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A new non-magnetic time-of-flight mass spectrometer.

Emil S. Koteles
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A NEW NON-MAGNETIC TIME-OF-FLIGHT
MASS SPECTROMETER

by

Emil S. Koteles

A Thesis
Submitted to the Faculty of Graduate Studies through the Department
of Physics in Partial Fulfillment of the Requirements for
the Degree of Master of Science at the
University of Windsor.

Windsor, Ontario

1964
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ABSTRACT

A new, non-magnetic, time-of-flight mass spectrometer has been constructed. It utilizes two localized radio frequency electric fields perpendicular to the ion beam to effect a velocity selection. The theory of the instrument is briefly presented as well as a description of the apparatus and the techniques employed to determine the mass differences of doublets. The components of the mass doublet, CO-N₂, differing in mass by one part in 2500, have been well resolved. The best resolution, measured at the base of the peaks, with the prototype instrument, has been about one part in 8000. Experimental values for the mass difference of O-CH₄ and the mass differences of CO-N₂-C₂H₄ are presented. Preliminary results indicate that it will be possible to make precision mass determinations in a new and unique way (without the use of a large magnetic field) with this new instrument.
I should like to express my gratitude to Dr. Arie Van Wyngaarden for his aid and guidance during this last year. I should also like to thank W. Grewe who constructed the apparatus.

I gratefully acknowledge the financial assistance which was extended to me, in the form of a bursary, by the National Research Council of Canada.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td><strong>CHAPTER I - Introduction</strong></td>
<td></td>
</tr>
<tr>
<td>A. Basic Principles of Mass Spectroscopy</td>
<td>1</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Filters</td>
<td>1</td>
</tr>
<tr>
<td>a. Energy Filters</td>
<td>1</td>
</tr>
<tr>
<td>b. Momentum Filter</td>
<td>3</td>
</tr>
<tr>
<td>c. Wien Velocity Filter</td>
<td>3</td>
</tr>
<tr>
<td>d. Cycloidal Filter</td>
<td>3</td>
</tr>
<tr>
<td>e. Angular Velocity Filter</td>
<td>4</td>
</tr>
<tr>
<td>3. Other Methods of Mass Analysis</td>
<td>4</td>
</tr>
<tr>
<td>4. Resolution and Precision</td>
<td>5</td>
</tr>
<tr>
<td>B. Types of Mass Spectroscopes</td>
<td>6</td>
</tr>
<tr>
<td>1. Magnetic Instruments</td>
<td>6</td>
</tr>
<tr>
<td>a. Magnetic Deflection Mass Spectroscopes</td>
<td>6</td>
</tr>
<tr>
<td>b. Cyclotron Resonance Mass Spectroscopes</td>
<td>7</td>
</tr>
<tr>
<td>c. Cycloidal Path Mass Spectrometers</td>
<td>8</td>
</tr>
<tr>
<td>2. Non-Magnetic Instruments</td>
<td>8</td>
</tr>
<tr>
<td>a. Pulsed Beam Mass Spectrometers</td>
<td>8</td>
</tr>
<tr>
<td>b. Energy-Gain Mass Spectrometers</td>
<td>8</td>
</tr>
<tr>
<td>c. Quadrupole Mass Spectrometer</td>
<td>9</td>
</tr>
<tr>
<td>d. Smythe-Fattnach Mass Spectrometer</td>
<td>9</td>
</tr>
<tr>
<td>C. The New Instrument</td>
<td>10</td>
</tr>
<tr>
<td>D. The Need for a New Non-Magnetic Mass Spectroscope</td>
<td>11</td>
</tr>
</tbody>
</table>

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# CHAPTER II - Theory of the New Instrument

A. Basic Principles 13  
B. Mass Resolution 14  
C. The Doublet Method of Mass Determination 16  
   1. Frequency Scanning 17  
   2. Accelerating Potential Scanning 17  
D. The Magnetic Analyser 18

# CHAPTER III - Description of the Apparatus

A. Introduction 20  
B. The Vacuum System 20  
C. The Ion Source 21  
D. The Radio Frequency Oscillator 22  
E. The Detection System 23  
F. The High Voltage Power Supply 25  
G. Doublet Scanning Apparatus 26

# CHAPTER IV - Technique

A. Alignment of the Collimating Slits 27  
B. The Measurement of Mass Doublets 27  
   1. Frequency Scanning 28  
   2. Accelerating Potential Scanning 29

# CHAPTER V - Results and Discussion

A. Resolution Achieved 32  
B. Mass Doublets Measured 33  
   1. Frequency Scanning 33  
   2. Accelerating Potential Scanning 34

# CHAPTER VI - Conclusion 38

REFERENCES 40

VITA AUCTORIS 41
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Experimental Data used in Plotting Calibration</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Curves of Voltmeter</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Tabulated Values of Doublet Mass Differences and</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Comparison with Previous Values</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1. Schematic Diagram of Non-Magnetic Time-of-flight Mass Spectrometer

2. Schematic Diagram of Ion Source

3. Schematic Diagram of Magnetic Electron Multiplier

4. Schematic Diagram of Voltage Scanning Circuit

5. A Recorder Plot of the Ion Current versus the Frequency for the Mass Doublet CO-N$_2$

6. A Recorder Plot of the Ion Current versus the Accelerating Potential for the Mass Doublet O-CH$_4$

7. A Recorder Plot of the Ion Current versus the Accelerating Potential for the Mass Triplet CO-N$_2$-C$_2$H$_4$

8. A Recorder Plot of the Ion Current versus the Frequency for the Mass Triplet CO-N$_2$-C$_2$H$_4$

9. Calibration Curve of Voltmeter, used in determining the Mass Separation of O-CH$_4$

10. Calibration Curve of Voltmeter, used in determining the Mass Separations of CO-N$_2$-C$_2$H$_4$
CHAPTER I

Introduction

A. Basic Principles of Mass Spectroscopy

1. Introduction

A mass spectroscope is an instrument which separates ions according to their charge to mass ratios. The ions, usually singly charged, are produced in a source, travel through a separation region and then are detected by photographic (mass spectrography) or electronic (mass spectrometry) methods.

The kinetic energy of individual ions, \( \frac{1}{2}Mv^2 \), is a function of two independent variables, the mass, \( M \), and the velocity, \( v \). Therefore, two independent operations must be performed on the ion beam in order to eliminate \( v \) and to obtain \( M \). Generally, this is accomplished by employing combinations of electric and magnetic fields arranged so as to select, from the ion beam, those ions with a certain energy, a certain momentum, or a certain velocity. A singly charged ion which passes successively through any two of these so called filters, will have its mass uniquely determined. It will have passed through a mass spectroscope.

2. Filters

a. Energy Filters

The simplest type of energy filter is the one in which ions, leaving a source, are accelerated by a constant potential, \( V \). If the initial energy of these ions can be neglected, then, after acceleration, they will all possess one kinetic energy given by

\[
\frac{1}{2}Mv^2 = qV
\]

where \( q \) is the charge on the ion. (Since mass spectrosocopy usually deals
with singly charged positive ions, from now on, in this thesis, the charge on an ion will be denoted by \( e \), the absolute value of the electronic charge. However, for precision mass measurements, the initial energies of the ions leaving the source cannot be neglected since this energy spread is superimposed on the constant energy, \( eV \), the ions receive during acceleration.

