 10. This was made using PROGRAM A3.

Once the file was organized the unknown spectra were compared with spectra on the tape using PROGRAM R3. This programme uses subroutines BIG and DIVER of PROGRAM R2.

4. 5. 2. Eight-Peak Tape - The programme EP was written to compare an unknown with the spectra in the Eight Peak Tape. Again it was necessary to reorder the spectra by increasing molecular weight. To do this it was first necessary to transfer the tape adding at the end of each record a code number corresponding to the collection letter, the molecular weight and a number corresponding to the order of the record inside of each spectrum (up to 4).

Owing to the time taken to do the whole job and the system of time priorities in the Computer Service it proved more convenient to divide the file in seven sections and transfer each of them using programmes similar to B1. The contents of each file was listed and afterwards reordered using the I.B.M. SORT facility. Each file was sorted in increasing order of molecular weight, code number, spectrum number inside each collection and order of the record inside each spectrum and then partly listed. The seven files were then merged with the same ordering criterion by using the I.B.M. MERGE facility, and the new completely ordered file was again listed.

To speed the search it was decided to organize a key to the File in which for each molecular weight from 2 to 9999 would be written the number of the record where spectra with this molecular weight started or zero if there were none. This was done by means of PROGRAM B2.

The new programme FN, which is still being used, after reading the molecular weight of the unknown looks for this molecular weight in the new file and if there are any compounds with this molecular weight reads the record number, closes the first file and goes straight into the eight peak file at the point where compounds with this molecular weight start and proceeds comparing spectra.

The storage space necessary on disc to store this file was not justified considering the frequency of the programme's use.

4. 5. 3. Time considerations - Though the number of operations required by the criterion of identification affects the central processing time, as shown by the difference between the time taken for calculating the divergence with twenty-five (DIV 25) and eight peaks (DIV 8) for the same file and compounds (see Table 4.3), the number of waits while effecting the search is much more relevant and this depends on the way the library and the search are organised as well as on the storage facilities available (tape or disc).

Table 4.3

Time considerations per unknown compound.

File conditions	Time in seconds (average).
Search of 3000 compounds C.S.T.	392 s
Search of 900 compounds C.S.T.	236 s
Search of 900 ordered compounds T.F.P.T.	16 s

Table 4.3 contd.

File conditions	Time in seconds (average).
Search of 900 compounds on disc (DIV 25) T.F.P.F.	8 s
Search of 900 compounds on disc (DIV 8) T.F.P.F.	5 s
Calculation of DIV 25 for 900 compounds (disc) T.F.P.F.	250 s
Search of 700 compounds E.P.T.	60 s
Search of 17500 compounds E.P.T. reordered	20 s

C.S.T. - complete spectra tape

T.F.P.T. - twenty five peak tape

T.F.P.F. - twenty five peak file

E.P.T. - eight peak tape.

The times taken in the various file conditions are indicated in Table 4.3.

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Chapter 5.

The Computation of some Molecular Weights

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THE COMPUTATION OF SOME MOLECULAR WEIGHTS

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Abstract—A method is described for deducing the molecular weight of a compound, the mass spectrum of which does not extend as far as the molecular weight. It is based upon the combination of fragment ions and restricted to limits determined by an approximate estimate of that weight.

THE ELECTRON-IMPACT of a molecule is usually considered to yield the molecular ion by the following process:

$$e + ABC \rightarrow \overset{+\cdot}{ABC} + 2e$$

so that the ion of greatest mass upon the mass spectrometer trace, neglecting isotopic ions, will reveal the compound's molecular weight. There are a not inconsiderable number of exceptions to this rule, both with the appearance of spectra which show ions of a mass in excess of the true molecular weight—as is often encountered with the mass-spectra of organic nitriles[1]—and in a considerable number of molecules in the mass spectra of which the parent ion is absent. It is with this latter class that one is now concerned. When such a situation is met some possible remedies are available. Often it is sufficient merely to increase the sample pressure in the spectrometer when, presumably as a consequence of an ion-molecule collision, the $[M + 1]^+$ ion is obtained. This method is not always desirable, nor in the case of combined mass spectrometry-gas chromatography, possible. Accordingly, one has considered this problem. Methods are already available in the literature whereby an accurate molecular weight may be obtained from effusiometric studies,[2] although these are often exacting experimentally.

In the present analysis a knowledge of the approximate molecular weight is an advantage in shortening the operational time and restricting the size of computer store needed. The estimate of the molecular weight may be so approximate that it can be assessed from the physical properties of the material or even from the incomplete mass spectrum. Having decided upon the approximate molecular weight a combinatorial programme is drawn up whereby the addition of one mass peak to another is accomplished, subject to the condition that their sum is within the limits established for the estimated molecular weight. The programme was extended to involve the addition of three ions, a process necessary in all but two cases. Still later the addition of four fragments was considered, but this either gave the same result as three or increased the number of false probable values. The consideration of two ions of the same mass appearing simultaneously in one fragmentation process did not alter the results sensibly.

RESULTS

The method consists in combining the masses of peaks to form sums both for possible molecular weights and for probabilities (as defined below) following the

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* Supported by the Instituto de Alta Cultura, Lisbon, Portugal.

argument that the maximum probability may reasonably be expected to correspond to the molecular weight of the compound under examination. About fifty compounds were examined by this method with the results given in the following Tables.

The method was not uniformly successful. For the compounds in Table 1 the correct value was always obtained; for the compounds in Table 2 the values obtained corresponded to the molecular weight minus one. In all cases in which spectra extending as far as the molecular weight were used, the mass referred to was also the more intense in this zone, suggesting there is a loss of hydrogen during ionization. In Table 3 are the other compounds which gave incorrect results, though in four cases they also coincide with the more intense value in the spectrum; two of them (tetradecafluoro-2-methylpentane and decafluorobutane) are particularly bad, as the mass

TABLE 1

No.	Name	Computed mass	Actual mass	Spectrum begins at *m*/*e*
API 1052	1-Hexanol	102	102	14
DOW 705	*t*-Butanol	74	74	14
DOW 1119	2-Methyl-2-butanol	88[a] [b]	88	13
API 565	2-Methyl-5-Ethylheptane	142	142	18
DOW 1823	*t*-Butylamine	83	83	14
API 1931	*iso*-Propyl acetate	102[a]	102	12
DOW 3280	2,2′,2″-Trifluoroethanol	100[a]	100	12
MCA 115	2,2′-Difluoropropane	80[a]	80	12
DOW 3911	2-Fluoro-2-Methylpropane	76	76	15
MCA 143	Perfluorobutyraldehyde	216	216	19

[a] Spectrum extended as far as molecular weight.

[b] Differs from the more intense in the last group of peaks in the spectrum.

TABLE 2[a]

No.	Compound	Computed mass	Actual mass	Spectrum begins at *m*/*e*
API 1053	2-Methyl-1-pentanol	101	102	14
DOW 703	*sec*-Butyl alcohol	73[b]	74	14
API 1056	2-Heptanol	115[b]	116	14
API 1116	1,1-Diethoxyethane	117[b]	118	18
DOW 766	1,1-Diethoxyethane	117[b]	118	15
API 1113	1,1-Dimethoxyethane	89[b]	90	12
DOW 691	3,4-Epoxy-1-butene	71[b]	72	12
DOW 5030	2-Methyl-1,3-dioxolane	87[b]	88	15
DOW 4673	Methyl-3,3-dioctyl-methacrylate	323	324	14
DOW 2564	Cyclohexylcyclohexane-carboxylate	213	214	15
API 1626	Heptafluorobutanoic acid	213	214	12

[a] In all cases where spectra extended as far as molecular weight, the value obtained was the more intense in the last group of peaks in the spectrum.

[b] Spectrum extended as far as molecular weight.

TABLE 3

No.	Compound	Computed mass	Actual mass	Spectrum begins at *m/e*
DOW 686	*iso*-Propyl alcohol	61[a, b]	60	15
API 1055	2-Ethyl-1-butanol	99, 100	102	14
DOW 1267	Glycerol	101[a, c]	92	13
API 1101	1,1-Di-*sec*-butoxyethane	172	174	12
API 1122	1,1-Di-*n*-hexoxyethane	228	230	18
DOW 4568	*n*-Decylether	294, 295, 297, 298	298	14
DOW 2944	Tri-*n*-butyrin	300, 301	302	15
DOW 946	3-Propiolactone	69[a, b]	72	12
API 795	*n*-Butylnitrite	101[a, c]	103	12
API 814	3-Methylbutyl nitrite	115	117	12
DOW 1342	Allyl acetate	101[a, c]	100	12
DOW 1960	Oxalic acid	91[a, c]	90	12
API 1152	Propanoic anhydride	115	130	2
DOW 3243	1-Fluoropropane	60[a, b]	62	12
DOW 3244	1-Fluorobutane	74[a, b]	76	14
DOW 1972	1,1,1-Trifluoroethane 2,2,2	85[a, b]	87	12
API 736	Tetradecafluoro-2-methylpentane	331[d]	338	12
API 445	Decafluorobutane	231[d]	238	12

[a] Spectrum extended as far as molecular weight.

[b] Differs from the more intense in the last group of peaks.

[c] Is the more intense in the last group of peaks.

[d] Does not correspond to any possible fragment of the molecule.

obtained does not correspond to a possible fragment of the molecule. This is always a possibility, considering one is not making any chemical hypothesis. In all cases the value of *m/e* from which the spectrum used starts is indicated, as from the theory that one should use the complete spectra, i.e. including the lower masses. This was not always possible, however, and is certainly one of the sources of error.

In Table 4 are all the compounds computed where there were more than one abundant isotope. In the case where there was only one atom of chlorine or bromine per molecule present one obtained very good agreement. When there was more than one atom present, although there is a series of very probable masses in the same zone, there is no relation between the computed probabilities and the calculated relative abundances.

DISCUSSION

Neglecting the presence of the naturally occurring isotopes deuterium, carbon-13, nitrogen-15, oxygen-18, etc., the abundances of which are so low as to make little difference to the analytical method and assuming that even if the parent molecular ion is too unstable for existence it will be, theoretically at least, the first formed:

$$[M]^{+\cdot} \rightarrow [X_a]^+ + X_b$$

or

$$[M]^{+\cdot} \rightarrow X_a + [X_b]^+$$

TABLE 4

No.	Name	Computed masses	Actual masses	Spectrum begins at *m/e*
DOW 430	Chlorotrifluoromethane	104 106[a]	104 106	12
MCA 137	1,1-Difluoro-1-chloroethane	100 102	100 102	19
API 128	Chloropentafluoroethane	154 156	154 156	19
API 792	2-Bromoethyl acetate	166 168[a]	166 168	18
MCA 125	1,1′,2-Trifluoro-1,2,2-Trichloroethane	190,189, 188[a]	186, 188, 190, 192	13
MCA 127	1,1-Dichlorotetrafluoroethane	173, 172 174[a]	170, 172, 174	19
MCA 131	1,3-Dichlorohexafluorocyclobutane	233, 234, 235	232, 234, 236	19
DOW 1098	1,2-Dichloroperfluorocyclobutane	233, 234, 235	232, 234, 236	12
DOW 1456	Acetyl chloride	77, 78, 79[a]	78, 80	12

[a] Spectrum extended as far as molecular weight.

The case in which the molecule only fragments in two parts and both ions $[X_a]^+$ and $[X_b]^+$ are present in the spectrum, though with different intensities, is considered first. The two ions will generally have different masses, but the sum of these masses will always be equal to the molecular weight of the compound.

The different ways in which the molecule dissociates can be represented in a general form by Process *n*:

$$2[M]^{+\cdot} \rightarrow [X_j]^+ + [X_k]^+ + X_j + X_k$$

when the ion $[X_j]^+$ has a probability of occurrence

$$p_{X_j^+} = \frac{I_{X_j^+}}{\sum\limits_j I_{X_j^+}}$$

where $I_{X_j^+}$ is the intensity of peak $[X_j]^+$ in the spectrum and the denominator is the sum of the intensities of all the peaks in the spectrum.

The probability that the decomposition of the molecule took place by process *n* is

$$p_n = p_{X_j^+} + p_{X_k^+}$$

and $\sum\limits_n p_n = \sum\limits_j p_{X_j^+} = 1$ by the definition of probability.

All possible combinations of the ions taken two by two (excluding the combination of two ions of the same mass) are considered and by summing their masses a series of probable values for the molecular weights is obtained. With each likely molecular weight is associated a probability equal to the sum of the probabilities of all the ions entering into binary combination to give that weight. As it was assumed that all the ions originate from only one kind of parent ion there will be at least one value M for which $\sum\limits_j p_{X_j^+} = 1$ and this is the necessary condition. As the only ions considered are those recorded by the collector, this hypothesis excludes processes in which a neutral fragment is subsequently released while the ion is still in the source. Recombination of ions may also lead to errors. Both processes are infrequent, however.

