Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand). This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.

- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.

- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.
http://researchspace.auckland.ac.nz/feedback

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library

Thesis Consent Form
A Fast Mobility Spectrometer for
Atmospheric Ions

A Thesis Presented to the
University of Auckland
for the degree of
Doctor of Philosophy

by

John Nevil Brownlee

September, 1973

Frontispiece (Plate 3.71):
General View of the Experimental Site
See section 3.7 for details
A FAST MOBILITY SPECTROMETER FOR ATMOSPHERIC IONS

ABSTRACT

The development of a mobility spectrometer which yields a complete spectrum every 25 seconds is described. The spectrometer uses a Differential Gerdien Chamber of the First Order with 8 collecting electrodes, giving a set of 8 "electrode charges" corresponding to each observed spectrum. A Least Squares iteration is used to fit the parameters of a function which describes the complete mobility spectrum. The spectrum function's parameters can be fitted reliably with standard deviations of 3% or better.

The spectrometer was used for observations of temporal variations in the atmospheric ion mobility spectrum at Auckland. These show a clear diurnal variation, and demonstrate that the spectrum can change significantly in an interval of 100 seconds. Atmospheric polar conductivities calculated from the mobility spectrum (which agreed well with independently measured conductivities) indicate that large ions can contribute as much as 40% of the total conductivity.
This thesis covers the development of a mobility spectrometer for atmospheric ions with time resolution significantly better than any other so far reported, and its use in studies of temporal variations of the atmospheric ion mobility spectrum at Auckland.

Relevant topics in Atmospheric Electricity are summarised in Chapter 1, which concludes with a complete statement of the aims of the investigation. Chapter 2 gives a detailed analysis of the ion currents collected by a generalised "Gerdien Chamber". Gerdien Chambers which are mechanically simple suffer the disadvantage that in computing a mobility spectrum the chamber's ion currents must be differentiated, with a consequent introduction of noise into the results. A new alternative method of spectrum computation is proposed, in which a "least squares" iteration is used to fit the parameters of a function which describes the spectrum. Although this lowers the mobility resolution available it greatly improves the accuracy with which the spectrum parameters may be determined. The chapter ends with a discussion of the design decisions required for the thesis spectrometer.

The spectrometer is a Differential Gerdien Chamber of the First Order, having eight collecting electrodes, each of which can be connected to a vibrating capacitor electrometer through a reed switch. Charges measured by the electrometer are punched onto paper tape at a maximum rate of one chamber electrode every 2.5 seconds. 5 seconds is allowed for synchronis-
ing information to be recorded so that all the electrodes are sampled (giving data for one complete spectrum) every 25 seconds. Practical details of the spectrometer are given in Chapter 3. Of particular interest here are the determination of the spectrometer's inter-electrode capacitances, the charges generated by the reed switches when they are opened, and the sequencing of the various spectrometer functions. The site where the spectrometer was installed is also described, together with the results of some preliminary experiments. Chapter 4 deals with the reduction of the large quantities of raw data produced by the spectrometer. A computer model of the spectrometer was developed, tested, and used in correcting the measured charges from the collecting electrodes for the effects of electrostatic interaction between them. "Leakage" currents to the electrodes, i.e. currents observed when in principle no ions could be collected, are discussed, together with the effect of resistive leakage of charge from the electrodes. In Chapter 5 a function is developed to represent the mobility spectrum. This has two parts: a delta function to represent the large ions, and a lognormal function to represent the small ions. Using the least-squares iteration mentioned above the parameters of this function can be fitted reliably with standard deviations of 3% or better.

Studies of temporal variations in the atmospheric ion mobility spectrum are discussed in chapter 6. These show that while the diurnal variation at Auckland is very similar to that at Glencree (Ireland) and Tokyo (Japan) the spectrum can change significantly in an interval of 100 seconds or less, indicating the clear demand for high time resolution in a spectrometer. Calculations of atmospheric polar conductivities (which compared
well with independently measured conductivities) indicate that large ions can contribute as much as 40% of the total conductivity. This is surprising, for electrical conduction in the atmosphere is commonly assumed to involve only the small (i.e. high-mobility) ions. A preliminary investigation of the spectrum of ions produced in the laboratory by point discharge at a metal point gave results which are consistent with a simple description of the point discharge process. Chapter 7 considers the limitations of the present spectrometer and suggests some possible improvements to it.

Throughout the thesis convenient metric prefixes are used for units, hence the unit of mobility is \( \text{cm}^2/\text{Vsec} \) rather than \( x10^{-4} \text{ m}^2/\text{Vsec} \). The prefix femto- is frequently used, particularly for currents: for example 2.7 fA means \( 2.7 \times 10^{-15} \text{ A.} \) All figures and tables have their section number as a prefix, so that fig. 6.32 is the second figure of section 6.3. Although the algorithms used in computer programs are fully discussed no program listings are given since they were written in a non-standard dialect of Fortran which was developed by the University Computer Centre and is no longer available.

Throughout this project my supervisor, Professor K.S. Kreielsheimer, has been tremendously helpful to me and it has been a real pleasure to work under him. Special thanks are due to Dr Murray Johns for our many valuable discussions, and particularly for his help in our joint development of the electrometer. I am indebted to the staff of the Physics Department Mechanical Workshop who built my spectrometer, and also to Miss June Magan who did all the typing for this thesis.
Since February 1971 I have been a lecturer in the University Computer Centre under its Director, Dr J.C.B. White, who has at all times been most understanding. Finally I must thank my family for their support and consideration over the past few years.

[Signature]

21 Sept 73
"A Fast Mobility Spectrometer for Atmospheric Ions"

Table of Contents

CHAPTER 1

INTRODUCTION
1.1 Nuclei, Ions, Mobility, Diffusion 1
1.2 Measurement of Mobility, Mobility Spectra 5
1.3 Ionic Equilibrium in the Atmosphere 10
1.4 Theories of the Ionic Combination Coefficients 13
1.5 Atmospheric Conductivity 18
1.6 Point Discharge 20
1.7 Scope of the Present Work 23

CHAPTER 2

THEORY OF THE GERDIEH MOBILITY SPECTROMETER
2.1 Analysis of the General Case 24
2.2 Classification of Chamber Types 29
2.3 Physical Significance of Critical Mobilities - An Alternative Analysis 32
2.4 Methods of Spectrum Determination 35
2.5 Design of the Mobility Spectrometer 38

CHAPTER 3

DETAILS OF THE SPECTROMETER
3.1 Physical Construction 42
3.2 The Electrometer 44
3.3 Measurement of Spectrometer Capacitances 45
3.4 Ion Currents to a Single Ring 47
CHAPTER 3  cont'd ..

3.5 Charge Separation by Reed Switches  48
3.6 Sequencing of the Spectrometer Relays  49
3.7 Site of the Experiments  51
3.8 Preliminary long-term Recording  52
3.9 Spectrometer Sequencing for Experiments  54

CHAPTER 4

DATA REDUCTION, CURRENTS TO THE SPECTROMETER RINGS

4.1 Fundamentals  55
4.2 Theory of Spectrometer Ring Interactions  57
4.3 Computer Model of Spectrometer Ring System  59
4.4 Sync Checking, Calculation of Input Currents  61
4.5 Leakage Current from the Rings  64
4.6 The Effect of an Open Reed Switch  66
4.7 Removal of Zero Offsets, Calculation of Block Means  68
4.8 Discussion of the Observed Ring Currents  70

CHAPTER 5

MOBILITY SPECTRUM CALCULATIONS

5.1 The Spectrometer Transform  73
5.2 Inverse Spectrometer Transforms  75
5.3 Properties of Mobility Spectrum Functions  77
5.4 Preliminary Tests on Mobility Spectrum Functions  80
5.5 Calculation of Optimal Spectrum Parameters  83
5.6 The "Complete" Mobility Spectrum Function  87
5.7 Accuracy of the Calculated Spectra  88
CHAPTER 6

OBSERVED MOBILITY SPECTRA

6.1 Experimental Details 91
6.2 Variation of Mobility Spectra over Fifteen-Minute Intervals 92
6.3 Diurnal Variation of Mobility Spectra 97
6.4 Comparison of Independently Measured Conductivities with those Computed from Mobility Spectra 101
6.5 The Dependence of $\lambda$ on $v$ and $A$ 104
6.6 Mobility Spectra of Ions Produced by Point Discharge 106

CHAPTER 7

CONCLUSION

7.1 Limitations of the Present Spectrometer 111
7.2 Suggestions for an Improved Spectrometer 112

Appendix 1: Details of the Spectrometer Electronics 114
Appendix 2: Least Squares Parameter Estimation 117
Appendix 3: The Transformed Lognormal Distribution 121

References:
CHAPTER 1

INTRODUCTION

1.1 Nuclei, Ions, Mobility, Diffusion

In the lower atmosphere a large number of aerosol particles of various types are constantly present. JUNGE (1955) classified these by their size into:

- giant particles — radii greater than $10^{-6}$ m;
- large particles — radii between $10^{-6}$ and $10^{-7}$ m;
- Aitken particles — radii less than $10^{-7}$ m.

While the larger particles are of special interest from the point of view of atmospheric pollution, in Atmospheric Electricity we are mainly interested in the Aitken particles, often referred to as "condensation nuclei", and in particles of this or smaller size, which when carrying an electric charge are called "atmospheric ions".

Condensation nuclei consist of substances which are soluble in water. They are the points at which water vapour will condense when the air about them becomes saturated. Their number density can therefore be measured by enclosing a volume of air, expanding it rapidly to produce supersaturation, and counting the number of drops which appear. The counting was done directly in the original Aitken nucleus counter, but this has been superseded by photoelectric counting (e.g. NOLAN and POLLAK (1947)). Condensation does not occur on particles of greater radius.
Atmospheric ions are of two kinds - large and small. A small ion consists of a single ionised molecule with a number of other molecules clustered about it, the "cluster" being held together by the charge and its induced polarisation. For example SISKNA (1969) concluded that the most important positive ions in air are hydronium ions (chemical symbol $\text{(H}_3\text{O})^+\text{(H}_2\text{O})_n^-$). WRIGHT (1936) considered the number of molecules in a cluster to be between 10 and 12. If a small ion loses its charge there are no longer any forces to hold the cluster together: the ion ceases to exist.

A condensation nucleus may become charged by the attachment of one or more small ions: the resulting charged particle is a "large ion". If the small ions each carry a charge of one electron (i.e. are singly charged) the large ions net charge may be 0, $\pm 1$, $\pm 2$, ... electrons. The maximum charge an ion can carry depends on its radius, being one electron for radii less than about $5 \times 10^{-8}$ m, two for radii between $5 \times 10^{-8}$ and $1 \times 10^{-7}$ m, hence small ions are invariably singly charged. At any time a large ion may revert to a condensation nucleus, neutralising its charge by attaching oppositely charged small ions.

Any atmospheric ion, when placed in an electric field, experiences a force proportional to its charge and the potential gradient of the field. This causes the ion to accelerate in the direction of the field, thus gaining kinetic energy. It will lose this energy in collisions with air molecules, ultimately reaching a limiting velocity at which its rate of energy loss in collisions balances the energy supplied by the field. The velocity attained by an ion in an electric field
of one volt per metre is called its "mobility", \( k \). For fields up to about \( 10^6 \) V/m the limiting velocity is found to be proportional to the field strength, so an ion's velocity, \( \nu \), in a uniform field \( E \), is given by

\[
\nu = kE \tag{1}
\]

and the units of mobility are \( \text{m}^2/\text{V}.\text{sec} \), i.e. \( \text{m}/\text{sec} \) per V/m. Small ions have mobilities in the range 2.0 \( \text{cm}^2/\text{V}.\text{sec} \) down to about 0.2 \( \text{cm}^2/\text{V}.\text{sec} \), while large ion mobilities are usually much smaller - MISAKI (1964) observed mobilities as low as 0.0000 42 \( \text{cm}^2/\text{V}.\text{sec} \) (4.2 \( \times 10^{-9} \) \( \text{m}^2/\text{V}.\text{sec} \)). Ions with mobilities between 0.2 and 0.002 \( \text{cm}^2/\text{V}.\text{sec} \) are often called "intermediate ions".

The mobility of an ion is influenced by a large number of factors such as the ambient pressure, the presence of other substances and the chemical nature of the ion's molecules, but the most important factor is its size (usually expressed as a radius). It would be useful to be able to calculate the size of an ion from its mobility, however there is no valid general law relating these quantities. For large ions, whose radii are generally greater than the mean free paths of their surrounding air molecules, Stokes' law (as modified by Milliken and Cunningham) is commonly used. This law may be written as

\[
F = 6\pi \eta r v \left( 1 + \frac{L}{r} (0.684 + 0.290 \exp[-1.25 \frac{r}{L}]) \right)^{-1} \tag{2}
\]
where $F = \text{acting force}$,

$\eta = \text{viscosity of the air}$,

$r = \text{ionic radius}$,

$v = \text{ionic velocity}$,

and $L = \text{mean free path of air molecules}$.

FUCHS (1964) gives a brief derivation of the above equation, and of others which may be useful for ions of lesser radius.

Several theoretical derivations of ionic mobility have been proposed, but these can only deal with ions of known species in pure gases (e.g. $\text{H}_3\text{O}^+$ in $\text{O}_2$). A survey of this field is given by LOEB (1955).

When a large number of ions of the same species are present in a gas they diffuse away from regions of high ion concentration. Their diffusion coefficient, $D$ (the number of ions per second diffusing through a surface of unit area because of a unit concentration gradient), is given by the formula

$$D = \frac{kT}{ne} \text{ m}^2/\text{sec}$$

..........(3)

where $ne = \text{the charge on the ion}$,

$k = \text{Boltzmann's constant}$,

$T = \text{absolute temperature}$,

and $k = \text{ionic mobility}$.

Diffusion is usually insignificant for small ions, but measurements of the rate of loss of nuclei by diffusion to the edges of a tube can be used with formulae such as that of GORMLEY &
Fig. 1.21 Apparatus for Mobility Measurement by the "Flight Time" Method.

Fig. 1.22 Ideal Ion Pulse as observed on an Oscilloscope.

Fig. 1.23 Ion Pulse observed by BRICARD, BABANE & MADELAINE (1969).
KENNEDY (1949) to determine nuclear radii.

1.2 Measurement of Mobility, Mobility Spectra

Consider the apparatus shown schematically in fig. 1.21. Positive ions are assumed to be produced at the left of the figure and may then drift in an electric field \( E \) maintained between two metal plates, of which the one on the right is connected to earth through a sensitive current measuring instrument, A. A gauze screen, at a known distance \( d \) from the collecting plate, is used as an "ion gate" to control the entry of ions to the measuring space between it and the collecting plate. The ion gate is used to provide a small "parcel" of ions, and the time taken by the parcel to travel the distance \( d \) is measured. If this transit time is \( t \) then the mobility of the ions in the parcel is

\[
k = \frac{d}{t} \cdot \frac{1}{E}
\]

We will call mobility measuring methods based on this apparatus "flight-time" methods.

This method was used by TYNDALL & GRINDLEY (1926) for the measurement of positive and negative small ion mobilities in air. Their apparatus employed a small quantity of radioactive material with a rotating metal shutter in front of it as a gated ion source instead of the continuous source of fig. 1.21 and an alternating square-wave electric field to allow the measuring section to be cleared of ions between measurement cycles. They determined the transit time by varying the repetition rate of their measurement cycle to find the rate
giving a maximum collected current, observed on an electrometer. Other more accurate flight-time methods are discussed by LOEB (1955).

If an oscilloscope were used as the current measuring instrument we might expect the observed current pulse to be square, as indicated in fig. 1.22. This, however, is seldom the case. Assuming that the parcel of ions leaving the ion gate has well-defined edges and only contains ions of one mobility, ions inside the parcel will diffuse outward, blurring its edges. It is also probable that the shape of the parcel will change as it moves through any distortions present in the applied field. The assumption of a single ionic mobility can only be true for the case of a known species of ion in a pure gas; the parcel will usually contain a mixture of ions of varying mobilities. These factors distort the edges of the observed current pulse so that the pulse shape observed by BRICARD, BABAINE & MADELAINE (1969) (reproduced in fig. 1.23) is much more typical.

Flight-time methods are capable of yielding absolute mobilities with high accuracy but are seldom used for atmospheric ion mobilities, for a number of reasons. They require the ions to be sampled periodically, and a time interval determined for each sample: this may be tedious to obtain and to record. They are obviously not well suited to situations where ions having a range of mobilities are present, i.e., they have poor resolving power. Other methods commonly used for atmospheric work may be referred to as "Gerdien Chamber" methods.
Fig. 1.24 Apparatus for Mobility Measurement by the "Gerdien Chamber" Method.

Fig. 1.25 Contours of Equal Ion Concentration, Showing Diurnal Variation of Atmospheric Mobility Spectrum - from MISAKI & KANAZAWA (1969).
An apparatus for the Gerdien Chamber method is illustrated in fig. 1.24. It consists of a chamber bounded on two sides by planar parallel metal electrodes between which an electric field is maintained. The collecting electrode (the lower one in the figure) is earthed, except for a short section which is earthed through the electrometer, A. We will call this section the "indicating" section. An ion starting from the driving electrode will move across the gap, reaching the collecting electrode in a time inversely proportional to its mobility, exactly as in the flight-time method. In this case, however, the air in the chamber is not stationary, but moving through it, and as indicated in fig. 1.24 the flow is always at right angles to the field with a uniform velocity everywhere. This means that high-mobility ions will reach the collecting electrode at points closer to the intake end, while those with lower mobilities will arrive further downstream. If ions are only allowed to enter the chamber through a small aperture in the intake (using some form of ion gate), and the indicating section is moved along the collecting electrode, then the mobility spectrum (i.e. the number of ions for every mobility) can be calculated from the current observed while the indicating section traverses the whole length of the chamber.

Ideally the widths of both ion gate aperture and indicating section should be negligibly small, but in practice finite widths must be used. This means that the ions actually observed (by the electrometer) will include a band of mobilities rather than just one single mobility. The width of this band determines the mobility resolution of the apparatus. A further practical limitation is imposed by the electrometer: the maximum obtainable electrometer sensitivity is only of the
order of $0.1 \text{ fA (10}^{-16}\text{A)}$, corresponding to about one thousand electrons per second. So as to collect enough ions to give a measurable current it is common to use indicating sections whose length is a significant fraction of the chamber length, and/or to dispense with the ion gate. A thorough analysis of such chambers is given in Chapter 2.

This method of mobility measurement was developed at the turn of the century by several workers, notably J. Zeleny, H. Ebert, H. Gerdien, and J.A. McClelland. More recently WHIPPLE (1960) and MISAKI (1961) measured atmospheric small ion mobilities in the range $0.1$ to $5 \text{cm}^2/\text{V}.\text{sec.}$ MISAKI (1964) also observed large ions with mobilities down to $4.2 \times 10^{-5} \text{cm}^2/\text{V}.\text{sec}$, and MISAKI & KANAZAWA (1969) investigated diurnal variations in atmospheric mobility spectra, using three separate Gerdien chambers to cover the range $0.00042$ to $4.22 \text{cm}^2/\text{V}.\text{sec.}$ DOLEZALEK & OSTER (1965) developed a Gerdien chamber apparatus for use in the upper atmosphere which uses an alternating electric field instead of the steady field we have discussed.

Atmospheric ion mobility spectra are normally drawn as histograms, on a logarithmic mobility scale. They show a single maximum (typically of 100 ions/cm$^3$) in the small ion range, usually between 1.1 and 1.5 cm$^2$/V.sec. The total small ion concentration is typically 1000 ions/cm$^3$. As mobility decreases the number of ions present remains low through the intermediate ion range, however below about 0.01 cm$^2$/V.sec the ion concentration increases rapidly. Figure 1.25, taken from MISAKI & KANAZAWA (1969), is a plot of mobility vs time of day with contours of equal ion concentration drawn in. To produce
this plot mobility spectra were measured at twenty minute intervals, and the contours interpolated between them. The position of the small ion peak remains steady throughout the day while its magnitude varies, being much greater in the hours before dawn than during the rest of the day. This presumably reflects the higher concentration of nuclei (from processes such as combustion) present during the day which remove small ions by attachment (see section 1.3). The large ion spectrum does not show regular variations, and it may vary greatly from time to time.

Though the Gerdien chamber provides a convenient apparatus for atmospheric ion mobility measurements it still has some drawbacks. It can only detect ions of one sign at any time, so if measurements of both positive and negative ions are required we must either use two separate chambers or use a single one for positive and negative ions alternately. Airflow through the chamber must be laminar: this is simple to achieve at a fixed location, but more difficult for spectrometers mounted in vehicles, particularly those in aeroplanes. Errors in determining any of the chamber parameters (e.g. the airflow rate) lead to inaccuracy in the mobility values obtained, hence although the apparatus yields reliable relative mobility values it is not well suited to absolute mobility measurements. Similarly stray electric fields near the chamber intake (such as those due to the difference in potential of the earthed intake and its surroundings) will deflect some fraction of the ambient ions away from their undisturbed paths to the collecting electrode. The observed ion concentrations are hence accurate relative to each other, but may not be truly representative of those in the free atmosphere. Finally
we must assume that the ionic population does not alter in the time it takes us to measure it. This time is usually about 20 minutes, though EICHMEIER (1967), (1968) required periods of five hours! Obviously the spectrum may change in this time, but to date no attention seems to have been paid to this problem. These limitations do not, however, prejudice the Gerdien chamber's acceptance as the obvious method for atmospheric ion research.

1.3 Ionic Equilibrium in the Atmosphere

Atmospheric small ions are continually being created by the action of various forms of ionising radiation. J.J. NOLAN (1950) states that the rate of production of small ion pairs per (cm$^3$.sec), q, may be written as

$$q = q_1 + q_2 + q_3 = 9.5 \text{ ion pairs/cm}^3\cdot\text{sec}$$

where

$$q_1 = 4.9, \quad q_2 = 3.1, \quad q_3 = 1.5.$$  \hspace{1cm} ...........(1)

In this equation $q_3$ is the ionisation due to cosmic rays, $q_2$ that due to radioactive material in the earth's crust, and $q_1$ that due to radioactive aerosols in the air. $q_2$ and $q_3$ may be considered stable at any given place, but $q_1$ may vary from almost zero to many times its average value. The production of large ions by direct ionisation is, however, negligible - instead large ions are created (and small ones destroyed) by the attachment of small ions to other particles. Obviously the number of ions formed per cm$^3$.sec in this way is proportional to the concentration of each of the two particles involved,
<table>
<thead>
<tr>
<th>Charge</th>
<th>Positive</th>
<th>Negative</th>
<th>Uncharged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large</td>
<td>$N_1$</td>
<td>$N_2$</td>
<td>$N_0$</td>
</tr>
<tr>
<td>Small</td>
<td>$n_1$</td>
<td>$n_2$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

Table 1.31 Symbols for Ion Concentrations

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Combining Ion Species</th>
<th>Approx Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{jp}$</td>
<td>large $j$ small same sign</td>
<td>varies with radius (see section 1.4)</td>
</tr>
<tr>
<td>$\mu_{je}$</td>
<td>large $j$ small opp sign</td>
<td></td>
</tr>
<tr>
<td>$n_{12}$</td>
<td>small $+1$ large $-1$</td>
<td></td>
</tr>
<tr>
<td>$n_{10}$</td>
<td>small $+1$ large $0$</td>
<td></td>
</tr>
<tr>
<td>$n_{21}$</td>
<td>small $-1$ large $+1$</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>$n_{20}$</td>
<td>small $-1$ large $0$</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>small $+1$ small $-1$</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>large $+1$ large $-1$</td>
<td>$10^{-9}$</td>
</tr>
</tbody>
</table>

Table 1.32 Ionic Combination Coefficients
and to a "combination coefficient" for the process. Table 1.31 sets out the symbols we will use to represent the concentration of large and small ions of each sign, while table 1.32 gives the symbols and approximate magnitudes for the various combination coefficients.