To obtain a more monoenergetic ion beam, the ions are usually passed through an electrostatic analyser. This energy filter is based on the principle that a radial electrostatic field, \( E \), between two cylindrical condenser plates of average radius, \( r \), will constrain charged particles to travel in a circular path. The electrostatic force, \( eE \), counterbalances the centrifugal force, \( \frac{Mv^2}{r} \). That is

\[
eE = \frac{Mv^2}{r}
\]

or

\[
\frac{1}{2}Mv^2 = \frac{1}{2}eEr
\]

Only those ions which have a kinetic energy given by Equation (3) will follow an arc of radius \( r \) and thus pass through the filter's slits. The energy spread of the ion beam, \( \Delta E \), is given by the energy resolution formula of the filter (Duckworth, 1958).

\[
\frac{\Delta E}{E} = \frac{S_i + S_o}{r}
\]

where \( S_i \) is the width of the entrance slit,

\( S_o \) is the width of the exit slit, and

\( E \) is the mean energy of the ion beam.

It is evident that \( \Delta E \) may be reduced to any desired amount by decreasing the slit widths and/or increasing the radius. Moreover, it is possible to construct the electrostatic analyser in such a manner that monoenergetic ions, entering the cylindrical condenser with a small angular divergence, are brought to a focus at the exit slit.
b. Momentum Filter

A uniform magnetic field acts as a momentum filter. The force on a charged particle moving with velocity $v$, in a magnetic field, $B$, is directed perpendicularly to the field. Thus ions are constrained to travel circular paths by a magnetic field directed normal to their plane of motion. Equating the centrifugal force, $\frac{Mv^2}{r}$, to the magnetic centripetal force, $evB$, it follows that

$$Mv = eBr$$  \hspace{1cm} (5)

That is, ions of a certain momentum follow an arc of radius, $r$. This filter can be constructed so as to display direction focusing properties similar to those of the electrostatic analyser.

c. Wien Velocity Filter

The Wien velocity filter employs homogeneous electric and magnetic fields set at right angles to each other. If the velocity of an ion passing through this filter is such that the magnetic force it experiences, $evB$, is equal to, but in a direction opposite to that of the electrostatic force, $eE$, acting on it, then the ion is not deflected and travels, in a straight line, through the filter's slits. By equating the two forces, the selected velocity is found to be

$$v = \frac{E}{B}$$  \hspace{1cm} (6)

d. Cycloidal Filter

This filter, and the one following, provide enough information by themselves on the mass of the ions that they constitute single filter mass spectrometers.

The cycloidal filter employs crossed electric and magnetic fields as does the Wien filter. Ions of a specific mass, which move with a velocity other than that given by Equation (6), travel in cycloidal paths
to a focus whose position is independent of their initial velocity or direction. By varying the electric field or the magnetic field, ions of different masses are brought to this focus point in turn. In this manner the mass spectrum of the ion beam can be analysed.

e. Angular Velocity Filter

The angular velocity filter operates using the cyclotron resonance principle of charged particles. Ions, in a uniform magnetic field, $B$, will describe circular paths about an axis parallel to the field with an angular velocity, $\omega$. This is readily determined by rearranging Equation (5).

\[
\omega = \frac{v}{r} = \frac{B \epsilon}{\mu} \tag{7}
\]

As this equation indicates, the angular velocity, $\omega$, is independent of the velocity, $v$, and the path radius, $r$, of the ion but depends directly on its charge to mass ratio. Thus a measure of an ion's cyclotron resonance velocity is a measure of its mass.

3. Other Methods of Mass Analysis

In addition to the techniques mentioned previously, there are other methods of effecting a mass analysis. For example, time-of-flight mass spectrometers measure the time required for an ion to travel a specified distance. Strictly speaking, only those mass spectrometers which make use of a direct timing mechanism with pulsed sources and detectors or which subject the ion beam to radio frequency fields can properly be termed time-of-flight instruments. Other so-called time-of-flight mass spectrometers are, in reality, angular velocity filters (I, A, 2, e). Time-of-flight instruments select from the ion beam, those ions possessing a certain velocity. Then, if the velocity of the
ion is characteristic of its mass (e.g. if the ions have passed through an acceleration energy filter) a velocity analysis of the ion beam reduces to a mass analysis. The new instrument operates in this manner.

Many other mass spectrometers have been constructed employing principles different from those mentioned but, with the exception of the quadrupole mass spectrometer (I, B, 2, c), their mass resolutions were very poor.

4. Resolution and Precision

The mass resolution of a mass spectroscope is a measure of its ability to separate ions of different masses. In this thesis the mass resolution shall be defined as the width of the mass peak at the base, \( \Delta M \), divided by the actual mass, \( M \). Thus an instrument with a resolving power of one part in 400 is just able to separate completely masses 399 and 400.

Frequently, in the literature, the peak width is taken at half of the peak height rather than at the base. This half width resolution equals twice the resolution at the base of the peaks for triangular peaks. Throughout the rest of this thesis, unless specifically stated otherwise, the term resolution shall refer to the resolution at the base of the peaks.

The precision of a mass spectroscope is not limited to its resolution since the position of a peak may be determined to some fraction of its width. In the case of photographic recording of a mass, this fraction is, roughly, one part in 50 and so, with a resolution of one part in 400, the mass value may be determined with a precision of one part in 20,000. In the case of electronic recording of masses, this fraction can be improved to about one part in 500 if peak-matching techniques (IV, B, 2) are employed.
B. Types of Mass Spectroscopes

1. Magnetic Instruments

a. Magnetic Deflection Mass Spectroscopes

As explained previously (I, A, 1) ions can have their masses uniquely specified by any combination of energy, momentum or velocity filters. Mass spectroscopes which employ a magnetic momentum filter as one of these two filters are termed magnetic deflection instruments.

Single focusing magnetic deflection mass spectroscopes possess direction focusing in the momentum filter only and have relatively low resolutions.

Double focusing instruments generally consist of an electrostatic analyser and a magnetic momentum filter. Both of these filters have direction focusing properties and the instrument is designed so that the velocity dispersion of one filter is compensated by an approximately equal and opposite velocity dispersion in the following filter. High resolutions (of the order of one part in 100,000 or better) are achieved as a result of the velocity focusing properties produced. In general, if an ion beam enters a filter with an angular divergence, \( \alpha \), and a velocity given by \( \nu = \nu_0 (1 + \beta) \), where \( |\alpha| \) and \( |\beta| \ll |I| \), then there will be aberrations in the final positions of the ions proportional to \( \alpha, \beta, \alpha^2, \beta^2, \ldots \). Mass spectroscopes which eliminate the aberrations proportional to \( \alpha \) and \( \beta \) through the use of suitable geometry are said to be first order double focusing. Second order double focusing instruments eliminate the aberrations proportional to first and second order terms. Although this advantageous situation of second order double focusing has yet to be realized in practice, an instrument possessing second order direction focusing and first order double focusing has been constructed.
(Nier and Roberts, 1951) and others, with theoretical resolutions of better than one part in a million are being developed.

b. **Cyclotron Resonance Mass Spectroscopes**

These instruments, which are essentially angular velocity filters (I, A, 2, e), differ only in the methods they employ to determine the cyclotron resonance frequencies, $\frac{\omega}{2\pi}$, of the ions.