Next one must prove that this value of M is unique (sufficient condition). To begin with, postulate that M is not unique and there is at least a second mass M′ which yields the same result. Thus there will exist a set of processes $p_{n'}$, all different from p_n since they reconstitute one mass M′ different from M, but also satisfying the condition $\sum_{n'} p_{n'} = 1$, that is, also involving all the masses in the spectrum.

Considering the process

$$2[\mathrm{M}]^{+\cdot} \rightarrow [\mathrm{X}_{\mathrm{max}}]^{+} + [\mathrm{X}_{\mathrm{min}}]^{+} + \mathrm{X}_{\mathrm{max}} + \mathrm{X}_{\mathrm{min}}$$

where $[\mathrm{X}_{\mathrm{max}}]^{+}$ and $[\mathrm{X}_{\mathrm{min}}]^{+}$ are the ions with the highest and lowest mass respectively, in the spectrum of the substance of molecular weight M.

$[\mathrm{X}_{\mathrm{max}}]^{+}$ and $[\mathrm{X}_{\mathrm{min}}]^{+}$ both have to appear in a process n', so there will be two combinations:

$$(1)\quad [\mathrm{X}_{\mathrm{max}}]^{+} + [\mathrm{X}_j]^{+} \rightarrow \mathrm{M}' \qquad \text{where} \qquad [\mathrm{X}_j]^{+} > [\mathrm{X}_{\mathrm{min}}]^{+}$$

$$(2)\quad [\mathrm{X}_{\mathrm{min}}]^{+} + [\mathrm{X}_k]^{+} \rightarrow \mathrm{M}' \qquad \text{where} \qquad [\mathrm{X}_k]^{+} < [\mathrm{X}_{\mathrm{max}}]^{+}.$$

From (1) the value of M′ obtained is necessarily greater than M while from (2) M′ is smaller than M. This is absurd and proves that in the case considered, only one value of M can exist satisfying the condition $\sum_{n} p_n = 1$.

While trying to compute the molecular weight based on this principle it became obvious that the molecule does not only fragment into two pieces but also in three. Attempts to use a similar method to demonstrate that there should be only one value of M with the same property when one simultaneously considers combination of the ions two by two and three by three failed.

So the molecule normally fragments by processes of both type *n* and *m*.

$$\text{Process } n \quad 2[\mathrm{M}]^{+\cdot} \rightarrow [\mathrm{X}_j]^{+} + [\mathrm{X}_k]^{+} + \mathrm{X}_j + \mathrm{X}_k$$

$$\text{Process } m \quad 3[\mathrm{M}]^{+\cdot} \rightarrow [\mathrm{X}_a]^{+} + [\mathrm{X}_b]^{+} + [\mathrm{X}_c]^{+} + 2\mathrm{X}_a + 2\mathrm{X}_b + 2\mathrm{X}_c$$

The probability that the decomposition of the molecule took place by process *n* is

$$p_n = a_{jn} p_{\mathrm{X}_j{}^{+}} + a_{kn} p_{\mathrm{X}_k{}^{+}}$$

where

$$p_{\mathrm{X}_j{}^{+}} = \frac{I_{\mathrm{X}_j{}^{+}}}{\sum_j I_{\mathrm{X}_j{}^{+}}} = \sum_n a_{jn} p_{\mathrm{X}_j{}^{+}} + \sum_m a_{jm} p_{\mathrm{X}_j{}^{+}}$$

since the probability of peak X_j in the spectrum is now the sum of the contributions from the probabilities of the ion being formed from fragmentations in two parts, plus the contribution from the probabilities of being formed by fragmentation into three parts.

In a similar way

$$\sum_n p_n + \sum_m p_m = 1$$

and there necessarily exists one value M which satisfies this relation.

While for the case in which there were only fragmentations into two, the value of p_n could be calculated in each case, it is now impossible to calculate p_n or p_m as the coefficients $a_{jn} \ldots, a_{jm} \ldots$ are not known. Since one is only interested in $\sum\limits_{m} p_n + \sum\limits_{m} p_m$ for each probable mass, however, this difficulty can be overcome by considering the total value of the probability of an ion the first time it appears, whether in a combination of two or three, giving a value of probable mass. One tried to prove that the value M which satisfied the relation

$$\sum_{n} p_n + \sum_{m} p_m = 1 \quad \text{(A)}$$

was unique. Again one assumed the existence of another mass M′ satisfying the same condition. Now the minimum mass in the spectrum can appear either by fragmentation into two parts or three. First the case where the minimum mass comes from a fragmentation into two parts, was considered.

$$[X_{\min^2}]^+ < [X_{\min^3}]^+$$

$$[X_{\min^2}]^+ + [X_{\max^2}]^+ \rightarrow M$$

$$[X_a]^+ + [X_b]^+ + [X_{\max^3}]^+ \rightarrow M$$

$$[X_a]^+ > [X_{\min^2}]^+ \quad \text{and} \quad [X_b]^+ > [X_{\min^2}]^+ \quad \text{so necessarily} \quad [X_{\max^2}]^+ > [X_{\max^3}]^+$$

For a value M′ to exist $[X_{\max^2}]^+$ has to appear at least in one combination of masses summing to give a mass M′.

If $[X_{\max}]^+$ appears in a combination of two masses

$$[X_{\max^2}]^+ + [X_r]^+ \rightarrow M'$$

and as $[X_r]^+ > [X_{\min}]^+$, M′ is necessarily greater than M. The same conclusion arises if $[X_{\max^2}]^+$ occurs in a combination of three ions, so that in this case one can conclude that although other values appear satisfying the relation (A), M will be the smallest one. Considering that the minimum mass came from a fragmentation into three parts, one was unable to discover any such relation between the real M and other possible values.

In the computation, however, it happened that the real value of the molecular weight, or the value indicated in the Tables, corresponded to a well defined maximum frequently followed by a series of values of a very high probability. In some cases, as in Printout No. 1, the probability at this point is equal to 1, but more often as in Printout No. 2, though very high, it was less than 1. This is attributed to the fact that in general very small peaks in the spectra are ignored.

In Printout No. 1 the difference between the probability of the molecular weight (M), and of [M − 1] and [M + 1] is very small. Artificial errors of 1% of the highest peak intensity were introduced in some of the spectra, but it made very little difference to the results. Some of the probabilities were slightly altered while the position of the maxima remained the same.

In the case of Printout No. 3 an incomplete spectrum was used for the calculation and yielded a badly defined result, in any case wrong. It was, however, possible to correct this, as the chemical composition was known, by introducing dummy peaks with intensities 0·0 at the possible missing masses (see Printout No. 4). This approximation was used in other instances but only to confirm results and in general it is advisable to use complete spectra.

PRINTOUT 1. MASPEC RUN-RESULTS FOR *iso*-PROPYL ACETATE-A.P.I.-1931

Mass number	Probability
80	0·8302
81	0·8283
82	0·8280
83	0·8290
84	0·8678
85	0·8739
86	0·9546
87	0·9974
88	0·9586
89	0·9569
90	0·9568
91	0·9568
92	0·9568
93	0·9568
94	0·9568
95	0·9568
96	0·9568
97	0·9568
98	0·9568
99	0·9977
100	0·9996
101	0·9997
102	1·0000
103	0·9997
104	0·9997
105	0·9997
106	0·9588
107	0·9569
108	0·9568
109	0·9568
110	0·9568
111	0·9568
112	0·9977
113	0·9996
114	1·0000
115	1·0000
116	1·0000
117	1·0000
118	1·0000
119	1·0000
120	1·0000

PRINTOUT 2. MASPEC RUN-RESULTS FOR *sec*-BUTYL ALCOHOL

Mass number	Probability
50	0·1063
51	0·0428
52	0·0762
53	0·1039
54	0·1011
55	0·1899
56	0·2676
57	0·3402
58	0·3551
59	0·8787
60	0·7879
61	0·7370
62	0·7313
63	0·6895
64	0·6638
65	0·2288
66	0·2678
67	0·2755
68	0·3200
69	0·3746
70	0·8177
71	0·8552
72	0·8597
73	0·9677
74	0·9649
75	0·9530
76	0·9447
77	0·9189
78	0·9168
79	0·8144
80	0·8242
81	0·8307
82	0·8599
83	0·8645
84	0·9676
85	0·9718
86	0·9737
87	0·9804
88	0·9823
89	0·9823
90	0·9820

Printout 3. Maspec run-results for 1,1-diethoxyethane-(DOW)

Mass number	Probability
100	0·9374
101	0·9385
102	0·9393
103	0·9921
104	0·9459
105	0·9432
106	0·9428
107	0·9419
108	0·9394
109	0·9381
110	0·9353
111	0·7399
112	0·9301
113	0·9200
114	0·9420
115	0·9428
116	0·9428
117	0·9445
118	0·9947
119	0·9979
120	0·9983
121	0·9983
122	0·9983
123	0·9463
124	0·9432
125	0·9419
126	0·9419
127	0·9402
128	0·9947
129	0·9979
130	0·9983
131	0·9983
132	1·0000
133	1·0000
134	1·0000
135	1·0000
136	1·0000
137	0·9983
138	0·9983
139	0·9983
140	0·9983

Printout 4. Maspec run-results for 1,1-diethoxyethane-(DOW)

Mass number	Probability
100	0·9394
101	0·9428
102	0·9428
103	0·9947
104	0·9459
105	0·9432
106	0·9428
107	0·9419
108	0·9410
109	0·9385
110	0·9385
111	0·9385
112	0·9393
113	0·9402
114	0·9428
115	0·9947
116	0·9979
117	1·0000
118	0·9983
119	0·9983
120	0·9983
121	0·9983
122	0·9983
123	0·9463
124	0·9432
125	0·9428
126	0·9428
127	0·9428
128	0·9947
129	0·9996
130	1·0000
131	1·0000
132	1·0000
133	1·0000
134	1·0000
135	1·0000
136	1·0000
137	0·9983
138	0·9983
139	0·9983
140	0·9983

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APPENDIX - LIST OF PROGRAMMES

Chapter 4

4.5.1

- PROGRAM SR
  SUBROUTINE BIG
  SUBROUTINE DIVER
- PROGRAM A1
  SUBROUTINE BIG
- PROGRAM A2
- PROGRAM R2
  SUBROUTINE BIG (as for SR)*
  SUBROUTINE DIVER
- PROGRAM A3
- PROGRAM R3
  SUBROUTINE BIG (as for SR)*
  SUBROUTINE DIVER (as for R2)*