If conditions remain steady a state of equilibrium must eventually be reached, in which the number of ions created per cm$^3$.sec is exactly balanced by the number destroyed by combination. Considering only the processes which are usually significant in the atmosphere we can write four equilibrium equations, one for each ion species:

\[
\begin{align*}
\text{small + ions} & \quad q = \alpha n_1 n_2 + \eta_{12} n_1 N_2 + \eta_{10} n_1 N_0 \\
\text{small - ions} & \quad q = \alpha n_1 n_2 + \eta_{21} n_2 N_1 + \eta_{20} n_2 N_0 \\
\text{large + ions} & \quad n_{10} n_1 N_0 = \eta_{21} n_2 N_1 \\
\text{large - ions} & \quad n_{20} n_2 N_0 = \eta_{12} n_1 N_2
\end{align*}
\]

These equations were first proposed by NOLAN & DE SACHY (1927), who found that although $N_1$ and $N_2$ were practically equal $n_1$ was normally greater than $n_2$, the ratio $n_1/n_2$ being about 1.2. Provided the ionisation rate $q$ remains steady any changes in ion concentration can be attributed to changes in the coefficients.

Measurements are often made of $Z$, the total concentration of charged and uncharged nuclei (using some form of nucleus counter - section 1.1). NOLAN, BOYLAN & DE SACHY (1925) verified that $Z$ is equal to the sum of the concentrations of charged and uncharged nuclei, or
\[ Z = N_0 + N_1 + N_2 \] ............(6)

If the nucleus concentration is much greater than that of small ions we may follow P.J. NOLAN (1956) and ignore the difference between positive and negative ions, writing

\[ n_1 = n_2 = n, \quad n_{10} = n_{20} = n_0 \]
\[ N_1 = N_2 = N, \quad n_{12} = n_{21} = n \] ............(7)

so that equations (4) and (5) reduce to

\[ n_0 N_0 = nN \] ............(8)

Let \[ n/n_0 = N_0/N = R \] ............(9)

Then \[ Z/N = (N_0 + 2N)/N = R + 2 \]

Equations (2) and (3) become

\[ q = an^2 + 2nnN \] ............(10)

or, from (9)

\[ q = an^2 + bnZ \] ............(11)

where \[ b = 2n_0 R/(R+2) \] ............(12)

If we write

\[ F = q - an^2 \] ............(13)
**Fig. 1.31** Variation in Ion Concentration when Nuclei from a Flame were introduced into a Sealed Room - from BURKE & DALU (1969).

**Fig. 1** Variation of discharge current (circles) and of nucleus concentration (crosses) with potential of point.

**Fig. 1.65** Small Ion (point current) and Nucleus Concentration near a point for various point Potentials - from NOLAN & O'TOOLE (1959).
in equation (11), then taking logarithms and differentiating we obtain

$$\frac{dF}{F} = \frac{db}{b} + \frac{dn}{n} + \frac{dZ}{Z}$$

...............(14)

Equation (11) implies a relationship between nucleus and small ion concentrations: if the nett small ion production rate, \(F\), is constant then the small ion concentration varies inversely with the nucleus concentration.

BURKE & DALU (1969) investigated the dependence of \(n\) upon \(Z\) using a sealed room 50 m\(^3\) in volume, into which were introduced nuclei from fog and from a flame. The variation thus produced in both \(n\) and \(Z\) was very striking - one of the records obtained is reproduced in fig. 1.31. Burke and Dalu measured \(n\) and \(Z\) directly, \(b\) by measuring the nuclear radius \(r\) (using a diffusion method) and calculating \(b\) using a formula given by KEEFE & NOLAN (1962) relating \(r\) and \(b\). They then calculated \(F\) from \(b\), \(n\) and \(Z\) using equation (11). Finally they plotted each of the terms in equation (14) against time to determine the relative contribution of each. Their conclusion was that "the variation of the nucleus concentration fully controls the variation of the small ions."

1.4 Theories of the Ionic Combination Coefficients

One application of mobility spectrometry is the determination of the size spectrum of aerosol particles in the condensation nucleus size range, as described by JUNGE (1955). MISAKI, OHTAKA & KANAZAWA (1972), for example, have used
this approach to observe a "very rapid progress of atmospheric pollution at a rural country site". To convert the observed mobility spectrum we may first calculate the radius corresponding to each mobility (using the Stokes-Millikan-Cunningham formula - section 1.1), then use a theoretical relation to compute the total number of particles (charged and uncharged) of this radius from the observed number of ions. For the larger particles at least we will have to allow for particles which are more than singly charged, as indicated by MISAKI (1964). In section 1.3 we obtained the formula, (equation (8))

\[ \frac{N_0}{N} = \eta/\eta_0 \] ............(1)

which gives the ratio of uncharged to singly charged ions. If \( \mu_{jp} \) is the combination coefficient for a large ion carrying charge \( j \) and a small ion of the same sign, and \( \mu_{je} \) that for the same large ion and a small one of opposite sign, we may write a more generalised form of (1) which includes large ions of any given charge:

\[ \frac{N_{j-1}}{N_j} = \frac{\mu_{je}}{\mu_{j-1p}} \] ............(2)

We see that the relations we require for the \( N \)'s are derived from the \( \mu \)'s, accordingly we now examine the various theories for combination coefficients.

WHIPPLE (1933) derived the formulae

\[ \eta_{12} = \eta_{10} + \frac{k_1e}{\varepsilon_0}, \quad \eta_{21} = \eta_{20} + \frac{k_2e}{\varepsilon_0} \] ............(3)
which account for the attachment of small ions to charged and uncharged nuclei due to both kinetic motion and electrostatic attraction. He assumed that a small ion (radius \( r \)) would be captured on entering a small (spherical) surface surrounding an oppositely charged nucleus (radius \( r \)). WRIGHT (1936) obtained the relation

\[
\eta_{10} = \eta_{20} = \pi r^2 c
\]

by considering the probable number of ions with velocity \( c \) (due to Brownian movement only) which collide with the nucleus in a given time, assuming that the small ion concentration remains constant.

In (1949) BRICARD used the Smoluchowsky theory of coagulation, which states that "the stream of particles moving towards the surface of an aerosol particle is proportional to its radius", to say that

\[
\mu_{1p} nN = N.r.4\pi D \frac{dn}{dx}_{x=r}
\]

where \( D \) is the diffusion coefficient of the small ions. He evaluated \( dn/dx \), the concentration gradient near the nucleus, considering both diffusion and electrostatic attraction. Since he regarded the nucleus as a conducting sphere rather than a point charge he allowed for the electrostatic image of the approaching small ion when determining the electric field. Bricard's resulting formulae are:

\[
\mu_{jp} = \frac{4\pi D_0}{I(\phi,j)}, \quad \mu_{je} = \frac{4\pi D_0}{I(\phi,-j)}
\]
where \( \phi = \frac{ek}{4\pi\varepsilon_0 Dr} \) (\( e \) is the charge on an electron)

and \( I(\phi, j) = \int_1^\infty \frac{1}{x^2} \exp (-\frac{1}{4x^2} \frac{1}{2x^2(x^2-1)}) dx \)

In (1962) BRICARD extended his theory to allow capture to take place when the small ion had approached to within one mean free path's length of the nucleus.

JUNGE (1955) stated that the BRICARD (1949) and WRIGHT (1936) theories are both based on invalid assumptions since both assume a stationary diffusion field for the aggregation process. He proceeded instead as follows: "If, on the average, one aerosol particle is present within the volume \( V \) (surface \( S \)) which has not attached at time \( t \), the rate of attachment of these uncharged particles is

\[
\mu_0 \rho = \int_0^V \int_0^S \frac{\partial n}{\partial t} \, dV = D \int_0^SV \, n \, dS = 4\pi Dr^2 \left( \frac{\partial n}{\partial x} \right)_x
\]

\[ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7) \]

To account for electrostatic attraction we use, similar to WHIPPLE (1933), the substitution

\[
\frac{\partial n}{\partial t} = D V^2 n + V(jknE)
\]

\[ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8) \]

where \( jE \) is the electric field through surface \( S \). Making this substitution and solving we obtain

\[
\mu_{jp} = 4\pi(Dr + jke), \quad \mu_{je} = 4\pi(Dr - jke)
\]

\[ \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (9) \]
The radii for which \( \mu_j \) become positive give the values of \( r \) below which the nucleus cannot carry \( j \) charges."

In (1956) P.J. NOLAN proposed that the Boltzmann distribution law should apply to charged nuclei, i.e. if \( N_j \) is the number of nuclei per cm\(^3\) with charge \( j \) then

\[
N_j = N_0 \exp\left(-\frac{j^2 e^2}{4 \pi \varepsilon_0 \kappa k T}\right)
\]

\[\text{.........(10)}\]

where \( \kappa \) = Boltzmann's constant
and \( T \) = absolute temperature.

This idea was developed further by KEEFE, NOLAN & RICH (1959), KEEFE & NOLAN (1961) and KEEFE & NOLAN (1962), yielding the relation

\[
\frac{Z}{N_0} = \sqrt{\frac{n}{m}} = M \sqrt{r'}
\]

\[\text{.........(11)}\]

where \( m = \frac{e^2}{4 \pi \varepsilon_0 \kappa k T} \)
and \( M \) is a constant.

Furthermore, if we write \( y = \exp(e^2/4 \pi \varepsilon_0 \kappa k T) \) then from (10)

\[
N_0/N_1 = y, \quad N_0/N_2 = y^4, \quad \ldots, \quad N_0/N_j = y^{j^2}
\]

\[\text{.........(12)}\]

hence the concentrations of nuclei carrying various charges can be determined.

From the foregoing discussion it is clear that there is little agreement on the theories of ionic combination coeffic-
ients. One of the main obstacles to such agreement is the
difficulty of gathering direct experimental evidence to
support any theory. Meanwhile each of the last three (i.e.
Bricard, Junge and Boltzmann) seems equally valid.

1.5 Atmospheric Conductivity

Because of the ions present atmospheric air has a small
but finite electrical conductivity, typically of the order of
5 to 10 × 10^{-15} \text{ mho.m}^{-1}. Consider a flat surface of area \( A \),
perpendicular to which there is an electric field \( E \). If there
are \( f(k) \) ions of one sign and mobility \( k \) per unit volume the
number of such ions driven through the surface each second by
the field will be

\[ N_k = A \cdot kE \cdot f(k) \] ........................(1)

We assume the ions are singly charged (i.e. have charge \( e \)), so
the current density through the surface is

\[ J = eN_k / A = e \cdot kf(k) \cdot E \text{ Ampere} \] ........................(2)

The conductivity due to ions of mobility \( k \) is thus

\[ \lambda_k = e \cdot kf(k) \text{ mho.m}^{-1} \] ........................(3)

and the total conductivity due to ions of one sign, or "polar
conductivity" is the integral of (3) over all mobilities. The
total conductivity due to positive ions is therefore
\[ \lambda_+ = e \int_0^\infty k f(k) dk \] ............(4)

Atmospheric conductivities are generally measured using a modified form of Gerdien chamber; the method was devised by H. Gerdien in 1905, and JOHNS (1972) gives a detailed modern account of its theory, design and experimental considerations. This independent conductivity measurement can be compared with that calculated by integrating a mobility spectrum to provide an indication of the reliability of a mobility spectrometer.

It is commonly assumed that the atmospheric conductivity is virtually determined by the small ion concentration - for example ISRAEL (1970) states that "since the mobility of small ions usually lies between 1 and 2 cm²/V·sec, whereas that of the intermediate and large ions is approximately 1/10 to 1/10,000 of this value, respectively, the conductivity of the air is almost exclusively due to the small ions". Since, however, there will often (particularly in polluted areas) exist many more larger ions than small ones, it is quite possible for the contribution from the larger ions to be significant. No investigations of this contribution have so far been made.

When only small ions (with an average mobility of \(k_+\) and \(k_-\) for positive and negative ions) are considered the polar conductivities become

\[ \lambda_+ = |e n_+ k_+|, \quad \lambda_- = |e n_- k_-| \] ............(5)

Considerable interest has been shown in the ratio
<table>
<thead>
<tr>
<th></th>
<th>( \lambda_-/\lambda_+ )</th>
<th>( n_+/n_- )</th>
<th>( k_+ )</th>
<th>( k_- )</th>
<th>( k_-/k_+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SAGALYN (1958)</strong></td>
<td>1.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SAGALYN (1958)</strong></td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HOPPEL &amp; KRAEKEVIK (1965)</strong></td>
<td>1.15</td>
<td>1.24</td>
<td></td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td><strong>SAGALYN (1958)</strong></td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>1.05</td>
</tr>
</tbody>
</table>

**Ground level**

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_-/\lambda_+ )</th>
<th>( n_+/n_- )</th>
<th>( k_+ )</th>
<th>( k_- )</th>
<th>( k_-/k_+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ISRAEL (1970) p.94</strong></td>
<td>0.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NOLAN, BOYLAN &amp; DESACHY (1925)</strong></td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ISRAEL (1970) p.194</strong></td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>J.J. &amp; P.J. NOLAN (1933)</strong></td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ISRAEL (1970) p.142</strong></td>
<td>1.37</td>
<td>1.89</td>
<td></td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td><strong>MISAKI &amp; KANAZAWA (1969)</strong></td>
<td>1.14</td>
<td>1.50</td>
<td></td>
<td>1.31</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.51  Experimental Values of Conductivity, Ion Concentration and Mobility Ratios for Atmospheric ions of each sign.
\[ \frac{\lambda_-}{\lambda_+} = \frac{(k_-/k_+)/(n_+/n_-)}{ \ldots \ldots \ldots (6) } \]

(assuming charges of equal magnitude on positive and negative ions).

Table 1.51 gives some of the various values reported for the three ratios in equation (6). At high altitudes, where there are no large ions and \( n_+ = n_- \), the conductivity and mobility ratios are the same, but at ground level, where large ions are plentiful, agreement with equation (6) is poor.

1.6 Point Discharge

Figure 1.61 shows a uniform electric field between two surfaces, such as might exist between the ionosphere and the earth (assumed to be at zero potential). Any location in the field will have a differing electrostatic potential due to the field. A conducting point attached to the lower surface will remove the potential at the tip producing a greatly intensified field there, as illustrated in fig. 1.62. If the field is sufficiently intense any free electrons present may be accelerated sufficiently to ionise other particles with which they collide, so releasing more electrons: this phenomenon is called "avalanche multiplication". Avalanching is most probable close to the point's tip; when this occurs a "point discharge" current (typically of the order of one microamp) flows through the point. Discharges of this type are also termed "corona discharge".
Fig. 1.61 Undisturbed Field at a Plane Surface.

Fig. 1.62 Field Near a Conducting Point on a Plane Surface.

Fig. 1.63 Observed Discharge Current Pulses from a Negative Point (Trichel Pulses).

Fig. 1.64 Observed Discharge Current Pulses from a Positive Point.
When the point is negative (relative to the upper surface) electrons avalanche outwards from it, leaving a cloud of slower moving positive ions surrounding the point. This space charge lowers the field near the point until further avalanching is stopped, then the positive ions drift in to the point and the cycle repeats. The first avalanche may easily start with electrons dislodged from the point when a positive ion collides with it. Since positive ions are plentiful in the air this will invariably occur as soon as the space charge has cleared. Discharge current from a negative point therefore consists of a regular series of current pulses called "trichel pulses" whose shape is indicated in fig. 1.63 - TRICHEL (1938).

On the other hand, when the point is positive avalanching is inward to the point, leaving a positive space charge as before. Two modes of discharge are then possible: in one the space charge acts as an extension of the point, forming a conducting streamer; in the other the discharge spreads back along the surface of the point, where the field is higher since there is less space charge. In either case the initial avalanche must begin in the air close to the point's tip. As indicated in section 1.3 the ionisation rate in air is low (only about 10 ion pairs formed per cm$^3$.sec), so there will be a significant (random) time delay between current pulses. Hence positive point discharge current consists of pulses with irregular time intervals between them, as in fig. 1.64.
The above descriptions are of course idealised - LOEB (1965) gives a detailed survey of the mechanisms of corona discharge. We note, however, that the discharge is comprised of a series of current pulses, whose frequency depends on the time taken to clear space charge from the vicinity of the point. This means that any wind past the point will help clear space charge, increasing the pulse frequency and hence the discharge current. Furthermore, such wind will reduce random fluctuations in the gap clearing time, improving the regularity of the pulse train.

Most interest in point discharge in the atmosphere has been in the following areas: the relation between the point current and the undisturbed potential at its tip, the relation between point discharge current through the air and height above the point, the difference (if any) between an artificial point such as a metal rod and a natural one, e.g. a tree, and the contribution of point discharge to the earth's charge balance. Little attention has so far been given to the ions produced, though BRICARD, BABANE & MADELAINE (1969) examined the mobility spectrum of ions formed by positive point discharge using a flight-time method (see section 1.2). NOLAN & KUFFEL (1957) and NOLAN & O'TOOLE (1959) investigated the ions and nuclei produced by negative point discharge. One of their plots of point current (carried away by positive small ions) and nucleus concentration vs point potential is reproduced in fig. 1.65. This indicates that whenever small ions are produced, nuclei are produced as well. These nuclei are very small, are uncharged, and tend to be drawn in to the point by the intense non-uniform field.
1.7 Scope of the Present Work

The scope of the investigations described in this thesis may be briefly summed up as follows:

I  To develop a mobility spectrometer capable of measuring a complete spectrum in a time significantly less than the twenty minutes commonly required (if necessary at the expense of mobility resolution).

II a) To observe mobility spectra over short periods of time, and hence to test the assumption that they do not change rapidly.

b) To observe mobility spectra continually for periods of the order of one day, reduce these to half-hourly averages, and thus determine the daily spectrum variations prevailing in Auckland.

c) To test the supposition that large ions do not contribute significantly to the atmospheric conductivity using the spectra obtained in b).

d) To make a preliminary study of the mobility spectra of ions produced by point discharge.
CHAPTER 2

THEORY OF THE GERDIEIN MOBILITY SPECTROMETER

2.1 Analysis of the General Case

Consider a Gerdier Chamber consisting of two parallel plates of infinite extent a unit distance apart with an electric field $E$ between them. Fig. 2.11 shows the chamber in a space described by co-ordinates $\xi$ and $\psi$. Air enters through the gap $[\psi_1, \psi_2]$ in the intake side of the chamber at a rate of one unit volume per second per unit depth, and is drawn through the chamber in the $+\xi$ direction. Assume that the air velocity is independent of $\psi$, i.e. uniform across the chamber, and is of magnitude $v$. Any positively charged ions present will move in the $+\psi$ direction with a velocity $v$, characteristic of the ion. For negative ions $v$ is negative, and the ions move to the upper ($\psi = 0$) plate. We wish to determine the current reaching the segment $[\xi_1, \xi_2]$ of the lower (collecting) plate in terms of the characteristic velocity $v$, and to find the relationship between $v$ and the mobility $k$ of an ion in some experimental space, $(\xi, p)$.

Since both components of an ion's velocity ($v$ and $\nu$) are constant, it will follow a straight line trajectory at an angle $\alpha$ given by

$$\alpha = \tan^{-1} \frac{v}{\nu} \quad \text{...........(1)}$$
<table>
<thead>
<tr>
<th>Region</th>
<th>Case A</th>
<th>Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>$\gamma_1 = 0$</td>
</tr>
<tr>
<td>Boundary 12</td>
<td>$\xi_1 = \xi_2$</td>
<td>$\gamma_{12} = (1 - \psi_2) \frac{\xi_2}{\xi_2}$</td>
</tr>
<tr>
<td>2</td>
<td>$\xi_1 = \xi_2$</td>
<td>$\gamma_2 = \frac{\xi_2 - \xi_1}{\xi_2 - \xi_1} = \frac{\xi_2}{\xi_2} - (1 - \psi_2)$</td>
</tr>
<tr>
<td>Boundary 23</td>
<td>$\xi_2 = \xi_3$</td>
<td>$\gamma_{23A} = (1 - \psi_2) \frac{\xi_3}{\xi_3}$</td>
</tr>
<tr>
<td>3</td>
<td>$\xi_1 = \xi_3$</td>
<td>$\gamma_{3A} = \frac{\xi_3 - \xi_1}{\xi_3 - \xi_1} = \frac{\xi_3}{\xi_3} - \psi_2$</td>
</tr>
<tr>
<td>Boundary 34</td>
<td>$\xi_2 = \xi_4$</td>
<td>$\gamma_{34A} = (1 - \psi_4) \frac{\xi_2}{\xi_2}$</td>
</tr>
<tr>
<td>4</td>
<td>$\xi_1 = \xi_4$</td>
<td>$\gamma_4 = \frac{\xi_4 - \xi_1}{\xi_4 - \xi_1} = (1 - \psi_4) \frac{\xi_4}{\xi_4}$</td>
</tr>
<tr>
<td>Boundary 45</td>
<td>$\xi_2 = \xi_5$</td>
<td>$\gamma_{45} = (1 - \psi_4) \frac{\xi_4}{\xi_4}$</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>$\gamma_5 = 0$</td>
</tr>
</tbody>
</table>

Table 2.11: Gerdien Chamber Collecting Efficiencies ($\gamma$) for all possible Characteristic Velocities ($u$).
In particular positive ions entering at points \((0, \psi_1), (0, \psi_2)\) will reach the lower plate at points \((\xi_U, 0), (\xi_L, 0)\), such that

\[
\frac{\nu}{V} = \frac{1-\psi_2}{\xi_L} = \frac{1-\psi_1}{\xi_U}
\] ............(2)

From fig. 2.11 we see that only a fraction of the ions entering through gap \([\psi_1, \psi_2]\) will reach segment \([\xi_1, \xi_2]\). We will call this fraction the "collecting efficiency", \(\gamma\). For \(\nu = \text{constant}\) \(\gamma\) is a function of the chamber geometry, and of \(\nu\). For small values of \(\nu\) both \(\xi_U\) and \(\xi_L\) may be greater than \(\xi_2\); hence \(\gamma = 0\). As \(\nu\) increases both \(\xi_L\) and \((\xi_U - \xi_L)\) decrease, sweeping back across \([\xi_1, \xi_2]\). The range of \(\nu\) can therefore be divided into five regions, and \(\gamma\) obtained for each. The five regions and their boundaries are detailed in Table 2.11 and a complete plot of \(\gamma\) vs \(\nu\) is given in fig. 2.12.

Table 2.11 shows two possible cases for region 3. Of these, case A applies if \(\nu_{23A}\) is reached before \(\nu_{34A}\);

\[
i.e. \quad (1-\psi_2) \cdot \frac{\nu}{\xi_1} < (1-\psi_1) \cdot \frac{\nu}{\xi_2}
\] ............(3)

This condition implies that \(\gamma(\nu_{34A})\) is greater than \(\gamma(\nu_{23A})\), hence the slope of the graph in region 3 is positive. In the particular case where the two sides of equation (3) are equal, the plot becomes triangular, with a peak value of 1.