Hays, Richards and Goudsmit (1951) developed a mass spectrometer in which the cyclotron frequency was determined by electronically measuring the time required for ions to travel a helical path of several revolutions, from source to detector, in a uniform magnetic field. Although the resolution did not depend on the mass of the ion, as is the case in most other instruments, it was limited since it did depend on the accuracy with which the travel time of the ions could be measured.

The omegatron, developed by Hipple, Somner and Thomas (1949) is, in reality, a small cyclotron. The ions are created in the center of a homogeneous magnetic field which is perpendicular to a radio frequency electric field. If the frequency of the r.f. field is equal to the cyclotron frequency, $\frac{\omega}{2\pi}$, of the selected ion, then this ion will gain energy and spiral outward to a detector. Space charge effects, inhomogeneities in the magnetic field, gas scattering and other difficulties limit the resolution of this instrument at the present, to one part in 10,000 for low masses.

Another mass spectrometer which employs the cyclotron resonance principle is the Mass Synchrometer developed by L. Smith (1951). It uses a radio frequency "pulser" to decelerate selected ions, causing them to travel paths of shorter radius and thus enter a detector. The half-width resolution of this instrument (one part in
30,000) is sufficient for precision mass determinations since peak
matching techniques are employed (IV, B, 2).

c. Cycloidal Path Mass Spectrometers

The principle of the cycloidal filter (I, A, 2, d) has
been used in the construction of a mass spectrometer by Bleakney and
Hipple (1938). The resolution of the original instrument was not very
high. However, cycloidal path mass spectrometers with mass resolutions
of one part in 1,200 have been developed (Robertson and Hall, 1956).

2. Non-Magnetic Instruments

a. Pulsed Beam Mass Spectrometers

The pulsed beam mass spectrometer is a time-of-flight
instrument. It consists, essentially, of a long evacuated tube with
a source at one end and a detector at the other. Pulses of ions,
homogeneous in energy or momentum, emitted by the source, spread out as
they travel down a field free drift tube to the detector. Then, the
accurate determination of the time taken for an ion to travel from the
source to the detector is a measure of its mass. The best instrument of
this type (Wiley and McLaren, 1955) has a mass resolution of one part
in 200.

b. Energy-Gain Mass Spectrometers

Bennett (1950) developed an instrument in which selected
ions with a particular initial velocity are accelerated preferentially
by axial radio frequency electric fields. Only these ions gain enough
energy to overcome a d.c. potential barrier and reach a detector.
Several mass spectrometers of this type have been constructed but the
maximum resolution achieved has been relatively poor.
c. **Quadrupole Mass Spectrometer**

Paul, Reinhard and Von Zahn built the first model of this unique mass spectrometer in 1958. Ions of a specific mass perform stable oscillations at a certain frequency. All the other ions execute oscillations whose amplitude increases exponentially to infinity causing them to strike one of the electrodes forming the quadrupole field. Only the selected ions are able to travel through this field to the detector. This instrument, which now has a half width resolving power of one part in 15,000 for masses whose \( A > 130 \), is the only non-magnetic mass spectrometer possessing a mass resolution comparable to those of magnetic instruments.

d. **Smythe-Mattauch Mass Spectrometer**

This instrument, developed by Smythe and Mattauch (1932), was the earliest time-of-flight mass spectrometer. Essentially, it is a velocity filter in which the ion beam is subjected to two lateral radio frequency electric fields. In the first field, formed by a parallel plate condenser, those ions with a velocity such that they traverse the field in a time interval which is equal to an integral number of cycles of the radio frequency emerge from the field displaced parallel to their original direction of motion. These ions enter the second identical r.f. field in a phase opposite to that in which they entered the first and so they experience a parallel displacement in the opposite direction. Thus the ions with the selected velocity travel undisplaced and undeviated through the system while all other ions are deflected away. Mass analysis is accomplished by combining this velocity filter with an electrostatic analyser. The presence of spurious "ghost" peaks and a low resolution lead to its abandonment.
C. The New Instrument

The new instrument, like that of Smythe and Mattauch, employs two lateral radio frequency electric fields arranged so that they function as a velocity selector. In the Smythe-Mattauch instrument, however, those ions travelling with the correct velocity are displaced twice with respect to their original direction of motion in such a manner that they experience no net displacement or deflection. In the new instrument the r.f. fields have a negligible effect on the ions travelling with the selected velocity. The purpose of these fields is to deflect, out of the ion beam, those ions with other velocities. Further, the parallel plate condensers used are very short and the ions traverse them in a time interval which is small compared with the period of the r.f. signal. Thus, essentially, the two condensers act as shutters in a manner analogous to the famous Fizeau toothed wheel experiment for light.

This technique was first utilized by Wiechert (1899) to measure the velocity of cathode rays. Later Hammer (1911, 1914) employed a similar technique in his investigations of the velocity of positive rays of hydrogen. In 1930, Perry and Chaffee, in order to determine the charge to mass ratio of electrons, used the energy of the electrons, obtained from the known accelerating potential, together with their observed velocity, found by employing two condenser shutters as in Hammer's research. The electrons, after falling through the constant potential, are able to pass through the first condenser during a short time interval when the amplitude of the r.f. signal is approximately zero. Then, if the velocity of the electrons is such that they reach the second condenser when the r.f. amplitude is again almost zero, they
are able to travel through the instrument without being deflected. The condition for this to occur is that the electrons must travel the distance between the two localized fields in a time interval equal to an even multiple of half a period of the r.f. signal. The basic principle of the new mass spectrometer is similar to this.

D. The Need for a New Non-Magnetic Mass Spectroscope

Precise mass measurements are extremely important to nuclear physicists in the evaluation of binding energies, in the investigation of nuclear shell structure and in the study of the processes involved in the release of nuclear energy. Until recently, all precision mass values were determined by large magnetic instruments since none of the resolutions of other mass spectroscopes was sufficient for accurate mass measurements. The values obtained appeared to contain systematic errors since they varied, from instrument to instrument, by amounts larger than the experimental errors. Frequently these values differed significantly from those derived from nuclear Q-values. (The Q-value of a nuclear reaction is the amount of energy gained or lost in the reaction. If the original nuclei were in their ground states and the product nuclei end up in their ground states, then the Q-value is a measure of the mass difference between the two groups of nuclei). Although recently, Nier and his co-workers (1956), using an enlarged version of the instrument described previously (I, B, I, a) and Smith (1958) employing the Mass Synchrometer (I, B, I, b) have obtained precision mass values which are in good agreement, it would nevertheless appear desirable to verify their results with non-magnetic mass spectroscopes.