4.5.2

- PROGRAM EP
  SUBROUTINE DIVER (as for FN)*
- PROGRAM B1
- PROGRAM B2
- PROGRAM FN
  SUBROUTINE DIVER

Chapter 5

- PROGRAM ME
  SUBROUTINE COMB

* To use the main programme, subroutines from where indicated should be used.

```
      REAL MOVER1,INTEN1,MOVERE,INTEN
      DIMENSION ICARD(20),IFORM(7),JJ(10),MOVER1(1000),
     XINTEN1(1000),MOVERE(1000),INTEN(1000),IFORM1(7),
     XIG1(27),IGC(27)
      INTEGER ONE/'1'/
      DATA I19,I20/'0000','0000'/
      READ (5,250)NUM,MWT1
  250 FORMAT(2I7)
      READ (5,251) (IFORM1(I),I=1,7)
  251 FORMAT (1X,7A4)
      READ(5,252) (MOVER1(J),INTEN1(J),J=1,NUM)
  252 FORMAT (5(F6.1,F7.3))
      WRITE (6,253)
  253 FORMAT (1X,'UNKNOWN SPECTRUM')
      WRITE (6,252) (MOVER1(J),INTEN1(J),J=1,NUM)
      CALL BIG(NUM,INTEN1,IG1,NG1)
      TOTAL1=0.0
       DO 286 NK=2,NG1
      I=IG1(NK)
      TOTAL1=TOTAL1+INTEN1(I)
  286 CONTINUE
      REWIND 10
  200 FORMAT(19A4,I4)
  201 READ (10,200,END=207) (ICARD(I),I=1,20)
      IF(ICARD(20).EQ.901)GO TO 777
      IF (I19.EQ.ICARD(19).AND.I20.EQ.ICARD(20)) GO TO 201
      I19=ICARD(19)
      I20=ICARD(20)
      READ (10,202) MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
  202 FORMAT (38X,I4,7A4,10A1)
      IF (MWT.NE.MWT1) GO TO 201
      DO 203 I=1,7
      IF (IFORM(I).NE.IFORM1(I))GO TO 201
  203 CONTINUE
      WRITE (6,213)
  213 FORMAT('1','PROBABLE COMPOUND')
      WRITE(6,200)(ICARD(I),I=1,20)
      IF (JJ(1).NE.ONE) GO TO 9997
      READ (10,200) (ICARD(I),I=1,20)
      WRITE(6,200)(ICARD(I),I=1,20)
      WRITE(6,214)
  214 FORMAT(38X,'****',38X)
      J=1
      K=7
  206 READ(10,204) (MOVERE(I),INTEN(I),I=J,K),(JJ(I),I=1,10)
      IF (JJ(2).EQ.ONE) GO TO 205
      J=J+7
      K=K+7
      GO TO 206
  204 FORMAT (7(1X,F5.1,F4.2),10A1)
  207 WRITE (6,208)
  208 FORMAT (1X,'END OF TAPE REACHED')
      GO TO 9999
  205 CONTINUE
      WRITE(6,216)
  216 FORMAT('1','SPECTRUM OF THE PROBABLE COMPOUND')
```

```
      WRITE(6,252)(MOVERE(I),INTEN(I),I=1,K)
      CALL BIG(K,INTEN,IGC,NGC)
      TOTAL2=0.00
      DO 295 NK=2,NGC
      J=IGC(NK)
      TOTAL2=TOTAL2+INTEN(J)
  295 CONTINUE
      IF(NG1-NGC)282,283,283
  282 NMAX=NG1
      GO TO 284
  283 NMAX=NGC
  284 CALL DIVER(IG1,IGC,MOVER1,MOVERE,INTEN1,INTEN,
     XTOTAL1,TOTAL2,NMAX,ICARD,MWT,IFORM)
      GO TO 201
  777 WRITE(6,779)
  779 FORMAT(1X,'IT COMPARED WITH 900 COMPOUNDS')
      GO TO 9999
 9997 WRITE (6,9998)
 9998 FORMAT(1X,'WRONG FORMAT')
 9999 REWIND 10
      CALL EXIT
      END
```

```
      SUBROUTINE BIG(NUM,B,IG,NUM1)
C
C THIS SUBROUTINE CHOOSES THE BIGGEST 25 PEAKS OF THE ARRAY
C OR IF THERE ARE LESS/OR 25 TAKES ALL OF THEM
C AND ARRANGES THEM IN DECREASING ORDER OF INTENSITY
C
      DIMENSION IG(27),B(1000)
      N=1
      IG(N)=0
      IF(NUM-25)2,1,1
    1 NUM1=26
      GO TO 3
    2 NUM1=NUM+1
    3 I=1
      J=2
    9 DO 11 NK=1,N
   10 IF(I.EQ.IG(NK))GO TO 19
   11 CONTINUE
      GO TO 20
   19 I=I+1
      IF(I.GT.NUM)GO TO 90
      GO TO 9
   20 DO 22 NK=1,N
   21 IF(J.EQ.IG(NK))GO TO 23
   22 CONTINUE
      GO TO 30
   23 J=J+1
      IF(J.GT.NUM)GO TO 89
      GO TO 20
   30 IF(J-I)31,23,31
   31 IF(B(J)-B(I))40,40,50
   40 IF(J.EQ.NUM)GO TO 89
      IF(I.EQ.NUM)GO TO 89
      IF(J.LT.I) J=I
      GO TO 23
   50 IF(J.EQ.NUM)GO TO 90
      IF(I.EQ.NUM)GO TO 90
      IF(I.LT.J)I=J
      GO TO 19
   89 N=N+1
      IG(N)=I
      GO TO 93
   90 N=N+1
      IG(N)=J
   93 IF(N-NUM1)3,94,94
   94 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DIVER(IG1,IGC,MOVER1,MOVERE,INTEN1,
     XINTEN,TOTAL1,TOTAL2,NMAX,ICARD,MWT,IFORM)
C
CTHIS SUBROUTINE CALCULATES THE DIVERGENCE BETWEEN THE UNKNOWN
C COMPOUND AND ONE COMPOUND FROM THE TAPE IF AT LEAST
C THE FIRST 2/5 OF THE BIGGEST PEAKS BOTH FROM
C THE UNKNOWN AND THE TAPE HAVE A MATCH
C
      REAL MOVER1,MOVERE,INTEN1,INTEN
      DIMENSION IG1(27),IGC(27),MOVER1(1000),MOVERE(1000),
     XINTEN1(1000),INTEN(1000),ICARD(20),IFORM(7)
C***TEMPORARY***
  300 FORMAT(1X,'OUT AT',F5.1)
C***TEMPORARY***
  301 MIN=NMAX-INT((NMAX-1)*0.6)
      SUM1=0
      SUM2=0
      S1=0
      S2=0
      KG=1
      N1=1
  302 KG=KG+1
      IF(KG-10)303,303,304
  303 KGM9=2
      GO TO 305
  304 KGM9=KG-9
  305 IF(KG-(NMAX-9))306,306,307
  306 KGP9=KG+9
      GO TO 308
  307 KGP9=NMAX
  308 I=IG1(KG)
      DO 309 N=KGM9,KGP9
      J=IGC(N)
      IF (MOVER1(I).EQ.MOVERE(J)) GO TO 313
  309 CONTINUE
      IF (KG-MIN)310,311,311
  310 IF(MOVER1(I).EQ.14.0)GO TO 3100
      IF(MOVER1(I).EQ.16.0)GO TO 3100
      IF(MOVER1(I).EQ.18.0)GO TO 3100
      IF(MOVER1(I).EQ.28.0)GO TO 3100
      IF(MOVER1(I).EQ.32.0)GO TO 3100
      IF(MOVER1(I).EQ.44.0)GO TO 3100
C***TEMPORARY***
      WRITE(6,300)MOVER1(I)
C***TEMPORARY***
      WRITE(6,501)
  501 FORMAT(1X,'NOT ENOUGH PEAKS HAVE A MATCH
     XSTOPPED WHILE CALCULATING SUM1')
      GO TO 503
 3100 WRITE(6,100)MOVER1(I)
  100 FORMAT (1X,F5.1,'IS VERY DIFFERENT IN THE UNKNOWN')
      N1=N1+1
      IF(KG.LT.NMAX) GO TO 302
      GO TO 314
  311 CONTINUE
      N1=N1+1
```

```
      PROB1=INTEN1(I)/TOTAL1
      R=INTEN1(I)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      WRITE(6,700)R,PROB1,S1
  700 FORMAT(1X,'R=',F7.5,2X,'PROB1=',F7.5,2X,'S1=',F16.4)
      IF(KG.GE.NMAX)GO TO 314
      GO TO 302
  313 PROB1=INTEN1(I)/TOTAL1
      RS=(INTEN1(I)+INTEN(J))/(TOTAL1+TOTAL2)
      R=INTEN1(I)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL1*(PROB1-RS)*ALOG(PROB1/RS)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      WRITE(6,700)R,PROB1,S1
      IF(KG.LT.NMAX)GO TO 302
  314 NUSED1=NMAX-N1
      KG=1
      N1=1
  402 KG=KG+1
      IF(KG-10)403,403,404
  403 KGM9=2
      GO TO 405
  404 KGM9=KG-9
  405 IF(KG-(NMAX-9))406,406,407
  406 KGP9=KG+9
      GO TO 408
  407 KGP9=NMAX
  408 J=IGC(KG)
      DO 409 N=KGM9,KGP9
      I=IG1(N)
      IF(MOVERE(J).EQ.MOVER1(I))GO TO 413
  409 CONTINUE
      IF(KG-MIN)410,411,411
  410 IF(MOVERE(J).EQ.14.0)GO TO 4100
      IF(MOVERE(J).EQ.16.0)GO TO 4100
      IF(MOVERE(J).EQ.18.0)GO TO 4100
      IF(MOVERE(J).EQ.28.0)GO TO 4100
      IF(MOVERE(J).EQ.32.0)GO TO 4100
      IF(MOVERE(J).EQ.44.0)GO TO 4100
C***TEMPORARY***
      WRITE(6,300)MOVERE(J)
C***TEMPORARY***
      WRITE(6,502)
  502 FORMAT(1X,'NOT ENOUGH PEAKS HAVE A MATCH
     XSTOPPED WHILE CALCULATING SUM2')
      GO TO 503
 4100 WRITE(6,200)MOVERE(J)
  200 FORMAT(1X,F5.1,'IS VERY DIFFERENT IN THE TAPE')
      N1=N1+1
      IF(KG.LT.NMAX)GO TO 402
      GO TO 414
  411 CONTINUE
      N1=N1+1
      PROB=INTEN(J)/TOTAL2
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
```

```
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      WRITE(6,701)R,PROB,S2
  701 FORMAT(1X,'R=',F7.5,2X,'PROB=',F7.5,2X,'S2=',F16.4)
      IF(KG.GE.NMAX)GO TO 414
      GO TO 402
  413 PROB=INTEN(J)/TOTAL2
      RS=(INTEN1(I)+INTEN(J))/(TOTAL1+TOTAL2)
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL2*(PROB-RS)*ALOG(PROB/RS)
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      WRITE(6,701)R,PROB,S2
      IF(KG.LT.NMAX)GO TO 402
  414 NUSED2=NMAX-N1
      RNORM=S1+S2
C***TEMPORARY***
      WRITE(6,400)SUM1,SUM2,TOTAL1,TOTAL2
  400 FORMAT(1X,'SUM1=',F10.5,1X,'SUM2=',F10.5,1X,
     X'TOTAL1=',F10.2,1X,'TOTAL2=',F10.2)
      WRITE(6,595)RNORM
  595 FORMAT(1X,'RNORM=',F16.6)
C***TEMPORARY***
      DIV=(SUM1+SUM2)/RNORM
      WRITE(6,504)NUSED1,NUSED2
  504 FORMAT(1X,I2,'=',I2,'HAVE A MATCH')
      WRITE(6,211)DIV
  211 FORMAT(1X,'DIVERGENCE=',F9.6)
       WRITE(6,210)(ICARD(I),I=1,20)
  210 FORMAT(20A4)
      WRITE(6,212) MWT,(IFORM(I),I=1,7)
  212 FORMAT(1X,'MOL. WEIGHT=',I4,2X,'FORMULA=',7A4)
  503 CONTINUE
      RETURN
      END
```

PROGRAM A1

```
      DIMENSION ICARD(20),IFORM(7),JJ(10),MOVERE(1000),
     XINTEN(1000),IGC(27),MOVER1(30),INTEN1(30)
      INTEGER ONE/'1'/
      DATA I19,I20/'0000','0000'/
      REWIND 10
      REWIND 11
  200 FORMAT(19A4,I4)
      READ(10,200)(ICARD(I),I=1,20)
      IF(I19.EQ.ICARD(19).AND.I20.EQ.ICARD(20))GO TO 201
      I19=ICARD(19)
      I20=ICARD(20)
  301 READ(10,300)ICARD(20)
  300 FORMAT(/////////76X,I4)
      IF(ICARD(20).LT.497)GO TO 301
  303 READ(10,200)(ICARD(I),I=1,20)
      IF(ICARD(20).LT.500)GO TO 303
      WRITE(6,501)
      WRITE(6,200)(ICARD(I),I=1,20)
  501 FORMAT(1X,'LAST LINE READ IN OLD TAPE')
      READ(10,202)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
      WRITE(11,202)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
      IF(JJ(1).NE.ONE)GO TO 9997
      READ(10,200)(ICARD(I),I=1,20)
      WRITE(6,200)(ICARD(I),I=1,20)
      WRITE(11,200)(ICARD(I),I=1,20)
      J=1
      K=7
  306 READ(10,204)(MOVERE(I),INTEN(I),I=J,K),(JJ(I),I=1,10)
      IF(JJ(2).EQ.ONE)GO TO 305
      J=J+7
      K=K+7
      GO TO 306
  305 CONTINUE
      CALL BIG(K,INTEN,IGC,NGC)
      K=0
      DO 395 NK=2,NGC
      J=IGC(NK)
      K=K+1
      MOVER1(K)=MOVERE(J)
      INTEN1(K)=INTEN(J)
  395 CONTINUE
      DO 397 K=NGC,28
      MOVER1(K)=0
      INTEN1(K)=0
  397 CONTINUE
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=1,7),(JJ(I),I=3,10)
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=8,14),(JJ(I),I=3,10)
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=15,21),(JJ(I),I=3,10)
      WRITE(11,224)(MOVER1(K),INTEN1(K),K=22,28),(JJ(I),I=3,10)
  201 READ(10,200,END=207) (ICARD(I),I=1,20)
      IF(I19.EQ.ICARD(19).AND.I20.EQ.ICARD(20)) GO TO 201
      I19=ICARD(19)
      I20=ICARD(20)
      WRITE(6,200)(ICARD(I),I=1,20)
      IF(ICARD(20).EQ.1001)GO TO 9999
      WRITE(11,200)(ICARD(I),I=1,20)
```