The ion concentrations in the incoming air can be described by a mobility spectrum function \(f(k)\), such that the number
of ions with mobility in the range \( k \) to \( k+dk \) is \( dn \),

i.e. \[ f(k) = \frac{dn}{dk} \] \( ............(4) \)

If the electric field in \((\xi, \psi)\) space, \( E \), is of unit magnitude, the characteristic velocity of an ion is equal to its mobility. In this case we may therefore write the collecting efficiency function as \( \gamma(k) \) \([=\gamma(\nu)]\). The number of ions reaching \([\xi_1, \xi_2]\) each second with mobilities in the range \( k \) to \( k+dk \) is

\[ dN = \gamma(k) \cdot f(k) \cdot dk \] \( ............(5) \)

Hence the total ion current reaching \([\xi_1, \xi_2]\) is

\[ I = e \int_{0}^{\infty} \gamma(k) \cdot f(k) \cdot dk \; \text{Ampere,} \] \( ............(6) \)

where \( e \) is the charge on a single ion.

We may thus obtain the current \( I \) for any given chamber, provided we can determine \( \gamma(k) \) for that chamber. We can write down \( \gamma(\nu) \) for the chamber using the plot of fig. 2.12. We now need to find the relationship between \( \nu \) and \( k \).

Consider a Gerdien Chamber in \((\xi, p)\) space, where the electric field is not necessarily uniform, but may be a function of \( p \). An ion's velocity in the field, \( \text{\(v\)} \), is given by

\[ \text{\textbf{\(W = \frac{dp}{dt} = p = kE(p)\)}} \] \( ............(7) \)
Fig. 2.13 Cylindrical "Differential Chamber of the First Order".
Since $W$ is not necessarily constant the ion's trajectory is no longer a straight line. To allow for this we may transform the chamber into $(\xi, \psi)$ space, where the ion's velocity, $v$, is constant. Assume that the relation between $(\xi, p)$ and $(\xi, \psi)$ space may be written

$$\psi = g(p) \quad \cdots \cdots \cdots (8)$$

Then

$$v = \dot{\psi} = \dot{p}g'(p) \quad \cdots \cdots \cdots (9)$$

Therefore (7)

$$v = kE(p)g'(p) \quad \cdots \cdots \cdots (10)$$

Hence

$$\psi = g(p) = \int \frac{v}{kE(p)} dp \quad \cdots \cdots \cdots (11)$$

Now $v$ and $k$ are constant and $E(p)$ can be determined for the given chamber; equation (11) may therefore be solved for $g(p)$. We may then obtain $\gamma(k)$ for the chamber, and thus find $I$ using equation (6). As an example of the method we will consider the cylindrical chamber shown in fig. 2.13a.

Let

$$\Delta \xi = \xi_2 - \xi_1 \quad \cdots \cdots \cdots (12)$$

For this chamber in $(\xi, \psi)$ space (fig. 2.13b), $\psi_1 = 0$, $\psi_2 = 1$. Thus the condition specified by equation (3) is satisfied hence case A, (fig. 2.12) holds. The plot of $\gamma$ vs $v$ is therefore as shown in fig. 2.13c.

The electric field in $(\xi, p)$ space is

$$E(p) = \frac{U}{p \log \frac{p_2}{p_1}} \quad \cdots \cdots \cdots (13)$$

where $U$ is the potential difference between $p_1$ and $p_2$. 
Substitute in (11):

\[ \psi = \int \frac{\nu p \log \frac{P_2}{P_1}}{kU} \cdot dp = \frac{\nu \log \frac{P_2}{P_1}}{kU} \cdot \left( \frac{p^2 + \text{const}}{2} \right) \]

.........(14)

But \( \psi = 0 \) when \( p = p_1 \):

\[ \text{const} = -\frac{p_1^2}{2} \]

\( \psi = 1 \) when \( p = p_2 \):

\[ \frac{kU}{\nu \log \frac{p_2}{p_1}} = \frac{(p_2^2 - p_1^2)}{2} \]

Thus

\[ k = \frac{\nu}{U} \log \frac{p_2}{p_1} \cdot \frac{(p_2^2 - p_1^2)}{2} \]

.........(15)

From (15) we define \( k_1 \) and \( k_2 \) corresponding to \( v_{15} \) and \( v_{34} \) (fig. 2.13c) and obtain

\[ k_1 = \frac{\nu}{\xi_1 U} \cdot \log \frac{p_2}{p_1} \cdot \frac{(p_2^2 - p_1^2)}{2} \]

.........(16)

\[ k_2 = \frac{\nu}{\xi_2 U} \cdot \log \frac{p_2}{p_1} \cdot \frac{(p_2^2 - p_1^2)}{2} \]

Mobilities such as \( k_1 \) and \( k_2 \) are referred to as "critical mobilities" for a chamber. They are discussed in section 2.2.

Comparing equations (15) and (16) we see that

\[ \frac{v}{\nu} = \frac{k}{\xi_1 k_1} = \frac{k}{\xi_2 k_2} \]

.........(17)

The plot of \( \gamma \) vs \( k \) is therefore as shown in fig. 2.13d. The slopes of its two component straight lines are
\[ S^p = \frac{\Delta E}{\xi_1 k_1} \]

and
\[ S^n = -\frac{1}{k_1} \]

\[ \ldots \ldots \ldots \ldots (18) \]

Finally we may substitute for \( \gamma \) in equation (6) to obtain

\[ I = e \int_0^{k_2} S^p k f(k) \, dk + e \int_{k_2}^{k_1} (1 - S^n k) f(k) \, dk \]

Ampere \[ \ldots \ldots \ldots \ldots (19) \]

The preceding analysis assumed a unit volume of air entering the chamber each second. If instead the flow rate is \( M_o \), then the collected current is just \( M_o \) times the \( I \) given by equation (19).

2.2 Classification of Chamber Types

In the preceding section we derived the collecting efficiency function, \( \gamma(k) \), for a generalised Gerdien chamber described by the four parameters \( \xi_1 \), \( \xi_2 \), \( \psi_1 \) and \( \psi_2 \). A number of simpler chambers (which are specialised cases of the general one) can be obtained by setting one or more of the describing parameters to fixed values. Such chambers were classified by TAMMET (1960) into "integral chambers" and "differential chambers" of the first and second orders. Their collecting efficiency functions (hereafter referred to as "CEF's") are discussed below, in terms of the mobility regions listed in table 2.11.
a) Undivided Intake, Undivided Collector.

\[ \psi_1 = 0 \]
\[ \psi_2 = 1 \]
\[ \xi_2 = 0 \]

Case A

b) Undivided Intake, Divided Collector.

\[ \psi_1 = 0 \]
\[ \psi_2 = 0 \]

Case A

c) Divided Intake, Undivided Collector.

\[ \xi_4 = 0 \]

Case B

Fig. 2.21 Collecting Efficiency Functions for Various Gerdien Chambers.
In an integral chamber neither the collecting electrode nor the air intake are divided, so that

\[ \xi_1 = 0, \quad \xi_2 > 0 \]

\[ \psi_1 = 0, \quad \psi_2 = 1 \]  \hspace{1cm} \ldots \ldots \ldots (1)

Relation (3) of section 2.1 therefore holds, so the CEF is case A of fig. 2.12. Since \( \psi_2 = 1 \) regions (1) and (2) are not present, similarly since \( \xi_1 = 0 \) there is no region (5). The CEF thus has only two regions: it is shown in fig. 2.71a.

First order differential chambers may have either a divided collecting electrode or a divided air intake (but not both). The CEF for a chamber with a divided collector, for which

\[ \xi_1 > 0, \quad \xi_2 > \xi_1 \]

\[ \psi_1 = 0, \quad \psi_2 = 1 \]  \hspace{1cm} \ldots \ldots \ldots (2)

was derived in section 2.1 (see fig. 2.13). It is reproduced as fig. 2.21b and is similar to that of fig. 2.21a except that region (5) is now present.

Fig. 2.21c shows the CEF for a chamber with a divided intake. In this case

\[ \xi_1 = 0, \quad \xi_2 > 0 \]

\[ 0 \leq \psi_1 < \psi_2 < 1 \]  \hspace{1cm} \ldots \ldots \ldots (3)
hence relation (3) (section 2.1) fails and case B of fig. 2.12 applies. Regions (1) and (2) are both present, but since $\xi_1 = 0$ there are no regions (4) or (5). The CEF therefore has three regions, the same number as that for the other first order chamber.

A differential chamber of the second order has

$$0 < \xi_1 < \xi_2$$
$$0 < \psi_1 < \psi_2 < 1$$

so its CEF is the complete one shown in fig. 2.12. Conditions (4) imply that regions (1), (2), (4) and (5) must always be present, but if

$$(1-\psi_2)/(1-\psi_1) = \xi_2/\xi_1$$

then $k_{23} = k_{34}$ and there is no region (3). The CEF may therefore have either four or five regions.

The names of the various chambers used by TAMMET (1960) refer to a method of computing mobility spectra which involved differentiating the currents collected by the Gerdien chamber (further discussed in sections 2.4 and 5.2). As an alternative classification scheme the following could be used:

- 2-region chamber = Integral chamber
- 3-region chamber = Differential chamber of first order
- 4-region chamber = Differential chamber of second order
- 5-region chamber = Differential chamber of second order
Fig. 2.31 "Integral" Gerdien Chamber.

Fig. 2.41 The Mobility Spectrometer Transform.
2.3 Physical Significance of Critical Mobilities - An Alternative Analysis

In section 2.1 we derived expressions for "critical mobilities" \( k_1 \) and \( k_2 \). These expressions (16) may be rewritten as follows: The capacitance of a cylindrical capacitor with the chamber's area and length is

\[
C = \frac{2\pi \xi}{\log p_2/p_1},
\]

\[........................(1)\]

while if we assume that air velocity is uniform across the chamber the volume rate per second is

\[
M_0 = v\pi (p_2^2 - p_1^2)
\]

\[........................(2)\]

Hence

\[
k_1 = \frac{M_0 \xi}{UC_1}, \quad k_2 = \frac{M_0 \xi}{UC_2},
\]

\[........................(3)\]

where \( C_1 \) and \( C_2 \) are the capacitances corresponding to lengths \( \xi_1 \) and \( \xi_2 \).

In equation (3) the capacitances are used merely as geometrical factors, but it is important to understand their physical significance. To do this, we will analyse the "Integral" Gerdien chamber, using a method similar to that of TAMMET (1960).

Consider the general "Integral" chamber shown in fig. 2.31. At any point within the chamber the velocity of an ion is

\[
\dot{v} = v + ke
\]

\[........................(4)\]
For a given value of $k$ the current reaching the single collecting electrode is the integral over a closed surface enclosing it of the product of ion density and velocity. Such a surface is shown dotted on fig. 2.31.

\[ i(k) = e \int f(k) \mathbf{v} \cdot ds \]

\[ = e f(k) \left\{ \int \mathbf{v} \cdot ds + k \int E \cdot ds \right\} \text{ using (4) } \quad \quad (5) \]

The first integral is zero, since all the air which enters the surface must also leave it, while the second is the integral of the electric field over a Gaussian surface.

Therefore

\[ i(k) = e f(k), \quad k \frac{Q}{\varepsilon} = e k f(k), \quad \frac{CU}{\varepsilon} \quad \quad \quad \quad \quad \quad \quad (6) \]

where $Q$ is the charge on the collecting electrode, and $C$ is its capacitance.

Again if all the ions of mobility $k$ are collected

\[ i(k) = e M_0 f(k) \quad \quad \quad \quad \quad \quad \quad (7) \]

Equations (6) and (7) are identical for all $k$ greater than $k_c$, the "critical" mobility. This is the mobility for which the ions entering at the outer edges of the intake are just collected, i.e. they follow paths like the one indicated on fig. 2.31.
From (6) and (7)

\[ k_c = \frac{M_0 \varepsilon}{U'C} \] ........................(8)

which is the same as equation (3) for \( k_1 \) and \( k_2 \).

We can now see that the capacitance in equations (3) and (8) represents the capacitance between the collecting and driving electrodes. This means that a measured value of this capacitance may be used in determining the critical mobility — a fact which is very useful for electrode configurations where the calculation of the capacitance of the collecting electrode is difficult.

The total current is obtained by integrating equation (5):

\[
I = \int_0^\infty \frac{eCU}{\varepsilon} \cdot kf(k) \, dk \\
= M_0 e \int_0^\infty \frac{k}{k_c} \cdot f(k) \, dk \quad \text{using (8)} \quad \text{............(9)}
\]

The range of integration may be divided at \( k_c \), since above this value equation (7) holds.

Hence \( I = M_0 e \left\{ \int_0^{k_c} \frac{k}{k_c} f(k) \, dk + \int_{k_c}^\infty f(k) \, dk \right\} \quad \text{............(10)} \)

Equation (10) is the usual form used for "Integral" chambers.

The current collected by the "First Order Differential" chamber of section 2.1 is merely the difference of the currents
for two integral chambers of lengths $\xi_2$ and $\xi_1$.

This method of analysis is simpler than that of section 2.1, and is valid for chambers where the cross-section varies with distance from the intake, such as the spherical centre electrode in a cylindrical outer one suggested by TAMMET (1962). It can, however, only be used for chambers using the whole of the intake area; the earlier method is required for the chambers having a divided air intake.

One other feature of this method should be noted: no mention was made of the spatial distribution of the airflow. Since there will always be a thin film of stationary air attached to the electrode surfaces, no ions can ever be carried onto them by the airflow alone - only the electric field will attract them. Hence for any "whole intake" chamber, only the total volume entering per second need be considered.

2.4 Methods of Spectrum Determination

Consider again equation (9) of section 2.3:

$$I = M_0 e \int_{0}^{\infty} \frac{k}{k_c} f(k) dk$$

which gives the output current from a spectrometer for given input spectra and critical mobilities. Since the critical mobility is a function of $M_0$, $U$ and $C$ [section 2.3, equation (8)], any of these three parameters may be varied to alter $k_c$. Driving potential $U$ is most commonly used, but NOLAN & KENNY (1952) varied the airflow rate $M_0$, while NAKATANI (1969) varied capacitance $C$ by changing the length of his collecting elec-
trode. Assuming that only one of \( M_0 \), \( U \) and \( C \) is used to alter \( k_c \), we may write equation (1) more generally as

\[
I(k_c) = g(k_c, f(k)) 
\]

\( ..........(2) \)

The spectrometer is thus a device which transforms an input spectrum function \( f(k) \) into an output current function \( I(k_c) \) using the transform \( g \), as indicated in fig. 2.41. Spectrum determination therefore requires two steps: we measure \( I \) for a range of values of \( k_c \), then we calculate \( f(k) \) using an inverse transform \( G \), where

\[
f(k) = G(k, I(k_c)) 
\]

\( ..........(3) \)

In the usual method of determining \( G \) the expression for the current is differentiated a number of times with respect to the parameter varied, to yield an expression giving the spectrum as a function of the differential. For example, when the driving potential is varied in an Integral chamber we may obtain [DOLEZALEK & OSTER (1965)]

\[
f(k') = \frac{-CU^3}{eeM_0^2} \cdot \frac{3^2I}{8U^2} 
\]

\( ..........(4) \)

Using this equation \( f(k') \) can be calculated for driving potential \( U \), where \( k' \) is the critical mobility corresponding to \( U \).

It is desirable to measure as many \((I, k_c)\) [or \((I, U)\)] pairs as possible, for two reasons. First the method is very prone to noise in the measurements since any current error will be magnified on differentiation. Second the number of values of the differential which can be calculated is of the same order as the number of pairs so that in principle any desired
mobility resolution can be obtained by taking enough readings. It may however take a considerable time to make the measurements, which conflicts with the assumption that $f(k)$ does not vary with time. In practice ten to twenty pairs are generally used, taken over a period of about twenty minutes.

The noise problem is reduced in the following new method. Assume that $f$ is a function $F$ with $m$ parameters (other than $k$),

\[ f(k) = F(k, c_1, c_2, \ldots, c_m) \]  \hspace{1cm} (5)

The spectrometer transform is known, so that for a chosen set of values of $c_i$ the currents for various $k_c$ can be calculated, since

\[ I' = g(k_c, F) \]  \hspace{1cm} (6)

The calculated currents are then compared with a set of measured ones, $I$, to obtain a residual

\[ R = \Sigma (I - I')^2 \]  \hspace{1cm} (7)

which indicates the "goodness of fit" of function $F$ to the input spectrum. These two steps are then iterated to obtain the best fit for $F$.

This method gives values of $f$ for all $k$ instead of a set of $f(k)$ for a few $k$ values, i.e. it lowers the mobility resolution while expanding the mobility range covered. This allows parameters of the spectrum (such as its mean and variance) to be obtained with improved accuracy. Chapter 5 examines the problems of choosing the function $F$ and performing the iterations.
2.5 Design of the Mobility Spectrometer

For the mobility spectrometer developed for this investigation, two parameters were initially specified. First the mobility range scanned by the spectrometer had at least to include all small ions; and second, time resolution was of greater importance than mobility resolution. This section summarises the decisions made in designing the spectrometer — details of the complete instrument are given in the following two chapters.

Flight-time methods are not well suited to continuous measurements of atmospheric ion mobilities: some form of Gerdien Chamber spectrometer is clearly appropriate. A cylindrical chamber with a full intake and divided collecting electrode was selected since it can be used as a series of first differential chambers with a common driving electrode and successively decreasing critical mobilities. This allows a number of currents corresponding to the various critical mobilities to be measured (at least in principle) simultaneously.

Either centre or outer electrode can be used for the collecting electrode: the outer was selected as allowing a simpler mechanical construction. The collecting electrode was divided into eight sections (hereafter referred to as "rings"), allowing the use of a simple electronic counter in the spectrometer controller. The choice of electrode diameters was somewhat limited by the range of suitable tubing available locally, so diameters of 4" and 1" and a length of 18" were arbitrarily chosen as giving a spectrometer of reasonable overall size. An airflow rate of about 5 litre/sec was selected, giving an
instrument resembling that of MISAKI (1960 and 1961).

Since mobility spectra are generally plotted on a logarithmic mobility scale it is useful to choose the ring lengths to give critical mobilities which are equally spaced on such a scale. Each ring has a critical mobility \( k_c \) which corresponds to the distance \( d \) from its trailing edge to the intake end of the first ring. If there are \( N \) rings whose cumulative lengths are \( d_1, d_2, ..., d_N \) numbering from the intake end, we require that

\[
\frac{k_n}{k_{n+1}} = \frac{d_{n+1}}{d_n} = \text{constant} = C
\]

for \( n = 1 \) to \( N - 1 \) ............(1)

Therefore

\[
\sum_{n=1}^{N-1} \frac{d_{n+1}}{d_n} = C^{N-1} = \frac{d_N}{d_1} = \frac{k_1}{k_N} = R
\]

so that

\[
\frac{d_{n+1}}{d_n} = N-1 \sqrt{\frac{1}{R}}
\]

Given the number of rings \( N \) and the total ring length \( (d_N) \) only \( R \), the ratio highest/lowest critical mobility, remains to be determined. Since we wish to cover the small-ion range we may assume the highest critical mobility \( (k_1) \) is about 1.0 cm\(^2\)/V.sec. A limit to the lowest critical mobility \( (k_N) \) is reached when the actual length of the shortest collect-
ing ring approaches the thickness of the ring separators. From equation (3) we see

\[ \frac{d_{n+2} - d_{n+1}}{d_{n+1} - d_n} = \frac{d_{n+1}}{d_n} = \sqrt{\frac{7}{R}} \]  

\[ \text{for } n = 1 \text{ to } 6, \text{ hence ring 2 is the shortest of rings 2 to 8.} \]

Furthermore

\[ \frac{(d_2 - d_1)/d_1}{d_1} = \sqrt{\frac{7}{R}} - 1 \]

\[ \text{so that for } R \text{ values in the range } 0 < R < 2^7, \text{ ring 2 is shorter than ring 1 and is therefore the shortest ring. The shortest ring length is thus [from (2)]} \]

\[ d_2 - d_1 = \frac{d_N}{R} \cdot (\sqrt{\frac{7}{R}} - 1) \]

1/32" sheet teflon (the thinnest available) was used for the ring separators: assuming a lower limit of 10 times the separator thickness allows us to solve equation (6), yielding an upper limit for R of about 40. An R value of 40 implies a \( k_8 \) value of about 0.02 cm\(^2\)/V.sec, but fig. 1.25 indicates that there are practically no ions with mobilities in the range 0.01 to 0.3 cm\(^2\)/V.sec, so rings 4 to 8 would collect only very small currents. Instead an R value of 5 was selected so that the spectrometer can cover the mobility range 0.2 to 1.0 cm\(^2\)/V.sec with collected currents of the same order of magnitude for all its rings.
For the design parameters chosen the maximum expected magnitude of current to a ring is approximately

\[ 5 \text{ litre/sec} \times 10^6 \text{ ions/litre} \times 1.6 \times 10^{-19} \text{ C} = 8 \text{ rings} \]

\[ = 1 \times 10^{13} \text{ Ampere} = 100 \text{ fA} \]

The cost of an electrometer with an adequate order of performance dictated the use of a single electrometer, time-shared between rings by a set of reed switches at its input. Rather than measure the current to a ring at "sample" intervals the electrometer is used to measure the charge collected on the ring during the interval since it was last sampled. The change in a ring's potential due to the charge collected on it is negligible compared to the driving potential, and this method yields a mean value of the current during the interval. Allowance must be made for electrostatic interaction between the rings as described in Chapter 4.
Air Intake

\( \frac{1}{32} \)" teflon separators

Sequencer

Ring mounting bars

Screening Plate

Electrometer

a) Elevation

b) End Plate
(Half Size)

FIG. 3.11  THE ION
Collecting Rings

Air Exhaust

Electrometer

End clamping ring

Scale 0.4'' = 1.0''

Clamp Screw

Teflon Insulator

1/8'' brass rods

Tunnel Insulators

c) Detail of Ring Mounting Bar (Actual Size)

d) Centre Electrode Mounting (Half Size)

MOBILITY SPECTROMETER
3.1 Physical Construction

The spectrometer is shown in plate 3.11, and detailed drawings of its construction are given in fig. 3.11. The centre electrode is a 1" diameter brass tube, supported by two sets of mounting rods at the exhaust end to minimise distortion of the field and airflow. The 8 outer (collecting) rings are sections of brass tube, having a 4" outside diameter and a 1/8" wall thickness. They are separated from each other by 1/32" teflon rings and are supported by four 1/16" teflon strips, mounted in brass bars.

Air is drawn into the spectrometer through a flared intake section, passes through the collecting section, and leaves via a similar flared exhaust section. The shape used for the intake and exhaust sections is that recommended by MISAKI (1960, 1961). Suction is provided by a centrifugal blower, connected to the spectrometer by about twenty feet of 3" diameter flexible tubing. A choke plate is mounted at the point of connection to the spectrometer to adjust the airflow. The air system thus approximates a constant volume sink, so that the air flow is stabilised. The airflow rate was measured by collecting the exhaust air from the blower in a large lightweight cylindrical polythene bag and measuring the volume per minute.
Outer Electrode Radius : 4.757 cm
Inner Electrode Radius : 1.269 cm
Driving Potential : 90.00 V
Air Flow Rate : 4.625 litre/sec

<table>
<thead>
<tr>
<th>Ring</th>
<th>Ring to inner electrode capacitance pF</th>
<th>Ring length cm</th>
<th>Cumulative Ring length cm</th>
<th>Critical Mobility cm²/Vsec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intake</td>
<td>1.07</td>
<td>2.56</td>
<td>2.56</td>
<td>4.40</td>
</tr>
<tr>
<td>1</td>
<td>3.83</td>
<td>9.15</td>
<td>11.71</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td>0.97</td>
<td>2.37</td>
<td>14.08</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>1.22</td>
<td>2.97</td>
<td>17.05</td>
<td>0.66</td>
</tr>
<tr>
<td>4</td>
<td>1.55</td>
<td>3.75</td>
<td>20.80</td>
<td>0.54</td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>4.71</td>
<td>25.51</td>
<td>0.44</td>
</tr>
<tr>
<td>6</td>
<td>2.46</td>
<td>5.94</td>
<td>31.45</td>
<td>0.36</td>
</tr>
<tr>
<td>7</td>
<td>3.11</td>
<td>7.47</td>
<td>38.92</td>
<td>0.29</td>
</tr>
<tr>
<td>8</td>
<td>3.95</td>
<td>9.41</td>
<td>48.33</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 3.11 Collecting System Parameters
The driving potential for the centre electrode is obtained from a 90 V dry battery. The battery and its polarity reversing relay are enclosed in a polystyrene box to minimise temperature variations in potential.