Determining mass values with such an instrument would be a check on whether similar systematic errors are present in all magnetic instruments.
Significant progress in this direction has been achieved by the quadrupole mass spectrometer (Von Zahn, 1962). The best resolution of the new instrument is comparable to that of the quadrupole mass spectrometer but, at present, is not sufficient for high precision mass determinations. However the instrument does show promise, not only as an apparatus for precision mass measurements, but also as an analytical tool.
A. Basic Principles

Figure 1 presents a schematic diagram of the apparatus. Here, positive ions produced in the source are accelerated by a positive potential, V, and enter slit S\textsubscript{2} homogeneous in energy if the initial energies of the ions can be neglected (I, A, 2, a). The ions then travel through a collimating stage, a short parallel plate condenser, C\textsubscript{1}, to which is applied a radio frequency electric field, a drift tube of length, L, a second parallel plate r.f. condenser, C\textsubscript{2}, a second collimating stage and finally enter a detection system consisting of a magnetic analyser and an electron multiplier. The two condensers are identical and are electrically connected to a radio frequency oscillator as shown in the diagram.

The acceleration energy filter produces ions of one kinetic energy given by

\[ \frac{1}{2}mv^2 = eV \]  

(8)

Therefore, after being accelerated, the ions enter slit S\textsubscript{2} with a velocity

\[ v = \sqrt{\frac{2eV}{M}} \]  

(9)

If ions of a particular mass pass through both C\textsubscript{1} and C\textsubscript{2} without being deflected, their time of flight, \[ \frac{L}{v} \], between the two condensers must be equal to an integral multiple, n, of half periods, \[ \frac{T}{2} \], of the radio frequency signal applied to these condensers. That is

\[ \frac{L}{v} = \frac{nT}{2} \]  

(10)

or

\[ f = \frac{nv}{2L} \]  

(11)
Fig. 1. Schematic Diagram of Non-Magnetic Time-of-flight Mass Spectrometer
where $f$ is the radio frequency. On substitution of Equation (9) into Equation (11), the basic equation of the instrument is derived.

$$f = \frac{n}{2L} \sqrt{\frac{2eV}{M}}$$  \hspace{1cm} (12)

or

$$f = nf_0$$  \hspace{1cm} (13)

The fundamental frequency, $f_0$, is the lowest frequency for which ions of mass, $M$, are able to travel through the system without being deflected. From the preceding, it is evident that, the drift tube with its r.f. condensers, together with the collimating stages constitute a velocity filter. This velocity filter, in conjunction with the acceleration energy filter, enables the instrument to separate ions according to their charge to mass ratios.

B. Mass Resolution

The ultimate mass resolution of the instrument is limited to the energy resolution of the energy filter. However, even if monoenergetic ions entered the velocity filter section, the mass resolution would not be infinitely large due to the finite widths of the collimating slits. It can be shown (R. Lum, 1964) that, for a sinusoidally varying r.f. signal of amplitude $V_y$, and constant frequency, monoenergetic ions of mass $M$ will be detected over a small range of accelerating potentials, $\delta V$, near the average accelerating potential, $V$. $\delta V$, the width of the ion peak at its base in a plot of ion current versus accelerating potential, should be given by

$$\delta V \approx \frac{16}{\pi} \left\{ \frac{V^2}{V_y} \right\} \left( \frac{d}{L} \right) \left( \frac{W}{L} \right) \left( \frac{1}{n} \right)$$  \hspace{1cm} (14)

or

$$\frac{\delta V}{V} \approx \frac{16}{\pi} \left\{ \frac{V}{V_y} \right\} \left( \frac{d}{L} \right) \left( \frac{W}{L} \right) \left( \frac{1}{n} \right)$$  \hspace{1cm} (15)

where $d$ is the distance between the centers of the plates of the two parallel condensers, $L$ is the horizontal length of the plates and $W$ is
the width of the collimating slits. This formula was derived assuming
that the time of flight through a condenser, $\frac{q}{v}$, was appreciably
smaller than half a period of the radio frequency, that all of the
collimating slits had widths, $W$, and that the length of both collimating
stages was equal to the length of the drift tube, L. The first two conditions
are satisfied in the present instrument but the last one is not. L is
approximately 110 inches, and, while the second collimating stage is also
110 inches, the first is only 50 inches. In future computations, a value
of 90 inches will be used as an average for L.

It can easily be shown, by differentiating Equation (12), that,
for a fixed frequency,

$$\frac{\Delta V}{V} = \frac{\Delta W}{W}$$

(16)

Therefore, on substitution of this equation into Equation (15), the
theoretical mass resolution at the base of the peaks is found to be

$$\frac{\Delta M}{M} \approx \frac{16}{\pi} \left( \frac{V}{V_0} \right) \left( \frac{d}{L} \right) \left( \frac{W}{L} \right) \left( \frac{1}{n} \right)$$

(17)

It is readily apparent that the resolution of the instrument is optimized
by increasing the quantities in the denominator and decreasing the
quantities in the numerator of the preceding equation. However, there
are practical limits. The mass resolution and the ion beam intensity
of this instrument, as in most mass spectroscopes, are not independent.
For example, reducing the value of the slit width, W, will increase the
mass resolution but it may also reduce the ion beam intensity to an
unmanageably small quantity. Further experimentation on this instrument
is necessary to determine the optimum practical values of the quantities
in Equation (17).
C. The Doublet Method of Mass Determination

In theory, it is possible to obtain absolute mass values by substituting experimental data into Equation (12). However, in practice, although $f$, $V$ and $e$, the electronic charge, might be known with sufficient precision, it would be very difficult to determine $L$ accurately enough to permit precision mass measurements. Generally, therefore, mass values are obtained by comparing unknown masses to an arbitrary standard; either $O^{16}$ (which is defined to be exactly 16 atomic mass units) or, more recently, $C^{12}$ (12 a.m.u.). Mass spectrometers which are used for precision mass determinations have such high resolutions, that masses differing by only one atomic mass unit are spread so far apart at the detection end of the instrument that it is difficult to compare their masses accurately. It is almost always impossible to compare masses directly with the standards. Because of this difficulty, the mass doublet method is used in precision mass determinations.

A mass doublet consists of a pair of ions whose masses are almost, but not quite, the same (e.g. $O$-$CH_4$). As they are so close together, the mass difference between the components of a doublet, $\Delta M$, can be determined with great precision by high resolution instruments. The mass values of the components of a doublet are then calculated by comparing the mass difference of the given doublet to mass differences obtained using other doublets composed of similar atoms. This procedure reduces, in effect, to solving simultaneous equations for the masses.