PROGRAM A1

```
      READ(10,202)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
  202 FORMAT(38X,I4,7A4,10A1)
      WRITE(11,202)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
      IF(JJ(1).NE.ONE)GO TO 9997
      READ(10,200)(ICARD(I),I=1,20)
      WRITE(6,200)(ICARD(I),I=1,20)
      WRITE(11,200)(ICARD(I),I=1,20)
      J=1
      K=7
  206 READ(10,204)(MOVERE(I),INTEN(I),I=J,K),(JJ(I),I=1,10)
      IF(JJ(2).EQ.ONE)GO TO 205
      J=J+7
      K=K+7
      GO TO 206
  204 FORMAT(7(1X,I5,I4),10A1)
  207 WRITE(6,208)
  208 FORMAT(1X,'END OF TAPE REACHED')
      GO TO 9999
  205 CONTINUE
      CALL BIG(K,INTEN,IGC,NGC)
      K=0
      DO 295 NK=2,NGC
      J=IGC(NK)
      K=K+1
      MOVER1(K)=MOVERE(J)
      INTEN1(K)=INTEN(J)
  295 CONTINUE
      DO 297 K=NGC,28
      MOVER1(K)=0
      INTEN1(K)=0
  297 CONTINUE
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=1,7),(JJ(I),I=3,10)
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=8,14),(JJ(I),I=3,10)
      WRITE(11,214)(MOVER1(K),INTEN1(K),K=15,21),(JJ(I),I=3,10)
      WRITE(11,224)(MOVER1(K),INTEN1(K),K=22,28),(JJ(I),I=3,10)
  214 FORMAT(7(1X,I5,I4),1X,'0',8A1)
  224 FORMAT(7(1X,I5,I4),1X,'1',8A1)
      GO TO 201
 9997 WRITE(6,9998)
 9998 FORMAT(1X,'WRONG FORMAT')
 9999 REWIND 10
      REWIND 11
      CALL EXIT
      END
```

PROGRAM A1

```
         SUBROUTINE BIG(NUM,B,IG,NUM1)
   C
   C THIS SUBROUTINE CHOOSES THE BIGGEST 25 PEAKS OF THE ARRAY
   C OR IF THERE ARE LESS/OR 25 TAKES ALL OF THEM
   C AND ARRANGES THEM IN DECREASING ORDER OF INTENSITY
   C
         INTEGER B
         DIMENSION IG(27),B(1000)
         N=1
         IG(N)=0
         IF(NUM-25)2,1,1
       1 NUM1=26
         GO TO 3
       2 NUM1=NUM+1
       3 I=1
         J=2
       9 DO 11 NK=1,N
      10 IF(I.EQ.IG(NK))GO TO 19
      11 CONTINUE
         GO TO 20
      19 I=I+1
         IF(I.GT.NUM)GO TO 90
         GO TO 9
      20 DO 22 NK=1,N
      21 IF(J.EQ.IG(NK))GO TO 23
      22 CONTINUE
         GO TO 30
      23 J=J+1
         IF(J.GT.NUM)GO TO 89
         GO TO 20
      30 IF(J-I)31,23,31
      31 IF(B(J)-B(I))40,40,50
      40 IF(J.EQ.NUM)GO TO 89
         IF(I.EQ.NUM)GO TO 89
         IF(J.LT.I)J=I
         GO TO 23
      50 IF(J.EQ.NUM)GO TO 90
         IF(I.EQ.NUM)GO TO 90
         IF(I.LT.J)I=J
         GO TO 19
      89 N=N+1
         IG(N)=I
         GO TO 93
      90 N=N+1
         IG(N)=J
      93 IF(N-NUM1)3,94,94
      94 CONTINUE
         RETURN
         END
```