The ring lengths were selected (section 2.5) so that their critical mobilities make equal steps on a logarithmic scale, with a ratio of 1:5 between the intake and exhaust rings. The complete collecting system parameters and corresponding critical mobilities are given in table 3.11. The (ring to centre electrode) capacitances in this table were calculated from the measured ring lengths, while the capacitance from centre electrode to intake section was directly measured and its effective length calculated.

The charges collected are measured with an electrometer, the input section of which is mounted on the bottom of the spectrometer case. Each ring in turn is connected to the electrometer input by a reed relay. ERG type MA/GO/J reed switches are used, since their specified minimum insulation resistance is $10^{15}$ ohms. The switches are carried in driving coils wound on brass bobbins to shield them from noise induced by the coil driving circuitry. The eight input relays are mounted in a brass bar, with their coil leads carried in a channel cut in the side of the bar. The leads from rings to relays to electrometer are further screened by the spectrometer case.
Fig. 3.21 The Electrometer Head Unit, Showing Mounting of Feedback Components.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input impedance</td>
<td>$&gt;10^{15}$ Ω</td>
</tr>
<tr>
<td>Input offset voltage</td>
<td>$&lt;20$ mV</td>
</tr>
<tr>
<td>Sensitivity (for 1 mV output)</td>
<td>0.1 fA</td>
</tr>
<tr>
<td>Short-term drift</td>
<td>$\sim 1$ fA/hour</td>
</tr>
<tr>
<td>Noise</td>
<td>$\pm 0.5$ fA</td>
</tr>
<tr>
<td>Usable sensitivity</td>
<td>1 fA</td>
</tr>
<tr>
<td>Output voltage range</td>
<td>$\pm 10$ V</td>
</tr>
<tr>
<td>Output impedance</td>
<td>$\sim 100$ Ω</td>
</tr>
</tbody>
</table>

Table 3.21 Electrometer Performance Specifications
Fig. 3.22 Circuit Used for Electrometer Calibration.

Fig. 3.23 Input and Output Voltages for the circuit of Fig. 3.22, with a Nominal $10^{13}$ Ω Resistor for $Z_F$.  ($Z_F$ calculated from these plots is $1.15 \times 10^{13}$ Ω)
3.2 The Electrometer

A vibrating capacitor [VAN Nieë & VAN ZELST (1964)] is used as the high-impedance input section of an operational amplifier, which may be connected as an integrator to measure charge or as an amplifier to measure current. The vibrating capacitor, its driving oscillator and signal preamplifier are contained in an aluminium box, which is mounted in the spectrometer under the collecting rings. The rest of the electrometer connects to the head unit by a nine-lead cable. Feedback components for the electrometer are mounted in the head unit. These may be either a high-value resistor, or a precision (teflon dielectric) capacitor with a shorting relay. The head unit with the capacitor mounted is shown in fig. 3.21. The electrometer output voltage is punched on to paper tape by a digital data recorder. The recorder voltage range is ±1.023 V in 1 mV steps: this quantisation sets an upper limit to the usable sensitivity of the electrometer.

The electrometer can be calibrated - i.e. the value of its feedback components, $Z_f$, measured - using the arrangement shown in fig. 3.22. The capacitance between ring 4 of the spectrometer and the centre electrode, $C_i$, is used as an input impedance to the electrometer. The other rings are earthed, thus guarding ring 4 which is at the input offset potential of the electrometer. $C_i$ is calculated from the dimensions of the spectrometer, so that $Z_f$ can be determined from measurements of the input and output voltages. Fig. 3.23 shows a sample record of these voltages, with a resistor for $Z_f$. A computer program was developed to perform these calculations, yielding values of the feedback components from the paper tape record.
a) Self Capacitance Circuit \(- c_{ii}\).

b) Induction Coefficient Circuit \(- c_{ij}\).

Fig. 3.31 Circuits Used in Measuring the Spectrometer Capacitances.
For use in the spectrometer the electrometer was connected as an integrator, with a 1 pF feedback capacitor: performance specifications for this configuration are listed in table 3.21. Further details of the electrometer circuit are given in Appendix 1.

3.3 Measurement of Spectrometer Capacitances

The relation between the charges on the spectrometer rings and their potentials is

$$q_i = C_{ij} \phi_j$$

where $q_i$ is the charge on ring $i$, $\phi_i$ is the potential of ring $i$, and $C$ is the capacitance matrix for the spectrometer.

The elements of $C$, $c_{ij}$ are either "coefficients of self capacitance" (capacitance of ring to earth) if $i=j$, or "coefficients of induction" (charge on ring $i$ / potential on ring $j$) if $i \neq j$ [RAMO, WHINERAY & VAN DZER (1965)]. In these definitions all rings other than $i$ and $j$ are assumed to be earthed.

All the spectrometer capacitances were measured, using the circuits of fig. 3.31a for self capacitance and fig. 3.31b for induction coefficients. The capacitance of the electrometer input lead, $C_L$, was 14.63 pF, so this value was subtracted from the observed self-capacitance values (see fig. 3.31a). The capacitances of the reed switches, $C_{si}$, were also measured.
<table>
<thead>
<tr>
<th>101.0</th>
<th>-24.9</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>-24.9</td>
<td>64.6</td>
<td>-25.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>-25.3</td>
<td>67.5</td>
<td>-24.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-24.7</td>
<td>72.8</td>
<td>-25.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-25.2</td>
<td>79.1</td>
<td>-25.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-25.5</td>
<td>86.7</td>
<td>-24.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-24.6</td>
<td>92.7</td>
<td>-25.0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-25.0</td>
<td>97.7</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.31 The Spectrometer Capacitance Matrix

All values are in pF, with a standard deviation of 1% for the non-zero capacitances.
Their values were all in the range 0.09 to 0.22 pF, which is negligible compared to the self capacitance of a ring or the capacitance between two adjacent ones. The magnitudes of the induction coefficients between any two non-adjacent rings were too small to be accurately measured, being of the same order as $C_{81}$. Table 3.31 shows the complete $C$ matrix. Capacitances on its leading, first upper, and first lower diagonals are accurate to within 1%, while all other capacitances are negligible.

The elements in the first upper and lower diagonals are the capacitances between adjacent rings. All are negative, since a negative potential on a ring induces a positive charge on its neighbours. They are all about 25 pF in magnitude: this is the value of a parallel plate capacitor whose plate area is that of the ring end faces with a $\frac{1}{32}$" teflon dielectric.

The self capacitances of the rings (leading diagonal elements) are of course much greater than those between the rings and centre electrode (given in table 3.11). They include a constant value of twice the inter-ring capacitance, capacitance between the rings and their four lateral supports, and the centre electrode capacitance. The latter two components depend on the ring length, monotonically increasing from $C_{22}$ to $C_{88}$, with $C_{11}$ slightly greater than $C_{88}$. 
Fig 3.41 Typical Ion Currents Collected on Ring 2.

Currents for 0 V, +80 V, -80 V driving potential plotted as "1", "2", "3" respectively.

Vertical bars indicate ±1 standard deviation for each 25 second interval.

Horizontal lines indicate mean current for whole record.

Fig. 3.51 Electrometer "Integrator" Test Circuit.
3.4 Ion currents to a Single Ring

The spectrometer was set up by an open window and a series of records made of the current collected on a single ring (with the other rings earthed).

Current values were recorded every 2.5 sec for 15 minutes with the (centre electrode) driving potential either positive, negative or zero.

Fig. 3.41 shows a sample record; the bars show the standard deviation of the current over 25 sec periods. Several features of these records stand out:

a) The mean positive current is always greater than the mean negative current, with both of the order of 5 fA.

b) The negative current shows wider fluctuations than the positive.

c) Some current is still observed when the driving potential is zero. The fluctuations so produced are less than for non-zero driving potentials, and the long-term mean current is stable. This means that the mean over a suitably long period, several minutes say, must be used for a measurement of zero offset. Currents observed with zero driving potential are discussed in sections 4.4 and 4.5.

These measurements did not involve any ring switching -
Fig. 3.52 Voltage Distributions Obtained using the circuit of Fig. 3.51.

Electrometer Output Voltages for 1 pF and 2 × 1 pF feedback capacitors plotted as "1" and "2".

Total number of points in each distribution = 1547.
the next step was to set the electrometer up as an integrator, and
test its input switching system.

3.5 Charge Separation by Reed Switches

To check the performance of the electrometer as an integrator, the circuit of fig. 3.51 was used. The reset switch is a reed relay, the same as those used for input switching. This circuit gave a random electrometer output voltage of the order of 20 mV (with the electrometer input on open circuit) immediately the reset switch was opened. Statistics of this voltage were gathered by closing the reset switch for one second in every five, and recording the voltage with it open. Some 1500 measurements were made using a 1 pF feedback capacitor. The experiment was then repeated using two 1 pF capacitors in series.

The results indicate that a charge is generated by the reed switch opening, which then appears across the capacitor giving the measured output voltage. If the charge distribution is stationary (i.e. time invariant) then both the means and standard deviations of the voltage distributions will be inversely proportional to the feedback capacitance.

The two observed voltage distributions are plotted in fig. 3.52, using the symbols "1" and "2" for the 1 pF and 2 x 1 pF cases respectively. Their means and standard deviations are

1 pF capacitor : 23 ± 33 mV
2x1 pF capacitor : 73 ± 115 mV
ratio of means : 3.2
ratio of standard devs : 3.5

These ratios are not 2.0 as might be expected, since 1 pF is the capacitor value when measured on a Q meter - in circuit the actual value will depend on strays. In use this value is measured by the procedure of section 3.3.

The above ratios are in reasonable agreement, hence the reed switches must be regarded as generating a random charge of about 20 fC when opened. Since this is of the same order as the charges to be measured, the electrometer output must be measured before and after each switch opening so that the "switch charges" can be allowed for.

3.6 Sequecing of the Spectrometer Relays

When the charge on a spectrometer ring is sampled three voltages must be measured. They are

\[ V_1 = \text{voltage after reset relay opens, no ring relay closed}, \]
\[ V_2 = \text{voltage after ring relay closed}, \]
\[ V_3 = \text{voltage after ring relay opened again}. \]

From these

\[ V_2-V_1 \text{ gives the charge removed from the ring,} \]
and \[ V_2-V_3 \text{ gives the charge returned to the ring from its relay.} \]
Fig. 3.61 Timing Diagram for the Sampling of a Single Ring.

Fig. 3.62 Timing Diagram for a Complete Spectrometer Scan.
A detailed description of the digital data recorder used is given by JOHNS (1972). The recorder uses a basic time interval of 5 sec, divided into 100 50 mS "cycles" numbered from 0 to 99. During each such interval any of the input data channels may be sampled (and its voltage punched on paper tape) in either one or two of the hundred cycles, for example channel 8 can be sampled only in cycles 24 and 74. The recorder was easily modified to provide a pulse on scans 16 and 66: using this pulse to initiate the sampling of a ring it was possible to record the three voltages described above on recorder channels 8, 12 and 15, at a maximum rate of one ring every 2.5 sec.

Fig. 3.61 gives a timing diagram for the sampling of a single ring. The initiating pulse was also used to step a decimal counter, the state of which selects the ring to be sampled. Of the ten usable states, states one to eight select rings one to eight, leaving two states for which no input relay is selected. State nine is unused, so its three voltages are the same (provided the electrometer system has no input leakage - this is useful as a check on the electrometer). For state zero the reset relay is not opened; since the reset resistor (≈10 MΩ) is much less than the electrometer input impedance (≈10^{15} Ω) its output is effectively short circuit to its input. State zero thus allows the electrometer's input offset potential to be recorded.

The complete spectrometer scan is given in fig. 3.62, together with an example of the corresponding electrometer output. Note that the output for state zero is always constant - this is used to check synchronization of the recorded output.
A control unit to produce all the required signals was constructed, using an integrated circuit decade counter, a diode matrix to decode its output, three timing univibrators, and a set of relay drivers. The complete unit can be mounted in the spectrometer next to the electrometer, and it requires only one control signal line (from the recorder). The control unit's circuit is given in appendix 1.

3.7 Site of the Experiments

The spectrometer was installed in a window overlooking the Physics Department roof. Plate 3.71 (frontispiece) gives a general view of the site with the spectrometer location arrowed. At the near end of the building are the instruments of the department's Atmospheric Electricity Station (AES), which measure the vertical electric field, positive and negative conductivity, and air-earth current. Of these the conductivity apparatus is the large raised box, the current antenna is the cylindrical cage on the left, and the field mill is the small square box suspended at the left corner of the raised central part of the roof. These instruments are connected to the digital recorder, which is installed in a control room at the AES end of the building.

A more detailed view of the spectrometer installation is given in plate 3.72. The top-hinged window is propped wide open to prevent rain from entering, and the spectrometer intake is screened by a sheet of stout cardboard to prevent the egress of draughts from inside. The intake is at a height of 60 cm from the roof. The adjacent area of roof is well shielded.
from wind by the super-structure of the physics building, and by adjacent buildings, so that air turbulence entering the intake was not a problem.

The University buildings are situated on a ridge, with the City of Auckland - the port, railway yards, and central business district - about \frac{1}{2} mile distant. Atmospheric conditions are hence those of an industrialized area. Probably the most significant contributor to atmospheric pollution (of both ions and nuclei) at the site is the exhaust from motor vehicles, though a heavy industrial area is some five miles south. Motor vehicle pollution should show a diurnal variation since there is little traffic between about 2300 and 0600 hours.

All the experiments described were performed here during the period May 1970 to July 1971.

3.8 Preliminary long-term Recording

A preliminary recording of five day's duration at the maximum recording rate was made, using positive and negative driving potential in successive quarter hours. Zero driving potential was used for half an hour in every twelve to check for zero drifts.

The electrometer was calibrated before and after the run. The two results for the ratio of input and feedback capacitances were:

before : 0.2588 ± 0.0084
Fig. 3.81  Sample of Current to Ring 1 from a Preliminary 5-day Experimental Run, with Weather Conditions Indicated.
after : 0.2578 ± 0.0059

The electrometer calibration is thus extremely stable, reflecting the rigid construction of the spectrometer and the feedback components.

The measured ring charges were converted to effective ring currents (as described in chapter 4), and their means for each quarter hour plotted. A section of the plot is shown in fig. 3.61, which gives the currents to ring 1 for 24 hours and the corresponding weather conditions. Plots for the other rings are similar.

The most obvious feature of these plots is that although the positive and negative ion currents lie on opposite sides of a zero value, this zero value drifts with time. The drift is most marked when rain begins, which suggests it is due to changes in the spectrometer insulation caused by rapid changes of humidity. No significant cross-correlation could however be detected between the currents from any pair of rings, ruling out the possibility of increased leakage between the rings. Leakage currents from the rings are further considered in section 4.4.

The results obtained in this way are useless because their zero value is not known with any degree of certainty. However, they demonstrate the need for much more frequent measurement of the zeros. From fig. 3.61 we see that a zero is required at least once an hour, preferably more often.
Fig. 3.91 Sequence of Events Used for Mobility Spectrum Observations.

Fig. 3.92 Spectrometer Driving Potential Supply.
3.9 Spectrometer Sequencing for Experiments

After the experiments described in section 3.8, an improved sequencing scheme for the spectrometer was devised; this is shown in fig. 3.91.

A measuring cycle takes 30 minutes, and is divided into 12 steps. Spectrometer driving potential is applied by the circuit of fig. 3.92. The control relay is energised from step 5 up to step 12 (i.e. back to step 0), while the potential's sign is determined by the reversing relay. This relay is part of a relay flip-flop, which is toggled at step 1 to set the sign for the present cycle. The recorder is turned on at steps 1 and 5, and off at steps 5 and 0; the gaps in recording allow the electrometer to clear the displacement charge produced by the change of driving potential.

This cycle of events is controlled by a large stepping switch, driven by a pulse from the data recorder every 2½ minutes. Hence the system will automatically record 15 minutes each of positive and negative ion currents every hour, interlaced with 10 minute zero records. A time between rings of 2.5 sec (the minimum possible) is used, allowing some 35 complete 25 sec spectrometer scans (see fig. 3.62) for each non-zero driving potential.

All experiments except those concerning point discharge were made using this cycle, however the system was easily adapted for point discharge investigation (see section 6.6).
Fig. 4.11 Spectrometer Output Voltage for Various Driving Potentials.

Scales: Vertical = 50 $\text{fC}$ / division, Horizontal = 1 sec / division.
CHAPTER 4

DATA REDUCTION, CURRENTS TO THE SPECTROMETER RINGS

4.1 Fundamentals

The experimental data punched on paper tape by the spectrometer is comprised of consecutive blocks of thirty voltages corresponding to the scans of the ten spectrometer states described in section 3.6. A chart recorder was connected in parallel with the digital recorder, allowing the spectrometer's operation to be monitored. Some samples of the charts produced with positive, negative, and zero driving potentials are given in fig. 4.11.

Every 2.5 seconds the electrometer reset relay is opened, giving an indicated charge (on fig. 4.11) of about -25 fC. Every tenth interval shows no such charge: this corresponds to spectrometer state zero, in which the electrometer remains reset. When a collecting ring is connected to the electrometer input its charge is transferred, giving a step in electrometer output. For non-zero driving potentials the sign of this step is the same as that of the driving potential, and its magnitude tends to vary with the ring length (being greatest for ring one, least for ring two, and rising for rings two toward eight). The current collected by a ring is approximately equal to the magnitude of the indicated charge divided by the collection time of 25 sec, but corrections (described below) must be made for the effect of charge on adjacent rings. When the ring is disconnected the ring relay produces a charge like
that produced by the electrometer reset relay. Since there is no ring connected during spectrometer state nine, the output for this state is steady after the reset relay opens.

For later computation of mobility spectra we require data in the form of currents to the spectrometer rings (i.e. "ring currents"). Several computer programs were developed to read raw data from paper tape and reduce it to this form. The steps involved in this reduction are discussed fully in sections 4.4 to 4.7; briefly these are

a) Check the synchronisation of the spectrometer scans.
b) Calculate the input currents from the observed charges.
c) Remove the measured zero offsets from the currents to give the ring currents.
d) Calculate the mean ring currents for specified time intervals.

The spectrometer can rapidly produce a prodigious quantity of raw data — for example the five days continuous recording of section 3.8 yielded some 432,000 measured voltages, punched into ten 750 ft reels of paper tape. Such large amounts of data require an appreciable time to process. The University computer was an IBM 1130 model 3C, with an 1134 paper tape reader whose maximum speed is only sixty characters per second. It took about 25 minutes merely to read one reel of tape, and another 15 minutes for its subsequent processing.

The computer was operated on a "partial open-shop" basis where intending users must make bookings for any run of over thirty minutes. Usage was such that an individual user could
only obtain one such booking every three weeks, so that the
five-day run took some three months to process. To minimize
the time between performing experiments and completing their
data reduction the duration of experiments was kept below
about twenty-four hours. This allowed a reasonable rate of
experimental progress while retaining enough data for diurnal
variations to be investigated.

4.2 Theory of Spectrometer Ring Interactions

In section 3.3 we discussed the spectrometer capacitance
matrix C, such that

\[ q = C \phi \] ...........(1)

We may invert C to obtain the elastance matrix S such that

\[ \phi = S q \] ...........(2)

Equation (2) describes the spectrometer with all rings free,
having charges \( q_i \) and resulting potentials \( \phi_i \). If we connect
one ring, say ring \( n \), to the electrometer input (whose input
offset potential is \( \psi \)) the system can then be described by a
new set of charges \( q_i' \) and potentials \( \phi_i' \).

Since all rings but \( n \) are isolated

\[ q_i = q_i' \text{ for } i \neq n \] 
and further

\[ \phi_n' = \psi \] ...........(3)
Now for ring $n$, (2) gives

$$\phi_n = \sum_{i=1}^{g} S_{ni} q_i$$

and

$$\phi_n' = \sum_{i=1}^{g} S_{ni} q_i'$$

Substituting from (3) we see

$$\psi = \phi_n - S_{nn} q_n + S_{nn} q_n'$$

so that

$$q_n - q_n' = \sum_{i=1}^{g} \frac{S_{ni} q_i - \psi}{S_{nn}}$$

In equation (7) $q_n'$ is the charge left on the ring after sampling, while $q_n - q_n'$ is the charge transferred to the electrometer when an input relay is closed, i.e. the "observed" charge. Two special cases of (7) are of interest: when $\psi = 0$ (no input offset), and either

a) $q_i = 0$ for every $i$ except $n$. In this case $q_n - q_n' = q_n$ and no charge remains on the ring.

or

b) $C$ is diagonal, i.e. there is no interaction between the rings. Here $S(=C^{-1})$ is also diagonal, so again no charge remains.
Variables:

NG: state of the spectrometer
PI(8): currents to each of rings 1 to 8 (i.e., charge removed each sample interval)
RQ(8): charges on rings 1 to 8
\( q_n' \): charge remaining on ring NG after sampling
CR: charge removed from ring NG

Fig. 4.31 Flowchart of Basic Spectrometer Subroutine, SRING.

Fig. 4.41 Test for a "Reset" Spectrometer Sample.
We may rewrite equation (7) to give \( q_n' \) explicitly:

\[
q_n' = \frac{\psi}{\text{S}n} - \sum_{i=1}^{n-1} \frac{S_{ni}}{\text{S}n} q_i - \sum_{i=n+1}^{n} \frac{S_{ni}}{\text{S}n} q_i \quad \ldots \ldots \quad (8)
\]

where the first sum is zero if \( n=1 \) and the second is zero if \( n=3 \).

4.3 Computer Model of Spectrometer Ring System

A computer model was developed to investigate the relation of observed charge to ring current. This consists of two parts - a subroutine named SRING which represents the ring system, and a program which supplies SRING with input currents.

A flowchart of SRING is given in fig. 4.31. The rings are represented by the array RQ which gives the charges on them, while the charge per sample interval (i.e. the current) reaching each ring is given by array PI and the variable NG indicates the state of the spectrometer (and hence the ring to be sampled). When SRING is called it steps to the next state by incrementing NG and adds the charge for that interval to the rings. If the state does not correspond to a ring no further action is required, except that when NG exceeds nine it must be reset to state zero. Otherwise, the charge left on the ring, \( q_n' \), is calculated using equation (8) of section 4.2, the charge removed is calculated, and the ring's charge is set to \( q_n' \). Finally the charge removed is scaled to give the calculated voltage at the electrometer output.
Fig. 4.32  Spectrometer Response to Triangular Driving Potential.
SRING thus gives the charge removed from "the next" ring for a specified set of ring currents, hence it is a model of the spectrometer sampling "the next" ring. The program using SRING calls it ten times to scan the rings, then prints the charges removed from the rings for that scan. The program is easily modified to provide any desired ring currents, and to allow the effect of various alterations to the input system to be studied. As an example of the use of the model we will calculate the charges obtained for two known voltage signals which are used for the driving potential, so that the ring currents are just the ring capacitances multiplied by the rate of change of driving potential.