In the new instrument, the mass difference between components of a doublet can be determined in two ways.
1. Frequency Scanning

If the accelerating potential remains constant, the two masses of a doublet are detected at slightly different frequencies [Equation (12)]. Therefore their mass difference can be determined in terms of a frequency difference. If ions of mass $M_1$ and $M_2 = M_1 + \Delta M$ are detected at frequencies $f_1 = n f_{01}$ and $f_2 = n f_{02}$ respectively, then, using Equation (12), it can be shown that

$$\frac{\Delta M}{M_1} = \frac{f_1^2 - f_2^2}{f_2}$$

(18)

If $M_1 \ll M_2 \ll M$ so that $f_1 \ll f_2 \ll f$, the preceding equation reduces approximately to

$$\frac{\Delta M}{M} \approx \frac{2 \Delta f}{f}$$

(19)

where $\Delta f = f_1 - f_2 = n (f_{01} - f_{02})$

2. Accelerating Potential Scanning

If the applied frequency remains constant, and the accelerating potential is varied, the components of the mass doublet will be detected at different values of the accelerating potential. Using Equation (12), it is easily shown that if ions of mass $M_1$ and mass $M_2 = M_1 + \Delta M$ are detected at accelerating potentials of $V_1$ and $V_2 = V_1 + \Delta V$ respectively, then

$$\frac{\Delta M}{M_1} = \frac{\Delta V}{V_1}$$

(20)

The mass difference is then observed in terms of a difference in accelerating potential.
D. The Magnetic Analyser

If the electron multiplier were mounted directly behind slit S7 (see Figure 1) and if the applied frequency were varied with the accelerating potential remaining constant, then the mass spectrum of the ion beam would be swept. This was actually done in preliminary experiments. At low frequencies the ions were detected at their fundamental frequencies (i.e. \( n = 1 \)). The heavier masses appeared at lower frequencies and the lighter masses were detected at higher frequencies. At much higher frequencies (say \( n = 200 \)), mass spectra corresponding to different \( n \) values overlapped. This complicated the analysis. Since large \( n \) values and therefore high frequencies were needed to improve the resolution for precision mass determinations [Equation (17)], a momentum filter was added to the detection system. This magnetic analyser selected from the ion beam the mass doublet being investigated. The resolution of this filter was low enough so that both components of the mass doublet were detected as a single peak. Thus the magnetic analyser did not improve the performance of the mass spectrometer directly but merely permitted operation at frequencies higher than normally possible.

Although this overlapping of orders at higher frequencies is a nuisance, it has the advantage that it becomes possible to directly determine precise mass differences between certain ions which differ in mass by several atomic mass units. This arises from the fact that ions, whose masses are approximately related by an integer squared, \( k^2 \), will have fundamental frequencies approximately related by an integer, \( k \) Equation (12). Suppose that \( M_2 \approx k^2 M_1 \) and that, at a constant frequency, masses \( M_1 \) and \( M_2 \) are detected at accelerating potentials.
$V_1$ and $V_2 = V_1 + \Delta V$ respectively. Then, it can be shown that

$$\frac{M_2 - k^2 M_1}{M_2} = \frac{\Delta V}{V_2}$$

(21)

This procedure reduces to the doublet method of precision mass determination for $k = 1$ [Equation (20)].
CHAPTER III

Description of the Apparatus

A. Introduction

The major portions of the apparatus, the collimating stages and the drift tube, were constructed of long brass tubes joined together by means of flanges soldered on their ends. The slits were mounted in the ends of these tubes. The source, since it was at high potential, was at the end of a glass tube which electrically insulated it from the rest of the instrument. The apparatus rested on a rigid, horizontal, steel frame and had a total length of approximately twenty-six feet.

As the instrument was assembled, each of the collimating slits was adjusted in turn using an accurate level until it was horizontal. In this manner all of the slits were mounted parallel to one another. But, having the slits parallel did not necessarily mean that they were all in line vertically. Therefore, adjustments were provided at several points along the instrument by which the slit assemblies could be raised or lowered. The final alignment of the slits was accomplished (IV, A) by means of Faraday cups which could be inserted into the path of the ion beam at three points along the instrument.

E. The Vacuum System

To ensure that the ions, on their journey from the source to the detector, did not collide with gas molecules and thus suffer changes in their velocity or direction, the entire instrument was evacuated. Care was taken that the system was vacuum tight. The flanges were sealed with rubber "O" rings. Electrical connections
to the inside of the system were made by means of Kovars. The Faraday cups were lowered into the ion beam by means of vacuum tight bellows.

A Speedivac rotary pump (model 1SC150B) with a pumping speed of 144 litres per minute and capable of an ultimate vacuum of $5 \times 10^{-3}$ mm Hg provided the fore-pumping. To bring the system down to operating pressures, four Speedivac oil diffusion pumps (model E02, model 102A and two of model F203) with a total pumping speed of over 300 litres per minute were positioned along the instrument. The pressure was monitored by means of three Veeco ion gages (model RG-75P) situated near the source, about the center of the apparatus and near the electron multiplier. The pressure obtained, a few times $10^{-6}$ mm Hg, was considered adequate because it was believed that the scattering of the ion beam by the residual gaseous atoms in the system would not effect, at this stage, the precision of the measurements.

C. The Ion Source

Figure 2 is a schematic diagram of the ion source. Gas was leaked into the ionization chamber through the thin metal tube at the rear of the source and subjected to bombardment by electrons evaporated from a hot tungsten filament. These electrons were accelerated by potentials of 45 to 180 volts supplied by 45 volt "B" batteries so that they passed through a slit into the ionization chamber. Here they suffered inelastic collisions with the gas molecules thus forming ions. It was originally intended to repel these ions through slit $S_1$ into the high voltage acceleration region between slits $S_1$ and $S_2$ by means of a small positive potential applied to the repeller plate at the rear of the ionization
chamber in order to produce large ion currents. However, a potential on the repeller plate introduces an energy spread amongst the ions if they are formed in different regions of the ionization chamber. Therefore, since sufficiently large ion currents (the measured ion current just past slit $S_2$ was of the order of $10^{-9}$ amps.) were observed with zero potential on the repeller, in an actual run the repeller plate was directly connected to the source. Then the energies of the ions in the source consisted of thermal energies, recoil energies suffered in the inelastic collisions with the electrons, and Coulomb repulsion energies which existed amongst neighbouring positive ions. The energy spread in the ion beam was primarily composed of these energies. Monoenergetic ion beams are usually produced by passing the ions from a source through an electrostatic analyser (I, A, 2, a).

The source assembly was mounted on a quartz plate which was chosen for its electrical insulation properties and its ability to withstand high temperatures. The source components and slit $S_2$ were constructed of stainless steel to inhibit high voltage sparking. Since the source was at a high potential, all of the voltages needed to operate it were provided by batteries. The filament current, which was regulated by a variable resistor, was supplied by a 12 volt lead storage battery. The rate at which gas flowed into the source through the gas inlet tube was controlled by means of a Speedivac variable leak.

D. The Radio Frequency Oscillator

The radio frequency signal was supplied to the condensers by a
General Radio Type 1330-A Bridge Oscillator which had a maximum output voltage of approximately 10 volts R.M.S. However, it was found that, by matching the inductance of the leads to the capacitance of the condensers, a resonant condition occurred and radio frequency amplitudes as high as 40 or 50 volts could be obtained across the condenser's plates. The operating frequency was approximately 15 megacycles per second as the output voltage tended to decrease for lower or higher frequencies.

The parallel plate condensers were identical. The distance, $d$, between the plates was 0.020 inches and their length, $l$, was 0.125 inches. They were mounted on insulators and electrical connections were made to them in the vacuum system by means of Kovars.