PROGRAM A2

```
$COMPILE         CEK002RT                                                  1
C    M.E.SILVA,CHEMISTRY
C PROGRAM TO TRANSFER 900 RECORDS TO 2ND FILE--ON TAPE B9674
      DIMENSION ICARD(20),IFORM(7),JJ(10),MOVER1(30),
     XINTEN1(30),JL(8)
      REWIND 11
      REWIND 12
  200 FORMAT(A4,I5,A3,16A4,I4)
  400 FORMAT(17A4,8A1,I4)
  303 READ(11,200)ICARD(1),NORD,IC,(ICARD(I),I=4,20)
      IF(ICARD(20).EQ.901)GO TO 999
      READ(11,202)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,10)
      IORD=10
      WRITE(6,201)ICARD(1),NORD,IC,(ICARD(I),I=4,18),NORD,IORD,MWT
  201 FORMAT(A4,I5,A3,15A4,I3,I2,I3)
      WRITE(12,201)ICARD(1),NORD,IC,(ICARD(I),I=4,18),NORD,IORD,MWT
  202 FORMAT(38X,I4,7A4,10A1)
      IORD=11
      WRITE(6,203)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      WRITE(12,203)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
  203 FORMAT(38X,I4,7A4,2A1,I3,I2,I3)
  304 READ(11,400)(ICARD(I),I=1,17),(JL(I),I=1,8),ICARD(20)
      IORD=12
      WRITE(6,305)(ICARD(I),I=1,17),(JL(I),I=1,4),NORD,IORD,MWT
      WRITE(12,305)(ICARD(I),I=1,17),(JL(I),I=1,4),NORD,IORD,MWT
  305 FORMAT(17A4,4A1,I3,I2,I3)
      READ(11,214)(MOVER1(K),INTEN1(K),K=1,7),(JJ(I),I=1,10)
      IORD=13
      WRITE(12,215)(MOVER1(K),INTEN1(K),K=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      READ(11,214)(MOVER1(K),INTEN1(K),K=8,14),(JJ(I),I=1,10)
      IORD=14
      WRITE(12,215)(MOVER1(K),INTEN1(K),K=8,14),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      READ(11,214)(MOVER1(K),INTEN1(K),K=15,21),(JJ(I),I=1,10)
      IORD=15
      WRITE(12,215)(MOVER1(K),INTEN1(K),K=15,21),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      READ(11,214)(MOVER1(K),INTEN1(K),K=22,28),(JJ(I),I=1,10)
      IORD=16
      WRITE(12,215)(MOVER1(K),INTEN1(K),K=22,28),(JJ(I),I=1,2),
     XNORD,IORD,MWT
  214 FORMAT(7(1X,I5,I4),10A1)
  215 FORMAT(7(1X,I5,I4),2A1,I3,I2,I3)
      GO TO 303
  999 WRITE(6,500)
  500 FORMAT(1X,'END OF 900 COMPOUNDS')
      REWIND 11
      REWIND 12
      STOP
      END

 $DATA
R***      UN=3

ROGRAMME WAS EXECUTING LINE       6 IN ROUTINE M/PROG WHEN TERMINATION OCCURRED

 TIME=      0.97 SEC,EXECUTION TIME=      0.03 SEC,OBJECT CODE=    3712 BYTES,AR
```

```
C***MAIN PROGRAM***
      REAL MOVER1,INTEN1,MOVERE,INTEN
      DIMENSION ICARD(20),IFORM(7),JJ(10),JL(4),MOVER1(100),
     XINTEN1(100),MOVERE(28),INTEN(28),IFORM1(7),IG1(27),IDARD(17)
  100 READ(5,250)NUM,MWT1
  250 FORMAT(2I7)
      READ(5,251)(IFORM1(I),I=1,7)
  251 FORMAT(1X,7A4)
      READ(5,252)(MOVER1(J),INTEN1(J),J=1,NUM)
  252 FORMAT(5(F6.1,F7.3))
      WRITE(6,253)
  253 FORMAT(1X,'*****UNKNOWN COMPOUND*****')
      WRITE(6,350)MWT1
  350 FORMAT(1X,'MOLECULAR WEIGHT=',I7)
      WRITE(6,351)(IFORM1(I),I=1,7)
  351 FORMAT(1X,7A4)
      WRITE(6,359)
  359 FORMAT(1X,'*****SPECTRUM*****')
      WRITE(6,252)(MOVER1(J),INTEN1(J),J=1,NUM)
      CALL BIG (NUM,INTEN1,IG1,NG1)
      REWIND 10
  201 FORMAT(A4,I5,A3,15A4,I3,I2,I3)
  303 READ(10,201,END=207)ICARD(1),NORD,IC,(ICARD(I),I=4,18),
     XNORD;IORD,MWT
  803 IF(MWT.EQ.MWT1)GO TO 304
      IF(MWT.GT.MWT1)GO TO 705
  202 FORMAT(//////A4,I5,A3,15A4,I3,I2,I3)
      READ(10.202,END=207)ICARD(1),NORD.IC,(ICARD(I),I=4,18),
     XNORD,IORD,MWT
      GO TO 803
  304 READ(10,203)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
  203 FORMAT(38X,I4,7A4,2A1,I3,I2,I3)
      DO 306 I=1,7
      IF(IFORM(I).NE.IFORM1(I))GO TO 307
  306 CONTINUE
      GO TO 308
  307 READ(10,204,END=207)ICARD(1),NORD,IC,(ICARD(I),I=4,18),
     XNORD,IORD,MWT
  204 FORMAT(/////A4,I5,A3,15A4,I3,I2,I3)
      GO TO 803
  308 WRITE(6,213)
  213 FORMAT('1','PROBABLE COMPOUND')
      WRITE(6,201)ICARD(1),NORD,IC,(ICARD(I),I=4,18)
      WRITE(6,215)MWT,(IFORM(I),I=1,7)
  215 FORMAT(1X,'MOLECULAR WEIGHT=',I4,4X,'FORMULA=',7A4)
      READ(10,205)(IDARD(I),I=1,17),(JL(I),I=1,4),
     XNORD,IORD,MWT
  205 FORMAT(17A4,4A1,I3,I2,I3)
      WRITE(6,605)(IDARD(I),I=1,17)
  605 FORMAT(1X,'***',17A4,'***')
      READ(10,214)(MOVERE(K),INTEN(K),K=1,7),
     X(JJ(I),I=1,2),NORD,IORD,MWT
      READ(10,214)(MOVERE(K),INTEN(K),K=8,14),
     X(JJ(I),I=1,2),NORD,IORD,MWT
      READ(10,214)(MOVERE(K),INTEN(K),K=15,21),
```

```
     X(JJ(I),I=1,2),NORD,IORD,MWT
      READ(10,214)(MOVERE(K),INTEN(K),K=22,28),
     X(JJ(I),I=1,2),NORD,IORD,MWT
  214 FORMAT(7(1X,F5.1,F4.2),2A1,I3,I2,I3)
      WRITE(6,216)
  216 FORMAT('1','**SPECTRUM OF THE PROBABLE COMPOUND**')
      WRITE(6,252)(MOVERE(I),INTEN(I),I=1,25)
      DO 300 I=1,25
      IF(INTEN(I).EQ.0.0)GO TO 305
  300 CONTINUE
      NGC=26
      GO TO 406
  305 NGC=I
  406 IF(NG1-NGC)282,283,283
  282 NMAX=NG1
      GO TO 284
  283 NMAX=NGC
  284 NEC=NMAX-1
      DO 301 J=1,NEC
      I=IG1(2)
      IF(MOVER1(I).EQ.MOVERE(J))GO TO 321
  301 CONTINUE
      GO TO 703
  321 DO 302 J=2,NMAX
      I=IG1(J)
      IF(MOVERE(1).EQ.MOVER1(I))GO TO 322
  302 CONTINUE
  703 WRITE(6,704)
  704 FORMAT(1X,'MISSING HIGHEST PEAK')
      WRITE(6,229)
      WRITE(6,219)
      GO TO 303
  322 CALL DIVER(MOVER1,MOVERE,INTEN1,INTEN,IG1,IGC,
     XNMAX,NUSED,DIV)
      WRITE(6,504)NUSED
  504 FORMAT(1X,I2,' MASSES WERE COMPARED')
      WRITE(6,505)DIV
  505 FORMAT(1X,'*****DIVERGENCE=',F6.4,'*****')
      WRITE(6,229)
      WRITE(6,219)
  229 FORMAT(' ')
  219 FORMAT('0',2X,76(1H*))
      GO TO 303
  705 WRITE(6,997)
  997 FORMAT(1X,'END OF COMPOUNDS WITH THE SAME MOLECULAR WEIGHT')
  700 FORMAT(I1)
      READ(5,700)ISTOP
      IF(ISTOP.EQ.1)GO TO 100
      GO TO 999
  207 WRITE(6,998)
  998 FORMAT(1X,'END OF FILE')
  999 REWIND 10
      CALL EXIT
      END
```

```
      SUBROUTINE DIVER(MOVER1,MOVERE,INTEN1,INTEN,
     XIG1,IGC,NMAX,NUSED,DIV)
C
C THIS SUBROUTINE CALCULATES THE DIVERGENCE
C BETWEEN THE UNKNOWN COMPOUND AND ONE
C COMPOUND FROM THE TAPE
      REAL MOVER1,MOVERE,INTEN1,INTEN
      DIMENSION MOVER1(100),INTEN1(100),MOVERE(26),
     XINTEN(26),IG1(26)
      TOTAL1=0.0
      DO 100 NK=2,NMAX
      I=IG1(NK)
      TOTAL1=TOTAL1+INTEN1(I)
  100 CONTINUE
      TOTAL2=0.0
      NEC=NMAX-1
      DO 101 K=1,NEC
      TOTAL2=TOTAL2+INTEN(K)
  101 CONTINUE
      N1=0
      SUM1=0
      SUM2=0
      S1=0
      S2=0
      K=2
  102 I=IG1(K)
      DO 103 J=1,NEC
      IF(MOVER1(I).EQ.MOVERE(J))GO TO 113
  103 CONTINUE
      IF(MOVER1(I).EQ.14.0)GO TO 3100
      IF(MOVER1(I).EQ.16.0)GO TO 3100
      IF(MOVER1(I).EQ.18.0)GO TO 3100
      IF(MOVER1(I).EQ.28.0)GO TO 3100
      IF(MOVER1(I).EQ.32.0)GO TO 3100
      IF(MOVER1(I).EQ.44.0)GO TO 3100
      N1=N1+1
      PROB1=INTEN1(I)/TOTAL1
      R=INTEN1(I)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      K=K+1
      IF(K.LE.NMAX)GO TO 102
      GO TO 201
  113 PROB1=INTEN1(I)/TOTAL1
      RS=(INTEN1(I)+INTEN(J))/(TOTAL1+TOTAL2)
      R=INTEN1(I)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL1*(PROB1-RS)*ALOG(PROB1/RS)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      K=K+1
      IF(K.LE.NMAX)GO TO 102
      GO TO 201
 3100 WRITE(6,300)MOVER1(I)
  300 FORMAT(1X,F5.1,'IS NOT IN THE TAPE')
      N1=N1+1
      K=K+1
      IF(K.LE.NMAX)GO TO 102
```

```
  201 J=1
  202 DO 203 K=2,NMAX
      I=IG1(K)
      IF(MOVERE(J).EQ.MOVER1(I))GO TO 213
  203 CONTINUE
      IF(MOVERE(J).EQ.14.0)GO TO 4100
      IF(MOVERE(J).EQ.16.0)GO TO 4100
      IF(MOVERE(J).EQ.18.0)GO TO 4100
      IF(MOVERE(J).EQ.28.0)GO TO 4100
      IF(MOVERE(J).EQ.32.0)GO TO 4100
      IF(MOVERE(J).EQ.44.0)GO TO 4100
      PROB=INTEN(J)/TOTAL2
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      J=J+1
      IF(J.LE.NEC)GO TO 202
      GO TO 301
  213 PROB=INTEN(J)/TOTAL2
      RS=(INTEN(J)+INTEN1(I))/(TOTAL1+TOTAL2)
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL2*(PROB-RS)*ALOG(PROB/RS)
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      J=J+1
      IF(J.LE.NEC)GO TO 202
      GO TO 301
 4100 WRITE(6,400)MOVERE(J)
  400 FORMAT(1X,F5.1,'IS NOT IN THE UNKNOWN')
      J=J+1
      IF(J.LE.NEC)GO TO 202
  301 NUSED=NEC+N1
      RNORM=S1+S2
C***TEMPORARY***
      WRITE(6,500)SUM1,SUM2,TOTAL1,TOTAL2
  500 FORMAT(1X,'SUM1=',F10.5,1X,'SUM2=',F10.5,1X,
     X'TOTAL1=',F10.2,1X,'TOTAL2=',F10.2)
      WRITE(6,595)RNORM
  595 FORMAT(1X,'RNORM=',F16.6)
C***TEMPORARY***
      DIV=(SUM1+SUM2)/RNORM
      RETURN
      END
```

```
      DEFINE FILE 9(862,8,E,MWT),10(900,422,E,KEY)
      REAL MOVERE,INTEN
      DIMENSION ICARD(20),IFORM(7),JJ(10),JL(4),MOVERE(28),
     XINTEN(28),IDARD(17),NTM(862)
      DO 100 I=1,862
      NTM(I)=0
  100 CONTINUE
  201 FORMAT(A4,I5,A3,15A4,I3,I2,I3)
      READ(11,201)ICARD(1),NORD,IC,(ICARD(I),I=4,18),NORD,IORD,MWT
      NTM(MWT)=NTM(MWT)+1
  203 READ(11,202,END=204)ICARD(1),NORD,IC,(ICARD(I),I=4,18)
     X,NORD,IORD,MWT
  202 FORMAT(//////A4,I5,A3,15A4,I3,I2,I3)
      NTM(MWT)=NTM(MWT)+1
      GO TO 203
  204 REWIND 11
      KEY=0
      NULL=0
      MWT=1
  205 IF(MWT.GT.862)GO TO 215
      IF(NTM(MWT).GT.0)GO TO 210
      WRITE(9'MWT,300)NULL,NTM(MWT)
  300 FORMAT(I3,I2)
      GO TO 205
  210 KEY=KEY+1
      WRITE(6,396)MWT,KEY,NTM(MWT)
  396 FORMAT(1X,'MWT=',I3,2X,'KEY=',I3,2X,'NTM=',I2)
      WRITE(9'MWT,300)KEY,NTM(MWT)