Consider first the assymmetric triangular waveform shown in fig. 4.32c. The program calculates the ring currents for positive and negative slopes of the driving waveform then calls SRING repeatedly, using the positive currents for the first 92 seconds, then the negative ones for the remaining 53 seconds of each successive 145 second period. The calculated removed charges are shown in fig. 4.32a, and may be compared with those measured by the actual spectrometer in fig. 4.32b. Note that the spectrometer takes about two scan periods to reflect the change in ring currents - for other driving waveforms this delay can be even longer, as demonstrated below.

The second waveform is a 90 V negative step, shown in fig. 4.33c. This waveform is applied to the spectrometer whenever the driving potential is changed during an experiment, so we are especially interested in the time required for the resulting charges to be completely removed. Here the program
Fig. 4.33 Spectrometer Response to Negative Step Driving Potential.

- **a)** Calculated.
- **b)** Observed.
- **c)** Input Potential.
initially puts a charge on each ring of the ring capacitance times the magnitude of the voltage step, then calls SRING repeatedly with zero currents to all rings. Ideally the electrometer could remove any amount of charge at a sample, but its output voltage is limited to ±15 V; SRING was therefore modified for this program to remove a maximum charge corresponding to this voltage. Figs. 4.33a and b show the calculated and observed charges - we see that all the charges are well within electrometer range after six sampling scans, and are negligible after about nine scans.

The calculated and observed charges show good agreement, particularly for the triangular case. Exact numerical agreement was of course unlikely as we have not allowed for the charges returned to the rings by their reed switches opening (see section 3.5). For the step driving potential agreement is less likely, since when the electrometer output voltage reaches its maximum value feedback is lost and the electrometer input need not necessarily remain at earth potential.

4.4 Sync Checking, Calculation of Input Currents

Two computer programs (GMS10 and GMS11) were developed to check the synchronisation of the spectrometer output and calculate the measured input currents. These accept spectrometer data as a serial input file from the digital recorder, and produce an output file which is effectively a matrix with eight columns, one for each ring. The operations performed and the algorithms used are described below.
Fig. 4.42 Flowchart of GMS11 Spectrometer Model Subroutine.
GMS10 begins by reading in all the data for a recorded block - this will be about 240 rows of 10 samples for a zero-driving-potential block, and about 360 rows for other blocks (see sections 3.6 and 3.9 for sequencing details). It then prints the start and finish times for the block. The next step is to find the first sample corresponding to state 0 of a scan, during which the electrometer remained reset. Fig. 4.41 illustrates the test for a reset sample: the sample is a reset one if its mean data value (which will be the electrometer offset) is within 30 mV of zero and all three data values are within 4 mV of each other. Synchronisation is found when two reset samples occur ten samples apart, then the rest of the block is checked to see that every tenth sample is a reset one. One further check is made - the block is scanned for reset samples other than those for state 0. A high incidence of such rows indicates a failure of the spectrometer sequencer.

GMS11 uses a spectrometer model very similar to that of section 4.3 to calculate the input currents. A flowchart of this is shown in fig. 4.42. Each sample yields two charges; the charge removed from the ring, CR, and the charge put back by the input relay, CPB. The model calculates CHRGED, the charge deposited on the ring since it was last sampled. CR plus the charge left on the ring, \( q_n' \), is the charge on the ring before sampling. CHRGED is then \( q_n \) minus the charge on the ring immediately after it was last sampled, LQ. Finally LQ and RQ (the charge on the ring) are reset, and PI (the current to the ring) updated. The calculation of \( q_n' \) thus uses the most recent estimates of PI at all times.
<table>
<thead>
<tr>
<th>Zero Blocks (zero driving potential)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Means:</strong></td>
</tr>
<tr>
<td>Ring 1</td>
</tr>
<tr>
<td>Uncorrected</td>
</tr>
<tr>
<td>Corrected</td>
</tr>
<tr>
<td>% change</td>
</tr>
</tbody>
</table>

**Standard deviations:**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected</td>
<td>0.39</td>
<td>0.28</td>
</tr>
<tr>
<td>Corrected</td>
<td>1.93</td>
<td>0.88</td>
</tr>
<tr>
<td>% change</td>
<td>17.99</td>
<td>252.51</td>
</tr>
<tr>
<td>(noise factor)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data Blocks (+ 90 V driving potential)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Means:</strong></td>
</tr>
<tr>
<td>Ring 1</td>
</tr>
<tr>
<td>Uncorrected</td>
</tr>
<tr>
<td>Corrected</td>
</tr>
<tr>
<td>% change</td>
</tr>
</tbody>
</table>

**Standard deviations:**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected</td>
<td>1.80</td>
<td>0.31</td>
</tr>
<tr>
<td>Corrected</td>
<td>2.19</td>
<td>0.64</td>
</tr>
<tr>
<td>% change</td>
<td>1.16</td>
<td>4.10</td>
</tr>
<tr>
<td>(noise factor)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.41 Typical Output Statistics from Program GMS11
Data from blocks 17 and 16 of experiment 112
The first scan of input data to GMS11 is used to initialize the spectrometer model variables: for ring I, PI(I) is set to one tenth of CR, RQ(I) to \((10-I)*PI(I)\), and LQ(I) to CPB. For the second scan the model is used to update the variables, but to allow the system to settle no output row is written. Following scans use the model normally, yielding the input currents and updating the electrometer input offset voltage OFST, so that each scan yields eight current values, one for each ring. These values are written to a row of the output file.

Since \(q_n'\) depends on the PI values (which are used in calculating RQ) we must assume that the currents do not change significantly over one spectrometer scan. As a performance check GMS11 calculates, for each block, the mean and standard deviation of:

- a) The uncorrected currents, QR
- b) The corrected currents, CHRGE
- c) The percentage change in current when corrected, 
  \[
  100 \times \frac{(QR - CHRGE)}{CHRGE}
  \]

If the currents remained constant an equilibrium situation would quickly be reached as demonstrated in section 4.3, in which case a) and b) would be equal, with c) zero. Normally however the currents vary with time, so that a) and b) differ. Here the mean of c) gives the magnitude of the corrections applied, while its standard deviation gives the range of these magnitudes. The standard deviation of c), which we will call the block's "noise factor", thus gives an indication of the reliability of a data block - high values correspond to a
Fig. 4.51  Sample of Observed Normal Ring Currents.

Data from blocks (13) to (17) of experiment 112:

Currents to rings 1, 2, 6, 8 plotted as "1", "2", "3", "4".
situation where the currents change rapidly and often, low values to one where changes are slow and seldom.

Table 4.41 gives some typical values of these statistics for blocks obtained with zero and non-zero driving potentials, i.e. for "zero" and "data" blocks. JOHNS (1972) found that although the mean current to a ring over a period of ten minutes with zero driving potential is substantially zero, the current at any instant may be of either sign and may vary rapidly in magnitude. This is reflected in the high values of noise factor for zero blocks, which are in the range 0 to 300. For data blocks mean currents are in the range 10 to 80 fA, while noise factors range from 0 to 6.

4.5 Leakage Current from the Rings

Fig. 4.51 shows a one-hour section of sample output from CMS11, the spectrometer data input program. Sections 1, 3 and 5 are "zero" blocks, while sections 2 and 4 are "data" blocks for negative and positive driving potential. We will call currents observed in the zero blocks "leakage currents"; fig. 4.51 shows that they can remain substantially constant (drift of less than 2 fA over the hour shown) which is reassuring after the results of the long-term experiment described in section 3.8. Means of the leakage currents over complete experimental runs (of between 5 and 24 hours duration) are given in Table 4.51.

When the driving potential is zero there is no way in which charges can reach the rings from the airflow through
<table>
<thead>
<tr>
<th>Experiment</th>
<th>leakage current fA to ring:</th>
<th>Electro- meter Input Offset mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>5.47  1.23 -4.68  6.88  2.21  3.15  3.76  7.22</td>
<td>-5</td>
</tr>
<tr>
<td>115</td>
<td>5.76  0.69 -1.87  3.82 -0.73  3.11  3.25  5.03</td>
<td>+25</td>
</tr>
<tr>
<td>121</td>
<td>3.32  1.14  0.02  6.79  16.66 -9.65  3.89  5.12</td>
<td>-5</td>
</tr>
<tr>
<td>137</td>
<td>3.47  12.47 -6.93  17.37 -14.64  2.98  5.62  8.65</td>
<td>+5</td>
</tr>
</tbody>
</table>

Table 4.51 Mean leakage Currents to Rings for Complete Experimental Runs

\[
\begin{align*}
|m_{11} - m_{12}| & > |m_{12} - m_{13}| \\
|m_{31} - m_{32}| & > |m_{32} - m_{33}|
\end{align*}
\]

- \(m_{11} - m_{12}\) and \(m_{31} - m_{32}\): opposite signs
- \(m_{11} - m_{12}\) and \(m_{12} - m_{13}\): same sign
- \(m_{31} - m_{32}\) and \(m_{32} - m_{33}\): same sign

Table 4.71 Conditions for a data block to be "open-ring"

(symbols refer to fig. 4.71c)
them. The existence of leakage currents therefore requires finite leakage resistances between rings and from rings to earth, and a source of potential at the rings.

The leakage resistances were initially measured using a Keithly model 602 electrometer; all were of the order of $10^{14}$ ohm. During later experiments a Keithly model 500 megohmmeter was used to check these leakage resistances. These remained better than $10^{13}$ ohm, the upper limit of the megohmmeter. For a maximum ring current of 100 fA to the ring with the lowest capacitance (ring 2) the potential of the ring after 25 sec is only about 40 mV. A leakage resistance of $10^{14}$ ohm would reduce this by about 0.5 percent, so the assumption of negligible resistance effects in the theory of section 4.2 is indeed justified.

One possible source of ring potential is the electrometer, since after a sample the ring is left at the electrometer input offset potential which may be as high as 25 mV. The ring then discharges through its leakage resistance, requiring charge from the electrometer to restore its potential when it is next sampled. Such leakage currents would have magnitudes of about 0.25 fA and the same sign as the electrometer input offset. Table 4.51 shows that the leakage currents are at least an order of magnitude too large, while their signs show no correlation with the electrometer offset.

The remaining source of potential is a contact potential. For leakage currents of the order of 5 fA this would need to be about 500 mV; a contact potential between adjacent rings could
produce pairs of currents such as those underlined on table 4.51. Furthermore humid conditions, by aiding the formation of water films on the insulators, would vary these potentials giving the large variations in leakage current observed in section 3.8.

The leakage currents may therefore be regarded as slowly changing currents independent of the ion currents to the rings. Hence they may be subtracted from the currents observed during a data block, giving the "true" ring currents. To allow for observed drifts leakage current values interpolated between the means of adjoining zero blocks must be subtracted from each row of the data block.

Should the leakage resistance from a ring to earth drop below $10^{-14}$ ohm the leakage current for that ring will increase; high leakage current means for a complete experimental run indicate a decreased reliability of the final current values. Lowered leakage resistances between rings, on the other hand, cannot be detected in this way. In such a case the only observable effect will be an increase in the apparent current to one ring at the expense of that to its neighbour.

4.6 The Effect of an Open Reed Switch

Results for some of the recording sessions showed that the reed switch connected to ring 3 had been open circuit for long periods of time. Obviously this meant that no current should have been detected from ring 3, but the currents from the adjacent rings, 2 and 4, were also highly anomalous.
Fig. 4.61 Sample of Observed Ring Currents with Reed Switch 3 Permanently Open.

Data from blocks (9) to (13) of experiment 121:
Currents to rings 2, 3, 4 plotted as "1", "2", "3".
Fig. 4.61 shows a one-hour section of this kind of record; compare this with the normal behaviour in fig. 4.51. At the beginning of each block of fig. 4.61 the current to ring 4 is high (of the order of 100 fA) and of the same sign as the change in driving potential, but during the block it decreases exponentially, with a time constant of about 7 scans, i.e. 175 sec. The current to ring 2 is of lesser magnitude, has opposite sign, and rises more slowly at the start of the block.

Consider the effect of changing the driving potential from 0 to +90 V at the transition between blocks 3 and 4. During the following few scans positive displaced charges are removed from the rings (as demonstrated in section 4.3). Since ring 3 is isolated its charge can only be removed by a leakage resistance from it; its capacitance to earth is 67.5 pF, which indicates a resistance value of $2.6 \times 10^{12}$ ohm. For the case of fig. 4.61 the leakage is from ring 3 to ring 4, so that during every scan positive charge is transferred to ring 4 giving the observed "discharging" current. Again during the first few scans ring 2 gains an excess negative charge, induced from earth by that on ring 3. As the charge on ring 3 decreases ring 2 relinquishes its (negative) charge to the electrometer, producing the observed negative current.

The currents to rings 2 and 4 (and zero current to ring 3) are recorded on paper tape and processed by the spectrometer input programs of section 4.4 to give calculated input currents like those of fig. 4.61. These programs assume no leakage between rings, so their output shows a current to ring 3 which reflects the movement of charges between this ring and its neighbours.
a) Observed: Block (3) from Fig. 4.61.

Fig. 4.62 Spectrometer Output Following a +90 V step in Driving Potential with Ring 3 Isolated.

b) Calculated: $2 \times 10^{12}$ ohm leakage between rings 3 and 4.
Records like that of fig. 4.61 thus arise from a) an open circuit reed switch, and b) a leakage resistance of the order of $10^{12}$ ohm to an adjacent ring; this is the only case where such a leakage can be detected from the calculated input currents. The effect can be simulated using the computer model of the spectrometer described in section 4.3 to generate data for the spectrometer input program. Fig. 4.62 shows one cycle of calculated input currents for a $\pm 90$ V change in driving potential, with a resistance of $2 \times 10^{12}$ ohm between rings 3 and 4. Block 3 of fig. 4.61 is given for comparison; it shows good agreement with the calculated currents.

Since the "open" ring's charge is removed after some 14 to 21 scans, and each block contains 22 (zero blocks) or 33 scans, the mean current for the last third of a block can be used as an estimate of the mean current for that block. This approach is used in the "block means" program of section 4.7 to estimate the mean currents to rings adjacent to an isolated one.

4.7 Removal of Zero Offsets, Calculation of Block Means

Before the calculated input currents in each data block can be used as ring currents for spectrum determination their leakage currents must be removed from them. The method employed is indicated in fig. 4.71a.

Mean currents are calculated for each of the zero blocks adjoining a data block, and a line joining them is used to obtain zero values at times within the block, $I_n'$. These zero values are then subtracted from their corresponding data values
c) Means of each third of adjacent "zero" blocks calculated by CMS21.
(symbols for the means are referenced in table 4.71)

Fig. 4.71 Algorithms Used to Remove Zero Offsets from Data Blocks.
giving the effective input ring currents, \( I_n \) (hereafter referred to as simply "ring currents").

If there are no "open-ring" data blocks (i.e. those during which a reed switch was open circuit) in a complete recording session the above procedure can always be used, allowing mean ring currents to be calculated for any number of scans up to the number of scans in a data block. For open-ring blocks however, only an estimated block mean can be calculated using the mean of the last third of each block as indicated in fig. 4.71b.

Program GMS21 was written to calculate block means for complete recording sessions. GMS21 selects which of the above algorithms to use as follows: The means of each third of the adjacent zero blocks are calculated. The block is then considered to be open-ring only if all the conditions in table 4.71 are satisfied.

GMS21 also checks that the sign of the ring currents alternates in successive data blocks, and calculates for each ring

a) The mean leakage current for the recording session
b) The number of open-ring data blocks
c) The number of data blocks having errors in sign

Table 4.51 gives some examples of mean leakage currents from GMS21.
<table>
<thead>
<tr>
<th>Block number</th>
<th>Driving potential Sign</th>
<th>Max Noise Factor</th>
<th>Ring number</th>
<th>Min Noise Factor</th>
<th>Ring number</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-</td>
<td>492.0</td>
<td>1</td>
<td>20.8</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>563.9</td>
<td>3</td>
<td>2.9</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>75.0</td>
<td>8</td>
<td>5.0</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>8.5</td>
<td>2</td>
<td>0.7</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>10.0</td>
<td>4</td>
<td>1.3</td>
<td>8</td>
</tr>
<tr>
<td>12</td>
<td>+</td>
<td>6.0</td>
<td>5</td>
<td>0.6</td>
<td>8</td>
</tr>
<tr>
<td>14</td>
<td>-</td>
<td>4.2</td>
<td>6</td>
<td>1.0</td>
<td>7</td>
</tr>
<tr>
<td>16</td>
<td>+</td>
<td>4.1</td>
<td>2</td>
<td>0.3</td>
<td>8</td>
</tr>
<tr>
<td>18</td>
<td>-</td>
<td>215.5</td>
<td>3</td>
<td>3.7</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>+</td>
<td>7.3</td>
<td>2</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>9.3</td>
<td>6</td>
<td>1.2</td>
<td>7</td>
</tr>
<tr>
<td>24</td>
<td>+</td>
<td>2.8</td>
<td>3</td>
<td>0.5</td>
<td>8</td>
</tr>
<tr>
<td>26</td>
<td>-</td>
<td>4.8</td>
<td>6</td>
<td>1.3</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4.81 Max and Min Noise factors for Data Blocks from Experiment 112
4.8 Discussion of the Observed Ring Currents

Fig. 4.81 is a plot of computed ring currents for a period of some 6½ hours. It is the output from the GMS11 computer program (section 4.4) for the data of experiment 112 (section 6.1). Symbols "1" to "8" are used to plot the current to each of rings 1 to 8, while the "8" symbol indicates a point where more than four of the ring currents have the same value. Blocks 13 to 17 are also shown on a larger scale in fig. 4.51.

Maximum and minimum noise factors (section 4.4) for the data blocks of fig. 4.81 are listed in table 4.81. Consider now the latter part of the spectrometer scan. After ring seven has been sampled it has only 25 seconds to collect a charge before ring eight is sampled. On the other side of ring eight is the spectrometer case which is at earth potential. There is thus little change in the charge on the conductors nearest ring eight, hence we may expect the computed corrections to its current (and therefore its noise factor) to be smaller than those for the other rings. Table 4.81 indicates, however, that the ring with lowest noise factor in this experiment was always either eight or seven, so the above explanation is inadequate. Another situation giving low noise factors occurs when the ring currents are only changing very slowly. Since the currents for the higher numbered rings are made up of ions of lower mobility we might infer from table 4.81 that changes in the spectrum of large ions are less rapid than those in the small ion spectrum. Unfortunately the mobility spectra for experiment 112 computed in section 6.2 do not show such a difference. Again, since ring eight collects the highest proportion of low-mobility ions its current should be the most stable. If it
Fig. 4.81  Computed Ring Currents for Experiment 112.

Current to rings 1 to 8 plotted as "1" to "8".
were sufficiently stable the first argument above would then apply to ring seven. It therefore appears that both the effects discussed are present. The maximum noise factor, on the other hand, will come from one of the rings for which the currents vary most rapidly. This should be one of the lower numbered rings, but we cannot predict more than this.

Ignoring for the moment the shaded portions of table 4.81 we see that the greatest noise factor observed was 10.0. The data blocks corresponding to the unshaded parts of the table are all reasonably smooth, hence we may regard 10.0 as a working upper limit to the noise factor of a "quiet" data block. A higher noise factor than 10.0 will indicate that the corrections of section 4.4 are unreliable, although of course the mean corrected currents for the block should still be valid. In "quiet" blocks the ring currents may change noticeably over intervals of some four spectrometer scans (100 seconds). These changes are most obvious for ring one, where the magnitude of the current is greatest, but it is not possible to infer from the plotted currents what changes were occurring in the mobility spectrum.

Blocks 2, 4, 6 and 18 (the shaded ones in table 4.81) have very high noise factors, and fig. 4.81 shows that these blocks each contain a sudden large disturbance to the ring currents. Since the spectrometer takes at least six scans (150 seconds) to recover from such a charge impulse (section 4.3) we cannot accurately determine the time for which the disturbance was present. None of the zero blocks have these bursts, hence they must be caused by the entry into the spectrometer of a parcel of air having a higher ion concentration
than usual. Such parcels of space charge were described by Hutchinson (1969) who found they occurred on days when thermal convection was present, and were moved about by the wind. Experiment 112 was carried out on a particularly calm fine day, with little wind, commencing at 0630 hours. The temperature was 13.5 °C at 0640 hours, rising to 18.5 °C by 0915 hours and reaching 21.5 °C at 1315 hours, while the relative humidity was 72% at 0640 hours, falling to 43% by 0915 hours where it remained until 1315 hours. Presumably these conditions were ideal for the formation of space charge clouds, for they were not repeated during the rest of the experiments and no more disturbances of this kind were found in the ring current records.
<table>
<thead>
<tr>
<th>Ring n</th>
<th>Mobility $k_n$ cm²/Vsec</th>
<th>Positive Slope $S_{np}$ Vsec/cm²</th>
<th>Negative Slope $S_{nn}$ Vsec/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intake</td>
<td>4.404</td>
<td>0.227</td>
<td>0.000</td>
</tr>
<tr>
<td>1</td>
<td>0.963</td>
<td>0.812</td>
<td>0.227</td>
</tr>
<tr>
<td>2</td>
<td>0.801</td>
<td>0.210</td>
<td>1.039</td>
</tr>
<tr>
<td>3</td>
<td>0.661</td>
<td>0.264</td>
<td>1.248</td>
</tr>
<tr>
<td>4</td>
<td>0.542</td>
<td>0.333</td>
<td>1.513</td>
</tr>
<tr>
<td>5</td>
<td>0.442</td>
<td>0.418</td>
<td>1.845</td>
</tr>
<tr>
<td>6</td>
<td>0.359</td>
<td>0.526</td>
<td>2.263</td>
</tr>
<tr>
<td>7</td>
<td>0.290</td>
<td>0.663</td>
<td>2.789</td>
</tr>
<tr>
<td>8</td>
<td>0.233</td>
<td>0.835</td>
<td>3.452</td>
</tr>
</tbody>
</table>

Table 5.11 Collecting Efficiency Functions for Single Rings
5.1 The Spectrometer Transform

The collecting efficiency function for a single ring was deduced in section 2.1 and is illustrated in fig. 2.13c. It has two sections: a straight line through the origin with slope $S^p_n$, and a straight line with negative slope $S^n_n$ reaching zero again at the critical mobility for the leading edge of the ring; the break point of the function is at the critical mobility for the trailing edge of the ring. In section 2.5 we defined the "cumulative length" of ring $n$, $d_n$, to be the distance of the trailing edge of ring $n$ from the intake edge of the first ring. Substituting for $\xi$ in equations (13) of section 2.1 yields

\[
S^p_n = \frac{d_n - d_{n-1}}{d_n} \cdot \frac{1}{k_n} \\
S^n_n = \frac{1}{k_{n-1}}
\]

where $k_n$ is the critical mobility for ring $n$ (corresponding to length $d_n$). For computational purposes it is convenient to calculate and store the two slopes for each ring; these are shown in table 5.11 and fig. 5.12a.

An alternative method of deriving the collecting efficiency functions is illustrated in fig. 5.12b. If all the rings
Fig. 5.12 a) Collecting Efficiency Functions for Rings 1 to 8.

Fig. 5.12 b) Alternative Derivation of Collecting Efficiency Functions.

[Note that the $\gamma$ scale differs from that of fig. 5.12a]
were connected together the resulting Integral Gerdien Chamber would have an efficiency function which was a straight line through the origin reaching a value of one at the critical mobility for the trailing edge of ring eight, \( k_8 \), and one for all higher mobilities. If only the first seven rings were grouped in this way, their efficiency function would reach unity at \( k_7 \). The efficiency function for ring eight is just the difference between these two - i.e. a triangle with base length \( k_7 \) and height \( 1 - \gamma_7(k_8) \). This process yields the efficiency functions for all rings except ring one, which has no ring below it. The upper critical mobility for ring one, labelled \( k_{\text{intake}} \) on the figure, corresponds to the effective length of the intake section of the spectrometer. This section had a measured capacitance value of 1.07 pF, giving an effective length of 2.56 cm.