E. The Detection System

The detection system (see Figure 1) consisted of the magnetic analyser, an electron multiplier, an electrometer amplifier and a chart recorder.

The magnetic field of the magnetic analyser was produced by two Alnico horseshoe permanent magnets. The field, which had a maximum strength of about 1200 gauss in the pole gap, could be varied by adjusting a soft iron shorting bar.

Figure 3 is a schematic diagram of the electron multiplier (Bendix model 306). It consisted of two parallel glass plates coated with resistive layers. Across these layers potential gradients were applied. Nine evenly spaced Alnico permanent magnets provided a uniform magnetic field of approximately 400 gauss, essentially perpendicular to the electric field.
Fig. 3. Schematic Diagram of Magnetic Electron Multiplier
When ions struck the cathode, secondary electrons were emitted. These electrons were accelerated by the electric field which had components perpendicular and parallel to the resistive layers. The presence of the magnetic field caused them to travel in cycloidal paths and thus to strike the resistive layer from which they were emitted, at a point lower in potential energy. This action liberated secondary electrons with a yield greater than one and each of these performed a similar type of motion under the influence of the crossed fields in the multiplier. In this manner a cascading action resulted and relatively high electron currents were collected at the anode. The current gain achieved was of the order of 10^7.

The potential gradients across the resistive strips were supplied by a John Fluke High Voltage D.C. Power Supply (model U12A). The gain was maximized by adjusting the potentials of the various components of the instrument to approximately the values shown in the diagram. The cathode was made of tungsten metal, which has a relatively high work function. Because of this the electron multiplier did not respond to visible light and had an extremely low dark current (less than 0.1 accidental electrons arising from the cathode per second).

The output of the electron multiplier was measured by a Keithley electrometer amplifier (model 621). With the radio frequency amplitude at zero, the ion current registered by the electrometer was of the order of 10^-6 amps. Since the gain of this multiplier was approximately 10^7, the incident ion current was of the order of 10^-13 amps. With the radio frequency potential at maximum, some of the smallest peaks detected had ion currents of approximately 10^-16.
amps which corresponds to about $10^3$ singly charged ions per second striking the cathode.

The output of the electrometer was fed to a Bauch and Lomb chart recorder (model V.0.M. - 5) which was equipped with an event marker. A rapid chart speed (20 inches per minute) was used in order to spread the peaks out on the recorder paper and thus make their shapes more discernible.

The whole detection system was arranged to record accurately the distance between the peaks of a mass doublet. No attempt was made to measure the absolute intensities of the mass components with any precision as this was of no consequence in the present investigations.

F. The High Voltage Power Supply

Since the ultimate resolution of the instrument depended on the energy resolution of the acceleration energy filter and since this depended, to a large extent, on the stability of the accelerating potential, $V$, a very stable high voltage was needed. A John Fluke high voltage power supply (model U30A), which received power from a Sorenson A.C. voltage regulator (model 2000S), was used. The output voltage had short term fluctuations of one part in $10^5$ which was hardly adequate for the method of doublet scanning used (IV, B, 2).

The high voltage was measured with a high degree of accuracy by connecting the output voltage to a voltage divider (John Fluke model 30D-30) whose resistance ratios were known with a precision of $\pm 0.01\%$ (see Figure 1). The output potential of this voltage divider was measured with a John Fluke differential voltmeter (model 321A) which is accurate to $\pm 0.01\%$. Thus the output of the high voltage power supply, H.V., could be determined with an accuracy of $\pm 0.02\%$. 

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**G. Doublet Scanning Apparatus**

To produce frequency scanning, the tuning capacitor of the radio frequency oscillator was simply driven by means of a pulley connected to a 1/4 r.p.m. synchronous motor.

The accelerating potential scanning technique, which was adopted to obtain preliminary results, required a more complicated apparatus. Figure 4 is a schematic diagram of the accelerating voltage scanning circuit. The output of the high voltage power supply, H.V., was connected to a ten turn 100 kΩ precision potentiometer (Spectrol, model 860) across which a battery, B, was connected. The slider of the potentiometer was connected to the source circuit and, therefore, fractional amounts, dV, of the battery voltage could be added to the high voltage, H.V. This incremental voltage, dV, was measured by a micro-ammeter, µA, (Simpson, model 139C) which, in series with a resistance Rm, was placed in parallel with the incremental voltage of the potentiometer. Thus the micro-ammeter together with the series resistor functioned as a voltmeter and the differential voltmeter mentioned previously was used to calibrate it. The slider was driven by a 25 r.p.m. reversible synchronous motor (Borg, model 1003-LSY) so that the incremental voltage could be varied linearly in time. Thus the potential of the source, V, was equal to the sum of a constant, H.V., and a variable, dV. Therefore varying the incremental voltage linearly in time was equivalent to varying the total accelerating potential linearly in time.
Fig. 4. Schematic Diagram of Voltage Scanning Circuit

Driven by Reversible Synchronous Motor

Resistive Voltage Divider

Differential Voltmeter

To Ion Source Circuit

$V = H \cdot V + dV$

H.V.
CHAPTER IV

Technique

A. Alignment of the Collimating Slits

The alignment of the collimating slits was a critical factor in the performance of the instrument. Many precautions were taken (III, A) and the following procedure performed to ensure that the slits were in line with the ion beam.

With the system evacuated and the output potential of the radio frequency oscillator at zero, the assembly of slit $S_1$ was first adjusted until a maximum current was observed in the Faraday cup situated between slits $S_2$ and $S_3$. Next, the ion current in the Faraday cup placed just beyond slit $S_4$ was maximized using further adjustments. Then, similarly, the current in a final Faraday cup situated near slit $S_6$ was adjusted to a maximum. Finally, the positions of the last slits were varied until the output of the electron multiplier was at a maximum. In this manner, the slits were lined up, one by one, to the ion beam. The widths of the collimating slits were so small ($0.005$ inches) that the slightest disturbance (such as a sudden temperature change) was enough to misalign the instrument. Therefore, before any experiment was performed, the apparatus was realigned.

B. The Measurement of Mass Doublets

With zero radio frequency potential, the magnetic analyser was adjusted so that the mass doublet being investigated was detected at an accelerating potential of approximately 25,000 volts. Then the mass difference between the components of a doublet could be determined in one of two ways (II, C).
1. Frequency Scanning

When the frequency was scanned chart recordings of the type shown in Figure 5 resulted. Plots of the ion current versus the radio frequency were obtained by placing markers on the chart paper at regular frequency intervals. The doublet peaks were detected at multiples of their fundamental frequencies. Thus, as indicated in the figure, the frequency difference between two adjacent peaks of the same mass was equal to the fundamental frequency, $f_0$, of that mass. The mass difference between the components of a doublet was related to the frequency difference, $\Delta f$, using Equation (19).