      KEY=KEY+NTM(MWT)-1
      GO TO 205
  215 WRITE(6,399)
  399 FORMAT(1X,'END OF FILE 9')
      KEY=1
  216 READ(11,211,END=400)ICARD(1),NORD,IC,(ICARD(I),I=4,18),
     XNORD,IORD,MWT
  211 FORMAT(A4,I5,A3,15A4,I3,I2,I3)
      READ(11,213)MWT,(IFORM(I),I=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
  213 FORMAT(38X,I4,7A4,2A1,I3,I2,I3)
      READ(11,305)(IDARD(I),I=1,17),(JL(I),I=1,4),
     XNORD,IORD,MWT
  305 FORMAT(17A4,4A1,I3,I2,I3)
      READ(11,225)(MOVERE(K),INTEN(K),K=1,7),(JJ(I),I=1,2),
     XNORD,IORD,MWT
  225 FORMAT(7(1X,I5,I4),2A1,I3,I2,I3)
      READ(11,225)(MOVERE(K),INTEN(K),K=8,14),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      READ(11,225)(MOVERE(K),INTEN(K),K=15,21),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      READ(11,225)(MOVERE(K),INTEN(K),K=22,28),(JJ(I),I=1,2),
     XNORD,IORD,MWT
      WRITE(6,398)KEY,MWT
  398 FORMAT(1X,'KEY=',I3,'MWT=',I4)
      WRITE(10'KEY,235)ICARD(1),NORD,IC,(ICARD(I),I=4,18),
     XMWT,(IFORM(I),I=1,7),(IDARD(I),I=1,17),
     X(MOVERE(K),INTEN(K),K=1,25)
```

```
235 FORMAT(A4,I5,A3,15A4,I4,7A4,17A4,25(1X,I5,I4))
    GO TO 216
400 WRITE(6,397)
397 FORMAT(1X,'END OF FILE 10')
    REWIND 11
    CALL EXIT
    END
```

```
      C***PROGRAM R3***
      C***MAIN PROGRAM***
            DEFINE FILE 9(862,8,E,MWT),10(900,422,E,KEY)
            REAL MOVER1,INTEN1,MOVERE,INTEN
            DIMENSION ICARD(18),IFORM(7),JJ(10),JL(4),IG1(27),
           XMOVERE(25),INTEN(25),IDARD(17),MOVER1(300),INTEN1(300)
        100 READ(5,250)NUM,MWT
        250 FORMAT(2I7)
            READ(5,252)(MOVER1(J),INTEN1(J),J=1,NUM)
        252 FORMAT(5(F6.1,F7.3))
            WRITE(6,253)
        253 FORMAT(1X,'*****UNKNOWN COMPOUND*****')
            WRITE(6,350)MWT
        350 FORMAT(1X,'MOLECULAR WEIGHT=',I7)
            WRITE(6,359)
        359 FORMAT(1X,'*****SPECTRUM*****')
            WRITE(6,252)(MOVER1(J),INTEN1(J),J=1,NUM)
            CALL BIG(NUM,INTEN1,IG1,NG1)
            READ(9'MWT,200)KEY,NTM
        200 FORMAT(I3,I2)
            NSUP=KEY+NTM-1
            WRITE(6,229)
            WRITE(6,219)
        229 FORMAT(' ')
        219 FORMAT('0',2X,76(1H*))
            WRITE(6,994)
        994 FORMAT(1X,'**PROBABLE COMPOUND**')
        236 READ(10'KEY,235)ICARD(1),NORD,IC,(ICARD(I),I=4,18),
           XMWT,(IFORM(I),I=1,7),(IDARD(I),I=1,17),
           X(MOVERE(K),INTEN(K),K=1,25)
        235 FORMAT(A4,I5,A3,15A4,I4,7A4,17A4,25(1X,F5.1,F4.2))
            WRITE(6,995)(IDARD(I),I=1,17),(IFORM(I),I=1,7),MWT
        995 FORMAT(1X,17A4,1X,7A4,1X,I4)
            DO 300 I=1,25
            IF(INTEN(I).EQ.0.0)GO TO 305
        300 CONTINUE
            NGC=26
            GO TO 406
        305 NGC=I
        406 IF(NG1-NGC)282,283,283
        282 NMAX=NG1
            GO TO 284
        283 NMAX=NGC
        284 NEC=NMAX-1
            DO 301 J=1,NEC
            I=IG1(2)
            IF(MOVER1(I).EQ.MOVERE(J))GO TO 321
        301 CONTINUE
            GO TO 703
        321 DO 302 J=2,NMAX
            I=IG1(J)
            IF(MOVERE(1).EQ.MOVER1(I))GO TO 322
        302 CONTINUE
        703 WRITE(6,704)
        704 FORMAT(1X,'MISSING HIGHEST PEAK')
            IF(KEY.LE.NSUP)GO TO 236
```

```
      GO TO 237
  322 CALL DIVER(MOVER1,MOVERF,INTEN1,INTEN,IG1,IGC,
     XNMAX,NUSED,DIV)
      WRITE(6,505)DIV
  505 FORMAT(1X,'*****DIVERGENCE=',F6.4,'*****')
  996 IF(KEY.LE.NSUP)GO TO 236
  237 WRITE(6,997)
  997 FORMAT(1X,'END OF COMPOUNDS WITH THE SAME MOLECULAR WEIGHT')
  700 FORMAT(I1)
      READ(5,700)ISTOP
      IF(ISTOP.EQ.1)GO TO 100
      CALL EXIT
      END
```

```
C
C PROGRAMME TO COMPARE WITH EIGHT PEAK TAPE
C
C THIS PROGRAMME IS ORGANIZED SO THAT ONLY
C COMPOUNDS WITH THE SAME MOLECULAR WEIGHT
C ARE COMPARED
C THERE IS A PRE FILTERING CONDITION THAT THE BIGGEST
C PEAK OF THE UNKNOWN MUST EXIST IN THE EIGHT
C BIGGEST PEAKS OF THE COMPOUND IN THE TAPE
C AND VICE-VERSA
C THE DATA SHOULD BE SUPPLIED IN DECREASING
C ORDER OF INTENSITY
      REAL MOVER1,MOVERE,INTPP
      DIMENSION MOVER1(8),MOVERE(8),RINTEN(8),INTEN(8),
     XINTEN1(8),NN(11),INAME(211)
      INTEGER A/'A'/,B/'B'/,C/'C'/,D/'D'/,E/'E'/,F/'F'/,
     XG/'G'/,L/'L'/,V/'V'/,W/'W'/,X/'X'/,Y/'Y'/,Z/'Z'/
   99 READ(5,341)MWT1
      READ(5,351)(MOVER1(J),RINTEN(J),J=1,8)
      DO 352 J=1,8
      INTEN1(J)=IFIX(RINTEN(J)+0.5)
  352 CONTINUE
      WRITE(6,340)
      WRITE(6,350)MWT1
      WRITE(6,359)
      WRITE(6,371)(MOVER1(J),INTEN1(J),J=1,8)
      WRITE(6,219)
  340 FORMAT(1X,'*****UNKNOWN COMPOUND*****')
  341 FORMAT(I7)
  350 FORMAT(1X,'MOLECULAR WEIGHT=',I7)
  359 FORMAT(1X,'******SPECTRUM******')
  371 FORMAT(4(F6.1,I6))
  351 FORMAT(4(F6.1,F7.2))
      DO 353 J=1,7
      JP=J+1
      IF(INTEN1(JP).GT.INTEN1(J))GO TO 360
  353 CONTINUE
      REWIND 12
      MES=0
  201 IF(LC.EQ.B.AND.NSPEC.EQ.456)GO TO 402
      IF(LC.EQ.B.AND.NSPEC.EQ.496)GO TO 402
      READ(12,100,END=999)LC,NSPEC,(MOVERE(I),I=1,8),(INTEN(I),I=2,8),
     XMOLW,INTPP,NC,NH,(NN(I),I=1,4)
  100 FORMAT(A1,I4,8F5.1,7I2,I4,F4.2,I2,I3,4I2)
      MES=MES+1
      IF(MES.EQ.699)GO TO 996
  404 CONTINUE
      IF(MWT1.EQ.MOLW)GO TO 101
  304 READ(12,200)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
     X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND
      IF(IND.EQ.1)GO TO 201
      READ(12,300)LC,NSPEC,(INAME(I),I=64,137),IND
      IF(IND.EQ.1)GO TO 201
      READ(12,300)LC,NSPEC,(INAME(I),I=138,211),IND
      GO TO 201
  402 READ(12,403)LC,NSPEC,(MOVERE(I),I=1,8),(INTEN(I),I=2,8),
```

```
     XMOLW,INTOP,ERROR,NC,NH,(NN(I),I=1,4)
  403 FORMAT(A1,I4,8F5.1,7I2,I4,F3.1,A1,I2,I3,4I2)
      GO TO 404
  101 DO 301 J=1,8
      IF(MOVER1(1).EQ.MOVERE(J))GO TO 321
  301 CONTINUE
      GO TO 304
  321 DO 302 J=1,8
      IF(MOVERE(1).EQ.MOVER1(J))GO TO 322
  302 CONTINUE
      GO TO 304
  322 INTEN(1)=100
      CALL DIVER(MOVER1,MOVERE,INTEN1,INTEN,
     XNUSED,DIV)
  202 READ(12,200)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
     X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND
  200 FORMAT(A1,I4,2I2,2I1,2I2,I1,63A1,I1)
      IF(IND.EQ.0)GO TO 203
      IF(IND.EQ.1) KP=1
      GO TO 210
  203 READ(12,300)LC,NSPEC,(INAME(I),I=64,137),IND
  300 FORMAT(A1,I4,74A1,I1)
      IF(IND.EQ.0) GO TO 204
      IF(IND.EQ.1)KP=2
      GO TO 210
  204 READ(12,300)LC,NSPEC,(INAME(I),I=138,211),IND
  218 WRITE(6,219)
  219 FORMAT('0',2X,76(1H*))
  210 IF(LC.EQ.A.OR.LC.EQ.B.OR.LC.EQ.C.OR.LC.EQ.D
     X.OR.LC.EQ.E.OR.LC.EQ.F.OR.LC.EQ.G) GO TO 220
  211 IF(LC.EQ.L)GO TO 221
  212 IF(LC.EQ.V) GO TO 222
  213 IF(LC.EQ.W)GO TO 223
  214 IF(LC.EQ.X) GO TO 224
  215 IF(LC.EQ.Y) GO TO 225
  216 IF(LC.EQ.Z) GO TO 226
  217 IF(LC.EQ.0) GO TO 227
  220 WRITE(6,230)NSPEC
      GO TO 240
  221 WRITE(6,231)NSPEC
      GO TO 240
  222 WRITE(6,232)NSPEC
      GO TO 240
  223 WRITE(6,233)NSPEC
      GO TO 240
  224 WRITE(6,234)NSPEC
      GO TO 240
  225 WRITE(6,235)NSPEC
      GO TO 240
  226 WRITE(6,236)NSPEC
      GO TO 240
  227 WRITE(6,237)NSPEC
      GO TO 240
  230 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-NUMBER-',I4)
  231 FORMAT(21X,'MASS SPECTRUM FROM LITERATURE',1X,I4)
  232 FORMAT(21X,'MASS SPECTRUM FROM API(MATRIX)',1X,I4)
```

```
 233 FORMAT(21X,'MASS SPECTRUM FROM MCA (NOW TRC)',1X,I4)
 234 FORMAT(21X,'MASS SPECTRUM FROM ASTM-NUMBER-',I4)
 235 FORMAT(21X,'MASS SPECTRUM FROM API-NUMBER-',I4)
 236 FORMAT(21X,'MASS SPECTRUM FROM DOW-NUMBER-',I4)
 237 FORMAT(21X,'MASS SPECTRUM FROM MSDC-NUMBER-',I4)
 240 WRITE(6,245)(INAME(I),I=1,63)
     IF(KP.EQ.1) GO TO 250
     WRITE(6,245)(INAME(I),I=64,137)
     IF(KP.EQ.2) GO TO 250
     WRITE(6,245)(INAME(I),I=138,211)
 245 FORMAT(' ',2(1H*),74A1,2(1H*))
 250 IF(INTPP.EQ.0)GO TO 251
     IF(INTPP.EQ.(-0.01))GO TO 252
     WRITE(6,260) MOLW,INTPP
     GO TO 259
 251 WRITE(6,261)MOLW
     GO TO 259
 252 DO 253 I=1,8
     IF(IFIX(MOVERE(I)).EQ.MOLW)GO TO 401
 253 CONTINUE
 401 WRITE(6,262)MOLW,INTEN(I)
 260 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
    X'INT. OF PARENT PEAK=',F4.2)
 261 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
    X'INT. OF PARENT PEAK LESS THAN 0.01')
 262 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
    X'INT.OF PARENT PEAK=',I3)
 259 WRITE(6,270)NC,NH,NN(1),NN(2),NN(3),
    XNN(4),NN(5),NN(6),NN(7),NN(8),NN(9),NN(10),NN(11)
 270 FORMAT(' ',1X,'FORMULA=C',I2,'.H',I3,'.N',I2,
    X'.O',I2,'.F',I2,'.CL',I2,'.BR',I2,
    X'.B',I2,'.SI',I1,'.P',I1,'.S',I2,'.D',I2,
    X'(PLUS ',I1,' OF OTHER(S))')
     WRITE(6,219)
     WRITE(6,229)
     WRITE(6,271)(MOVERE(I),INTEN(I),I=1,8)
 229 FORMAT(' ')
 271 FORMAT(30X,F5.1,12X,I3)
     WRITE(6,504)NUSED
 504 FORMAT(1X,I2,'WERE USED')
     WRITE(6,505)DIV
 505 FORMAT(1X,'*****DIVERGENCE=',F6.4,'*****')
     WRITE(6,229)
     WRITE(6,219)
     GO TO 201
 360 WRITE(6,361)
 361 FORMAT(1X,'DATA INTRODUCED IN WRONG ORDER')
     STOP
 996 WRITE(6,997)
 997 FORMAT(1X,'END OF 700 SPECTRA')
     REWIND 12
     READ(5,700)ISTOP
 700 FORMAT(I1)
     IF(ISTOP.EQ.1)GO TO 99
     STOP
 999 WRITE(6,998)
```

```
  998 FORMAT(1X,'END OF TAPE')
      REWIND 12
      STOP
      END
```