The current to ring \( n \) is given by equation (19) of section 2.1. We may re-write this equation as:

\[
I_n = M_0 \int_0^{k_n} S_n k f(k) dk + M_0 \int_{k_n}^{k_{n-1}} (1-S_n k) f(k) dk \text{ Ampere}
\]

............(2)

with \( f(k) \), the mobility spectrum function, giving the number of ions with mobilities in the range \( k \) to \( k+dk \). This equation is the spectrometer transform outlined in section 2.4. It gives the ring current as a function of \( f(k) \), \( k_n \) and \( k_{n-1} \), i.e.

\[
I_n = g(k_n, k_{n-1}, f(k)).
\]

............(3)
5.2 Inverse Spectrometer Transforms

Consider a spectrometer with only two collecting electrodes whose (cumulative) lengths are \( d_{n-1} \) and \( d_n \). Their corresponding critical mobilities, \( k_n \) and \( k_{n-1} \), are given by equation (3) of section 2.3,

\[
k_c = \frac{M_o e}{UC}
\]

so that

\[
\frac{k_n}{k_{n-1}} = \frac{d_{n-1}}{d_n} = \frac{1}{\alpha}
\]

where \( \alpha \) is a constant factor.

Assume that \( d_n > d_{n-1} \) so that \( \alpha > 1 \). The factor \( \alpha \) is fixed by the spectrometer geometry if there are only two rings, but in our 8-ring spectrometer the ring lengths were chosen (in section 2.5) using equation (2) above. The spectrometer transform may therefore be written as

\[
I = M_o e \left\{ \int_0^{k_n} S_n f(k) dk + \int_{k_n}^{ak_n} f(k) dk - \int_{k_n}^{ak_n} S_n^n f(k) dk \right\}
\]

Substituting for \( d_n \) and \( k_{n-1} \) in equations (1) of section 5.1 we see that
\[ S_n^p = (1 - \frac{1}{\alpha}) \cdot \frac{1}{k_n} \]
\[ S_n^n = \frac{1}{\alpha} \cdot \frac{1}{k_n} \] ............(4)

Using these expressions for the slopes the right-hand side of equation (3) becomes a function of \( k_n \) only. Each of its three integrals may therefore be differentiated with respect to \( k_n \) by introducing auxiliary variables such as \( u = k_n \), \( v = \alpha k_n \), and differentiating using the Chain Rule. After differentiating and simplifying we obtain

\[ \frac{\partial I}{\partial k_n} = \frac{M_o e}{k_n} \left\{ \int_0^{k_n} S_n^p k f(k) dk - \int_{k_n}^{\alpha k_n} S_n^n k f(k) dk \right\} \] ............(5)

Substituting from equation (3) yields

\[ \frac{\partial I}{\partial k_n} = \frac{M_o e}{k_n} \int_{k_n}^{\alpha k_n} f(k) dk - \frac{I}{k_n} \] ............(6)

This equation may be used to find the number of ions in the range \( k_n \) to \( k_{n-1} \) and is thus an inverse spectrometer transform. It is more common to use a derivative with respect to the experimentally varied quantity since any required form can be obtained from (6): WHIPPLE (1960) for example, used

\[ \frac{\partial}{\partial k_{n-1}} \{ I \} = \frac{1}{U} \frac{M_o e}{k_{n-1}} \int_{k_n}^{\alpha k_n} f(k) dk \] ............(7)

where \( U \) was the chamber's driving potential.
To use an inverse transform one measures the current \( I \) for a range of values of \( k_n \) (normally some 10 to 15 values), calculates the derivative for all except the highest and lowest values, then calculates the spectrum integral for each derivative. The resulting spectrum is a histogram with bars for each interval \([k_n, k_{n-1}]\) whose height represents the number of ions with mobilities lying in the interval. If \( r \) measurements are made then up to \( r-2 \) bars can be used, and in principle any desired mobility resolution may be achieved merely by narrowing the interval \([k_n, k_{n-1}]\), i.e. by using an \( a \) value close to unity.

The accuracy of the calculated spectrum depends very much on the accuracy of the current measurements, especially since any error will be magnified on differentiation. It is therefore highly desirable to use a spectrum function having less than \( r-2 \) parameters so as to obtain improved parameter estimates. The following sections examine possible spectrum functions and the method of obtaining estimates of their parameters.

5.3 Properties of Mobility Spectrum Functions

In principle any function with \( m \) parameters

\[
f = f(k, c_1, c_2, \ldots, c_m)
\]

\((1)\)

could be used as a mobility spectrum function, but we must ultimately select one to use for all our spectrum determinations. For each set of observed currents and each proposed function we may find an optimal set of parameter values, then
calculate (using the spectrometer transform) a set of "predicted currents". If the function is a good model of the actual observed spectrum the predicted and observed currents will agree well, otherwise we must discard the function. Such agreement, although highly desirable, is not a sufficient reason for choosing a particular function. We must consider what other properties the chosen function should have.

Any spectrum function must have at least two parameters, one of which should be a linear scale factor, $A$ - i.e. we consider that

$$f(k, A, c_2, \ldots, c_m) = A f'(k, c_2, \ldots, c_m) \quad \quad \quad (2)$$

The function $f'$ is of course normalised, i.e.

$$\int_0^\infty f'(k, c_2, \ldots, c_m) dk = 1 \quad \quad \quad (3)$$

so that the scale factor $A$ represents the total number of ions per unit volume of air, while the remaining parameters correspond to quantities of the spectrum function such as its mean and variance. Obviously we would like to determine as many spectrum parameters as possible; we must therefore decide on the number we can reliably use. We should first try functions with only two parameters, then three parameters, and so on. Each extra parameter will improve the fit of predicted to observed currents, until finally we have an interpolating function which has eight parameters and gives a perfect fit. We may then decide the number of parameters at which the introduction of one more does not significantly improve the fit.
We cannot measure $f(k)$ we must instead measure $g(k)$ and $h(k)$.

Fig. 5.31 Mobility Spectrum Functions for Positive and Negative Driving Potential.

1. Good agreement between predicted and observed currents.
2. One parameter is a linear scale factor.
3. At least two and less than eight parameters.
4. Zero for zero mobility, undefined for mobilities of opposite sign to spectrometer driving potential.
5. Zero for mobilities greater than some limiting value.
6. Sensitive to changes in its parameters, particularly for mobilities in the range $k_8$ to $k_1$.

Table 5.31 Properties of a Mobility Spectrum Function
As well as finding optimal values for the parameters we can calculate estimates of their variance. In general as the number of parameters is increased the variance of each will also increase. This introduces another limit to the number of reliable parameters, since an extra parameter whose value cannot be determined precisely enough will not yield any further information about the observed spectrum, however much it improves the fit.

As mentioned in section 1.1 the mobility of an ion depends on its charge, mass, and size, which implies an upper limit to ionic mobilities— that of a free electron. A mobility spectrum function must hence be zero for all mobilities above some limiting value. Furthermore since every ion carries some charge no ion can have zero mobility, hence a spectrum function is also zero for a mobility value of zero. Again the spectrometer can only yield information about ions of the same sign as its driving potential: we cannot simultaneously determine the spectrum for both positive and negative mobilities. Instead we must measure each sign separately and concatenate the results, so the spectrum function is zero for all mobilities with sign opposite to the driving potential. Fig. 5.31 summarises these properties.

Consider the collecting efficiency functions of fig. 5.12a. For every mobility in the range zero to \( k_8 \) each ring collects a constant proportion of the incoming ions. This means that no detail of the mobility spectrum in this range can be resolved since if we chose a delta function with height A and mobility \( k \) as our spectrum model, i.e.
\[ f = \Lambda(k, A, K) = \begin{cases} A & \text{when } k = K \\ 0 & \text{otherwise} \end{cases} \] ...........(4)

then we could not distinguish between

\[ \Lambda(k, A, K) \quad \text{and} \quad \Lambda(k, A/\beta, \beta K). \]

For mobilities greater than \( k_1 \) only the first ring collects any ions, so again no detail can be resolved.

Since the spectrometer can only resolve details of the mobility spectrum in the range \( k_0 \) to \( k_1 \) we would like a spectrum function for which variations in the parameters alter the function in this mobility range. To speed up the parameter fitting process (section 5.5) it is also desirable that the function is sensitive to such parameter variations. Finally, since the function will be evaluated a large number of times, we would prefer one which is simple to compute - provided it is still a realistic model.

Table 5.31 summarises all the above properties of a mobility spectrum function.

5.4 Preliminary Tests on Mobility Spectrum Functions

A computer program was developed to test any given spectrum function. The program reads in sets of observed currents \( I_n \), calculates predicted currents \( I'_n \), then computes the residual
a) Square step.

\[ f = \frac{A}{2\pi} \text{ when } m - r \leq k \leq m + r, \]
\[ 0 \text{ otherwise} \]

b) Semicircle.

\[ f = \frac{2A}{\pi r^2} \sqrt{r^2 - (k-m)^2} \text{ when } m - r \leq k \leq m + r, \]
\[ 0 \text{ otherwise} \]

c) Histogram.

d) Line Spectrum.

Fig. 5.41 (abcd) Examined Mobility Spectrum Functions.
\[
R = \sum_{n=1}^{6} (I_n - I'_n)^2
\]

\[\ldots\ldots\ldots\ldots\ldots(1)\]

for a range of values of the spectrum parameters. Several functions were evaluated in this way; these are discussed below, and illustrated in fig. 5.41.

a), b) Square Step and Semicircle:

These are both three parameter functions, the parameters being total ion density A, mean mobility m, and mobility half-range r. They are also very simple to compute and both gave a minimum residual of the order of 250 for values of m and r of about 0.35 and 0.15 respectively. For both of them the fit was sensitive to changes in m but was insensitive to changes in r, making them useful only as two-parameter functions.

Unfortunately both functions have discontinuities at m−r and m+r which are not easily explained physically, especially since the value of r is not particularly critical.

c), d) Histogram and Line Spectrum:

The histogram function is interesting since it is the one given by the conventional inverse spectrometer transform, while the line spectrum is similar except that it uses delta functions instead of bars. Normally the edges of the intervals are fixed by the critical mobilities used leaving the heights to be determined, but alternatively the heights could be fixed and the critical mobilities determined, or a case intermediate between these two could be used.
e) Gaussian.

\[ f = \frac{A}{\sigma \sqrt{2\pi}} e^{-\frac{(k-\mu)^2}{2\sigma^2}} \]

f) Rayleigh.

\[ f = \frac{Ak}{\sigma^2} e^{-\frac{k^2}{2\sigma^2}} \]

g) Lognormal.

\[ f = \frac{A}{k\sigma \sqrt{2\pi}} e^{-\frac{(\ln k - \mu)^2}{2\sigma^2}} \]

Fig. 5.41 (efg) Examined Mobility Spectrum Functions.
Obviously these functions have discontinuities also, rendering them physically unattractive. In conventional spectrum determinations the widths of the bars are (hopefully) made sufficiently small that they can be regarded as samples from a continuous function. Since we have only eight measured points covering the mobility range 0.2 to 1.0 cm²/Vsec this is not a valid assumption in our case.

e) Gaussian Distribution:

The gaussian distribution function gave minimum residuals of about 250 with mean and standard deviation (μ and σ) values of about 0.2 and 0.5 respectively. The fit was sensitive to changes in either μ or σ, allowing the gaussian to be used either as a two- or a three-parameter function.

From the μ and σ values just stated we see that the function is not zero for zero or negative mobilities, it cannot therefore be used as a spectrum function.

f) Rayleigh Distribution:

This function is very similar to e), but it is only a two-parameter function. It is zero at zero mobility, undefined for negative mobilities, and gave minimum residuals of about 250, for σ values of about 0.3.

g) Lognormal Distribution:

The lognormal distribution can be regarded as a normal distribution drawn on a logarithmic scale. Like f) its value is zero for zero mobility and undefined when the mobility is negative. Minimum residuals of 20 to 50 were obtained with
Fig. 5.42 Lognormal Curves for Various Values of $\mu$ and $\sigma$.

Fig. 5.51 "Actual" and "Model" Mobility Spectrometers.
values of -3.0 and +1.5 for $\mu$ and $\sigma$. Furthermore the fit was sensitive to changes in either $\mu$ or $\sigma$ allowing its use with three or two parameters.

Since the lognormal function gave much the best fit of all the functions tested, without having discontinuities, it was the obvious choice for a spectrum function. The properties of the lognormal distribution are well treated in the monograph by AITCHISON & BROWN (1957), but briefly if $A(x)$ is lognormal then

$$A(x) = N(\log x)$$ ............(2)

where $N$ is the normal distribution function. This implies that

$$A(x) \cdot dx = \frac{1}{x \sigma \sqrt{2\pi}} \exp \left\{- \frac{(\log x - \mu)^2}{2\sigma^2} \right\} \cdot dx$$ ............(3)

The distribution has a mean of $\exp\{\mu + \frac{1}{2}\sigma^2\}$, a mode of $\exp\{\mu - \sigma^2\}$ and is positive skew. Fig. 5.42 shows some lognormals with a range of values for $\mu$ and $\sigma$ and an $A$ value of one.

5.5 Calculation of Optimal Spectrum Parameters

The upper half of fig. 5.51 illustrates the mobility spectrometer system. An (unknown) spectrum of ions is drawn in on the left and transformed by the spectrometer into a set of currents which are recorded. In the lower half of the figure is a model of the system. Instead of the spectrometer we use its transform to convert the input spectrum into currents, and now the form of the spectrum is known although the values
of its parameters have yet to be determined.

We wish to determine the optimal values of the model spectrum's parameters so as to achieve the best fit of predicted to observed currents. The "Method of least Squares" (outlined in Appendix 2) allows us to obtain minimum variance estimates of the parameters, and estimates of their standard deviations. The function to be fitted is

\[ g(n, A, \mu, \sigma) = g(f'(k, A, \mu, \sigma), k_n) \quad \ldots \ldots \ldots (1) \]

which gives the current to ring \( n \). Since this is non-linear, we require expressions for

\[ \frac{\partial g}{\partial A}, \frac{\partial g}{\partial \mu}, \text{ and } \frac{\partial g}{\partial \sigma}. \]

All these can be written down using the lognormal distribution function [equation (3), section 5.4] for \( f' \) and the spectrometer transform [equation (2), section 5.1], then using suitable transformations the integrals can be expressed in terms of the error function, \( \text{erf}(X) \), where

\[ \text{erf}(X) = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{X} \exp(-t^2) dt \quad \ldots \ldots \ldots (2) \]

For computing purposes polynomial approximations for \( \text{erf}(X) \) are given by HASTINGS (1955). The algebraic manipulations required are lengthy and tedious: their resulting expressions are given in Appendix 3. A computer program was written to perform the least squares calculations. In the course of its development a number of slight variations to the method were
found useful - these are explained below.

Since the current to each ring is measured separately there was no reason to suppose that errors in the currents were not independent. A diagonal variance-covariance matrix \( M_f \) was therefore used, giving a diagonal weight matrix \( W^{-1} \) which simplified the operations required in setting up the normal equation matrices. Equal weights of one were used, except that currents less than 0.25 fA (the smallest observable current step, corresponding to a change in electrometer output of one mV) were given weights of zero. When this occurred the number of observed currents was thereby effectively reduced.

In solving the normal equations the matrix \( A'M_f^{-1}A \) must be inverted, which requires that it be well-conditioned (i.e. have a large determinant value). If one of the parameters has only a small effect on the function's value at the expansion point \( (x_1^0, \ldots, x_m^0) \) then its row in the \( A \) matrix will have small elements, giving an ill-conditioned normal matrix. To avoid this problem it is **essential** to scale the rows of the normal matrix before inverting. To do this we may set up a diagonal matrix of scale factors, \( Q \), where

\[
q_{ij} = 0 \text{ when } i \neq j \\
q_{ii} = \text{scale factor for row } i
\]

and the scale factors are chosen to bring all the \( A \) matrix elements to within the same order of magnitude.

In use the product \( Q.A \) replaces \( A \) in the normal equations.
Writing the unscaled equations as

\[(A'M_f^{-1}A)\hat{X} = C\hat{X} = A'M_f^{-1}F\] ..........(3)

these become

\[(A'QM_f^{-1}QA)\hat{Y} = D\hat{Y} = A'QM_f^{-1}F\] ..........(4)

Without scaling the solution to the normal equations is

\[X = A^{-1}F\] ..........(5)

which becomes

\[Y = A^{-1}Q^{-1}F\] ..........(6)

so that

\[x_i = q_i y_i\] ..........(7)

and

\[c^{-1}_{ii} = q_id^{-1}_{ii}q_i\] 

Equation (7) gives the formulae for obtaining the values and estimated standard deviations of the unscaled parameters. With this modification convergence of the iterations was generally rapid and reliable: without it the normal matrix was singular in about 60% of the cases examined.
Fig. 5.62 Approximate Plots of Lognormals from Points Marked X on fig 5.61.
Fig. 5.61 Typical Contours of Residual (R) for a Lognormal Spectrum Function.

Fig. 5.63 "Complete" Mobility Spectrum Function.
5.6 The "Complete" Mobility Spectrum Function

The least squares program developed in section 5.5 was used to fit the lognormal spectrum function to a range of observed spectra, and its performance evaluated. Contrary to expectation reliable fits were not realised, with \( \mu \) and \( \sigma \) both iterating to large (absolute) values. To investigate this behaviour plots like that of fig. 5.61 were produced. These plots gave the minimum residual, \( R \), for ranges of values of \( \mu \) (ordinate) and \( \sigma \) (abscissa); similar plots giving the optimal value of \( A \) were also produced. From fig. 5.61 we see that with the scale values chosen the contours of equal \( R \) form a valley running at about 45 degrees to the axes, with a floor which slopes down (decreasing \( R \)) in the direction shown by the arrows. This means the least squares iterations will attempt to "walk" down the valley, with \( \mu \) decreasing and \( \sigma \) increasing. In principle the process should find the minimum \( R \) but in practice the slope of the valley floor is so gentle that the normal matrix usually becomes poorly conditioned long before the minimal point is reached.

Fig. 5.62 gives plots of lognormal functions corresponding to the points marked X on fig. 5.61. As the residual decreases the mode of the function moves down while the total density \( A \) increases, keeping the upper tail of the function substantially unchanged. Recalling section 5.4 it is now obvious that the least squares process is attempting to fit only the upper tail of the function, since the spectrometer can only yield details for the mobility range \( k_8 \) to \( k_1 \). Clearly a better spectrum function is required.
So far we have been attempting to fit the entire mobility spectrum with a single continuous function. There is, however, no doubt that two such functions, one for large ions, the other for small ones, would be an equally valid model. For our spectrometer all the large ions \((k < 0.1 \text{ cm}^2/\text{Vsec})\) have mobilities below \(k_8\), so we will only be able to obtain an estimate of their total number. Since we cannot determine their mobilities we lose nothing by using a delta function of height \(\nu\) at mobility \(k_8\) [equation (4) section 5.3] for the large ion spectrum function. Again a lognormal is a sensible choice for the small ion function, giving the complete (four-parameter) function shown in fig. 5.63.

Contours of residuals similar to fig. 5.61 were produced for the complete spectrum function, giving a series of plots corresponding to various values of \(\nu\) for each observed spectrum. In about 50% of the cases a clear minimum was obtained for all values of \(\nu\), typically with \(\mu\) and \(\sigma\) values near -0.2 and +0.5 respectively. The remaining cases generally had a shallow valley (like that of fig. 5.61) running parallel to the \(\mu\) axis, indicating that the fit is insensitive to \(\sigma\). The function may therefore be used only as a three-parameter function by assuming an arbitrarily chosen value of say +0.5 for \(\sigma\). Similarly we can use it as a two-parameter function, assuming values of -0.2 and +0.5 for \(\sigma\) and \(\mu\).

5.7 Accuracy of the Calculated Spectra

The upper part of table 5.7 gives standard deviations for all the measured quantities required in the spectrum calculat-
### Measured Quantities

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>σ</th>
<th>% σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Driving Potential</td>
<td>$U$</td>
<td>V</td>
<td>90.00</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Airflow Rate</td>
<td>$M_0$</td>
<td>litre/sec</td>
<td>4.825</td>
<td>0.024</td>
<td>0.57</td>
</tr>
<tr>
<td>Chamber electrode radii</td>
<td>$d_p$</td>
<td>cm</td>
<td>1.269</td>
<td>0.001</td>
<td>0.08</td>
</tr>
<tr>
<td>Cumulative Ring lengths</td>
<td>$d_n$</td>
<td>cm</td>
<td>9.15</td>
<td>0.04</td>
<td>0.44</td>
</tr>
<tr>
<td>Critical Mobility</td>
<td>$k_n$</td>
<td>cm$^2$/Vsec</td>
<td>0.96</td>
<td>0.005</td>
<td>0.87</td>
</tr>
<tr>
<td>Ring Currents</td>
<td>$I_n$</td>
<td>fA</td>
<td>4.00</td>
<td>0.125</td>
<td>3</td>
</tr>
</tbody>
</table>

### Spectrum parameters for the two-parameter function

<table>
<thead>
<tr>
<th>Ion Concentration</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>σ</th>
<th>% σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large ion concentration</td>
<td>$\nu$</td>
<td>ions/cm$^3$</td>
<td>120</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>Small ion concentration</td>
<td>$A$</td>
<td>ions/cm$^3$</td>
<td>60</td>
<td>1.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### Spectrum parameters for the three-parameter function

<table>
<thead>
<tr>
<th>Ion Concentration</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>σ</th>
<th>% σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large ion concentration</td>
<td>$\nu$</td>
<td>ions/cm$^3$</td>
<td>120</td>
<td>2.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Small ion concentration</td>
<td>$A$</td>
<td>ions/cm$^3$</td>
<td>60</td>
<td>2.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Small ion mode (on log scale)</td>
<td>$\mu$</td>
<td>-</td>
<td>-0.25</td>
<td>0.1</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.71 Standard Deviations for the Measured and Derived Quantities
ions. Of these the driving potential, airflow rate and ring diameters require no further explanation. The length of each separate ring was measured with negligible error, then the rings were clamped together with 1/32 " teflon spacers. The error in their cumulative lengths is assumed to be half the thickness of a single spacer, including an allowance of 5% for variations in spacer thickness. Ring one, being the shortest, has the largest standard deviation; all the other rings have smaller deviations, even allowing for their increased number of spacers (each with its 5% thickness variation). Critical mobilities are calculated from the quantities above, giving a worst case standard deviation of about 0.9%. The ring currents could be measured to within one millivolt of electrometer output, i.e. to within 0.25 fA, so their worst case standard deviation is about 3% (for ring two).

Calculated standard deviations for the fitted spectrum parameters are given in the lower part of table 5.7. For the two-parameter function ($\mu = -0.2, \sigma = +0.5$) the standard deviations are of the order of 3%, the same as that for the ring currents. Standard deviations for $v$ and $A$ with the three-parameter function are, as expected, increased, while the parameter values are of course unchanged. However the third parameter, $\mu$, has a very high standard deviation - so high that it is obviously unusable. Accordingly, the two-parameter "complete" function was used for all later spectrum calculations.

The spectrometer performance can be summarised as follows: We assume as our model of the observed mobility spectrum a
delta function of height \( \nu \) at mobility 0.233 cm\(^2\)/Vsec and a lognormal function with total density \( A \) and values of -0.2, +0.5 for \( \mu, \sigma \). These values of \( \mu \) and \( \sigma \) give the mean of the lognormal distribution a value of 0.928 cm\(^2\)/Vsec.