At the present, this method of determining mass differences was considered too inaccurate for several reasons. It was discovered that the dial markings of the tuning capacitor of the radio frequency oscillator were accurate to only about $\pm 0.5\%$. Also, the dial calibration was logarithmic. Thus the frequency variation was logarithmic in time while the chart recorder plotted the ion current linearly in time. This made it difficult to determine $\Delta f$ with precision. Further, there was no assurance that a phase difference did not exist between the radio frequency fields on the two condensers. Such a phase difference would have effectively changed the length of the drift tube, $L$. Serious errors in the measurement of mass differences would have resulted if this phase difference had varied as the frequency was swept. Primarily for these reasons, preliminary results were obtained by employing accelerating voltage scanning. However, since, with proper techniques, frequencies can be measured with greater accuracy than voltages, it is anticipated that, in the near future, frequency scanning will be used for precision mass determinations.
Figure 5. A Recorder Plot of the Ion Current versus the Frequency for the
Mass Doublet CO-N2
2. Accelerating Potential Scanning

Chart recordings of the type pictured in Figure 6, which is a recorder plot of the ion current versus the accelerating potential for the mass doublet O-CH$_3^+$, were obtained when, at a constant radio frequency, the accelerating potential was varied linearly in time. To obtain these graphs, the following steps were taken.

The output potential of the high voltage power supply was set at about 25,000 volts and $dV$ was set at approximately half its maximum value. With this accelerating potential, the constant frequency was chosen to be the average of the two frequencies at which the doublet components were detected (at some given $n$ value). In this case, by varying $dV$, one doublet component was detected at a slightly lower accelerating voltage and the other at a slightly higher voltage. The synchronous motor which drove the slider of the potentiometer (III, G) also rotated a threaded shaft on which an arm moved vertically. This arm, by activating micro-switches connected to the electrical circuit of the motor caused the motor to reverse direction after about eight revolutions. Thus, after rotating the slider of the potentiometer eight times in one direction, the motor would reverse, rotate eight times in the opposite direction and reverse again. In this manner, the motor was arranged so as to reverse after a doublet had been scanned, and so continuous scanning of the accelerating potential was achieved.

Markers were placed on the chart recorder paper at regular intervals corresponding to the scale markings of the microammeter. Thus, since both the chart recorder paper and the accelerating potential varied linearly in time, plots of ion current versus the accelerating potential were obtained on the recorder paper.
Figure 6. A Recorder Plot of the Ion Current versus the Accelerating Potential for the Mass Doublet O-CH$_4$
The accelerating voltage difference, $\Delta V$, between the two components of a doublet [Equation (20)] was determined from the chart recorder plots in the following manner. The voltmeter was calibrated with the differential voltmeter. Figure 9 and Figure 10 present the calibration curves of the voltmeter for a 135 volt battery and a 180 volt battery respectively. The measured distance between the doublet peaks, on the recorder paper, was converted to a potential difference by comparing this distance to the measured distance from the 5 (or 10) marker to the 20 marker for which the corresponding potential difference was known from the calibration curve. In this manner $\Delta V$ was determined and, on its substitution into Equation (20), together with the appropriate values for $M$ and $V$, the mass difference for the doublet $\Delta M$, was determined.

It was found that the probable error in the position of the markers on the recorder paper was relatively small (usually less than $\pm 0.06\%$). The major errors occurred in the calibration curves of the voltmeter. As a result of the relatively large linearity tolerance of the precision potentiometer ($\pm 0.25\%$), the calibration curves approximated straight lines only about their centers. Therefore, during an experiment, care was taken that the doublet peaks were detected near the centers of the curves. Even so, two straight lines with slopes differing by as much as $0.3\%$ could be drawn through the "center" points of a calibration curve. It was decided to use mean straight lines drawn through these "center" points for measurement purposes and to assign probable percentage errors of $\pm 0.15\%$ to the slopes.

A further difficulty was presented by the relative instability of the high voltage power supply. Fluctuations of the order of $\pm 0.2$ volts
Figure 9. Calibration Curve of Voltmeter, used in determining the Mass Separation of $\text{O-CH}_4$.
Figure 10. Calibration Curve of Voltmeter, used in determining the Mass Separations of C0-N2-C2H4.
at 25,000 volts were observed in the high voltage output. Thus the accelerating potential, $V$, was quite stable. However, since these variations took place as the doublet peaks were slowly scanned, fluctuations in $\Delta V$ of $\pm 0.5$ volts occurred. Because $\Delta V$ was only of the order of tens of volts at 25,000 volts, these fluctuations caused serious error. Since the voltage fluctuation appeared to be random, the average voltage difference, $\Delta V$, was found fairly accurately by taking a large number of observations, albeit with an appreciably larger probable error. Peak matching, a method of determining mass differences by electronically superimposing the two peaks of a mass doublet on an oscilloscope, should largely eliminate this problem as, in this case, the doublet peaks are swept as fast as 60 times a second. Peak matching should also improve the precision of the instrument since it is usually possible to gain a factor of 500 or better over the mass resolution using this technique.
CHAPTER V
Results and Discussion

A. Resolution Achieved

The theoretical resolution of this new mass spectrometer is approximately given by Equation (17). In the prototype instrument, the values of the variables in this equation were:

\[ V \approx 25,000 \text{ volts} \]
\[ V_y = 45 \text{ volts} \]
\[ d = 0.020 \text{ inches} \]
\[ l = 0.125 \text{ inches} \]
\[ w = 0.005 \text{ inches} \]
\[ L = 90 \text{ inches} \]

Upon substitution of these values into the resolution equation, the theoretical resolution becomes

\[ \frac{\sigma M}{M} \approx \frac{1}{40} \times \frac{1}{n} \]  \hspace{1cm} (22)

The value of \( n \) can be determined from chart recordings of the ion current versus the radio frequency. For example, in Figure 5, a recorder plot of the ion current versus the frequency for the mass doublet CO-N\(_2\), \( f_0 \) is found directly to be approximately 75 kcps. Since the frequency at which the doublets are observed is about 15.15 mcps, using Equation (13), \( n \) is found to be approximately 200. Therefore, the theoretical mass resolution of the present instrument is about one part in 8000 at the base of the peaks. The experimental mass resolution for the peaks in Figure 5 can be calculated using the following equation derived from Equation (12).

\[ \frac{\sigma M}{M} \approx \frac{2 \Delta f}{f} \]  \hspace{1cm} (23)
In this case, the average width of the peaks at the base is about 1.15 kcps and therefore the observed mass resolution is one part in 6500. The fact that the observed resolution is somewhat lower than the theoretical resolution seems to be the result of an intensity effect. This effect is shown in Figure 8 which is a recorder plot of the ion current versus the frequency for the mass triplet CO-N_2-C_2H_4. It will be noted that the peak width, \( \Delta f \), decreases as the ion current decreases. The best resolution, observed with low ion currents, has been about one part in 8000 in agreement with the theory.

B. Mass Doublets Measured

1. Frequency Scanning

Although frequency scanning was not used in these present investigations to obtain accurate doublet mass differences, a sample calculation will be presented to illustrate the application of Equation (19). In Figure 5, the average experimental values for the CO-N_2 doublet are

\[
\Delta f \approx 30.7 \text{ kcps}
\]

\[
f \approx 15.15 \text{ mcps}
\]

and \( M \approx 28 \text{ a.m.u.} \).