J

```
C PROGRAM TO TRANSFER TAPE J9769 TO TAPE B9901
      DIMENSION MOVERE(8),INTEN(8),NN(11),INAME(211)
      INTEGERA/'A'/,B/'B'/,C/'C'/,D/'D'/,E/'E'/,F/'F'/,
     XG/'G'/,L/'L'/,V/'V'/,W/'W'/,X/'X'/,Y/'Y'/,Z/'Z'/
      INTEGER ZERO/'0'/
      REWIND 12
      DO 888 K=1,2500
      READ(12,887)
  887 FORMAT(//////////)
  888 CONTINUE
      ICOUNT=25000
   99 IF(ICOUNT.GE.30000)GO TO 997
      READ(12,100,END=999)LC,NSPEC,(MOVERE(I),I=1,8),
     X(INTEN(I),I=2,8),MOLW,INTPP,NC,NH,(NN(I),I=1,4)
  100 FORMAT(A1,I4,8I5,7I2,I4,I4,I2,I3,4I2)
      IF(LC.EQ.A)LK=1
      IF(LC.EQ.B)LK=2
      IF(LC.EQ.C)LK=3
      IF(LC.EQ.D)LK=4
      IF(LC.EQ.E)LK=5
      IF(LC.EQ.F)LK=6
      IF(LC.EQ.G)LK=7
      IF(LC.EQ.L)LK=8
      IF(LC.EQ.V)LK=9
      IF(LC.EQ.W)LK=10
      IF(LC.EQ.X)LK=11
      IF(LC.EQ.Y)LK=12
      IF(LC.EQ.Z)LK=13
      IF(LC.EQ.ZERO)LK=14
      IK=1
      WRITE(10,101)LC,NSPEC,(MOVERE(I),I=1,8),(INTEN(I),I=2,8),
     XMOLW,INTPP,NC,NH,(NN(I),I=1,4),LK,MOLW,IK
  101 FORMAT(A1,I4,8I5,7I2,I4,I4,I2,I3,4I2,I2,I4,I1)
      ICOUNT=ICOUNT+1
  102 READ(12,200)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
     X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND
  200 FORMAT(A1,I4,2I2,2I1,2I2,I1,63A1,I1)
      IK=2
      WRITE(10,201)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
     X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND,LK,MOLW,IK
  201 FORMAT(A1,I4,2I2,2I1,2I2,I1,63A1,I1,I2,I4,I1)
      ICOUNT=ICOUNT+1
      IF(IND.EQ.1)GO TO 99
      READ(12,300)LC,NSPEC,(INAME(I),I=64,137),IND
  300 FORMAT(A1,I4,74A1,I1)
      IK=3
      WRITE(10,301)LC,NSPEC,(INAME(I),I=64,137),IND,LK,MOLW,IK
  301 FORMAT(A1,I4,74A1,I1,I2,I4,I1)
      ICOUNT=ICOUNT+1
      IF(IND.EQ.1)GO TO 99
      READ(12,300)LC,NSPEC,(INAME(I),I=138,211),IND
      IK=4
      WRITE(10,301)LC,NSPEC,(INAME(I),I=138,211),IND,LK,MOLW,IK
      ICOUNT=ICOUNT+1
      GO TO 99
  997 WRITE(6,996)ICOUNT
```

```
      996 FORMAT(1X,'END OF ',I5,' RECORDS')
      999 WRITE(6,998)ICOUNT
      998 FORMAT(1X,I5,' RECORDS TRANSFERRED')
          CALL EXIT
          END
```

```
      DIMENSION IJUNK(20)
      MARK=2
      IREL=0
      INULL=0
      ICOUNT=1
      WRITE(12,200)MARK,ICOUNT
  200 FORMAT(I4,I5)
      WRITE(6,300)MARK,ICOUNT
  300 FORMAT(1X,'MOLECULAR WEIGHT',I4,'STARTS AT RECORD NUMBER',I5)
  101 READ(10,100,END=207)(IJUNK(I),I=1,20),LK,MOLW,IK
  100 FORMAT(20A4,I2,I4,I1)
      IF(MOLW.NE.MARK)GO TO 205
      IREL=IREL+1
      GO TO 101
  205 MARK=MARK+1
      IF(MOLW.GT.MARK)GO TO 206
      ICOUNT=ICOUNT+IREL
      WRITE(12,200)MOLW,ICOUNT
      WRITE(6,300)MOLW,ICOUNT
      IREL=1
      GO TO 101
  206 WRITE(12,200)MARK,INULL
      WRITE(6,300)MARK,INULL
      GO TO 205
  207 WRITE(6,400)
  400 FORMAT(1X,'END OF TAPE')
      CALL EXIT
      END
```

```
      C COMPOUNDS WITH THE SAME MOLECULAR WEIGHT
      C ARE COMPARED
      C THERE IS A PRE FILTERING CONDITION THAT THE BIGGEST
      C PEAK OF THE UNKNOWN MUST EXIST IN THE EIGHT
      C BIGGEST PEAKS OF THE COMPOUND IN THE TAPE
      C AND VICE-VERSA
      C THE DATA SHOULD BE SUPPLIED IN DECREASING
      C ORDER OF INTENSITY
            REAL MOVER1,MOVERE,INTPP
            DIMENSION MOVER1(8),MOVERE(8),RINTEN(8),INTEN(8),
           XINTEN1(8),NN(11),INAME(211),NUMBER(10),IPLACE(10)
            DIMENSION INEXT(10),ICOMP(10)
            INTEGER A/'A'/,B/'B'/,C/'C'/,D/'D'/,E/'E'/,F/'F'/,
           XG/'G'/,L/'L'/,V/'V'/,W/'W'/,X/'X'/,Y/'Y'/,Z/'Z'/
            INTEGER ZERO/'0'/
            REWIND10
            I=0
            IP=0 LNEAR=0
         99 READ(5,341)MWT1
            WRITE(6,350)MWT1
            IF(I)51,51,52
         51 IDIGIT=MWT1-2
            IF(IDIGIT.EQ.0)GO TO 93
            GO TO 94
         53 WRITE(6,996)
        996 FORMAT(1X,'NO COMPOUNDS OF THIS MOLECULAR WEIGHT')
            IF(IP.GE.IMAX)GO TO 990
            GO TO 54
         52 IDIGIT=MWT1-1-INEXT(I)
            IF(IDIGIT.EQ.0)GO TO 93
         94 DO 95 K=1,IDIGIT
            READ(10,92)
         92 FORMAT(1X)
         95 CONTINUE
         93 READ(10,90)MARK,ICOUNT
         90 FORMAT(I4,I5)
            WRITE(6,80)MARK,ICOUNT
         80 FORMAT(1X,'MOLW=',I4,'ICOUNT=',I5)
            I=I+1
            IPLACE(I)=ICOUNT
            NUMBER(I)=MWT1
         56 READ(10,90)MARK,ICOUNT
            ICOMP(I)=ICOUNT
            INEXT(I)=MARK
            IF(ICOUNT.EQ.0)GO TO 56
            WRITE(6,80)MARK,ICOUNT
            IMAX=I
            READ(5,700)ISTOP
        700 FORMAT(I1)
            IF(ISTOP.EQ.1)GO TO 99
            DO 88 K=1,35042
            READ(10,92,END=87)
         88 CONTINUE
         87 WRITE(6,86)
         86 FORMAT(1X,'END OF FIRST FILE')
         54 IP=IP+1
```

```
      IF(NEAR.EQ.1)GO TO 58
      IF(IPLACE(IP).EQ.0)GO TO 53
      IR=IP-1
      IF(IR.EQ.0)GO TO 57
      ICOUNT=IPLACE(IP)-ICOMP(IR)-1
      GO TO 58
   57 ICOUNT=IPLACE(IP)-1
   58 WRITE(6,55)IP
   55 FORMAT(1X,'COMPOUND NUMBER ',I2)
      READ(5,351)(MOVER1(J),RINTEN(J),J=1,8)
      DO 352 J=1,8
      INTEN1(J)=IFIX(RINTEN(J)+0.5)
  352 CONTINUE
      WRITE(6,340)
      WRITE(6,359)
      WRITE(6,371)(MOVER1(J),INTEN1(J),J=1,8)
      WRITE(6,219)
  340 FORMAT(1X,'*****UNKNOWN COMPOUND*****')
  341 FORMAT(I7)
  350 FORMAT(1X,'MOLECULAR WEIGHT=',I7)
  359 FORMAT(1X,'******SPECTRUM******')
  371 FORMAT(4(F6.1,I6))
  351 FORMAT(4(F6.1,F7.2))
      DO 353 J=1,7
      JP=J+1
      IF(INTEN1(JP).GT.INTEN1(J))GO TO 360
  353 CONTINUE
      IF(NUMBER(IP).EQ.2)GO TO 201
      IF(NEAR.EQ.1)GO TO 101
      DO 354 K=1,ICOUNT
      READ(10,92)
  354 CONTINUE
  201 READ(10,100,END=999)LC,NSPEC,(MOVERE(I),I=1,8),(INTEN(I),I=2,8),
     XMOLW,INTPP,NC,NH,(NN(I),I=1,4),LK,MOLW,IK
  100 FORMAT(A1,I4,8F5.1,7I2,I4,F4.2,I2,I3,4I2,I2,I4,I1)
      IF(NUMBER(IP).EQ.MOLW)GO TO 101
      IF(NUMBER(IP).LT.MOLW)GO TO 995
  101 DO 301 J=1,8
      IF(MOVER1(1).EQ.MOVERE(J))GO TO 321
  301 CONTINUE
      NEAR=0
  304 READ(10,200)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
     X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND,LK,MOLW,IK
      IF(IND.EQ.1)GO TO 201
      READ(10,300)LC,NSPEC,(INAME(I),I=64,137),IND,LK,MOLW,IK
      IF(IND.EQ.1)GO TO 201
      READ(10,300)LC,NSPEC,(INAME(I),I=138,211),IND,LK,MOLW,IK
      GO TO 201
  321 DO 302 J=1,8
      IF(MOVERE(1).EQ.MOVER1(J))GO TO 322
  302 CONTINUE
      GO TO 304
  322 INTEN(1)=100
      CALL DIVER(MOVER1,MOVERE,INTEN1,INTEN,
     XNUSED,DIV)
  202 READ(10,200)LC,NSPEC,(NN(I),I=5,6),(NN(I),I=7,8),
```

```
      X(NN(I),I=9,10),NN(11),(INAME(I),I=1,63),IND,LK,MOLW,IK
  200 FORMAT(A1,I4,2I2,2I1,2I2,I1,63A1,I1,I2,I4,I1)
      IF(IND.EQ.0)GO TO 203
      IF(IND.EQ.1) KP=1
      GO TO 210
  203 READ(10,300)LC,NSPEC,(INAME(I),I=64,137),IND,LK,MOLW,IK
  300 FORMAT(A1,I4,74A1,I1,I2,I4,I1)
      IF(IND.EQ.0) GO TO 204
      IF(IND.EQ.1)KP=2
      GO TO 210
  204 READ(10,300)LC,NSPEC,(INAME(I),I=138,211),IND,LK,MOLW,IK
  218 WRITE(6,219)
  219 FORMAT('0',2X,76(1H*))
  210 IF(LC.EQ.A)GO TO 220
      IF(LC.EQ.B)GO TO 421
      IF(LC.EQ.C)GO TO 422
      IF(LC.EQ.D)GO TO 423
      IF(LC.EQ.E)GO TO 424
      IF(LC.EQ.F)GO TO 425
      IF(LC.EQ.G)GO TO 426
  211 IF(LC.EQ.L)GO TO 221
  212 IF(LC.EQ.V) GO TO 222
  213 IF(LC.EQ.W)GO TO 223
  214 IF(LC.EQ.X) GO TO 224
  215 IF(LC.EQ.Y) GO TO 225
  216 IF(LC.EQ.Z) GO TO 226
  217 IF(LC.EQ.ZERO)GO TO 227
  220 WRITE(6,230)NSPEC
      GO TO 240
  421 WRITE(6,431)NSPEC
      GO TO 240
  422 WRITE(6,432)NSPEC
      GO TO 240
  423 WRITE(6,433)NSPEC
      GO TO 240
  424 WRITE(6,434)NSPEC
      GO TO 240
  425 WRITE(6,435)NSPEC
      GO TO 240
  426 WRITE(6,436)NSPEC
      GO TO 240
  221 WRITE(6,231)NSPEC
      GO TO 240
  222 WRITE(6,232)NSPEC
      GO TO 240
  223 WRITE(6,233)NSPEC
      GO TO 240
  224 WRITE(6,234)NSPEC
      GO TO 240
  225 WRITE(6,235)NSPEC
      GO TO 240
  226 WRITE(6,236)NSPEC
      GO TO 240
  227 WRITE(6,237)NSPEC
      GO TO 240
  230 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-A-',I4)
```

```
      231 FORMAT(21X,'MASS SPECTRUM FROM LITERATURE',1X,I4)
      232 FORMAT(21X,'MASS SPECTRUM FROM API(MATRIX)',1X,I4)
      233 FORMAT(21X,'MASS SPECTRUM FROM MCA (NOW TRC)',1X,I4)
      234 FORMAT(21X,'MASS SPECTRUM FROM ASTM-NUMBER-',I4)
      235 FORMAT(21X,'MASS SPECTRUM FROM API-NUMBER-',I4)
      236 FORMAT(21X,'MASS SPECTRUM FROM DOW-NUMBER-',I4)
      237 FORMAT(21X,'MASS SPECTRUM FROM MSDC-NUMBER-',I4)
      431 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-B-',I4)
      432 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-C-',I4)
      433 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-D-',I4)
      434 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-E-',I4)
      435 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-F-',I4)
      436 FORMAT(21X,'MASS SPECTRUM FROM ICI,LTD-G-',I4)
      240 WRITE(6,245)(INAME(I),I=1,63)
          IF(KP.EQ.1) GO TO 250
          WRITE(6,245)(INAME(I),I=64,137)
          IF(KP.EQ.2) GO TO 250
          WRITE(6,245)(INAME(I),I=138,211)
      245 FORMAT(' ',2(1H*),74A1,2(1H*))
      250 IF(INTPP.EQ.ZERO)GO TO 251
          IF(INTPP.EQ.(-0.01))GO TO 252
          WRITE(6,260) MOLW,INTPP
          GO TO 259
      251 WRITE(6,261)MOLW
          GO TO 259
      252 DO 253 I=1,8
          IF(IFIX(MOVERE(I)).EQ.MOLW)GO TO 401
      253 CONTINUE
      401 WRITE(6,262)MOLW,INTEN(I)
      260 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
         X'INT. OF PARENT PEAK=',F4.2)
      261 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
         X'INT. OF PARENT PEAK LESS THAN 0.01')
      262 FORMAT(11X,'MOLECULAR WEIGHT=',I4,1X,
         X'INT.OF PARENT PEAK=',I3)
      259 WRITE(6,270)NC,NH,NN(1),NN(2),NN(3),
         XNN(4),NN(5),NN(6),NN(7),NN(8),NN(9),NN(10),NN(11)
      270 FORMAT(' ',1X,'FORMULA=C',I2,'.H',I3,'.N',I2,
         X'.O',I2,'.F',I2,'.CL',I2,'.BR',I2,
         X'.B',I2,'.SI',I1,'.P',I1,'.S',I2,'.D',I2,
         X'(PLUS ',I1,' OF OTHER(S))')
      229 FORMAT(' ')
          WRITE(6,504)NUSED
      504 FORMAT(1X,I2,'WERE USED')