The spectrometer permits us to obtain an estimate of the parameters \( \nu \) and \( A \) every 25 seconds, with standard deviations of less than 3 percent.
<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Date</th>
<th>Start Time</th>
<th>Duration (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>WED 21 OCT 70</td>
<td>0630</td>
<td>6½</td>
</tr>
<tr>
<td>115</td>
<td>SAT 7 NOV 70</td>
<td>1045</td>
<td>9</td>
</tr>
<tr>
<td>117</td>
<td>SUN 8 NOV 70</td>
<td>2400</td>
<td>5½</td>
</tr>
<tr>
<td>121</td>
<td>TUE 17 NOV 70</td>
<td>1030</td>
<td>24</td>
</tr>
<tr>
<td>126</td>
<td>MON 23 NOV 70</td>
<td>2130</td>
<td>19</td>
</tr>
<tr>
<td>130</td>
<td>SAT 28 NOV 70</td>
<td>1000</td>
<td>24</td>
</tr>
<tr>
<td>134</td>
<td>TUE 8 DEC 70</td>
<td>2115</td>
<td>13</td>
</tr>
<tr>
<td>137</td>
<td>SAT 12 DEC 70</td>
<td>2115</td>
<td>7</td>
</tr>
<tr>
<td>140</td>
<td>SAT 19 DEC 70</td>
<td>2300</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 6.11 Times of Mobility Spectrum Observations
CHAPTER 6

OBSERVED MOBILITY SPECTRA

6.1 Experimental Details

In October 1970 the spectrometer was installed on the Physics Department roof, as described in section 3.7. Its sequencing was set up according to the scheme of section 3.9, allowing the recording of 15 minute data blocks for positive or negative ions each alternate half hour. During the next few months a series of experimental runs were made, details of which are given in Table 6.11. The experiment numbers in Table 6.11 are serial numbers of the reels of paper tape on which the spectrometer output was punched. They are not consecutive since the digital recorder is continually in use recording information from the department's Atmospheric Electricity Station.

All the data blocks collected were converted to corrected ring currents, their zero offsets removed and means calculated, using the computer programs of section 4.4 and 4.7. The resulting 120 hours of half-hourly-mean ring currents are discussed fully in sections 6.3 to 6.5. The reed switch connected to ring three was found to be open-circuit for long periods of time. This occurred throughout experiments 121, 126 and 130, and during most of experiment 134, allowing only 84 of the 240 data blocks to be examined for short-term variations in mobility spectrum, as discussed in section 6.2.
6.2 Variation of Mobility Spectra over Fifteen-Minute Intervals

Mobility spectra were computed for all of the valid data blocks obtained in section 6.1, using the least-squares procedure of section 5.5 to fit the spectrum model described in section 5.6. This yielded a series of fifteen-minute records giving the mobility spectrum every 25 seconds. In some of the "noisy" blocks (section 4.8) the iteration failed to converge, leaving missing points in the record. Since this never occurred in a "quiet" block such missing points were given values interpolated between the fitted spectra adjacent to them.

In correcting the ring currents for electrostatic interaction between the rings we need to know the charge on all the rings the instant any one was sampled. We assumed (section 4.4) that the charge on each ring was \([\text{time since last sample of ring}]^g \cdot [\text{current to ring as determined at last sample}]\). This assumption is satisfactory provided the ring currents do not change significantly during the 25 seconds required for a spectrometer scan, but it clearly reduces the spectrometer's useable time resolution to less than the theoretical maximum of two scan periods. When the computed spectra were plotted the presence of noise with a 50 second period was apparent, indicating the need for some smoothing of the plots. BLACKMAN & TUKEY (1959) define a smoothed function as "the result of weighted averaging of nearby values of the original function" : the weighting scheme used was

\[
\hat{f}_n = \frac{1}{4} (\hat{f}_{n-1} + 2\hat{f}_n + \hat{f}_{n+1})
\]  

.........(1)
Fig. 6.21 Mobility Spectra from Experiment 112.

Large, small ion concentrations plotted as "1", "2" on scales 1, 2. R. M. S. ring current error plotted as "3" on scale 3.

Scales: Vertical: 1 = 3 fA/division.
        2 = 2 fA/division.
        3 = 0.5 fA/division.

Horizontal = 1 Spectrometer Scan (25 sec)/division.

Driving Potential: +90 V, -90 V in alternate blocks as indicated.

Blocks 2, 4, 6, 18 are "noisy" blocks.
where \( f_n \) is the nth unsmoothed value,
and \( f_n' \) is the nth smoothed value.

This effectively gives a low-pass filter whose relative gain is 0.8 for a frequency of 1/200 Hz, 0.4 for 1/100 Hz, and negligible for frequencies above 1/50 Hz. All the spectra were smoothed, so the most rapid periodic variation they can show has a period of some 200 seconds, though changes over intervals of 100 seconds should be apparent.

Mobility spectra for experiment 112 are shown in fig. 6.21. These were computed from the ring currents plotted in fig. 4.81, and have been smoothed as described above. Interpolated points occurring in the noisy blocks (2, 4, 6 and 18) are circled on the plot. It is simple to show that the value of an interpolated point is not altered by smoothing. For example if \( f_n \) is a single interpolated point,

\[
i.e. \quad f_n = \frac{1}{2}(f_{n-1} + f_{n+1})
\]

\[\ldots\ldots\ldots(2)\]

then substituting for \( f_n \) in (1) above yields \( f_n' = f_n \). A valid data point adjacent to an interpolated one may however change, which is why some of the interpolated points on fig. 6.21 are local extrema. The spectrum model has two components: a delta function of height \( v \) at mobility 0.233 cm\(^2\)/Vsec representing the large ions, and a lognormal function with area A, \( \mu = -0.2 \) and \( \sigma = 0.5 \) representing the small ions, giving a mean small-ion mobility of 0.928 cm\(^2\)/Vsec. The spectrum fitting process yields the ion concentrations \( v \) and \( A \) with standard deviations of about 3% (section 5.7). In fig. 6.21 the symbols "1" and "2" represent large and small ion concentrations (v
and A) respectively. Also plotted (using symbol "3") is the ring current error for each spectrum, which is the root-mean-square value of the difference between the measured ring currents and those calculated from the fitted spectrum. In quiet blocks this error is typically 2.5 fA. The horizontal straight lines drawn on each block are the concentrations of large and small ions computed from the block's mean ring currents. Note that since the inverse spectrometer transform is inherently non-linear this need not be the same as the mean of the fitted concentrations.

On examining the quiet blocks a number of features become apparent. First there is in general much less variation of the large-ion concentration than of the small. While the large-ion concentration is usually within 5% of its mean it may differ from it by as much as 20%, whereas the small-ion concentration is normally only within some 10% of its mean, and may differ from it by some 45%. This indicates that the population of small ions is less stable than that of large ions, possibly because there are many more large ions than small.

Secondly the ion concentrations may change markedly over periods of five to ten spectrometer scans (125 to 250 seconds). Consider, for example, blocks 12, 14, 20, 22 and 26, all of which show such changes. Note that while the large and small ion concentrations usually alter at the same time, the magnitude of their changes may differ considerably. This is particularly apparent in block 14, where the small-ion concentration changes most, while in block 26 it is the large-ion concentration which does so. Short-term changes of this kind
probably correspond to the incidence of parcels of ion-laden air like those mentioned in section 4.8 drifting in the wind past the spectrometer air intake. The drop in small-ion concentration in block 14 would thus mark the passing of a parcel of ion-free air.

Thirdly several of the blocks show a steady drift of ion concentration over intervals of ten minutes or more. This is demonstrated by blocks 16 and 24, where the large-ion concentration increases by 24% and 44% respectively over an interval of 32 scans (13 1/3 minutes), and by block 20, where the small-ion concentration rises from 52 to 102 ions/cm$^3$ (i.e. nearly doubles) in an interval of only 26 scans (10 5/6 minutes). These steady drifts are evidence of long-term variations extending over periods of hours. One such variation is the diurnal variation examined in section 6.3; others may correspond to slow changes in meteorological conditions (though these were very steady all through experiment 112).

Ring currents for each of the noisy blocks (2, 4, 6 and 18) showed a sudden disturbance, which completely violated the assumption of small changes in ring current between scans. However the computed spectra for these blocks are completely normal until the disturbance begins and after it has passed - block 4 shows this very clearly. The disturbance itself is undoubtedly due to a cloud of space charge passing the spectrometer, since in all four noisy blocks the small-ion concentration rose very rapidly to several times its block mean level and remained high while the disturbance was present. In blocks 6 and 18 there is no significant change in large-ion
concentration, whereas in blocks 2 and 4 the large-ion concentration returns to normal in about half the time taken by the small ions. This suggests that the space-charge cloud contained mainly small ions but the information given by the spectrometer is not sufficiently reliable to confirm this. A study of the ionic composition of such clouds might be an interesting topic for later research, though this would require improved spectrometer time resolution.

The observations of this section may be summarised as follows:

a) Steady drifts in the mobility spectrum parameters over quarter-hour intervals are apparent, indicating the presence of longer-term variations. These drifts could completely invalidate a spectrum computed from a sequence of current measurements for increasing critical mobilities.

b) The atmospheric ion mobility spectrum changes significantly over time intervals of the order of 100 seconds, hence a truly representative spectrum for a quarter-hour period can only be obtained by averaging a series of spectra measured at short intervals during the quarter-hour.

c) The existence of parcels of ion-laden air ("space-charge clouds") moving about in the wind has been demonstrated, but the spectrometer could not give details of their mobility spectrum.
Fig. 6.31 ½ Hour Mean Spectra for Experiments 112 and 121.

Large Ion Concentration (u) and Small Ion Concentration (A) plotted as "1" and "2" on Scale A.

R.M.S. Current Error plotted as "3" on Scale B.
6.3 Diurnal Variation of Mobility Spectra

A mean mobility spectrum was computed for every quarter-hour data block obtained from the experiments listed in table 6.11. These series of spectra were plotted using the same plotting symbols as those of fig. 6.21, ("1" and "2" for large and small ion concentrations, "3" for ring current error) with broken lines joining the plotted points for negative ions and continuous lines those for positive ions. Samples of these plots for experiments 112 and 121 are given in fig. 6.31. The ring current error for a quarter-hour mean spectrum should obviously be less than that for the 25-second spectra observed during the quarter-hour. This is demonstrated by experiment 112, for which fig. 6.21 gives a typical 25-second value of 2.5 fA, whereas the quarter-hour value shown by fig. 6.31 is typically only 1.0 fA. The spectra plots show short-term variations over time intervals of up to five hours, and indicate the presence of a slower variation with a period of the order of a day.

Since the longest of the mobility spectra records available covered only a twenty-four hour interval it was not sensible to attempt a full time-series analysis of them, so the exact period of the "diurnal" variation could not be determined. Instead all the records were smoothed (using the weighting scheme of section 6.2) and the smoothed records plotted on a single graph whose time axis covered an interval of twenty-four hours. Smooth curves were then drawn through half-hourly means of the plotted spectra, giving an "estimated average day" of mobility spectra. Figures 6.32, 6.33, 6.34 and 6.35 are plots obtained for the concentrations of
Fig. 6.32 Observed Diurnal Variation of Large Negative Ion Concentration \( (V) \).

Fig. 6.33 Observed Diurnal Variation of Small Negative Ion Concentration \( (A) \).
Fig. 6.34 Observed Diurnal Variation of Large Positive Ion Concentration ($n_+^+$).

Fig. 6.35 Observed Diurnal Variation of Small Positive Ion Concentration ($A_+^+$).
large negative, small negative, large positive and small positive ions respectively. On each of these plots the smooth curve is the estimated average value, while the vertical bars indicate the range of values observed. Fig. 6.37 is a similar plot for the vertical component of the earth's electric field (F V/m), using values of F recorded by the field mill which forms part of the Atmospheric Electricity Station ("AES") mentioned in section 3.7. All five of the above parameters are shown together (without their range indications) in fig. 6.36. The overall accuracy of this procedure is unfortunately low (seldom yielding better than 20% standard deviation), nevertheless the plots show a clear cyclic variation over the course of a day. It is interesting to compare fig. 6.36 with similar ones obtained by J.J. NOLAN & P.J. NOLAN (1933) at Glencree in Ireland (reproduced here as fig. 5.38), and MISAKI & KANZAWA (1969) at Tokyo (given as fig. 1.25).

Consider first the small-ion concentrations. These rise steadily during the night to a maximum at about 0400 hours. The maximum is more pronounced for positive ions than negative, though we lack sufficient resolution to be certain of this. At night the only sources of small ions are radioactive material in the atmosphere and the earth's crust, both of which are reasonably stable. An increase in small-ion concentration must therefore be caused by a decrease in nucleus concentration, which lowers the rate small ions are lost by recombination. A morning maximum is also evident at Tokyo, where it occurs at 0400 hours, and at Glencree where it does not occur until about 0800 hours. After 0400 hours the small ion concentrations decrease somewhat, then rise again to reach a second maximum at about 1400 hours. A second maximum is apparent at
Tokyo (though MISAKI & KANAZAWA (1969) do not point this out), and also at Glencree. This early afternoon maximum is presumably due to an increase in small-ion production by solar radiation. There are thus two main effects contributing to the small-ion population; an inverse relation between small-ion and nucleus concentrations, and a direct dependence of small-ion production on solar radiation. Both effects are always present, but the relative importance of each differs between the records examined (for Auckland, Tokyo and Glencree).

Note that all the small-ion concentration extrema mirror exactly those of the vertical field strength, F. This is reasonable, for clearly an increase in the concentration of small ions in the lower atmosphere will increase the conductivity there, thus lowering the effective electric field. Since F was measured by an independent instrument (the AES field mill), this provides a clear verification of the spectrometer results.

The large-ion concentrations show a maximum at about 1100 hours. From midday they fall steadily until about 0400 hours, then rise again rather more rapidly. During the night industrial activity and vehicular traffic are at a minimum but they build up in the morning, mainly during the interval between about 0700 and 0900 hours. These two sources produce large numbers of nuclei and of large ions, giving the observed rise in large-ion concentration. Atmospheric nuclei are continually removed by the processes of coagulation and sedimentation, hence an equilibrium nucleus concentration should eventually be reached. This occurs at about 1100 hours, the time of max-
Fig. 6.37 Observed Diurnal Variation of Electric Field Strength ($F$).

Fig. 6.38 Diurnal Variation of Atmospheric Ion Concentration at Glencree - from NOLAN & NOLAN (1933).
imum concentration. In the afternoon industry and traffic diminish again, particularly during the interval from 1600 to 1800 hours, so the large-ion concentration decreases as the nuclei are removed. The observed maximum at 1100 is, however, sharper than can be entirely accounted for by the above argument since it implies that the large-ion concentration should remain steady from 1100 hours (when equilibrium is reached) until about 1600 hours (when the rate of nucleus production drops). We noted in the preceding paragraph that small-ion concentration exhibits a maximum at 1400 hours, so we might expect an early afternoon maximum in the concentration of large ions formed by the combination of small ions and nuclei. A combination of both the above effects affords a reasonable explanation for the observed variations. At Glencree nucleus concentration had its maximum at about 1500 hours, some four hours later than at Auckland. This four-hour lag is also apparent for the small-ion maxima. Apart from the fact that the Glencree measurements were made forty years ago at a small village (rather than in a city) there is no apparent reason for it. The large-ion spectra for Tokyo did not show regular daily variations.

The positive small-ion concentration is always greater than that for negative small ions, the ratio varying between about 1.1 (at midday) and nearly 2.0 (at midnight). For large ions the polar concentrations are almost identical from about 1800 to 0600 but during the day there are more negative large ions than positive. Such variations in the ratio of positive/negative ion concentrations do not seem to admit to any simple explanation.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Electrode radius</td>
<td>10 mm</td>
</tr>
<tr>
<td>Outer electrode radius</td>
<td>50 mm</td>
</tr>
<tr>
<td>Electrode length</td>
<td>300 mm</td>
</tr>
<tr>
<td>Driving potential</td>
<td>94 V</td>
</tr>
<tr>
<td>Airflow rate</td>
<td>4 m³/minute</td>
</tr>
<tr>
<td>Critical Mobility</td>
<td>6 cm²/Vsec</td>
</tr>
</tbody>
</table>

Table 6.41 Parameters of Atmospheric Electricity Station Gerdien Chambers
This section has demonstrated a number of effects which contribute to the diurnal variation of the atmospheric ion mobility spectrum at Auckland. The observed variation agrees well with similar ones at both Tokyo and Glencree. The resolution of the plotted variations is somewhat poor, resulting from the use of a number of short records for the analysis rather than a single long one. Since each record required a considerable amount of data processing it is obvious that one drawback of the spectrometer is the high rate at which it produces raw data. Provided this difficulty is resolved the detailed observation of diurnal mobility spectrum variations at regular intervals for various sites would form the basis of a worthwhile future research project. Studies of this kind should be particularly helpful in the field of pollution control, while an investigation of the variations of positive/negative ion concentration ratios might provide useful data for the theory of ionic equilibrium.

6.4 Comparison of Independently Measured Conductivities with those Computed from Mobility Spectra

The Physics Department's Atmospheric Electricity Station mentioned in section 3.7 includes a pair of "Integral" Gerdien Chambers for measuring the atmospheric polar conductivities. The parameters of these chambers are listed in table 6.41, while complete details of the whole station are given by KASEMIR & DOLEZALEK (1961). Both chambers are mounted vertically, side by side in a large raised metal box, with their air intakes at the bottom at a height of about one metre above the roof. Conductivity readings are recorded automatically at
Fig. 6.41 Comparison of Calculated and Directly Observed Atmospheric Conductivities for Positive Ions.

Data from experiment 130:
Large, small ion concentration plotted as "1", "2" on scales 1, 2.
Observed Conductivity plotted as "3" on scale 3.
Calculated Conductivity plotted as "4" on scale 4.
Fig. 6.43 Comparison of Calculated and Directly Observed Atmospheric Conductivities for Negative Ions.

Data from experiment 130:

Large, small ion concentration plotted as "1", "2" on scales 1, 2.
Observed Conductivity plotted as "3" on scale 3.
Calculated Conductivity plotted as "4" on scale 4.
suitable intervals by the digital recorder used for the spectrometer.

As mentioned in section 1.4, atmospheric conductivity can be calculated from the mobility spectrum, since (ignoring signs)

\[ \lambda = e \int_{0}^{\infty} k f(k) dk \]  

\ldots \ldots (1)  

For the mobility spectrum function used (section 5.6) this becomes

\[ \lambda = e \{ k_L \cdot \nu + k_s \cdot A \} \quad \text{mho/m} \]  

\ldots \ldots (2)  

where

- \( k_L = 0.233 \ \text{cm}^2/\text{Vsec}, \)
- \( \nu = \text{concentration of large ions/cm}^3, \)
- \( k_s = \text{mean of lognormal distribution with} \ u = -0.2, \)
- \( \sigma = 0.5 \ (0.928 \ \text{cm}^2/\text{Vsec}), \)
- \( A = \text{concentration of small ions/cm}^3. \)

Conductivities were calculated from most of the spectra obtained in section 6.3 and compared with those observed at the same time by the Atmospheric Electricity Station. As samples of these comparisons figs. 6.42 and 6.44 give scattergrams for experiment 130, while figs. 6.41 and 6.43 are plots of the mobility spectrum parameters \( \nu \) (plotted as "1") and \( A \) (as "2") together with calculated ("4") and observed ("3") conductivities for the same experiment. Of these figures 6.41 and 6.42 represent positive ions, while 6.43 and 6.44 represent negative ions. Since for a given ion polarity spectra
Fig. 6.42 Scattergram of Calculated vs Observed Positive Atmospheric Conductivity. (Data from experiment 130).

Fig. 6.44 Scattergram of Calculated vs Observed Negative Atmospheric Conductivity. (Data from experiment 130).
are only available for alternate half-hours, every second point of the mobility spectrum plots is the average of its neighbours. The observed conductivities plotted are an average of twelve readings taken at \( 2\frac{1}{2} \) minute intervals.

The most striking feature of these comparisons is the difference in magnitude of the two conductivities. The one calculated from the spectrum is only a quarter of the directly measured one, the two conductivity ranges being 0.5 to 2.5 fmho/m and 2 to 10 fmho/m respectively. The range of conductivities observed by JOHNS (1972) at Auckland was 2 to 7 fmho/m, with values in the range of 5 to 6 fmho/m being most common. It therefore seems that the calculated conductivities are somewhat low, though certainly of the right order of magnitude. The two measuring instruments are sited some twenty metres apart (see plate 3.71, the frontispiece), and the Atmospheric Electricity Station site is less screened from winds than that of the spectrometer. JOHNS (1972) noted a 10 to 25 percent difference between conductivities measured by two different methods at points only 2 metres apart, so the difference noted above is hardly surprising. The scattergrams for experiment 130 show a clear correlation between calculated and observed conductivities. This correlation is also apparent in figs. 6.41 and 6.43, particularly after about 1600 hours. Section 6.5 examines the dependence of conductivity on \( v \) and \( A \) in detail, however we may note here that the calculated conductivity is more sensitive to changes in \( A \), the small-ion concentration, than to those in \( v \).

In this section we have demonstrated the correlation
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Large ions $v_v/v_-$ std-dev</th>
<th>Small ions $A_/A_-$ std-dev</th>
<th>Conductivities $\lambda_v/\lambda_-$ std-dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>115</td>
<td>0.9</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>117</td>
<td>1.1</td>
<td>5.5</td>
<td>2.1</td>
</tr>
<tr>
<td>121</td>
<td>1.1</td>
<td>2.9</td>
<td>2.1</td>
</tr>
<tr>
<td>126</td>
<td>1.2</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>130</td>
<td>1.0</td>
<td>2.6</td>
<td>1.5</td>
</tr>
<tr>
<td>134</td>
<td>1.3</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>137</td>
<td>1.2</td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>140</td>
<td>0.8</td>
<td>1.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Mean: 1.08 0.09 2.43 0.24 1.59 0.13

Table 6.51  Ratios of Positive/Negative Ion Concentration and Conductivity

<table>
<thead>
<tr>
<th>Experiment</th>
<th>% Small Ion Contribution</th>
<th>$A_/A_- \cdot P_-/P_+$</th>
<th>$\lambda_v/\lambda_-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>112</td>
<td>56 5</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>115</td>
<td>55 6</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>117</td>
<td>29 3</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>121</td>
<td>57 3</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>126</td>
<td>49 3</td>
<td>2.0</td>
<td>1.7</td>
</tr>
<tr>
<td>130</td>
<td>44 4</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>134</td>
<td>76 5</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>137</td>
<td>56 4</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>140</td>
<td>66 5</td>
<td>1.7</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Mean: 54.3 1.5 66.0 1.4 1.84 1.59

Table 6.52  Percentage Small Ion Contribution to Polar Conductivities
between conductivities calculated from our mobility spectra and those measured independently with a different instrument. Agreement between the two instruments is by no means perfect, since they generally differ by a factor of four; it is however sufficient to demonstrate that both instruments do detect the same variations in conductivity over intervals of several hours.

6.5 The Dependence of λ on ν and A

Table 6.51 lists the ratios of positive/negative large-ion concentrations (ν+/ν−), small-ion concentrations (A+/A−), and polar conductivities calculated from these using equation (2) of section 6.4 (λ+/λ−). Note that although ν+/ν− and A+/A− are good estimates of the ion number density ratios, N+/N− and n+/n−, we cannot estimate ratios of the form N/n (large-ion to small-ion densities), for ν would be equal to N only if all the large ions had a mobility of 0.233 cm²/Vsec. ν+/ν− ranges from 0.8 to 1.3 with a mean close to 1.0, indicating that over long periods of time the mean concentrations of positive and negative large ions are equal. On the other hand A+/A− ranges from 1.1 to more than 2.9 (though the value of 5.5 for experiment 117 is anomalously high), so there are always more positive small ions than negative ones. The mean A+/A− ratio of 2.4 is much higher than the NOLAN & DE SACHY (1927) n+/n− ratio of 1.2, suggesting that positive ions are being preferentially admitted to the spectrometer. Since all the experiments were performed in fine weather with a positive potential gradient this may well be an electrode effect, where negative ions are repelled from the earthed roof on which the
spectrometer is mounted.