Substituting these values into

\[
\Delta M \approx \frac{2 \Delta f \times M}{f}
\]

(19)

yields

\[
\Delta M (\text{CO-N}_2) \approx 1.13 \times 10^{-2} \text{ a.m.u.}
\]

This agrees, within experimental error, with other, more accurate values (see Table II).
Figure 8. A Recorder Plot of the Ion Current versus the Frequency for the Mass Triplet CO-N$_2$-C$_2$H$_4$. 

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2. Accelerating Potential Scanning

The mass differences of the doublet O-CH\textsubscript{3} and the triplet CO-N\textsubscript{2}-C\textsubscript{2}H\textsubscript{4} were determined using the techniques described in the last chapter.

A typical recorder plot of the ion current versus the accelerating potential for the mass doublet O-CH\textsubscript{3} is shown in Figure 6. The resolution of the instrument while this doublet was being investigated was approximately one part in 3000. The value of the high voltage, H.V., was 24,721.2 ± 4.9 volts and of the battery, B, was 135 volts. The points of the corresponding calibration curve for the voltmeter (Figure 9) are tabulated in Table I. The average measured distance between the doublet peaks on the recorder paper was 3.686 inches and the corresponding distance from marker 10 to marker 20 was 3.738 inches.

The error was calculated by taking into account the probable percentage errors of the measured peak distance and the measured distance from marker 10 to marker 20 (±0.09 % and ±0.07 % respectively for 23 measurements), the probable percentage error in the slope of the voltmeter calibration curve (±0.15 %) and the possible percentage error in the accelerating potential (±0.02 %). These factors added up to a total error in the mass difference, ΔM, of about ±0.2 %.

Figure 7 is a chart recorder plot of the ion current versus the accelerating potential for the mass triplet CO-N\textsubscript{2}-C\textsubscript{2}H\textsubscript{4}. The resolving power of the instrument during this investigation was approximately one part in 5000. The values of the high voltage, H.V., and the battery, B, were 22,330.2 ± 4.5 volts and 180 volts respectively. The data presented in Table I for the 180 volt battery were plotted to obtain the calibration curve shown in Figure 10. From 20 measurements,
Figure 7. A Recorder Plot of the Ion Current versus the Accelerating Potential for the Mass Triplet CO-N₂-C₂H₄
the average distance, on the recorder paper, from marker 5 to marker 20 was 5.639 inches and the measured distances between the doublet peaks of CO-N₂, N₂-C₂H₄, and CO-C₂H₄ were 0.441 inches, 0.9831 inches and 1.4245 inches respectively.

The errors were calculated in a manner similar to that used in determining the error in ΔM for the doublet O-CH₄. An error of ±1.3% was found for the mass difference of CO-N₂ whereas the mass differences of N₂-C₂H₄ and CO-C₂H₄ had errors of ±0.5% and ±0.6% respectively. These errors were much larger than the error in the O-CH₄ doublet mass difference because the high voltage was somewhat more unstable when this triplet was recorded.

The results of these investigations of the mass differences of the doublet O-CH₄ and the triplet CO-N₂-C₂H₄ are presented in Table II together with previous values reported by others. All these values are based on O¹⁶ as the standard. It is apparent that the mass differences of the doublets, measured with the new instrument, agree, within experimental error, with the previous, more accurate values. This agreement suggests the absence of large systematic errors. This conclusion is strengthened by the observation that the mass differences of O-CH₄ and CO-C₂H₄ which should be equal, are the same, within experimental error.

The asymmetrical shape of the O¹⁶ peak (Figure 6) gives rise to interesting speculation. Historically, the O-CH₄ doublet has been the most stubborn in resisting attempts to obtain a consistent value for its mass difference. Recently, it has been suggested (private communication with Dr. H. E. Duckworth) that this may be due, in part, to the large amounts of kinetic energy (of the order
### Table I. Experimental Data used in Plotting Calibration Curves of Voltmeter

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### Table II. Tabulated Values of Doublet Mass Differences and Comparison with Previous Values

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<th>Previous Work</th>
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<td>CO-N₂</td>
<td>1.128 ± 0.014</td>
<td>1.12853 ± 0.00007*</td>
<td>1.1237 ± 0.00011#</td>
</tr>
<tr>
<td>N₂-C₂H₄</td>
<td>2.517 ± 0.013</td>
<td>2.51586 ± 0.00008*</td>
<td>2.516086 ± 0.0000040#</td>
</tr>
<tr>
<td>CO-C₂H₄</td>
<td>3.647 ± 0.022</td>
<td>3.639733 ± 0.000035#</td>
<td>3.639730 ± 0.0000011#</td>
</tr>
<tr>
<td>O-CH₄</td>
<td>3.692 ± 0.007</td>
<td>3.63933 ± 0.00009</td>
<td>3.639733 ± 0.000011#</td>
</tr>
</tbody>
</table>

*Quisenberry, Scolman and Nier, (1956).

of electron volts) which the oxygen atoms may receive when the oxygen molecule is split in the process of ionization. The energy spread of these energetic oxygen atoms might also depend, to some extent, on the geometry of the ion source. If this were true, different values for the mass difference O-CH₄ would have been observed by mass spectrometers which employed different types of sources. For the present, the interpretation of the consistent asymmetrical shape of the O¹⁶ peak produced by this apparatus will be limited to the observation that the "tail" is composed of O¹⁶ atoms which have lower energies than the atoms of the "mean".
CHAPTER VI

Conclusion

The results of these preliminary investigations of mass doublets are very encouraging. They suggest that precision mass determinations will be possible with this new type of instrument in the immediate future. If such mass values could be obtained, they would be especially significant since they would be the first precise mass measurements made with a mass spectroscope which does not employ large magnetic fields. The new instrument is also suitable for use as an analytical tool in certain fields of chemistry and physics since it is relatively inexpensive compared to other mass spectroscopes of comparable performance.

Experimentation in the future will be concentrated on attempts to improve the mass resolution and the precision of the instrument. The latter will be accomplished by applying peak matching techniques to mass doublet determinations. It is believed that the resolving power can be improved by a factor of four or better without serious loss in ion current intensity by increasing the operating frequency of the radio frequency signal by the same factor. With a resolving power of one part in $30,000$ and using peak matching, it should be possible to determine masses to a precision of one part in $15 \times 10^6$ or better. Since the resolution of the instrument can be no better than the resolution of the energy filter, future plans call for an electrostatic analyser to replace the acceleration energy filter. Not only would this new energy filter improve the energy resolution, but it would also largely remove doubts about the influence of the source $(V, B, 2)$ on the mass separation of doublet components.
Finally, plans are in preparation to add another electron multiplier to the magnetic analyser. This modification of the detection system will make it possible to detect simultaneously two masses differing in mass by several atomic mass units. Thus mass difference determinations of the type described previously (II, D) will be possible.
REFERENCES


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1940 - born in Windsor, Ontario on April 1.
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1958 - graduated from Assumption High School, Windsor, Valedictorian.
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