          WRITE(6,505)DIV
      505 FORMAT(1X,'*****DIVERGENCE=',F6.4,'*****')
          WRITE(6,229)
          WRITE(6,219)
          GO TO 201
      360 WRITE(6,361)
      361 FORMAT(1X,'DATA INTRODUCED IN WRONG ORDER')
          STOP
      995 WRITE(6,994)
      994 FORMAT(1X,'END OF COMPOUNDS WITH THE SAME MOLECULAR WEIGHT')
          IP=IP+1
          IF(NUMBER(IP).EQ.MOLW)NEAR=1
```

```
      IP=IP+1
      IF(IP.LT.IMAX)GO TO 54
  990 WRITE(6,991)
  991 FORMAT(1X,'END OF JOB')
      REWIND 10
      STOP
  999 WRITE(6,998)
  998 FORMAT(1X,'END OF TAPE')
      REWIND 10
      STOP
      END
```

```
      SUBROUTINE DIVER(MOVER1,MOVERE,INTEN1,INTEN,
     XNUSED,DIV)
C
C THIS SUBROUTINE CALCULATES THE DIVERGENCE BETWEEN
C THE UNKNOWN COMPOUND AND ONE COMPOUND
C FROM THE TAPE
      REAL MOVER1,MOVERE
      DIMENSION MOVER1(8),MOVERE(8),INTEN1(8),INTEN(8)
      TOTAL1=0.0
      DO 100 K=1,8
      TOTAL1=TOTAL1+INTEN1(K)
  100 CONTINUE
      TOTAL2=0.0
      DO 101 K=1,8
      TOTAL2=TOTAL2+INTEN(K)
  101 CONTINUE
      N1=0
      SUM1=0
      SUM2=0
      S1=0
      S2=0
      K=1
  102 DO 103 J=1,8
      IF(MOVER1(K).EQ.MOVERE(J))GO TO 113
  103 CONTINUE
      IF(MOVER1(K).EQ.14.0)GO TO 3100
      IF(MOVER1(K).EQ.16.0)GO TO 3100
      IF(MOVER1(K).EQ.18.0)GO TO 3100
      IF(MOVER1(K).EQ.28.0)GO TO 3100
      IF(MOVER1(K).EQ.32.0)GO TO 3100
      IF(MOVER1(K).EQ.44.0)GO TO 3100
      N1=N1+1
      PROB1=INTEN1(K)/TOTAL1
      R=INTEN1(K)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      K=K+1
      IF(MOVER1(K).EQ.0.0)GO TO 200
      IF(INTEN1(K).LT.1)GO TO 200
      IF(K.LT.9)GO TO 102
      GO TO 201
  113 PROB1=INTEN1(K)/TOTAL1
      RS=(INTEN1(K)+INTEN(J))/(TOTAL1+TOTAL2)
      R=INTEN1(K)/(TOTAL1+TOTAL2)
      SUM1=SUM1+TOTAL1*(PROB1-RS)*ALOG(PROB1/RS)
      S1=S1+TOTAL2*R*ALOG(TOTAL2*PROB1/0.0001)
      K=K+1
      IF(MOVER1(K).EQ.0.0)GO TO 200
      IF(INTEN1(K).LT.1)GO TO 200
      IF(K.LT.9)GO TO 102
      GO TO 201
 3100 WRITE(6,300)MOVER1(K)
  300 FORMAT(1X,F5.1,'IS VERY DIFFERENT IN THE UNKNOWN')
      N1=N1+1
      K=K+1.
      IF(MOVER1(K).EQ.0.0)GO TO 200
```

```
      IF(K.LT.9)GO TO 102
      GO TO 201
  200 N1=N1+9-K
  201 J=1
  202 DO 203 K=1,8
      IF(MOVERE(J).EQ.MOVER1(K))GO TO 213
  203 CONTINUE
      IF(MOVERE(J).EQ.14.0)GO TO 4100
      IF(MOVERE(J).EQ.16.0)GO TO 4100
      IF(MOVERE(J).EQ.18.0)GO TO 4100
      IF(MOVERE(J).EQ.28.0)GO TO 4100
      IF(MOVERE(J).EQ.32.0)GO TO 4100
      IF(MOVERE(J).EQ.44.0)GO TO 4100
      PROB=INTEN(J)/TOTAL2
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      J=J+1
      IF(MOVERE(J).EQ.0.0)GO TO 301
      IF(INTEN(J).LT.1)GO TO 301
      IF(J.LT.9)GO TO 202
      GO TO 301
  213 PROB=INTEN(J)/TOTAL2
      RS=(INTEN(J)+INTEN1(K))/(TOTAL1+TOTAL2)
      R=INTEN(J)/(TOTAL1+TOTAL2)
      SUM2=SUM2+TOTAL2*(PROB-RS)*ALOG(PROB/RS)
      S2=S2+TOTAL1*R*ALOG(TOTAL1*PROB/0.0001)
      J=J+1
      IF(MOVERE(J).EQ.0.0)GO TO 301
      IF(INTEN(J).LT.1)GO TO 301
      IF(J.LT.9)GO TO 202
      GO TO 301
 4100 WRITE(6,300)MOVERE(J)
  400 FORMAT(1X,F5.1,'IS VERY DIFFERENT IN THE TAPE')
      J=J+1
      IF(MOVERE(J).EQ.0.0)GO TO 301
      IF(J.LT.9)GO TO 202
  301 NUSED=8-N1
      RNORM=S1+S2
      DIV=(SUM1+SUM2)/RNORM
      RETURN
      END
```

```
C   ***PROGRAM MASPEC***
C
C THIS PROGRAM PROCESSES DATA FROM A MASS SPECTROMETER.
C FOR COMPLETE INFORMATION REFER TO PROGRAM SPECIFICATION
C
C THIS SECTION READS THE MASS NUMBERS AND ABUNDANCES
C AND CALCULATES THE PROBABILITY OF EACH MASS PEAK
C WARNING= THE TOTALITY OF THE INTEGER MASS NUMBERS
C MUST BE SUPPLIED IN INCREASING ORDER BECAUSE
C THE PROGRAM DEPENDS ON THAT.
      INTEGER A/'MIN'/,B/'MAX'/,C/'END'/
      INTEGER END
      DIMENSION NTIT(8),NALM(300),ALREL(300),
     XMASS(70),PROB(70),PROBL(300)
  100 MIN=A
      MAX=B
      END=C
    1 READ(5,500)MFLAG,MINT,(NTIT(I),I=1,10)
      IF(MFLAG.NE.MIN)GO TO 1
      MIN=MINT
    2 READ(5,500)MFLAG,MINT
      IF(MFLAG.NE.MAX)GO TO 2
      MAX=MINT
      NUM=0
    3 READ(5,501)MFLAG,MINT,REL
      IF(MFLAG.EQ.END)GO TO 4
      IF(NUM.EQ.300)GO TO 5
      IF(NUM.EQ.0)GO TO 8
      IF(MINT.LT.NALM(NUM))GO TO 6
    8 NUM=NUM+1
      NALM(NUM)=MINT
      ALREL(NUM)=REL
      GO TO 3
    5 WRITE(6,600)
    7 STOP
    6 WRITE(6,601)
      GO TO 7
    4 CONTINUE
      WRITE(6,653)
      WRITE(6,652)
      WRITE(6,650)(NTIT(I),I=1,10)
      WRITE(6,652)
      WRITE(6,653)
      WRITE(6,654)(NALM(I),ALREL(I),I=1,NUM)
      WRITE(6,655)MIN,MAX
      WRITE(6,653)
      WRITE(6,652)
      WRITE(6,653)
      SUM=0.0
      DO 109 K=1,NUM
      SUM=SUM+ALREL(K)
  109 CONTINUE
  800 DO 11 K=1,NUM
      PROBL(K)=ALREL(K)/SUM
   11 CONTINUE
  500 FORMAT(A4,2X,I3,20X,10A4)
```

```
    501 FORMAT(A4,2X,I3,11X,F6.2)
    600 FORMAT(4X,'***TOO MANY INPUT CARDS-JOB ABANDONED***')
    601 FORMAT(4X,'***INPUT SEQUENCE ERROR-JOB ABANDONED***')
    650 FORMAT('0',4X,'MASPEC RUN-LIST OF INPUT DATA FOR',1X,10A4)
    652 FORMAT('0',2X,76(1H*))
    653 FORMAT('0')
    654 FORMAT(5(3X,I3,1X,F7.3,2X))
    655 FORMAT(' ',25X,'RANGE IS FROM',1X,I3,1X,'TO',1X,I3)
        CALL COMB(NUM,NALM,MIN,MAX,PROBL,MASS,PROB,KR)
  C
  C THIS PART ORDERS THE ARRAY MASS(K) IN INCREASING
  C ORDER AND WRITES THE MASSES AND CORRESPONDING PROBABILITIES
  C
        WRITE(6,652)
        WRITE(6,301)(NTIT(I),I=1,10)
        WRITE(6,652)
        WRITE(6,302)
    301 FORMAT('0',4X,'MASPEC RUN-RESULTS FOR',1X,10A4)
    302 FORMAT(' ',24X,'MASS NUMBER',10X,'PROBABILITY',24X)
    310 DO 320 K=1,KR
        IF(MIN.EQ.MASS(K))GO TO 325
    320 CONTINUE
        PROBE=0.0
        WRITE(6,330)MIN,PROBE
        GO TO 326
    325 WRITE(6,330)MASS(K),PROB(K)
    326 MIN=MIN+1
        IF(MIN.LE.MAX)GO TO 310
    330 FORMAT(23X,I5,24X,F6.4,22X)
    700 FORMAT(I1)
        READ(5,700)ISTOP
        IF(ISTOP.EQ.1)GO TO 100
        CALL EXIT
        END
```

```
      SUBROUTINE COMB(MM,NALM,MIN,MAX,PROBL,MASS,PROB,KR)
C THIS SUBROUTINE GENERATES ALL THE SINGLE, DOUBLE,TRIPLE,
C AND QUADRUPLE COMBINATIONS OF MASSES WHOSE SUM
C FALLS INSIDE THE RANGE DETERMINED BY MIN AND MAX
C  ONCE EACH COMBINATION IS ORGANIZED THE VALUE
C OF PROBL OF THE CORRESPONDING MASSES IS ADDED
C IN PROB(MASS) IF IT HAS NOT YET BEEN INCLUDED
C
      DIMENSION IRRAY(70,300),NALM(300),MASS(70),
     XPROB(70),PROBL(300)
C***TEMPORARY***
      WRITE(6,777)
  777 FORMAT(14X,'PROBABILITIES')
      WRITE(6,887)(NALM(I),PROBL(I),I=1,MM)
  887 FORMAT(1X,5(I3,2X,F6.4,4X))
C***TEMPORARY***
      DO 99 KR=1,70
      DO 98 I=1,300
      IRRAY(KR,I)=0
   98 CONTINUE
   99 CONTINUE
      KR=0
C
C GENERATE SINGLE COMBINATIONS
C
      WRITE(6,888)
  888 FORMAT(1X,'SINGLE COMBINATIONS')
      I=0
  103 IF(I.GE.MM)GO TO 100
      I=I+1
      IF(NALM(I)-MIN)103,102,101
  101 IF(NALM(I)-MAX)102,102,100
  102 KR=KR+1
      MASS(KR)=NALM(I)
      PROB(KR)=PROBL(I)
      IRRAY(KR,I)=1
      GO TO 103
  100 CONTINUE
C
C GENERATE DOUBLE COMBINATIONS
C
      K=0
      L=0
      WRITE(6,997)
  997 FORMAT(1X,'DOUBLE COMBINATIONS')
      IZ=MM
      IY=IZ-1
      I=0
  110 IF(I.GE.IY)GO TO 111
      I=I+1
      J=I
  112 IF(J.GE.IZ)GO TO 110
      J=J+1
      NAL=NALM(I)+NALM(J)
      IF(NAL.LT.MIN)GO TO 112
      IF(NAL.GT.MAX)GO TO 113
```

```
      DO 115 KN=1,KR
      IF(NAL.EQ.MASS(KN))GO TO 114
  115 CONTINUE
      KR=KR+1
      MASS(KR)=NAL
      PROB(KR)=PROBL(I)+PROBL(J)
      IRRAY(KR,I)=1
      IRRAY(KR,J)=1
      GO TO 112
  114 IF(IRRAY(KN,I).EQ.0) PROB(KN)=PROB(KN)+PROBL(I)
      IRRAY(KN,I)=1
      IF(IRRAY(KN,J).EQ.0)PROB(KN)=PROB(KN)+PROBL(J)
      IRRAY(KN,J)=1
      GO TO 112
  113 IZ=J-1
      IY=IZ-1
      GO TO 110
  111 CONTINUE
C
C GENERATE TRIPLE COMBINATIONS
C
      WRITE(6,495)
  495 FORMAT(1X,'START TRIPLE')
      IZ=MM
      IY=IZ-1
      IX=IY-1
      I=0
  120 IF(I.GE.IX)GO TO 121
      IZ=MM
      IY=IZ-1
      IX=IY-1
      I=I+1
      J=I
  122 IF(J.GE.IY)GO TO 120
      J=J+1
      K=J
  123 IF(K.GE.IZ)GO TO 122
      K=K+1
      NAL=NALM(I)+NALM(J)+NALM(K)
      IF(NAL.LT.MIN)GO TO 123
      IF(NAL.GT.MAX)GO TO 124
      DO 125 KN=1,KR
      IF(NAL.EQ.MASS(KN))GO TO 126
  125 CONTINUE
      KR=KR+1
      MASS(KR)=NAL
      PROB(KR)=PROBL(I)+PROBL(J)+PROBL(K)
      IRRAY(KR,I)=1
      IRRAY(KR,J)=1
      IRRAY(KR,K)=1
      GO TO 123
  126 IF(IRRAY(KN,I).EQ.0)PROB(KN)=PROB(KN)+PROBL(I)
      IRRAY(KN,I)=1
      IF(IRRAY(KN,J).EQ.0) PROB(KN)=PROB(KN)+PROBL(J)
      IRRAY(KN,J)=1
      IF(IRRAY(KN,K).EQ.0) PROB(KN)=PROB(KN)+PROBL(K)
```

```
         IRRAY(KN,K)=1
         GO TO 123
     124 IZ=K-1
         IY=IZ-1
         IX=IY-1
         GO TO 122
     121 CONTINUE
   C GENERATE QUADRUPLE COMBINATIONS
   C
         WRITE(6,496)
     496 FORMAT(1X,'START QUADRUPLE')
         IZ=MM
         IY=IZ-1
         IX=IY-1
         IW=IX-1
         I=0
     130 IF(I.GE.IW)GO TO 131
         IZ=MM
         IY=IZ-1
         IX=IY-1
         IW=IX-1
         I=I+1
         J=I
     132 IF(J.GE.IX)GO TO 130
         IZ=MM
         IY=IZ-1
         IX=IY-1
         IW=IX-1
         J=J+1
         K=J
     133 IF(K.GE.IY)GO TO 132
         K=K+1
         L=K
     134 IF(L.GE.IZ)GO TO 133
         L=L+1
         NAL=NALM(I)+NALM(J)+NALM(K)+NALM(L)
         IF(NAL.LT.MIN)GO TO 134
         IF(NAL.GT.MAX)GO TO 135
         DO 136 KN=1,KR
         IF(NAL.EQ.MASS(KN))GO TO 137
     136 CONTINUE
         KR=KR+1
         MASS(KR)=NAL
         PROB(KR)=PROBL(I)+PROBL(J)+PROBL(K)+PROBL(L)
         IRRAY(KR,I)=1
         IRRAY(KR,J)=1
         IRRAY(KR,K)=1
         IRRAY(KR,L)=1
         GO TO 134
     137 IF(IRRAY(KN,I).EQ.0)  PROB(KN)=PROB(KN)+PROBL(I)
         IRRAY(KN,I)=1
         IF(IRRAY(KN,J).EQ.0)  PROB(KN)=PROB(KN)+PROBL(J)
         IRRAY(KN,J)=1
         IF(IRRAY(KN,K).EQ.0)  PROB(KN)=PROB(KN)+PROBL(K)
         IRRAY(KN,K)=1
         IF(IRRAY(KN,L).EQ.0)  PROB(KN)=PROB(KN)+PROBL(L)
```

```
      IRRAY(KN,L)=1
      GO TO 134
  135 IZ=L-1
      IY=IZ-1
      IX=IY-1
      IW=IX-1
      GO TO 133
  131 CONTINUE
      RETURN
      END
```