Consider again equation (2) of section 6.4:

\[
\lambda = \varepsilon(k_L \cdot \nu + k_S \cdot A) \text{ mho/m}
\]  \hspace{1cm} ........(1)

It is commonly assumed (section 1.5) that large ions do not contribute significantly to the atmospheric conductivity, hence we might regard \(k_L \cdot \nu\) as insignificant compared with \(k_S \cdot A\), and write

\[
\lambda = \varepsilon k_S \cdot A \text{ mho/m}
\]  \hspace{1cm} ........(2)

Since we have used the same \(k_S\) for ions of both signs we would then expect

\[
\frac{\lambda_+}{\lambda_-} = \frac{A_+}{A_-}
\]  \hspace{1cm} ........(3)

Comparing these ratios on table 6.51 it is clear that agreement, while occasionally good, is generally rather poor, rendering the above assumption suspect.

Defining \(p\) to be the percentage contribution to polar conductivity made by small ions,

\[
i.e., \quad p = 100.\varepsilon k_S A/\lambda
\]  \hspace{1cm} ...........(4)

we obtain

\[
\frac{\lambda_+}{\lambda_-} = \frac{(A_+/A_-)}{(p_-/p_+)}
\]  \hspace{1cm} ...........(5)
instead of equation (3). Values of \( p \) were calculated for all the experiments, and are listed in table 6.52. The mean positive and negative percentages differ by more than 10%, which reflects the excess of observed positive ions noted above. Their values are 54% for negative and 66% for positive ions, while percentages greater than 75 are rare. This leaves contributions of 40% or more from large ions, which are undoubtedly significant.

Values of \( (A_+/A_-)/(p_-/p_+) \) are also listed in table 6.52; these show much better agreement with \( \lambda_+ / \lambda_- \) than did \( A_+/A_- \). We must therefore conclude that, at least for the conditions prevailing at Auckland during the experiments, it is definitely invalid to assume that large ions do not contribute significantly to the atmospheric conductivity.

6.6 Mobility Spectra of Ions Produced by Point Discharge

A primary requirement for the study of point-discharge ions is a point at which a steady discharge can be maintained for a reasonable time. Since the discharge is limited by the buildup of space charge at its tip the point should be well ventilated - NOLAN & O'TOOLE (1959), for example, mounted their point at the centre of a brass tube through which they pumped up to 20 litres of air per minute. When the point is at a negative potential the discharge is maintained by electrons dislodged from its tip by incoming positive ions. If the current density at the tip is high its shape is continually altered by the bombardment, so the location at which discharge occurs may move randomly about, always remaining at the spot.
Fig. 6.61 Point-plane Electrode Configuration set up in front of the Mobility Spectrometer.

Fig. 6.62 Sequence of Events as used for Point Discharge Mobility Spectra Observations.
where the field is strongest. To minimise this "sputtering" effect the current density should be kept low, which means that very sharp points (such as sewing needles) should be avoided.

A variety of electrode configurations were tested, and the one shown in fig. 6.61 selected for later use. This has an earthed sheetmetal plate some 25 cm square held at an angle of $45^\circ$ to the horizontal, and a 1/16 " diameter stainless steel rod with a rounded end mounted at a distance of 2.5 cm from the plate as shown. The point is supported by a perspex insulator, and has a lead attached to its lower end for connection to a high-voltage power supply. A discharge current of about one microamp is drawn when a potential of 6 kV is applied between the point and the earthed plate. The point and spectrometer were set up on the laboratory bench for preliminary studies, as illustrated in fig. 6.61. With the point more than 50 cm from its air intake, the spectrometer’s ring currents were greatly increased when the point power supply was switched on, but these currents were not at all steady. As the point was moved closer to the spectrometer the ring currents increased in magnitude and became more stable, probably because of the improved ventilation of the point by the intake air stream. With the point very close to the intake however, the displacement current to the rings when the point potential was suddenly changed became troublesome. A distance of 15 cm was chosen, giving reasonably steady ring currents with no apparent displacement current problems.

For observing point discharge mobility spectra the sequencing scheme shown in fig. 6.62 was set up. In a half-hour cycle this scheme allows five minutes to observe the
ambient atmospheric ion spectrum, ten minutes to observe the ions created by the discharge, and five minutes after the discharge ceases. A series of experimental runs were made, using each of the four possible combinations of point potential and spectrometer driving potential. Mobility spectra at 25 second (one spectrometer scan) intervals were computed for each experiment: these spectra were interpolated, smoothed and plotted, exactly as described in section 6.2.

The resulting plots (see figs. 6.63 and 6.64) have several common features. While the point is off they are, of course, very similar to those of section 6.2, but when it is switched on the rms current error immediately jumps from its usual value of around 2.5 fA up to 10 fA or more. This change indicates that, as we would expect, the mobility spectrum of ions from the point is less stable than that of the undisturbed air. Later, when the point is turned off, the spectrum returns to normal over a period of five or six spectrometer scans (up to 150 seconds). This interval is probably the settling time of the spectrometer ring system (section 4.3) rather than a property of the point-discharge ions.

If the spectrometer driving potential is of opposite sign to the point potential the mobility spectrum does not alter significantly when the point is turned on. In these cases the spectrum fitting process often fails to converge so that half or more of the plotted points have to use interpolated values, which greatly reduces the significance of the plots. We must therefore conclude that no significant number of ions leave the point carrying charges with signs opposite to that of its potential.
Fig. 6.63 Mobility Spectra for Negative Ions produced by Negative Point Discharge.

Large, small ion concentration plotted as "1", "2" on scales 1, 2. R.M.S. current error plotted as "3" on scale 3.
Fig. 6.63 gives a typical plot of the mobility spectrum of negative ions from a negative point. Both large and small ion concentrations rise quickly from their ambient values of 60 and 25 ions/cm$^3$ to much higher ones of about 275 large ions/cm$^3$ and up to 900 small ions/cm$^3$ when the discharge starts. The small-ion concentration varies rapidly through the range 50 to 900 ions/cm$^3$ demonstrating the random nature of point discharge. The large ion concentration, on the other hand, is relatively stable, varying slowly between about 200 and 350 ions/cm$^3$. In negative point discharge any positive ions formed are attracted back to the tip, and negative ions can only be formed by attachment of electrons to uncharged nuclei. NOLAN & O'TOOLE (1959) found that nuclei produced by the discharge are initially of molecular size, so they will form small ions when they attach one or more electrons. This implies that the large ions we observe must be formed by the attachment of the plentiful small ions to larger nuclei drawn past the point in the spectrometer intake air stream. The comparatively constant large-ion concentration thus reflects a steady concentration of nuclei in the ambient room air.

A similar plot for positive ions from a positive point is given in fig. 6.64. Again the large ion concentration rises from an ambient value (of 75 ions/cm$^3$) to a new one of 130 ions/cm$^3$, varying between about 110 and 150 ions/cm$^3$. Now, however, the small ion density decreases from its ambient (45 ions/cm$^3$) to some 20 ions/cm$^3$. Near a positive point small positive ions are formed in the electron avalanching process, but many of them will recombine with electrons, giving a much lower effective creation rate than that for the negative ions
Fig. 6.64 Mobility Spectra for Positive Ions produced by Positive Point Discharge.

Large, small ion concentration plotted as "1", "2" on scales 1, 2. R.M.S. current error plotted as "3" on scale 3.
mentioned above. Fig. 6.64 suggests that most of the remaining small ions then combine with uncharged nuclei in the air stream, hence the difference between these two situations lies purely in the different effective rates of small ion production.

The investigations described above can only be described as preliminary though some interesting results were obtained which are consistent with a simple description of the point-discharge process. For any future work an improved mobility spectrometer would be desirable, either with better mobility resolution (to study the difference between positive and negative discharges), better time resolution (to study the correlation between changes in spectrum parameters and movement of the discharge over the point's tip caused by sputtering), or both.
7.1 Limitations of the Present Spectrometer

In Chapter 6 we discussed three different studies undertaken using the present mobility spectrometer. For each of these the spectrometer performance was sufficient to yield worthwhile results, but the need for better performance became apparent.

One obvious limitation is the low mobility resolution achieved. This is particularly serious for the large-ion part of the spectrum, where we have only a single delta function in our spectrum model. As against this the two parameters of the fitted spectra are not only frequent (every 25 seconds), which was the primary design objective stated in section 1.7, but also accurate (standard deviations of 3%). For studies of rapidly changing phenomena, like the space-charge clouds observed in section 6.2, or the fluctuations in point-discharge ion spectra of section 6.6, time resolution is all-important. Both these cases really require better time resolution than is available, and since it is clear that any spectrometer design must compromise between time and mobility resolutions, we must accept low resolution of mobilities. On the other hand studies of long-term variations, such as those described in sections 6.3, 6.4 and 6.5, demand better mobility resolution. From the observations of short-term spectrum variations described in section 6.2 it appears that an interval of 100 sec-
onds would be sufficiently short to give reliable average spectra for quarter-hour periods. A spectrometer taking 100 seconds to scan the spectrum should be capable of better mobility resolution - such an instrument is considered in section 7.2.

Another (less serious) limitation is the large volume of data produced by the spectrometer. Any decrease in this volume would certainly improve its usefulness. A final disadvantage is the spectrometer's dependence on a large, fixed, digital recorder. The use of a smaller, more portable recorder would make the whole spectrometer a reasonably portable, and therefore more versatile, instrument.

7.2 Suggestions for an Improved Spectrometer

Several improvements to the present spectrometer appear attractive. The mounting arrangements for its collecting rings are unnecessarily complicated, and could be replaced with a simple vee-block support. This would consist of two flat plates topped with sheet teflon, inclined at 45 degrees to the horizontal so that the rings and their teflon separating washers automatically sit in correct alignment.

The system of time-sharing a single electrometer between the rings was an economic necessity, but (as explained in chapters 3 and 4) it limits the overall spectrometer performance. A set of eight electrometers, one connected directly to each ring, would dramatically improve spectrometer performance. Each ring would be at its electrometer's input potential
(virtual earth) instead of being electrically isolated, so charge leakage from the rings would be practically eliminated. Electrostatic interaction between the rings would be impossible, so the spectrometer's time resolution would equal its scan time of 25 seconds. The reed switches would be used to select an electrometer output rather than a ring, eliminating the charge separation problem at the electrometer inputs and reducing by one third the number of measurements required for each scan. Alternatively each electrometer could be connected to a separate channel of the digital recorder: this would allow the time resolution to be increased up to half the recorder's maximum sampling rate (one sample every 2½ seconds). With one electrometer per channel it might also be possible to use them as amplifiers instead of as integrators, thus eliminating the reset reed switches and their charge separation problem.

Improved mobility resolution could be obtained without compromising time resolution simply by adding more rings. The cost of adding an electrometer with each extra ring makes this proposition unattractive. Alternatively we could scan a wider mobility range by varying the driving potential periodically. Using a recorder channel for each electrometer would allow the following sequence to be used: change potential, open all reset relays, wait for integrating time, measure charges (on all rings simultaneously), close reset relays. Using an integration time of 25 seconds (as at present) this approach, permitting 32 points covering an extended mobility range to be obtained in little more than 100 seconds, looks most promising.
Fig. A.11 Schematic Diagram of the Vibrating Capacitor Electrometer.

[Circled numbers refer to figures in JOHNS (1972)]
APPENDIX 1

DETAILS OF THE SPECTROMETER ELECTRONICS

The electrometer design was jointly developed by myself and Dr M.D. Johns, who has already described its operation in section 3.4 of his doctoral thesis [JOHNS (1972)]. The circled figures on the blocks of the functional diagram of the electrometer given in fig. A.11 refer to circuit diagrams in JOHNS (1972).

The vibrating capacitor head unit and its detector unit together function as an operational amplifier. When measuring charge the "reset" relay is open, so the feedback impedance is a 1 pf capacitor, and the "damping" relay is closed, so the feedback loop's gain can be adjusted using the potentiometer in series with the detector's signal input. When the electrometer is reset the "reset" relay is closed. In this state the electrometer's output is connected to its input through the 22 MΩ discharging resistor, hence it acts as an amplifier. It was impossible to stabilise the feedback loop for both "measuring" and "reset" states without significantly degrading the time response for measuring, so the "damping" relay was installed to stabilise the "reset" loop by simply lowering its gain.

Performance specifications for the complete electrometer are listed in table 3.21 and its head unit is illustrated in fig. 3.21. It has proved to be highly reliable throughout all
Fig. A.12 Functional Diagram of the Spectrometer Sequencer.
the experiments.

Requirements for the spectrometer sequencing unit were discussed in section 3.6. Fig. A.12 is a functional diagram of the complete unit, and circuits of the various blocks follow in figs. A.13 to A.17. None of these circuits is in any way unusual so they are not discussed further.

An initiating pulse from the digital recorder (see section 3.6) is used to close a relay at the recorder end of the line. The circuit of fig. A.13 converts this contact closure to a negative-going spike which is used to trigger univibrators U1 and U2. The positive-going edge of U1's output steps a Fairchild CWL 9958 decade counter to select the next state of the spectrometer's sampling scan. The counter output is decoded by the circuits of figs. A.15, A.16 and A.17 to give ten signal lines, one of which is earthed in each of the spectrometer states. Of these ten lines one (state 9) is unused, while those for states 1 to 8 feed the low-potential end of the ring-selecting relays. The high-potential end of all the relays is driven by the output of univibrator U3. A tenth signal line drives a resistor which is used for spectrometer state zero, and is combined with the output from univibrator U1 to control the electrometer "reset" relay.

The sequence of operations is therefore as follows. When an initiating pulse arrives the decade counter is stepped, selecting the spectrometer state for this sample. At the same time U1 and U2 are triggered, and (unless the unit is now in state zero) the electrometer "reset" relay is opened. After a time interval determined by U2, U3 is triggered supplying
Fig. A.13  Line Receiver and Differentiator.

Fig. A.14  Univibrators (3x).

Fig. A.15  Diode Matrix Drivers (4x).
Fig. A.16 Diode Matrix (1 out of 10 decode).

Fig. A.17 Relay Drivers (10x).
power to the relay drivers. The relay selected by the counter closes, connecting its ring to the electrometer input. When U3 resets the selected relay opens, then when U1 resets the electrometer "reset" relay is closed again to await the next initiating pulse.

The entire sequencing unit was built on a 6½" x 4" piece of "spotboard" so that it would fit easily into the limited space available inside the spectrometer case. It has been absolutely reliable at all times, but its extremely compact construction makes it somewhat difficult to modify.
APPENDIX 2

LEAST SQUARES PARAMETER ESTIMATION

The method of least squares is well covered in reference works such as HAMILTON (1964) and ROLLET (1965), but a summary is included here for completeness.

Suppose we have a quantity $f$ which is a known function of $m$ parameters $x_1$ to $x_m$, and we make $n$ (where $n$ is greater than $m$) measurements of $f$, $f_i$, each of which has a random error $e_i$. These assumptions specify a set of "observational equations"

$$f_i = a_{i1}x_1 + a_{i2}x_2 + \ldots + a_{im}x_m + e_i$$

or in matrix form

$$F_{n,1} = A_{n,m}X_{m,1} + E_{n,1} \quad \cdots \cdots \cdots (1)$$

Assume the errors $e_i$ have a joint distribution with zero means (so that the expectation value of $e$ is zero), i.e. that

$$\varepsilon(F) = F^0 = AX, \quad \cdots \cdots \cdots (2)$$

and a variance-covariance matrix $M_f$ of rank $n$, so that the elements of $M_f$ are $m_{ij}$ where

$$m_{ii} = \text{variance} (f_i)$$

and $m_{ij} = \text{covariance}(f_i, f_j)$ when $i \neq j$. 
Note that we have assumed here only that the errors \( e_i \) have come from a population with finite second moments. Let \( \hat{X} \) be a chosen set of values of \( X \), and define a "residual vector" \( V_{n,1} \) as

\[
V = F - \hat{F} = F - A\hat{X}
\] ............(3)

Then the generalised weighted sum of squares of the residuals is the quadratic form \( s = V'M_f^{-1}V \), and the optimum set of values for \( \hat{X} \) is the one which minimises \( s \). \( \hat{X} \) is given by the "normal equations"

\[
(A'M_f^{-1}A)\hat{X} = A'M_f^{-1}F
\] ............(4)

so that \( \hat{X} = (A'M_f^{-1}A)^{-1}A'M_f^{-1}F \) ............(5)

\( \hat{X} \), the "least squares estimate" of \( X \), can also be shown to be the estimate which minimises the variance of the estimate of any linear function of \( X \).

If \( M_f \) is known only to within a scale factor,

i.e. \( M_f = \sigma^2 N \) with \( \sigma^2 \) unknown,

then \( M_f^{-1} = \frac{1}{\sigma^2}N^{-1} \) ............(6)

When equation (6) is substituted into the normal equations (4), \( \sigma^2 \) cancels out, so that \( \hat{X} \) is independent of the scale of the variance-covariance matrix. The matrix \( N^{-1} \) is called the
"weight matrix" and \( \sigma^2 \) is the variance of an observation with unit weight.

The variance-covariance matrix for the least squares estimate is

\[
M_{\hat{X}} = \varepsilon\{(\hat{X}-X)(\hat{X}-X)\}'
\]

which yields

\[
M_{\hat{X}} = \sigma^2 (A'N^{-1}A)^{-1}
\]  \hspace{1cm} (7)

so that if the variance of an observation of unit weight is known the variances and covariances of the parameters \( \hat{X} \) can be calculated.

If \( \sigma^2 \) is unknown an unbiased estimate of it is

\[
\sigma^2 = \frac{V'N^{-1}V}{n-m}
\]  \hspace{1cm} (8)

This estimate may be used in equation (7) to obtain unbiased estimates of the \( M_{\hat{X}} \) matrix.

If the functions \( f_i \) are non-linear functions of variables \( x_1 \) to \( x_m \) we may expand them as a Taylor Series about the point \((x_1^0, x_2^0, \ldots, x_m^0)\), the terms to the first order being

\[
f_i = f_i(x_1^0, x_2^0, \ldots, x_m^0) + \frac{\partial f_i}{\partial x_1} (x_1 - x_1^0) + \ldots
\]

\[
+ \frac{\partial f_i}{\partial x_m} (x_m - x_m^0)
\]
or \[ f_i - f_i^0 = \sum_{j=1}^{m} \frac{\partial f_i}{\partial x_j} (n_j - x_j^0) \]

or \[ \Delta f_i = \sum_{j=1}^{m} \frac{\partial f_i}{\partial n_j} \Delta x_j \] \[\text{.........(9)}\]

If the above expansion is valid we have linearised the equations so that the previous formula can be used, with the matrix of partial derivatives for A and the vector of deviations from the values of the functions at the expansion point for F. The normal equations are solved for the differences \( \Delta x_j \), and the values \( x_i^0 \) adjusted accordingly. This process is continued until all the \( \Delta x \)'s are very small, i.e. the process has converged. Since at each stage the values \( x_j^0 \) are assumed known accurately the estimated variance-covariance matrix for the \( \Delta x \)'s may also be used for the \( x \)'s.
APPENDIX 3

THE TRANSFORMED LOGNORMAL DISTRIBUTION

This appendix lists the expressions required by the least squares fitting process described in section 5.5.

Let:

\[ \phi(x) = \frac{1}{2} \text{erf}(x) \]  \hspace{1cm} (1)

\[ I_c = A \left[ \phi(U_3) - \phi(L_3) \right] \]  \hspace{1cm} (2)

\[ L_2 = \frac{\log k_n - \mu - \sigma^2}{\sigma \sqrt{2}} \]  \hspace{1cm} (3)

\[ U_2 = \frac{\log k_{n-1} - \mu - \sigma^2}{\sigma \sqrt{2}} \]  \hspace{1cm} (4)

\[ L_3 = \frac{\log k_n - \mu}{\sigma \sqrt{2}} \]  \hspace{1cm} (5)

\[ U_3 = \frac{\log k_{n-1} - \mu}{\sigma \sqrt{2}} \]  \hspace{1cm} (6)

\[ M = \exp\{\mu + \frac{1}{2} \sigma^2\} \]  \hspace{1cm} (7)

The current to ring \( n \) is then

\[ I_n = S_{n}^{PAM} \left[ \frac{1}{2} + \phi(L_2) \right] + I_c - S_{n}^{PAM} \left[ \phi(U_2) - \phi(L_2) \right] \]  \hspace{1cm} (8)
Its differentials with respect to $A$, $\mu$, and $\sigma$ are

\[
\frac{\partial I_n}{\partial A} = \frac{I_n}{A} \quad \ldots \ldots \ldots(9)
\]

\[
\frac{\partial I_n}{\partial \mu} = I_n - I_c + \frac{A}{\sigma \sqrt{2\pi}} \left[ \exp\{-L_3^2\} - \exp\{-U_3^2\} \right. \\
\left. + S_n^M \exp\{-U_2^2\} - (S_n^P + S_n^R) M \exp\{-L_2^2\} \right] \\
\ldots \ldots \ldots(10)
\]

and

\[
\frac{\partial I_n}{\partial \sigma} = \sigma (I_n - I_c) + \frac{A}{\sigma \sqrt{\pi}} \left[ L_3 \exp\{-L_3^2\} - U_3 \exp\{-U_3^2\} \right. \\
\left. + S_n^M \exp\{-U_2^2\} (U_2 + \sigma \sqrt{2}) \right. \\
\left. - (S_n^P + S_n^R) M \exp\{-L_2^2\} (L_2 + \sigma \sqrt{2}) \right] \\
\ldots \ldots \ldots(11)
\]
REFERENCES

   Cambridge University Press (Dept of Applied Economics Monographs 5).


   Geofisica Pura E Applicato, Milano, 51, 238-242.


Geofisica Pura E Applicato, Milano, 50, 155-160.

KEEFE, D., & NOLAN, P.J., 1962: Combination Coefficients of Ions and Nuclei.


University of California Press.

University of California Press.

Papers in Meteorological and Geophysics, Tokyo, 11, 348-355.

Papers in Meteorological and Geophysics, Tokyo, 12, 247-276.


NOLAN, P.J., & POLLAK, L.W., 1947: Calibration of a Photo-electric Nucleus Counter.


Permagon Press, London.

Recent Advances in Atmospheric Electricity,
Permagon Press, London.

SISKNA, R., 1969: Role of the Water Substance in the Structure and By-production of Ions in the Ambient Atmospheric Air.
Planetary Electrodynamics, 207-230,

TAMMET, H.F.,


TRICHEL, G.W.,

1938: The Mechanism of Negative Point to Plane Corona Near Onset.

TYNDALL, A.M. & GRINDLEY, G.C.,

1926: The Mobility of Ions in Air (Parts 1 and 2).

VAN NIE, A.G., and ZAAALBERG VAN ZELST, J.J.

1964: A Vibrating Capacitor Driven by a High-frequency Electric Field.

WHIPPLE, F.J.W.,

1933: Relations Between the Combination Coefficients of Atmospheric Ions.

WHIPPLE, E.C. Jr.,

1960: An Improved Technique for Obtaining Atmospheric Ion Mobility Distributions.

WRIGHT, H.L.,

1936: The Size of Atmospheric Nuclei.